The Hydroformylation Reaction

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1. Introduction

The reaction of 1-alkenes with carbon monoxide and hydrogen in the presence of a catalyst gives the corresponding homologous aldehydes (Eq. 1). The discovery

(1)

of this reaction was made by Roelen in 1938 using $Co_2(CO)_8$ as the catalyst at high temperature (120–170°) and high pressure of carbon monoxide/hydrogen (200–300 bar). (1, 2) This reaction has been called the “Oxo reaction”, “Roelen reaction” or “hydroformylation”. (3, 4) Hydroformylation is a general term indicating that both a hydrogen and a formyl group are introduced to unsaturated bonds, especially olefins.

Later this reaction was developed as an industrial process, i.e., the Oxo Process, for the production of alkanals from 1-alkenes using a cobalt or rhodium catalyst. (3, 4) Most noteworthy is the conversion of propene to butanal, which can be subsequently hydrogenated to 1-butanol or converted to 2-ethylhexanol by self-aldol condensation. (3, 4) 2-Ethylhexanol, a crucial intermediate for the production of ester-type plasticizers, is the most important bulk chemical produced by the Oxo Process. (3, 4) A variety of transition metal catalysts other than $Co_2(CO)_8$ have been investigated, including phosphine complexes of cobalt and hydridocobalt clusters. Platinum and ruthenium complexes show reasonably good catalytic activities, but modified cobalt catalysts are still much more advantageous. However, various rhodium complexes demonstrate higher catalytic activity (10^3–10^4 times) than the cobalt complexes. Although the price of rhodium is higher than cobalt, reactions using rhodium catalysts require lower temperature (50–80°) and pressure (10–50 atm).

Other important commercial applications of hydroformylation include the production of long-chain alcohols from C_5–C_{17} isomeric linear alkenes. (3-5)

These long-chain alcohols serve as intermediates for lubricants, plasticizers and detergents. (5) The hydroformylation of ethene to propanal is another important Oxo Process. (5)

Excellent reviews appeared in 1970s (6-9), 1980's (3, 4, 10-15) and 1990s. (16-19) An exhaustive review of the Oxo Processes of 1-alkenes and other hydroformylation reactions appeared in 1980 and covered all aspects of the hydroformylation reaction from its discovery to 1978. (3)

In this chapter, the authors put clear emphasis on the scope of the hydroformylation reaction in organic synthesis. In this context, there is a relevant review in 1987 of the hydroformylation of functionalized alkenes. (5) The hydroformylation reaction now can be performed under very mild conditions using a variety of functionalized alkenes. (20) Reactions in aqueous biphase, (21-23) supercritical carbon dioxide (24-30) or fluorous biphase (31, 32) have recently emerged in response to separation and environmental issues. In fact, a highly efficient Oxo Process using a water-soluble rhodium catalyst, $HRh(CO)(TPPTS)_3$ [TPPTS = $P(C_6H_4SO_3Na$-*m*)], in aqueous biphasic conditions has been commercialized by Ruhrchemie/Rhône-Poulenc for the production of butanal. (21-23) Asymmetric hydroformylation of prochiral olefins catalyzed by enantiopure rhodium complexes has been developed to the level that practical applications appear possible. (33-42) Although the reactions of formaldehyde, oxiranes, and others with carbon monoxide and hydrogen in the presence of transition metal catalyst could be considered as variations of hydroformylation, this chapter only deals with hydroformylation of carbon-carbon multiple bonds.

2. Mechanism

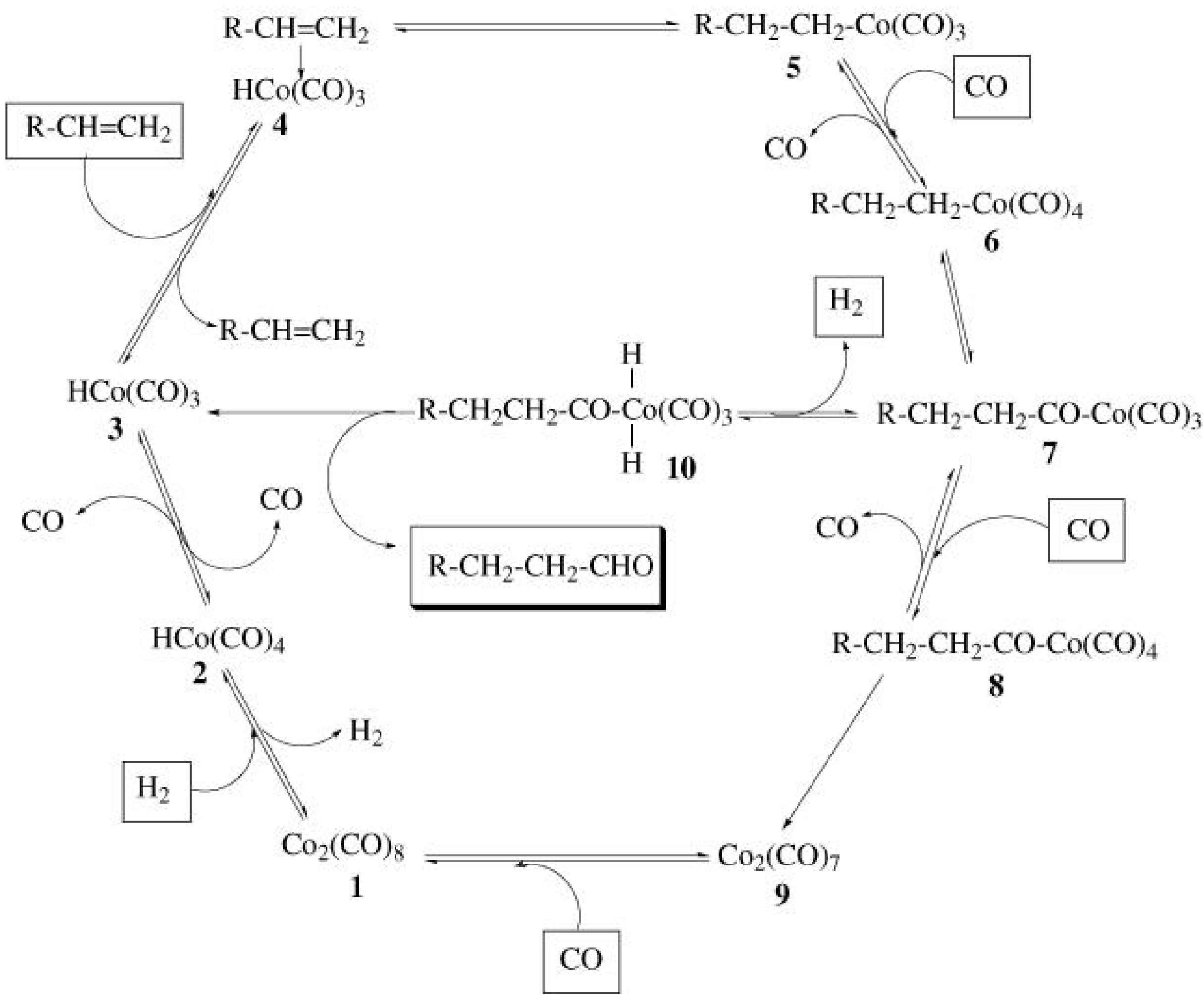
Extensive mechanistic studies have been performed on the cobalt-catalyzed hydroformylation of olefins. Studies of the mechanism of hydroformylations catalyzed by rhodium and platinum complexes, which were developed later, greatly benefited from the accumulated knowledge on the cobalt counterpart. The rapid advances in organometallic chemistry in the 1960s and 1970s also made significant contributions to the detailed understanding of the individual steps involved in this reaction. Direct observation of reactive intermediates by high pressure IR spectroscopy helped confirm catalytic cycles proposed on the basis of kinetics. Deuterium labeling provides important information about a possible equilibrium between the starting olefin, intermediates, and products, which is useful for the determination of the rate-determining step. (4, 43-51) ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies (and ^{195}Pt NMR for platinum catalysts) have been extensively used for direct observation and structural characterization of reactive intermediates. (34, 52-62) Theoretical studies on the energy analysis of possible intermediates in the catalytic cycle have been advanced to give more insight into and better understanding of the mechanism of hydroformylation. (63-66)

These mechanistic studies have established the crucial unit processes involved in the hydroformylation of olefins, although some mechanistic details await further investigation. (3, 4, 64) It has been shown that there are three crucial unit processes: (1) reaction of a hydrido-metal species with an olefin to form an alkyl-metal species, (2) alkyl migration to a carbonyl ligand of the metal, i.e., net carbon monoxide insertion to the alkyl-metal bond ("migratory insertion"), forming an acyl-metal species, and (3) hydrogenolysis of the acyl-metal species, giving an aldehyde and regenerating the hydrido-metal species.

2.1. Cobalt-Catalyzed Hydroformylation

The generally accepted mechanism for the hydroformylation of olefins catalyzed by $Co_2(CO)_8$ was first proposed by Heck and Breslow (67) and is depicted in Scheme 1 for the formation of a linear aldehyde. The proposed mechanism includes the generation of $HCo(CO)_4$ from $Co_2(CO)_8$ and hydrogen as the first step, followed by the three crucial unit processes mentioned above. Instead of hydrogenolysis of the acyl-cobalt species, $RCH_2CH_2CO\text{-}Co(CO)_4$, reductive cleavage of the acyl-cobalt species with $HCo(CO)_4$ is also possible to regenerate $Co_2(CO)_8$.

Scheme 1.



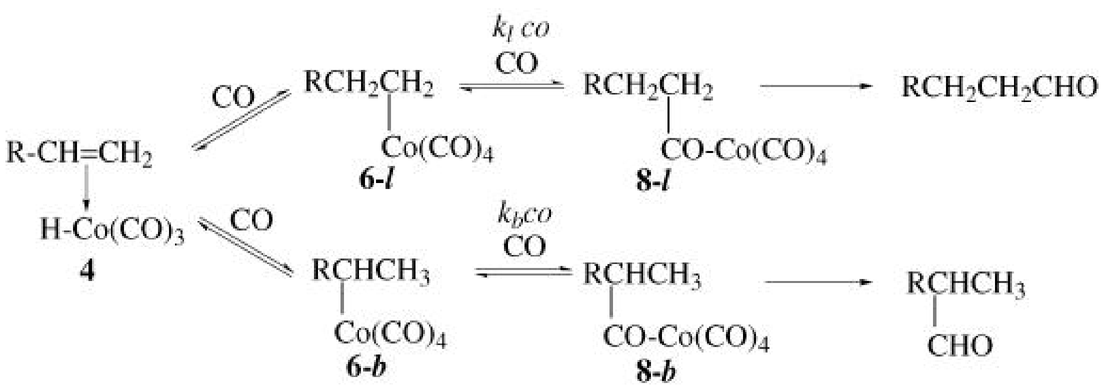
A series of carefully designed model reactions, simulations, analogies with stoichiometric reactions, kinetic and IR spectroscopic studies at the same temperature and pressure as those of the industrial Oxo Process confirmed the validity of the Heck-Breslow mechanism with some modifications. (3, 4) For instance, IR spectroscopic studies under industrial Oxo Process conditions have revealed the virtually complete conversion of $Co_2(CO)_8$ (**1**) to $HCo(CO)_4$ (**2**). (68) Although the formation of alkyl- and acyl-cobalt carbonyl complexes can be observed in model reactions, no alkyl-cobalt complexes have been detected under the conditions of the industrial process, i.e., only acyl- $Co(CO)_4$ **8** is observed. (69-71)

In the Heck-Breslow mechanism, formal reductive cleavage of the acyl-Co complex **8** with molecular hydrogen or $HCo(CO)_4$ (**2**) is proposed. However, it is more than likely that the actual acyl-Co complex that reacts with molecular hydrogen is the coordinatively unsaturated (16-electron) acyl- $Co(CO)_3$ **7**, and the oxidative adduct **10** is formed from **7**, which then reductively eliminates to give aldehyde and $HCo(CO)_3$ (**3**) (Scheme 1). (4, 43)

With regard to the two possible mechanisms for the formation of aldehyde from the acyl-Co complex **8**, it is still not certain which one is operating under catalytic conditions although either one can take place under stoichiometric conditions. Supporting evidence for the hydrogenolysis route (72, 73) as well as the bimolecular route involving $HCo(CO)_4$ (**2**) (74-77) has been presented.

Although Scheme 1 shows only the formation of a linear aldehyde, a mixture of linear (major) and branched (minor) aldehydes is obtained in the hydroformylation of 1-alkenes (Scheme 2). The regioselectivity of this reaction should be determined at the alkyl-Co complex formation step (**4**→ **5** or **6**) and/or the subsequent acyl-Co complex formation step (**6** → **7** or **8**). The *stoichiometric* hydroformylation of 1-propene in the absence of free carbon monoxide gives 70% branched aldehyde $(CH_3)_2CHCHO$ and 30% linear aldehyde $CH_3(CH_2)_2CHO$, (3, 78-80) which appears to be consistent with the Markownikow rule since $HCo(CO)_3$ is a strong acid. This result indicates that regioselectivity is determined at the alkyl-Co complex formation step (**4**→ **5**) under these conditions. However, the stoichiometric reaction *in the presence of* free carbon monoxide as well as the *catalytic* reaction exhibit reversed regioselectivity, i.e., the reactions give 70% linear aldehyde and 30% branched aldehyde. (3, 81) The results clearly indicate that acyl-Co complex formation (**6** → **8**) is the regioselectivity-determining step, i.e., the migratory insertion should be easier for the linear alkyl-Co(CO) complex than that for the branched counterpart mainly for steric reasons ($k_l co > k_b co$). Under optimized conditions (110°, 150 bars, H_2:CO = 1), a linear/branched aldehyde ratio of 4/1 is achieved in the hydroformylation of 1-propene. (3)

Scheme 2.



One factor that complicates the mechanistic understanding of this reaction is the fact that the olefin-Co, alkyl-Co and acyl-Co complexes are in equilibrium. The existence of equilibrium among these intermediate complexes is consistent with the observations of (1) olefin isomerization (3, 82-87) and (2) virtually statistical isotope scrambling on using 1,1,2-trideuterio-1-propene, (79, 80) 6,6,6-trideuterio-1-hexene (79) or 1-[^{14}C]-propene. (81) Isomerization and isotope scrambling are suppressed at high carbon monoxide pressures (>100 bars) and temperatures up to 140°. (3, 34, 6, 84) This fact clearly indicates that vacant coordination sites are necessary for the observed isomerization and isotope scrambling. These observations are also consistent with kinetic studies. (3, 88, 89)

When the enantiomerically enriched alkene (*S*)-3-methyl-1-hexene is employed, 3-ethyl-1-hexanal is formed with 70% retention of configuration together with 4-methyl-1-heptanal and 2,3-dimethyl-1-hexanal, in spite of the fact that the precursor of this product should be achiral 2-ethyl-1-pentene generated through isomerization of (*S*)-3-methyl-1-hexene. (82, 90-92) In order to accommodate this result, a 1,2-hydrogen shift mechanism has been proposed that does not include a true σ carbon-Co bond and is faster than the dissociation of olefin from the olefin-Co complex, which appears to be generally accepted. (3, 4, 6, 90)

A variety of ligand-modified cobalt catalysts have been investigated (3) and a commercial process known as the Shell Process was developed. (3, 93-95) The Shell Process uses tributylphosphine as the modifier, which generates $HCo(CO)_3PBu_3$ as the active catalyst species (68, 96) and is substantially more stable than $HCo(CO)_4$. This process gives a higher linear/branched ratio (7.3/1, i.e., 88% linear and 12% branched for the reaction of 1-propene), but the products are alcohols and not aldehydes, and ca. 15% of 1-propene is hydrogenated to propane. These characteristics may be ascribed to steric and electronic effects of the bulky and electron-donating phosphine ligand.

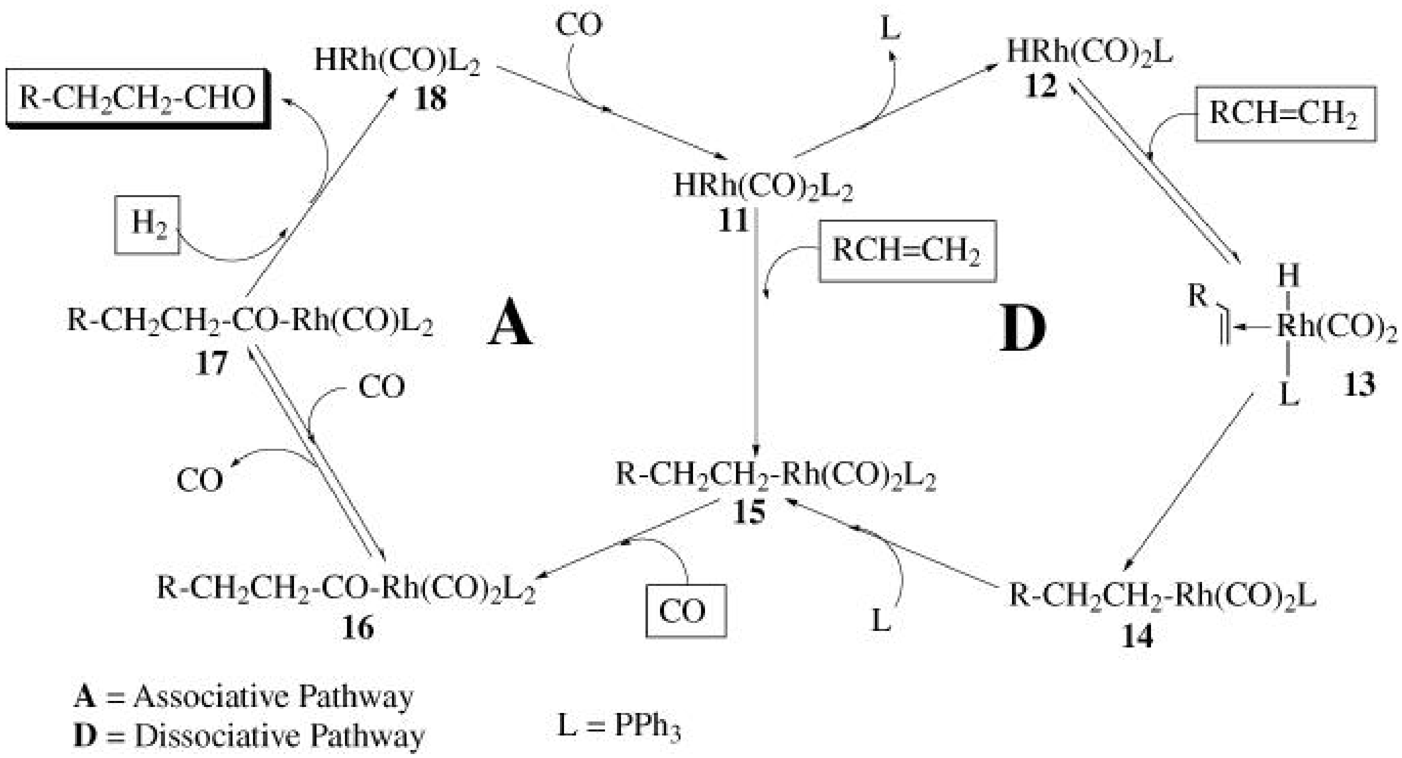
2.2. Rhodium-Catalyzed Hydroformylation

Mechanistic studies of rhodium-catalyzed hydroformylation of olefins have shown that the basic feature of the catalyst cycle is more or less the same as that of the cobalt-catalyzed reaction. (3, 4) When unmodified rhodium carbonyls, e.g., $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, are used as catalysts, there is an equilibrium among $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, and $HRh(CO)_n$ (n = 3 or 4) in the presence of carbon monoxide and hydrogen, which complicates the mechanistic study. (3, 4) Nevertheless, $HRh(CO)_n$ (n = 3) is postulated as the active catalyst species, (3, 4, 9) and the formation of $HRh(CO)_4$ is observed by FT-IR analysis. (97)

Although the unmodified rhodium carbonyl catalyst $HRh(CO)_n$ shows high activity, it gives a low regioselectivity and tends to hydrogenate or isomerize olefins, (3) i.e., this catalyst is not practically useful.

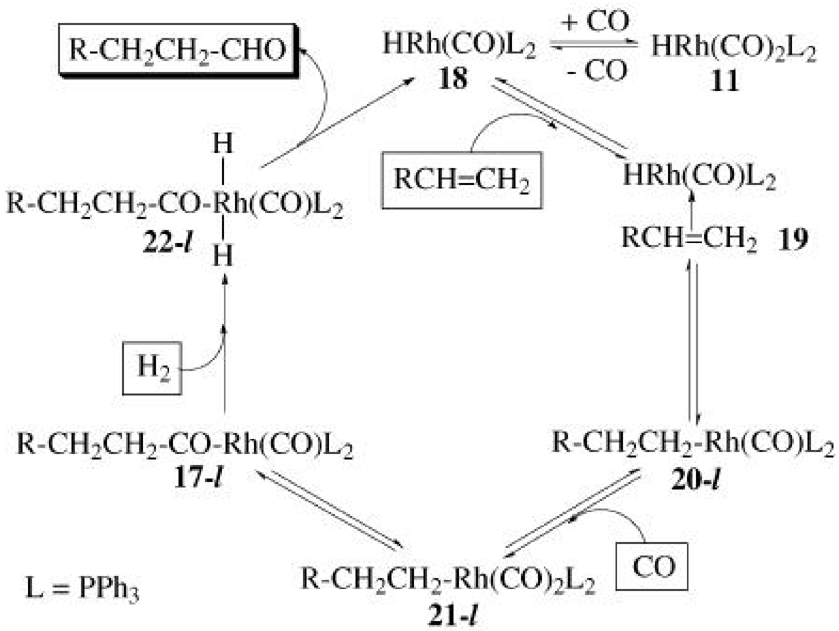
Most mechanistic studies on ligand-modified rhodium catalysts have been performed using $HRh(CO)(PPh_3)_3$, (3, 4) which was introduced as a hydroformylation catalyst in 1968. (98, 99) These extensive mechanistic studies on the basis of IR, ^1H and ^{31}P NMR spectroscopies have revealed that $HRh(CO)_2(PPh_3)_2$ (**11**) (an 18-electron species, generated by losing one triphenylphosphine ligand from $HRh(CO)(PPh_3)_3$ and acquiring one carbon monoxide ligand) is a key active catalyst species, which readily reacts with ethylene at 25°. (99) Two mechanisms, an associative pathway and a dissociative pathway, were proposed, (3, 6, 99, 100) depending on the concentration of the catalyst (Scheme 3, only the formation of a linear aldehyde is shown for clarity).

Scheme 3.



According to the proposed mechanisms, the associative pathway (**A**) dominates at catalyst concentrations >6 × 10^{-3} mol/L, while the dissociative pathway (**D**) that includes the generation of a more active catalyst species, $HRh(CO)_2(PPh_3)$ (**12**), through loss of another triphenylphosphine ligand becomes predominant at concentrations <6 × 10^{-3} mol/L. (99) The fact that carbon monoxide and excess triphenylphosphine inhibit the reaction (99) strongly suggests formation of the pentacoordinated acyl-Rh species **16** (18-electron species) that does not react with molecular hydrogen because of the lack of a vacant coordination site for molecular hydrogen to undergo oxidative addition. (4, 43) Under the industrial reaction conditions producing *n*-butanal from propene with high selectivity, the use of a large excess of triphenylphosphine is required, which certainly favors the associative pathway. In the associative pathway, it was originally assumed that coordination of an olefin to $HRh(CO)_2(PPh_3)_2$ (**11**) would take place to generate a hexacoordinated 20-electron π -olefin-Rh species. (4, 101) However, this appears to be unlikely based on the generally accepted 18-electron rule. (43, 102) Thus, a modified mechanism that can accommodate these points has been proposed as shown in Scheme 4. (43) In this mechanism, (1) coordinatively unsaturated $HRh(CO)(PPh_3)_2$ (**18**) (16-electron species) is generated from **11**, and **18** is the active catalyst, (2) **18** forms the π -olefin-Rh complex **19** (18-electron species), (3) **19** gives the alkyl-Rh complex **20** (16-electron species), (4) carbon monoxide coordinates to **20** to form the saturated alkyl-Rh complex **21**, (5) a migratory insertion takes place to give the unsaturated acyl-Rh complex **17**, (6) oxidative addition of molecular hydrogen to **17** gives the acyl-Rh dihydride complex **22** (18-electron species), and (7) a reductive elimination takes place to give an aldehyde and regenerate **18**.

Scheme 4.



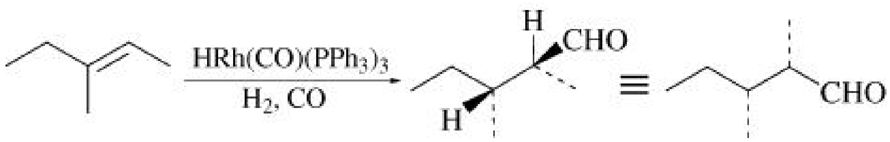
Although Scheme 4 shows only linear alkyl-Rh and acyl-Rh intermediates (**20-l**, **21-l**, **17-l**, and **22-l**), the branched counterparts of these intermediates (**20-b**, **21-*b***, **17-b**, and **22-*b***) as well as branched aldehyde $R(CH_3)CHCHO$ should be formed when the alkyl-Rh complex formation step yields the branched alkyl-Rh intermediate, $R(CH_3)CH$-$Rh(CO)(PPh_3)_2$ (**20-b**), that follows the same subsequent steps as those discussed above (see also Scheme 2). The fact that excess triphenylphosphine decreases the reaction rate, but increases the linear/branched ratio of the resulting aldehyde and suppresses hydrogenation and rearrangement of olefin, indicates that the regioselectivity of the reaction is determined in the step that forms the alkyl-Rh complex from the π -olefin-complex **19**. (43)

For reductive cleavage of acyl-Rh complex **17**, it is generally accepted that molecular hydrogen is the hydrogen donor as shown in Scheme 4. However, this step could be effected alternatively by another hydrido-Rh complex, $HRh(CO)_2(PPh_3)_2$, in a manner similar to that discussed for the cobalt-catalyzed reaction. With regard to this possibility, intriguing results have been reported: (a) silica-bonded rhodium complexes are found to be inactive when these complexes are completely site isolated, whereas these complexes become active when the site isolation is such that only a pair of rhodium complexes are close enough to undergo the bimolecular reductive cleavage of an acyl-Rh complex by a hydrido-Rh complex; (103) (b) a homogeneous binuclear rhodium complex with a specially designed tetraphosphine ligand, that places two rhodium metals in an appropriate space so that the bimolecular reductive cleavage is feasible, shows exceptional acceleration of the reaction rate. (104, 105) Although these findings cannot eliminate the generally accepted reductive cleavage step with molecular hydrogen, it is strongly indicated that bimolecular reductive cleavage involving two rhodium species is operative under certain reaction conditions.

Ab initio molecular orbital studies on the whole catalytic cycle of hydroformylation of ethylene catalyzed by $HRh(CO)_2(PH_3)_2$ has been performed, (63, 64) which points out the significance of the coordinating solvent, ethylene in this case, and identifies the oxidative addition of molecular hydrogen to the pentacoordinate acyl-Rh complex (**17**→**22**) as the rate-determining step. In fact, this step is the only endothermic process in the catalytic cycle.

As discussed above, kinetic studies on the effect of partial pressures of hydrogen and carbon monoxide on the reaction rate indicate that the oxidative addition of molecular hydrogen to the Rh complexes with phosphine (3, 43) or diphosphite (55) ligands is the slowest step in the whole process. Further mechanistic studies, however, have revealed that the rate-determining step of the reaction depends on the nature of the ligand employed, and in some cases alkene insertion into the Rh-H bond becomes the slowest step as observed for the Rh-BINAPHOS–catalyzed reactions. (51) It has also been shown that alkene insertion to the Rh-H bond is irreversible for the formation of linear alkyl-Rh species in general, while this step may become reversible for the formation of branched alkyl-Rh species, depending on the reaction conditions and the nature of the alkene. (51)

It has been shown that hydrometalation of the olefin (step 3: **19** → **20**) proceeds by complete *cis* addition, and the subsequent migratory insertion of carbon monoxide (step 4: **21**→ **17**) takes place with retention of configuration. (4, 43-45, 106) Thus, the hydroformylations of (*E*)- and (*Z*)-3-methyl-2-pentenes give *syn*- and *anti*-2,3-dimethylpentanals, respectively, in a stereospecific manner (Eqs. 2 and 3). (4, 44) Some *E*-*Z* isomerization of the olefins takes place during the reaction, complicating the analysis, but deuterium labeling experiments reveal the completely stereospecific *cis*-addition of hydrogen and a formyl group to the double bond. (4, 43-45)



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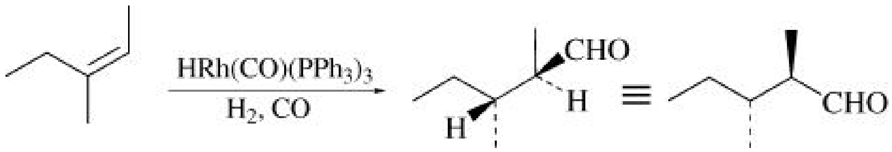
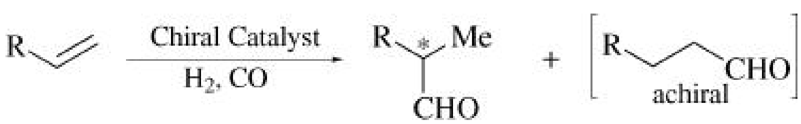


(3)

2.3. Asymmetric Hydroformylation

When an appropriate chiral ligand is introduced to a catalyst, the differentiation of two enantiofaces of a prochiral olefin is conceptually possible in the hydroformylation reaction. There are three classes of alkenes from which enantiomerically enriched aldehydes can be obtained (Eqs. 4–6). The asymmetric hydroformylation



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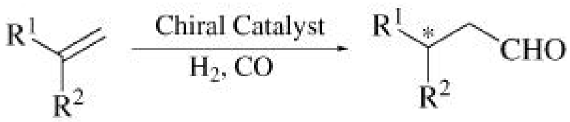

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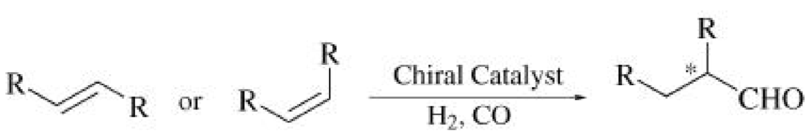


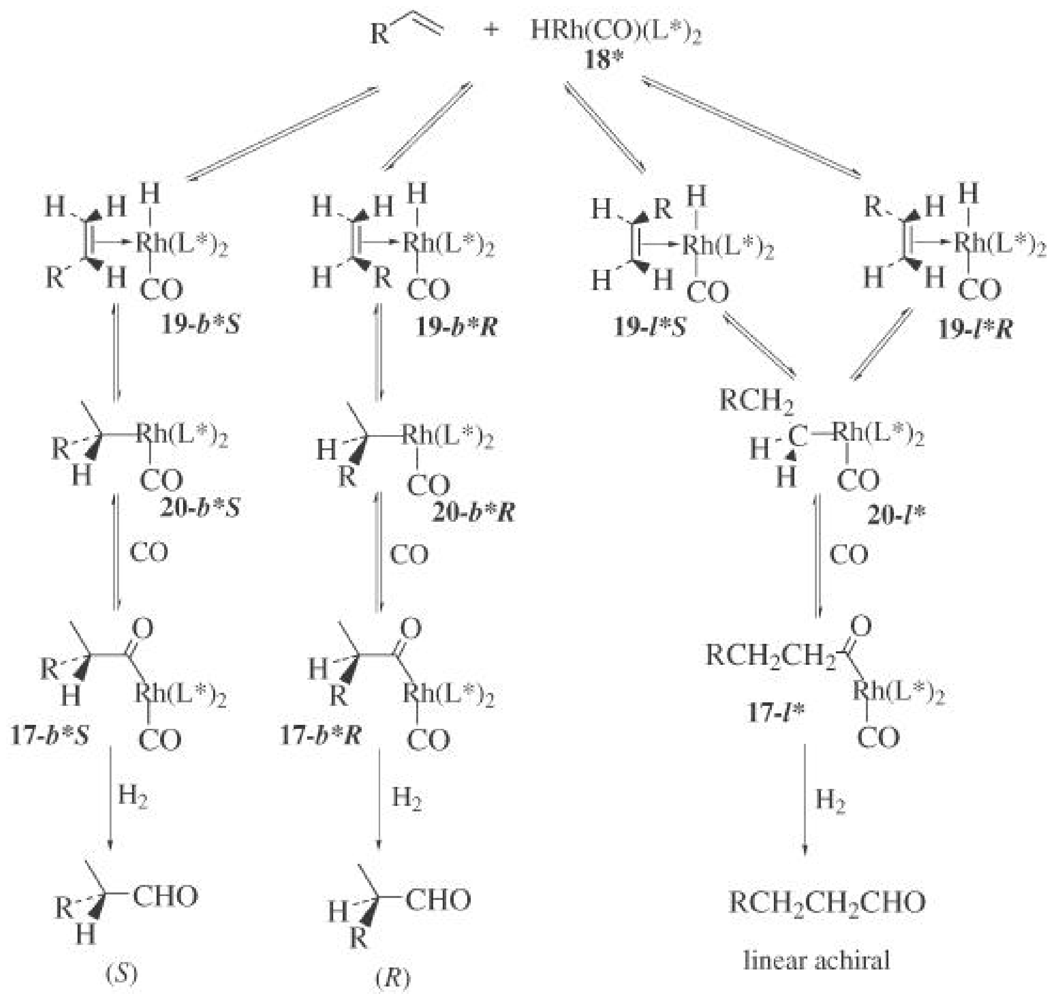
(6)

of 1-alkenes to give the corresponding branched aldehydes regioselectively and enantioselectively (Eq. 4) is the most general process, but it is more complicated than the other two ways (Eqs. 5 and 6) because of the formation of achiral linear aldehydes in substantial amounts as undesirable products.

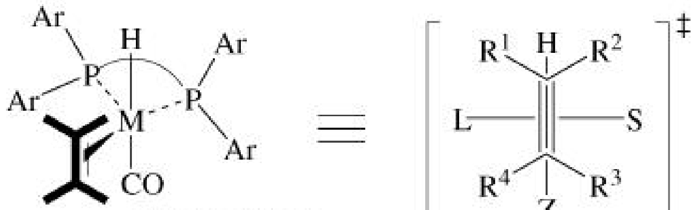
Extensive mechanistic studies have been performed on reactions catalyzed by rhodium and platinum complexes containing enantiopure C_2-symmetric diphosphine ligands. (54, 107-112) As discussed above, (1) the formation of the π-olefin-Rh(H) complex **19**, (2) stereospecific *cis* addition of the hydridorhodium to the coordinated olefin to form the alkyl-Rh complex **20** (and then **21**), and (3) the migratory insertion of a carbonyl ligand giving the acyl-Rh complex **17** with retention of configuration, have been established in the hydroformylation of 1-alkenes or substituted ethenes. Thus, it is reasonable to assume that the enantioselectivity of the reaction giving a branched aldehyde is determined at the diastereomeric (1) π -olefin-Rh complex **19** formation step, (2) alkyl-Rh complex **20** formation step, or (3) acyl-Rh complex **17** formation step.

As Scheme 5 illustrates, when a 1-alkene reacts with hydridorhodium complex with a chiral diphosphine ligand **18***, two diastereomeric π -olefin-Rh complexes, **19*-*S*** and **19*-*R***, are formed, in which the *Si* face and *Re* face of the 1-alkene coordinate to the Rh catalyst, respectively. The π -olefin-Rh complex, 19*-***S*** has two rotamers, **19*-bS** and **19*-lS**, that are relevant to the *cis* addition of the hydridorhodium. The π -olefin-Rh complex **19*-bS** gives the branched (*S*)-aldehyde via the alkyl-Rh complex **20*-bS** and the acyl-Rh complex **17*-bS**, whereas **19*-lS** leads to the formation of the linear achiral aldehyde. In the same manner, the π -olefin-Rh complexes **19*-bR** and **19*-lR** give the branched (*R*)-aldehyde and the linear achiral aldehyde, respectively.

Scheme 5.



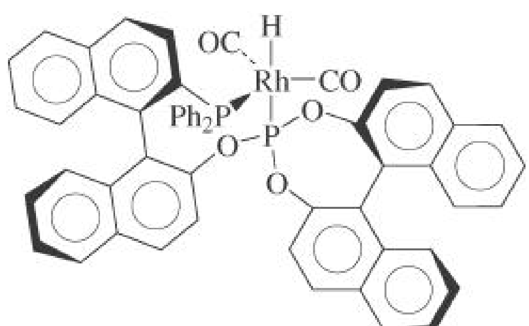
Based on the apparent importance of the relative population of the four isomers of the π -olefin-Rh complexes **19*** in determining enantioselectivity as well as regioselectivity, an empirical rule was proposed for prediction of the absolute configuration of the major aldehyde and regioselectivity in the asymmetric hydroformylation of prochiral olefins catalyzed by rhodium and platinum complexes with C_2-symmetrical chiral diphosphine ligands. (107, 108, 111) This simple quadrants model assumes the trigonal bipyramidal configuration of π -olefin-M complex **19*** (M = Rh or Pt) in the transition state of the alkyl-Rh complex formation (early transition state model) and defines the large (L) and small (S) ligands based on experimental results in a consistent manner (Z = CO). This model was successfully applied to the reactions of simple aliphatic olefins such as butenes, 2-methyl-1-butene, 2,3-dimethyl-1-butene, and norbornene. However, this model failed to give meaningful explanation and prediction for the reactions of unsaturated esters and vinylarenes such as styrene and 2-phenylpropene.



19* M = Rh, Pt

Another crucial step for asymmetric induction is the formation of alkyl-M complex **20***, i.e., the rate of olefin insertion to the M-H bond should be different in each π -olefin-M complex **19*** and this difference should be reflected in the final ratio of two enantiomeric aldehydes. (33) This possibility should be examined in the future.

Most of the molecular models for the mechanistic studies of asymmetric hydroformylation catalyzed by C_2-symmetric chiral diphosphine-Rh complexes are based on a trigonal bipyramidal structure in which two phosphorus atoms occupy equatorial positions as exemplified in **19***. In fact, recent NMR and X-ray crystallographic studies on $HRh(CO)_2$(diphosphite) complexes support this type of trigonal bipyramidal structure. (55-58) However, a different trigonal bipyramidal structure plays a key role in the hydroformylation of prochiral olefins (e.g., 94% ee for styrene, b/l = 88/12; 97% ee for (*E*)-1-phenyl-1-propene, b/l = 97/3) catalyzed by a rhodium complex with a phosphine-phosphite chiral ligand, BINAPHOS. (34) It has been shown, on the basis of NMR and IR data, that $HRh(CO)_2$(BINAPHOS) complex (**23**) takes a trigonal bipyramidal configuration in which the phosphine moiety occupies an equatorial position and the phosphite moiety as well as the hydride apical positions. (34, 113) A recent molecular modeling study has indicated that the outstanding properties of BINAPHOS can be ascribed to a combination of the unique coordination mode, adequate numbers of



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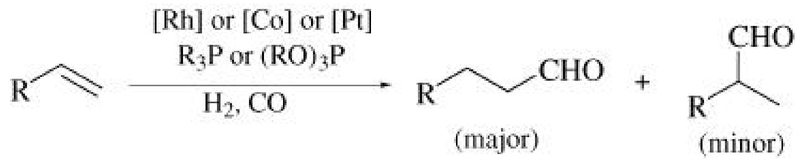
chiral centers and the matched pair configurations (*R,S* or *S,R*) of two binaphthyl moieties. This model provides a good explanation for the observed excellent enantioselectivity and branched/linear ratio. (114, 115)

3. Scope and Limitations

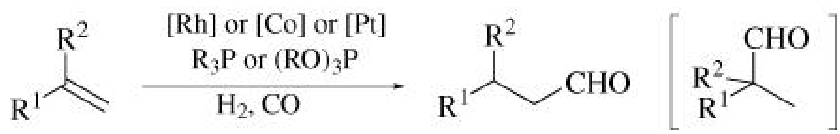
3.1. Simple Olefins

The phosphine and phosphite complexes of rhodium, cobalt, and platinum are commonly used as catalysts for hydroformylation of olefins (Eq. 7). Other



(7)

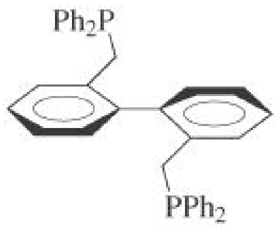
metal carbonyl complexes of ruthenium, (116, 117) iridium, (118-120) osmium, (121) manganese, (25, 122, 123) iron, (124-126) palladium, (127, 128) and rhenium (129) also possess catalytic activity. (3) In general, the reaction of vinylidene type olefins shows excellent regioselectivity with conventional catalysts because of the significant difference in the steric environment between the two ends of the olefinic bond (Eq. 8). (130, 131)



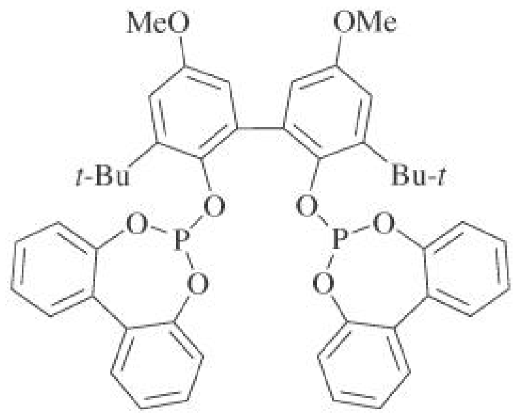
(8)

However, in order to attain high regioselectivity in the hydroformylation of simple 1-alkenes, a large excess of phosphines or phosphites should be added to cobalt and rhodium catalysts such as $Co_2(CO)_8$, $HRh(CO)(PPh_3)_3$, and $Rh(acac)(CO)_2$, which decreases the reaction rate. (3)

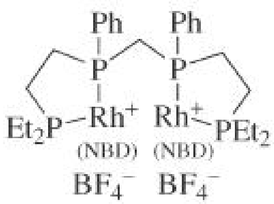
Many catalyst systems with phosphine and phosphite ligands have been developed to enhance the linear selectivity of the reaction. (104, 132-219) For example, rhodium complexes of BISBI (**24**) (linear/branched ^{3} 66.5), (132, 133, 141, 142, 149, 155, 158, 220-225) BIPHEPHOS (**25**) (l/b ^{3} 40/1), (134, 135, 160, 161) and a homobimetallic rhodium complex with “racemic-et, ph-P4” (**26**) (l/b ^{3} 27.5) (104, 226, 227) can achieve excellent linear selectivity in the hydroformylation of propene and 1-hexene. Rhodium catalyst systems with water-soluble phosphine ligands have been studied extensively (21, 180, 228-240) and it has been demonstrated that $HRh(CO)(TPPTS)_3$ [TPPTS = $P(C_6H_4SO_3Na\text{-}m)_3$] can achieve high linear selectivity. (21) In order to achieve easy separation of the product aldehydes from the catalyst, amphiphilic (241, 242) as well as thermoregulated (243) ligands have been developed. The amphiphilic ligands act on the interface of a biphasic mixture, while the thermoregulated ligands have the ability to change their solubilities as a function of temperature, allowing the catalyst species to transfer back and forth between an aqueous and an organic phase. Electrochemically prepared dimeric platinum-diphosphine complexes such as $[Pt_2(H)_2(\mu\text{-DIOP})(DIOP)_2][SnCl_3]$ (**27**) can also achieve high regioselectivity (l/b ³ 49). (244-246)



BISBI (**24**)



BIPHEPHOS (**25**)



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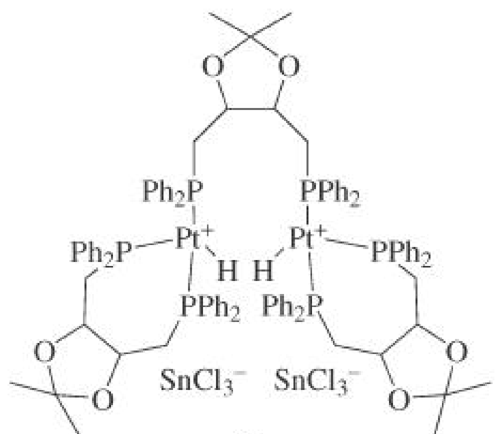
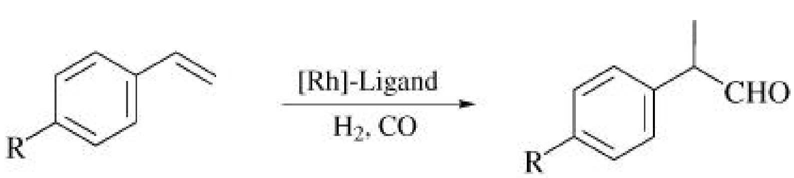


27

Rhodium complexes with a bis(diphenylmethyl)norbornane **28**, (247) a bis(dioxaphospholane) **29**, (248, 249) and α , α -TREDIP (**30**) (250) as well as a zwitterionic rhodium-borate complex **31** (251) give 2-phenylpropanal with 97–99% selectivity in the hydroformylation of styrene (Eq. 9).



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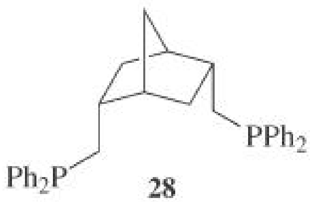

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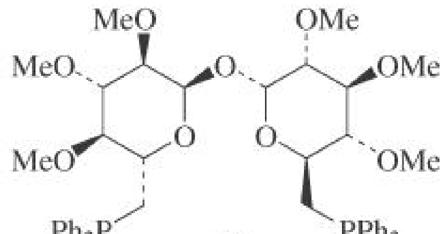

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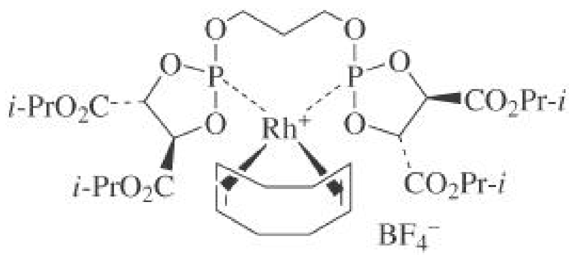

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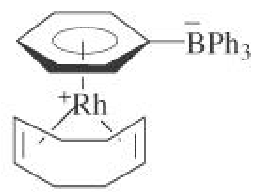
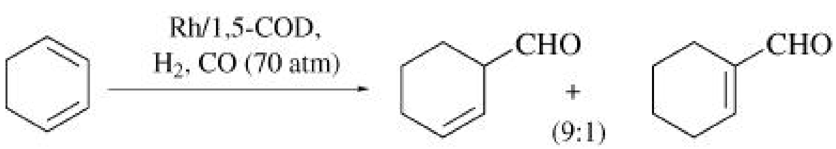


31

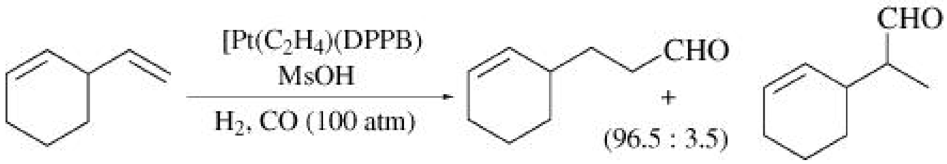
3.2. Dienes and Polyenes

The hydroformylation of conjugated dienes such as 1,3-butadiene, isoprene, and 1,3-pentadiene gives mixtures of regioisomers, isomerized aldehydes, and di-aldehydes depending on the conditions and catalysts used. (252-256) The reaction of 1,3-butadiene provides 1,6-hexanedial and has relevance to nylon production. (257, 258) The reaction of 1,3-cyclohexadiene catalyzed by a rhodium complex gives a 9:1 mixture of regioisomers (Eq. 10). Recently, high regioselectivity as well as enantioselectivity has been accomplished in the asymmetric hydroformylation of 1,3-dienes.

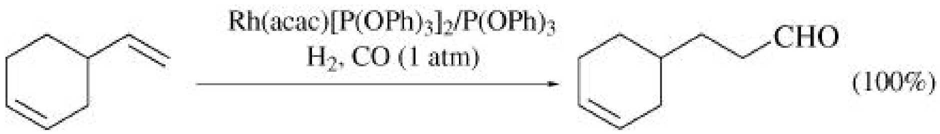


(10)

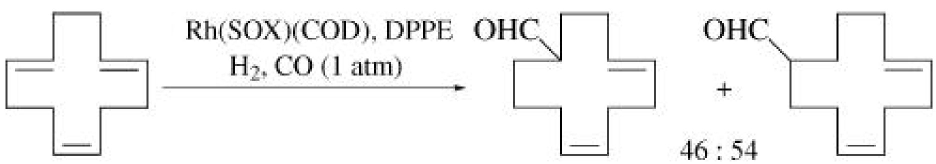
With nonconjugated dienes, the terminal olefin moiety reacts preferentially with both Pt and Rh catalyst systems (Eqs. 11, 12). (259-264) The reaction of (*E, E, Z*)-cyclododeca-1,5,9-triene gives two regioisomers (Eq. 13). (265)



(11)

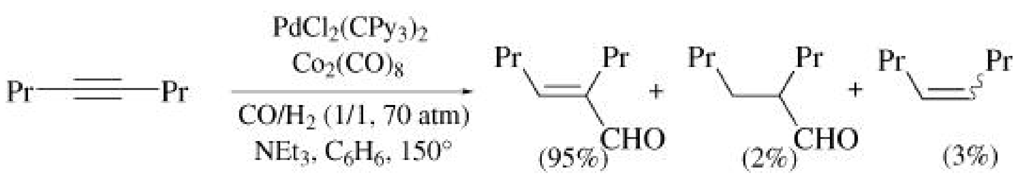


(12)



(13)

The hydroformylation of alkynes is usually accompanied by extensive hydrogenation, producing saturated aldehydes or alkenes. However, the use of bimetallic catalytic systems, such as Pd-Co, Pd-W or Pd-Fe, can achieve excellent yields in the hydroformylation of symmetric internal alkynes, affording conjugated unsaturated aldehydes (Eq. 14). (266)

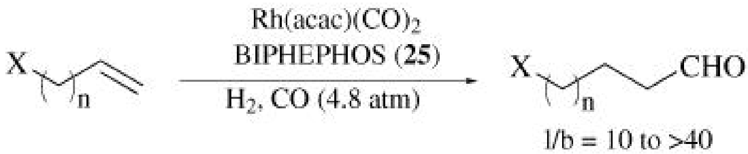


(14)

3.3. Functionalized Olefins

3.3.1. Functionalized Alkenes

Regioselective hydroformylation of functionalized alkenes has been extensively studied. (5, 135, 267, 286) The rhodium complex with BIPHEPHOS (**25**) is an excellent catalyst for regioselective hydroformylation of functionalized terminal alkenes to give aldehydes (Eq. 15). (135) A zwitterionic



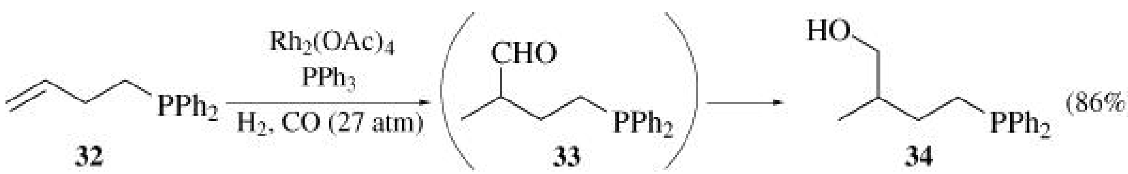
(15)

X = MeCO-. MeOC(O), PhC(O)OC(O), Et_2NCO, $(EtO)_2CH$, $(CH_2CO)_2N$; n = 0 to 8

rhodium complex, $[Rh(DPPB)(COD)][BPh_4]$ (DPPB = $Ph_2P(CH_2)_4PPH_2$), is also a good catalyst for the reaction of allyl alkanoates, yielding aldehydes with 91–95% regioselectivity. (267, 287)

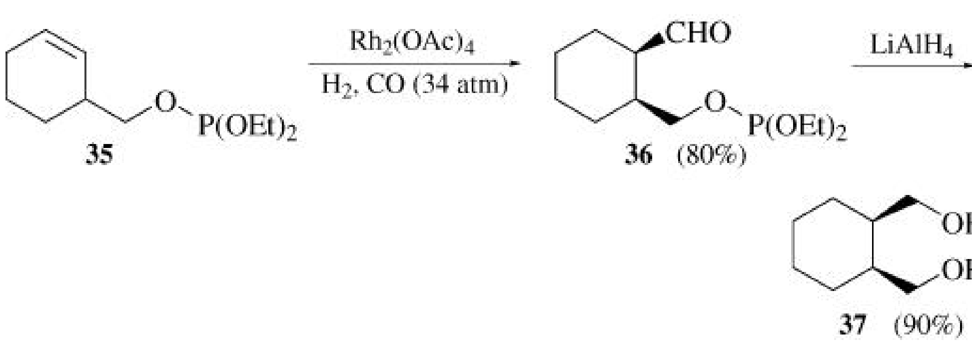
3.3.2. Functional Group–Directed Hydroformylation

Phosphine and phosphite moieties in olefinic substrates exert strong directing effects on the regioselectivity of hydroformylation. For example, hydroformylation of 4-(diphenylphosphino)-1-butene (**32**) catalyzed by $Rh_2(OAc)_4/4PPh_3$ gives branched aldehyde **33**, which subsequently is reduced to provide the corresponding alcohol **34** as the sole product (Eq. 16). (288, 289) Under the same conditions, 1-hexene affords the linear aldehyde



(16)

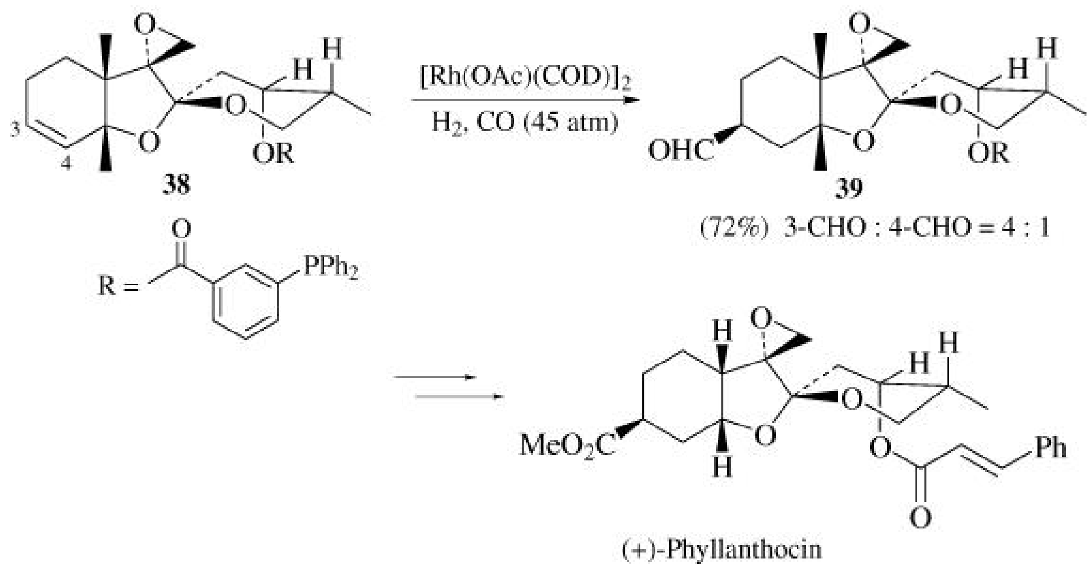
as the major product. Similar strong directing effects of a phosphite moiety are observed in reactions of cyclic and acyclic alkenylphosphites, e.g., cyclohexenyl phosphite **35** is converted to *cis*-1,2-bis(hydroxymethyl)cyclohexane (**37**) with 100% regio- and stereoselectivity after reduction of the intermediate aldehyde **36** (Eq. 17). (290, 291) The use of phosphite as an intramolecular directing group



(17)

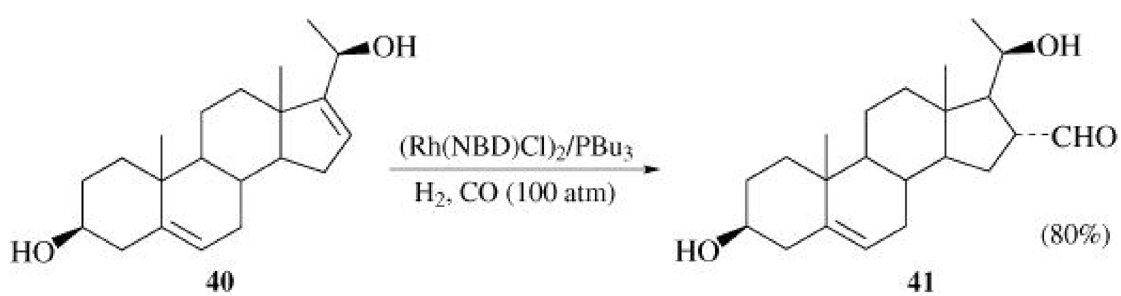
is attractive for organic syntheses since the phosphite moiety can be easily introduced and then readily removed after regioselective hydroformylation.

Intramolecular phosphine-directed hydroformylation has been successfully applied as a key step in the synthesis of (+)-phyllanthocin (Eq. 18). (292)



(18)

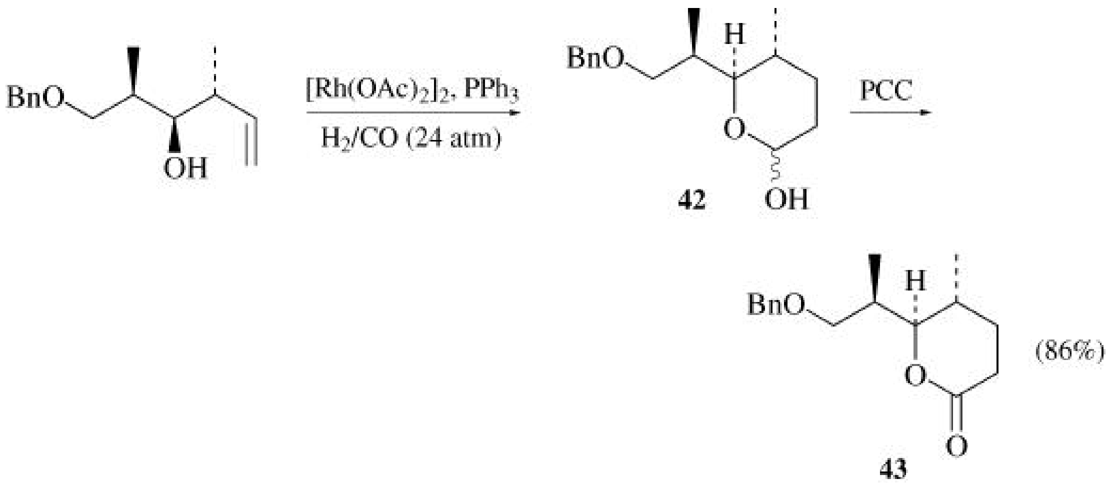
Hydroxy-directed hydroformylation of (20*R*)-3 β -dihydroxypregna-5,16-diene (**40**) catalyzed by $Rh_2Cl_2(NBD)_2/PBu_3/NEt_3$ gives 16 α -aldehyde **41** in 80% yield after recrystallization (Eq. 19). (293)



(19)

3.3.3. Alkenyl and Alkynyl Alcohols

Rhodium-catalyzed hydroformylation of unsaturated alcohols provides useful intermediates for organic syntheses. (294-312) For example, hydroformylation of homoallylic alcohols gives isolable lactols **42**, (313) which can be oxidized to the corresponding lactones **43** (Eq. 20). (314)The



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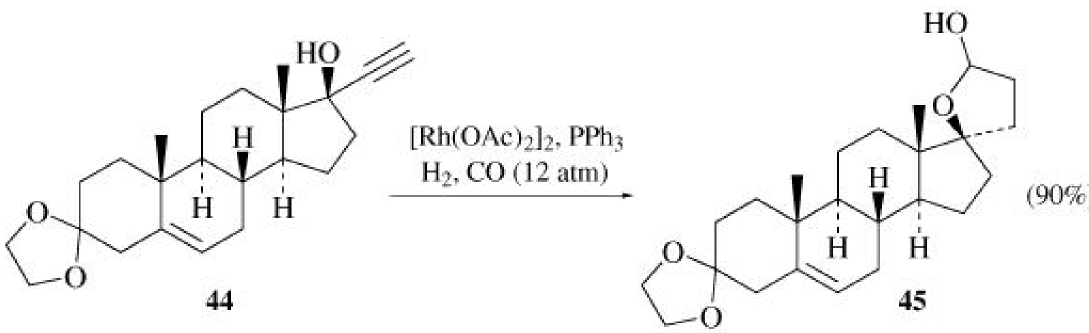
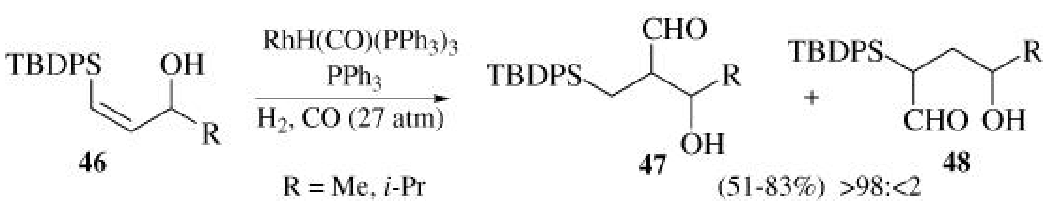
propargyl alcohol moiety of steroid **44** reacts selectively to give lactol **45** with the trisubstituted olefin left intact (Eq. 21). (748)



(21)

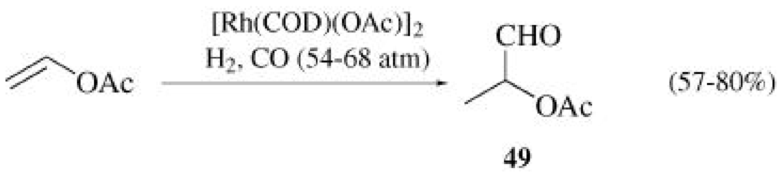
As an approach to the synthesis of aldols, hydroformylation of (*Z*)- β -silylallyl alcohols **46** catalyzed by $RhH(CO)(PPh_3)_3$/ PPh_3 gives **47** with high regioselectivity (>98%) (Eq. 22). (315)



(22)

3.3.4. Alkenyl Esters

Hydroformylation of vinyl acetate gives exclusively the branched aldehyde **49** (Eq. 23), (316-318) while the linear aldehyde **50** is the predominant product in the reaction of allyl acetate (Eq. 24). (267)



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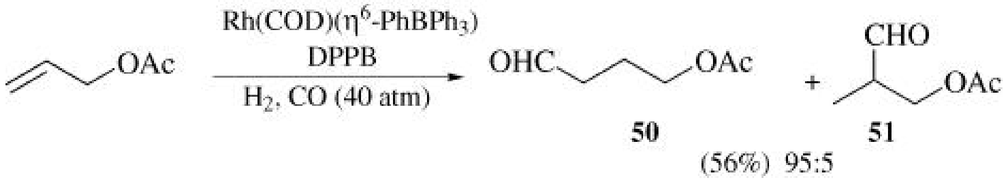
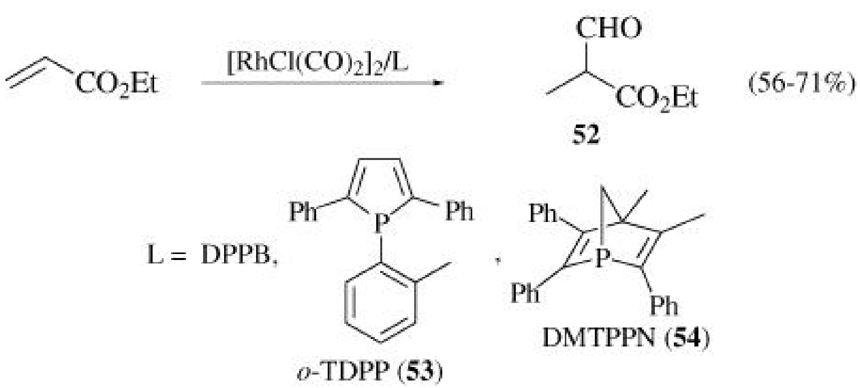


(24)

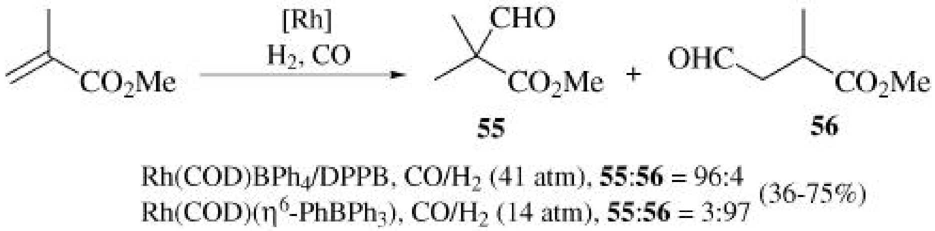
3.3.5. α , β -Unsaturated Esters

Hydroformylation of α , β -unsaturated esters and diesters generally gives α -formyl esters, (319-323) but with some exceptions. (324) Hydroformylation of ethyl acrylate is catalyzed by the $Rh_2Cl_2(CO)_2$/phosphine/NEt_3 system under mild conditions (20–40°, H_2/CO (1/1, 20 atm) to give ethyl 2-formylpropanoate (**52**) with high regioselectivity (98–100%) (Eq. 25). (319) A



(25)

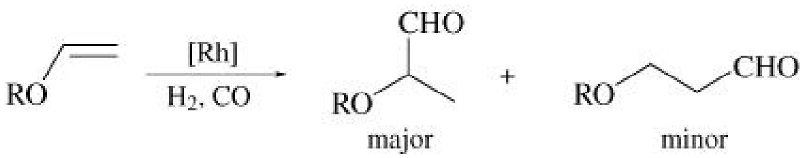
phosphole (*o*-TDPP) (**53**), a phosphanorbornadiene (DMTPPN) (**54**), and DPPB are particularly effective ligands for this reaction. Regioselectivity of hydroformylation of methyl methacrylate is highly dependent on the catalyst used and reaction temperature, and can provide 2-formyl-2-methylpropanoate (**55**) or 3-formyl-2-methylpropanoate (**56**) selectively (Eq. 26). (251, 325)



(26)

3.3.6. Vinyl Ethers

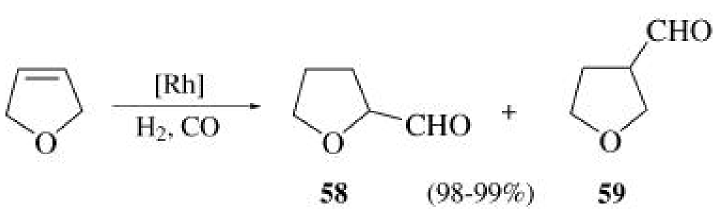
Hydroformylation of vinyl ethers provides efficient routes to alkoxy aldehydes. (326-331) The reaction of terminal vinyl ethers gives mixtures of regioisomers, the branched aldehyde being the major product (Eq. 27). (332) The



(27)

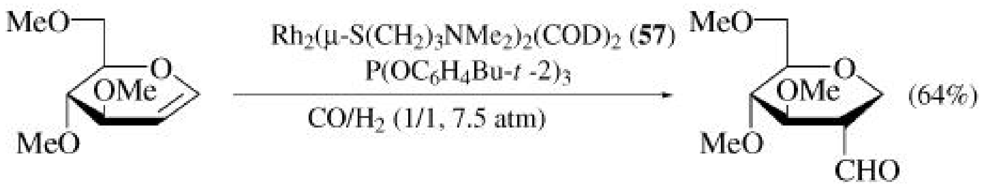
regioselectivity depends on the substituent R, e.g., methyl vinyl ether gives methoxypropanal with a b/l ratio of 54/46, while a b/l ratio of 95/5 is observed for phenyl vinyl ether. (332)

Hydroformylation of 2,3- or 2,5-dihydrofuran gives a mixture of 2- and 3-formyltetrahydrofuran (**58**, **59**), since isomerization of the double bond appears to take place extensively (Eq. 28). (333) Under optimized conditions using $Rh_2[\mu\text{-}S(CH_2)_3NMe_2]_2(COD)_2$ (**57**)



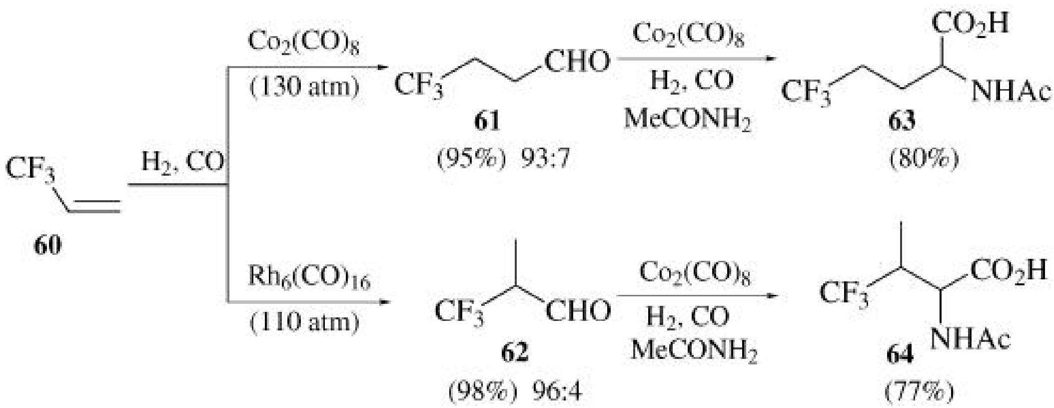
(28)

and 10 equivalents of PPh_3 or $P(OMe)_3$, 3-for-myltetrahydrofuran (**59**) is obtained from 2,5-dihydrofuran with 99% regioselectivity. (333, 334) In contrast, reactions of dihydro-2*H*-pyrans with the same catalyst system do not occur selectively. (333) However, this catalyst system has been successfully applied to achieve regio- and stereoselective hydroformylation of glucal derivatives (Eq. 29). (335) Alkenyl acetals can be employed as substrates for hydroformylation, giving the corresponding monoacetals of alkanedials. (336-340)

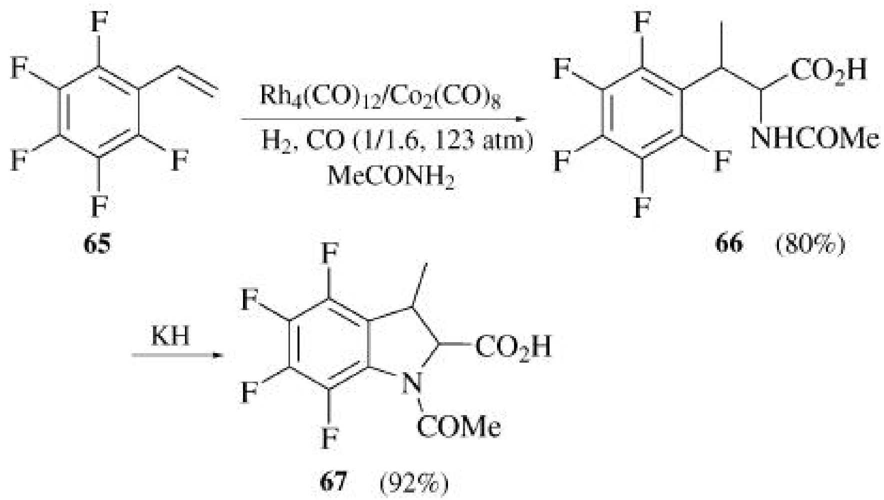
 (29)

3.3.7. Halogenated Alkenes

Hydroformylation of vinyl chloride gives 2-chloropropanal, a versatile intermediate for agrochemical and pharmaceutical agents. (341-353) The hydroformylation of 3,3,3-trifluoropropene (**60**) catalyzed by $Co_2(CO)_8$ gives 3-trifluoromethylpropanal (**61**) with high linear selectivity (l/b = 93/7), while reactions catalyzed by rhodium complexes afford 2-trifluoromethylpropanal (**62**) with excellent branched selectivity (l/b = 5/95 - 3/97) (Eq. 30). (354, 355) These trifluoromethylpropanals are further transformed to *N*-acetyltrifluoronorvaline (**63**) and *N*-acetyltrifluorovaline (**64**) through

 (30)

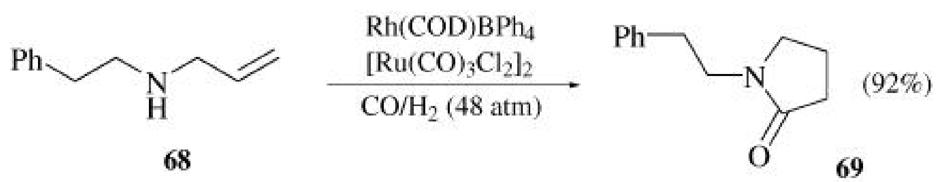
amidocarbonylation in high yields (Eq. 30). (356) The rhodium complex-catalyzed hydroformylation of other fluoroolefins, $R_fCH = CH_2$ (R_f = F, perfluoroalkyl, C_6F_5), also gives the corresponding branched aldehydes with 92–100% selectivities. (355, 357, 358) The hydroformylation-amidocarbonylation of pentafluorostyrene (**65**) catalyzed by $Rh_4(CO)_{12}$/ $Co_2(CO)_8$ affords 3-methylpentafluorophenylalanine (**66**) in one step with 98% regioselectivity; **66** is readily cyclized to tetrafluoroindole **67** (Eq. 31). (359)



(31)

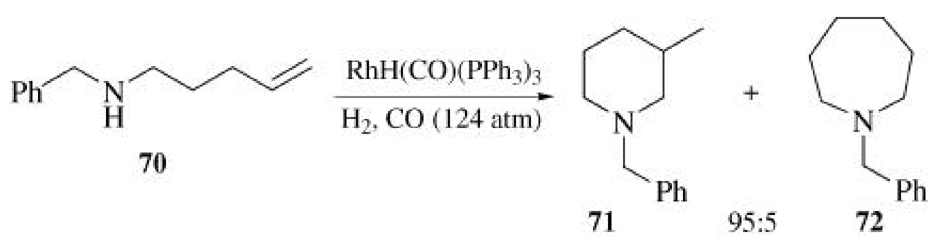
3.3.8. Alkenylamines and Alkenylamides

Hydroformylations of olefins bearing amine or amide groups often give nitrogen heterocycles through condensation of the resulting aldehyde and the amine or amide moiety. (248, 278, 313, 360-364) The reaction of *N*-allyl-*N*-(2-phenylethyl)amine (**68**) catalyzed by a Rh/Ru mixed system gives pyrrolidinone **69** exclusively in high yield (Eq. 32). (360)



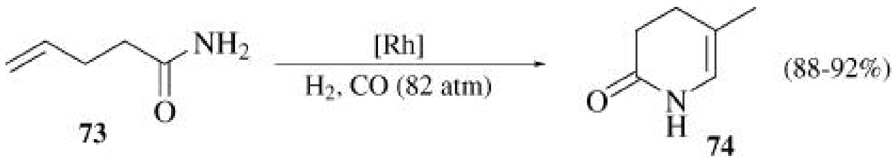
(32)

Amine-directed hydroformylation of 5-benzylamino-1-pentene (**70**) catalyzed by $RhH(CO)(PPh_3)_3$ affords methylpiperidine **71** with 95% regioselectivity via the branched aldehyde intermediate (Eq. 33). (362) In the same manner, reaction of



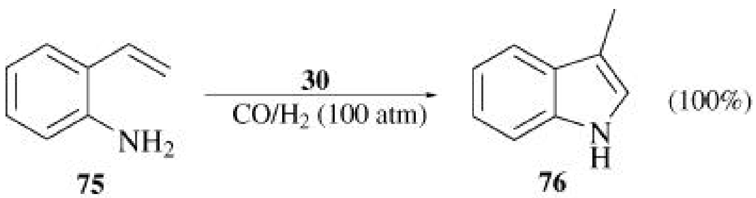
(33)

4-pentenamide **73** catalyzed by $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $RhH(CO)(PPh_3)_3$ or $Rh_4(CO)_{12}$ leads to the exclusive formation of methyldihydropyridone **74** in excellent yield (Eq. 34). (363)



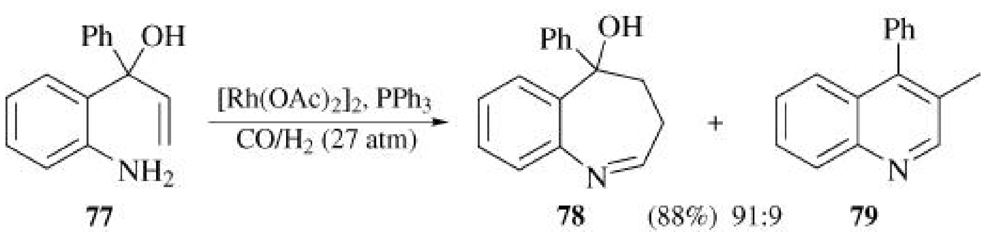
(34)

Hydroformylation of 2-aminostyrene (**75**) catalyzed by the diphosphite-Rh complex **30** gives 3-methylindole (**76**) in quantitative yield (Eq. 35). (248) In a similar



(35)

manner, reaction of 2-amino-1-(1-hydroxy-2-propenyl)benzene (**77**) affords a 91:9 mixture of didehydrobenzoazepine **78** and quinoline **79** in high yield (Eq. 36). (313, 361) A tricyclic benzimidazole **81** is formed in one step in high yield from 1-alkenylamino-2-aminobenzene **80** (Eq. 37). (364)



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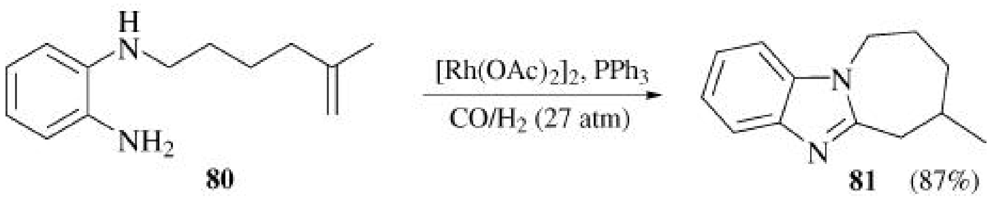
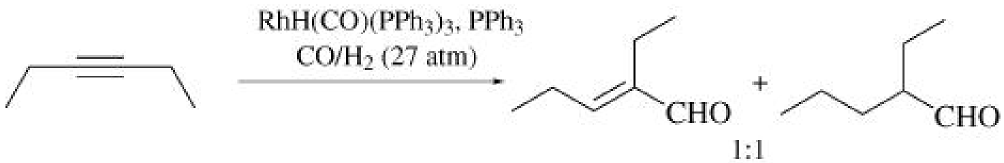


(37)

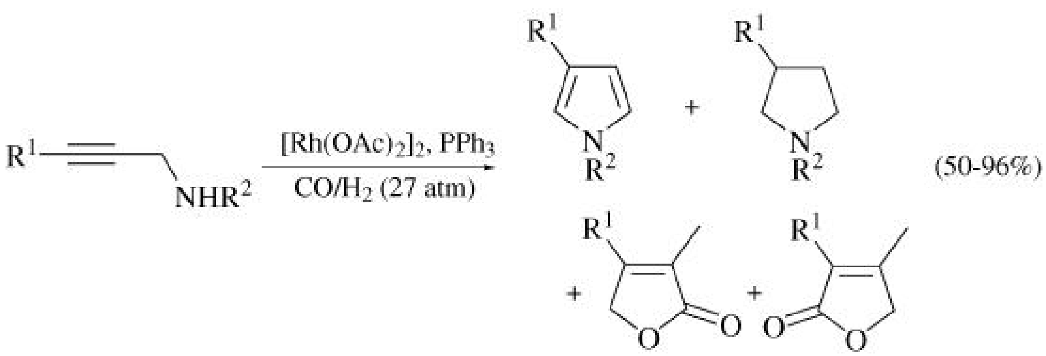
3.3.9. Miscellaneous

Substrates containing phosphorus, sulfur and silicon functional groups, e.g., -P(O)R_2, (288, 365) -P(O)(OR^1)R^2, (366) -SR, (367-370) -S(O)R, (369, 371) -SO_2R, (369, 371) -CH$(SR)_2$, (135, 367, 372-374) -SiR_3, (118, 315, 368, 375, 376) -OSiR_3, (135) and -Si$(OR)_3$, (375, 377) undergo hydroformylation with rhodium and cobalt catalysts to give the corresponding aldehydes. Phosphine and phosphite moieties possess strong directing effects as described above (see Eqs. 16, 17). Although hydroformylation of alkynes gives the corresponding conjugated aldehydes in moderate yield accompanied by saturated aldehydes (Eq. 38), (368, 378, 379) reactions of functionalized alkynes



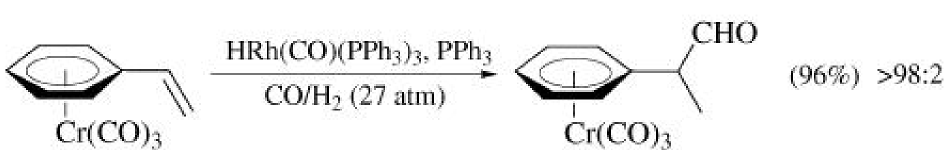
(38)

often give carbocyclic or heterocyclic compounds. (380-383) Propargylamines form pyrroles, usually accompanied by lactone byproducts arising from deamination, as well as hydrogenated byproducts (Eq. 39). (380, 384) Alkenes bearing organometallic



(39)

moieties such as vinylferrocene, (385, 386) vinylbenzene- $Cr(CO)_3$, (387) and indene- $Cr(CO)_3$ (387, 388) are good substrates for hydroformylation. The benzene-chromium moiety has a strong directing effect to form the branched aldehyde in excellent regioselectivity (Eq. 40). (387) Hydroformylation of oxiranes gives 1,3-diols or



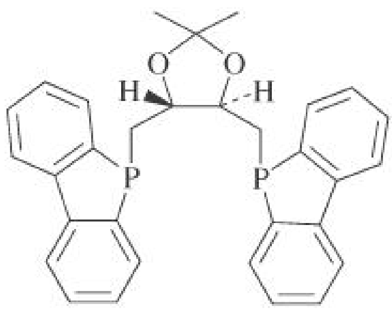
(40)

3-hydroxyaldehydes. (389-393) The hydroformylation of polymers bearing unsaturated tethers or pendant groups is useful for the production of polymers with formylalkyl groups. (394-397)

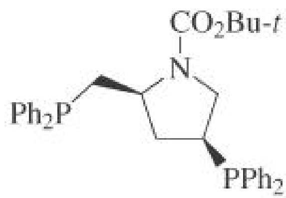
3.4. Asymmetric Hydroformylation

Asymmetric hydroformylation of prochiral olefins has been investigated both for the elucidation of reaction mechanism and for development of a potentially useful method for asymmetric organic synthesis. Rhodium and platinum complexes have been extensively studied, and cobalt complexes to a lesser extent. A variety of enantiopure or enantiomerically enriched phosphines, diphosphines, phosphites, diphosphites, phosphine-phosphites, thiols, dithiols, *P,N*-ligands, and *P,S*-ligands have been developed as chiral modifiers of rhodium and platinum catalysts. (33, 398-403)

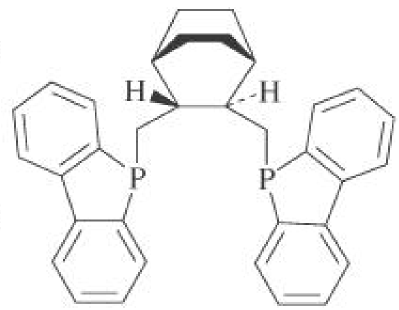
In spite of extensive studies on the asymmetric hydroformylation of olefins using chiral rhodium and platinum complexes, enantioselectivities had not exceeded 60% ee until the reaction of styrene catalyzed by $PtCl_2$(DBP-DIOP)/ $SnCl_2$ (**82**) was reported to attain 95% ee in 1982. (404) Although the value was corrected to 73% ee in 1983, (405) this result spurred further studies of the reaction (Eq. 41) in connection with possible commercial synthesis of anti-inflammatory drugs such as (*S*)-ibuprofen and (*S*)-naproxen. The catalyst $PtCl_2$(BPPM)/ $SnCl_2$ (**83**) is useful for asymmetric hydroformylation of styrene and its derivatives, yielding the branched aldehyde **86**. (406) For example, this catalyst gave the corresponding aldehyde in 70–80% ee for styrene, 80% ee for *p*-isobutylstyrene, and 81% ee for 2-ethenyl-6-methoxynaphthalene. Although the branched/linear ratios were low (0.5–0.7), the enantioselectivities achieved were considerably higher than those realized with any other chiral catalyst system at that time. A chiral platinum catalyst, $PtCl_2$(BCO-DBP)/ $SnCl_2$ (**84**), also achieved 86% ee for the reaction of styrene with much better branched/linear ratio (4:1). (407) Higher enantioselectivity (91% ee) for the hydroformylation of styrene was achieved with the platinum-bis(phosphite) **85**-Sn system, although regioselectivities did not exceed a branched/linear ratio of 60/40. (408)



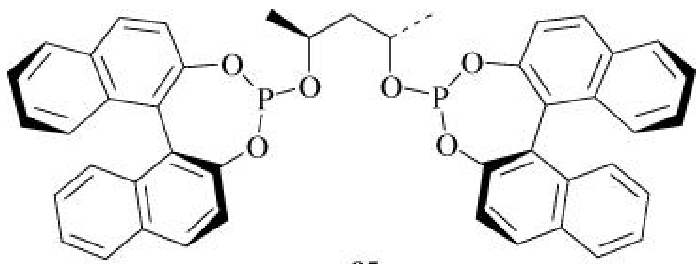
DBP-DIOP (**82**)



BPPM (**83**)



BCO-DBP (**84**)

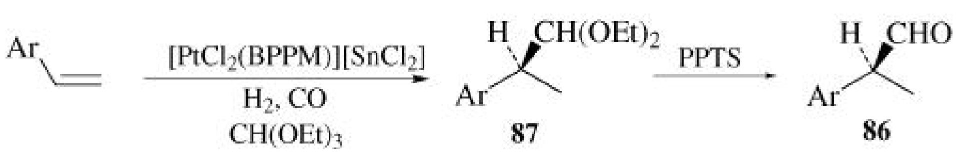


85

86

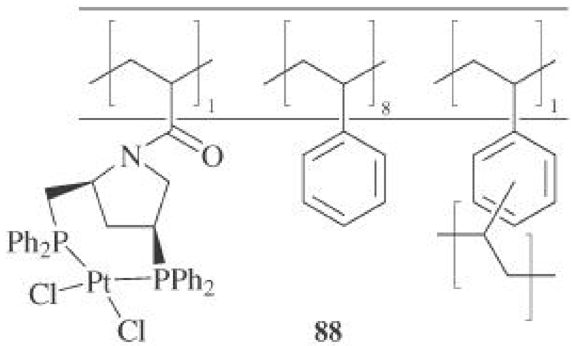
(41)

One of the difficulties in achieving high enantioselectivity in asymmetric hydroformylation is the propensity of chiral aldehydes **86** to racemize under the reaction conditions. Accordingly, if the chiral aldehyde can be converted to a less labile derivative in situ, higher enantioselectivity might be anticipated. In fact, when asymmetric hydroformylation of styrene and its derivatives catalyzed by $PtCl_2$(BPPM)/ $SnCl_2$ is carried out in triethyl orthoformate, the diethylacetals of chiral aldehydes **87** are obtained with >96% ee (Eq. 42). (406, 409, 410) It is reported



(42)

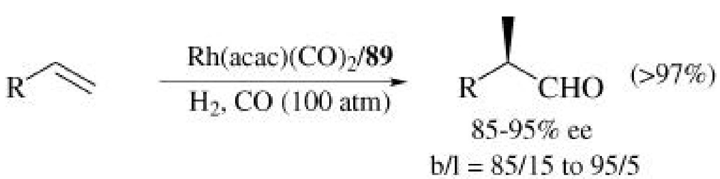
that a chiral platinum-phosphine catalyst anchored on cross-linked beads **88** bearing BPPM as the pendant group gives virtually the same enantioselectivity (up to



88

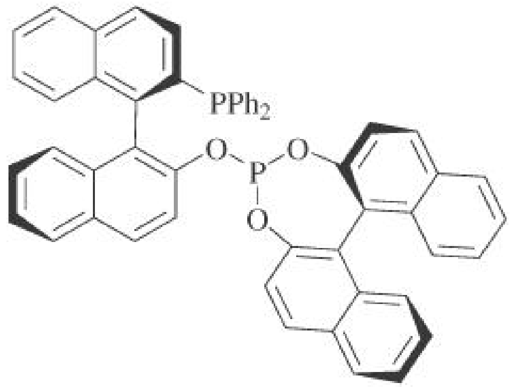
>98% ee at 22% conversion) as that attained by the homogeneous catalyst system in the reaction of styrene. (406, 410-412) Hydroformylations in triethyl orthoformate are slow, but enantioselectivities are excellent. Because of the low reaction rate and low regioselectivity, this protocol does not appear to be practical.

A breakthrough in asymmetric hydroformylation has been realized by using rhodium complexes with a novel phosphine-phosphite ligand, (*R,S*)-BINAPHOS (**89**). (34) The Rh(acac)$(CO)_2$-BINAPHOS (**89**) catalyst can achieve excellent enantioselectivities (85–95% ee) in the hydroformylations of a variety of prochiral olefins such as vinyl acetate, *N*-vinylphthalimide, styrene and its derivatives, and 1,3-dienes (34, 36, 413) with high branched/linear ratios (84/16–92/8) and good reaction rates at 60–80° (Eq. 43). A similar phosphine-phosphite ligand, (*S,R*)-BIPHENPHOS (**90**), has also been developed, and its Rh complex can achieve the same high level of enantioselectivity as (*R,S*)-BINAPHOS. (414, 415)

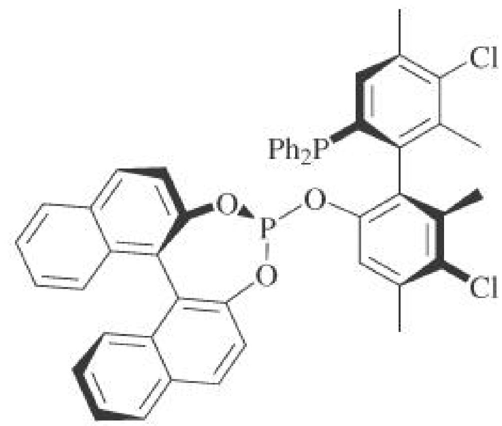


(43)

R = AcO, phthalimido, phenyl, tolyl, 4-isobutylphenyl

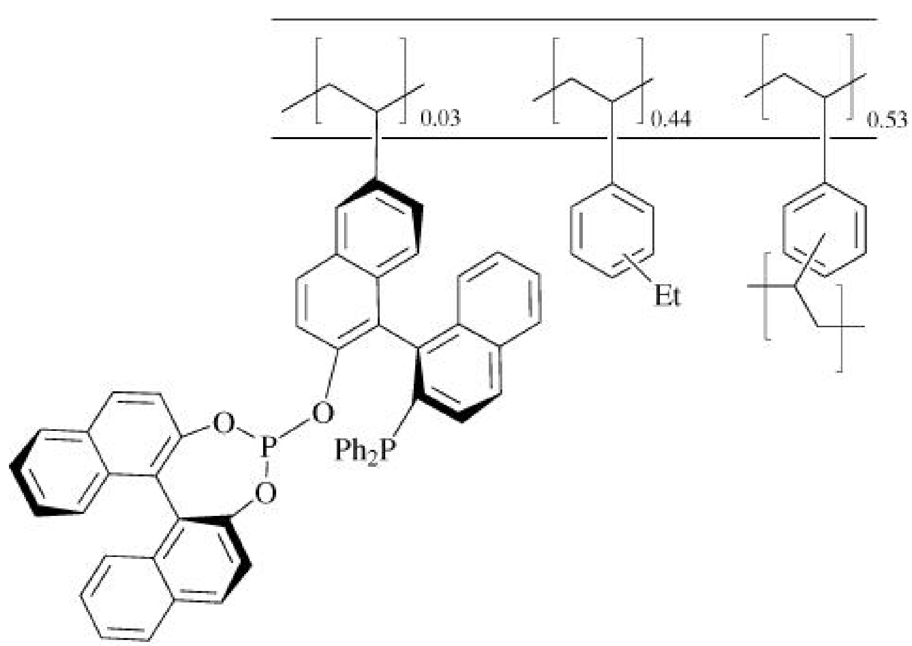


(*R,S*)-BINAPHOS (**89**)



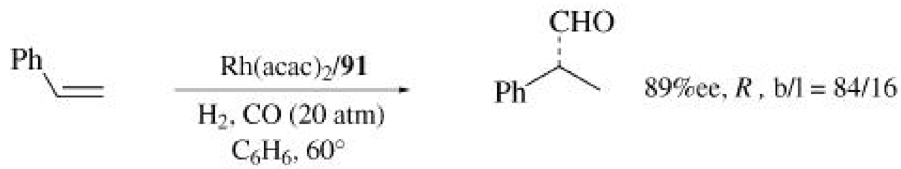
(*S,R*)-BIPHEMPHOS (**90**)

A rhodium complex with a polymer-supported (*R,S*)-BINAPHOS (**91**) has achieved high enantioselectivities similar to those obtained in the homogeneous system, showing promise for the development of practical heterogenized reusable chiral catalysts (Eq. 44). (416)



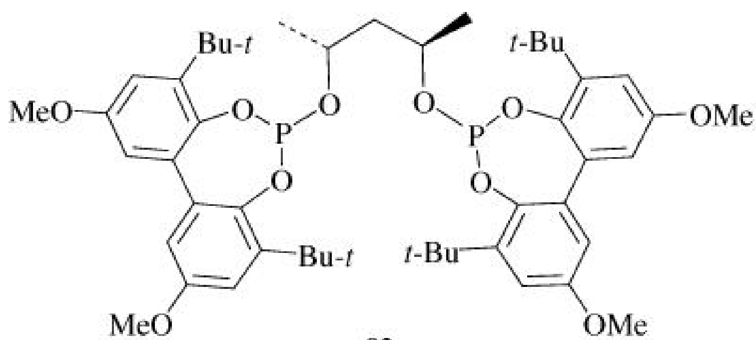
91

The Rh complex with the chiral diphosphite ligand **92** derived from (*R,R*)-pentane-2,4-diol has shown enantioselectivity up to 90% ee with 98% branched

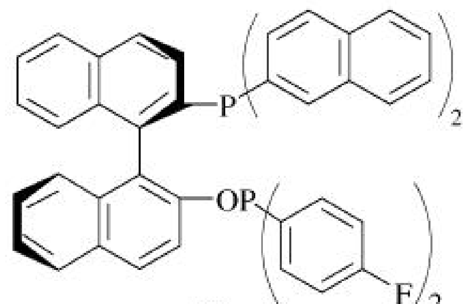


(44)

aldehyde selectivity. (38, 417) Phosphine-phosphinite ligands such as **93** show high asymmetric induction and high regioselectivity in the Rh-catalyzed hydroformylation of 4-vinyl- β -lactams. (418)

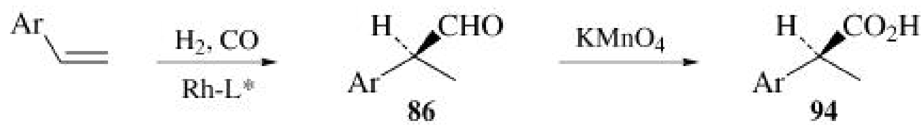


92



93

Chiral aldehydes with high enantiopurity obtained through asymmetric hydroformylation serve as useful intermediates for pharmaceutical drugs. (419) For example, (*S*)-2-arylpropanals (**86**) can be oxidized to the corresponding (*S*)-2-arylpropanoic acids **94**, which are anti-inflammatory drugs such as (*S*)-ibuprofen (**94a:** Ar = 4-isobutylphenyl), (*S*)-naproxen (**94b:** Ar = 6-methoxynaphthyl), and (*S*)-suprofen (**94c:** Ar = 4-(2-thienylcarbonyl)phenyl) (Eq. 45). (406)



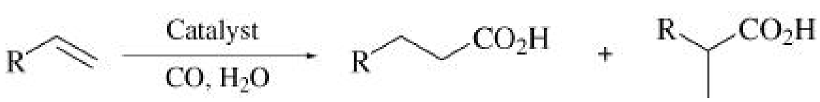
(45)

4. Comparison with Other Methods

Hydroformylation is a useful catalytic method for the synthesis of aldehydes from alkenes and alkynes. There are no other methods that compete directly with hydroformylation for the synthesis of alkyl aldehydes. However, when the desired compounds are carboxylic acids or esters, and aldehydes are used as their intermediates, there are other methods that can give the desired compounds directly from alkenes, i.e., hydrocarbohydroxylation and hydrocarbalkoxylation catalyzed by transition metal complexes. (4, 420) The hydroformylation of alkynes does not cleanly afford conjugated alkenyl aldehydes mainly because of extensive hydrogenation associated with the process. For the synthesis of conjugated alkenyl aldehydes, the formylation of aryl halides, alkenyl iodides, alkenyl triflates, and allylic halides is a convenient method. The silylformylation of alkynes also provides an efficient method, although a silyl group is incorporated in the product along with a formyl group.

4.1. Hydrocarbohydroxylation and Hydrocarbalkoxylation

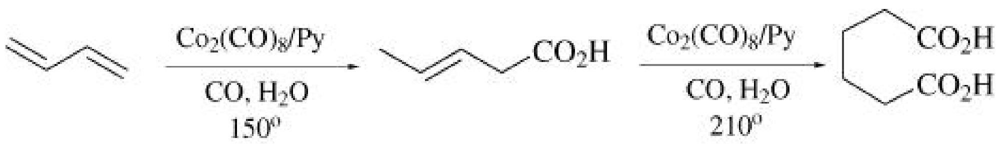
The hydrocarbohydroxylation of 1-alkenes is promoted by nickel, cobalt, platinum, and palladium catalysts to give linear and branched alkanoic acids in differing ratios (Eq. 46). (4, 420, 421) Nickel catalysts, e.g., $Ni(CO)_4$, $NiCl_2$, NiI_2 and



(46)

Raney Ni, favor formation of the branched product, while $Co_2(CO)_8$/pyridine, $H_2PtCl_6/SnCl_2$, and $PdCl_2(PPh_3)_2$/ HCl catalyst systems give the linear carboxylic acid as the predominant product. (420) The nickel and cobalt catalysts usually require high temperature (150–250°) and high carbon monoxide pressure (150–250 atm). Although platinum and palladium catalysts can promote the reaction at lower temperatures, often an extremely high pressure (700–800 atm) is required. (420, 421) Although the platinum catalyst $H_2PtCl_6/SnCl_2$ can only promote the reaction of 1-alkenes, (422) other catalysts can be used for internal olefins, cyclo-alkenes, and vinylidenealkanes. (421)

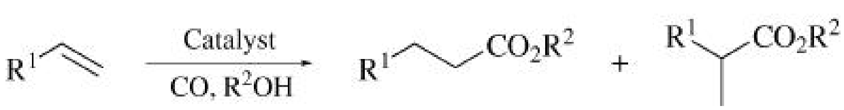
The reaction of 1,3-butadiene catalyzed by $PdCl_2(PPh_3)_2$/ HCl (120–140°, 700 atm) (421) and $Co_2(CO)_8$/pyridine (160°, 250 atm) forms 3-buten-1-oic acid in high yield, and this can be further transformed to adipic acid in a reasonable yield using the cobalt catalyst at higher temperature (210°) (Eq. 47). (420)

 (47)

A palladium complex generated in situ by mixing $Pd(OAc)_2$ with DPPB and HCO_2H (2 equivalents) is an excellent catalyst system for the hydrocarbohydroxylation of a variety of terminal olefins, which gives linear acids with excellent regioselectivity (74–100%) at 150° and 6.8 atm of carbon monoxide. (423) For example, the reactions of 2,4,6-trimethylstyrene, 3,3-dimethyl-1-butene, 2,2-dimethyl-4-pentanal, and 4-vinylcyclohexene (Eq. 48) give the corresponding linear acids as the only products in high yields (75–98%).

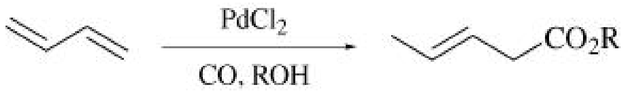
(48)

In a manner similar manner, the hydrocarbalkoxylation (commonly called hydroesterification) of alkenes in the presence of alcohols can be effected by the nickel, cobalt, platinum, and palladium catalysts described above (Eq. 49). (4, 420, 421)



(49)

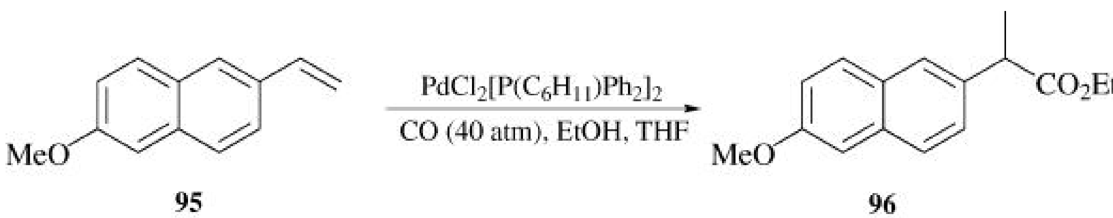
The reaction of 1,3-butadiene catalyzed by $PdCl_2$ gives an alkyl 3-pentenoate (Eq. 50), whereas the $Pd(OAc)_2(PPh_3)_2$-catalyzed reaction yields an alkyl 3,8-nonadienonate via a dimerization-carbonylation process (Eq. 51). (4, 424)



(50)

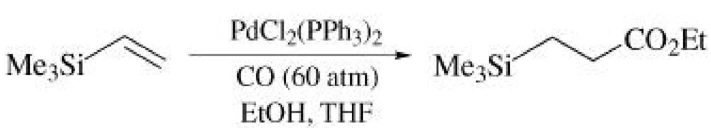
(51)

An (*R,S*)-naproxen ester **96** is obtained through regioselective hydrocarbalkoxylation of 6-methoxy-2-naphthylethene (**95**) catalyzed by $PdCl_2[P(c\text{-}C_6H_{11})Ph_2]_2$ with 100% regioselectivity in 95% yield (Eq. 52). (425)

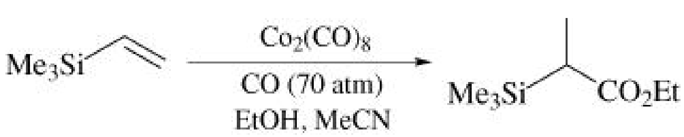


(52)

The hydrocarbalkoxylation of trimethylvinylsilane catalyzed by $PdCl_2(PPh_3)_2$ gives 3-(trimethylsilyl)propanoate with 95–100% selectivity, while the $Co_2(CO)_8$-catalyzed reaction affords 2-(trimethylsilyl)propanoate with 91–100% selectivity (Eqs. 53, 54). (426) A platinum complex, $PtCl_2(AsPh_3)_2$, can also give the linear product with 100% selectivity. The reactions of other vinylsilanes bearing different



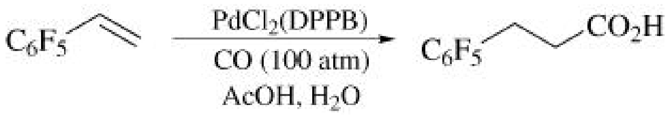
(53)



(54)

substituents on silicon show the regioselectivity switching between the palladium and the cobalt catalysts as well. Highly regioselective hydrocarbohydroxylation of trimethylvinylsilane can be effected by $PdCl_2(PPh_3)_2$, giving 3-(trimethylsilyl)propanoic acid in 95% yield. (426)

The hydrocarbohydroxylation of pentafluorostyrene catalyzed by $PdCl_2$(DPPB) in AcOH/ H_2O gives 3-(pentafluorophenyl)propanoic acid with >99% selectivity, whereas the hydrocarbalkoxylation of pentafluorostyrene catalyzed by $PdCl_2(PPh_3)_2$ in MeOH/benzene yields methyl 2-(pentafluorophenyl)propanoate with 95% selectivity (Eqs. 55, 56). (427)



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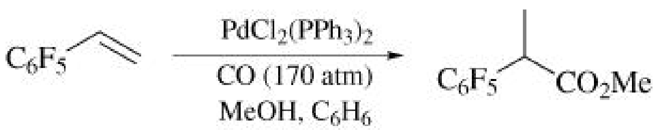
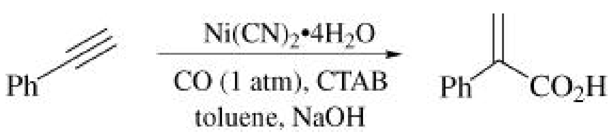


(56)

The hydrocarbohydroxylation of phenylacetylene catalyzed by $Ni(CN)_2$ under mild phase transfer conditions using cetyltrimethylammonium bromide (CTAB) gives atropic acids in excellent yield (Eq. 57). (428)

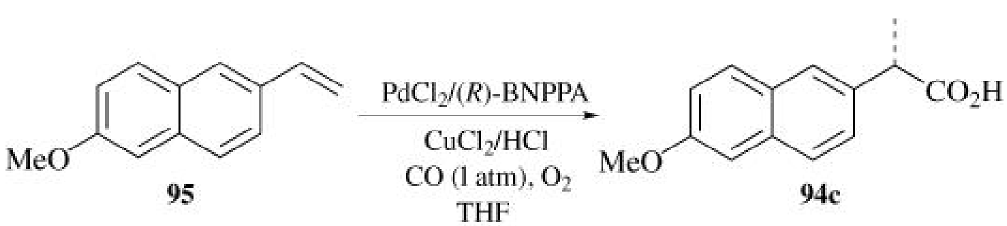


(57)

4.2. Asymmetric Hydrocarbohydroxylation and Hydrocarbalkoxylation
Asymmetric hydrocarbalkoxylation of alkenes has been studied since early 1970s, but the number of papers published on this subject is much less than that on asymmetric hydroformylation. This is mainly due to the fact that these reactions catalyzed by palladium complexes with chiral phosphine ligands usually require a very high pressure of carbon monoxide, which is rather difficult for academic laboratories to provide. However, new processes that do not require high pressure have been developed, which make these potentially useful reactions in organic synthesis more attractive. Apparently, it has been difficult to achieve high enantioselectivity in these reactions. (111) For example,

until 1997 the best enantioselectivity attained in asymmetric hydrocarbalkoxylation was 69% ee (at 8% conversion) in the reaction of 2-phenylpropene with *tert*-butyl alcohol catalyzed by a palladium complex with DBP-DIOP (**82**) (100° and 220–240 atm of CO), giving *tert*-butyl 3-phenylbutanoate. (429) A closely related catalyst system, $PdCl_2$/DIOP, catalyzed the reaction of methyl methacrylate (100° and 370–400 atm of CO) to give methylsuccinic acid monomethyl ester with 49% ee. (430, 431) Although an improved process for asymmetric hydrocarbalkoxylation under mild conditions (50° and 1 atm of CO) was developed in 1982 using $Pd(dba)_2$, neomen-thyldiphenylphosphine, and trifluoroacetic acid in methanol, (432) there appears to have been no further development of this catalyst system. However, quite recently a similar system, $Pd(OAc)_2$/BPPFA/*p*-toluenesulfonic acid, has achieved 86% ee in the reaction of styrene. (433) Very recently, a $PdCl_2$/ $CuCl_2$/diphosphine catalyst system with a unique chiral diphosphine, 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-idiol, was reported to achieve 99% ee, (434) which is very encouraging and warrants further investigation.

For asymmetric hydrocarbohydroxylation, an efficient catalyst system consisting of $PdCl_2$, $CuCl_2$, and (*R*)-1,1¢-binaphthyl-2,2¢-diyl hydrogen phosphate (BNPPA) was introduced in 1990, and can promote the reaction at ambient temperature and pressure. (435) The reactions of 4-isobutylstyrene and 6-methoxy-2-naphthylethene (**95**) promoted by the $PdCl_2$/ $CuCl_2$/(*R*)-(–)-BNPPA catalyst give (*S*)-ibuprofen (**94a**) with 83–84% ee and (*S*)-naproxen (**94b**) with 91% ee, respectively (Eq. 58). (436) Although 10–25 mol% of the chiral palladium catalyst is required to promote the reaction efficiently, this process has high potential because of mild reaction conditions and high enantioselectivity achieved.



(58)

4.3. Formylation of Halides and Triflates (437)

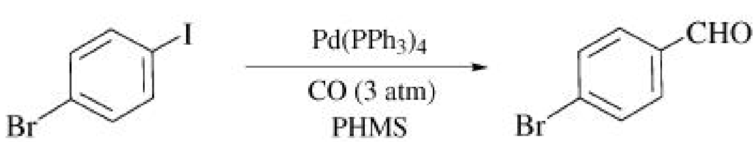
Catalytic formylation of aryl, heteroaryl, and vinylic halides in the presence of an amine, carbon monoxide, and hydrogen using a palladium complex such as $PdCl_2(PPh_3)_2$ provides a convenient route to conjugated aldehydes in good to excellent yields (Eq. 59). (438) The use of iodo substrates secures excellent yields.

$$\mathrm{ArX + NEt_3 \xrightarrow[\text{CO/H}_2\text{ (100 atm)}, \ \mathrm{NEt_3}]{\mathrm{PdCl_2(PPh_3)_2}} ArCHO + Et_3N{\bullet}HX} \qquad (59)$$

Allylic halides can be used as the substrates, but the yields of the resulting β , γ -unsaturated aldehydes are modest (38–42%). (439) When 1,3-bis(diisopropylphosphino)propane (DIPPP) is used as the ligand for palladium catalyst, and sodium formate as the hydrogen source, aryl chlorides are converted to the corresponding aldehydes in excellent yield under mild conditions (Eq. 60).

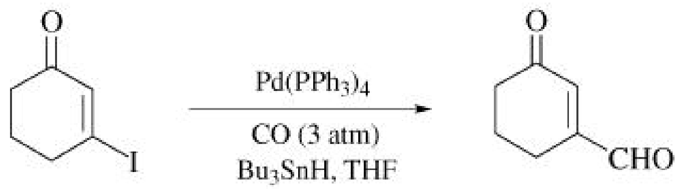
$$\mathrm{ArCl + HCO_2Na \xrightarrow[\text{CO (6 atm)}]{\mathrm{Pd(DIPPP)_2}} ArCHO + CO_2 + NaCl} \qquad (60)$$

The use of a silicon hydride or a tin hydride in place of molecular hydrogen allows the formylation of aryl halides to proceed under much milder conditions. The reactions of aryl and benzylic bromides/iodides catalyzed by $Pd(PPh_3)_3$ in the presence of poly(methylhydrosiloxane) (PHMS) at 80° and 3 atm of carbon monoxide afford the corresponding aldehydes in 48–96% yields. (440) When 1-bromo-4-iodobenzene is used as the substrate, 4-bromobenzaldehyde is formed exclusively in 95% yield (Eq. 61). (440)



(61)

Almost the same procedure except for using tributyltin hydride as the hydrogen source provides a convenient and versatile method for the synthesis of aldehydes from aryl iodides/bromides, benzylic and vinylic halides, vinylic triflates, and allylic halides. (441) This protocol allows the reactions to proceed at ca. 50° and 1–3 atm of carbon monoxide, and a variety of functional groups can be tolerated (Eqs. 62–64). (441)



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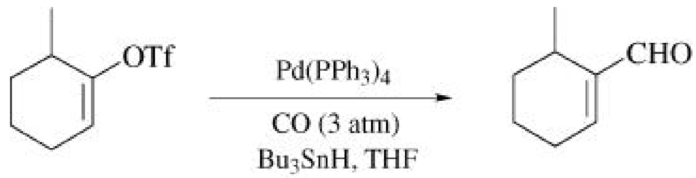

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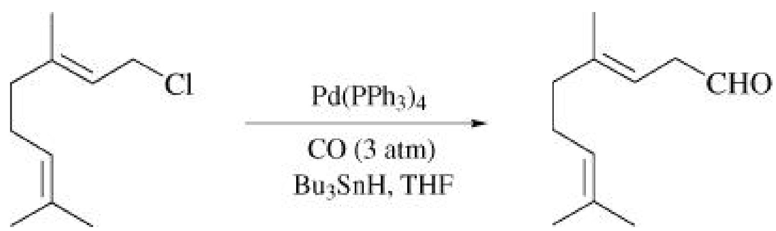
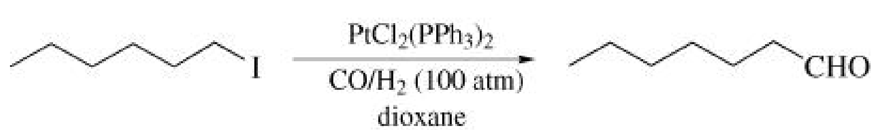


(64)

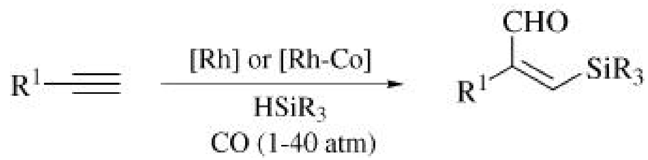
Primary and secondary alkyl iodides can be formylated with the platinum complex $PtCl_2(PPh_3)_2$, instead of palladium complexes as the catalyst in good to high yield at 120° and 100 atm of carbon monoxide and hydrogen (1:1) in the presence of potassium carbonate (Eq. 65). (442)



(65)

4.4. Silylformylation of Alkynes

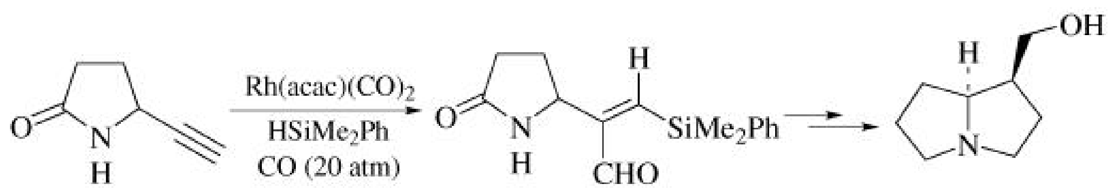
Silylformylation of 1-alkynes gives 1-silyl-2-formyl-1-alkenes with excellent regio- and stereoselectivity (Eq. 66). (443-445) This reaction is catalyzed by rhodium



(66)

or rhodium-cobalt complexes such as $Rh_4(CO)_{12}$, (443-445) $Rh_2Co_2(CO)_{12}$, (444, 445) Rh(CN-Bu-*t*)$_4$Co(CO)$_4$, (445) Rh(acac)(CO)$_2$, (445) $Rh_2(pfb)_4$ (pfb = perfluorobutyrate), (446) and (η^6-$C_6H_5BPh_3$)Rh(COD) (**29**) (447).

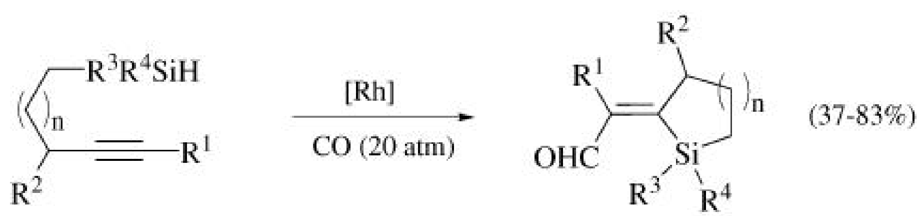
When internal alkynes are used, a mixture of regioisomers is formed. (443) A mixture of *Z* and *E* isomers in varying ratios is obtained depending on the catalyst species and reaction conditions. (443, 446) Functional groups such as olefin, hydroxy, ester, ether, amide and nitrile are tolerated. (443, 445-447) The reaction of 5-ethynylpiperidin-2-one (**96**) was successfully applied to the synthesis of isoretronecanol (**98**) (Eq. 67). (445, 448)



96 **97** (98%) (±)-Isoretronecanol (**98**)

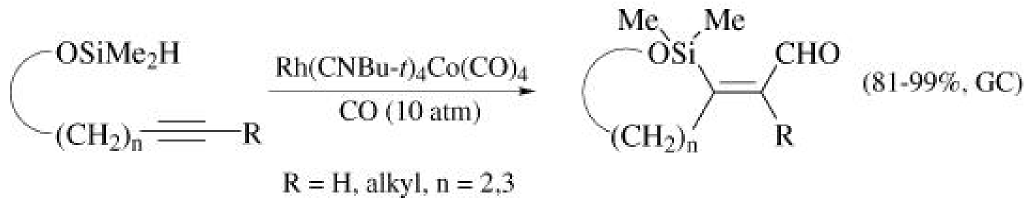
(67)

Although the reaction of 1-alkynes always affords 2-formyl products as shown in Eq. 66, this regiochemistry can be completely reversed using intramolecular silylformylation via *exo-dig* cyclization of alkynylsilanes (449) and alkynyloxysilanes (450) (Eqs. 68–70).

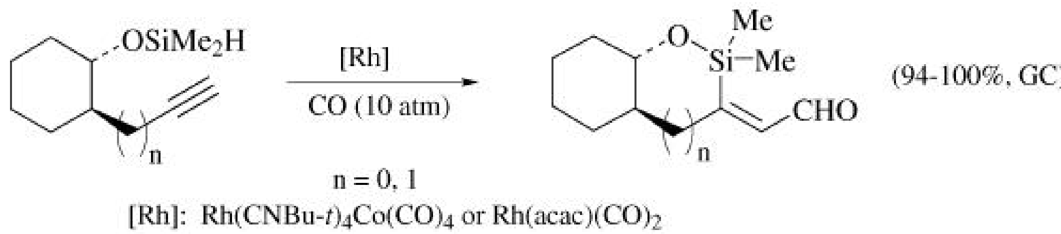


(68)

R^1 = H, alkyl, Ph; R^2 = H, Me; R^3, R^4 = Me, Ph; n = 1, 2
[Rh]: (η^6-$C_6H_5BPh_3$)Rh(COD) (**29**), 40°; $Rh_4(CO)_{12}$/NEt_3, 90°


OSiMe2H
(CH2)n
R
Rh(CNBu-t)4Co(CO)4
CO (10 atm)
R = H, alkyl, n = 2,3
Me
Me
OSi
CHO
(CH2)n
R
(81-99%, GC)

(69)


OSiMe2H
n
[Rh]
CO (10 atm)
n = 0, 1
[Rh]: Rh(CNBu-t)4Co(CO)4 or Rh(acac)(CO)2
O
Me
Si
Me
CHO
n
(94-100%, GC)

(70)

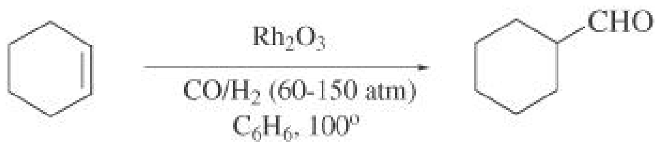
5. Experimental Conditions

Hydroformylation is usually carried out under catalytic conditions. The alkene, catalyzed by metal complexes under carbon monoxide and hydrogen in hydrocarbon, alkyl halide or ether solvent, generates the hydroformylation product. Rhodium catalysts are preferred for laboratory syntheses because of their higher activity and selectivity. Improvements in regioselectivity and yields have been found when the reaction is carried out in the presence of added donor ligands such as trialkylphosphines, or under UV irradiation. Catalysts supported on polymers have been used for easy separation of product and reuse of catalysts.

5.1.1. Carbon Monoxide

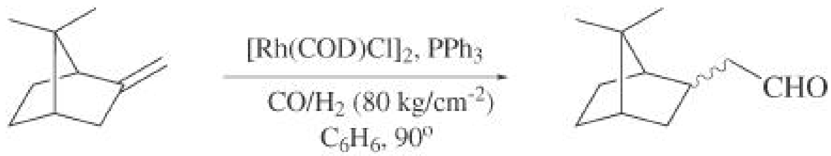
Carbon monoxide is a colorless, odorless gas, liquefying at –191.5°. It is readily available, at pressures of up to about 100 bar, in a variety of cylinder sizes, so that experiments can be run at 80 bar without a compressor. The acute toxicity of carbon monoxide reflects its high affinity for hemoglobin. It is stated (451) that 400–500 ppm of carbon monoxide in air can be breathed for an hour without appreciable effect, while levels above 1000 ppm are dangerous, and at more than 4000 ppm it causes death within an hour. The previously cited reference gives a Threshold Limit Value of 50 ppm. Carbon monoxide must always be used in an efficient fume cupboard, keeping emissions into the laboratory atmosphere to an absolute minimum. If carbon monoxide is in routine use it is recommended that an electronic detection system be installed to provide continuous monitoring of the laboratory atmosphere. For atmospheric pressure reactions, conventional rubber tubing or clear PVC tubing can be employed in laboratories, with appropriate securing clips, for delivering carbon monoxide to the reaction system. Higher pressures require the use of stainless steel tubing and couplings.

6. Experimental Procedures



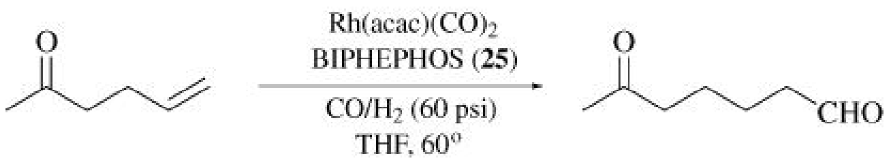
6.1.1. Cyclohexanecarboxaldehyde [Hydroformylation of an Alkene Under Classical Homogeneous Conditions] (452)

To a stainless steel 0.5 L pressure vessel equipped with a 450-atm manometer and a temperature recorder was added 0.2 g (0.8 mmol) of rhodium(III) oxide. The vessel was then sealed and evacuated to 0.1 mm Hg pressure. A solution of 82 g (1 mol) of cyclohexene in 140 mL of anhydrous benzene was introduced by suction into the vessel. The vessel was placed in a heatable shaking device and pressured to 75 atm with carbon monoxide, then the total pressure was increased to 150 atm with hydrogen. Shaking was begun and the vessel was heated to an internal temperature of 100°. When the internal temperature reached 100°, the pressure began to fall. When the pressure had fallen to 60 atm, rocking was stopped and carbon monoxide was introduced to 105 atm and then hydrogen to 150 atm. Rocking was started again, and the process was continued until no appreciable pressure decrease occurred. Approximately two hours was required, and the pressure decrease corresponded to the consumption of 2 moles of gas. The vessel was rapidly cooled to room temperature and the residual gas was carefully vented. The vessel was opened, and the slightly yellow reaction mixture was transferred immediately to a 2-L round-bottomed flask containing a freshly prepared solution of 200 g of sodium hydrogen sulfite in 400 mL of water. The flask was fitted with a stopper and was occasionally shaken at room temperature for a period of 3 hours. The resulting precipitate was collected by suction filtration on a sintered-glass funnel and washed with 500 mL of ether. After drying in air, the bisulfite derivative was transferred to a 2-L distillation flask containing 1 L of 20% aqueous potassium carbonate. The resulting mixture was distilled, and the azeotropic mixture of water and aldehyde (bp 94–95°) was collected under nitrogen. The aldehyde was separated from the lower aqueous layer as a colorless liquid and dried over 10 g of anhydrous sodium sulfate. The drying agent was removed by filtration, and the product was distilled under reduced pressure using a Claisen distillation apparatus to give 92–94 g (82–84%) of cyclohexanecarboxaldehyde, bp 52–53° (18 mm), n^{25}_{D} 1.4484. A purity of about 98% was established by GC analysis.



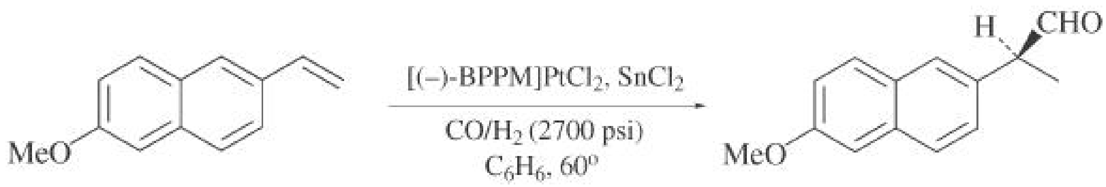
6.1.2. (7,7-Dimethylnorborn-2R-yl)-Acetaldehyde [Hydroformylation of an Alkene Under Homogeneous Conditions] (453)

A 200 mL autoclave was charged with 5.0 g (37 mmol) of (+)- α -fenchene, 45.3 mg (0.18 mmol) of the dimer of rhodium(I) chloride-1,5-cyclooctadiene, 95 mg (0.36 mmol) of triphenylphospine, 0.5 mL of triethylamine and 25 mL of benzene, and the reaction was carried out at 90° for 16 hours under a synthesis gas pressure of 80 kg/cm^2 (CO pressure 40 kg/cm^2; H_2 pressure 40 kg/cm^2). The solvent was evaporated, and the residue was fractionally distilled under reduced pressure to give 5.7 g (93.4%) of the product. The *exo/endo* ratio of the product was determined to be 85:15 by ^1H NMR; bp 54–55° (0.2 mm); ^1H NMR ($CDCl_3$) δ : *exo form* 9.71 (t, *J* = 7.9 Hz, 1 H, C*H*O), 2.60 (ddd, *J* = 2.1, 5.9, 9.6 Hz, 2 H, CH_2CHO), 1.08 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3); *endo form* 9.76 (t, *J* = 7.9 Hz, 1 H, C*H*O), 1.08 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3); MS (m/z): 166 (M^+), 151, 133, 123, 122 (base), 107, 95, 81, 79, 69, 67, 55, 41. Anal. Calcd for $C_{11}H_{18}O$: C, 79.52; H, 10.84. Found: C, 79.40; H, 10.86.



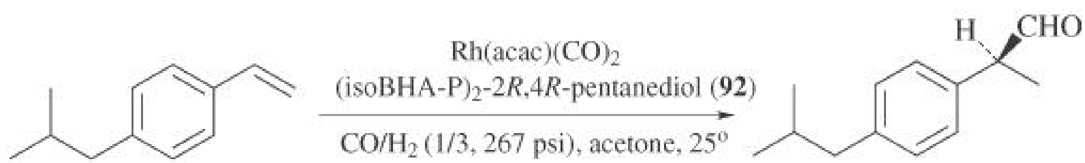
6.1.3. 6-Oxoheptanal (135)

Into a Fisher-Porter bottle, fitted with a pressure coupling closure complete with gas inlet, pressure gauge, and pressure release valve, was added (acetylacetonato)dicarbonylrhodium (28 mg, 0.109 mmol, 0.54 mol%), BIPHEPHOS (**25**) (320 mg, 0.408 mmol), THF (36 mL), and 5-hexen-2-one (2.32 mL, 20 mmol). The reaction vessel was degassed three times and purged with CO/H_2 (1:1 mixture) for several minutes. The reaction vessel was pressurized at room temperature to 60 psi with CO/H_2 (1:1 mixture) and then heated at 60° for 18 hours. After cooling to room temperature, the pressure was released and the solution concentrated. The resulting oil was purified by Kugelrohr distillation to give a colorless oil, 6-oxoheptanal (2.21 g, 86% yield).



6.1.4. (S)-2-(6-Methoxy-2-Naphthyl)Propanal [Asymmetric Hydroformylation of a Vinylarene Under Homogeneous Conditions] (406)

A deoxygenated solution of 1.0 g (5.4 mmol) of 6-methoxy-2-naphthylethene in 15 mL of benzene was charged into a 125-mL Parr Monel bomb with 16 mg (0.02 mmol) of [(–)-BPPM] $PtCl_2$ and 11 mg (0.05 mmol) of stannous chloride dihydrate. The bomb was sealed, pressurized to 2700 psi, and heated with stirring at 60° for 9 hours. At the end of the reaction, the bomb was quenched in a dry ice bath, the pressure was vented, and the mixture was eluted with benzene through an MPLC apparatus to afford 350 mg (30.1%) of the branched aldehyde (b/n = 0.7): mp 145°; 81% ee (determined by ^{1}H NMR using $Eu(hfc)_3$ as chiral shift reagent); ^{1}H NMR δ 9.7 (d, *J* = 4.1 Hz, 1 H), 7.7-7.1 (m, 6 H), 3.9 (s, 3 H), 3.7 (dq, *J* = 6.3, 4.1 Hz, 1 H), 1.6 (d, *J* = 6.3 Hz, 3 H). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.50; H, 6.54. Found: C, 78.38; H, 6.59.



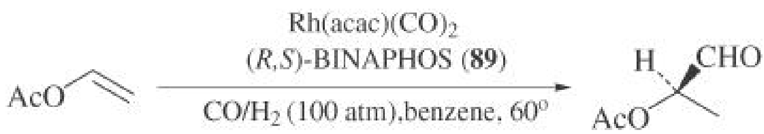
6.1.5. (S)-2-(4-Isobutylphenyl)Propanal [Asymmetric Hydroformylation of a Vinylarene under Homogeneous Conditions] (38)

A catalyst solution was prepared consisting of 0.011 g of (acetylacetonato)dicarbonylrhodium (1500 ppm rhodium), 0.765 g of $(isoBHA\text{-}P)_2$-(2*R*,4*R*)-pentanediol (**92**) (4:1 ligand to rhodium ratio), 5 g of 4-isobutylstyrene, and 24.5 g of acetone. This solution was charged to a 100 mL reactor and charged to a pressure of 67 psi with hydrogen gas and 200 psi with carbon monoxide (at ambient temperature). The rate of the reaction was determined by monitoring the drop in pressure as syngas was consumed. The reaction rate was approximately 0.1 g-mole/L/h. When the rate had slowed because of consumption of starting material, the reaction mixture was removed from the reactor under a nitrogen atmosphere. A portion of the reaction mixture was analyzed by GC to determine product composition. An

isomer ratio of 66:1 [2-(4-isobutylphenyl)propanal:
3-(4-isobutylphenyl)propanal] was observed.

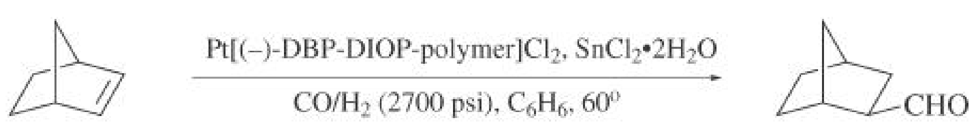
6.1.5.1. Determination of Enantiomeric Purity

Three mL of the solution was diluted in 50 mL of acetone and treated with 0.3 g of potassium permanganate and 0.32 g magnesium sulfate to effect oxidation of the product aldehydes to their respective acids. The mixture was stirred at room temperature for 30 minutes after which time the solvent was removed under reduced pressure. The residue was extracted three times with 50 mL of hot water. The three aqueous solutions were then combined, filtered, and washed with 50 mL of chloroform. The aqueous layer was acidified with hydrochloric acid to a pH of 2 and then extracted with 50 mL of chloroform. The chloroform was removed in vacuo and the resulting residue dissolved in 0.5 mL of toluene. This solution was analyzed by GC on a chiral β -cyclodextrin column which separated the two enantiomers of the resulting 2-arylpropanoic acid. This analysis indicated a 91:9 ratio of the *S* and *R* enantiomers for an ee of 82%.



6.1.6. (S)-2-Acetoxypropanal [Asymmetric Hydroformylation of a Vinyl Ester Under Homogeneous Conditions] (34)

A solution of vinyl acetate (532.3 mg, 6.19 mmol), Rh(acac)$(CO)_2$ (4.0 mg, 1.55×10^{-2} mmol), and (*R,S*)-BINAPHOS (**89**) (17.7 mg, 3.34×10^{-2} mmol) in benzene (10 mL) placed in a Schlenk tube was degassed by freeze-thaw cycles. It was then transferred into a 50 mL autoclave, and the mixture was stirred at 60° for 36 hours under hydrogen and carbon monoxide pressure (1:1 ratio, total 100 atm). ^{1}H NMR analysis of the reaction mixture showed that the conversion was >99% and the branched and normal aldehydes (2-acetoxypropanal and 3-acetoxypropanal) were formed in 86:14 ratio. The enantiomeric excess of (*S*)-2-acetoxypropanal (92%) was determined by GC using a chiral capillary column.



6.1.7. exo-Norbornanecarboxaldehyde [Asymmetric Hydroformylation of an Alkene Using a Cross-Linked Polymer-Supported Catalyst Under Heterogeneous Conditions] (411)

6.1.7.1. Preparation of the Polymer-Supported Ligand

A solution of 500 mg of poly(vinylpyrrolidone) (M_r 40000) in 60 mL of water was degassed by two freeze-pump-thaw cycles, transferred to a 250 mL Morton creased flask containing a variable speed stirrer, and heated to 65° under argon. A mixture of 441.5 mg (0.77 mmol) of (4*R*,5*R*)-2-(*p*-styryl)-4,5-bis[(dibenzophospholyl)methyl]-1,3-dioxolane, 648.2 mg (6.22 mmol) of styrene, 101.1 mg (0.77 mmol) of divinylbenzene, 50 mg of azobis(isobutyronitrile), and 2 mL of toluene was deoxygenated and added to the flask. The suspension was stirred for 20 hours, cooled, treated with 30 mL of methanol, and stirred for 30 minutes. The beads were filtered in a glove bag, washed with 50 mL of methanol, 50 mL of THF, 50 mL of benzene, and 50 mL of methanol, and dried under reduced pressure to afford 972.2 mg (80%) of 20–60 μm polymer beads: solid state ^{31}P NMR (CP/MAS) δ -24.8 (broad signal with a shoulder at δ -18.8). Anal. Calcd: P, 4.01. Found: P, 4.18.

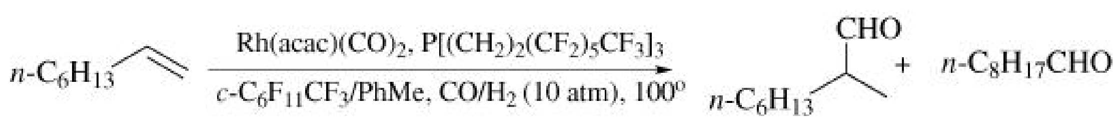
6.1.7.2. Preparation of the Polymer-Supported Catalyst

A solution of 0.12 mmol of bis(benzonitrile)dichloroplatinum(II) in 10 mL of benzene was added to a refluxing suspension of an amount of polymer beads containing 0.21 mmol of dibenzophosphole ligand in 5 mL of benzene. Reflux was continued for 40 hours under argon. The mixture was filtered in a glove bag, washed with 10 mL of dichloromethane and 10 mL of benzene, and dried under reduced pressure to afford the polymer-supported catalyst **I** in 98.6% yield: solid state ^{31}P NMR (CP/MAS) δ 2.0 (1*J* (Pt,P) = 3549 Hz), –24.7 (uncoordinated ligand). Anal. Calcd: Pt, 6.99. Found: Pt, 5.96.

A 125 mL Parr Monel bomb was charged with 0.02 mmol of the Pt polymer-supported catalyst **I** and 0.04 mmol of stannous chloride dihydrate. The bomb was brought into an argon-filled glove bag and charged with 8.7 mmol of norbornene dissolved in 3 mL of benzene. The bomb was sealed, pressurized, and vented three times with the synthesis gas mixture (1:1 $CO:H_2$) and then pressurized to 2700 psi and heated with stirring in an oil bath at 60° for 4 hours. At the end of the reaction, the bomb was opened in a glove bag. Catalyst **I** was recovered by filtration. The reaction mixture was analyzed by GC to determine the conversion (100%) and the aldehyde selectivity (87%). ^{1}H NMR of the mixture in the presence of $Eu(hfc)_3$ determined that the *exo*-norbornanecarboxaldehyde was obtained in 20% *ee*.

6.1.8. n-Heptanal and 2-Methylhexanal [Hydroformylation of an Alkene using Water-Soluble Complexes as Catalytic Precursors in a Two-Phase System] (23)

A mixture of 5.0 mL (40 mmol) of 1-hexene, 157.6 mg (0.1 mmol) of Rh_2(µ -S-*t*-Bu)$_2$(CO)$_2$(TPPTS)$_2$ and 568 mg (1.00 mmol) P($C_6H_4SO_3$Na-*m*)$_3$ (TPPTS) in 30 mL of distilled and nitrogen-saturated water was introduced into the autoclave under vacuum. This was heated to 80°, with stirring; after 5 minutes the syngas (CO/H_2 = 1/1) was introduced at the working pressure (10 bar). After 18 hours, the solution was transferred from the autoclave into a Schlenk tube. The composition of the solution was determined by GC on an Intersmat I.G.C. 131 apparatus equipped with a 3 m × 0.125 in. diameter column of OV17 on chromosorb WHP. The reaction conversion was 100% and the aldehyde selectivity was 97% (*n*-heptanal/2-methylhexanal = 36).



6.1.9. n-Nonanal and 2-Methyloctanal [Fluorous Biphase Hydroformylation of Alkene using Recycle Catalyst] (31)

A mixture of 12.9 mg (0.05 mmol) Rh(acac)(CO)$_2$ in 35 mL of toluene and 2.14 g (2.00 mmol) P[(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$]$_3$ in 35 mL of *c*- $C_6F_{11}CF_3$ was charged to a 300 mL autoclave under 5 atm CO/H_2 (1:1) and heated to 100°. A 75 mL pressure bomb was charged with 2.52 g (158 mmol) of 1-decene and attached to the autoclave. When the temperature in the autoclave reached 100°, the 1-decene was added by using 10 atm CO/H_2 (1:1) pressure, which was maintained during the reaction. After the reaction was complete, the reactor was cooled to room temperature. The autoclave was depressurized, and the two-phase system was separated in a separatory funnel under N_2. The upper phase was recharged to the cleaned and catalytically inactive autoclave. A solution of 30 mL of 1-octene in 35 mL of toluene was added under 5 atm CO/H_2 (1:1) and heated to 100°. The pressure was increased to 10 atm CO/H_2 (1:1) and maintained for 24 hours. A GC analysis of the reaction mixture showed only trace amounts of conversion of 1-octene. In contrast, when the lower phase was charged to the autoclave, the hydroformylation of 1-octene proceeded to give 85% nonanals with *n/i* ratio of 2.9 and 8% octenes.

6.1.10. (E,Z)-3-Pentenal and 4-Pentenal [Hydroformylation of an Alkene Catalyzed by Mesitylene-Solvated Rhodium Atoms] (254)

Rhodium metal (82.8 mg, 0.8 mmol) was evaporated during 40 minutes and co-condensated with mesitylene (30 mL) at liquid-nitrogen temperature, using a glass metal-atom reactor. The matrix obtained was warmed to about –40° and the resulting brown solution siphoned under argon into a Schlenk tube and manipulated at –30° under argon.

To a portion of the above co-condensate containing 5.2 mg of rhodium were added 22 mg (0.05 mmol) of bis(diphenylphosphino)ethane and 32.5 mmol of 1,3-butadiene, and the solution so obtained was introduced by suction into an evacuated 80 mL stainless steel autoclave. When carbon monoxide was introduced to the desired pressure (60 atm), and the autoclave was rocked and heated to 80°, hydrogen gas was rapidly introduced to give a 1:1 gas composition (total pressure 120 atm). After 4 hours, the reaction mixture was analyzed by GC to determine the conversion (78%) and the aldehydes yield (76%). The ratio of 3-pentenal/4-pentenal was 96/4. (*E,Z*)-3-Pentenal (*E*/*Z* = 75/25): ^{1}H NMR δ 9.62 (t, *J* = 2 Hz, 1 H, C*H*O, *E*), 9.64 (t, *J* = 1.8 Hz, 1 H, C*H*O, *Z*); 5.38–5.90 (m, 2 H, C*H* = C*H*, *E* + *Z*); 3.12–3.20 (m, 2 H, CH_2, *Z*); 3.05–3.10 (m, 3 H, CH_2, *E*); 1.65–1.78 (m, 3 H, CH_3, *E*); 1.55–1.72 (m, 3 H, CH_3, *Z*); GC-MS (m/e) 84 (M^+), 69, 55 (100). 4-Pentenal: ^{1}H NMR δ 9.75 (t, *J* = 1.5 Hz, 1 H, C*H*O); 5.04–5.07 (m, 1 H, -C*H* =); 4.94–5.02 (m, 2 H,=CH_2); 2.45–2.55 (m, 2 H, -CH_2-CHO); 2.35–2.40 (m, 2 H, -CH_2-CH_2); GC-MS (m/e) 84 (M^+), 83, 55 (100), 41.

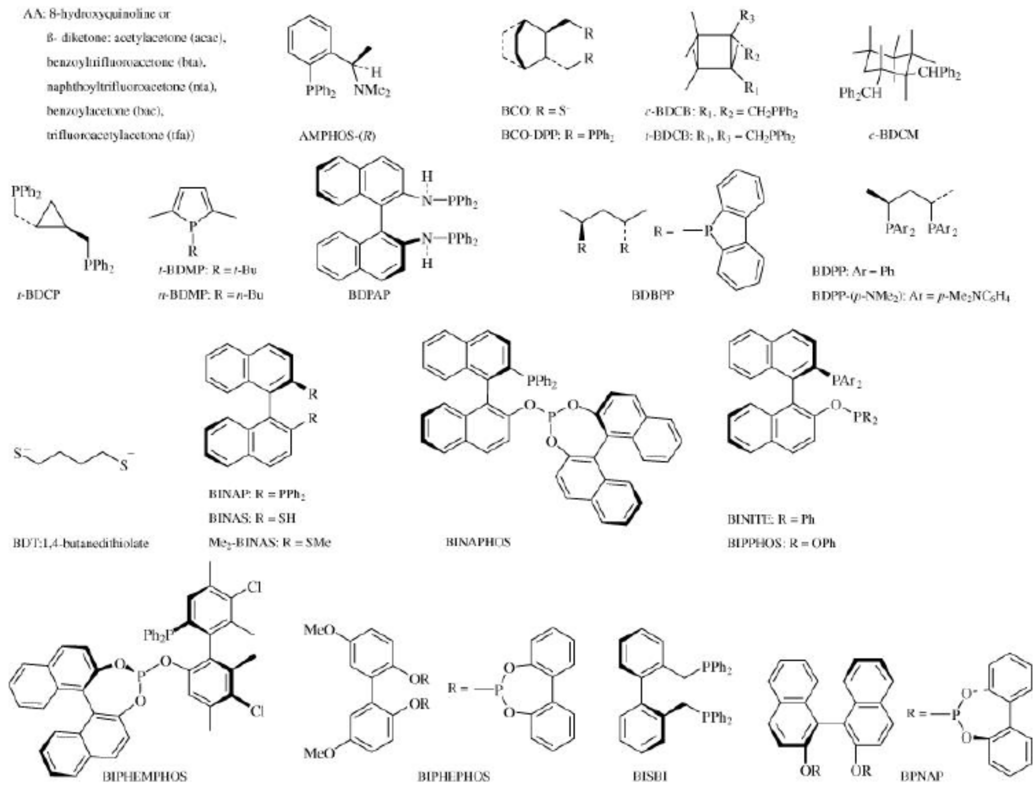
7. Tabular Survey

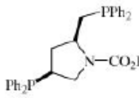
As mentioned in the Introduction, the exhaustive review by Cornils on the hydroformylation reactions that appeared in 1980 compiled publications including patents and patent applications since its discovery in 1938 till sometime in 1978. (3) Accordingly, the tabular survey in this chapter covers relevant examples abstracted from the literature from 1978 through 1998, and additional examples from crucial references up to November, 1999 have also been included. Because of the emphasis on the scope of the hydroformylation reactions as synthetic methods, patents and patent applications dealing with improvements of the well-established industrial Oxo-Process are not included. The tabular survey starts from the hydroformylation of simple olefins, dienes, and polyenes in Tables I and II. Then, Tables III–IX are categorized according to different functional groups attached to olefinic substrates. Table X covers asymmetric hydroformylations of prochiral olefins, and Table XI summarizes the hydroformylation of acetylenes. Within each table the substrate compounds are listed according to increasing carbon numbers. Reaction conditions including solvent, temperature, pressure, and time are presented as they are available from the original references. The pressure unit differs from a paper to another paper, i.e., atmosphere (atm), bar, kg/cm^2, pounds per square inch (psi), and pascal (Pa). Although it might be confusing, the authors intentionally did not convert the reported pressures to a uniform pressure unit. The relations between different pressure units are as follows: 1 atm = 1.01325 bar = 1.03323 kg/cm^2 = 14.696 psi = 101.325 Pa. Yields and percent enantiomeric excess (% ee) are given in parentheses. A dash indicates that no yield is given in the reference.

The following abbreviations are used in the tables:

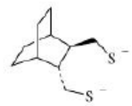
Ac	acetyl
acac	acetylacetonato
Bipy	2,2¢-bipyridine
COD	cycloocta-1,5-diene
Cy	cyclohexyl
ee	enantiomeric excess
Pht	*o*-phthalyl
py	pyridine
Pz	pyrazolate
THF	tetrahydrofuran

The following catalysts and their abbreviations are listed in alphabetical order and are used throughout the Tabular Survey.

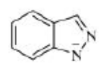




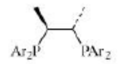
BPPM



BSCOS

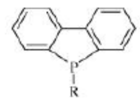


btz = benzotriazolate



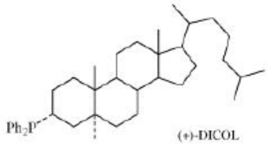
CHIRAPHOS: Ar = Ph

CHIRAPHOS-(p-NMe$_2$): Ar = p-Me$_2$NC$_6$H$_4$

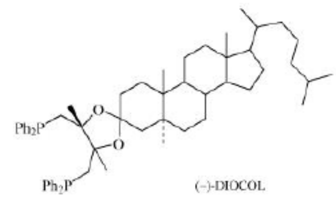


DBP-Et: R = Et

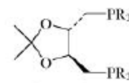
DBP-Ph: R = Ph



(+)-DICOL



(–)-DIOCOL



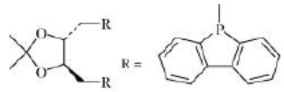
DIOP: R = Ph

DIOP-NMe$_2$: R = p-Me$_2$NC$_6$H$_4$

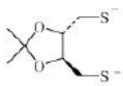
m-CF$_3$-DIOP: R = m-CF$_3$C$_6$H$_4$

CyDIOP: R = cyclohexyl

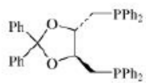
EtDIOP: R = ethyl



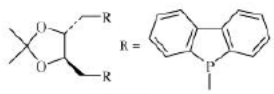
DIOP-BNP



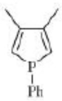
DIOS



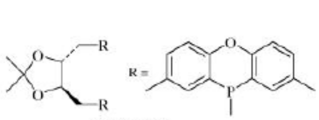
DIPH-DIOP



DIPHOL

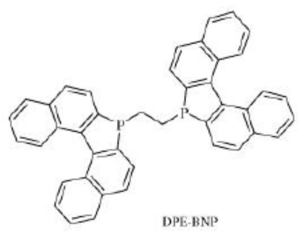


DMPP



DMPP-DIOP

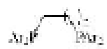
DMTPP



DPE-BNP

PPh$_2$C$_6$H$_4$SO$_3^-$-m

DPM



[illegible]

[illegible]

[illegible]

[illegible]

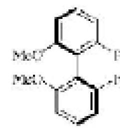
DPPF

[illegible]

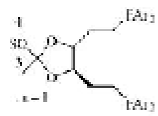
[illegible]

[illegible]

[illegible]



MOBIPH



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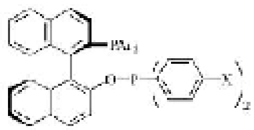
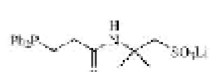


[illegible]

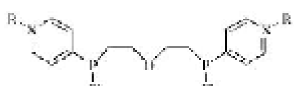
[illegible]

PC

PEVV



PNS



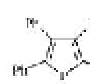
POP: X = C, R = H

POPam: X = C, R = CH$_2$NEt$_2$

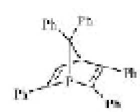
POPpy: X = N, R = H

P-P = diphosphine

PPN = [Ph$_3$P=]$_2$N



PTP

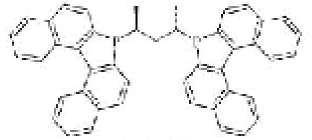


PPPN

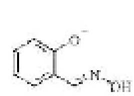
PROLOPHOS

PROPHOS

pz = pyrazolate



Skewphos BNP



SOX

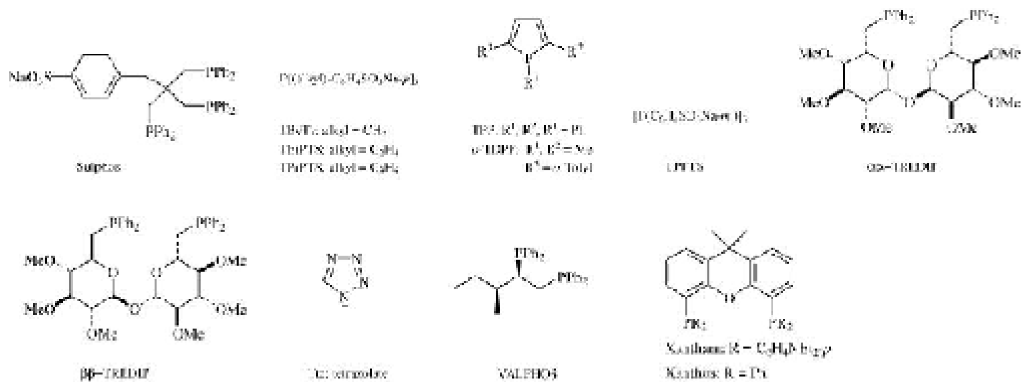


Table I. Hydroformylation of Alkyl-Substituted Monoolefins

View PDF

Table II. Hydroformylation of Dienes and Polyenes

View PDF

Table III. Hydroformylation of Unsaturated Alcohols

View PDF

Table IV. Hydroformylation of Unsaturated Aldehydes and Ketones

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Table V. Hydroformylation of Unsaturated Esters

View PDF

Table VI. Hydroformylation of Unsaturated Ethers and Acetals

View PDF

Table VII. Hydroformylation of Unsaturated Halogen Compounds

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Table VIII. Hydroformylation of Unsaturated Nitrogen Compounds

View PDF

Table IX. Hydroformylation of Other Functionally Substitued Olefins

View PDF

Table X. Asymmetric Hydroformylation

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Table XI. Hydroformylation of Alkynes

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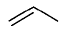
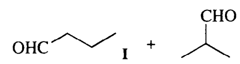
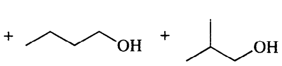
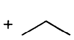
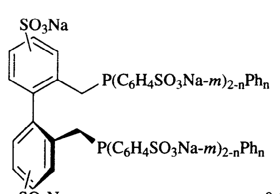
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	CO/H_2 (47/67, 114 bar), THF, 120°, 16 h	 I + II	454

Catalyst	Turnover[a]	I/II
$[Rh(CpCo(P(O)(OMe)_2)_3]_2(CO)_3$	30	0.7
$[Rh(CpCo(P(O)(OMe)_2)_3]_2(CO)_3/PPh_3$	50	1.7
$Rh(CpCo[P(O)(OMe)(O[CH_2]_3CH{=}CH_2)]_3)(CO)_2$	280	0.6
$Rh(CpCo(P(O)(OMe)(OC_3H_6CH{=}CH_2))_3)(CO)_2/PPh_3$	390	2.6
$Rh(CpCo(P(O)(OMe)(OC_3H_6CN))_3)(CO)_2$	340	0.7
$Rh(CpCo(P(O)(OMe)(OC_3H_6CN))_3)(CO)_2/PPh_3$	690	2.2

CO/H_2 (1/1, 7.4 bar), di-*n*-butyl phthalate, 90°, 5 h — 455

Catalyst precursor	Ligand	L/[Rh]	Turnover[a]	I/II
$RhH(CO)(PPh_3)_3$	—	0	68.8	1.63
$RhH(CO)(C_{60})(PPh_3)_2$	—	0	57.3	1.38
$RhH(CO)(PPh_3)_3$	PPh_3	13	64.6	2.91
$RhH(CO)(C_{60})(PPh_3)_2$	C_{60}[b]	13	44.8	1.19
$RhH(CO)(C_{60})(PPh_3)_2$	PPh_3	13	55.3	3.00
$RhH(CO)(PPh_3)_3$	PPh_3	40	64.8	4.23
$RhH(CO)(C_{60})(PPh_3)_2$	PPh_3	40	49.5	4.25

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ru(saloph)(CO), CO/H_2 (1/1, 27 atm), 120°, 4 h	I (60)	456
	$[NEt_4][HRu_3(CO)_{11}]$, CO (3.3 bar), H_2 (1.7 bar), diglyme, 75°, 66 h	I + II (—), I:II = 98.6:1.4	457, 458
	$Fe_3Rh_2(CO)_{14}C$ on SiO_2, CO/H_2 (1/1), 162°	I (—) + II (—) +  III (—) + IV (—) +  V (—); (I + II):(III + IV):V = 17:28:55, (I + III):(II + IV) = 70:30	459
	$HRuCo_3(CO)_{12}$ on carbon, CO/H_2 (1/1), 194°	I (—) + II (—) + III (—) + IV (—) + V (—) (I + II):(III + IV):V = 1:4:95, (I + III):(II + IV) = 96:4	460
	$Co(OAc)_2/P(Bu\text{-}n)_3$, *hν*, 80°, MeOH, CO/H_2 (1/1, 85 bar), 24 h	I + II (16), I:II = 99:1	461, 462
	RhNaY (Rh 3.4%), CO/H_2 (1/3, 1 atm), 150°	I + II (—), I:II = 1.9:1, V/(I + II) = 3.4	463-465
	 n = 0,1; $Rh(OAc)_3$, P/Rh = 6.7, pH = 5, 125°, CO/H_2 (1/1, 725 psi), H_2O	I (87) + II (—), I:II = 96.9:3.1; III + IV (1)	466
	$Co_2(CO)_8$, CO/H_2 (1/1, 192 psi), $scCO_2$[d]		467

Pressure (psi)	Temp	I:II	I + II
2400	78°	4.2	—
2400	88°	4.1	—
2400	98°	3.1	—
2400	108°	2.7	—
1350	88°	2.7	—
1650	88°	3.0	—
2100	88°	4.2	—
2700	88°	4.3	—

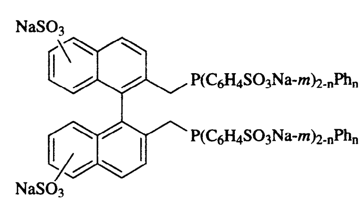
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(COD)OAc]_2$, PPh_3, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 90 °	I (61)	468

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

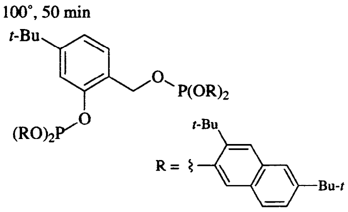
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ru_3(CO)_{12}$, ligand, L/Rh=8, $MeCONMe_2$, CO/H_2 (1/1, 80 atm), 120°, 20 h		469

Ligand	I + II	I:II
None	(25)	84:16
1,10-phenanthroline	(73)	95:5
2,9-Me_2-1,10-phenanthroline	(76)	92:8
$Me_2N(CH_2)_2NMe_2$	(31)	95:5
$Me_2N(CH_2)_3NMe_2$	(33)	96:4
$Me_2N(CH_2)_4NMe_2$	(57)	96:4
$Me_2N(CH_2)_6NMe_2$	(62)	96:4
2,2'-bipyridyl	(24)	93:7
py	(79)	91:9
PPh_3	(0)	—

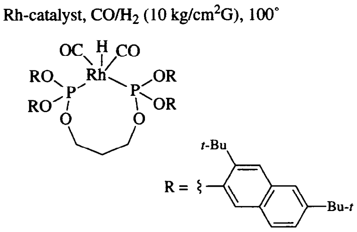
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazolin-2-ylidine)rhodium, PhMe, CO/H_2	**I** + **II** (—), **I**:**II** = 1	470
	$Rh(acac)(CO)_2$, PPh_3, P/Rh = 10, PhMe, CO/H_2 (1/1, 50 atm), 100°, <5 min	**I** + **II** (>96), **I**:**II** = 2	471
	$Rh(acac)(CO)_2$, TPPTS, P/Rh = 10, 90 min, $PhMe/H_2O$ = 4/3, CO/H_2 (1/1, 50 atm), 100°	**I** + **II** (—), **I**:**II** = 5	471
	$Rh(acac)(CO)_2$/TPPTS on 60 Å silica gel, P/Rh = 10, PhMe, 24% wt H_2O, 100°, CO/H_2 (1/1, 50 atm), 90 min	**I** + **II** (—), **I**:**II** = 2.8	471
	[Rh], P/Rh = 10-50, 110-130°, CO/H_2 (1/1, 20-60 atm)	**I** + **II** (—), **I**:**II** = 99	241

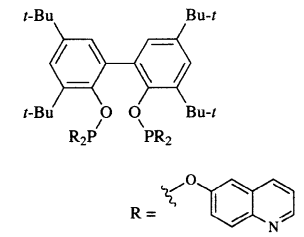
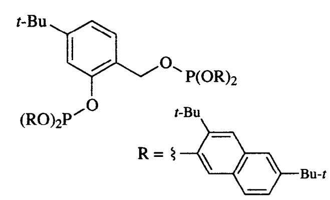
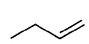
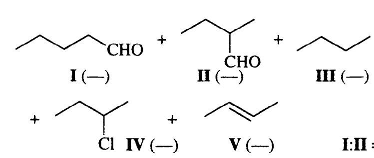


Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ru_3(CO)_{12}$, 1,10-phenanthroline, $AcNMe_2$, 120°, 20 h	**I** (73) + **II** (—) + **V** (1), **I**:**II** = 20.3	472
	$HRh(CO)_2L$, CO/H_2 (10kg/cm^2), 100°, 50 min	**I** (62) + **II** (37)	473



Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh-catalyst, CO/H_2 (10 kg/cm^{2}G), 100°	**I** (55) + **II** (43)	474



Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(OAc)(COD)]_2$, PhMe, H_2/CO (9 kg/cm^2 G) 70°, 1 h 	I:II = 49	475
	$HRh(CO)_2L$, CO/H_2 (10 kg/cm^2), 100°, 50 min 	I (62) + II (37)	473
	$[Rh(OAc)(CO)]_2$, P/Rh = 8, CO/H_2 (1/1), N_2	I (87) + III (1)	476
	$Rh(CO)(PPh_3)_3$, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, DPPB, diphosphite/DPPB/Rh = 56/2/1, $N(CH_2CH_2OH)_3$, *i*-PrOH, CO/H_2 (40 atm), 55°, 2 h	I + II (87)	477
C_4 	$PtCl_2(CO)(PPh_3)$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 140 atm), 80°, 1.5 h	 I:II = 87:13	478
	$PtCl_2(PPh_3)_2$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 140 atm), 80°, 1.5 h	I (—) + II (—) + III (—) + V (—) I:II = 92:8	478
	$HPtCl(PPh_3)_2$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 140 atm), 80°, 1.5 h	I (—) + II (—) + III (—) + V (—) I:II = 95:5	478
	$Rh(acac)(CO)_2$, phosphine ligand, P/Rh = 12, CO/H_2 (1/5, 1500 kPa), 2-ethylhexyl acetate, 110°		479

Phosphine ligand	Rate ($M^{-1}min^{-1}$)	Conv. (%)	I : II : III : V
$Me_3SiCH_2CH_2PPh_2$	330	50	67 : 19 : 6 : 8
$Me_2Si(CH_2CH_2PPh_2)_2$	123	50	78 : 12 : 4 : 6
$MeSi(CH_2CH_2PPh_2)_3$	77	50	82 : 9 : 3 : 6
$Si(CH_2CH_2PPh_2)_4$	41	50	83 : 10 : 2 : 6
PPh_3	430	50	59 : 18 : 5 : 19

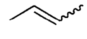
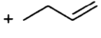
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PtCl_2(COD)/SnCl_2/P(OPh)_3/(PPN)Cl$ (1/5/2/1), 80°, CH_2Cl_2, 0.5 h, CO/H_2 (1/2, 140 atm)	I (—) + II (—) + III (—) + IV (—) + V (—) I:II = 93:7	480
	$PtCl_2(CO)(PPh_3)$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 140 atm), 80°, 2 h	I (—) + II (—) + III (—) + IV (—) +  VI (—) I:II = 18:82	478
	$PtCl_2(PPh_3)_2$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 140 atm), 80°, 2 h	I (—) + II (—) + III (—) + IV (—) + VI (—) I:II = 16:84	478
	$HPtCl(PPh_3)_2$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 140 atm), 80°, 2 h	I (—) + II (—) + III (—) + VI (—) I:II = 9:91	478

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

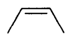
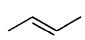
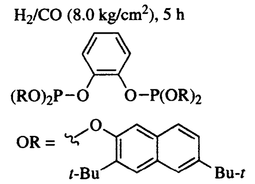
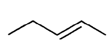
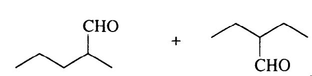
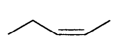
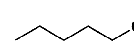
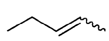
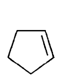
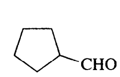
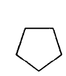
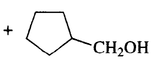
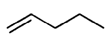
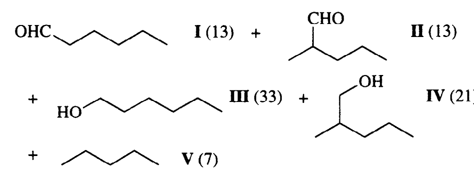
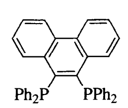
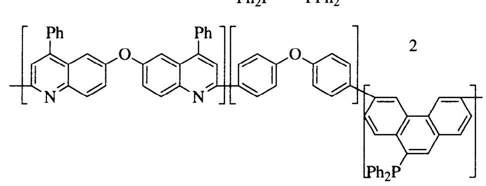
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PtCl_2(COD)$, PPh_3, (PPN)Cl, $SnCl_2$, CO/H_2 (1/1, 140 atm), CH_2Cl_2, 80°, 2 h	**I** (—) + **II** (—) + **III** (—) + **IV** (—) **I**:**II** = 8:92	481
	$PtCl_2(COD)$, $SnCl_2$, $P(OC_6H_4OMe\text{-}4)_3$, CO/H_2 (1/1, 140 atm), CH_2Cl_2, 120°, 2 h	**I** (—) + **II** (—) + **III** (—) + **IV** (—) + **VI** (—) **I**:**II** = 68:32	482
	$PtCl_2(COD)/SnCl_2/P(OPh)_3/(PPN)Cl$ (1/5/1/1), 80°, CH_2Cl_2, 0.5 h, CO/H_2 (1/2, 140 atm)	**I** (—) + **II** (—) + **III** (—) + **IV** (—) + **VI** (—) **I**:**II** = 8:92	480
	1. $Pt(SnCl_3)Cl(DIOP)$, CO (90 atm), D_2 (35 atm), 80°, 3 h, PhEt 2. Ag_2O, NaOH, H_2O 3. CH_2N_2, Et_2O	$CH_3CH_{1.18}D_{.82}CH_{.9}D_{1.1}CH_{1.92}D_{.08}CO_2Me$ **I** (—) + $CH_3CH_{1.09}D_{.91}CH(CH_{2.95}D_{.05})CO_2Me$ **II** (—) **I**:**II** = 20:80	483, 484
	1. $Rh_4(CO)_{12}$, CO (90 atm), D_2 (90 atm), 100°, 17 h, PhEt 2. Ag_2O, NaOH, H_2O 3. CH_2N_2, Et_2O	$CH_3CH_{.92}D_{1.08}CH_{.83}D_{1.17}CH_2CO_2Me$ **I** (—) + $CH_3CH_{.94}D_{1.06}CH_{.92}D_{.08}(CH_{2.86}D_{.14})CO_2Me$ **II** (—) **I**:**II** = 14:86	483
	1. $Co_2(CO)_8$, CO (430 atm), D_2 (70 atm), 100°, 6.5 h, PhEt 2. Ag_2O, NaOH, H_2O 3. CH_2N_2, Et_2O	$CH_3CH_{1.5}D_{.5}CH_{1.81}D_{.19}CH_{1.55}D_{.45}CO_2Me$ **I** (—) + $CH_3CH_{1.41}D_{.59}CH_{.66}D_{.34}(CH_3)CO_2Me$ **II** (—) **I**:**II** = 65:35	483
	$Rh(acac)(CO)_2$, ligand, PhMe, 100°, H_2/CO (8.0 kg/cm^2), 5 h  ligand = $(RO)_2P$–O / O–$P(OR)_2$; OR = ; *t*-Bu, Bu-*t*	**I** (81)	485
C_5 	RhCl(CO)(DPPB), C_6H_6, 55°, 12 h, CO/H_2 (1/1, 90 atm)	 CHO **I** (44) + CHO **II** (44)	486
	$Ru_3(CO)_{12}$, C_6H_6, 150°, CO (50 atm), H_2 (45 atm)	**I** + **II** +  CHO **III** + *n*-C_5H_{12} (11) **I** + **II** + **III** (30), **I**:**II**:**III** = 24:3.4:72.6	487
	$Co_2(CO)_8$/DIPHOS (1/1), C_6H_6, 140°, 24 h, CO/H_2 (1/1, 1100-1150 psi)	**I** + **II** + **III** (98), **III**/(**I** + **II**) = 1.8	488
	$Co_2(CO)_8$/DIPHOS (1/3), C_6H_6, 140°, 24 n, CO/H_2 (1/1, 1100-1150 psi)	**I** + **II** + **III** (24), **III**/(**I** + **II**) = 3.4	488
	Polystyrene resin-$C_6H_4CH_2PPh_2Co(CO)_3$-$Co(CO)_3Ph_2PCH_2C_6H_4$-polystyrene resin, P/Co = 0.67, CO/H_2 (1/1, 1100-1150 psi), C_6H_6, 140°, 24 h	**I** + **II** + **III** (98), **III**/(**I** + **II**) = 1.94	488
	Polystyrene resin-$C_6H_4CH_2PPh_2Co(CO)_3$-$Co(CO)_3Ph_2PCH_2C_6H_4$-polystyrene resin, DIPHOS, P/Co = 2.67, C_6H_6, 140°, 24 h, CO/H_2 (1/1, 1100-1150 psi)	**I** + **II** + **III** (50), **III**/(**I** + **II**) = 4.61	488
	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2$, 150°, 22.5 h, CO/H_2 (1/1, 77.1-68.2 bar)	**I** + **II** + **III** (95), **III**/(**I** + **II**) = 0.6	489
	$RhH(CO)(PPh_3)_3$, $PPh_2(CH_2)_2PPh_2$, P/Rh = 21, CO/H_2 (1/1, 800 psi), 120°, C_6H_6, 21 h	**I** + **II** (90)	490
	Styrene-divinylbenzene (1%) resin-$(C_6H_4PPh(CH_2)_2PPh_2)RhH(CO)(PPh_3)$, P/Rh = 21, CO/H_2 (1/1, 100 psi), C_6H_6, 140°, 21 h	**I** + **II** + **III** (91), **III**/(**I** + **II**) = 0.72	490
	$HCo(CO)_4$, CO (0.1 bar), H_2 (100 bar), *n*-heptane, 25°	 CHO **I** (—) +  **II** (—)	491

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	cis-$PtCl_2(PPh_3)_2/SnCl_2{\cdot}2H_2O$ (1:5), $CHCl_3$, CO/H_2 (1/1, 100 bar), 90°, 4 h	**I** (79) + **II** (3)	492
	Rh(acac)$[P(OPh)_3]_2$, $P(OPh)_3$, 80°, CO/H_2 (10 atm), 1 h	**I** (100)	393
	$Ru_3(CO)_{12}$, $P(C_6H_{11})_3$, HCO_2Me, H_2O, 180°, 10 h	**II** (47) +  (43)	493
	Polystyryl-$(CH_2)_4P(Bu\text{-}n)_2$-$Co_2(CO)_8$, *n*-C_8H_{18}, CO/H_2 (1/2, 480-510 psi), 180°, 14 h		494
	$[Rh(COD)OAc]_2$, PPh_3, L/Rh = 10, CO/H_2 (1/1, 20 atm), PhH, 90 °	**I** (78)	468
	$Rh(acac)_3(CO)_2$, 1-butyl-1-methyl-imidazolium hexafluorophosphate, PPh_3, CO/H_2, C_7H_{16}/PhMe, 82°, 2 h	**I** (75) + **II** (24)	495
	cis-$PtCl_2(PPh_3)_2/SnCl_2{\cdot}2H_2O$ (1:5), C_6H_6, CO/H_2 (1/1, 100 bar), 90°, 4 h	**I** + **II** (86), **I**:**II** = 93:7, **V** (7); 2-pentenes (5)	492
	$Rh(OAc)_3$, TPPTS, polyethylene glycol, H/CO (1/1, 30 bar), 125°, 3h	**I** + **II** (70), **I**:**II** = 96 : 4	496
	RhCl(CO)(DPPB), C_6H_6, 55°, 12 h, CO/H_2 (1/1, 90 atm)	**I** (57) + **II** (43)	486
	$Rh_4(CO)_{12}/PPh_3$ (1/5), C_6H_6, 25°, 6 h, CO/H_2 (1/1, 1 atm)	**I** + **II** (99), **I**:**II** = 3.7	497
	$Rh_4(CO)_{12}/P(OPh)_3$ (1/4), C_6H_6, 25°, 24 h, CO/H_2 (1/1, 1 atm)	**I** + **II** (28), **I**:**II** = 16.3	497
	$[Rh(CO)_2Cl]_2$, CO/H_2 (1/1, 600 psi), C_6H_6, 100-110°, 16-18 h		498

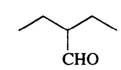
Phosphine ligand	P/Rh	Conv. (%)	I:II
none	—	100	0.76
PPh_3	2	99	0.88
DIPHOS	2	82	0.86
1,2-$(PPh_2)_2C_6H_4$	2	73	1.55
	7	94	3.20
	2	100	0.91

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PPN$[HRu(CO)_4]$, CO/H_2 (1/1, 300 atm), DMF, 150°, 16.5 h	**I** + **II** (56), **I**:**II** = 90.1:9.9; **III** + **IV** (3), **III**:**IV** = 93.9:6.1; **V** (3); 2-pentenes (14)	499
	$Fe_4Rh_2C(CO)_{16}$, CO/H_2 (1/1, 60 atm), 100°, 6 h	**I** + **II** (—), **I**:**II** = 1:1; pentane (traces)	500
	$[Fe_3Rh_3C(CO)_{15}][PPh_4]$, 100°, 5 h, CO/H_2 (1/1, 60 atm)	**I** + **II** (—), **I**:**II** = 1:1; pentane (traces)	500
	$Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$, C_6H_6, 130°, CO/H_2 (1/1, 400 psi), 168 h	**I** + **II** (50), **I**:**II** = 3.2	501
	$Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$, C_6H_6, 130°, CO/H_2 (1/1, 800 psi), 150 h	**I** + **II** (89), **I**:**II** = 1.7	501

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PtCl_2(PhCN)_2$, Ligand, $SnCl_2{\cdot}2H_2O$, Pt/P/Sn = 1/2/5, CO/H_2 (1/1, 100 kg/cm²), C_6H_6, 100°		502

Ligand	Time (h)	Conv. (%)	**I** : **II** : pentane : 2-pentenes
PPh_3	24	4	72.7 : 6.3 : 8 : 13
$Ph_2P(CH_2)_4PPh_2$	10	100	64.6 : 6.4 : 14 : 15
trans-1,2-$(Ph_2PCH_2)_2$-*c*-C_6H_{10}	18	100	68.4 : 7.6 : 13 : 10
trans-1,2-$(Ph_2PCH_2)_2$-*c*-C_5H_8	4	100	70.1 : 2.9 : 9 : 18
DIOP	4	100	67.2 : 2.8 : 10 : 20
trans-1,2-$(Ph_2CH_2)_2$-*c*-C_4H_6	3	100	78.2 : 0.8 : 6 : 13
trans-2,3-bis(diphenyl-phosphinomethyl)norbornane	2	100	71.3 : 0.7 : 8 : 20
trans-1,2-$(Ph_2PO)_2$-*c*-C_5H_8	5	99	51.7 : 3.3 : 12 : 33
1,2-$(Ph_2PCH_2)_2C_6H_4$	10	95	61.9 : 6.1 : 10 : 22

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_4(CO)_{12}/PPh_2H/P(OPh)_3$ (1/2/4), C_6H_6, 25°, 4 h, CO/H_2 (1/1, 1 atm)	**I** + **II** (78), **I**:**II** = 8.7	497
	$Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$, PhMe, 100°, CO/H_2 (1/1, 800 psi), 17 h	**I** (64) + **II** (15) + **III** (7)	503
	$MeCCo_2(CO)_6NiCp$, THF, 130°, 24 h, CO/H_2 (1/1, 600 psi)	**I** + **II** (88), **I**:**II** = 0.6; **III** + **IV** (11)	504
	$PhPFeCo_2(CO)_9$, THF, 130°, 24 h, CO/H_2 (1/1, 600 psi)	**I** + **II** (89), **I**:**II** = 1.4; **III** + **IV** (1)	504
	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2$, 130°, 23 h, CO/H_2 (1/1, 62.0-55.4 bar)	**I** + **II** + **III** + **IV** +  **VI** **I** + **II** + **VI** (95), **I**/(**II** + **VI**) = 2.7; **III** + **IV** (3)	489
	$Co_4(CO)_6(\mu_2\text{-}CO)_2(PPh_3)_2(\mu_4\text{-}PPh)_2$, PPh_3, 150°, 72.3 h, CO/H_2 (1/1, 41.4 bar)	**I** + **II** + **VI** (52), **I**/(**II** + **VI**) = 3.8; **III** + **IV** (5)	489

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Pt(PhCN)_2Cl_2$/1,2-$(Ph_2PCH_2)_2$-*c*-C_4H_6/ $SnCl_2$ (1/1/5), CO/H_2 (1/1, 100 atm), 70°, C_6H_6, 2 h	**I** + **II** + 2-pentene (8) + *n*-pentane (4) **I** + **II** (89), **I**:**II** = 99:1	505
	$Ru(CO)_3(PPh_3)_2$, PPh_3, P/Ru = 20, C_6H_6, CO/H_2 (1/1, 1000 psi), 140°	**I** + **II** (—), **I**:**II** = 3.4	506
	$Ru(CO)_3$(Ph_2P-polystyrene-1% divinylbenzene resin$)_2$, P/Ru = 3.1, C_6H_6, CO/H_2 (1/1, 1000 psi), 140°	**I** + **II** (—), **I**:**II** = 3.7	506
	$Co_2(CO)_8$, Phosphine, P/Co = 2.2, C_6H_6, CO/H_2 (4/5, 45 atm), 160°		507

Phosphine	Relative rate	(**I**+**III**):(**II**+**IV**+**VI**)
DBP-Ph	1.3	72 : 28
PPh_3	1.0	66 : 34
DBP-Et	0.9	77 : 23
PPh_2Et	0.7	79 : 21
P(Bu-*n*$)_3$	0.6	87 : 13

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, phosphine, P/Rh = 21, CO/H_2 (1/1, 100 psi), C_6H_6, 80°		490

Phosphine	Conversion (%)	**I**/(**II**+**VI**)
None	99	3.5
PPh_3	98	6.7
$Ph_2P(CH_2)_2PPh_2$	92	1.1
$Ph_2P(CH_2)_3PPh_2$	89	0.9
$Ph_2P(CH_2)_4PPh_2$	93	1.2

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Styrene-divinylbenzene (1%) resin-($C_6H_4PPh(CH_2)_2PPh_2$)RhH(CO)(PPh_3), P/Rh = 2.1, CO/H_2 (1/1, 200 psi), C_6H_6, 60°, 21 h	**I** + **II** (89), **I**:**II** = 2.7	490
	$Ru_3(CO)_{12}$, KOH (3.05 N), MeOH, 135°, CO (800 psi), 0.5 h	**I** + **II** (—), **I**:**II** = 32.3	508

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

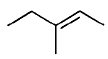
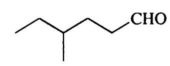
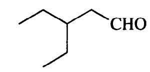
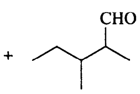
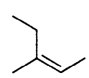
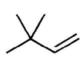
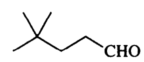
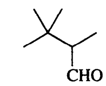
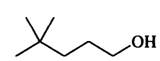
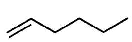
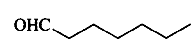
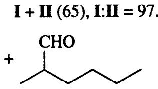
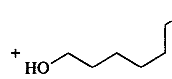
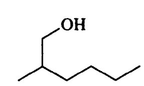
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(CO)_2Cp$-20% divinylbenzene-polystyrene copolymer, PPh_3, P/Rh = 20, C_6H_6, 110°, CO/H_2 (1/1, 1500 psi), 5 h	**I** + **II** (91), **I**:**II** = 2.06	509
C_6 	$Pt(PPh_3)_2Cl_2$, $SnCl_2 \cdot 2H_2O$, CO/H_2	 **I** (—) +  **II** (—) +  **III** (—) **I**:**II**:**III** = 33:58:9 *erythro*:*threo* = 21:79	484
	$Pt(PPh_3)_2Cl_2$, $SnCl_2 \cdot 2H_2O$, CO/H_2	**I** + **II** + **III** (*erythro*:*threo* = 32:68) **I**:**II**:**III** = 32:57:11	484
	$RhH(CO)(PPh_3)_3$, C_6H_6, 80°, CO/H_2 (1/1, 80 kg/cm²)	 **I** +  **II** **I** + **II** (97), **I**:**II** = 95:5	375
	$Rh_6(CO)_{16}$, C_6H_6, CO/H_2 (1/1, 80 kg/cm²), 80°	**I** + **II** (91), **I**:**II** = 96:4	375
	$[Rh(COD)(OAc)]_2$, CO/H_2, 25°	**I** (57-80)	316
	$Rh(acac)(CO)_2$, $P(OC_6H_3Me$-4-Bu-*t*-2$)_3$, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 70°	**I** (64)	468
	$[Pt(C_2H_4)(DPPB)]/CH_3SO_3H$ (1/1), 100°, CH_2Cl_2, CO/H_2 (1/1, 100 atm), 19 h	**I** + **II** +  (17) **I** + **II** (65), **I**:**II** = 97.6:2.4	259
	$Ru_3(CO)_{12}$-2,2'-bipyridine, PhMe, CO/H_2 (1/1, 50 bar), 100°, 66 h	 **I** (21) +  **II** (30) +  **III** (13) +  **IV** (9)	510
	$Ru_3(CO)_{12}$-2,2'-bipyridine, PhMe, Et_3N, CO/H_2 (1/1, 50 bar), 100°, 17 h	[**I** + **II**] (2) + **III** (47) + **IV** (20)	510
	$Ru_3(CO)_{12}$-2,2'-bipyridine on silica f22, CO/H_2 (1/1, 50 bar), 100°, 17 h, PhMe	[**I** + **II**] (0) + **III** (36) + **IV** (17)	510
	$Ru_3(CO)_{12}$-2,2'-bipyridine on magnesium silicate x-104/2, CO/H_2 (1/1, 50 bar), 100°, 17 h, PhMe	**I** (29) + **II** (13) + **III** (13) + **IV** (3)	510
	Rh(SOX)(COD), PPh_3, L/Rh = 5, PhMe, CO/H_2 (1/1, 0.1 MPa), 60°, 10 h	**I** + **II** (—), **I**:**II** = 83.9:16.1	511
	Rh(SOX)(COD), DPPE, L/Rh = 5, PhMe, CO/H_2 (1/1, 0.1 MPa), 60°, 10 h	**I** + **II** (—), **I**:**II** = 45.3:54.7	511
	$Rh(SOX)(CO)_2$, CO/H_2 (1/1, 1.0 MPa, PhMe, 60°	Ligand, P/Rh, Conv. (%), **I**:**II** $P(OPh)_3$, 2, 12, 73:27 PPh_3, 2, 29, 81:19 DPPE, 2, 37, 51:49 DPPP, 2, 94, 48:52	512
	$[Rh(SBu$-*t*$)(CO)]_2(C_5H_5)Zr(CH_2PPh_2)_2$, CO/H_2 (1/1, 20 bar), THF, 80°, 2 h	**I** + **II** (99), **I**:**II** = 1.9:1	513
	$[RhCl(CO)_2]_2$, PPh_3, L/Rh = 5, Et_3N, PhMe, CO/H_2 (1/1, 20 bar), 80°, 20 min	**I** + **II** (6), **I**:**II** = 71:29	514
	$[RhCl(CO)_2]_2$, DMTPPN, L/Rh = 5, Et_3N, PhMe, CO/H_2 (1/1, 20 bar), 80°, 20 min	**I** + **II** (27), **I**:**II** = 68:32	514
	$[RhCl(CO)_2]_2$, PPPN, L/Rh = 5, Et_3N, PhMe, CO/H_2 (1/1, 20 bar), 80°, 20 min	**I** + **II** (62), **I**:**II** = 68:32	514
	$Rh_2(\mu$-SBu-*t*$)_2(CO)_2(TPPTS)_2$, TPPTS, 80°, L/Rh = 6, CO/H_2 (1/1, 10 bar), H_2O, 18 h	**I** + **II** (100), **I**:**II** = 36:1	515, 23
	$RhH(C_2H_4)[CH_3C(CH_2PPh_2)_3]$, THF, CO/H_2 (1/1, 30 atm), 100°, 3 h	**I** + **II** (—), **I**:**II** = 80:20	516

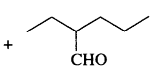
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pt(DIOP)Cl_2/$SnCl_2$, propylene carbonate, C_6H_6, CO/H_2 (1/1, 100 atm), 90°, 2 h	**I** (52) + **II** (—) + *n*-hexane **III** (20) **I**:**II** = 1.9:1	245
	Pt(DIOP)Cl_2/Sn/e^-, propylene carbonate, C_6H_6, CO/H_2 (1/1, 100 atm), 90°, 4 h	**I** (87) + **II** (—) + **III** (7) + 2-hexene (5) **I**:**II** = 57:1	245
	CO/H_2 (1/1, 5 atm), $ClCH_2CH_2Cl$, 80°		517

Catalyst	P/Rh	Time (h)	Conv. (%)	I:II
[Rh(COD)$(PPh_3)_2$]ClO_4/PPh_3	5	5	3	3.4:1
[Rh(COD)$(P(OPh)_3)_2$]ClO_4/P$(OPh)_3$	10	19	22	4.8:1
[Rh(COD)(OMe)$]_2$/P$(OMe)_3$	5	3	36	5.3:1
[Rh(COD)(OAc)$]_2$/P$(OMe)_3$	5	3	18	4.6:1
[Rh(COD)(OAc)$]_2$/P$(OPh)_3$	5	3	53	1.5:1
[Rh(COD)(OAc)$]_2$/PPh_3	5	3	82	2.8:1
[Rh(COD)(OAc)$]_2$/PPh_3	10	3	78	5.3:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[2,6-$(CH_2O(CH_2)_3PPh_2)_2C_5H_3N$]-[ZnCl(μ-Cl)Rh(CO)]$BF_4$, CO/$H_2$	**I** + **II** (—)	518
	[Rh(COD)(spiro(4-*tert*-butylcyclohexane) diaziridine)]ClO_4, PPh_3, 80°, 5.5 h, CO/H_2 (1/1, 5 atm)	**I** + **II** (26), **I**:**II** = 1.7:1	519
	Rh(acac)$(CO)_2$, diphosphine, C_6H_6, 34°, CO/H_2 (1/1, 6 atm)		133, 520

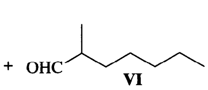
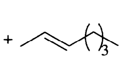
Diphosphine	I:II	Yield (%)
BISBI	66.5:1	(—)
T-BDCP	12.1:1	(—)
DIOP	8.5:1	(—)
DIPHOS	2.1:1	(—)
2,5-bis(diphenylphosphinomethyl)-bicyclo[2.2.1]heptane	2.9:1	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[RuH(CO)$(NCMe)_2(PPh_3)_2$][BF_4], PhMe, CO/H_2 (2/1, 100 bar), 150°, 20 h	**I**+**II** (10), **I**:**II** = 0.9, **III**+**IV** (60), hexane+hex-2-ene (30)	521
	$Rh_4(CO)_{12}$, CO/H_2	**I** + **II** +  **V** **I**:**II**:**V** = 54:38:8 (—)	367
	CO/H_2 (1/1, 1000 psi), PhMe, 100°, 3 h		522

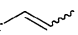
Catalyst	I : II : V	Yield (%)
[Rh(CO)$(PPh_3)_2]_4SiW_{12}O_{40}$	57 : 36 : 7	(95)
[Rh(CO)$(PPh_3)_2]_3PW_{12}O_{40}$	51 : 39 : 10	(95)
[Rh(CO)$(PPh_3)_2]_3PMo_{12}O_{40}$	54 : 38 : 8	(92)
[Rh(CO)$(PPh_3)_2]_4SiMo_{12}O_{40}$	60 : 34 : 5	(93)
[Rh(CO)$(PPh_3)_2]_4PVMo_{11}O_{40}$	64 : 33 : 3	(96)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2(OAc)_4$, PEt_3, L/Rh = 11.4, scCO_2 (250 bar), 100 °		523

P_{CO}(bar)	P_{H2}(bar)	Time (h)	C_7-aldehydes(%)	I/II	heptanol (%)
10	10	1	38	2.5	—
5	20	1	35	2.6	—
20	20	1	82	2.4	2.3
20	20	2	89	2.5	8.1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[Rh$(Hdmg)_2(PPh_3)$]$_2$, CO/H_2 (1/1, 1MPa), THF, 80°	**I** + **II** + **V** +  **VI** +  **VII**	524

[Rh] (x 10^{-6} mol)	Additive	Time (min)	V (%)	VI (%)	VII (%)	I+II (%)	I/II
7.0	—	440	3	29	4	65	2.0
7.8	—	205	3	26	16	55	1.9
7.6	—	250	1	26	4	68	2.5
11.6	PPh_3	130	—	25	—	75	3.4
4.8	—	280	—	27	3	68	2.4
9.5	—	245	—	28	6	65	2.3
5.3	PPh_3	105	—	23	5	72	3.1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(R^1COCHCOR^1)(CO)_2$, Ligand, CO/H_2 (2/1, 1 atm), PhMe, 50°, 6 h	I + II + n-Pr  (VI)	525

R^1	Ligand	I + II	I/II	VI
Me	$P(OCH_2)_3CEt$	(21)	6.3	(8)
$4-C_8H_{17}OC_6H_4$	$P(OCH_2)_3CEt$	(29)	6.7	(11)
Me	$P(OCH_2)_3CC_8H_{17}$	(26)	6.4	(16)
$4-C_8H_{17}OC_6H_4$	$P(OCH_2)_3CC_8H_{17}$	(20)	8.8	(7)
Me	$P(OCH_2)_3CCH_2O_2CC_6H_{13}$	(25)	9.8	(15)
$4-C_8H_{17}OC_6H_4$	$P(OCH_2)_3CCH_2O_2CC_6H_{13}$	(21)	9.5	(13)
Me	$P(OCH_2)_3CCH_2O_2CC_{11}H_{23}$	(17)	8.0	(13)
$4-C_8H_{17}OC_6H_4$	$P(OCH_2)_3CCH_2O_2CC_{11}H_{23}$	(22)	8.2	(12)
$4-C_8H_{17}OC_6H_4$	$P(OEt)_3$	(2)	5.0	(3)
Me	$P(OPh)_3$	(17)	5.9	(25)
$4-C_8H_{17}OC_6H_4$	$P(OPh)_3$	(21)	7.3	(25)
Me	$P(OC_6H_3Me\text{-}4\text{-}Bu\text{-}t\text{-}2)_3$	(23)	1.2	(75)
$4-C_8H_{17}OC_6H_4$	PPh_3	(5)	6.3	(4)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 30 atm), $n-C_7H_{16}$, 120°, 24 h	I + II + VI + EtCH=CHEt (VII)	526

Catalyst	Conversion (%)	I	II	VI	VII
$Ru_2(CO)_4(OAc)_2(PBu_3)_2$	18.6	(3)	(1)	(13)	(1)
$Ru(CO)_4(PBu_3)$	59.8	(2)	(1)	(55)	(2)
$Ru_4(CO)_8(OAc)_4(PBu_3)_2$	71.7	(7)	(2)	(60)	(3)
$Ru(CO)_5$	86.5	(11)	(2)	(69)	(5)
$Ru(CO)_2(OAc)_2(PBu_3)_2$	0.1	(tr)	(0)	(0)	(0)
$Ru(CO)_3(PBu_3)_2$	2.7	(tr)	(tr)	(tr)	(1)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2/SiO_2$, PhMe, CO/H_2 (1/1, 40 kg/cm^2), 130°, 6 h	I + II + III + IV (100)	527
	$Rh_2(\mu\text{-}SBu\text{-}t_2(CO)_2[P(OMe)_3]_2$, 80°, CO/H_2 (5 bar)	I + II (100)	528-531
	$[Co(CO)_3(Ph_2PCH_2CH_2NMe_3)]_2(PF_6)_2$ on macroreticular resin, C_6H_6, 100°, CO/H_2 (2/3, 80 atm), 24 h	I (70) + II (30)	532
	$[Co(CO)_3(PMePh_2)]_2$, C_6H_6, 100°, CO/H_2 (2/3, 80 atm), 24 h	I (82) + II (18)	532
	$Cp_2Zr(CH_2PPh_2)_2RhH(PPh_3)$, 3 PPh_3, THF, CO/H_2 (1/1, 20 bar), 80°, 160 min	I (72) + II (28)	533
	$Cp_2Zr(CH_2PPh_2)_2$, $RhH(PPh_3)_4$, THF, CO/H_2 (1/1, 20 bar), 80°, 140 min	I (73) + II (26)	533
	Cation-exchanged Rh zeolite A (2% Rh), PhMe, 50°, 22 h, CO/H_2 (1/1, 20 atm)	I (42) + II (42) + V (13)	534
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, L/Rh = 4, CO/H_2 (1/1, 11 atm), C_6H_6, 40°, 5 h	I (73) + II (16) + VI (7)	535
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, L/Rh = 2, CO/H_2 (1/1, 1 atm), C_6H_6, 40°, 5 h	I (61) + II (3) + VI (27)	535
	$Co_2(CO)_8/Ru_3(CO)_{12}$, Ru/Co = 0.99, 110°, CO/H_2 (1/1, 80 kg/cm^2), C_6H_6, 1.5 h	I + II (50), I:II = 3.1	536
	$Co_2(CO)_8/[NP(OPh)_{1.7}(OC_6H_4PPh_2)_{0.3}]_n$, P/Co = 4, CO/H_2 (1:2, 2000 psi), 190-195°, 7 h	I (3) + III (85)	537
	$Co_2(CO)_8/PPh_2$-linked polystyrene, P/Co = 2.7, CO/H_2 (1:2, 2000 psi), 190-195°, 7 h	I (33) + III (52)	537
	$K[Ru(EDTA\text{-}H)Cl]\cdot 2H_2O$, 130°, 12 h, CO/H_2 (1/1, 50 atm), $EtOH/H_2O$ (80/20)	I (100)	538
	$[Rh(CO)_2(PPh_3)_3][HC(SO_2CF_3)_2]$, CO/H_2 (1/1, 1000 psi), PhMe, 20 h	I (73)	539

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions			Product(s) and Yield(s) (%)			Refs.
	$Cp_2Zr(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 1 atm), 50°, 60 h			**I** (80) + **II** (5)			540
	CO/H_2 (1/1, 5 bar), PhMe, 80°						541
	Catalyst	Time (h)		**I+II**	**I:II**	Conversion (%)	
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2$(DPPB)	8		(—)	70.5:29.5	96	
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2$(DPPP)	6		(—)	64.3:35.7	97	
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2$(DPPF)	5		(—)	83.1:16.9	95	
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2$(DPPR)	5		(—)	73.0:27.0	98	
	$[Rh(COD)(DPPF)]ClO_4$	8		(—)	78.3:21.7	98	
	$[Rh(COD)(DPPR)]ClO_4$	10		(—)	88.1:11.9	75	
	$RhH[MeC(CH_2PPh_2)_3](C_2H_4)$, THF, 100°, CO/H_2 (1/1, 30 atm), 3 h			**I** + **II** (69), **I**:**II** = 83.9:16.1			542
	CO/H_2 (1/1, 5 bar), PhMe, 80°						543
	Catalyst	Time (min)	**I** + **II**	**I**:**II**			
	$Rh_2(\mu\text{-}pz)(\mu\text{-}SBu\text{-}t)(CO)_2[P(OMe)_3]_2$	104	(98)	1.56			
	$Rh_2(\mu\text{-}pz)(\mu\text{-}SBu\text{-}t)(CO)_2[P(OPh)_3]_2$	110	(98)	1.27			
	$Rh_2(\mu\text{-}pz)(\mu\text{-}SBu\text{-}t)(CO)_2(PPh_3)_2$	125	(80)	1.38			
	$Rh_2(\mu\text{-}btz)(\mu\text{-}SBu\text{-}t)(CO)_2[P(OMe)_3]_2$	184	(99)	1.5			
	$Rh_2(\mu\text{-}btz)(\mu\text{-}SBu\text{-}t)(CO)_2[P(OPh)_3]_2$	200	(96)	1.08			
	$Rh(acac)[P(OPh)_3]_2$, $P(OR)_3$, P/Rh = 1.1, PhMe, CO/H_2 (1 atm), 40°						544
	$P(OR)_3$, R =			**I** + **II**	**I**:**II**	**VI**	
	2-MeC_6H_4			(70)	10.0	(30)	
	3-MeC_6H_4			(80)	5.4	(20)	
	3,5-$Me_2C_6H_3$			(75)	7.4	(25)	
	2,4,6-$Me_3C_6H_2$			(66)	5.2	(33)	
	2,6-$Me_2C_6H_3$			(67)	5.0	(33)	
	2-ClC_6H_4			(71)	2.6	(29)	
	2-$O_2NC_6H_4$			(63)	2.9	(37)	
	$PtCl_2(PPh_3)_2$, $SnCl_2$, CH_2Cl_2, CO/H_2 (1/1, 100 atm), 80°, 3 h			**I** + **II** + *n*-hexane (5) + hexenes (28) **I** + **II** (63), **I**:**II** = 93:7			545-548
	$[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$, PPh_3, L/Rh = 2, CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 80°, 20 h			**I** + **II** (82), **I**:**II** = 3.5			549
	$[Rh(\mu\text{-}SC_6H_4F)(CO)_2]_2$, PPh_3, L/Rh = 2, CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 80°, 20 h			**I** + **II** (94), **I**:**II** = 3.2			549
	$Rh(acac)[P(OPh)_3]_2$/3-picoline (1.1), CO/H_2 (1/1, 1 atm), 40°, 3-4 h			**I** + **II** (90), **VI** (10)			550
	$RhH(PEt_3)_3$, PEt_3, THF, 120°, 16 h, CO/H_2 (55 atm)			**I** + **II** (80), **I**:**II** = 1.58; **III** + **IV** (27), **III**:**IV** = 5.08			551
	$RhH(PEt_3)_3$, EtOH, 120°, 16 h, CO/H_2 (65 atm)			**III** + **IV** (100), **III**:**IV** = 2.07			551
	$RhH(PEt_3)_3$, MeOH, 144°, 16 h, CO (20 atm)			**III** + **IV** (85), **III**:**IV** = 1.4			552
	$K[Ru(saloph)Cl_2]$, EtOH, 130°, CO/H_2 (1/1, 21 atm)			**I** + **II** (—), **I**:**II** = 75:25			553
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2[P(C_6H_4SO_3Na\text{-}m)_3]_2$, CO (8 x 10^5 Pa), H_2O, pH 4.8, 80°, 15 h			**I** + **II** (75), **I**:**II** = 23:1			554-557
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 20, 50°, CO/H_2 (1/1, 300 psi), 22 h			**I** (73) + **II** (27)			558-560
	$RhH(CO)(PPh_3)_3$, $Cp_2Zr(CH_2PPh_2)_2$, CO/H_2 (1/1, 5 bar), 80°, PhMe, 1 h			**I** + **II** (95), **I**:**II** = 2.6:1			561
	$RhH(CO)(PPh_3)_3$, $[Cp_2Zr(CH_2PPh_2)]_2O$, CO/H_2 (1/1, 5 bar), 80°, PhMe, 0.5 h			**I** + **II** (95), **I**:**II** = 2.7:1			561
	RhNaY, PEt_3, CO/H_2 (1/1, 300 psi), PhMe, 100°, 14 h			**I** + **II** (90), **I**:**II** = 2.3:1			562

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 5 bar), 80°		563, 564

Catalyst precursor	Solvent	Turnover (min^{-1})[a]	I/II
$Rh_2(\mu\text{-}Tz)_2(CO)_4/2PPh_3$	PhMe	3.37	1.7
$Rh_2(\mu\text{-}Tz)_2(CO)_4/2P(OMe)_3$	PhMe	1.75	1.6
$Rh_2(\mu\text{-}Tz)_2(CO)_4/2P(OPh)_3$	PhMe	1.10	2.1
$Rh_2(\mu\text{-}Tz)_2(COD)_2/2PPh_3$	PhMe	3.07	1.5
$Rh_2(\mu\text{-}Tz)_2(COD)_2/2P(OMe)_3$	PhMe	5.18	2.4
$Rh_2(\mu\text{-}Tz)_2(COD)_2/2P(OPh)_3$	PhMe	3.30	1.3
$Rh_2(\mu\text{-}Ttz)_2(CO)_4/2PPh_3$	PhMe	0.70	2.4
$Rh_2(\mu\text{-}Ttz)_2(CO)_4/2P(OMe)_3$	PhMe	1.50	1.3
$Rh_2(\mu\text{-}Ttz)_2(CO)_4/2P(OPh)_3$	PhMe	6.28	1.5
$Rh_2(\mu\text{-}Pz)_2(CO)_2[P(OPh)_3]_2$	PhMe	6.00	2.77
$Rh_2(\mu\text{-}Pz)_2(CO)_4/2P(OPh)_3$	*n*-C_7H_{16}	7.90	3.07
$Rh_2(\mu\text{-}MePz)_2(CO)_4/2P(OPh)_3$	*n*-C_7H_{16}	7.70	2.93
$Rh_2(\mu\text{-}Pz)_2(COD)_2/2P(OPh)_3$	*n*-C_7H_{16}	20.6	2.32

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2[\mu\text{-}S(CH_2)_3NMe_2]_2(COD)_2$, PPh_3, L/Rh = 40, CO/H_2 (1/1, 5x10^5 Pa), 80°, $ClCH_2CH_2Cl$	**I** + **II** (87), **I**:**II** = 93:7	565
	$Co_2Rh_2(CO)_{12}$ on support, C_6H_6, 80°, CO/H_2 (1/1.2, 55 kg/cm^2), 8 h		566

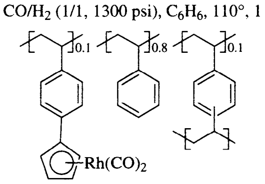
Support	I/II	Conversion (%)
None	1.0	96.4
Poly(*N*-vinyl-2-pyrrolidone)	0.75	95.9
Poly(styrene-*co*-maleic anhydride)	0.86	97.1
Aminated copolymer of styrene-maleic anhydride (NH_3)	0.63	95.1
Aminated copolymer of styrene-maleic anhydride [$(CH_2NH_2)_2$]	0.58	95.3
Poly(2-vinylpyridine)	1.05	88.1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[Rh_2(COD)(4-thio-1-methylpiperidine)$_2$] $[BF_4]_2/P(OMe)_3$ (1/2), CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 80°, 5 h	**I** + **II** (40), **I**:**II** = 3.4	567
	$Pt(DIOP)_2Cl_2/Sn/e^-$, CO/H_2	**I** + **II** (—), **I**:**II** = 98:2	244
	$[Rh(CO)_2Cl]_2$, phosphine, P/Rh = 1, Et_3N, PhMe, CO/H_2 (1/1, 20 bar), 80°, 30 min		568, 569

Phosphine	I + II	I : II
TPP	(95)	80:20
PPh_3	(91)	71:29
PPP	(50)	73:27
t-BDMP	(25)	68:32
DMPP	(13)	67:33
n-BDMP	(5)	65:35

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(anthranilate)$(CO)_2$, $P(OPh)_3$, P/Rh = 2.7, CO/H_2 (1/1, 1 atm), PhMe, 40°	**I** + **II** (83) + **VI** (17)	570
	$HCo(CO)_2(PBu_3)_2$, PBu_3, *hv*, MeOH, CO (1.5 atm), H_2 (40 atm), 30°, 6 h	**I** (30) + **II** (tr) + **III** (3) + hexane (14)	571
	$PtCl(TPPTS)_2(SnCl_3)$ on glass, P/Pt = 2, CO/H_2 (1/1, 1000 psi), PhMe, 100°, 120 h	**I** + **II** (26), **I**:**II** = 11.5	572
	$HRh[P(OPh)_3]_4/Cp_2Zr(CH_2PPh_2)_2$ (1/2.6), CO/H_2 (1/1, 5 bar), C_6H_6, 55°, 70 min	**I** + **II** (85), **I**:**II** = 5.5	573
	$PhCCo_3(CO)_9$, CO/H_2 (1/1, 900-1015 psi), PhMe, 100°, 26 h	**I** (64) + **II** + **V** **II** + **V** (20)	574
	$(OC)_9Co_3CCO_2CH_2CH_2COMe{=}CH_2$-derived polymer, CO/H_2 (1/1, 1000 psi), PhMe, 100°, 23 h	**I** (64) + **II** + **V** **II** + **V** (19)	574

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 1300 psi), C_6H_6, 110°, 1 h 	**I** + **II** (—), **I**:**II** = 2:3	575
	$Rh(AA)[P(OPh)_3]_2$, $P(OPh)_3$, C_6H_6, 85°, CO/H_2 (1/1, 12.6-12.7 atm), 1 h		576

AA	**I** : **II** : (2+3-hexenes) : *n*-hexane
8-hydroxyquinoline	62.5 : 13.5 : 18.0 : 11.0
benzoylacetone	54.0 : 21.0 : 0.0 : 24.0
acetylacetone	55.0 : 17.3 : 5.0 : 28.0
trifluoroacetylacetone	75.0 : 18.0 : 4.0 : 8.0
naphthoyltrifluoroacetone	42.0 : 13.0 : 25.0 : 14.0
benzoyltrifluoroacetone	54.0 : 19.0 : 15.0 : 23.0

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH_2(O_2COH)[P(Pr\text{-}i)_3]_2$, CO (15 atm), H_2O, THF, 115°, 20 h	**I** (42) + **II** (35)	577
	$[Rh(NBD)Cl]_2$, $Ph_2PCH_2CH_2NMe_3^+NO_3^-$, AMPHOS/Rh = 3, CO/H_2 (1/1, 40 atm), pH = 6.8, H_2O, 90°, 24 h	**I** + **II** + **III** + **IV** + hexenes (5) + hexane (3) **I** + **II** (86), **I**:**II** = 4.6; **III** + **IV** (1)	578
	trans-$[RhCl(CO)L_2]$, C_6H_6, 80°, 4 h, CO/H_2 (1/1)		579

Ligand	Pressure (atm)	I	II	V	1-hexene	2-hexene	hexane
PPh_3	100	(26)	(15)	(3)	(0)	(57)	(0)
$P(C_6H_4Et\text{-}4)_3$	100	(27)	(14)	(3)	(tr)	(52)	(4)
$P(C_6H_4Bu\text{-}n\text{-}4)_3$	100	(28)	(11)	(tr)	(34)	(27)	(0)
$P(C_6H_4C_5H_{11}\text{-}n\text{-}4)_3$	100	(12)	(5)	(0)	(79)	(5)	(tr)
$P(Bu\text{-}n)_3$	100	(20)	(21)	(8)	(tr)	(51)	(tr)
$P(Bu\text{-}n)_3$	80	(9)	(7)	(2)	(tr)	(82)	(1)
$P(C_8H_{17}\text{-}n)_3$	80	(4)	(2)	(0)	(82)	(12)	(0)
$P(C_{16}H_{33}\text{-}n)_3$	80	(tr)	(tr)	(0)	(94)	(5)	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Pt(PR_3)(CO)Cl_2/SnCl_2{\cdot}2H_2O$ (1/2), 80°, acetone, CO/H_2 (1/1, 600 psi), 2 h		580

PR_3	I	Internal aldehyde
$P(C_6H_4F\text{-}4)_3$	(47)	(3)
$P(Bu\text{-}n)_3$	(45)	(4)
PEt_3	(37)	(3)
PPh_3	(34)	(2)
$P(C_6H_4Me\text{-}4)_3$	(34)	(2)
$P(C_6H_{11})_3$	(27)	(4)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)[P(py)_3]_2/P(py)_3$ (1/20), PhCOMe, CO/H_2 (1/1, 2 atm), 60°	**I** + **II** (—), **I**:**II** = 13:1	581
	$RhH(CO)(PPh_3)_3$, Phosphine Ligand, CO/H_2 (1/1, 793 kPa), PhMe		582

Phosphine ligand	L/Rh	Temp	**I** : **II** : (**VI** + **VII**) : hexane
$PEtPh_2$	20	100°	73.0 : 23.0 : 4.0 : 0.0
DPPE	5	105°	54.6 : 45.2 : 0.2 : 0.0
DPPP	5	105°	57.7 : 47.3 : 0.0 : 0.0
DPPB	5	105°	75.0 : 24.0 : 0.0 : 0.4
(+)-DIOP	2	106°	83.0 : 17.0 : 0.2 : 0.1
t-BDCB	2	106°	87.0 : 11.0 : 1.0 : 0.6
c-BDCB	5	100°	78.0 : 21.0 : 0.6 : 0.6
t-BDCH	5	103°	52.0 : 46.0 : 1.0 : 0.0

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(COD)(PPh_3)(py)]PF_6$, PPh_3, P/Rh = 4, Et_3N, CO/H_2 (1.05/1, 50 cmHg), 25°, C_6H_6	**I** + **II** (—), **I**:**II** = 89.5: 10.5	583
	$RhCl(CO)[PPh_2\text{-poly(methylsiloxanes)}]_2$, CO/H_2 (1/1, 1000 psi), C_6H_6, 100°, 3 h	**I** (47) + **II** (50) + 2-hexene (2)	584

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

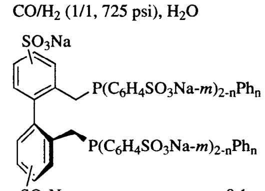
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst, amine, CO/H_2 (1/1, 50 bar), 100°, 17 h		585

Catalyst	Amine	Solvent	I+II+V	I/(II+V)	III+IV	III/IV
$FeCl_3$	—	EtOH	(0)	—	(0)	—
$FeCl_3$	Et_3N	EtOH	(0)	—	(0)	—
$RuCl_3{\cdot}3H_2O$	—	acetone	(6)	—	(0)	—
$RuCl_3{\cdot}3H_2O$	Et_3N	acetone	(16)	—	(0)	—
$CoCl_2{\cdot}6H_2O$	—	acetone/PhMe	(97)	0.7	(0)	—
$CoCl_2{\cdot}6H_2O$	Et_3N	acetone/PhMe	(75)	2.4	(0)	—
$RhCl_3{\cdot}3H_2O$	—	EtOH	(41)	0.2	(0)	—
$RhCl_3{\cdot}3H_2O$	Et_3N	PhMe	(1)	—	(98)	0.7
$IrCl_3$	—	PhMe	(18)	0.2	(1)	—
$IrCl_3$	Et_3N	PhMe	(12)	1.0	(2)	—
$Fe_3(CO)_{12}$	—	PhMe	(7)	—	(0)	—
$Ru_3(CO)_{12}$	—	PhMe	(96)	1.0	(2)	—
$Os_3(CO)_{12}$	—	CH_2Cl_2	(14)	2.2	(0)	—
$Co_2(CO)_8$	—	PhMe	(84)	2.0	(1)	—
$Co_2(CO)_8$	Et_3N	PhMe	(85)	1.7	(0)	—
$Co_4(CO)_{12}$	—	PhMe	(74)	2.8	(1)	—
$Co_4(CO)_{12}$	Et_3N	PhMe	(82)	2.2	(0)	—
$Rh_2(CO)_4Cl_2$	—	PhMe	(99)	0.8	(0)	—
$Rh_2(CO)_4Cl_2$	Et_3N	PhMe	(0)	—	(97)	0.7
$Rh_4(CO)_{12}$	—	PhMe	(95)	0.6	(0)	—
$Rh_4(CO)_{12}$	Et_3N	PhMe	(0)	—	(100)	1.0
$Rh_4(CO)_8[P(OPh)_3]_4$	—	PhMe	(96)	1.6	(1)	—
$Rh_4(CO)_8[P(OPh)_3]_4$	Et_3N	PhMe	(94)	1.2	(1)	—
$Co_2Rh_2(CO)_{12}$	—	PhMe	(95)	0.3	(0)	—
$Co_2Rh_2(CO)_{12}$	Et_3N	PhMe	(0)	—	(98)	0.8
[PPN][$RuRh_5(CO)_{16}$]	—	$PhMe/CH_2Cl_2$	(98)	0.7	(0)	—
[PPN][$RuRh_5(CO)_{16}$]	Et_3N	$PhMe/CH_2Cl_2$	(77)	0.7	(16)	1.5

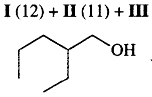
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	NaY zeolites entrapped rhodium carbonyl clusters, C_6H_{14}, CO/H_2 (1/1, 80 atm), 80°, 3 h	**I** + **II** + **V** (—), **I**:**II**:**V** = 51:41:8	586
	$Rh(acac)(CO)(PPh_3)/PPh_3$ (1/13.4), amine, CO/H_2 (1/1, 1 MPa), PhMe, 353 K		587

Amine	Amine/Rh	I+II+V	I/(II+V)	2-hexene
None	—	(69)	5.5	(12)
Ph_3N	10	(85)	5.8	(—)
$(PhCH_2)_3N$	10	(71)	5.8	(8)
$PhNH_2$	10	(73)	3.7	(4)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Co_2Rh_2(CO)_{12}$ on Dowex MWA-1 resin, CO/H_2 (1/1, 50 bar), PhMe, 100°, 17 h	**II** (2) + **III** (39) + **IV** (56)	588
	$Co_2Rh_2(CO)_{12}$ on Dowex MSC-1 (-SO_3Na) resin, CO/H_2 (1/1, 50 bar), PhMe, 100°, 17 h	**I** + **II** (90), **I**:**II** = 0.9	588
	$Rh_4(CO)_{12}/Co_4(CO)_{12}$ (2.6) on Dowex MWA-1 resin, CO/H_2 (1/1, 50 bar), PhMe, 100°, 17 h	**III** + **IV** (99), **III**:**IV** = 1.1	588
	$Rh(OAc)_3$, P/Rh = 6.7, pH = 5.2, 155°, CO/H_2 (1/1, 725 psi), H_2O	**I** (30) + **II** (—), **I**:**II** = 94.6:5.4	466
	(Polymer-N=C)$_2$Rh(acac)(CO), PhMe, CO/H_2 (1/1, 12 MPa), 120°, 5 h	**I** (12) + **II** (11) + **III** (38) + **IV** + **V** (6) +	589

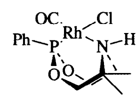
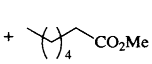
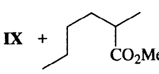
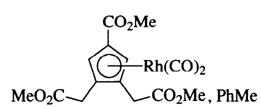


n = 0.1



VIII **IV** + **VIII** (33)

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Pt(C_2H_4)(DPPB)]/CH_3SO_3H$ (1/1), PhMe, CO/H_2 (1/1, 100 atm), 100°, 24 h	**I** + **II** (58), **I**:**II** = 94.9:5.1; **III** + **IV** (5)	259
	$Co_2(CO)_6[P(C_6H_4SO_3Na\text{-}m)_3]_2$/glass (CPG 340), CO/H_2 (1/1, 800 psi), H_2O, PhMe, 190°, 8 h	**I** + **II** (—), **I**:**II** = 2.2; **III** + **IV** (—), **III**:**IV** = 1.12	590
	$RhCl(CO)(DPPB)$, C_6H_6, 55°, 12 h, CO/H_2 (1/1, 90 atm)	**I** (53) + **II** (46)	486
	$[Rh_2(COD)(4\text{-thio-1-methylpiperidine})_2][BF_4]_2/P(OPh)_3$ (1/2), CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 80°, 5 h	**I** + **II** (82), **I**:**II** = 1.7	567
	$RuCl_2[N(CH_2CH_2PPh_2)_3]$, PhMe, 150°, CO/H_2 (1/1, 100 atm), 10 h	**I** (—) + *n*-hexane (—) **I**:*n*-hexane = 35:65	591
	 , CO/H_2	**I** + **II** (85)	592
	$RhH_2(O_2COH)(PPr\text{-}i_3)_2$, $(CH_2O)_n$, THF, 120°, 20 h	**I** + **II** + **III** + **IV** +  **IX** +  **X** **I** + **II** (67), **I**:**II** = 41:59; **III** + **IV** (4), **III**:**IV** = 61:39; **IX** + **X** (13), **IX**:**X** = 80:20, *n*-hexane (3)	593
	 , PhMe		594

PPh_3/Rh	Temp	Time (h)	P (bar)	CO/H_2	I:II:V	I+II+V
0	100°	3.5	70	1/1	44:44:12	(90)
5	80°	3.0	42	4/6	75:25:0	(91)
5	60°	12.0	56	4/6	75:25:0	(75)

Ref. 594

Catalyst	Temp	Time (h)	P (bar)	CO/H_2	Solvent	I:II:V	I+II+V
$(MeO_2CCp)Rh(CO)_2$	100°	3.5	70	1/1	PhMe	51:44:5	(85)
$(Cp)Rh(CO)_2$	100°	5.0	70	1/1	PhMe	55:38:7	(87)
$(MeO_2CCp)Rh(CO)_2$/5 PPh_3	80°	3.0	42	4/6	PhMe	74:26:0	(90)
$(Cp)Rh(CO)_2$/5 PPh_3	80°	6.0	42	4/6	PhMe	75:25:0	(29)

Ref. 595

Catalyst	PR_3	P/Rh	Solvent	CO/H_2 (1/1, bar)	Conv. (%)	I:II
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	—	—	PhMe	30	76	52:48
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	—	—	PhMe	70	56	56:44
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	PPh_3	2	PhMe	30	96	73:26
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	PPh_3	2	PhMe	70	97	74:27
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	PPh_3	4	PhMe	30	94	75:25
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	PPh_3	4	PhMe	70	98	73:27
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	PPh_3	2	$(CH_2Cl)_2$	30	94	74:26
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	$P(OC_6H_4Bu\text{-}t\text{-}2)_3$	2	$(CH_2Cl)_2$	30	36	65:35
$Rh_2(\mu\text{-}S(CH_2)_2S)(COD)_2$	$P(OPh)_3$	2	$(CH_2Cl)_2$	30	90	77:26
$Rh_2(\mu\text{-}S(CH_2)_4S)(COD)_2$	PPh_3	1	$(CH_2Cl)_2$	5	84	68:31
$Rh_2(\mu\text{-}S(CH_2)_4S)(COD)_2$	PPh_3	2	$(CH_2Cl)_2$	5	96	72:28

$Rh(acac)(CO)_2$, $P(NC_4H_4)_3$, C_6H_6, 90 min, CO/H_2 (1/1, 10 atm) — Ref. 596

P/Rh	Temp	Conversion (%)	I	II	I:II	VI	VII
1.8	60°	100	(61)	(17)	3.1	(19)	(3)
2.8	60°	100	(69)	(15)	4.1	(14)	(2)
4.1	30°	53.5	(44)	(2)	27.7	(8)	(0)
4.1	40°	90.5	(78)	(3)	31.0	(10)	(0)
4.1	60°	100	(70)	(7)	9.9	(23)	(0)
4.1	70°	100	(64)	(10)	5.5	(24)	(2)
4.1	80°	100	(64)	(14)	4.0	(20)	(2)
5.4	60°	100	(71)	(4)	19.8	(25)	(0)
7.1	60°	100	(85)	(3)	29.9	(21)	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, xantham, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80 °, 24 h	**I** + **II** + 2-hexene + 3-hexene **I**+**II** (96.2), **I**:**II** = 48	225

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, P(NC$_4$H$_4$)$_3$, P/Rh = 2.8, CO/H$_2$ (1/1, 10 atm), C$_6$H$_6$, 60°, 90 min		596

[Rh]/[1-hexene]	TON	I	II	I:II	VI	VII
2.5	4800	(68)	(11)	6.1	(20)	(0)
4.1	2900	(65)	(12)	4.9	(22)	(1)
5.1	2300	(65)	(15)	3.7	(18)	(3)
6.7	1800	(66)	(14)	4.1	(18)	(2)
8.2	1500	(68)	(15)	4.0	(15)	(2)
19.0	632	(69)	(15)	4.1	(14)	(2)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, PPh(NC$_4$H$_4$)$_2$, C$_6$H$_6$, CO/H$_2$ (1/1, 10 atm), 60 °		596

P/Rh	Time (h)	I	II	I:II	VI	VII
1.7	1.5	(66)	(18)	3.4	(15)	(2)
2.6	1.5	(66)	(21)	2.1	(10)	(4)
4.7	1.5	(75)	(11)	6.1	(12)	(1)
6.0	1.5	(83)	(7)	11.5	(10)	(0)
8.0	1.5	(85)	(6)	14.8	(9)	(0)
13.0	3	(81)	(6)	14.5	(4)	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, PPh$_2$(NC$_4$H$_4$), C$_6$H$_6$, H$_2$/CO (1/1, 10 atm), 60 °	**I** + **II** + **VI**	596

P/Rh	Temp	Time (min)	Conversion (%)	I	II	I:II	VI
2.3	60°	90	88.9	(65)	(22)	6.0	(3)
4.7	60°	90	92.4	(71)	(20)	3.6	(2)
6.4	60°	90	94.5	(73)	(19)	3.8	(2)
9.2	60°	120	91.5	(73)	(15)	4.9	(3)
9.2	70°	90	92.8	(75)	(16)	4.8	(3)
13.6	60°	190	87.1	(74)	(9)	8.6	(4)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, P(OC$_6$H$_3$Me-4-Bu-*t*-2)$_3$, L/Rh = 10, CO/H$_2$ (1/1, 20 atm), C$_6$H$_6$, 70 °	**I** (66) + alkenes (9)	468
	Co$_2$(CO)$_6$(L)$_2$, H$_2$/CO (8/1, 45 atm), dioxane, 150°, 3 h		597

Ligand	I	II	V	III	IV	VIII	hexane	hexenes
CO	(30)	(13)	(6)	(25)	(15)	(2)	(8)	(1)
P(Bu-*n*)$_3$	(42)	(19)	(7)	(11)	(6)	(2)	(10)	(4)
P(C$_3$H$_6$OCH$_3$)$_3$	(41)	(18)	(8)	(12)	(7)	(2)	(9)	(4)
P(CH$_2$CH$_2$CO$_2$CH$_3$)$_3$	(38)	(17)	(7)	(15)	(8)	(3)	(9)	(4)
P(CH$_2$CH$_2$CN)$_3$	(26)	(17)	(7)	(6)	(5)	(tr)	(10)	(29)

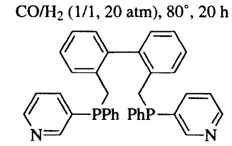
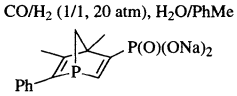
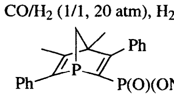
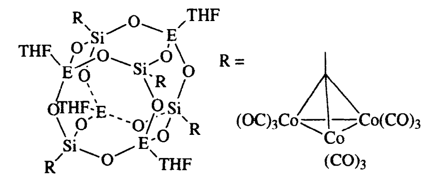
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, ligand, L/Rh = 10, PhMe, CO/H$_2$ (1/1, 20 atm), 80°, 20 h 	**I** (90) + **II** (2) + internal isomers (8), **I**:**II** = 49	224
	[Rh(CO)$_2$Cl]$_2$, ligand, L/Rh = 1, 80°, CO/H$_2$ (1/1, 20 atm), H$_2$O/PhMe (1/1) 	**I** + **II** (89), **I**:**II** = 0.88	598
	[Rh(CO)$_2$Cl]$_2$, ligand, L/Rh = 1, 80°, CO/H$_2$ (1/1, 20 atm), H$_2$O/PhMe (1/1) 	**I** + **II** (66), **I**:**II** = 1	598
	Co$_3$(CO)$_9$CSi(OH)$_3$, CO/H$_2$ (1/1, 126 atm), PhMe, 120°, 12 h	**I** + **II** + **V** (—), **I**:(**II**+**V**) = 3.75	599
	Co$_3$(CO)$_9$CSi[O(CH$_2$)$_2$(OCH$_2$CH$_2$)$_n$OH]$_3$, CO/H$_2$ (1/1, 70 atm), PhMe, 120°, 8 h	**I** + **II** + **V** (—), **I**:(**II**+**V**) = 0.73	599

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

CO/H_2 (70 bar), 120°, 18 h, toluene — 600



E	Conversion (%)	TON	I + II	I:II	internal hexenes
Al	86.9	4633	(96)	2	(3)
Ga	87.5	3525	(91)	1.6	(7)
In	46.0	2186	(52)	0.8	(37)

$PtCl_2(phosphine)_2$, $SnCl_2$, P/Rh = 2, PhMe, CO/H_2 (1/1, 1000 psi), 100°, 8 h — 601

Ligand	TOF	I + II	I:II
$P(CH_2Ph)_3$	71	(17)	3.5
$P(C_2H_4Ph)_3$	62	(49)	5.6
$P(C_3H_6Ph)_3$	53	(42)	7.2

$PtCl_2$ (phosphine)$_2$ on glass, $SnCl_2$, P/Rh = 2, CO/H_2 (1/1, 1000 psi), $PhMe/H_2O$, 100°, 8 h — 601

Ligand	TOF	I + II	I:II
TPPTS	5.7	(5)	10.3
TBeTS	4.5	(4)	3.7
TEtPTS	3.0	(2)	5.8
TPrPTS	2.6	(2)	8.7

$HRh[P(OPh)_3]_4$, $Cp_2ZrH(CH_2PPh_2)$, CO/H_2 (1/1, 10 atm), PhMe, 80° — 602

[Zr]:[Rh]	Time (min)	Conv. (%)	I + II	I:II	V	2-hexenes
0	160	100	(77)	3.0	(8)	(26)
1	95	100	(40)	4.0	(1)	(45)
2	345	100	(71)	3.4	(—)	(35)
4	280	100	(45)	2.8	(—)	(35)
8	515	47	(18)	2.1	(—)	(—)

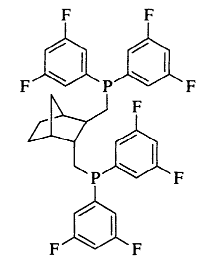
$HRh(CO)[P(OPh)_3]_3$, $Cp_2ZrH(CH_2PPh_2)$, CO/H_2 (1/1, 10 atm), PhMe, 80° — 602

[Zr]:[Rh]	Time (min)	Conv. (%)	I + II	I:II	V	2-hexenes
0	135	100	(71)	0.5	(24)	(4)
1	200	100	(73)	4.2	(2)	(28)
1.7	100	97	(59)	3.2	(—)	(17)
3	235	100	(58)	3.2	(—)	(44)
9.2	505	66	(15)	2.0	(—)	(43)

$Co_2(CO)_6(phosphine)_2$, phosphine, dioxane, H_2/CO (8/1, 45 atm), 3 h — 597

Phosphine	Temp.	P/Rh	I	II	III	IV	V	VIII	hexane	hexenes
$P(C_3H_6OMe)_3$	150°	0	(41)	(18)	(12)	(7)	(8)	(2)	(9)	(4)
$P(C_3H_6OMe)_3$	150°	1.3	(10)	(2)	(1)	(tr)	(1)	(0)	(4)	(81)
$P(C_3H_6OMe)_3$	150°	6.5	(7)	(1)	(1)	(0)	(tr)	(0)	(5)	(86)
$P(C_3H_6OMe)_3$	180°	6.5	(10)	(1)	(11)	(2)	(1)	(1)	(15)	(59)
$P(C_3H_6OMe)_3$	150°	10	(2)	(tr)	(tr)	(0)	(0)	(0)	(5)	(92)
$P[(CH_2)_2CN]_3$	150°	0	(26)	(17)	(6)	(5)	(7)	(tr)	(10)	(29)
$P[(CH_2)_2CN]_3$	150°	10	(tr)	(tr)	(0)	(0)	(0)	(0)	(tr)	(99)
$P[(CH_2)_2CO_2Me]_3$	150°	0	(38)	(17)	(15)	(8)	(7)	(4)	(9)	(4)
$P[(CH_2)_2CO_2Me]_3$	150°	10	(tr)	(tr)	(0)	(0)	(tr)	(0)	(5)	(95)

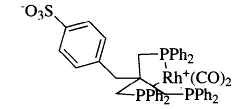
Conditions	Product(s) and Yield(s) (%)	Refs.
$(C_5Me_5)Rh(C_6F_5)_2$, PPh_3, L/Rh = 3, 80°, H_2/CO (1/1, 30 bar), 24 h	I:II=75:25, I + II (55)	603
$(C_5Me_5)Rh(HC_6F_4\text{-}p)_2$, PPh_3, L/Rh = 3, 80°, H_2/CO (1/1, 30 bar), 24 h	I:II=73:27, I + II (78)	603

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, 100°, CO/H_2 (1/1, 110 psi) 	I + II (—), I:II=7.2	604
	$Rh(CO)_2$-zeolite X, phosphine, P/Rh = 10, H_2/CO, 120°, 17 h		605

PR_3	H_2/CO (atm)	Solvent	I + II	I:II	III + IV	III:IV	Diethyl acetals
PPh_3	50	PhMe	(79)	3.3	(21)	3.5	(—)
PPh_3	50	EtOH	(38)	2.9	(52)	100:0	(10)
PEt_3	50	EtOH	(—)	—	(80)	2.5	(—)
PEt_3	20	EtOH	(—)	—	(100)	2.4	(—)
$P(Pr\text{-}n)_3$	50	EtOH	(—)	—	(32)	3.5	(—)
PEt_2Ph	50	EtOH	(—)	—	(40)	21	(30)
PEt_2Ph	20	EtOH	(—)	—	(60)	10.1	(30)

$Rh(CO)_2$-zeolite Y, phosphine, P/Rh = 10, H_2/CO (50 atm), 120°, 17 h — 605

PR_3	Solvent	I + II	I:II	III + IV	III:IV	Diethyl acetals
PPh_3	PhMe	(60)	(3.8)	(15)	(3.9)	(—)
PPh_3	EtOH	(35)	(5)	(36)	(100:0)	(30)
PEt_3	EtOH	(—)	(—)	(70)	(5.1)	(—)
$P(Pr\text{-}n)_3$	EtOH	(—)	(—)	(80)	(5.3)	(—)
PEt_2Ph	EtOH	(—)	(—)	(30)	(24)	(30)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(sulphos)(CO)_2$, CO/H_2 (1/1, 30 bar), H_2O/MeOH/isooctane (1/1/1), 80°, 5 h 	I (37) + II (17) + III (trace) + hexane (1) + 2-hexenes (33) + 3-hexenes (2)	606
	$[(CpFe(\eta^5\text{-}C_5H_4PPh_2))_2Co(CO)_3]$ $[Co(CO)_4]$, CO/H_2 (1/2, 2000 psi), PhMe, 170°, 3 h	I + II (7); III + IV (61), II:IV = 1.9	607
	$Co_2(CO)_8$, ligand, L/Co = 5, 190 °, H_2/CO (800 psi)		601

Ligand	Medium	H_2/CO	Time (h)	I + II	I:II	III + IV	III:IV	hexane
$P(CH_2Ph)_3$	PhMe	1/1	4	(39)	3.1	(13)	—	(—)
$P(C_2H_4Ph)_3$	PhMe	1/1	4	(24)	5.3	(9)	—	(—)
$P(C_3H_6Ph)_3$	PhMe	1/1	4	(21)	9.4	(30)	31	(16)
$P(C_3H_6Ph)_3$	PhMe	9/1	4	(0)	—	(53)	8.8	(19)
$P(C_3H_6Ph)_3$	PhMe	1/9	4	(25)	10.6	(13)	50	(13)
TPrPTS	$PhMe/H_2O$ (2/1)	1/1	8	(35)	1.3	(1)	1.2	(18)
TPrPTS	$PhMe/H_2O$ (2/1)	9/1	8	(11)	0.7	(0)	—	(48)
TPrPTS	$PhMe/H_2O$ (2/1)	1/9	8	(38)	2.3	(0)	—	(14)
TPrPTS	glass ($PhMe/H_2O$)	1/1	8	(15)	3.6	(0)	—	(31)
TPrPTS	glass ($PhMe/H_2O$)	9/1	8	(9)	3.6	(0)	—	(44)
TPrPTS	glass ($PhMe/H_2O$)	1/9	8	(27)	3.7	(0)	—	(20)

$Rh(acac)(CO)_2$, $Cp_2ZrH(CH_2PPh_2)$, PhMe, H_2/CO (1/1, 10 atm), 80°, 3.5 h — 608

Zr/Rh	Conv. (%)	I + II	2-hexene	I:II
1.4	56	(35)	(21)	1.8-2
2.7	84	(69)	(15)	1.8-2

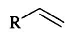
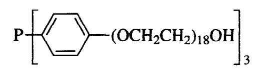
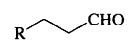
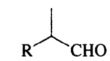
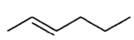
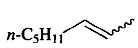
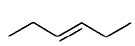
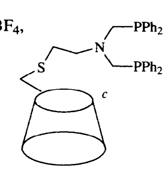
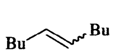
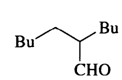
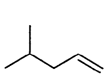
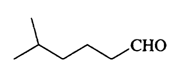
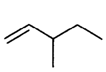
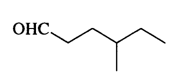
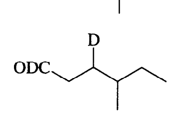
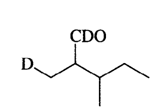
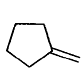
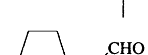
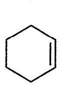
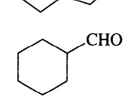
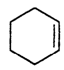
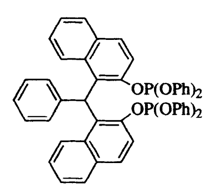
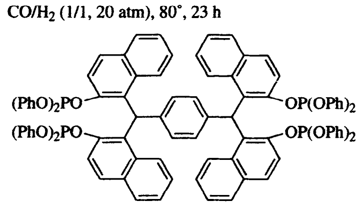
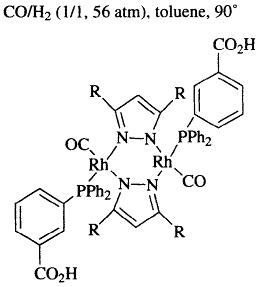
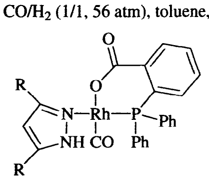
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $Cp_2Zr(CH_2PPh_2)_2$, PhMe, H_2/CO (1/1, 10 atm), 80°, 3.5 h		608
	Zr/Rh — Conv. (%)	I + II — 2-hexene — I:II	
	0.9 — 86	(52) — (34) — 1.8-2	
	1.2 — 99	(85) — (13) — 1.8-2	
	$RhCl_3$, phosphine, P/Rh = 13, 100°, 7 h, $PhMe/H_2O$ (2/3), pH = 6, CO/H_2 (1/1, 5 MPa) 	 I +  II	243
	R — Conv. (%)	I + II	
	C_4H_9 — 93.6	(91)	
	C_6H_{13} — 97.9	(86)	
	$C_{10}H_{21}$ — 96.0	(83)	
	$Ru_3(CO)_{12}$-2,2'-bipyridine on silica f22, CO/H_2 (1/1, 50 bar), 150°, 17 h, PhMe	**I** + **II** (0), **III** + **IV** (33-97), **III** : **IV** = 1.1-0.9	510
	$[Rh(CO)(PPh_3)_2]_4SiW_{12}O_{40}$, PhMe, CO/H_2 (1/1, 1000 psi), 100°, 3 h	**I** + **II** + **V** (96), **I**:**II**:**V** = 13:57:30	522
	$Pt(acac)_2$, TfOH, DPPF, H_2/CO (700 psi), 100°, 20 min	**I** + **II** + **V** + **III** (—), **I**:**II**:**V**:**III** = 20.7:1.7:0.3:0.7	609
	$HRh[P(OPh)_3]_4$, CO/H_2 (1/1, 10 atm), PhMe, 80°, 260 min	**I** (13) + **II** (48) + **V** (34)	602
	$HRh(CO)[P(OPh)_3]_3$, CO/H_2 (1/1, 10 atm), PhMe, 80°	**I** (16) + **II** (53) + **V** (32)	602
	$HRh(CO)[P(OPh)_3]_3$, $Cp_2ZrH(CH_2PPh_2)$, Zr/Rh = 1.5, CO/H_2 (1/1, 10 atm), PhMe, 80°	**I** (10) + **II** (51) + **V** (43)	602
	$[Rh(CO)(PPh_3)_2]_4SiW_{12}O_{40}$, PhMe, CO/H_2 (1/1, 1000 psi), 100°, 3 h	**I** + **II** + **V** (92), **I**:**II**:**V** = 10:40:50	522
	$[Rh(COD)(diphosphine)]BF_4$, 60°, 70 h, H_2O (30% DMF), CO/H_2 (1/1, 100 atm) 	**II** + **V** (—), **V**:**II** = 90:4	223
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrin-(Me-*o*)$_2$-2,6), P/Rh=5, CO/H_2 (1/1, 50 atm), 80°, 6 h	 I (2)	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh=5, CO/H_2 (1/1, 50 atm), 80°, 6 h	I (2)	610
	$[Rh(COD)OAc]_2$, PPh_3, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 90°	 I (78)	468
	$Rh(acac)(CO)_2$, $P(OC_6H_3Me\text{-}4\text{-}Bu\text{-}t\text{-}2)_3$, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 70°	I (64)	468
	$[Rh(COD)OAc]_2$, PPh_3, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 90 °	 I (91)	468
	Rh_2O_3, PPh_3, C_6H_6, CO/D_2 (1/1, 70 atm), 100°, 20 h	 (89) +  (11)	611
	$RhH(CO)(PPh_3)_3$, C_6H_6, rt, 4 d, CO/H_2 (1/2, 1 atm)	 (34)	368
	$[Rh(OAc)(COD)]_2$, $P(OPh)_3$, L/Rh = 2.5, CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 80°	 I (—)	517
	Rh_2O_3, C_6H_6, CO/H_2 (1/1, 150 atm), 100°, 2 h	I (82-84)	452

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$, H$_2$O, per(β-cyclodextrin-(Me-*o*)$_2$-2,6), P/Rh = 5, CO/H$_2$ (1/1, 50 atm), 80°, 2 h	**I** (5)	610
	Rh(acac)(CO)$_2$, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$, H$_2$O, P/Rh = 5, CO/H$_2$ (1/1, 50 atm), 80°, 2 h	**I** (4)	610
	Co(acac)$_2$, *n*-C$_7$H$_{16}$, CO/H$_2$ (1/1, 150 atm), 110°, 12 h	**I** (74)	452
	Co$_2$(CO)$_8$, C$_6$H$_6$, CO/H$_2$ (1/1, 150 atm), 120°, 8 h	**I** (80)	452
	Rh(acac)(CO)$_2$, P/Rh=2, PhMe, CO/H$_2$ (1/1, 20 atm), 80°, 23 h 	**I** (78)	612
	Rh(acac)(CO)$_2$, P/Rh=2, PhMe, CO/H$_2$ (1/1, 20 atm), 80°, 23 h 	**I** (80)	612
	CO/H$_2$ (1/1, 56 atm), toluene, 90° 	see below	613

R	Conversion after 1 h (%)	**I** (%)
H	37	37
Me	40	40

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H$_2$ (1/1, 56 atm), toluene, 90° 	see below	613

R	Conversion after 1 h (%)	**I** (%)
H	11	9
Me	31	31

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(COD)(OAc), P(OC$_6$H$_4$Bu-*t*-2)$_3$, L/Rh = 10, C$_6$H$_6$, 90°, 0.5-2 h, CO/H$_2$ (1/2, 18 bar)	**I** (—)	614
	CO/H$_2$ (1/1, 80 atm), C$_6$H$_6$, 120°, 8 h	see below	615

Catalyst	**I**
Rh$_2$(μ-Cl)(μ-SCH$_2$-polystyrene resin)(CO)$_2$(PBu-*t*$_3$)$_2$	(—)
Rh$_2$(μ-Cl)[μ-S(C$_6$H$_4$Me-4)](CO)$_2$(PPh$_2$-polystyrene resin)$_2$	(—)
Rh$_2$(μ-Cl)[μ-S(C$_6$H$_4$Cl-4)](CO)$_2$(PPh$_2$-polystyrene resin)$_2$	(—)
Rh$_2$(μ-Cl)[μ-S(CH$_2$)$_3$SiO$_3$-silica 60](CO)$_2$(PBu-*t*$_3$)$_2$	(—)
Rh$_2$(μ-Cl)[μ-S(CH$_2$)$_3$SiO$_3$-alumina 90](CO)$_2$(PBu-*t*$_3$)$_2$	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[(η^5-C$_5$H$_5$)Rh$_2$(μ-CO)(μ-Ph$_2$PPy)(CO)Cl], CO/H$_2$ (1/1, 80 atm), C$_6$H$_6$, 80°, 24 h	**I** (~93)	616

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

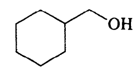
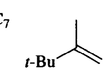
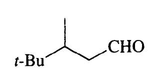
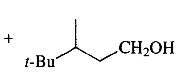
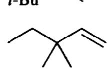
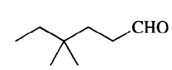
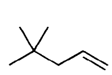
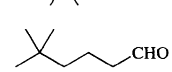
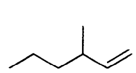
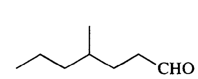
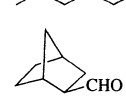
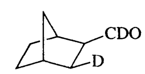
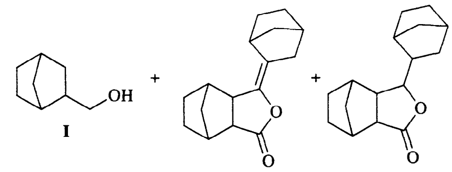
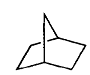
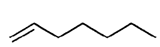
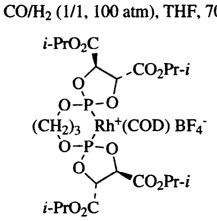
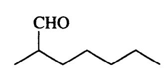
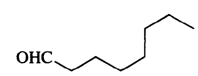
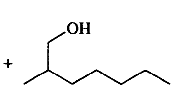
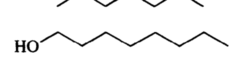
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	cis-[Rh{P(Bu-*t*)$_3$}(CO)]$_2$(μ-Cl){μ-P(Bu-*t*)$_2$}, CO/H$_2$ (1/1, 80 atm), PhMe, 120°, 20 h	**I** (94) + cyclohexane (6)	617
	Poly(*N*-vinyl-2-pyrrolidone)-Co$_2$Rh$_2$(CO)$_{11}$, CO/H$_2$ (1/1.2, 55 kg/cm^2), C$_6$H$_6$, 80°, 8 h	**I** +  **II** **I** + **II** (—), **I**:**II** = 64.1:35.9	566
	Ru$_3$(CO)$_{12}$, P(C$_6$H$_{11}$)$_3$, HCO$_2$Me, H$_2$O, 180°, 10 h	**II** (60) + cyclohexane (9)	493
	[Pt(C$_2$H$_4$)(DPPB)]/CF$_3$SO$_3$H (1/1), PhMe, CO/H$_2$ (1/1, 100 atm), 100°, 48 h	**I** (24) + **II** (2) + cyclohexane (1)	259
	Rh$_2$(CO)$_2$[P(Bu-*t*)$_3$]$_2$(μ-Cl)(μ-SBu-*t*), CO/H$_2$ (1/1, 80 atm), 120°, 23 h	**I** (100)	618
	Rh$_2$(CO)$_2$[P(Bu-*t*)$_3$]$_2$(μ-Cl)[μ-S(CH$_2$)$_2$SiO$_3$-silica gel], CO/H$_2$ (1/1, 80 atm), 120°, 20 h	**I** (75)	618
	Rh$_2$(CO)$_2$[P(Bu-*t*)$_3$]$_2$(μ-Cl)[μ-S(CH$_2$)$_3$SiO$_3$-silica gel], CO/H$_2$ (1/1, 80 atm), 120°, 20 h	**I** (85)	618
	Rh$_4$(CO)$_{12}$, CO/H$_2$ (1/1, 34 atm), 125°, *n*-hexane	**I** (—)	619
	K[Ru(saloph)Cl$_2$], EtOH, 130°, CO/H$_2$ (1/1, 21 atm)	**I** (—)	553
	cis-PtCl$_2$(PPh$_3$)$_2$/SnCl$_2$·2H$_2$O (1:5), CO/H$_2$ (1/1, 100 bar), CHCl$_3$, 90°, 6 h	**I** (53) + Cyclohexane (3)	492
	Rh$_4$(CO)$_{12}$/P(OPh)$_3$ (1/6), PhMe, 50°, 48 h, CO/H$_2$ (1/1, 1 atm)	**I** (90)	620
	Co$_2$Rh$_2$(CO)$_{12}$/P(OPh)$_3$ (1/6), PhMe, 50°, 48 h, CO/H$_2$ (1/1, 1 atm)	**I** (51)	620
	Co$_2$(CO)$_8$, Ru$_3$(CO)$_{12}$, Ru/Co = 9.9, THF, CO/H$_2$ (1/1, 80 kg/cm^2), 110°, 4 h	**I** (100)	621, 536, 622
	Rh(acac)[P(OPh)$_3$]$_2$, P(OPh)$_3$, 80°, CO/H$_2$ (10 atm), 4.5 h	**I** (44)	260
	Co(acac)$_2$(H$_2$O)$_2$, C$_6$H$_6$, 353 K, 4 h, CO/H$_2$ (1/1, 9.4x10^3 KN/m^2)	**I** (20) + **II** (19) + cyclohexane (13)	623
	Co$_2$Rh$_2$(CO)$_{12}$ on Dowex MWA-1 resin, CO/H$_2$ (1/1, 50 bar), PhMe, 100°, 16-19 h	**II** (77)	588
C$_7$ 	Na$_2$[Rh$_{12}$(CO)$_{30}$], H$_2$/CO (1/1, 120 atm), 100°, 90 min	 (56) +  (tr)	624
	[Rh (COD)OAc]$_2$, PPh$_3$, L/Rh = 10, CO/H$_2$ (1/1, 20 atm), C$_6$H$_6$, 90°	 (77)	468
	Rh(acac)(CO)$_2$, P(OC$_6$H$_3$Me-4-Bu-*t*-2)$_3$, L/Rh = 10, CO/H$_2$ (1/1, 20 atm), C$_6$H$_6$, 70°	 **I** (79) + alkenes (15)	468
	[Rh(COD)OAc]$_2$, PPh$_3$, L/Rh = 10, CO/H$_2$ (1/1, 20 atm), C$_6$H$_6$, 90 °	**I** (85)	468
	[Rh(COD)OAc]$_2$, PPh$_3$, L/Rh = 10, CO/H$_2$ (1/1, 20 atm), C$_6$H$_6$, 90 °	 (91)	468
	Pt(C$_2$H$_4$)(DPPB)/MeSO$_3$H, PhMe, CO/H$_2$ (1/1, 100 atm), 100°, 5 h	 **I** (98)	625
	Pt(C$_2$H$_4$)(DPPB)/MeSO$_3$H, PhMe, CO/H$_2$ (1/1, 50 atm), 100°, 5 h	**I** (93)	625
	HRh(CO)(PPh$_3$)$_3$, PhMe, 1 h CO/H$_2$ (1/1, 100 atm), 100°	**I** (99)	625
	Pt(DPPB)Cl$_2$/SnCl$_2$, PhMe, CO/H$_2$ (1/1, 100 atm), 100°, 1 h	**I** (98)	625

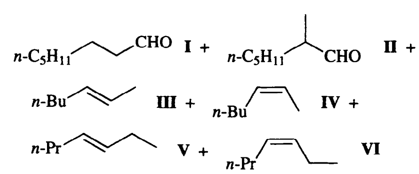
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Pt(C_2H_4)(DPPB)/MeSO_3H$, PhMe, CO/D_2 (1/1, 50 atm), 100°, 5 h	 (81)	625
	1. $Co_2(CO)_8$-$Ru_3(CO)_{12}$, C_6H_6, 90°, 4 h, CO/H_2 (1/1, 80 kg/cm^2) 2. $NaBH_4$	 I + II + III	626

Catalyst Co:Ru	Conv. (%)	I	II	III
1:0	41	(9)	(19)	(1)
0:1	3	(1)	(tr)	(0)
1:1	83	(29)	(21)	(4)
1:5	93	(38)	(12)	(3)
1:10	99	(55)	(15)	(tr)

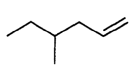
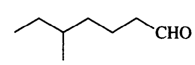
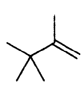
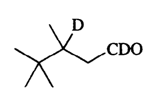
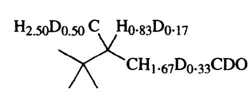
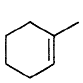
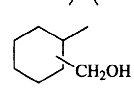
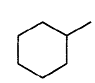
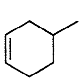
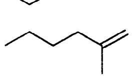
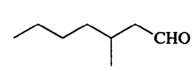
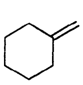
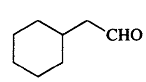
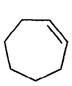
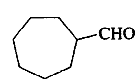
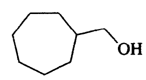
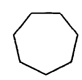
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ru_3(CO)_{12}$, $P(C_6H_{11})_3$, HCO_2Me, H_2O, 180°, 10 h	I (86) +  (9)	493
	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	 I +  II I + II (—); I:II = 60:40	248
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 20 h	I (—) + II (—) + starting material (11) I:II = 48:52	251
	$[Rh(COD)(PPh_3)_2]ClO_4/PPh_3$, L/Rh = 10, CO/H_2 (1/1, 5 atm), $(ClCH_2)_2$, 80°, 5 h	I + II (—), I:II = 1:3.7	517
	$Pt(COD)_2$, Ph_2POH, phosphines, C_6H_6, CO/H_2 (1/2, 50 bar), 100°, 1 h	I + II +  III +  IV	627-630

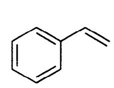
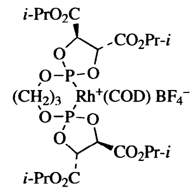
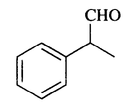
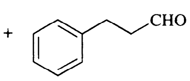
Catalyst	I + II	I:II	III + IV	III:IV	heptane	heptenes
$Pt(COD)_2/PPh_2OH/PPh_3$ (1/1/1)	(10)	10:90	(9)	10:90	(1)	(30)
$Pt(COD)_2/PPh_2OH/PPh_3$ (1/1/2)	(3)	10:90	(6)	10:90	(tr)	(10)
$Pt(COD)_2/PPh_2OH$ (1/2)	(4)	10:90	(2)	10:90	(2)	(80)
$Pt(COD)_2/PPh_2OH/DPPE$ (1/1/1)	(24)	10:90	(3)	10:90	(1)	(33)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[RhCl(COD)]_2$, PPh_3, P/Rh = 1, C_6H_6, CO/H_2 (1/1, 30 bar), 45°	 I:II:III:IV:V:VI = 69:31:34:13:4:3	631
	$[RhCl(COD)]_2$, PPh_2-polystrene, P/Rh = 1, C_6H_6, CO/H_2 (1/1, 30 bar), 45°	I:II:III:IV:V:VI = 51:49:31:16:7:4	631
	Rh(anthranilate)$(CO)_2$, $P(OPh)_3$, P/Rh = 3.1, CO/H_2 (1/1, 1 atm), PhMe, 40°	I + II (78) + hept-2-ene (22)	570
	$[Rh_2(\mu\text{-}S(CH_2)_3NMe_2(CH_2Ph))_2(COD)_2][PF_6]_2$, 2 PR_3, CO/H_2 (1/1, 5 bar), 80°, $ClCH_2CH_2Cl$		632

PR_3	Time (min)	Conv. (%)	I/II
PPh_3	330	93	2.57
$P(OPh)_3$	570	40	0.70
$P(OMe)_3$	420	8	3.44

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh_2(\mu\text{-}S(CH_2)_3NMe_2(CH_2Ph))_2(CO)_4][PF_6]_2$, 10 PPh_3, CO/H_2 (1/1, 5 bar), 80°, $ClCH_2CH_2Cl$, 5 h	**I** + **II** (78), **I**:**II** = 3.33	632
	$Rh_4Cl_4(CO)_4(O_2)_2(PPh_2OBu\text{-}i)_2$, $PPh_2OBu\text{-}i$, CO/H_2 (1/1, 1000 psi), DMA, 90°, 24 h	**I** + **II** (—), **I**:**II** = 69:22	633
	$[Rh(NBD)\{P(C_6H_4R\text{-}4)_3\}_2]ClO_4$, CO/H_2	**I** + **II** + *n*-BuCH(Et)CHO **VII** (—)	634
	R — Time (min) for 50% conversion	**I** : (**II** + **VII**)	
	MeO — 29	68 : 32	
	Me — 27	68 : 32	
	F — 18	64 : 36	
	Cl — 21	47 : 53	
	Catalyst, CO/H_2 (1/1, 50 atm), Me_2CO, 80°		635
	Catalyst	Selectivity *n*-octanal (**I**/Products)	
	$[Rh(Pz)\{P(OPh)_3\}_2]_2$	58	
	$[Rh(Pz)(CO)P(OPh)_3]_2$	43	
	$[Rh(Pz)(COD)]_2$	37	
	$[Rh(Pz)(COD)]_2$ + 16 PPh_3	74	
	$[Rh(MePz)(COD)]_2$ + 16 PPh_3	73	
	$[Rh(Me_2Pz)(COD)]_2$	37	
	$[Rh(Pz)(CO)PPh_3]_2$ + 2 PPh_3	63	
	$[Rh(MePz)(CO)PPh_3]_2$ + 2 PPh_3	64	
	$[Rh(Pz)(CS)PPh_3]_2$ + 2 PPh_3	68	
	$[Rh(Me_2Pz)(CS)PPh_3]_2$ + 2 PPh_3	70	
	$[Rh(HMe_2Pz)(CS)(PPh_3)_2]ClO_4$	64	
	$HRh(CO)(PPh_3)_2PPh_2$-polystyrene, polystyrene-PPh_2=CH_2, THF, CO/H_2 (1/1, 120 lb/in^2), 60°, 16 h	**I** (45) + **II** (10) + *n*-$C_9H_{19}CHO$ (12) + *n*-$C_{11}H_{23}CHO$ (2) + *n*-$C_{13}H_{27}CHO$ (tr)	636
	$[Rh(NBD)Cl]_2/PPh_3$ (1/10), Me_2CO, 100°, CO/H_2 (3/11, 38 atm)	**I** + **II** (—), **I**:**II** = 83.5:16.5	637
	$[Rh(COD)OAc]_2$, PPh_3, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 90 °	**I** (77)	468
	$[Rh(COD)OAc]_2$, PPh_3, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 90 °	 (77)	468
	$Rh_4(CO)_{12}$, C_6H_6, CO/D_2 (1/1, 200), 100°	 (99)	638
	$Co_2(CO)_8$, C_6H_6, CO/D_2 (1/1, 200), 100°	 (99)	638
	"	 **I** (33) +  **II** (40)	493
	"	**I** (50) + **II** (6)	493
	Rh(COD)(OAc), $P(C_6H_4OBu\text{-}t\text{-}2)_3$, L/Rh = 10, C_6H_6, 70°, 30-60 min, CO/H_2 (1/2, 18 bar)	 (—)	614
	Rh(COD)(OAc), $P(C_6H_4OBu\text{-}t\text{-}2)_3$, C_6H_6, 75°, CO/H_2 (1/2, 20 bar)	 (—)	614
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, 80°, CO/H_2 (10 atm), 3 h	 (24)	260
	$Ru_3(CO)_{12}$, $P(C_6H_{11})_3$, HCO_2Me, H_2O, 180°, 10 h	 (60) +  (24)	493

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	CO/H_2 (1/1), THF, 70°, 16 h 	 I +  II	248, 639
		Pressure (atm) / I : II / Yield (%): 10 / 50 : 50 / (—); 24 / 75 : 25 / (—); 56 / 98 : 2 / (—); 100 / 97.5 : 2.5 / (—)	
	$[Rh(CO)_2Cl]_2$, $PPhMe_2$, C_6H_6, CO/H_2, 60°	I + II (—), I:II = 96:4	640
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	I (—) + II (—) + starting material (11) I:II = 97.3:2.7	251
	$[RhCl(CO)_2]_2$, L/Rh = 5, Et_3N/Rh = 10, CO/H_2 (1/1, 20 bar), PhMe, 40°, 6 h		641, 642

Ligand	Conv. (%)	I:II	I + II
TPP	100	84:16	(90)
PPh_3	87	94:6	(99)
PPPN	82	91:9	(99)
o-TDPP	75	80:20	(84)
PPP	49	87:13	(100)
DMTPPN	32	94:6	(100)
t-BDMP	0	—	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[Rh(NBD)(2,5-bis(diphenylphosphino-methyl)bicyclo[2.2.1]heptane)ClO_4, CO/H_2 (1/1, 40 atm), C_6H_6, 25°, 72 h	I + II (—), I:II = 97:3	247
	$[Rh(COD)Cl]_2$, CO/H_2 (1/1, 600 psi), $CHCl_3$, 80°		643

Ligand	Time (h)	Yield (%)	I:II
$Ph_2P(CH_2)_2PPh_2$	4	(32)	92:8
$Ph_2P(CH_2)_2C_5H_4N$-2	1	(76)	91:9
$Ph_2PCH_2NMe_2$	1.5	(59)	94:6
$Ph_2P(CH_2)_2NMe_2$	1.5	(87)	91:9
$Ph_2P(CH_2)_3NMe_2$	1.5	(85)	97:3
$Ph_2PC_5H_4N$-2	1.5	(66)	98:2

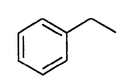
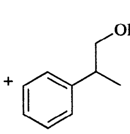
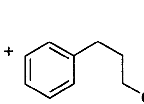
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$(\mu_3\text{-MeC})Co_3(CO)_7(\mu\text{-}Ph_2PCH_2PMe_2)$, PhMe, CO/H_2 (1/1, 80 bar), 105°, 67 h	I + II (23)	644
	$Pt(DIOP)Cl_2/Sn/e^-$, propylene carbonate, C_6H_6, CO/H_2 (1/1, 100 atm), 90°, 7 h	I (—) + II (74) +  III (8) I:II = 1:4	245
	$Pt(DIOP)Cl_2/Fe/e^-$, propylene carbonate, C_6H_6, CO/H_2 (1/1, 100 atm), 90°, 7 h	I (—) + II (90), I:II = 1:9	245
	$PtCl_2(PPh_3)_2$, $SnCl_2\cdot 2H_2O$, MEK, 70°, CO/H_2 (1/1, 100 atm), 4 h	I + II (—), I:II = 65:35	645
	1. $Pt(DIOP)_2Cl_2/Fe/e^-$, propylene carbonate/ C_6H_6 (40/60) 2. CO/H_2 (4/1, 100 bar), 90°, 24 h	I + II + III (—), I:II:III = 9:90:1	244
	$Pt(C_2H_4)((+)\text{-DIOP})$/3 $MeSO_3H$, PhMe, CO/H_2 (1/1, 100 atm), 100°, 4 h	I + II + III (5) +  IV +  V; I + II (58), I:II = 15.6:84.4; IV + V (7), IV:V = 4.4:95.6	646
	$Pt(C_2H_4)((+)\text{-DIOP})/SnCl_2$, PhMe, CO/H_2 (1/1, 100 atm), 100°, 4 h	I + II (85), I:II = 41.3:58.7; III (12); IV + V (3), IV:V = 32.3:67.8	646
	$Pt(C_2H_4)(1,2\text{-}(CH_2PPh_2)_2C_6H_4)/SnCl_2$, PhMe,$CO/H_2$ (1/1, 100 atm), 100°, 4 h	I + II (84), I:II = 44.8:55.2; III (15)	646

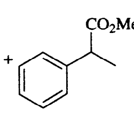
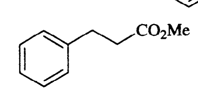
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PtCl_2$((+)-DIOP)/3 $SnCl_2$, PhMe, CO/H_2 (1/1, 100 atm), 100°, 4 h	I + II (77), I:II = 49.8:50.2; III (14)	646
	PPN[$HRu(CO)_4$], CO/H_2 (1/1, 300 atm), DMF, 150°, 16.5 h	I + II (43), I:II = 95.9:4.1; III (3); IV + V (52), IV:V = 93.2:6.8	499
	$PtCl_2$(bisphosphine), $SnCl_2$, PhMe, 100°, CO/H_2 (1/1, 80 bar), 4 h		131
	Biphosphine	Conv. (%) / I + II / I:II	
	$Ph_2PCH_2PPh_2$	2 / (80) / 55:45	
	$Ph_2P(CH_2)_2PPh_2$	9 / (72) / 72:28	
	$Ph_2P(CH_2)_3PPh_2$	76 / (86) / 27:73	
	$Ph_2P(CH_2)_4PPh_2$	71 / (80) / 43:57	
	cis-$PtCl_2(PPh_3)_2$/$SnCl_2 \cdot 2H_2O$ (1:5), CO/H_2 (1/1, 100 bar), $CHCl_3$, 90°, 4 h	I + II + III (4) I + II (50), I:II = 46:54	492
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 5, PhMe, CO/H_2 (5 bar), 80°, 2 h	I + II (100), I:II = 58:42	647
	$Rh_2(\mu$-SBu-$t)_2(PPh_3)_2$, PPh_3, L/Rh = 10, CO/H_2 (5 bar), $ClCH_2CH_2Cl$, 80°, 2 h	I + II (100), I:II = 89.2:10.6	647
	$Rh_2(\mu$-SBu-$t)_2[P(OPh)_3]_2$, PhMe, CO/H_2 (5 bar), 80°, 2 h	I + II (100), I:II = 33.5:66.5	647
	[Rh(COD)(TPPTS)$_2$]ClO_4, H_2O, 80°, CO/H_2 (1/1, 5 bar), 18 h	I + II (86), I:II = 70:30	647
	$Rh_2(\mu$-SBu-$t)_2(CO)_2(TPPTS)_2$, H_2O, 80°, CO/H_2 (1/1, 5 bar), 18 h	I + II (100), I:II = 78.8:21.2	647
	$RhH_2(O_2COH)[P(Pr$-$i)_3]_2$, CO (15 atm), H_2O, THF, 115°, 20 h	I (23) + II (57) + III (16)	577
	$Rh_2Cl_2(CO)_4$, Phosphine, P/Rh = 4, PhMe, CO/H_2 (1/1, 100 atm), 140°		507
	Phosphine	Relative Rate / I : II	
	DBP-Ph	1.1 / 77 : 23	
	PPh_3	1.0 / 74 : 26	
	DBP-Et	0.9 / 86 : 14	
	PPh_2Et	0.7 / 77 : 23	
	$P(Bu$-$n)_3$	0.2 / 83 : 17	
	$RhH(CO)(PPh_3)_3$, PPh_3, C_6H_6, CO/H_2 (1/1)		648
	P/Rh / Pressure (psi) / Temp.	I + II / I:II	
	3 / 100 / 60°	(100) / 11.0	
	3 / 400 / 60°	(100) / 13.9	
	3 / 800 / 60°	(97) / 15.0	
	3 / 800 / 80°	(96) / 10.6	
	3 / 800 / 120°	(100) / 4.6	
	5.3 / 800 / 60°	(100) / 14.7	
	14.3 / 800 / 60°	(100) / 13.0	
	Polystyrene-1% divinylbenzene resins-$(C_6H_4PPh_2)_xRhH(CO)(PPh_3)_{3-x}$, P/Rh = 3.3, C_6H_6, CO/H_2 (1/1, 800 psi), 60°	I + II (98), I:II = 12.9	648
	$RhH(CO)[Ph_2P(CH_2)_2PPh_2](PPh_3)$, $Ph_2P(CH_2)_2PPh_2$, C_6H_6, CO/H_2 (1/1)		648
	P/Rh / Pressure (psi) / Temp.	I + II / I:II	
	3 / 100 / 60°	(24) / 1.4	
	3 / 400 / 60°	(100) / 9.0	
	3 / 800 / 60°	(100) / 11.9	
	16.7 / 400 / 60°	(55) / 26.5	
	16.7 / 400 / 80°	(72) / 21.8	
	16.7 / 400 / 120°	(100) / 12.3	

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Co_2(CO)_8$/pyridine (1/2), C_6H_6, 60°, CO/H_2 (1/1, 80 atm), 20.5 h	**I** + **II** (35), **I**:**II** = 87:13	649
	$[Rh(COD)Cl]_2$, ligand, $CHCl_3$, 80°, 1.5 h, CO/H_2 (1/1, 600 psi)		650

Ligand	Conv. (%)	I:II
none	7	95:5
2-PPh_2-C_5H_4N	66	98:2
2-$P(O)Ph_2$-C_5H_4N	61	92:8
$Ph_2PCH_2NMe_2$	59	94:6
$Ph_2P(O)CH_2NMe_2$	100	91:9
$Ph_2P(O)CH_2CH_2NMe_2$	74	91:9
2-$CH_2P(O)Ph_2$-C_5H_4N	63	87:13
2-$CH_2CH_2P(O)Ph_2$-C_5H_4N	23	91:9

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_4(CO)_{12}$, C_6H_6, CO/H_2 (1/1, 170 atm), 20°, 15 h	**I** + **II** (—), **I**:**II** = 98:2	651
	$Rh_4(CO)_{12}$, C_6H_6, CO/H_2 (1/1, 170 atm), 130°, 0.2 h	**I** + **II** (—), **I**:**II** = 64:36	651
	$Rh_4(CO)_{12}/PPh_3$ (1/5), PhMe, 25°, CO/H_2 (1/1, 1 atm)	**I** + **II** (—), **I**:**II** = 14.5	620
	$Co_2Rh_2(CO)_{12}/PPh_3$ (1/3), PhMe, 25°, CO/H_2 (1/1, 1 atm)	**I** + **II** (—), **I**:**II** = 8.6	620
	$[Pt(C_2H_4)(DPPB)]/CH_3SO_3H$ (1/1), PhMe, CO/H_2 (1/1, 100 atm), 100°, 22 h	**I** + **II** (79), **I**:**II** = 10.8:89.2; **III** (3); **IV** + **V** (6)	259
	$RhH(CO)(PPh_3)_3/Ph_2PPy$ (2/1), C_6H_6, CO/H_2 (1/1, 70 atm), 40°, 8 h	**I** + **II** (>99), **I**:**II** = 16.0	616
	$MeCCo_2(CO)_6NiCp$, THF, 60°, 141 h, CO/H_2 (1/1, 800 psi)	**I** + **II** (89), **I**:**II** = 7.6	504
	$RhH_2(O_2COH)[P(Pr\text{-}i)_3]_3$, $(CH_2O)_n$, THF, 120°, 20 h	**I** + **II** + **III** + **IV** + **V** +  **VI** +  **VII** **I** + **II** (26), **I**,**II** = 37:63; **III** (23); **IV** + **V** (14), **V**:**VI** = 25:75; **VI** + **VII** (12), **VI**:**VII** = 17:83	593
	$[Rh(COD)(OMe)]_2$, CO/H_2	**I** + **II** (79), **I**:**II** = 95:5	316
	Rh/C (5%), DPPB, HCO_2H, CO (8.5 atm), DME, 100-105°, 18-24 h	**I** + **II** (67), **I**:**II** = 87:13	374
	Rh/C (5%), DPPB, HCO_2H, CO (8.5 atm), DME, 110-120°, 24 h	**I** + **II** (50), **I**:**II** = 58:42	374
	(see below)		652

Catalyst	P (atm)	Temp.	Conv. (%)	(I+II)/(I+II+III) (%)	I/II
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	40	45°	17.50	97.15	17.98
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	40	75°	92.58	99.36	6.96
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	40	100°	97.31	98.88	2.33
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	60	45°	34.78	98.77	20.55
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	60	75°	98.68	99.62	20.06
$[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$	60	100°	99.54	99.62	11.49
$[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$	50	75°	1.76	99.99	—
$[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$	60	75°	3.40	88.27	—
$[Ru(Ph_2PPy)_3Cl]Cl$	60	75°	1.18	63.93	—
$[Rh(CO)_2Cl_2][AsPh_4]$	50	75°	12.61	71.42	~9.00

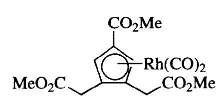
Catalyst	Temp.	Time (h)	CO/H_2 (bar)	Solvent	I + II	I:II
$(MeO_2CCp)Rh(CO)_2$	100°	3	40/60 (70)	PhMe	(94)	73:27
$(Cp)Rh(CO)_2$	100°	3	40/60 (70)	PhMe	(92)	58:42
$(MeO_2CCp)Rh(CO)_2$/5 PPh_3	80°	3	40/60 (56)	PhMe	(99)	99:1
$(Cp)Rh(CO)_2$/5 PPh_3	80°	3	40/60 (56)	PhMe	(25)	99:1
$(MeO_2CCp)Rh(CO)_2$/5 PPh_3	60°	1	40/60 (56)	PhMe/MeOH (1/4)	(85)	99:1

Ref. 594 applies to the table above.

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$(CO)_4\overline{W(\mu\text{-}PPh_2)_2Rh}H(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 380 psi), 50°, 20 h	**I** + **II** (>99), **I**:**II** = 98:2	371
	CO/H_2 (1/1), PhMe		653

Catalyst	Rh/PPh$_3$	P (atm)	Temp.	Time (h)	Conv. (%)	I	I/II
$Rh_2(OAc)_3[(C_6H_4)PPh_2](AcOH)_2$	—	5	80°	20	95	(51)	1.0
"	—	30	80°	2	100	(74)	2.8
$Rh_2(OAc)_2[(C_6H_4)PPh_2]_2(AcOH)_2$ (head-to-tail)	—	5	80°	20	79	(47)	0.9
"	—	30	80°	2	100	(75)	3.0
"	—	30	60°	6	100	(92)	11.5
"	1/1	5	80°	20	97	(69)	2.2
"	1/1	30	80°	3	99	(89)	8.1
$Rh_2(OAc)_2[(C_6H_4)PPh_2]_2(AcOH)_2$ (head-to-head)	—	30	60°	6	100	(93)	13.3
"	1/1	5	80°	20	96	(71)	2.5
$Rh_2(OAc)_4$	1/1	30	80°	20	100	(85)	5.7
"	1/2	5	80°	20	99	(76)	3.2
$HRh(CO)(PPh_3)_3$	—	5	80°	20	100	(58)	1.4
"	—	30	80°	2	36	(87)	6.7
$HRh(CO)(PPh_3)_3$/AcOH	—	30	80°	2	40	(87)	6.8



594

PPh$_3$/Rh	Temp.	Time (h)	CO/H_2 (40/60, bar)	Solvent	I + II	I:II
0	100°	3	70	PhMe	(99)	58:42
5	80°	3	56	PhMe	(98)	94:6
5	60°	10	56	PhMe	(100)	97:3
5	60°	1	56	PhMe/MeOH (1/4)	(94)	95:5

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	cis-[RhCl(NBD){(*R*,*R*)-5,11,17,23-tetra-*tert*-butyl-25,27-bis[(1-phenylethyl)carbamoylmethoxy]-26,28-bis(diphenylphosphinomethoxy)calix[4]arene}]BF_4, CO/H_2 (1/1, 40 atm), CH_2Cl_2/C_6H_6, 40°, 48 h	**I** + **II** (—), **I**:**II** = 95:5	654
	$RhCl(CO)(DPM)_2$-poly(vinylbenzyltriethylammonium chloride on silica, 85°, *c*-C_6H_{12}, H_2O, EtOH, CO/H_2 (1/1, 750 psi), 15 h	**I** + **II** (56), **I**:**II** = 6:1	655-657
	Rh(SOX)(COD), PhMe, 60°, CO/H_2 (1/1, 0.1 MPa)		511

Phosphine or Phosphite	P/Rh	Turnover	Yield (%)	I:II
$P(OPh)_3$	2	43	(—)	39.8 : 60.2
DPPM	2	0	(—)	—
DPPE	2	267	(—)	96.0 : 4.0
DPPE	5	90	(—)	97.4 : 2.6
DPPP	1	74	(—)	93.8 : 6.2
DPPP	2	194	(—)	95.4 : 4.6
DPPP	5	213	(—)	94.5 : 5.5

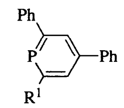
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	SiO_2-PAMAM-PPh_2, $[Rh(CO)_2Cl]_2$, CH_2Cl_2, H_2/CO (1/1, 1000 psi), 25°, 22 h		658

PAMAM generation	conversion (%)	I : II
1	98	27 : 1
2	>99	30 : 1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, ligand, PhMe, CO/H_2 (1/1, 20 bar)	**I** + **II** (—)	659

Ligand	P/Rh	Temp.	Time (h)	Conv. (%)	TOF (h^{-1})	I:II
PPh_3	5	25°	3	8	7.5	24:1
PPh_3	20	90°	73	28.1	2.9	—
$P(OC_6H_3(Bu\text{-}t)_2\text{-}2,4)_3$	5	25°	3	17.6	16.4	20:1
$P(OC_6H_3(Bu\text{-}t)_2\text{-}2,4)_3$	10	90°	1	28.8	214	—

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, PhMe, CO/H_2 (1/1, 20 bar)	I + II (—)	659

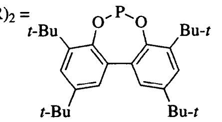


R^1	P/Rh	Temp.	Time (h)	Conv. (%)	TOF (h^{-1})	I:II
Ph	5	25°	3	30.8	28.7	20:1
Ph	10	90°	1	28.6	214	—
Me	4	90°	1	12.2	92	—

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh=5, CO/H_2 (1/1, 50 atm), 80°, 2 h	I + II (65), I:II=8	610
	$[Rh(CO)_2Cl]_2$, $PPhMe_2$, C_6H_6, CO/H_2, 60°	I + II (—), I:II = 96:4	640
	$Rh(acac)(CO)_2$, ligand, CO/H_2 (1/1, 20 bar), PhMe		660

$(RO)_2P—O—(CH_2)_n—O—P(OR)_2$

$P(OR)_2$ =



n	L/Rh	Temp.	Conv. (%)	I:II	TOF
2	20	80°	25	88:12	3710
3	2.5	40°	31	84:16	1890

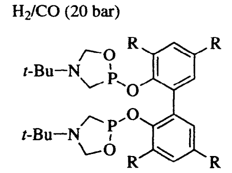
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Pt(BDT)(P\text{-}P)_2$, $SnCl_2$, Sn/Rh = 20, H_2/CO (1/2, 100 atm), THF, 125°		661

P-P	Time (h)	I + II	I:II	PhEt	Alcohol
$(PPh_3)_2$	60	(50)	19:81	(6)	(11)
DPPB	24	(11)	37:63	(4)	(1)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PtCl_2(DPPP)$, SnX_2, AgY, H_2/CO (1/1), PhMe, 100°	I + II + III	60

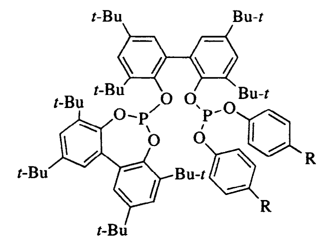
X	Y	Sn/Ag/Pt	Time (h)	Conv. (%)	I + II	I:II
Cl	—	2/0/1	4	76	(86)	27:73
Cl	TfO	2/0.5/1	25	86	(73)	54:46
Cl	TfO	2/1/1	20	94	(75)	52:48
Cl	TfO	2/2/1	35	98	(70)	67:33
F	F	2/2/1	100	60	(72)	54:46

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, L/Rh = 5, PhMe, H_2/CO (20 bar)		662

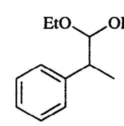
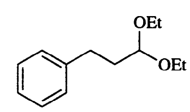
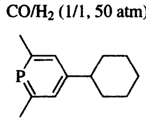
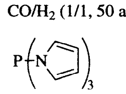
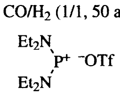
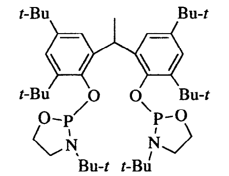


R	Temp.	Time (h)	Conv. (%)	I:II	TOF
H	40°	4.0	2	80:20	10
Bu-*t*	80°	3.5	68	75:25	480
Bu-*t*	40°	23	20	89:11	25

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	cis-[RhCl(NBD){(*R,R*)-5,11,17,23-tetra-*tert*-butyl-25,27-bis[(1-phenylethyl) carbamoylmethoxy]-26,28-bis(diphenyl-phosphinomethoxy)calix[4]arene}]BF_4, CO/H_2 (1/1, 40 atm), CH_2Cl_2/C_6H_6, 40°, 48 h	I + II (—), I:II = 95:5	654
	RhCl(CO)(DPM)$_2$-poly(vinylbenzyltriethyl-ammonium chloride on silica, 85°, c-C_6H_{12}, H_2O, EtOH, CO/H_2 (1/1, 750 psi), 15 h	I + II (56), I:II = 6:1	655-657
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	I (—) + II (—) + starting material (11) I:II = 97.3:2.7	251

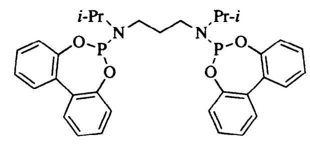
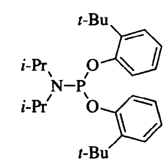
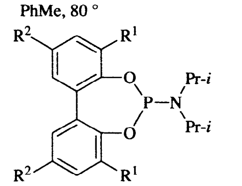
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, ligand, L/Rh = 20, CO/H$_2$, PhMe 		660

R	H$_2$/CO (bar)	Temp.	Conv. (%)	I:II	III	TOF
H	1 (20)	40°	13	84:16	(—)	47
H	6 (35)	120°	13	16:84	(16)	6175
MeO	1 (20)	80°	25	63:37	(—)	320
Ph	1 (20)	80°	18	51:49	(—)	320

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, BIPHEPHOS, L/Rh = 20, CO/H$_2$ (1/1, 20 bar), PhMe, 40°	I:II = 77:23, I + II (27)	660
	Rh$_2$(μ-OMe)$_2$(COD)$_2$, 10 PPh$_3$, HC(OEt)$_3$, PPTS, CO/H$_2$ (1/1, 50 bar), 60°, 24 h	 (93) +  (7)	663
	Rh(acac)(CO)$_2$, phosphine, P/Rh = 2, CO/H$_2$ (1/1, 50 atm), 20 °, 22 h 	I (77) + II (3), I:II = 26.6	664
	Rh(acac)(CO)$_2$, phosphine, P/Rh = 20, CO/H$_2$ (1/1, 50 atm), 20 °, 22 h 	I (7) + II (1), I,II=6	664
	Rh(acac)(CO)$_2$, phosphine, P/Rh = 20, CO/H$_2$ (1/1, 50 atm), 20 °, 22 h	I (7) + II (1), I:II=6	664
	Rh(acac)(CO)$_2$, phosphine, P/Rh = 2, CO/H$_2$ (1/1, 50 atm), 20 °, 22 h 	I (4) + II (—), I:II=100:0	664
	Rh(acac)(CO)$_2$, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$, H$_2$O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H$_2$ (1/1, 50 atm), 80°, 2 h	I + II (100), I:II=11	610
	Rh(acac)(CO)$_2$, ligand, L/Rh = 5, PhMe, CO/H$_2$ (20 bar), 80° 		662

Isomer	Time (h)	Conv. (%)	I:II	TOF
dl	23.0	3	84:16	3
meso	20.2	11	79:21	15

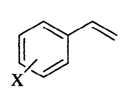
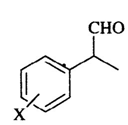
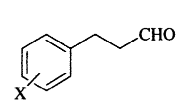
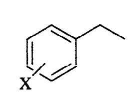
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, ligand, L/Rh = 5, PhMe, CO/H$_2$ (20 bar), 40°, 21.5 h 	I + II (—), I:II = 74:26	662
	Rh(acac)(CO)$_2$, ligand, L/Rh = 10, PhMe, CO/H$_2$ (20 bar), 80°, 20.3 h 	I + II (—), I:II=92:8	662
	Rh(acac)(CO)$_2$, ligand, CO/H$_2$ (20 bar), PhMe, 80 ° 		662

R^1	R^2	L/Rh	Temp.	Time (h)	Conv. (%)	I:II	TOF
Bu-*t*	MeO	100	40°	42.3	66	93:7	90
H	H	50	80°	3.0	97	85:5	1860

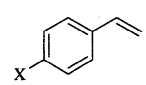
Rh(sox)(CO)$_2$, toluene, CO/H$_2$ (1/1), 60 ° — 512

Ligand	P/Rh	P (MPa)	Time (h)	Conv. (%)	I:II
PPh$_3$	2	0.1	7	3.0	70:30
PPh$_3$	2	1	5	98.0	100:0
DPPE	2	0.1	7	29.9	93:7
DPPE	2	1	4	91.0	100:0

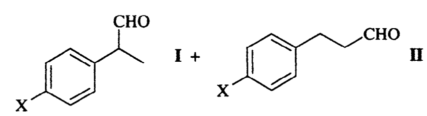
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	A. Co$_2$(CO)$_8$, CO/H$_2$ (1/1, 160 atm), 105°, 4-5 h B. Rh-Al$_2$O$_3$, CO/H$_2$ (1/1, 160 atm), 85°, 2-5 h	 I +  II +  III	665

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

X	A I	A II	A III	B I	B II	B III
H	(44)	(31)	(25)	(80)	(19)	(1)
2-Me	(27)	(46)	(27)	(69)	(30)	(1)
3-Me	(41)	(30)	(29)	(76)	(20)	(4)
4-Me	(40)	(23)	(37)	(78)	(20)	(2)
2,6-$(Me)_2$	(11)	(59)	(30)	(72)	(19)	(9)
2-OMe	(37)	(40)	(23)	(78)	(20)	(2)
3-OMe	(42)	(31)	(27)	(80)	(19)	(1)
4-OMe	(45)	(24)	(31)	(72)	(20)	(8)
2-Cl	(24)	(56)	(20)	(84)	(15)	(1)
3-Cl	(40)	(36)	(20)	(83)	(15)	(2)
4-Cl	(38)	(33)	(29)	(79)	(19)	(2)
2,6-$(Cl)_2$	(11)	(79)	(10)	(97)	(1)	(2)
3,4-$(Cl)_2$	(36)	(34)	(29)	(86)	(12)	(2)



$HRh(PPh_3)_4$, CO/H_2 (1/1, 62 kg/cm^2), 70°



666

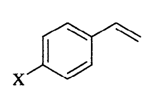
X	I + II	I : II
NO_2	(75)	96.2 : 3.8
Br	(100)	94.7 : 5.3
Cl	(100)	95.4 : 4.6
H	(100)	92.8 : 7.2
OPh	(93)	93.0 : 7.0
Me	(99)	91.4 : 8.6
OMe	(97)	91.8 : 8.2

$[Rh(NBD)(ligand)]BF_4$, PhH, 55°, CO/H_2 (1/1, 200 psi), 24 h — 667

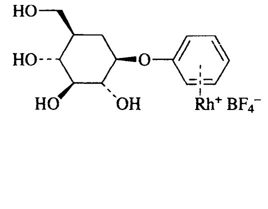
Ligand	X	I : II
DPPE	H	3.5
$[(C_6F_5)_2PCH_2]_2$	H	13.3
DPPE	Me	3.2
$[(C_6F_5)_2PCH_2]_2$	Me	19
DPPE	MeO	4
$[(C_6F_5)_2PCH_2]_2$	MeO	16
DPPE	Cl	3.2
$[(C_6F_5)_2PCH_2]_2$	Cl	10
DPPE	NO_2	24
$[(C_6F_5)_2PCH_2]_2$	NO_2	100:0

Rh-PEVV, CO/H_2 (1/1, 41.4 atm), H_2O — 242

X	Ligand	Temp.	Time (h)	Conv. (%)	I + II	I:II
H	—	40°	22	13	(13)	17.3
H	10 PPh_3	40°	24	12	(12)	17.9
Cl	—	40°	24	12	(12)	15.3
Me	—	40°	22	14	(14)	9
Me	—	28°	24	4	(4)	36.7



CO/H_2 (2/1, 500 psi),hexane, H_2O, 40°, 22 h



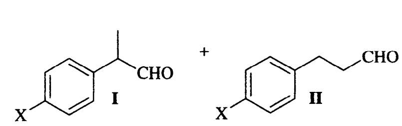


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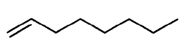
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.

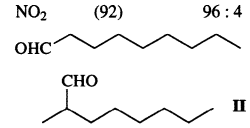
R	I + II	I:II
H	100	95:5
F	100	91:9
Cl	100	93:7
Br	100	93:7
Me	100	92:8
MeO	90	90:10

[Rh(COD)(OAc)]$_2$, CH_2Cl_2, 25°, 16 h, CO/H_2 (1/1, 800-1000 psi) — 316

X	I + II	I:II
H	(94)	96 : 4
OMe	(98)	95 : 5
Me	(98)	95 : 5
Cl	(98)	97 : 3
NO_2	(92)	96 : 4

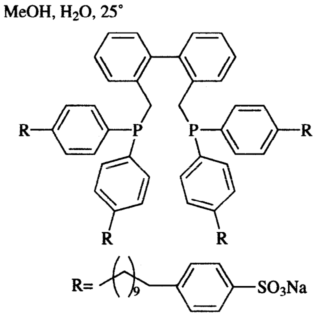


$Rh_2(\mu\text{-SBu-}t)_2(CO)_2(\text{Res-PPh}_2)_2$, 80°, CO/H_2 (1/1, 0.37 MPa), 15 h — 669



I (76) + **II** (8) + internal octenes (4)

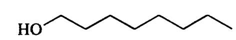
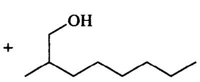
Rh(acac)(CO)$_2$, CO/H_2 (210 psi), MeOH, H_2O, 25° — **I+II** (83), **I:II** (91:9) — 670



Conditions	Product(s) and Yield(s) (%)	Refs.
Rh(SOX)(COD), PPh_3, L/Rh = 5, toluene, CO/H_2 (1/1, 0.1 MPa), 60°, 10 h	**I** + **II** (—), **I**:**II** = 84.6:15.4	511
Rh(SOX)(COD), DPPE, L/Rh = 5, toluene, CO/H_2 (1/1, 0.1 MPa), 60°, 10 h	**I** + **II** (—), **I**:**II** = 54.5:45.5	511
Rh(acac)(CO)$_2$, DPPETS, L/Rh = 3, 15 h, CO/H_2 (1/1, 200 psi), MeOH/H_2O, 120°	**I** + **II** (—), **I**:**II** = 3.2:1	671
Rh(acac)(CO)$_2$, TPPTS, L/Rh = 10, 15 h, CO/H_2 (1/1, 200 psi), MeOH/H_2O, 120°	**I** + **II** (—), **I**:**II** = 4:1	671, 672
Rh(acac)(CO)$_2$, $P(CH_2C_6H_4SO_3Na\text{-}p)_3$, 15 h L/Rh = 2.5, CO/H_2 (1/1, 200 psi), H_2O, 120°	**I** + **II** (—), **I**:**II** = 1.6:1	672
Rh(acac)(CO)$_2$, $P[(CH_2)_2C_6H_4SO_3Na\text{-}p]_3$, L/Rh = 2, CO/H_2 (1/1, 200 psi), H_2O, 120°, 15 h	**I** + **II** (—), **I**:**II** = 2:1	672
$Rh_2[\mu\text{-S}(CH_2)_3Si(OMe)_3]_2$ condensed with SiO_2, $P(OCH_3)_3$, P/Rh = 7.8, toluene, H_2/CO (1/1, 1atm), 60°, 11h	**I** + **II** (57), **I**/**II** = 12, octenes (28)	673
Rh(acac)(CO)$_2$, Ligand, L/Rh = 20, CO/H_2 (1/1, 20 bar), PhMe, 80°		674

Ligand	Time (min)	Conv. (%)	**I** : **II** : internal octenes
PPh_3	120	81.2	72.6 : 25.9 : 1.5
$Ph_2P(C_6H_4OH\text{-}3)$	120	76.6	73.1 : 26.1 : 0.8
$Ph_2P(C_6H_4CO_2H\text{-}4)$	70	1.1	73.6 : 26.4 : —
$Ph_2P(C_6H_4CH_2NEt_2\text{-}4)$	120	76.2	73.3 : 26.0 : 0.3
$PhP(C_6H_4CH_2NEt_2\text{-}4)_2$	120	72.6	73.0 : 26.1 : 0.8
$Ph_2P(C_6H_4CH_2NPh_2\text{-}4)$	120	83.3	73.1 : 26.5 : 0.3
$PhP(C_6H_4CH_2NPh_2\text{-}4)_2$	120	85.0	72.8 : 26.0 : 1.2
4-$PPh_2C_5H_4N$	120	92.9	72.0 : 25.0 : 3.2
3-$PPh_2C_5H_4N$	120	86.3	71.7 : 25.6 : 2.7
$PhP(C_5H_4N\text{-}3)_2$	120	94.9	71.3 : 25.3 : 3.3

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[Rh(NBD)(2,5-bis(diphenylphosphino-methyl)bicyclo[2.2.1]heptane)ClO_4, CO/H_2 (1/1, 40 atm), C_6H_6, 50°, 6 h	**I** + **II** (—), **I**:**II** = 59:41	247
	[$(CO)_2(PPh_3)Co(\mu\text{-}PBu\text{-}t_2)Rh(CO)(HPBu\text{-}t_2)$], CO/H_2 (5/3, 40 bar), *c*-C_6H_{12}, 70°, 24 h	**I** + **II** (—), **I**:**II** = 64:36	675
	RuO_2-2,2'-bipyridine, Bu_4PBr, 180°, 4 h, CO/H_2 (1/2, 1200 psi)	**I** (tr) + **II** (tr) +  **III** (69) +  **IV** (11)	676
	[$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(TPPTS)_2$], TPPTS, CO/H_2 (1/1, 0.5 MPa), H_2O, cosolvent, 80°, 15 h		677

Cosolvent (22% w/w)	Conv. (%)	I/(I + II)
none	18	95.5
EtOH	92	82.7
MeOH	83	89.6
MeCN	80	83.6
Me_2CO	90	86.2

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, Ligand, H_2O, MeOH, CO/H_2 (19.5 atm), 120°		678

Ligand	L/Rh	I + II	I/II
TPPTS	2	(47)	2.4
$P(C_6H_4[(CH_2)_3C_6H_4SO_3Na\text{-}p]\text{-}p)_3$	2	(88)	3.0
$P(C_6H_4[(CH_2)_6C_6H_4SO_3Na\text{-}p]\text{-}p)_3$	2	(84)	3.3
TPPTS	10	(78)	3.6
$P(C_6H_4[(CH_2)_3C_6H_4SO_3Na\text{-}p]\text{-}p)_3$	10	(85)	8.0
$P(C_6H_4[(CH_2)_6C_6H_4SO_3Na\text{-}p]\text{-}p)_3$	10	(88)	9.5

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[Rh(COD)(OAc)]$_2$, CO/H_2	**I** + **II** (57-80), **I**:**II** = 52:48	316
	[Rh(COD)(OMe)]$_2$, CO/H_2	**I** + **II** (—), **I**:**II** = 55:45	316
	[Rh(COD)($OCOCPh_3$)]$_2$, CO/H_2	**I** + **II** (—), **I**:**II** = 55:45	316
	Rh(acac)$(CO)_2$, $Ph_2P(4\text{-}HO_2CC_6H_4)$, CO/H_2 (1/1, 20 bar), 80°, THF, 250 min	**I** + **II** (—), **I**:**II** = 72.9:25.9	674
	Et_3N, H_2O, PhMe, 80°, CO/H_2 (1/1, 3 MPa)		679

Catalyst	Time (h)	I	II	Octane	Oct-2-ene
$Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(PPh_3)_2$	20	(72)	(24)	(0)	(0)
$Ru_2(\mu\text{-}O_2CMe)_2(CO)_4[P(OPh)_3]_2$	17	(65)	(25)	(6)	(0)
$Ru_2(\mu\text{-}O_2CPh)_2(CO)_4(PPh_3)_2$	16	(63)	(19)	(0)	(0)
$Ru_2(\mu\text{-}O_2CCF_3)_2(CO)_4(PPh_3)_2$	16	(45)	(14)	(0)	(0)
$Ru_2(\mu\text{-}O_2CCMe_3)_2(CO)_4(PPh_3)_2$	18	(11)	(4)	(0)	(0)
$Ru_2(\mu\text{-}O_2CCMe_3)_2(CO)_4[P(OPh)_3]_2$	22	(64)	(18)	(16)	(2)
$Ru_2(\mu\text{-}O_2CMe)_2(CO)_4[P(OMe)_3]_2$	20	(73)	(24)	(0)	(0)
$Ru_2(\mu\text{-}O_2CMe)_2(CO)_4(PBu_3)_2$	20	(3)	(1)	(0)	(0)

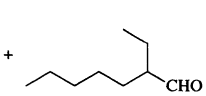
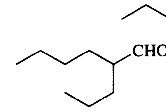
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ru_2(\mu\text{-}O_2CPh)_2(CO)_4(PPh_3)_2$, Et_3N, PhMe, 80°, CO/H_2 (1/1, 3 MPa)	**I** (69) + **II** (29) + octane (2)	679
	[$Ru_2(\mu\text{-}OAc)_2(CO)_4(PPh_3)_2$], P/Ru = 5, H_2O, THF, CO/H_2 (1/1, 3 MPa), 85°, 20 h	**I** (12) + **II** (4)	680
	$Cp_2Yb(\eta\text{-}OC)Co(CO)_3$, Et_2O/THF = 4/1, CO/H_2 (3/2, 6.5 MPa), 135°, 5 h	**I** + **II** (75), **I**:**II** = 1.10-1.15	681
	[$(\eta^5\text{-}C_5H_5)Rh_2(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)(CO)Cl$], CO/H_2 (1/1, 80 atm), C_6H_6, 80°, 14 h	**I** (48) + **II** (35) +  (7) +  (5)	616

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

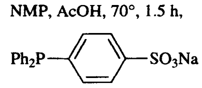
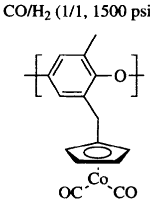
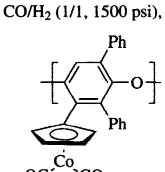
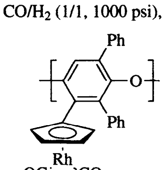
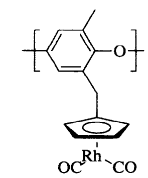
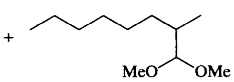
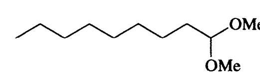
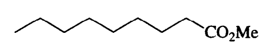
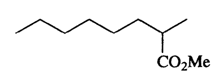
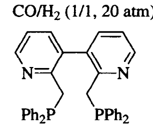
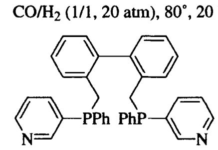
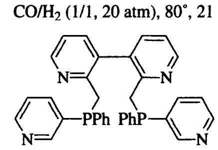
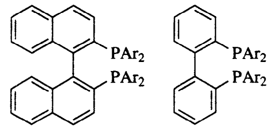
Reactant	Conditions			Product(s) and Yield(s) (%)	Refs.
	$Co(OAc)_2/P(Bu\text{-}n)_3$ (1/10), *hν*, MeOH, 85°, 26 h, CO/H_2 (1/1, 80 bar)			**I** + **II** (—), **I**:**II** = 90:10	461, 462, 682
	$Rh(acac)(CO)_2$, $P[(CH_2)_6C_6H_4SO_3Na\text{-}p]_3$, L/Rh = 2.5, CO/H_2 (1/1, 200 psi), H_2O, 120°, 15 h			**I** + **II** (—), **I**:**II** = 2.2:1	672
	$Rh(acac)(CO)_2$, $P(OC_6H_3Me\text{-}4\text{-}Bu\text{-}t\text{-}2)_3$, L/Rh = 50, CO/H_2 (1/7, 80 bar), PhMe, 80°			**I** + **II** (—), **I**:**II** = 2:1	683
	Rh/C (5%), $P(OPh)_3$, CO/H_2 (1/1), PhMe, 90°			**I** + **II** (72-84)	684
	Pressure (psi)	Time (min)		**I**:**II**	
	80-100	50		86:14	
	280-300	20		80:20	
	560-600	25		74:26	
	2500	25		69:31	
	Rh/C (5%), PR_3, PhMe, CO/H_2 (1/1, 80-100 psi)			**I** + **II** (72-84)	684
	R	Temp.	Time (min)	**I** : **II**	
	n-Bu	90°	225	71:29	
	Ph	90°	35	82:18	
	n-BuO	110°	60	81:19	
	PhO	90°	50	86:14	
	$2\text{-}MeC_6H_4O$	90°	52	78:22	
	$2\text{-}PhC_6H_4O$	90°	95	52:48	
	$4\text{-}PhC_6H_4O$	90°	70	85:15	
	$4\text{-}ClC_6H_4O$	90°	55	93:7	
	$4\text{-}MeOC_6H_4O$	90·	270	83:17	
	$Rh(acac)(CO)_2$, $P[(CH_2)_2C_6F_{13}\text{-}n]_3$, 100°, CO/H_2 (1/1, 150 psi), $c\text{-}C_6F_{11}CF_3$, PhMe			**I** + **II** (85), **I**:**II** = 2.9	31
	$Rh(acac)(CO)_2$, CO/H_2 (10 atm), NMP, AcOH, 70°, 1.5 h, 			**I** (80), **II** (20)	685
	CO/H_2 (1/1, 1500 psi), C_6H_6, 135°, 12 h 			**I** + **II** (—), **I**:**II** = 2.4	686
	CO/H_2 (1/1, 1500 psi), C_6H_6, 135°, 12 h 			**I** + **II** (—), **I**:**II** = 1.3	686
	CO/H_2 (1/1, 1000 psi), 24 h, $n\text{-}C_6H_{14}$, 50° 			**I** + **II** (—), **I**:**II** = 1.2	686

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 1000 psi), C_6H_6, 50°, 24 h 	**I** + **II** (—), **I**:**II** = 0.6	686
	$RhH(CO)(PPh_3)_3/PPh_3$ (1/200), diphosphine, CO/H_2 (1/1, 1 atm), PhMe, 85°		687
	Diphosphine	**I** : **II** : 2-octene	
	None	77 : 7 : 14	
	$Ph_2P(CH_2)_2PPh_2$	82 : 12 : 5	
	$Ph_2P(CH_2)_3PPh_2$	81 : 13 : 5	
	$Ph_2P(CH_2)_4PPh_2$	86 : 10 : 3	
	$RhCl_3$, NBD, *hv*, CO/H_2 (1/1, 75 bar), MeOH, 20°, 21 h	**I** (1) + **II** (3) +  (40) +  (30) +  (3) +  (13)	688
	$Rh(COD)BF_4$, ligand, 60°, PhMe, 18 h, L/Rh = 1.2, CO/H_2 (1/1, 100 atm)	**I** + **II** (—)	689
	Ligand	**I**:**II**	
	$PhN(CH_2PPh_2)_2$	62:38	
	p-$CF_3C_6H_4N(CH_2PPh_2)_2$	60:40	
	p-$Me_2NC_6H_4N(CH_2PPh_2)_2$	65:35	
	DPPP	63:37	
	$Rh(acac)(CO)_2$, ligand, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80°, 21 h 	**I** (89) + **II** (4) + internal isomers (7), **I**:**II** = 24	224
	$Rh(acac)(CO)_2$, ligand, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80°, 20 h 	**I** (90) + **II** (2) + internal isomers (8), **I**:**II** = 51	224
	$Rh(acac)(CO)_2$, ligand, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80°, 21 h 	**I** (89) + **II** (3) + internal isomers (8), **I**:**II** = 30	224
	Rh(hfacac)(COD), P[*m*-$F(CF_2)_6(CH_2)_2C_6H_4]_3$, L/Rh = 6, CO/H_2 (1/1, 60 atm), 60 °, $scCO_2$[d] (160 atm), 19 h	**I**:**II** = 4.6:1, **I** + **II** (—)	690

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, $MeOH/H_2O$ (1/1), CO/H_2 (210 psi), 120 °, 5 h		691

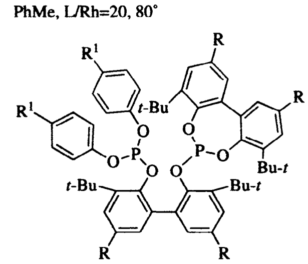


A B

Ar = m-$C_6H_4(CH_2)_3C_6H_4SO_3Na$-$p$

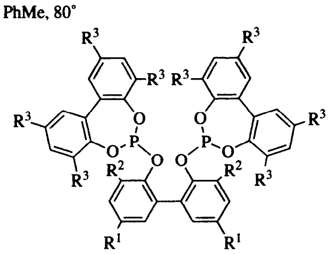
Ligand	P/Rh	I + II	I : II
A	2	(29)	74/26
A	3	(31)	74/26
A	5	(14)	75/25
A	7	(5)	70/30
B	2	(45)	68/32
B	3	(57)	76/24
B	5	(69)	88/12
B	7	(73)	94/6
B	9	(67)	97/3
B	14	(30)	98/2
TPPTS	2	(30)	68/32
TPPTS	3	(37)	70/30
TPPTS	5	(52)	75/25
TPPTS	7	(54)	76/24
TPPTS	9	(69)	76/24

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ru_3(CO)_{12}$, 1,10-phananthroline, L/Rh = 4, CH_3CONMe_2, CO/H_2 (1/1, 100 atm), 120°, 20 h	I + II (55) + internal octenes (25) + octane (3) I:II=95:5	469
	$Rh(acac)(CO)_2$, ligand, CO/H_2 (1/1, 20 bar), PhMe, L/Rh=20, 80°		660



R	R^1	Conv. (%)	I:II:internal alkenes	TOF
Bu-*t*	H	26	73:4:23	2450
Bu-*t*	MeO	29	96:4:0	2700
Bu-*t*	Ph	19	95:5:0	2275
Bu-*t*	Cl	21	95:5:0	3375
MeO	H	35	82.3:1.7:16	1750

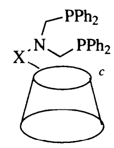
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, CO/H_2 (1/1, 20 bar), PhMe, 80°		660



R^1	R^2	R^3	Conv. (%)	I	II	Internal alkenes	TOF
MeO	Bu-*t*	H	31	(82)	(—)	(18)	3600
Bu-*t*	Bu-*t*	H	37	(72)	(1)	(27)	6120
H	H	Bu-*t*	21	(48)	(39)	(13)	520

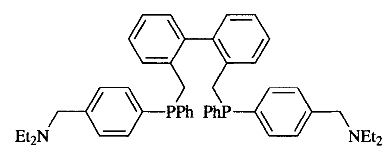
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, BISBI, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80 °, 21 h	I (90) + II (2) + internal isomers (8), I:II = 41	224
	$Rh(COD)_2BF_4$, L/Rh = 0.55, DAB-dendr-$[N(CH_2PPh_2)_2]_{16}$	I + II (—), I:II = 60:40	692

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	[Rh(COD)(diphosphine)]BF_4, 18 h, H_2O (30% DMF), CO/H_2 (1/1, 100 atm)		223



X	Temp.	TON	I:II
CH_2	60°	3179	75:25
$CH_2S(CH_2)_2$	80°	3172	76:24
$CH_2S(CH_2)_3$	60°	3170	69:31
$CH_2S(CH_2)_4$	60°	3170	67:33

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, ligand, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80°, 21 h	**I** (91) + **II** (3) + internal alkenes (6) **I**:**II** = 32	224

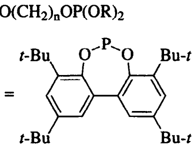


Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh (acac)$(CO)_2$, diphosphine ligand, PhMe, L/Rh = 10, CO/H_2 (1/1, 20 atm), 80°		225

Phosphine ligand	Time (h)	Conv. (%)	I + II	I:II	Isomers
POP	20	67.0	(100)	7.5	0.0
POPpy	20	88.0	(99)	8.9	0.7
POPam	21	71.5	(100)	7.3	0.0
xanthos	24	61.6	(96)	46	3.9
xantham	24	67.9	(96)	49	4.0

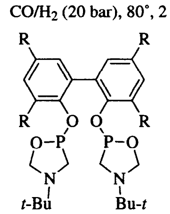
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, ligand, CO/H_2 (1/1, 20 bar), PhMe, 80° $(RO)_2PO(CH_2)_nOP(OR)_2$		660

$P(OR)_2$ =



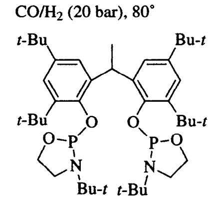
n	L/Rh	Conv. (%)	I:II:internal alkenes	TOF
2	20	21	61.5:38.5:0	11100
3	2.5	27	55:25:20	1550

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, ligand, L/Rh = 5, PhMe, CO/H_2 (20 bar), 80°, 2 h		662



R	Conv. (%)	I:II:internal alkenes	TOF
H	49	68:31:1	650
Bu-*t*	72	71:16:13	810

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, ligand, L/Rh = 5, PhMe, CO/H_2 (20 bar), 80°		662

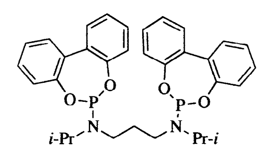


Isomer	Time (h)	Conv. (%)	I:II:internal octenes	TOF
dl	19.5	98	68:13:19	110
meso	1.3	54	82:9:9	950

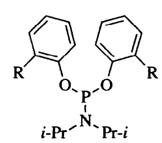
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	trans-RhCl(CO)$(P(C_6H_4CF_3\text{-}p)_3)_2$, $scCO_2$[d], H_2/CO (68 atm), 70°, 27 h	**I** + **II** (—), **I**/**II** = 2.4	693

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PhN(CH_2PPh_2)_2Rh(COD)BF_4$, H_2/CO	**I** + **II** (—), **I**:**II** = 62:38	692
	n-$PrN(CH_2PPh_2)_2Rh(COD)BF_4$, H_2/CO	**I** + **II** (—), **I**:**II** = 61:39	692
	$Rh(acac)(CO)_2$, ligand, L/Rh = 5, PhMe, CO/H_2 (20 bar), 80°, 3.5 h	**I** + **II** (—), **I**:**II**:internal octenes = 91:4:5	662

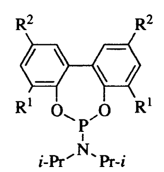


$Rh(acac)(CO)_2$, ligand, CO/H_2 (20 bar), PhMe, 80° — 662



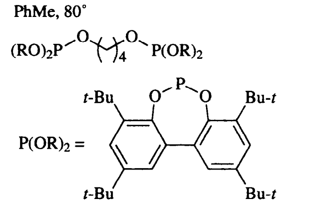
R	L/Rh	Time (h)	Conv. (%)	**I**:**II**:internal octenes	TOF
H	50	3.5	93	59:30:11	1200
Bu-*t*	100	0.3	22	48:19:33	1110

$Rh(acac)(CO)_2$, ligand, PhMe, H_2/CO (20 bar) — 662



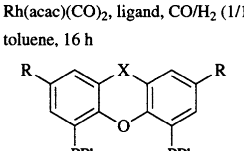
R^1	R^2	L/Rh	Temp.	Time (h)	Conv. (%)	**I**:**II**:internal octenes	TOF
Bu-*t*	MeO	100	80°	3.2	98	54:34:12	730
Bu-*t*	MeO	250	40°	21.8	24	56:37:7	50
Bu-*t*	MeO	1000	80°	42.6	77	61:27:12	80
H	H	100	80°	2.1	93	65:31:4	2160

$Rh(acac)(CO)_2$, ligand, CO/H_2 (1/1, 20 bar), PhMe, 80° — 660

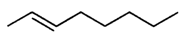
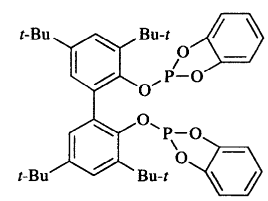
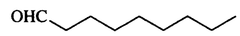
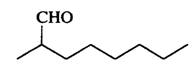
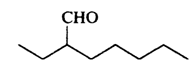
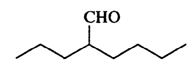
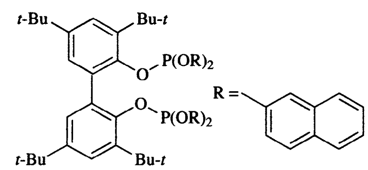
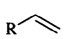
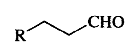
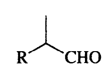


n	L/Rh	Conv. (%)	**I**:**II**:internal alkenes	TOF
2	20	21	62:38:0	11100
3	2.5	27	55:25:20	1550

$Rh(acac)(CO)_2$, ligand, CO/H_2 (1/1, 10 bar), toluene, 16 h — 694



Ligand	R	X	Temp.	I/II	I	isomerization(%)
Sixantphos	H	Si(Me$_2$	40°	35	(96)	<1
Thixanphos	Me	S	40°	47.6	(97)	1
Xantphos	H	C(Me)$_2$	40°	57.1	(98)	0
BISBI			40°	58.2	(96)	2.9
Sixantphos	H	Si(Me$_2$	80°	34	(94)	3
Thixanphos	Me	S	80°	41	(93)	4.7
Xantphos	H	C(Me)$_2$	80°	53.5	(98)	0.5
BISBI			80°	80.5	(90)	9.3

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, L (Rh : L = 1 : 2.04), H_2/CO (20 kg/cm^2), heptane, 100°, 2 h, 	 I (53) +  II (27) +  III (11) +  IV (10)	695
	Rh(acac)$(CO)_2$, Ph_3PO, 100°, 3 h, 	I + II + III + IV (59), I:II:III:IV = 54:28:10:8	696
	Rh(acac)$(CO)_2$, P/Rh = 9, C_6H_{12}, H_2O, n-$C_6H_{13}P(C_6H_4SO_3Na$-$m)_2$ on glass, CO/H_2 (1/1, 54 atm), 75°, 5 h	 I +  II	601

R	I:II	(I + II)/alkane	I + II
C_6H_{13}	2.3	10/1	(—)
C_8H_{17}	2.2	10/1	(—)
$C_{10}H_{21}$	2.3	10/1	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh-PEVV, CO/H_2 (1/1, 41.4 atm), H_2O		242

R	Temp.	Time (h)	Conv. (%)	I + II	I:II	2-alkene
C_6H_{13}	90°	22	89	(57)	2.45	(22)
$C_{10}H_{21}$	60°	4	70	(49)	1.95	(21)
n-BuO	100°	5	5	(5)	0.35	(0)

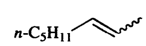
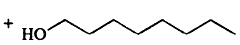
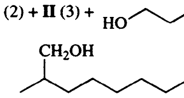
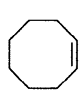
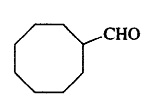
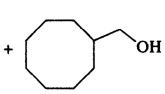
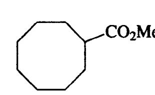
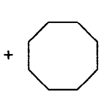
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	RuO_2, Bu_4PBr, CO/H_2 (1/2, 83 bar), 180°, 4 h	I (2) + II (3) +  III (32) +  IV (34), I:II=89:11	676
	$Ru_3(CO)_{12}$, 1,10-phananthroline, L/Rh=4, DMF, CO/H_2 (1/1, 100 atm), 120°, 20 h	I + II (20) + internal octenes (62) + octane (tr) I:II=89:11	469
	$Rh_2(CO)_2[P(Bu$-$t)_3]_2(\mu$-Cl)[μ-S$(CH_2)_nSiO_3$-silica gel], CO/H_2 (1/1, 80 atm), 120°, 15 h	 I; n = 2 (80); n = 3 (100)	618
	$RhH_2(O_2COH)[P(Pr$-$i)_3]_2$, $(CH_2O)_n$, THF, 120°, 20 h	I (59) +  II (12) +  III (11) +  IV (5)	593
	K[Ru(saloph)Cl_2], EtOH, 130°, CO/H_2 (1/1, 21 atm)	II (—)	553
	$Ru_3(CO)_{12}$, $P(C_6H_{11})_3$, HCO_2Me, H_2O, 180°, 10 h	II (15) + IV (77)	493
	Rh(acac)$[P(OPh)_3]_2$, $P(OPh)_3$, 80°, CO/H_2 (10 atm), 3 h	I (20)	697
	$RhH_2(O_2COH)[P(Pr$-$i)_3]_2$, CO (15 atm), H_2O, THF, 115°, 20 h	I (54)	577

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

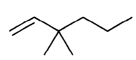
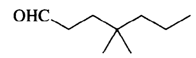
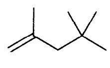
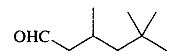
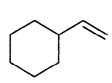
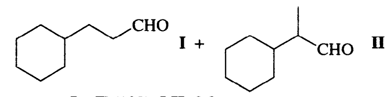
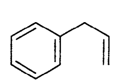
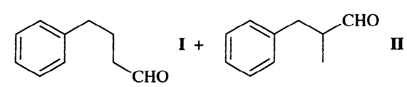
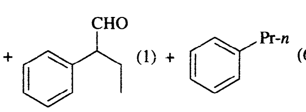
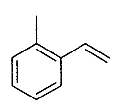
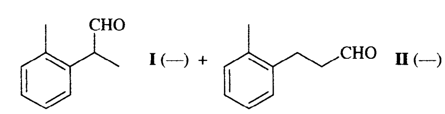
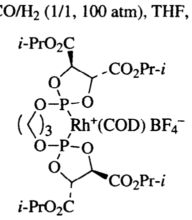
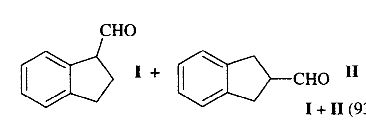
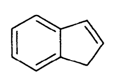
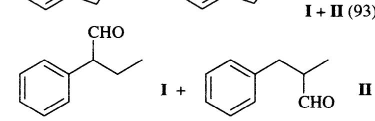
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 60°, 22 h	 (—) + starting material (31)	251
	Poly(*N*-vinyl-2-pyrrolidone)-$Co_2Rh_2(CO)_{11}$, CO/H_2 (1/1.2, 55 kg/cm^2), C_6H_6, 80°, 8 h	 (—)	566
	Rh(acac)$(CO)_2$, $P(C_6H_4SO_3Na$-*m*$)_3$, H_2O, per(β-cyclodextrinMe_2-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 2 h	 **I** + **II** (100), **I**:**II**=3.8	610
	Rh(acac)$(CO)_2$, $P(C_6H_4SO_3Na$-*m*$)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 2 h	**I** + **II** (34), **I**:**II**=9	610
	Rh(acac)$(CO)_2$, $P(OC_6H_3Me$-4-Bu-*t*-2$)_3$, L/Rh = 10, CO/H_2 (1/1, 20 atm), PhH, 70°	**I** (78) + alkenes (16)	468
C_9 	$[Rh(OAc)_2]_2$, PPh_3/Rh = 2, CO/H_2 (1/1, 400 psi), 60°, 20 h	 **I** + **II** (—), **I**:**II** = 7:3	313
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 60°, 22 h	**I** + **II** (—), **I**:**II** = 44:56	251
	cis-$PtCl_2(PPh_3)_2/SnCl_2{\cdot}2H_2O$ (1:5), CO/H_2 (1/1, 100 bar), $CHCl_3$, 4 h	**I** (70) + **II** (16) +  (6)	492
	5% Rh/C, DPPP, HCO_2H, CO (8.5 atm), DME, 100-105°, 18-24 h	**I** + **II** (45), **I**:**II** = 44:56	368
	Rh(acac)$(CO)_2$, $P(C_6H_4SO_3Na$-*m*$)_3$, H_2O, per(β-cyclodextrinMe_2-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 2 h	**I** + **II** (99), **I**:**II**=1.9	610
	Rh(acac)$(CO)_2$, $P(C_6H_4SO_3Na$-*m*$)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 2 h	**I** + **II** (48), **I**:**II**=2.8	610
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	 **I**:**II** = 95:5	251
	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	**I** + **II** (—), **I**:**II** = 97:3	248
	Rh(CO)$[P(C_6H_{11})_3]_2$Cl, 120°, 10 h, CO/H_2 (1/1, 300 atm)	 **I** + **II** (93), **I**:**II** = 77:23	698, 699
	"	 **I** + **II** (—) **I**:**II** = 94:6	248
	Rh(acac)$(CO)_2$, $P(C_6H_4SO_3Na$-*m*$)_3$, H_2O, per(β-cyclodextrinMe_2-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** + **II** (10), **I**:**II** = 14	610
	Rh(acac)$(CO)_2$, $P(C_6H_4SO_3Na$-*m*$)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** + **II** (2), **I**:**II**=11	610

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TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

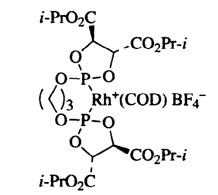
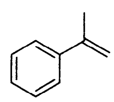
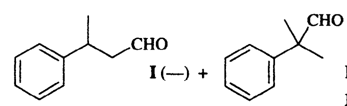
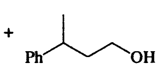
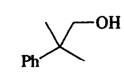
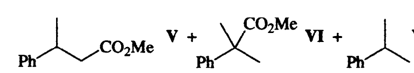
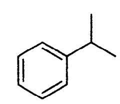
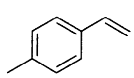
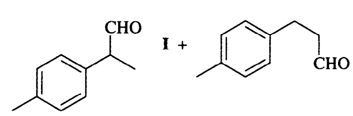
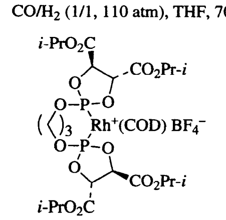
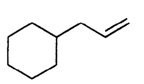
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	I + II (—), I:II = 93:7	248
	"	 I (—) + II (—) I:II > 99:1	248
	$[Rh(COD)Cl]_2$, $Ph_2P(CH_2)_2C_5H_4N$-2, CO/H_2 (1/1, 600 psi), $CHCl_3$, 80°, 19 h	I + II (15), I:II > 99:1	643
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 60°, 43 h	I (—) + starting material (25)	251
	$RhH_2(O_2COH)[P(Pr\text{-}i)_3]_2$, $(CH_2O)_n$, THF, 120°, 20 h	I + II +  III +  IV +  V + VI + VII (5) I + II (54), I:II = 97:3; III + IV (12), III:IV = 95:5; V + VI (28), V:VI = 95:5	593
	$PtCl_2[Ph_2P(CH_2)_3PPh_2]$, $SnCl_2$, PhMe, CO/H_2 (1/1, 80 bar), 4 h	I (51) +  (13) + starting material (36)	131
	$[(\eta^5\text{-}C_5H_5)Rh_2(\mu\text{-}CO)(\mu\text{-}Ph_2PPy)(CO)Cl]$, CO/H_2 (1/1, 80 atm), C_6H_6, 80°, 4 h	I + II (—), I:II = 25:1	616
	$RhH_2(O_2COH)[P(Pr\text{-}i)_3]_2$, CO (15 atm), H_2O, THF, 115°, 20 h	I (80) + II (5)	577
	Rh/C (5%), DPPB, HCO_2H, CO (8.5 atm), DME, 110-120°, 24 h	I + II (40), I:II = 100:0	368
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	 I + II I + II (—) I:II = 98:2	251
	CO/H_2 (1/1, 110 atm), THF, 70°, 16 h 	I + II (100), I:II = 96:4	248
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh=5, CO/H_2 (1/1, 50 atm), 80°, 1.5 h	I + II (48), I:II = 6.7	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 1.5 h	I + II (100), I:II=10	610

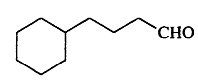
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(SOX)(COD), PhMe, 60°, CO/H_2 (1/1, 0.1 MPa)		511

Phosphine or Phosphite	P/Rh	Turnover[a]	Yield	I:II
$P(OPh)_3$	2	28	(—)	37.5 : 62.5
$P(OPh)_3$	5	0	(—)	—
PPh_3	2	10	(—)	74.7 : 25.3
PPh_3	5	43	(—)	87.5 : 12.5
DPPE	2	10	(—)	95.7 : 4.3
DPPE	5	48	(—)	97.5 : 2.5
DPPP	2	19	(—)	95.6 : 4.4
DPPP	5	76	(—)	96.0 : 4.0

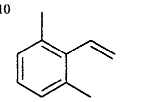


$Rh(acac)(CO)_2$, $P(OC_6H_3Me\text{-}4\text{-}Bu\text{-}t\text{-}2)_3$, L/Rh = 10, CO/H_2 (1/1, 20 atm), PhH, 70°

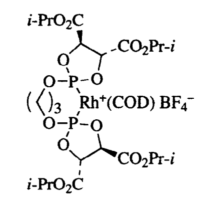


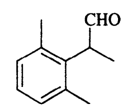
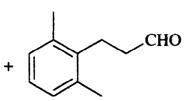
(66) + alkenes (17) — Refs. 468

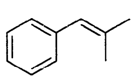
C_{10}



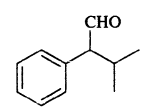
CO/H_2 (1/1, 100 atm), THF, 70°, 16 h

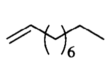


 I +  II — I + II (—), I:II = 97:3 — Refs. 248

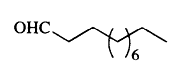
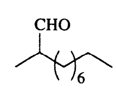
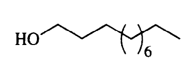
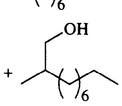


"

 (—) — Refs. 248



$Ru_3(CO)_{12}$-2,2'-bipyridine on silica f22, CO/H_2 (1/1, 50 bar), 150°, 17 h, PhMe

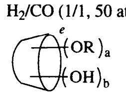
 I +  II +  III +  IV

I + II (5), III (36), IV (51) — Refs. 510

$RhH(CO)(PPh_3)_3$, CO/H_2 (1/1, 27.2 atm), 50° — Refs. 700

Solvent	Yield	I/II
C_6H_6	(—)	1.56
PhMe	(—)	1.22
EtOH	(—)	1.13
n-BuOH	(—)	2.92
n-$C_7H_{15}OH$	(—)	4.54

$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, P/Rh = 5, cyclodextrin, H_2/CO (1/1, 50 atm), H_2O, 80° — Refs. 701



Cyclodextrin	R	Cyclodextrin/Decene	a	b	Time (h)	Conv. (%)	I + II	I:II
α	—	0.014	0	18	8	10	(9)	3.2
γ	—	0.014	0	24	8	9	(6)	2.5
β	—	0.014	0	21	8	19	(15)	2.1
β	Me	0.014	12.6	8.4	8	76	(69)	1.8
β	Me	0.028	12.6	8.4	6	100	(95)	1.9
β	Me	0.014	21	0	8	30	(17)	2.5
β	COMe	0.014	21	0	8	6	(4)	2.6
β	COMe	0.014	14	7	8	46	(26)	2.6
β	$CH_2CH(OH)Me$	0.014	6.3	14.7	8	32	(27)	2
β	SO_3Na	0.014	9	12	8	7	(5)	2.8

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

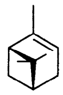
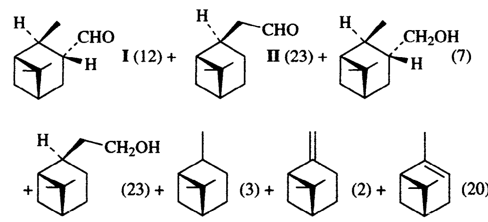
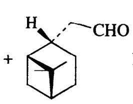
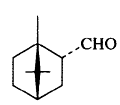
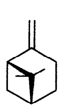
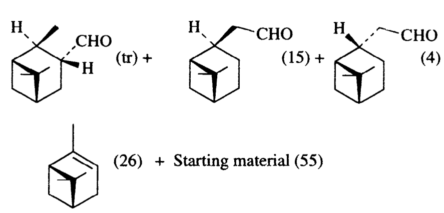
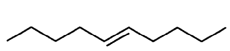
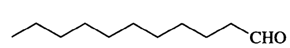
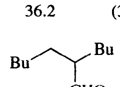
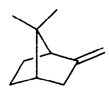
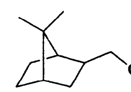
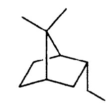
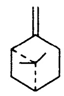
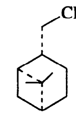
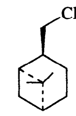
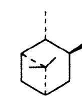
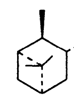
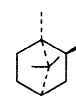
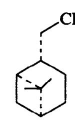
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(COD)Cl]_2$, $Ph_2P(CH_2)_2C_5H_4N$-2, CO/H_2 (1/1, 600 psi), $CHCl_3$, 80°, 2 h	**I** + **II** (100), **I**:**II** = 41:59	248
	$Rh_2(CO)_2[P(Bu\text{-}t)_3]_2(\mu\text{-Cl})[\mu\text{-S}(CH_2)_3SiO_3$-silica gel], CO/H_2 (1/1, 80 atm), 120°, 15 h	**I** (46) + **II** (46)	618
	$Rh(acac)(CO)_2$, $P(m\text{-}C_6H_4SO_3Na)_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** + **II** (95), **I**:**II**=1.9	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** + **II** (6), **I**:**II**=2.7	610
	Rh/C (5%), DPPB, HCO_2H, CO (8.5 atm), DME, 110-120°, 24 h	**I** + **II** (41), **I**:**II** = 41:59	368
	$Rh(acac)(CO)_2$, $P[(CH_2)_2(C_6F_{13}\text{-}n)]_3$, CO/H_2 (1/1, 150 psi), $c\text{-}C_6F_{11}CF_3$, PhMe, 100°, 11 h	**I** + **II** (80), **I**:**II** = 2.9	31
	$Rh_2(CO)_2[P(Bu\text{-}t)_3]_2(\mu\text{-Cl})[\mu\text{-S}(CH_2)_2SiO_3$-silica gel], CO/H_2 (1/1, 80 atm), 120°, 15 h	**I** (46) + **II** (45)	618
	$Rh_6(CO)_{16}$, PhMe, 130°, 48 h, CO/H_2 (1/1, 600 psi)		702
	$Rh_2(\mu\text{-SBu-}t)_2(CO)_2(P(OPh)_3)_2$, 85°, 4 d, CO/H_2 (1/1, 1.25 MPa), $ClCH_2CH_2Cl$	**I** (—) +  **III** (—) **I**:**III** = 40:60	703
	Rh catalyst, CO/H_2 (1/1, 650 bar), 70°	**I** + **II** + **III** (—), **I**:(**II** + **III**) = 8:1	699, 704
	$Co_2(CO)_8$, CO/H_2 (1/1, 200-300 bar), 110-120°	 (—)	704
	$Rh_6(CO)_{16}$, CH_2Cl_2, 60°, 17 h, CO/H_2 (1/1, 600 psi)		702
	$PtCl(CO)(PR_3)_2]ClO_4/SnCl_2\cdot H_2O$, 100°, CH_2Cl_2, CO/H_2 (1/1, 2000 psi), 3 h	 **I** + branched aldehydes **II** + decane **III**	705
	PR$_3$	Conv. (%) / **I** / **II** / **III**	
	$P(Bu\text{-}n)_3$	36.3 / (5) / (28) / (1)	
	PPh_3	37.6 / (5) / (31) / (2)	
	$P(PhCl)_3$	22.9 / (2) / (20) / (tr)	
	$P(OPh)_3$	72.5 / (10) / (51) / (12)	
	$P(OPhCl)_3$	50.8 / (8) / (37) / (7)	
	$AsPh_3$	36.2 / (3) / (26) / (8)	
	$Rh(acac)(CO)_2$, $P(m\text{-}C_6H_4SO_3Na)_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	 **I** (2)	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** (2)	610

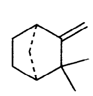
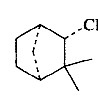
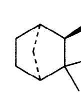
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(COD)Cl]_2$, 2 PPh_3, Et_3N, C_6H_6, 90°, CO/H_2 (1/1, 80 kg/cm²), 16 h	 I +  II I + II (93) I:II = 85:15	453
	$Rh_6(CO)_{16}$, 2 PPh_3, Et_3N, C_6H_6, 70°, CO/H_2 (1/1, 80 kg/cm²), 17 h	I + II (81), I:II = 87:13	453
	Rh-Co, CO/H_2 (1/1, 60 atm)	 I +  II +  III +  IV +  V	706

Catalyst	Solvent	Temp.	Time (h)	Conv. (%)	I	II	III + IV + V
$Co_2Rh_2(CO)_{12}$	PhMe	100°	1	32	(2)	(95)	(3)
$Rh_4(CO)_{12}/2Co_2(CO)_8$	PhMe	100°	1	31	(2)	(92)	(4)
$Rh_4(CO)_{12}/2(Ph_3P)_2NCl$	THF	125°	8	33	(11)	(82)	(5)
$Rh_4(CO)_{12}/400PPh_3$	PhMe	100°	5	62	(94)	(2)	(<1)
$Rh_4(CO)_{12}/80PCy_3$	PhMe	125°	5	51	(85)	(12)	(2)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(\mu\text{-SBu-}t)(CO)\{P(OPh)_3\}]_2$, CO/H_2 (1/1), toluene, 78°	 I (*cis*) +  II (*trans*)	707

Ligand	P (bar)	P/Rh	Conv. (%)	Isomerization (%)	de (%) (*cis*/*trans*)
$P(OPh_3)$	13	4	45	3	82 (91/9)
PPh_3	20	2.5	87	1	81 (90.5/9.5)
dppb	20	3	14	0	85 (92.5/7.5)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(\mu\text{-SBu-}t)(CO)\{P(OPh)_3\}]_2$, CO/H_2 (1/1), toluene, 78°	 I (*cis*) +  II (*trans*)	707

Ligand	P (bar)	P/Rh	Conv. (%)	Isomerization (%)	de (%)
$P(OPh_3)$	20	2	57	—	26

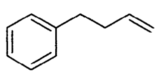
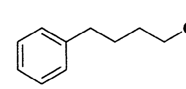
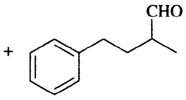
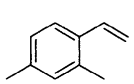
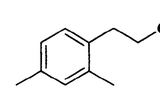
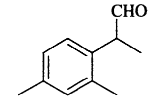
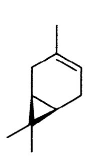
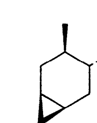
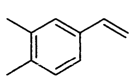
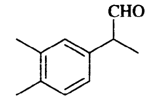
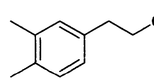
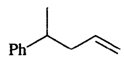
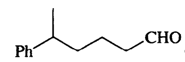
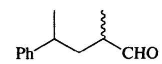
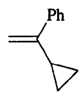
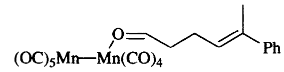
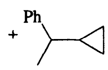
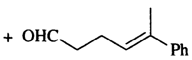
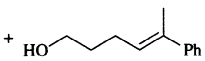
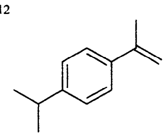
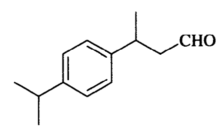
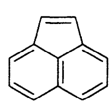
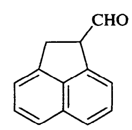
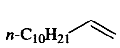
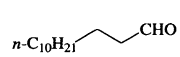
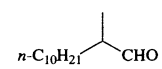
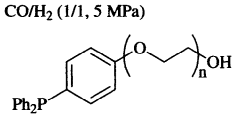
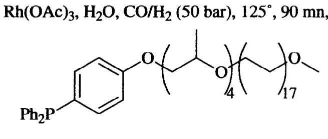
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 1.5 h	 I +  II I + II (99), I:II=1.4	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 1.5 h	I + II (37), I:II=3	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 12 h	 I +  II I + II (100), I:II=4.8	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 12 h	I + II (32), I:II=2.6	610
	Rh Catalyst, CO/H_2 (600 bar), <120°	 (—) + isomeric aldehydes (—)	699
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 47°, 22 h	 I (—) +  II (—) I:II = 97:3	251

TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	$[RhCl(CO)_2]_2/PPh_3$ (1/4), C_6H_6, 90°, CO/H_2 (120 atm), 4 h	 (67) +  (33) diastereomers ratio 1:1	708
	$HMn(CO)_5$, C_6D_6, 50°, 1 h	 (37) +  (5) +  (26) +  (28)	122
C_{12}			
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 400 psi), $CHCl_3$, 80°, 23 h	 (—) + starting material (29)	251
	Rh(SOX)(COD), PhMe, 75°, 10 h, CO/H_2 (1/1, 0.1 MPa)	 **I** (—)	511
	$Rh(COD)BPh_4$, CO/H_2, $CHCl_3$	**I** (98)	251
	$[RhCl(CO)_2]_2$, PPh_3, C_6H_6,100°, 1 h, CO/H_2 (1/1, 100 atm)	**I** (79)	709
	$[Rh(COD)Cl]_2$, CO/H_2 (1/1, 700 atm), 100°, C_6H_6	**I** (54)	710, 699
	$Rh_2O_3{\cdot}5H_2O$, Ligand, L/Rh = 330, 90°, CO/H_2 (1/1, 100 psi), 135 min Ligand NPh_3 PPh_3 $AsPh_3$ $SbPh_3$ $BiPh_3$	 **I** +  **II** Conv. (%) — I/II 5.8 — 1.8 86.9 — 8.7 85.8 — 3.5 8.5 — 9.1 0.0 — —	711
	$RhH(CO)(PPh_3)_3$, PPh_3, Ph_2POH, n-$C_{12}H_{25}C_6H_5$, CO/H_2 (1/1, 1 atm), 85°, 30 min	**I** (75) + **II** (7) + 2-dodecene (16) + dodecane (2)	712
	$Rh(acac)(CO)_2$, $P(OC_6H_3Me$-4-Bu-t-2$)_3$, L/Rh = 10, CO/H_2 (1/1, 20 atm), C_6H_6, 70°	**I** (63) + alkenes (19)	468
	$RhCl_3$, phosphine, P/Rh = 13, 100°, 7 h, PhMe/H_2O (2/3), pH = 6, CO/H_2 (1/1, 5 MPa) 	n — Conv. (%) — I + II 16 — 95.5 — (88) 25 — 96.5 — (85)	243
	$Rh(OAc)_3$, H_2O, CO/H_2 (50 bar), 125°, 90 mn, 	**I** + **II** (93.4), **I**:**II** = 72/28	713
	Rh (acac)$(CO)_2$, xantham, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80 °, 24 h	**I** + **II** + 2-undecene + 3-undecene +4-undecene **I** + **II** (96), **I**:**II** = 51	225

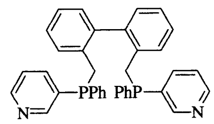
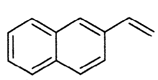
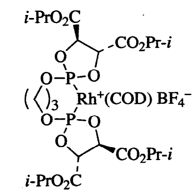
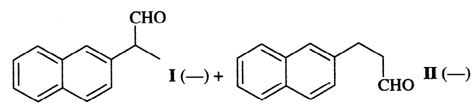
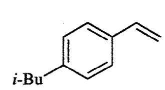
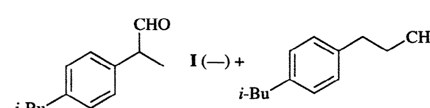
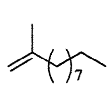
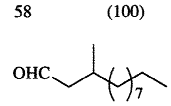
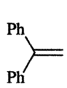
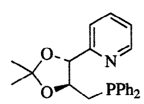
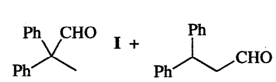
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, L/Rh = 10, PhMe, CO/H_2 (1/1, 20 atm), 80°, 20 h 	**I** (90) + **II** (2) + internal isomers (8), **I**:**II** = 54	224
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** + **II** (55), **I**:**II**=1.9	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	**I** + **II** (4), **I**:**II**=2.5	610
	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	 **I** (—) + **II** (—) **I**:**II** = 98:2	248
	Rh(COD)BF_4, ligand, 60°, PhMe, 18 h L/Rh = 1.2, CO/H_2 (1/1, 100 atm)	**I** + **II** (—)	689
	Ligand	**I**:**II**	
	$PhN(CH_2PPh_2)_2$	91:9	
	$p\text{-}CF_3C_6H_4N(CH_2PPh_2)_2$	93:7	
	$p\text{-}Me_2NC_6H_4N(CH_2PPh_2)_2$	95:5	
	DPPP	93:7	
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	**I** + **II** (—), **I**:**II** = 96.5:3.5	251
	Rh/C (5%), DPPP, HCO_2H, CO (8.5 atm), DME, 100-105°, 18-24 h	**I** + **II** (56), **I**:**II** = 82:18	368
	Rh/C (5%), DPPP, HCO_2H, CO (8.5 atm), DME, 110-120°, 24 h	**I** + **II** (67), **I**:**II** = 54.5:45.5	368
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 23 h	 **I** (—) + **II** (—) **I**:**II** = 90:10	251
	[Rh(NBD)(2,5-bis(diphenylphosphino-methyl)bicyclo[2.2.1]heptane)ClO_4, CO/H_2 (1/1, 40 atm), C_6H_6, 50°, 13 h	**I** + **II** (—), **I**:**II** = 92:8	247
	$[RhCl(CO)_2]_2$, L/Rh = 5, Et_3N/Rh = 10, CO/H_2 (1/1, 20 bar), PhMe, 25°, 6 h		641
	Ligand	Conv. (%) / **I** + **II** / **I**:**II**	
	TPP	79 / (100) / 83:17	
	PPh_3	29 / (100) / 94:6	
	PPPN	58 / (100) / 90:10	
	Rh(COD)BPh_4, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	 (—)	251
C_{14} 	$Rh(acac)(CO)_2$, L/Rh = 2.5, C_6H_6, CO/H_2 (1/1, 80 atm), 80°, 18 h L = 	 **I** + **II** **I** + **II** (21), **I**:**II** = 1:99	714

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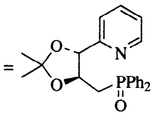
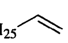
TABLE I. HYDROFORMYLATION OF ALKYL-SUBSTITUTED MONOOLEFINS (*Continued*)

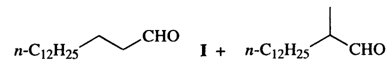
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst, H_2/CO (100 atm), PhH, 80°	I + II + PhCHMe (III)	715

Catalyst	H_2/CO	Temp.	Time (h)	Conv. (%)	I + II	I:II	III
HRh(CO)(PPh$_3$)$_3$	1/1	80°	48	81.7	(81)	96:4	(<1)
HRh(CO)(PPh$_3$)$_3$	1/1	120°	48	>99	(51)	>99	(49)
HRh(PPh$_3$)$_4$	1/1	80°	48	57.4	(53)	99	(4)
HRh(PPh$_3$)$_4$	1/1	90°	114	>99	(81)	98:2	(20)
[Rh(CO)$_2$Cl]$_2$	1/1	80°	48	75.2	(75)	>99	(>1)
[Rh(CO)$_2$Cl]$_2$	1/3	80°	48	61.2	(57)	>99	(4)
Rh(acac)(CO)$_2$	1/1	80°	24	46.4	(43)	99	(3)

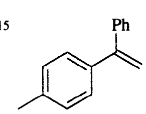
Rh(acac)(CO)$_2$, L/Rh = 2.5, C_6H_6, CO/H_2 (1/1, 80 atm), 80°, 18 h — I + II (61), I:II = 1:99 — 714

L =


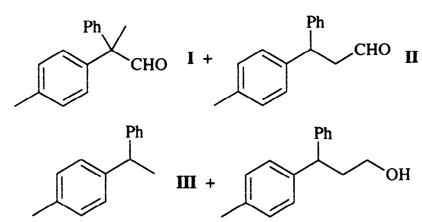
n-C$_{12}$H$_{25}$



I + II

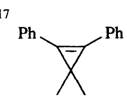
Conditions	Product(s) and Yield(s) (%)	Refs.
Rh(acac)(CO)$_2$, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	I + II (39), I:II=1.6	610
Rh(acac)(CO)$_2$, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 6 h	I + II (4), I:II=2.5	610
Rh(acac)(CO)$_2$, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$, H_2O, per(β-cyclodextrinMe$_2$-*o*-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 2 h	I + II (100), I:II=11	610

C$_{15}$


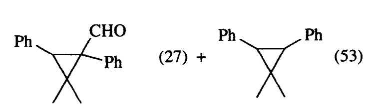
Catalyst, H_2/CO (1/1, 100 atm), C_6H_6 — 715


I + II + III + IV

Catalyst	Temp.	Time (h)	Conv. (%)	I + II	I:II	III	IV
HRh(CO)(PPh$_3$)$_3$	90°	48	72.1	(64)	>99	(8)	(—)
HRh(PPh$_3$)$_4$	90°	72	40	(35)	>99	(5)	(—)
HRh(PPh$_3$)$_4$	120°	66	>99	(66)	97:3	(4)	(30)
[Rh(CO)$_2$Cl]$_2$	90°	24	95	(88)	>99	(7)	(—)
[Rh(CO)$_2$Cl]$_2$	100°	24	>99	(46)	>99	(53)	(1)
Rh(acac)(CO)$_2$	90°	24	70	(67)	98:2	(3)	(—)

C$_{17}$


HMn(CO)$_5$, CO (1 atm), hexane, 55°, 5 h — 716


(27) + (53)

cis:*trans* = 87:13   *cis*:*trans* = 87:13

[a] Turnover = Mol substrate x conversion / mol catalyst

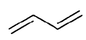
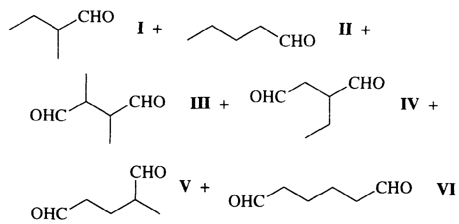
[b] C$_{60}$ = fullerene

[c] The barrel-like structure is a β-cyclodextrin

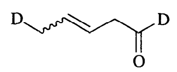
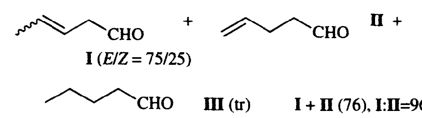
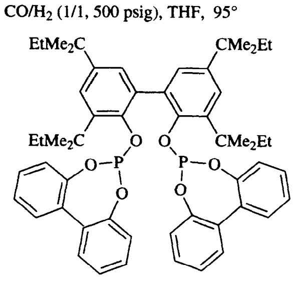
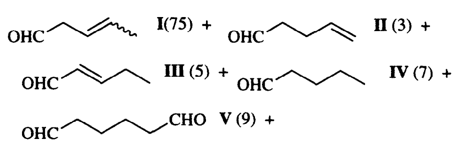
[d] scCO$_2$ = supercritical carbon dioxide.

[e] The barrel-like structure is a cyclodextrin.

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	$[Rh(COD)(OAc)]_2$, DPPE, L/Rh = 4, PhMe, CO/H_2 (1/2, 12 bar), 120°	Saturated C_5 aldehydes **I** (—) + unsaturated C_5 aldehydes **II** (—) **I**:**II** > 90:10; *n*:*iso* = 99:1	253
	Rh_2O_3, phosphine ligand, C_6H_6, 3 h, CO/H_2 (1/1, 200 atm)		252

Phosphine ligand	Temp.	I + II	I : II	III + IV + V + VI	III : IV : V : VI
PMe_2Ph	130°	(41)	15 : 85	(31)	1 : 18 : 61 : 20
$PMe_2(C_6H_4Me\text{-}2)$	130°	(14)	28 : 37	(1)	14 : 4 : 51 : 31
$PMe_2(C_6H_4Me\text{-}3)$	130°	(59)	34 : 66	(14)	1 : 8 : 65 : 26
$PMe_2(C_6H_4Me\text{-}4)$	130°	(40)	14 : 86	(38)	1 : 24 : 62 : 13
$PMe_2(C_6H_4Pr\text{-}i\text{-}4)$	130°	(46)	10 : 90	(28)	2 : 25 : 60 : 14
$PMe_2(CH_2Ph)$	130°	(50)	8 : 92	(14)	0 : 14 : 68 : 8
$PMe_2(C_6H_4OMe\text{-}4)$	130°	(43)	6 : 89	(18)	2 : 18 : 49 : 31
PhP(Et)Me	130°	(23)	16 : 83	(40)	1 : 26 : 59 : 14
PEt_2Ph	130°	(45)	6 : 94	(30)	2 : 23 : 59 : 16
Et_2PPEt_2	130°	(54)	8 : 91	(22)	2 : 55 : 46 : 2
Bu_2PPBu_2	130°	(64)	5 : 93	(14)	2 : 51 : 43 : 5
Ph_2PPPh_2	140°	(44)	18 : 82	(19)	1 : 63 : 37 : 0
$HPBu_2$	130°	(64)	18 : 81	(14)	2 : 45 : 53 : 1
$HPPh_2$	130°	(17)	23 : 76	(46)	0 : 82 : 17 : 1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh/mesitylene, DPPE, L/Rh = 1, 80°, CO/D_2 (1/1, 120 atm)	 (—)	227
	Rh/mesitylene, DPPE, L/Rh = 1, 80°, CO/H_2 (1/1, 120 atm), 4 h	 **I** (*E*/*Z* = 75/25) ... **II** + ... **III** (tr) **I** + **II** (76), **I**:**II**=96:4	254
	$Rh(acac)(CO)_2$, L, L/Rh = 12, CO/H_2 (1/1, 500 psig), THF, 95° 	 **I**(75) + **II** (3) + **III** (5) + **IV** (7) + **V** (9) + branched dialdehyde (1)	717

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 2MPa), L/Rh = 10, toluene, 100°, 3 h	**I** + **II** + **V**	718

Ligand	I	II+V
PPh_3	100	—
$Ph_2P(CH_2)_2$	94	6
$Ph_2P(CH_2)_3$	89	11
$Ph_2P(CH_2)_4$	76	24
$Ph_2P(CH_2)_5$	84	16
T-BDCP	74	26
T-BDCPn	68	32
CHDIOP	68	32
DIOP	65	35
BISBI	87	13

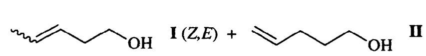
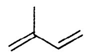
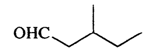
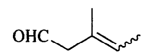
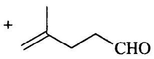
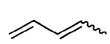
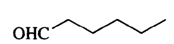
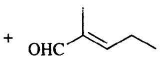
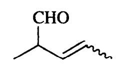
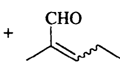
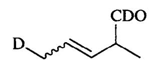
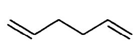
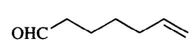
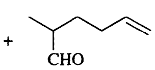
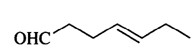
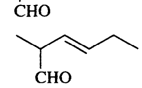
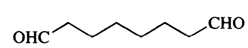
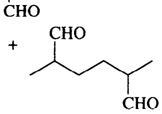
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, Et_3P, CO/H_2 (1/1, 600 psi), 80°	 **I** (*Z*,*E*) + **II** Conversion = 90 %, **I**+**II** (87)	719

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(COD)(OAc)]_2$, DPPE, L/Rh = 5, C_6H_6, CO/H_2 (1/1, 12 bar), 120°	 I (—) + other products II (—) I:II = 40:60	253
	Rh/mesitylene, DPPE, L/Rh = 1, 80°, CO/H_2 (1/1, 120 atm), 8 h	 I +  II; *E/Z* = 38/62; I + II (65), I:II = 90:10	254
	$[Rh(COD)(OAc)]_2$, DPPE, L/Rh = 5, C_6H_6, CO/H_2 (1/2, 12 bar), 120°	 I (—) +  II (—) I:II = 10:60	253
	Rh/mesitylene, DPPE, L/Rh = 1, 80°, CO/H_2 (1/1, 120 atm), 3 h	 I +  II + other aldehydes (III); *E/Z* = 18/82; I + II + III (68), I:II:III = 90:6:4	254
	Rh/mesitylene, DPPE, L/Rh = 1, 80°, CO/D_2 (1/1, 120 atm)	 (—)	254
	NaY zeolites entrapped rhodium carbonyl clusters, CO/H_2	Dialdehydes (60) + monoaldehydes (40)	585
C_6 		 I +  II +  III +  IV +  V +  VI	697

Catalyst	H_2/CO	Pressure (atm)	Temp.	I + II	III + IV	V + VI
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	1:1	10	30°	(70)	(16)	(0)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	1:1	10	40°	(38)	(32)	(30)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	1:1	10	50°	(3)	(25)	(70)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	1:1	6	50°	(5)	(54)	(41)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	3:7	10	50°	(15)	(0)	(59)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	1:1	10	60°	(0)	(17)	(83)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	1:1	10	80°	(0)	(0)	(100)
$Rh(acac)(CO)(PPh_3)/PPh_3$	1:1	10	50°	(25)	(0)	(75)
$Rh(acac)(CO)(PPh_3)/PPh_3$	1:1	6	50°	(80)	(0)	(20)
$Rh(acac)(CO)(PPh_3)/PPh_3$	1:1	10	60°	(0)	(0)	(100)

$Rh(acac)(CO)_2$, $Cp_2Zr(CH_2PPh_2)_2$, PhMe, H_2/CO (1/1, 10 atm), 80°, 2 h — 608

Zr/Rh	Time (h)	I + II	I:II
1.1	2	(26)	2
1.8	5	(30)	1.6
3.9	4	(10)	1.5

$Rh(acac)(CO)_2$, $Cp_2ZrH(CH_2PPh_2)$, PhMe, H_2/CO (1/1, 10 atm), 80°, 6 h — 608

Zr/Rh	Time (h)	I + II	I:II
1.0	4	(7)	—
3.5	6	(40)	1.2
5.5	8	(25)	1.7

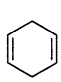
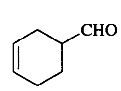
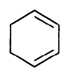
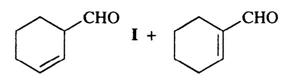
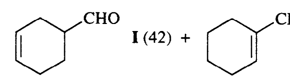
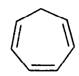
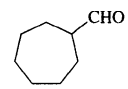
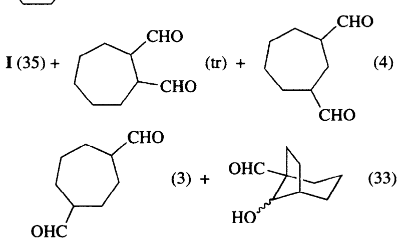
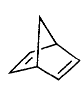
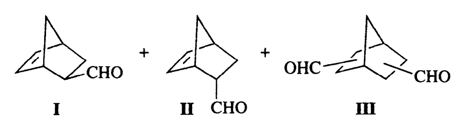
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, 80°, 3 h, CO/H_2 (10 atm)	 I (55)	260
	$Rh(acac)(CO)(PPh)_3$, PPh_3, 80°, 3 h, CO/H_2 (10 atm)	I (71)	260
	Rh/substrate (270), CO/H_2 (1/1, 70 atm), PhMe, 50°, 48 h	I (—)	720

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh/substrate (270), CO/H_2 (1/1, 70 atm), PhMe, 50°, 48 h	 **I** + **II** (—) **I**:**II** = 90:10	720
	Rh(acac)[$P(OPh)_3]_2$, $P(OPh)_3$, 80°, 3 h, CO/H_2 (10 atm)		260
	Rh(acac)(CO)(PPh_3)$_3$, PPh_3, 80°, 3 h, CO/H_2 (10 atm)	**I** (30) + **II** (43)	260
C_7 	Rh_2O_3, THF, CO/H_2 (1/1, 210 bar), 190°, 2.5 h	 **I** (71)	721
	Rh_2O_3/P(Bu-*n*)$_3$ (1/40), THF, CO/H_2 (1/1, 210 bar), 130°, 16 h	**I** (35) + 	721
	$Co_2(CO)_8$, THF, CO/H_2 (1/1, 210 bar), 150°, 7.5 h	**I** (69)	721
	CO/H_2 (1/1, 100 atm), PhMe		625

Catalyst precursor	Temp.	Time (h)	I + II	I:II	III
Pt(C_2H_4)(DPPB)/$MeSO_3H$	100°	4	(68)	89:11	(11)
Pt(C_2H_4)(DPPB)/$MeSO_3H$	100°	19	(13)	26:74	(86)
Pt(C_2H_4)(DPPB)/$MeSO_3H$	70°	8	(20)	96:4	(2)
Pt(C_2H_4)(DPPB)/$MeSO_3H$	70°	22	(50)	86:14	(10)
Pt(dppb)Cl_2/$SnCl_2$	100°	0.5	(4)	95:5	(79)
HRh(CO)(PPh_3)$_3$	100°	0.5	(4)	95:5	(95)
HRh(CO)(PPh_3)$_3$	50°	6	(22)	99:1	(4)
Pt(DPPB)Cl_2/$SnCl_2$	50°	4	(39)	100:0	(6)
Pt(DPPB)Cl_2/$SnCl_2$	50°	7	(22)	100:0	(2)
Pt(DPPB)Cl_2/$SnCl_2$	50°	22	(8)	96:4	(74)

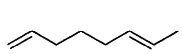
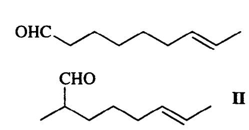
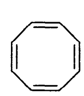
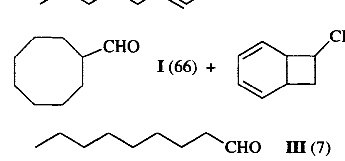
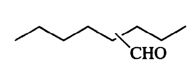
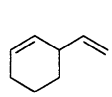
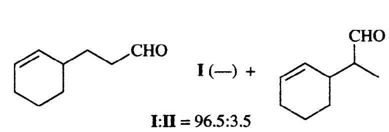
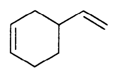
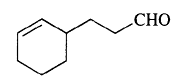
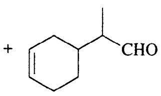
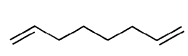
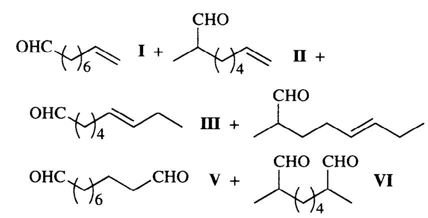
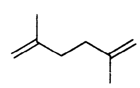
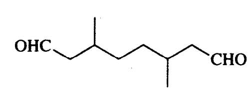
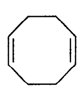
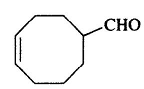
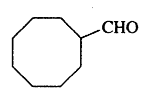
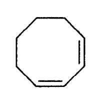
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhCl_3·3H_2O$, *hν*, CO/H_2 (1/1, 80 bar), MeOH, 25°, 18 h	**I** + **II** + **III** (—), (**I** + **II**):**III** = 10:90	682
C_8 	RhH(CO)(PPh_3)$_3$, C_6H_6, CO/H_2 (1/2), 12 h, rt	 **I** + **II** (47), **I**:**II** = 12:1	369
	$Co_2(CO)_8$, CO/H_2 (1/1, 210 bar), THF, 160°, 14 h		722
	Rh_2O_3, CO/H_2 (1/1, 210 bar), THF, 160°, 4 h	**I** (59) + **II** (7) + **III** (1) +  (3)	722
	[Pt(C_2H_4)(DPPB)]/CH_3SO_3H (1/1), PhMe, CO/H_2 (1/1, 100 atm), 100°, 22 h	 **I**:**II** = 96.5:3.5	259

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrinMe_2-o-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 1.5 h	**I** + **II** (100), **I**:**II**=3.3	610
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 1.5 h	**I** + **II** (40), **I**:**II**=10	610
	Rh-PEVV, CO/H_2 (1/1, 41.4 atm), H_2O, 100°, 2 h	 **I** +  **II** **I** + **II** (24) **I**:**II** = 5.65	242
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, 40°, CO/H_2 (1 atm), 6 h	**I** (100)	260
			697

Catalyst	Temp.	Pressure (atm)	Time (h)	I + II	III + IV	V + VI
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	50°	6	2.5	(0)	(37)	(63)
$Rh(acac)(CO)(PPh_3)/PPh_3$	50°	6	2	(28)	(7)	(65)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	50°	10	3	(0)	(27)	(73)
$Rh(acac)(CO)(PPh_3)/PPh_3$	50°	10	3	(0)	(0)	(100)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	60°	6	2	(0)	(48)	(52)
$Rh(acac)(CO)(PPh_3)/PPh_3$	60°	6	5	(0)	(6)	(94)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	60°	10	3	(0)	(53)	(47)
$Rh(acac)(CO)(PPh_3)/PPh_3$	60°	10	3	(0)	(0)	(100)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $Cp_2ZrH(CH_2PPh_2)$, PhMe, H_2/CO (1/1, 10 atm), 80°, 6 h	**I** + **II** (59), **I**:**II** = 1.3	608
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 65°, 23 h	 (90)	428
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 70 atm), PhMe, 20°, 48 h	 **I** (—)	720
	$HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 70 atm), PhMe, 20°, 48 h	**I** (—)	720
	Rh/1,5-COD, CO/H_2 (1/1, 70 atm), PhMe, 20°, 48 h	**I** (—)	720
	CO/H_2 (10 atm), 80°, 3 h	**I** +  **II** +  **III**	260

Catalyst	CO/H_2	I	II	III
$Rh(acac)[P(OPh)_3]_2/P(OPh)_3$	1/1	(0)	(67)	(33)
$Rh(acac)[P(OPh)_3]_2/P(OPh)_3$	3/2	(25)	(50)	(25)
$Rh(acac)(CO)(PPh_3)/PPh_3$	1/1	(16)	(72)	(12)
$Rh(acac)(CO)(PPh_3)/PPh_3$	3/2	(33)	(63)	(1)

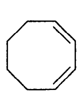
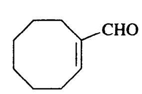
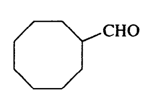
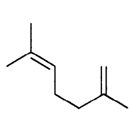
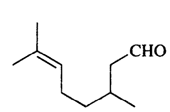
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh/COD-1,3, CO/H_2 (1/1, 70 atm), PhMe, 20°, 48 h	 (—)	720
	$Rh(acac)(CO)(PPh_3)$, PPh_3, 80°, 5 h, CO/H_2 (1/1, 10 atm)	 (20) + Starting material (80)	260
C_9 	$[Rh(COD)Cl]_2$, CO/H_2 (600 bar), 80°	 (—)	699, 723

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES (*Continued*)

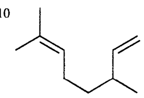
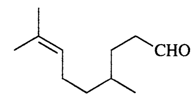
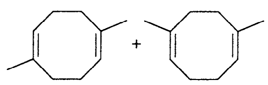
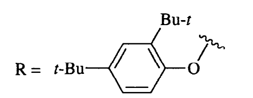
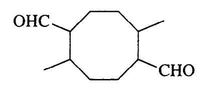
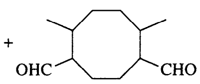
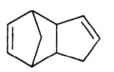
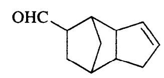
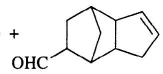
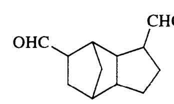
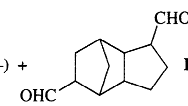
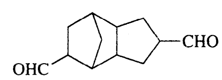
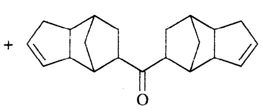
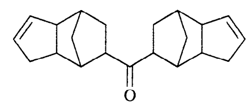
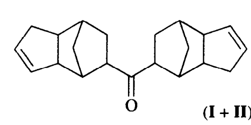
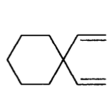
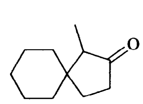
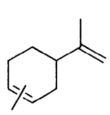
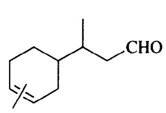
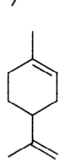
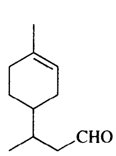
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	Rh catalyst, CO/H_2 (600 bar), 70°	 (—)	699
	$Rh(acac)(CO)_2$, $(RO)_3P$, toluene, CO/H_2 (90 atm), 60° 	 I +  II **I** + **II** = 55	724
	$Rh_4(CO)_{12}$, $Co_2(CO)_8$, PPh_3, 110°, 3 h, CO/H_2 (1/1, 40 atm)	 **I** (—) +  **II** (—) +  **III** (—) +  **IV** (—) +  **V** (—) (**I** + **II**):(**III** + **IV** + **V**) = 5.5:94.5	725
	$Rh_4(CO)_{12}$, $Co_2(CO)_8$, PPh_3, 90°, 3 h, CO/H_2 (1/1, 1 atm)	**I** (—) + **II** (—) +  **VI** (—) +  **VII** (—) +  **VIII** (—) (**I** + **II**):(**VI** + **VII** + **VIII**) = 32.4:67.6	725
	$[Rh(COD)(OAc)]_2$, DPPE, L/Rh = 5, C_6H_6, CO/H_2 (1/2, 18 bar), 95°	**I** + **II** (—)	253
	$Rh_4(CO)_{12}$, $Co_2(CO)_8$, PPh_3, 70°, 3 h, CO/H_2 (1/1, 1 atm)	**I** + **II** + **III** + **IV** + **V** + **VI** + **VII** + **VIII** (—) (**I** + **II**):(**III** + **IV** + **V**):(**VI** + **VII** + **VIII**) = 97.7:1.4:0.9	725
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, 60°, 3 h, CO/H_2 (10 atm)	**I** + **II** (57)	260
	$Rh(acac)[P(OPh)_3]_2$, $P(OPh)_3$, 80°, 3 h, CO/H_2 (10 atm)	**I** + **II** (81)	260
	$Rh(acac)(CO)(PPh)_3$, PPh_3, 60°, 3 h, CO/H_2 (10 atm)	**I** + **II** (69)	260
	$Rh(acac)(CO)(PPh)_3$, PPh_3, 80°, 3 h, CO/H_2 (10 atm)	**I** + **II** (89)	260
	$[RhCl(COD)]_2$, CO/H_2 (2/1, 30 bar), MeOH, 60°, 16 h	 (90)	726
	Rh(COD)(OAc), $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, L/Rh = 15, 90°, 0.5-3 h, CO/H_2 (1/2, 14 bar)	 (—)	614
	$Rh(COD)BPh_4$, CO/H_2, $CHCl_3$	 I (—)	251

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES (*Continued*)

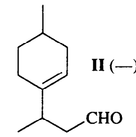
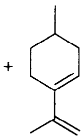
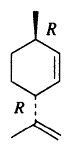
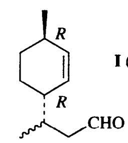
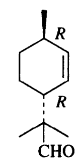
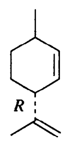
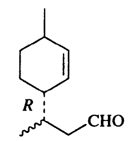
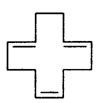
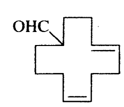
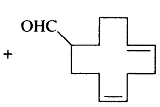
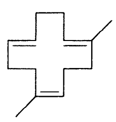
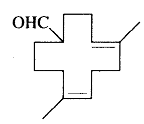
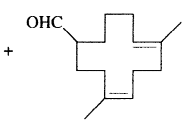
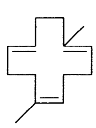
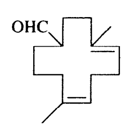
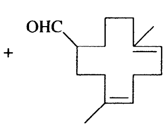
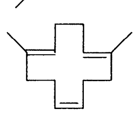
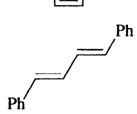
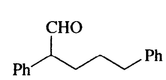
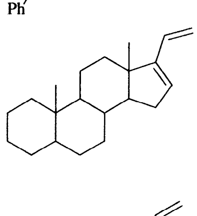
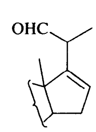
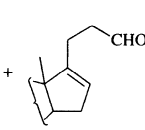
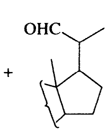
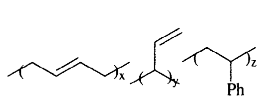
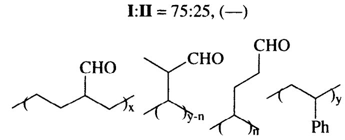
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2(\mu$-SBu-$t)_2(CO)_2(P(OMe)_3)_2$, 16 h, $ClCH_2CH_2Cl$, CO/H_2 (1/1, 0.5 MPa), 85°	I (—) +  II (—) +  III (—) I:II = 70:30	703
	$Rh_2(\mu$-SBu-$t)_2(CO)_2(P(OPh)_3)_2$, 16 h, $ClCH_2CH_2Cl$, CO/H_2 (1/1, 0.5 MPa), 85°	I (—) + III (—)	703
	$Rh_2(\mu$-SBu-$t)_2(CO)_2(PPh_3)_2$, 16 h, $ClCH_2CH_2Cl$, CO/H_2 (1/1, 0.5 MPa), 85°	I (—)	703
	$Rh_2(\mu$-SPh$)_2(CO)_2(P(OPh)_3)_2$, 16 h, $ClCH_2CH_2Cl$, CO/H_2 (1/1, 0.5 MPa), 85°	I (—)	703
	$[Rh(\mu$-SBu-$t)(CO)\{P(OPh)_3\}]_2$, P/Rh = 2, CO/H_2 (1/1, 12-13 bar), toluene, 78°, 18 h	 I (89) +  II (11)	707
	$[Rh(\mu$-SBu-$t)(CO)\{P(OPh)_3\}]_2$, P/Rh = 6, CO/H_2 (1/1, 5 bar), toluene, 78°, 18 h	 (—) de = 22%	707
C_{12} 	Rh(SOX)(COD), DPPE, L/Rh = 1, PhMe, CO/H_2 (1/1, 0.1 MPa), 60°	Monoaldehyde (—)	511
	Rh Catalyst, CO/H_2 (500 psi), 90°	 I +  II I + II (—) I:II = 46:54	265
	"	 (—) +  (—)	265
	"	 (—) +  (—)	265
	"	No reaction	265
C_{16} 	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 200 atm), C_6H_6, 60°, 6 h	 (68)	381
C_{21} 	$[Rh(NBD)Cl]_2$, PPh_3, 100°, 3 h, CO/H_2 (1/1, 80 bar)	 I +  II +  III I:II = 75:25, (—)	727
 Styrene-Butadiene copolymer (SBR)	Rh-catalyst, H_2/CO (1/1), THF, 40°		728

TABLE II. HYDROFORMYLATION OF DIENES AND POLYENES (*Continued*)

Reactant	Conditions			Product(s) and Yield(s) (%)		Refs.
Polymer	Catalyst	H_2-CO (psi)	Time (h)	Conv. (%)	Hydroformylation (%)	
Duradene 707	$HRh(CO)(PPh_3)_3$	200	19	27	28	
	$[Rh(COD)Cl]_2$	200	19	6	5	
	$[Rh(COD)_2]BF_4$	200	22	16	15	
	$[Rh(COD)dppb]BF_4$	200	19	6	6	
	$[Rh(COD)]BPh_4$	200	18	3	3	
Duradene 709	$HRh(CO)(PPh_3)_3$	800	72	80	81	
	$[Rh(COD)Cl]_2$	800	44	100	87	
	$[Rh(COD)_2]BF_4$	800	44	100	98	
	$[Rh(COD)dppb]BF_4$	800	46	36	38	

TABLE III. HYDROFORMYLATION OF UNSATURATED ALCOHOLS

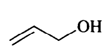
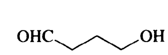
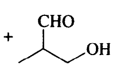
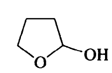
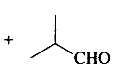
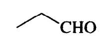
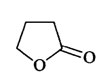
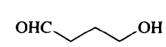
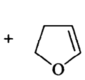
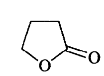
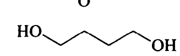
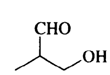
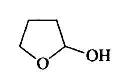
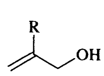
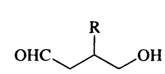
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	$RhH(CO)(PPh_3)_3$, $(Ph_2PC_5H_4)_2Fe$, P/Rh = 20, C_6H_6, CO/H_2 (1/1, 800 psi), 60°, 22 h	 **I** +  **II** + *n*-PrOH **III** **I** + **II** + **III** (—), **I**:**II**:**III** = 87.4:11.1:1.5	729
	$RhH(CO)(PPh_3)_3$, PPh_3, P/Rh = 20, C_6H_6, CO/H_2 (1/1, 100 psi), 60°, 5.7 h	**I** + **II** (—), **I**:**II** = 67.1:32.9	729
	$[Rh(PPh_3)_3]^+$/montmorillonite, EtOH, 70°, CO/H_2 (1/1, 60 atm)	**I** (96) + **II** (4)	730
	$HRh(CO)(PPh_3)_3$, PPh_3, PhCOMe, CO/H_2 (1/1, 55 bar), 60°	 **I** (96) +  **II** (4)	731
	$Rh(acac)(CO)_2$, reDPMNr, L/Rh = 4, toluene, CO/H_2 (1/1, 9 atm), 55°, 6 h	**I** (89) + **II** (11) +  **III** (tr)	732
	$Co_2(CO)_8$, TMEDA, $PhCH_2CN$, 84°, CO/H_2 (1/2, 69 bar), 18 h	 (90) + **II** (5) + **III** (5)	731
	$K[Ru(EDTA\text{-}H)Cl]\cdot 2H_2O$, H_2O, 90-130°, CO/H_2 (1/1, 50 atm)	 (35) +  (25) +  (25) +  (1)	733, 734
	$Rh(acac)(CO)_2$, $P(OC_6H_3[Bu\text{-}t]_2\text{-}2,4)_3$, BDPB, CO/H_2 (100 atm), 110°, 4 h	 **I** +  **II** **I** + **II** (91) **I**:**II** = 43:57	735
C_4 	$RhCl(CO)(PPh_3)_2$, C_6H_6, Et_3N, 80°, CO/H_2 (1/1, 80 atm)	 (80-90) R = Me; *t*-Bu; *s*-Bu	736

TABLE III. HYDROFORMYLATION OF UNSATURATED ALCOHOLS (*Continued*)

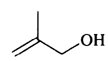
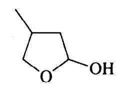
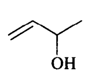
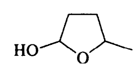
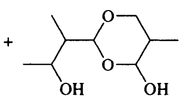
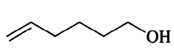
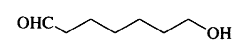
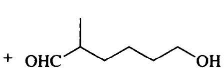
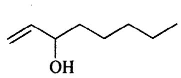
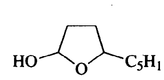
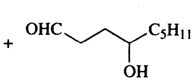
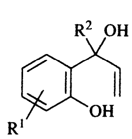
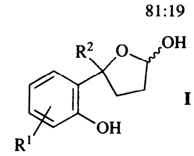
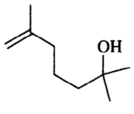
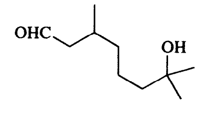
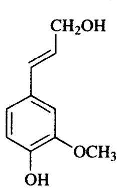
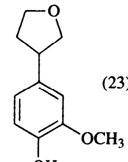
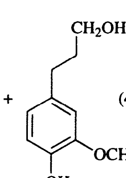
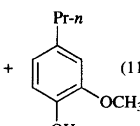
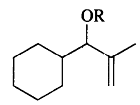
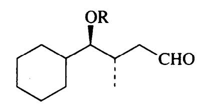
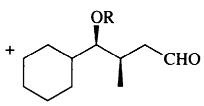
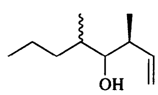
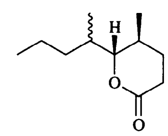
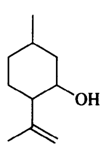
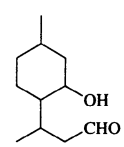
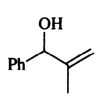
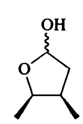
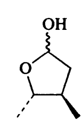
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, P$[OC_6H_3$(Bu-*t*$)_2$-2,4$]_3$, 90°, N$(CH_2CH_2OH)_3$, H_2/CO (3/1, 90 kg/cm^2), 2.5 h	 **I** (78)	737
	Rh(acac)$(CO)_2$, P$[OC_6H_3$(Bu-*t*$)_2$-2,4$]_3$, H_2/CO (90 atm), toluene, N$(CH_2CH_2OH)_3$ 90°, 2 h	**I** (65)	738
	Rh(acac)$(CO)_2$, ligand, L/Rh = 3, PhMe, CO/H_2 (1/1, 10 atm) Ligand — Temp. DPPB — 60° P(C_6H_4OMe-*p*$)_3$ — 60° PPh_3 — 60° P(C_6H_4Me-*p*$)_3$ — 60° DPPE — 80° P(C_6H_4Me-*m*$)_3$ — 60° P($OC_6H_3Me_2$-*m,m'*$)_3$ — 60° P(OC_6H_4Me-*o*$)_3$ — 60° P$(OPh)_3$ — 60°	 **I** (—) +  **II** (—) **I**:**II** 100:0 100:0 100:0 100:0 87:13 37:63 54:46 100:0 100:0	739
C_6 	Rh(acac)$(CO)_2$, ligand, L/Rh = 3, CO/H_2 (1/1, 10 atm), PhMe, 60° Ligand DPPB P(OC_6H_4Me-*m*$)_3$	 **I** (—) +  **II** (—) **I**:**II** 82:18 68:32	739
C_8 	Rh(acac)$(CO)_2$, ligand, L/Rh=3, PhMe, CO/H_2 (1/1, 10 atm), 60 ° Ligand DPPB P(C_6H_4OMe-4$)_3$ PPh_3 P(OC_6H_4OMe-3$)_3$ P($OC_6H_3Me_2$-3,5$)_3$ P$(OPh)_3$	 **I** (—) +  **II** **I**:**II** 100:0 100:0 100:0 100:0 100:0 81:19	739
C_9 	[Rh(OAc)$_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 60°, 20 h	 **I** R^1 — R^2 — **I** H — H — (70) H — Me — (95) 5-OMe — H — (91) 5-Me — Me — (80) 4-OMe — Me — (98) H — Ph — (83) 4-OMe — Ph — (100)	313
	[Rh(COD)Cl$]_2$, CO/H_2 (1/1, 600 bar), 100°, C_6H_6, 5 h	 (90)	699, 740
C_{10} 	1. $CoCO_3$, CO/H_2 (1/1, 100 atm), C_6H_6, 170°, 24 h 2. H_2 (100 atm), 150°, 3 h 3. HCl	 (23) +  (46) +  (11)	741

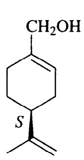
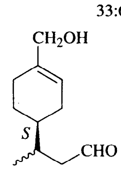
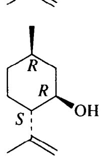
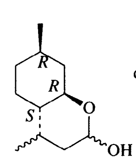
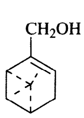
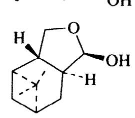
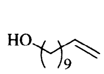
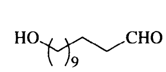
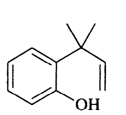
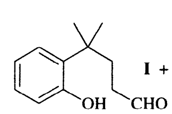
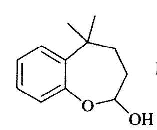
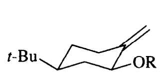
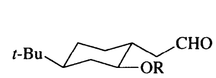
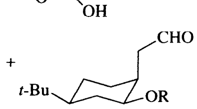
TABLE III. HYDROFORMYLATION OF UNSATURATED ALCOHOLS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, CO/H_2 (1/1, 80 atm), PhMe, 80°, 48 h	 I +  II	742
	1. $[Rh(OAc)_2]_2$, PPh_3, EtOAc, 100°, 6 h, CO/H_2 (1/1, 350 psi) 2. PCC, CH_2Cl_2, 3 h	 (81)	314
	$(CH_2Cl)_2$, CO/H_2 (1/1, 0.5 MPa), 85°, 16 h		703
	$Rh(acac)(CO)_2$, phosphine ligand, PhMe, CO/H_2 (1/1, 20 bar), 90°, 6-24 h	 I +  II I + II (83-95)	743

R	I + II	I : II
H	(96)	52:48
Ac	(84)	78:22
Piv	(89)	82:18
TBDMS	(91)	75:25
TBDPS	(96)	69:31

Catalyst	Conv. (%)	Yield
$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(P(OMe)_3)_2$	48.5	(—)
$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(P(OPh)_3)_2$	67.5	(—)
$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PPh_3)_2$	28	(—)
$Rh_2(\mu\text{-}SPh)_2(CO)_2(P(OPh)_3)_2$	9	(—)

Phosphine ligand	I:II
PPh_3	50:50
$P(OPh)_3$	45:50
P(*N*-pyrrolyl)$_3$	33:66

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(\mu\text{-}SBu\text{-}t)(CO)\{P(OPh)_3\}]_2$, P/Rh = 2, CO/H_2 (1/1, 12-13 bar), toluene, 78°,18 h	 (100)	707
	$[Rh(\mu\text{-}SBu\text{-}t)(CO)\{P(OPh)_3\}]_2$, P/Rh = 2, CO/H_2 (1/1, 13 bar), toluene, 78°, 16 h	 de 60%	707
	$[Rh(\mu\text{-}SBu\text{-}t)(CO)\{P(OPh)_3\}]_2$, P/Rh = 2, CO/H_2 (1/1, 100 bar), toluene, 85°, 16 h	 (82) + myrtanal (9)	707
C_{11} 	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 n:iso > 40:1, (53)	135
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 60°, 20 h	 I +  II I + II (85) I:II = 4:6	313
	$Rh(acac)(CO)_2$, CO/H_2 (1/1, 80 atm), PhMe, 40°, 45 h	 I +  II	742

R	I + II	I:II
H	(85)	67:33
Piv	(95)	64:36

TABLE III. HYDROFORMYLATION OF UNSATURATED ALCOHOLS (*Continued*)

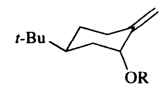
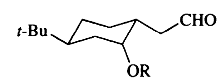
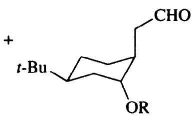
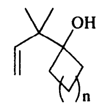
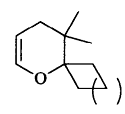
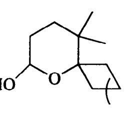
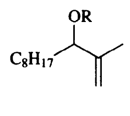
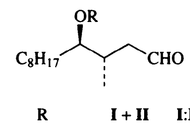
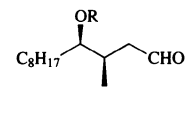
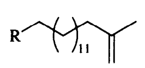
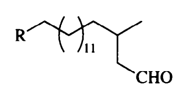
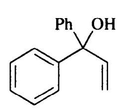
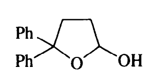
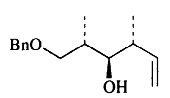
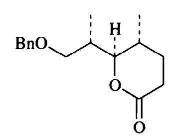
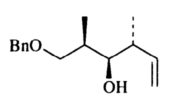
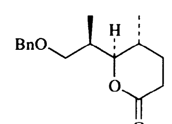
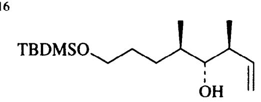
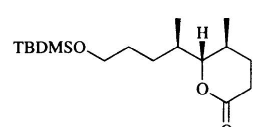
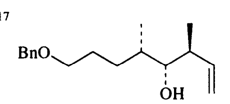
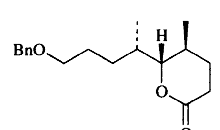
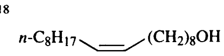
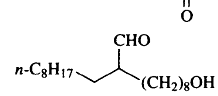
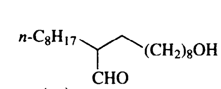
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, CO/H$_2$ (1/1, 80 atm), PhMe, 40°, 45 h	 I +  II R | I + II | I:II H | (84) | 36:64 Piv | (99) | 20:80	742
	[Rh(COD)Cl]$_2$ or Rh(acac)(CO)$_2$, CO/H$_2$ (30/20 bar), dioxane, 110°	 I +  II n | I | II 2 | (39) | (48) 3 | (95) | (—)	744
	Rh(acac)(CO)$_2$, CO/H$_2$ (1/1, 60 atm), PhMe, 80°, 48 h	 I +  II R | I + II | I:II H | (99) | 53:47 PhCO | (99) | 54:46 Piv | (90) | 61:39 TBDPS | (99) | 61:39	742
C$_{15}$			
	Rh(acac)(CO)$_2$, CO/H$_2$ (1/1), toluene	 I R | P (atm) | Temp. | I OTs | 80 | 40° | (84) OH | 80 | 60° | (92) OTBS | 80 | 60° | (90)	745
	[Rh(OAc)$_2$]$_2$, PPh$_3$, L/Rh = 4, CO/H$_2$ 60°, 29 h	 (84)	313
	1. [Rh(OAc)$_2$]$_2$, PPh$_3$, EtOAc, 100°, 6 h, CO/H$_2$ (1/1, 350 psi) 2. PCC, CH$_2$Cl$_2$, 3 h	 (85)	314
	1. [Rh(OAc)$_2$]$_2$, PPh$_3$, EtOAc, 100°, 6 h, CO/H$_2$ (1/1, 350 psi) 2. PCC, CH$_2$Cl$_2$, 3 h	 (86)	314
C$_{16}$			
	1. [Rh(OAc)$_2$]$_2$, PPh$_3$, EtOAc, 100°, 6 h, CO/H$_2$ (1/1, 350 psi) 2. PCC, CH$_2$Cl$_2$, 3 h	 (80)	314
C$_{17}$			
	1. [Rh(OAc)$_2$]$_2$, PPh$_3$, EtOAc, 100°, 6 h, CO/H$_2$ (1/1, 350 psi) 2. PCC, CH$_2$Cl$_2$, 3 h	 (86)	314
C$_{18}$			
	HRh(CO)[P(PhSO$_3$Na-*m*)$_3$]$_3$ on CPG-240, CO/H$_2$ (1/1, 5.1 MPa), cyclohexane, 75°, 5.5 h	 (—) +  (—)	746, 747

TABLE III. HYDROFORMYLATION OF UNSATURATED ALCOHOLS (*Continued*)

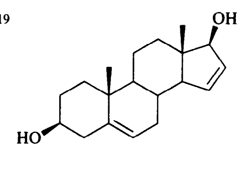
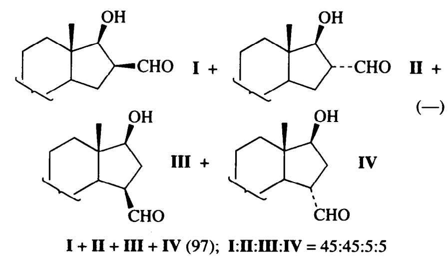
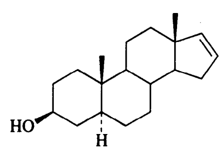
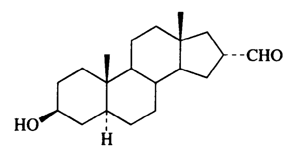
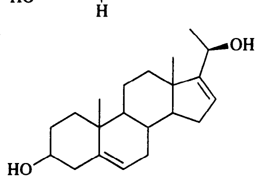
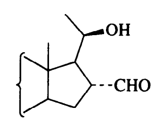
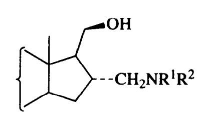
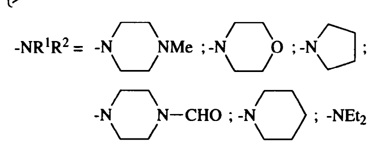
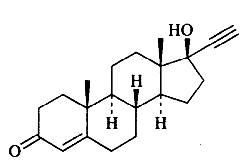
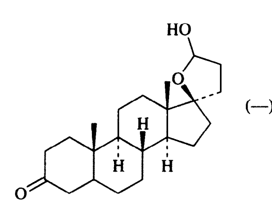
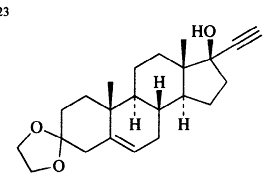
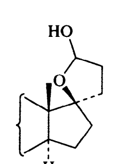
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19} 	$[Rh(NBD)Cl]_2$, PBu_3, CO/H_2	 I + II + III + IV (97); I:II:III:IV = 45:45:5:5	293
	$[Rh(NBD)Cl]_2$, PBu_3, CO/H_2	 (72) + Aldehyde isomer (28)	293
C_{21} 	$[Rh(NBD)Cl]_2$, PBu_3, Et_3N, C_6H_6, CO/H_2 (100-120 bar), 120°	 (80)	293
	$[Rh(NBD)Cl]_2$, PBu_3, R^1R^2NH, C_6H_6, CO/H_2 (120 bar), 120°	 (47-82) 	293
	$[Rh(OAc)_2]_2$, PPh_3, CO/H_2 (12 bar)	 (—)	748
C_{23} 	$[Rh(OAc)_2]_2$, PPh_3, CO/H_2 (1/1, 12 bar), EtOAc, 80°, 20 h	 (90)	748

TABLE IV. HYDROFORMYLATION OF UNSATURATED ALDEHYDES AND KETONES

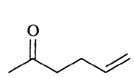
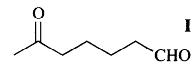
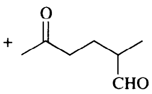
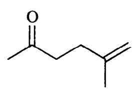
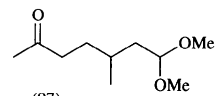
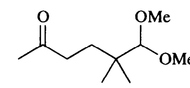
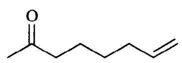
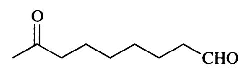
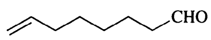
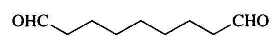
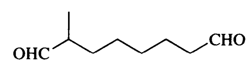
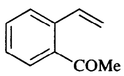
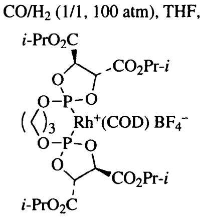
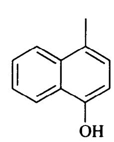
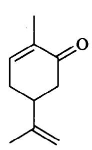
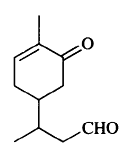
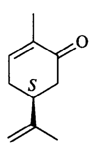
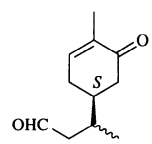
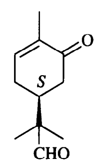
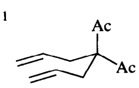
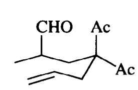
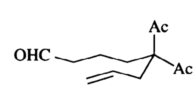
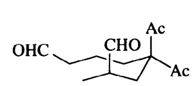
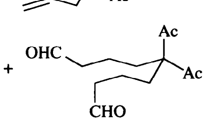
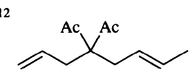
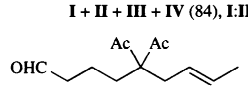
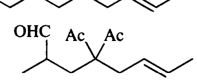
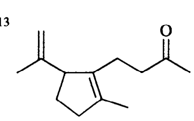
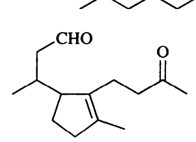
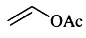
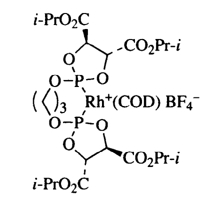
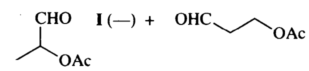
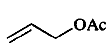
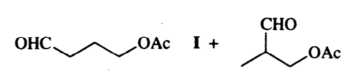
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Rh(CO)$_2$(acac), DIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°, 18 h	 I +  II; I + II (86), I:II > 40:1	135
	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	I + II (27), I:II = 36:63	368
C_7 	Rh_2(μ-OMe)$_2$(COD)$_2$, PPTS, 10 P(OC$_6$H$_4$Bu-*t*-2)$_3$, (MeO)$_2$CMe$_2$, CO/H_2 (1/1, 50 bar), 60°, 24 h	 (97) +  (3)	663
C_8 	Rh(CO)$_2$(acac), BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 n:iso > 40:1, (87)	135
C_9 	Rh(acac)(CO)$_2$, TPPSNa, polyethylene glycol dimethyl ether, H_2/CO (90 kg/cm^{2}G), 90°, 4 h	 I (41) +  II (—)	749
	Rh(acac)(CO)$_2$, TPPSNa, CO/H_2 (90 kg/cm^{2}G), 100°, 6 h	I (97)	750
C_{10} 	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	 (51)	248
	Rh(COD)BPh$_4$, CO/H_2, CHCl$_3$	 (—)	251
	[Rh(μ-SBu-*t*)(CO){P(OPh)$_3$}]$_2$, CO/H_2 (1/1, 12-13 bar),toluene, 78°, 18 h	 (98) +  (2)	707
C_{11} 	RhH(CO)(PPh$_3$)$_3$, C_6H_6, rt, 10 h, CO/H_2 (1/2, 1 atm)	 I +  II +  III +  IV; I + II + III + IV (84), I:II:III:IV = 5:45:1.5:29.5	369
C_{12} 	RhH(CO)(PPh$_3$)$_3$, C_6H_6, CO/H_2 (1/2, 1 atm), rt, 4 d	 I +  II; I + II (63), I:II = 2.5:1	369
C_{13} 	[RhCl(COD)]$_2$, C_6H_6, 100°, CO/H_2 (1/1, 700 bar), 7 h	 (—)	669, 750

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS

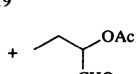
A. Esters of Unsaturated Alcohols

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	 I (—) + II (—) I:II > 99:1	248
	Rh(COD)BPh_4, CO/H_2 (1/2, 300 psi), $CHCl_3$, 55°, 22 h	I + II (—), I:II = 94.5:5.5	251
	Rh(acac)$[P(OPh)_3]_2$, $P(OPh)_3$, L/Rh = 2.6, CO/H_2 (1/1, 1atm), 40°, 6 h	I (63) + II (—)	751
	$RhH[P(OPh)_3]_4$, CO/H_2 (1/1, 1atm), 40°, 4.5 h	I (67) + II (—)	751
	Rh(acac)$(CO)_2$, $P(OPh)_3$, L/Rh = 2.6, CO/H_2 (1/1, 1atm), 40°, 3.5 h	I (81) + II (—)	751
	Rh(anthranilate)$(CO)_2$, $P(OPh)_3$, P/Rh = 4.1, CO/H_2 (1/1, 1 atm), PhMe, 40°	I (38)	570
	$[Rh(COD)(OAc)]_2$, CO/H_2	I + II (57-80), I:II > 99:1	316
	5% Rh/C, DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	I + II (30), I:II = 82:18	368
	$(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 380 psi), 50°, 22 h	I + II (72), I:II = 75:25	372
	CO/H_2 (40 atm), CH_2Cl_2, 80°, 12 h	 I + II	267

Catalyst	Phosphine	Catalyst:Phosphine	I + II	I:II
Rh(COD)(η^6-$PhBPh_3$)	—	—	(71)	36:64
Rh(COD)(η^6-$PhBPh_3$)	DPPB	1:1	(76)	40:60
Rh(COD)(η^6-$PhBPh_3$)	DPPB	1:2	(56)	95:5
Rh(COD)(η^6-$PhBPh_3$)	DPPB	1:4	(53)	91:9
$[Rh(COD)(PPh_3)_2]BPh_4$	—	—	(68)	20:80
$[Rh(COD)(PPh_3)_2]BPh_4$	DPPB	1:2	(55)	94:6
Rh(COD)(η^6-$PhBPh_3$)	PPh_3	1:1	(67)	56:44
Rh(COD)(η^6-$PhBPh_3$)	PPh_3	1:4	(74)	42:58
Rh(COD)(η^6-$PhBPh_3$)	$P(C_6H_4NMe_2\text{-}4)_3$	1:4	(63)	37:63

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 55 bar), 90°		731

Catalyst-Promoter	I + II	I:II
$Co_2(CO)_8$-Ph_3GeH	(—)	48:36
$Co_2(CO)_8$-Ph_2S	(—)	57:11
$Co_2(CO)_8$-2,2'-dipyridyl	(—)	66:14
$Co_2(CO)_8$-succinonitrile	(—)	61:19

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Co_2(CO)_8$, CO/H_2 (200 bar), 125°	I (64) + II (—) +  III (—) I:II:III = 70:15:15	731
	$(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 380 psi), 50°, 22 h	I + II (70), I:II = 89:11	372
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, H_2/CO (1/1, 600 psi)		752

Temp.	Time, (h)	Conv. (%)	I + II	I:II
145°	36	100	(56)	100:0
130°	36	100	(82)	86:14
100°	48	100	(92)	47:53
65°	60	100	(92)	30:70
rt	216	0	(—)	—

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

A. Esters of Unsaturated Alcohols (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(COD)Cl]_2$/DPPB in mormorilonite, CH_2Cl_2, H_2/CO		752

H_2/CO (psi)	Temp.	Time (h)	Conv. (%)	I + II	I:II
1000/100	100°	36	100	(90)	35:65
750/250	100°	45	100	(91)	38:62
250/750	100°	30	100	(90)	38:62
100/1000	130°	24	85	(81)	77:23
1000/100	55°	48	100	(93)	25:75

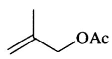
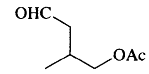
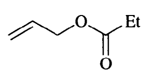
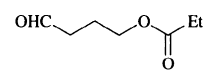
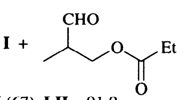
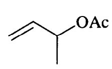
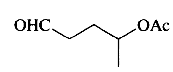
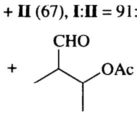
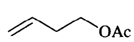
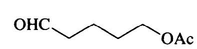
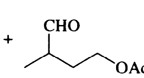
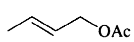
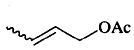
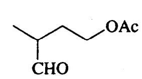
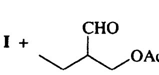
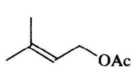
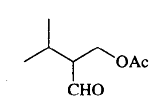
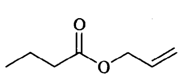
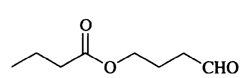
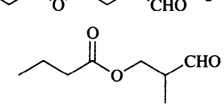
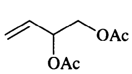
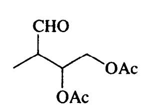
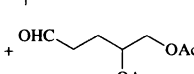
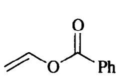
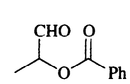
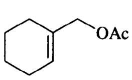
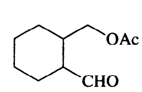
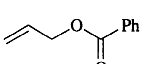
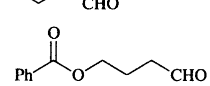
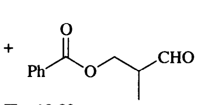
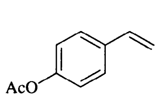
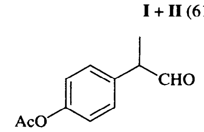
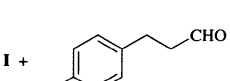
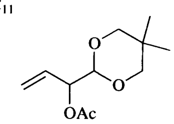
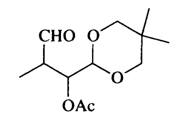
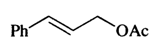
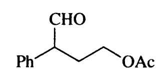
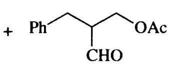
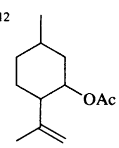
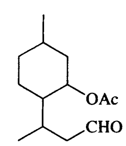
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$Rh(COD)(\eta^6\text{-}PhBPh_3)$, DPPB, CH_2Cl_2, CO/H_2 (40 atm), 80°, 12 h	(0)	267
	$[Rh(COD)Cl]_2$ in mormorilonite, 150°, H_2/CO, CH_2Cl_2, 20 h	 (97)	752
	$Rh(COD)(\eta^6\text{-}PhBPh_3)$, DPPB, CH_2Cl_2, CO/H_2 (40 atm), 80°, 12 h	 I +  II I + II (67), I:II = 91:9	267
	$Rh(COD)(\eta^6\text{-}PhBPh_3)$, DPPB, CH_2Cl_2, CO/H_2 (40 atm), 80°, 12 h	 I +  II I + II (69) I:II = 97:3	267
	$Rh(COD)(\eta^6\text{-}PhBPh_3)$, DPPB, CH_2Cl_2, CO/H_2 (40 atm), 80°, 12 h	 I +  II I + II (87) I:II = 70:30	267
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, CO/H_2, 50°, 30 h	I + II (66), I:II = 39:61	752
	$Rh(COD)(\eta^6\text{-}PhBPh_3)$, DPPB, CH_2Cl_2, CO/H_2 (40 atm), 80°, 12 h	Aldehydes (0)	267
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, CO/H_2, 50°, 30 h	I + II (66), I:II = 39:61	752
	$[Rh(COD)Cl]_2$ in mormorilonite, 50°, H_2/CO, CH_2Cl_2, 96 h	 I +  II I + II (93) I:II = 30:70	752
C_7 	Rh catalyst, CO/H_2 (600 bar), 80°	 (—)	699
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, 60°, H_2/CO (1/1, 600 psi), 20 h	 I +  II I + II (93) I:II = 30:70	752
C_8 	Rh catalyst, CO/H_2 (600 bar), 80°	 I (—) +  II (—) I:II = 80:20	699, 753
C_9 	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	 (83)	368
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, CO/H_2, 130°, 120 h	 (43)	752
C_{10} 	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, CO/H_2, rt, 264 h	 I +  II I + II (61), I:II = 18:82	752
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, per(β-cyclodextrinMe$_2$-o-2,6), P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 0.75 h	 I +  II I + II (100), I:II=11	610

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

A. Esters of Unsaturated Alcohols (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $P(C_6H_4SO_3Na\text{-}m)_3$, H_2O, P/Rh = 5, CO/H_2 (1/1, 50 atm), 80°, 0.75 h	I + II (70), I:II=8.3	610
C_{11} 	Rh catalyst, CO/H_2 (600 bar), 80°	 (—)	699, 754
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, CO/H_2, 110°, 20 h	 I +  II I + II (89) I:II = 64:36	752
	$[Rh(COD)Cl]_2$ in mormorilonite, CH_2Cl_2, CO/H_2, rt, 216 h	I + II (58), I:II = 17:83	752
C_{12} 	$(CH_2Cl)_2$, CO/H_2 (1/1, 0.5 MPa), 85°, 16 h		703

Catalyst	Conv. (%)	Yield
$Rh_2(\mu\text{-SBu-}t)_2(CO)_2(P(OMe)_3)_2$	35.5	(—)
$Rh_2(\mu\text{-SBu-}t)_2(CO)_2(P(OPh)_3)_2$	84.5	(—)
$Rh_2(\mu\text{-SBu-}t)_2(CO)_2(PPh_3)_2$	11	(—)
$Rh_2(\mu\text{-SPh})_2(CO)_2(P(OPh)_3)_2$	15.5	(—)

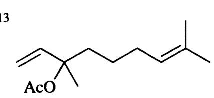
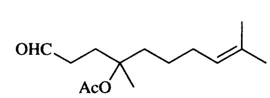
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	$Rh(COD)(\eta^6\text{-}PhBPh_3)$, DPPB, CH_2Cl_2, CO/H_2 (40 atm), 80°, 12 h	 (29)	267

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

B. Esters of Unsaturated Acids

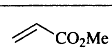
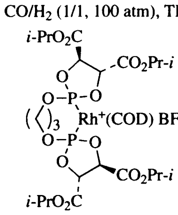
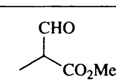
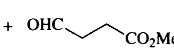
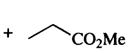
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h 	 I (—) +  II (—) I:II >99:1	248
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 60°, 22 h	I + II (—), I:II = 30:70	251
	[Rh(NBD)(2,5-bis(diphenylphosphino-methyl)bicyclo[2.2.1]heptane)ClO_4, CO/H_2 (1/1, 40 atm), C_6H_6, 40°, 38 h	I + II (—), I:II = 41:59	247
	$Rh(anthranilate)(CO)_2$, $P(OPh)_3$, P/Rh = 7.4, CO/H_2 (1/1, 1 atm), PhMe, 40°	II (23) +  III (15)	570
	$Co_2(CO)_8$, PhMe, CO/H_2 (1/1, 50 kg/cm^2), 120°, 132 min	I + II (77), I:II = 1:19.4	755
	$Co_2(CO)_8$, $Ph_2P(CH_2)_2PPh_2$, PhMe, CO/H_2 (1/1, 50 kg/cm^2), 120°, 35 min	I + II (84), I:II = 1:18.3	755

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

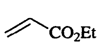
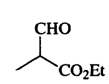
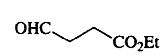
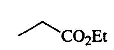
B. Esters of Unsaturated Acids (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 600 psi)), CH_2Cl_2, 80°, 18 h		756

Catalyst	Ligand	L/Rh	Conv. (%)	Yield (%) [GC (Isolated)]	I:II
Rh(COD)(η^6-$PhBPh_3$)	—	0	71	51 (35)	76:24
Rh(COD)(η^6-$PhBPh_3$)	DPPB	2	100	93 (68)	97: 3
Rh(COD)(η^6-$PhBPh_3$)	$P(OPh)_3$	4	96	90 (57)	98: 2
[Rh(COD)(DPPB)]BF_4	—	0	34	25 (18)	79:21
[Rh(COD)(DPPB)]BF_4	DPPB	2	100	89 (63)	99: 1
$[Rh(COD)Cl]_2$	—	0	16	5 (—)	75:25
$[Rh(COD)Cl]_2$	DPPB	1	33	25 (16)	91: 9
$[Rh(COD)Cl]_2$	DPPB	2	100	94 (71)	98: 2
$[Rh(COD)Cl]_2$	DPPB	3	100	94 (70)	99: 1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, ligand, H_2/CO (1/1, 50 bar), $PhMe/H_2O$		757

Ligand	L/Rh	$PhMe/H_2O$	Temp.	Time (h)	Conv. (%)	I + II	I:II	III
PNS	2	4	80°	4	100	(73)	1.8	(27)
PNS	2	2	80°	6	100	(77)	2.7	(23)
PNS	2	2	50°	21	81	(58)	14	(23)
TPPMS	4	2	50°	8	100	(83)	63	(17)
PNS	4	2	50°	21	100	(60)	22	(40)
PC	4	2	50°	21	100	(76)	22	(24)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, TPPMS, P/Rh = 4, 50°, $PhMe/H_2O$ = 2, CO/H_2 (1/1, 50 atm), 8 h	I + II (83) + III (17), I:II = 63	757
	$Rh(acac)(CO)_2$, PPh_3, P/Rh = 10, PhMe, CO/H_2 (1/1, 50 atm), 50°, 140 min	I + II (95), I:II >200	471
	$Rh(acac)(CO)_2$, TPPTS, P/Rh = 10, 120 min, $PhMe/H_2O$ = 4/3, CO/H_2 (1/1, 50 atm), 50°	I + II (97), I:II = 128	471
	$Rh(acac)(CO)_2$/TPPTS on 60Å silica gel, P/Rh = 10, PhMe, 24% wt H_2O, 50°, CO/H_2 (1/1, 50 atm), 60 min	I + II (97), I:II = 177	471
C_5 	Rh(COD)BPh_4, DPPB, L/Rh = 2, CH_2Cl_2, CO/H_2 (1/1, 600 psi), 80°, 12 h	 I +  II I + II (79) I:II = 98:2	325
	CO/H_2 (1/1), C_6H_6, 17 h	I + II +  III	758

Catalyst	Temp.	Pressure (atm)	I	II	III
$Rh(acac)(CO)_2/PMe_3$	40°	1	(0)	(0)	(7)
$Rh(acac)(CO)_2/P(OPh)_3$	40°	1	(21)	(58)	(20)
$Rh(acac)(CO)_2/P(OPh)_3$	60°	1	(1)	(52)	(47)
$Rh(acac)(CO)_2/P(OPh)_3$	80°	1	(0)	(28)	(38)
$Rh(acac)(CO)_2/P(OPh)_3$	40°	10	(82)	(7)	(3)
$Rh(acac)(CO)_2/P(OPh)_3$	40°	30	(96)	(1)	(1)
$Rh(acac)(CO)_2/P(OC_6H_4Me\text{-}4)_3$	40°	1	(27)	(46)	(23)
$Rh(acac)(CO)_2/P(OC_6H_4Cl\text{-}4)_3$	40°	1	(17)	(37)	(10)
$Rh(acac)(CO)_2/P(OC_6H_4Me\text{-}2)_3$	40°	1	(4)	(2)	(4)
$Rh(acac)(CO)_2/P(OPr\text{-}i)_3$	40°	1	(8)	(tr)	(88)
$Rh(acac)(CO)_2/P(OMe)_3$	40°	1	(16)	(tr)	(11)
$Rh(acac)(P(OPh)_3)_2/P(OPh)_3$	40°	1	(14)	(75)	(11)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, PPh_3, P/Rh = 10, PhMe, CO/H_2 (1/1, 50 atm), 50°, 165 min	I + II (94), I:II = 137	471
	$Rh(acac)(CO)_2$, TPPTS, P/Rh = 10, $PhMe/H_2O$ = 4/3, CO/H_2 (1/1, 50 atm), 30 min, 50°	I + II (97), I:II = 121	471
	$[Rh(CO)_2Cl]_2$, 10 Ligand, Et_3N, PhMe, CO/H_2 (1/1, 20 bar), 25°, 12 h		514, 319

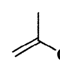
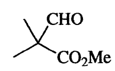
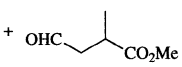
Ligand	I	I:II
DPPB	(56)	100:0
o-TDPP	(57)	100:0
PPPN	(71)	100:0
DMTPPN	(70)	100:0

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

B. Esters of Unsaturated Acids (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$/TPPTS on 60Å silica gel, P/Rh = 10, PhMe, 37% wt H_2O, 50°, CO/H_2 (1/1, 50 atm), 25 min	**I** + **II** (97), **I**:**II** = 115	471
	[RhCl(CO)$_2$]$_2$, P/Rh = 4, PhEt, 150°, CO/H_2 (1/1, 100 atm)		759

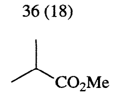
Phosphine	Time (min)	Conv. (%)	I : II : III
none	36	6	28.6 : 66.7 : 4.8
PPh$_3$	180	27	71.5 : 27.0 : 1.5
Ph$_2$P(CH$_2$)$_2$PPh$_2$	42	100	64.2 : 2.6 : 32.0
Ph$_2$P(CH$_2$)$_3$PPh$_2$	22	100	72.3 : 2.9 : 24.8
Ph$_2$P(CH$_2$)$_4$PPh$_2$	5	100	85.4 : 2.3 : 12.3
Ph$_2$P(CH$_2$)$_5$PPh$_2$	550	100	49.9 : 17.0 : 33.1
Cy$_2$P(CH$_2$)$_2$PCy$_2$	7	100	79.9 : 3.8 : 16.3
Cy$_2$P(CH$_2$)$_4$PCy$_2$	12	100	67.2 : 1.1 : 31.7
DBP-(CH$_2$)$_2$-DBP	76	100	32.1 : 17.3 : 50.5

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(COD)BPh$_4$, CO/H_2 (1/2, 300 psi), CHCl$_3$, 60°, 22 h	 **I** +  **II** **I** + **II** (—) **I**:**II** = 45:55	251
	Rh(COD)BPh$_4$, DPPB, L/Rh = 2, CH$_2$Cl$_2$, CO/H_2 (1/1, 600 psi), 130°, 24 h	**I** + **II** (75), **I**:**II** = 96:4	325
	[Rh(NBD)Cl]$_2$/PPh$_3$/Et$_3$N (1/2/15), C$_6$H$_6$, CO/H_2 (1/1, 80 bar), 100°, 3 h	**I** + **II** (—), **I**:**II** = 93:7	760
	[Rh(NBD)Cl]$_2$/PBu$_3$ (1/2), C$_6$H$_6$, CO/H_2 (1/1, 15 bar), 100°, 3 h	**I** + **II** (—), **I**:**II** = 18:82	760
	Styrene-divinylbenzene (1%) resin-(C$_6$H$_4$PPh$_2$)$_3$RhH(CO), P/Rh = 20, 80°, CO/H_2 (1/1, 400 psi), C$_6$H$_6$, 21-24 h	**I** + **II** (65), **I**:**II** = 95:5	761
	CO/H_2 (1/1, 600 psi)), CH$_2$Cl$_2$, 100°, 18 h		756

Catalyst	Ligand	L/Rh	Conv. (%)	Yield (%) [GC (Isolated)]	I:II
Rh(COD)(η[6]-PhBPh$_3$)	—	0	98	96 (78)	20:80
Rh(COD)(η[6]-PhBPh$_3$)	DPPB	2	72	72 (54)	91:9
[Rh(COD)(DPPB)]BF$_4$	—	0	29	24 (22)	16:84
[Rh(COD)(DPPB)]BF$_4$	DPPB	2	no reaction	0 (0)	—
[Rh(COD)Cl]$_2$	—	0	100	53 (47)	16:84
[Rh(COD)Cl]$_2$	DPPB	2	no reaction	0 (0)	—

Rh(COD)(η[6]-PhBPh$_3$), CO/H_2 (1/1), CH$_2$Cl$_2$ — 756

Pressure (psi)	Temp.	Time (h)	Conv. (%)	Yield (%) [GC (Isolated)]	I:II
600	50°	66	83	76 (67)	70:30
600	60°	64	86	84 (71)	53:47
600	84°	18	93	90 (73)	25:75
600	100°	18	98	96 (78)	20:80
600	130°	18	100	94 (77)	6:90
200	130°	18	39	36 (18)	3:97

[RhCl(CO)$_2$]$_2$, P/Rh = 4, C$_6$H$_6$, 150°, CO/H_2 (1/1, 100 atm) — **I** + **II** +  **III** — 759

Phosphine	Time (min)	Conv. (%)	I : II : III
none	16	100	7.2 : 73.4 : 19.6
PPh$_3$	200	100	38.5 : 56.1 : 5.4
Ph$_2$P(CH$_2$)$_2$PPh$_2$	105	100	79.5 : 17.6 : 2.9
Ph$_2$P(CH$_2$)$_3$PPh$_2$	250	51	45.9 : 17.5 : 36.6
Ph$_2$P(CH$_2$)$_4$PPh$_2$	360	92	75.5 : 19.2 : 5.3
Ph$_2$P(CH$_2$)$_5$PPh$_2$	420	98	14.7 : 74.3 : 11.0
Cy$_2$P(CH$_2$)$_2$PCy$_2$	450	98	50.2 : 44.7 : 5.1
Cy$_2$P(CH$_2$)$_4$PCy$_2$	280	98	54.9 : 40.5 : 4.7

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh$_4$(CO)$_{12}$, CO/H_2 (1/1, 110 atm), PhMe, 120°, 78 h	**I** (97) + **II** (tr) + **III** (3)	762

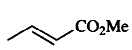
TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

B. Esters of Unsaturated Acids (*Continued*)

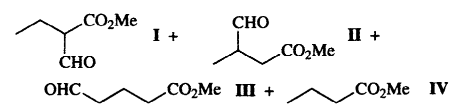
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, PPh_3, CO/H_2 (1/1), C_6H_6		761

P/Rh	Pressure (psi)	Temp.	Time (h)	Conv. (%)	I:II
3	50	80°	22	63	25:75
3	200	80°	18	82	57:43
3	800	80°	8	100	94:6
3	800	30°	91	86	99:1
3	800	150°	6	69	16:84
3	100	80°	5	57	31:69
6	100	80°	24	90	46:54
20	100	80°	23	87	70:30
40	100	80°	22	64	66:34
20	200	150°	18	56	2:98

172

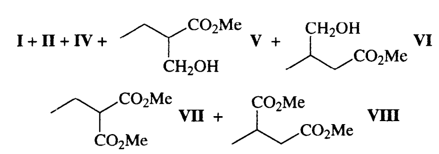


$[RhCl(CO)_2]_2$, P/Rh = 4, C_6H_6, 150°, CO/H_2 (1/1, 100 atm) — Ref. 759



Phosphine	Time (min)	Conv. (%)	I : II : III : IV
none	160	100	0.0 : 51.7 : 30.0 : 18.0
PPh_3	210	100	17.2 : 52.6 : 12.6 : 17.6
$Ph_2P(CH_2)_2PPh_2$	150	100	22.9 : 2.0 : 0.0 : 75.1
$Ph_2P(CH_2)_3PPh_2$	210	93	8.8 : 4.6 : 0.0 : 86.6
$Ph_2P(CH_2)_4PPh_2$	240	92	80.1 : 5.2 : 0.0 : 14.7
$Ph_2P(CH_2)_5PPh_2$	360	94	3.6 : 40.6 : 27.9 : 28.0
$Cy_2P(CH_2)_2PCy_2$	360	71	43.5 : 2.6 : 0.1 : 53.8
$Cy_2P(CH_2)_4PCy_2$	210	40	41.4 : 28.2 : 4.7 : 25.7

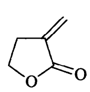
$RhH_2(O_2COH)[P(Pr\text{-}i)_3]_2$, $(CH_2O)_n$, THF, 120°, 20 h — Ref. 593



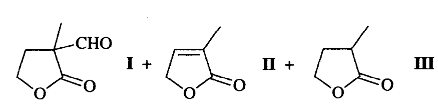
I + II (19), I:II = 48:52; IV (49); V + VI (5); VII + VIII (17), VII:VIII = 43:57

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, PPh_3, P/Rh = 10, PhMe, CO/H_2 (1/1, 50 atm), 50°, 360 min	I + II (44), I:II = 77	471
	$Rh(acac)(CO)_2$, TPPTS, P/Rh = 10, 720 min, $PhMe/H_2O$ = 4/3, CO/H_2 (1/1, 50 atm), 50°	I + II (81), I:II >200	471
	$Rh(acac)(CO)_2$/TPPTS on 60Å silica gel, P/Rh = 10, PhMe, 24% wt H_2O, 50°, CO/H_2 (1/1, 50 atm), 60 min	I + II (96), I:II >200	471

173



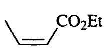
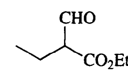
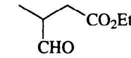
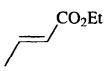
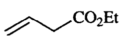
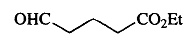
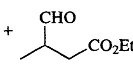
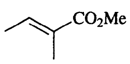
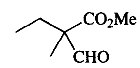
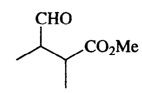
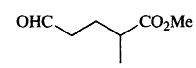
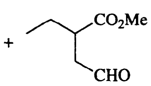
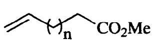
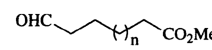
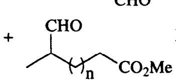
CO/H_2 (1/1, 600 psi), CH_2Cl_2 — Ref. 756



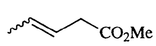
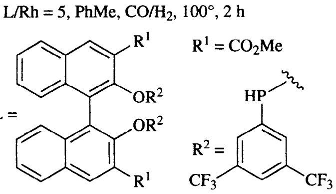
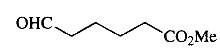
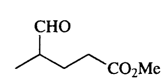
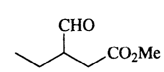
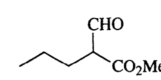
Catalyst	Temp.	Time (h)	Conv. (%)	I : II : III	I
$Rh(COD)(\eta^6\text{-}PhBPh_3)$	60°	24	100	0 : 94 : 6	(0)
$Rh(COD)(\eta^6\text{-}PhBPh_3)$ + DPPB (2)	60°	24	90	92 : 5 : 3	(—)
$Rh(COD)(\eta^6\text{-}PhBPh_3)$	100°	18	100	0 : 89 : 11	(0)
$Rh(COD)(\eta^6\text{-}PhBPh_3)$ + DPPB (2)	100°	18	100	82 : 11 : 7	(69)
$Rh(COD)(\eta^6\text{-}PhBPh_3)$ + DPPB (4)	100°	18	100	80 : 10 : 10	(—)
$Rh(COD)(\eta^6\text{-}PhBPh_3)$	130°	24	100	0 : 61 : 39	(0)
$Rh(COD)(\eta^6\text{-}PhBPh_3)$ + DPPB (4)	130°	24	100	67 : 9 : 24	(49)
$[Rh(COD)(DPPB)]BF_4$	100°	18	100	0 : 86 : 14	(0)
$[Rh(COD)(DPPB)]BF_4$ + DPPB (2)	100°	18	100	81 : 13 : 6	(70)
$[Rh(COD)Cl]_2$	100°	18	100	0 : 96 : 4	(0)
$[Rh(COD)Cl]_2$ + DPPB (2)	100°	18	100	81 : 14 : 5	(67)

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

B. Esters of Unsaturated Acids (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(COD)BPh$_4$, DPPB, L/Rh = 2, CH_2Cl_2, CO/H$_2$ (1/1, 600 psi), 130°, 24 h	I (56)	325
C$_6$ 	Rh(COD)BPh$_4$, DPPB, L/Rh = 2, CH_2Cl_2, CO/H$_2$ (1/1, 600 psi), 130°, 12 h	 I +  II; I + II (60), I:II = 99:1	325
	Rh(COD)BPh$_4$, DPPB, L/Rh = 2, CH_2Cl_2, CO/H$_2$ (1/1, 600 psi), 130°, 12 h	I + II (68), I:II = 98:2	325
	PtCl$_2$(PPh$_3$)$_2$/SnCl$_2$ (1/5), MEK, 70°, 4 h, CO/H$_2$ (1/1, 10 MPa)	 I +  II; I + II (96), I:II = 80:20	763
	[RhCl(CO)$_2$]$_2$, Ph$_2$P(CH$_2$)$_2$PPh$_2$, P/Rh = 4, CO/H$_2$ (1/1, 100 atm), 150°, 24 h	 major +  (—) +  (—) +  (19)	759
	Rh$_4$(CO)$_{12}$, TPPTSNa, P/Rh = 60, H$_2$/CO (1/1, 100 bar), 120°, pH = 7	 I +  II	764

n	Time (h)	Conv. (%)	I	II	I:II	Internal alkenes
1	27	22	(19)	(3)	85:15	(—)
2	21	99	(89)	(9)	91:9	(1)
6	13	92	(85)	(7)	93:7	(—)
7	3	86	(71)	(12)	86:14	(2)
10	4	82	(58)	(13)	82:18	(10)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(CO)$_2$(*t*-BuCOCH=CHCOBu-*t*), L, L/Rh = 5, PhMe, CO/H$_2$, 100°, 2 h; L =  R^1 = CO$_2$Me	 I (—); I : (I + other aldehydes) = 0.97; I : (all products) = 0.64	765
	PtCl$_2$(sixantphos), SnCl$_2$, Sn:Pt = 1, CO/H$_2$ (1:1), CH_2Cl_2	I +  II +  III +  IV	766

P/Pt	P (bar)	temp	I : (II+III+IV)	Hydrogenation (%)	Byproducts (%)
1	50	100°	2.7	1	(4)
1	10	100°	10.5	10	(1)
1	10	80°	11.1	2	(tr)
1	10	120°	8.8	23	(1)
8	10	80°	18.0	2	(1)

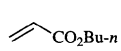
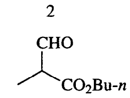
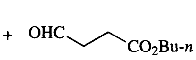
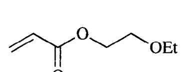
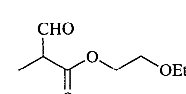
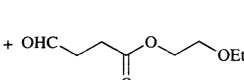
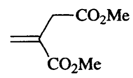
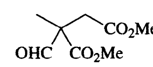
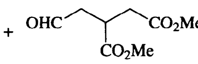
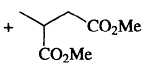
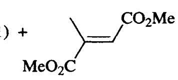
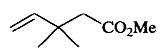
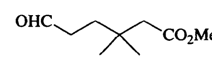
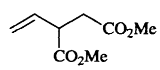
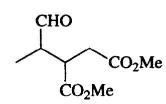
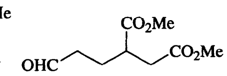
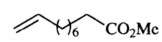
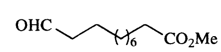
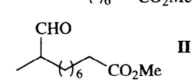
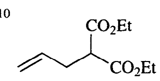
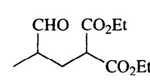
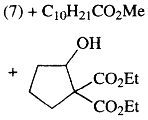
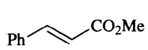
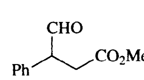
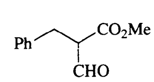
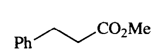
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_7$ 	Rh(acac)(CO)$_2$, PPh$_3$, P/Rh = 10, PhMe, CO/H$_2$ (1/1, 50 atm), 50°, 150 min	 I +  II; I + II (96), I:II = 140	471
	Rh(acac)(CO)$_2$, TPPTS, P/Rh = 10, 90 min, PhMe/H$_2$O = 4/3, CO/H$_2$ (1/1, 50 atm), 50°	I + II (98), I:II = 123	471
	Rh(acac)(CO)$_2$/TPPTS on 60Å silica gel, P/Rh = 10, PhMe, 37% wt H$_2$O, 50°, CO/H$_2$ (1/1, 50 atm), 120 min	I + II (98), I:II = 121	471
	Rh(acac)(CO)$_2$, PPh$_3$, P/Rh = 10, PhMe, CO/H$_2$ (1/1, 50 atm), 50°, 240 min	 I +  II; I + II (87), I:II = 62	471

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

B. Esters of Unsaturated Acids (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)$(CO)_2$, TPPTS, P/Rh = 10, 40 min, $PhMe/H_2O$ = 4/3, CO/H_2 (1/1, 50 atm), 50°	I + II (94), I:II = 72	471
	Rh(acac)$(CO)_2$/TPPTS on 60Å silica gel, P/Rh = 10, PhMe, 37% wt H_2O, 50°, CO/H_2 (1/1, 50 atm), 40 min	I + II (97), I:II = 103	471
	$RhH(CO)(PPh_3)_3$, PhMe, 100°, 8 h, CO/H_2 (1/1, 80 bar)	 I (37) +  II (8) +  III (41) +  IV (9)	767
	$Rh_4(CO)_{12}$, PhMe, 100°, 17 h, CO/H_2 (1/1, 80 bar)	I (8) + II (34) + III (58)	767
	$Rh_4(CO)_{12}$, PPh_3, L/Rh = 4, PhMe, 100°, 7 h, CO/H_2 (1/1, 80 bar)	I (42) + II (9) + III (45) + IV (4)	767
C_8			
	Rh-PEVV, CO/H_2 (1/1, 41.4 atm), H_2O, 100°, 2 h	 (21)	242
	Rh(aca)$(CO)_2$, PhMe, H_2/CO (100 atm), 8 h, tris(2,4-di-*tert*-butylphenyl) phosphite	 I (74) +  II (26)	768
	$Rh_4(CO)_{12}$, TPPTSNa, P/Rh = 60, H_2O $C_7H_{15}SO_3Na$, H_2/CO (1/1, 100 bar), 120°, pH = 7, 10 h	 I (80) +  II (6) I:II = 93:7 + internal alkenes (7) + $C_{10}H_{21}CO_2Me$ (2)	764
C_{10}			
	1. $RhH(CO)(PPh_3)_3$, C_6H_6, rt, 10 h, CO/H_2 (1/2, 1 atm) 2. Silica	 I +  II; I + II (87) I:II = 28:66	369
	CO/H_2 (1/1, 100 atm), C_6H_6	 I +  II +  III	769

Catalyst	Temp.	Time (h)	I:II	I + II	III
Rh_2O_3	120°	7	100:0	(69)	(31)
$RhH(CO)(PPh_3)_3$	80°	7	72:28	(58)	(12)
$[Rh(COD)Cl]_2$	80°	7	100:0	(40)	(20)
$Rh(COD)(BPh_4)$	80°	22	94:6	(79)	(16)
$[Rh(CO)_2Cl]_2$	80°	16	95:5	(52)	(18)
$RhH(PPh_3)_4$	80°	7	91:9	(57)	(11)
$RhCl(CO)(PPh_3)_2$	100°	7	62:38	(32)	(14)

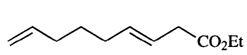
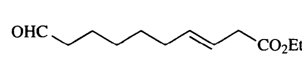
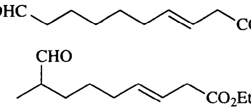
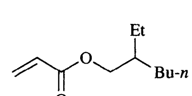
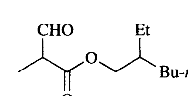
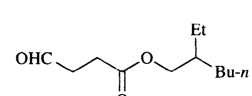
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	$RhH(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/2, 1 atm), rt, 4 d	 (61) +  (—)	369
	Rh(acac)$(CO)_2$, PPh_3, P/Rh = 10, PhMe, CO/H_2 (1/1, 50 atm), 50°, 150 min	 I +  II; I + II (93), I:II = 63	471

TABLE V. HYDROFORMYLATION OF UNSATURATED ESTERS (*Continued*)

B. Esters of Unsaturated Acids (*Continued*)

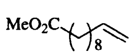
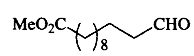
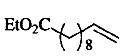
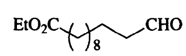
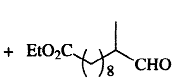
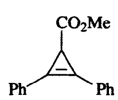
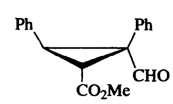
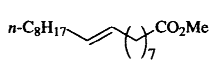
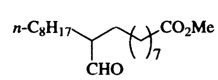
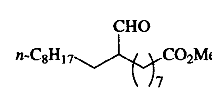
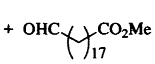
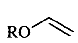
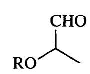
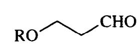
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, TPPTS, P/Rh = 10, 20 h, PhMe/H$_2$O = 4/3, CO/H$_2$ (1/1, 50 atm), 50°	I + II (97), I:II = 59	471
	Rh(acac)(CO)$_2$/TPPTS on 60Å silica gel, P/Rh = 10, PhMe, 37% wt H$_2$O, 50°, CO/H$_2$ (1/1, 50 atm), 20 h	I + II (93), I:II = 79	471
C$_{12}$ 	Rh(CO)$_2$(acac), BIPHEPHOS, THF, CO/H$_2$ (1/1, 70 psi), 60°	 (91) *n:iso* > 40:1	135
C$_{13}$ 	Rh$_2$H$_2$(CO)$_2$[Ph$_2$P(O(CH$_2$)$_2$)$_{400}$OPPh$_2$]$_3$-poly(2-hydroxyethylmethacrylate) network coating on porous silica, c-C$_6$H$_{12}$, CO/H$_2$ (1/1, 800 psi), 85°, 4 h	 I +  II I + II (42), I:II = 2:1	770
	RhCl(CO)(DPM)$_2$-poly(vinylbenzyltriethylammonium chloride) on silica, c-C$_6$H$_{12}$, H$_2$O, EtOH, 85°, CO/H$_2$ (1/1, 750 psi), 15 h	I + II (42), I:II = 8:1	655
C$_{17}$ 	HCo(CO)$_4$, CO (1 atm), hexane, rt, 1.5 h	 (18-22)	771, 772
C$_{19}$ 	Co$_2$(CO)$_8$, CO/H$_2$ (3500-4500 psi), 100-150°	 I + I + II (50-90)  II +  (4-16)	773-775
	Rh/C, PPh$_3$, PhMe, 100-110°, 4-6 h, CO/H$_2$ (1/1, 1000-2000 psi)	I + II (90-99)	775, 773

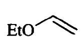
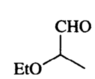
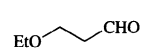
TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	$Rh_4(CO)_{12}$, C_6H_6, CO/H_2 (1/1, 100 atm), 100°	 **I** (—) +  **II** (—)	332

R	I:II
Me	78:22
Et	76:24
n-Bu	76:24
i-Pr	72:28
t-Bu	63:37
$PhCH_2$	76:24
Ph	95:5

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(CO)_2Cl]_2/PPh_3$ (1/6), C_6H_6, 100°, CO/H_2 (1/1, 100 atm)	**I** (—) + **II** (—)	332

R	I:II
Me	54:46
Et	54:46
n-Bu	53:47
i-Pr	52:48
t-Bu	53:47
$PhCH_2$	67:33
Ph	95:5

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 100 atm)	 **I** +  **II**	332

Temp.	Time (h)	I + II	I:II
100°	0.5	(97)	76:24
80°	0.8	(96)	77:23
50°	4.0	(90)	78:22
20°	15.0	(50)	82:18

TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS (*Continued*)

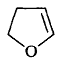
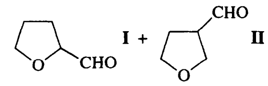
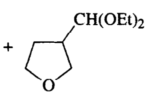
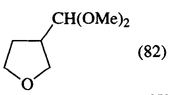
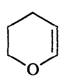
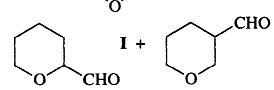
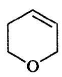
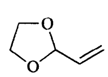
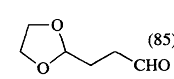
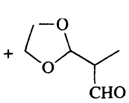
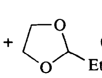
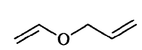
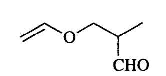
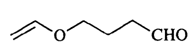
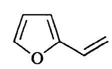
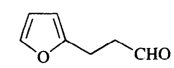
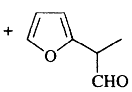
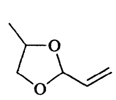
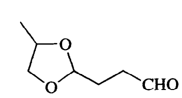
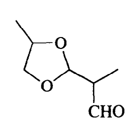
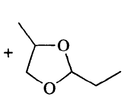
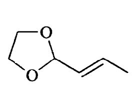
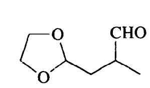
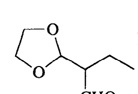
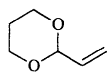
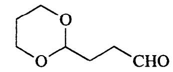
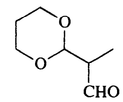
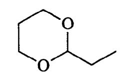
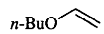
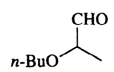
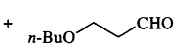
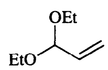
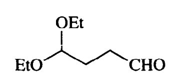
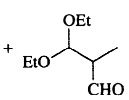
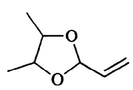
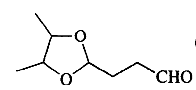
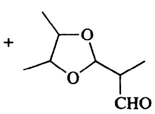
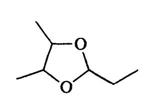
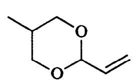
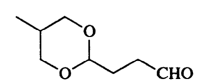
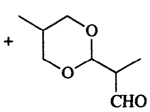
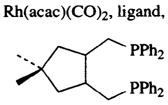
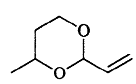
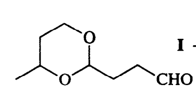
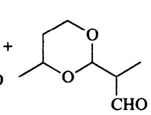
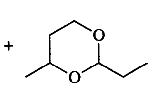
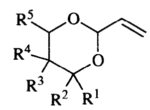
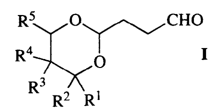
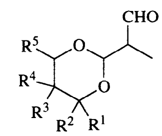
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2$, CH_2Cl_2, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, L/Rh = 20, 80°, CO/H_2 (1/1, 5 bar), 20 h	 I + II (100) I:II = 77:23	333
	$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2$, CH_2Cl_2, $P(OPh)_3$, L/Rh = 2, CO/H_2 (1/1, 5 bar), 80°, 20 h	I + II (99), I:II = 49:51	333
	$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2$, CH_2Cl_2, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, L/Rh = 2, 80°, CO/H_2 (1/1, 5 bar), 20 h	I + II (98), I:II = 69:31	333
	$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2$ (1 mol%), PPh_3, L/Rh = 10, CO/H_2 (1/1, 30 bar), $(CH_2Cl)_2$, 80°, 8 h	I + II (99), I:II = 1:99	333, 334
	$Rh_2(\mu\text{-}OMe)_2(COD)_2$, 10 PPh_3, CO/H_2 (1/1, 50 bar), $HC(OEt)_3$, 60°, 48 h	II (96) +  III (4)	663
	$Rh_2(\mu\text{-}OMe)_2(COD)_2$, 10 PPh_3, 60°, CO/H_2 (1/1, 50 bar), $(MeO)_2CMe_2$, 48 h	II (100)	663
	$Rh_2(\mu\text{-}OMe)_2(COD)_2$, 10 PPh_3, $HC(OEt)_3$, PPTS, CO/H_2 (1/1, 50 bar), 60°, 4 h	II (8) + III (92)	663
	$Rh_2(\mu\text{-}OMe)_2(COD)_2$, 10 PPh_3, PPTS, 60°, CO/H_2 (1/1, 50 bar), $(MeO)_2CMe_2$, 24 h	II (18) +  (82)	663
	$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2$, 120°, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, L/Rh = 10, 8 h, CO/H_2 (1/1, 75 bar)	 I + II (83) I:II = 67:33	333
	$Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2$, 120°, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, L/Rh = 10, 8 h, CO/H_2 (1/2, 75 bar)	I + II (81), I:II = 68:32	333
	$RhH(CO)(PPh_3)_3$, $P(OPh)_3$, L/Rh = 50, CO/H_2 (1/1, 3 bar), 100°	 (85) +  (10) +  (5)	776
	$[Rh(COD)(OAc)]_2$, CO/H_2	 I +  II I + II (57-80), I:II = 81:19	316
C_6			
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(PPh_3)_2$, PPh_3, L/Rh = 10, PhMe, CO/H_2 (5 bar), 80°	 I +  II I + II (99) I:II = 14:86	647
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2[P(OMe)_3]_2$, $ClCH_2CH_2Cl$, CO/H_2 (5 bar), 80°	I + II (59), I:II = 52:48	647
	$RhH(CO)(PPh_3)_3$, PPh_3, L/Rh = 5, PhMe, CO/H_2 (5 bar), 80°, 2 h	I + II (99), I:II = 26:74	647
	$[Rh(COD)(TPPTS)_2]ClO_4$, H_2O, 80°, CO/H_2 (1/1, 5 bar), 18 h	I + II (99), I:II = 36:64	647
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(TPPTS)_2$, H_2O, 80°, CO (5 bar), 18 h	I + II (62), I:II = 56:44	647
	$Rh_6(CO)_{16}$, $P(OMe)_3$, 110°, CO/H_2 (1/1, 6.5 atm)	 I +  II I + II (88) I:II = 81:19	373, 777
	$RhH(CO)(PPh_3)_3$, $P(OPh)_3$, L/Rh = 50, CO/H_2 (1/1, 3 bar), 100°	I (85) + II (9) +  (6)	776
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 80°, CO/H_2 (1/1, 100 atm), 3 h	 I +  II I + II (90) I:II = 70:30	373

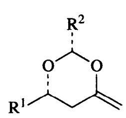
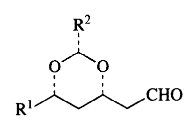
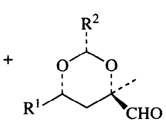
TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, $P(OPh)_3$, L/Rh = 50, CO/H_2 (1/1, 3 bar), 100°	 (85) +  (10) +  (5)	776
	$[Rh(COD)(OAc)]_2$, CO/H_2	 **I** +  **II** **I** + **II** (57-80) **I**:**II** = 72:28	316
C_7 	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 **I** +  **II** **I** + **II** (80) **I**:**II** = 10:1	135
	Rh_2O_3, C_6H_6, CO/H_2 (1/1, 200 atm), 110°, 30 min	**I** + **II** (63), **I**:**II** = 1:1.82	373, 778
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 80°, CO/H_2 (1/1, 100 atm), 1.5 h	**I** + **II** (98), **I**:**II** = 58:42	373, 779
	$RhH(CO)(PPh_3)_3$, $P(OPh)_3$, L/Rh = 50, CO/H_2 (1/1, 3 bar), 100°	 (86) +  (8) +  (6)	776
	$Rh_6(CO)_{16}$, $P(OMe)_3$, 110°, CO/H_2 (1/1, 7.1 atm)	 **I** +  **II** **I** + **II** (92) **I**:**II** = 87:13	373, 780, 781
	$Rh(acac)(CO)_2$, ligand, CO/H_2 	**I** (99)	782
	$Rh_6(CO)_{16}$, $P(OPh)_3$, 90°, CO/H_2 (1/1, 2.7 atm)	 **I** +  **II** **I** + **II** (95) **I**:**II** = 95.5:4.5	373, 783
	$RhH(CO)(PPh_3)_3$, $P(OPh)_3$, L/Rh = 50, CO/H_2 (1/1, 3 bar), 100°	**I** (82) + **II** (12) +  (6)	776
	$Rh(acac)(CO)_2$, PR_3, P/Rh = 50, 100°, CO/H_2 (1/1, 1 MPa), 4 h		784

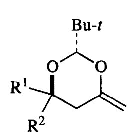
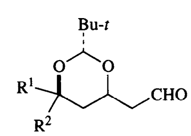
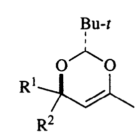
R	Conv. (%)	I:II
$3,5\text{-}F_2C_6H_3$	32.6	85:15
$3,5\text{-}Cl_2C_6H_3$	31.8	83:17
$4\text{-}CF_3C_6H_4$	25.6	81:19
$3\text{-}CF_3C_6H_4$	29.4	80:20
$3\text{-}ClC_6H_4$	33.7	80:20
$2\text{-}MeC_6H_4$	3.3	78:22
$3\text{-}FC_6H_4$	73.0	77:23
$4\text{-}ClC_6H_4$	81.9	74:26
$3,4\text{-}F_2C_6H_3$	23.0	73:27
$2\text{-}Me\text{-}4\text{-}ClC_6H_3$	3.6	71:29
$2\text{-}ClC_6H_4$	12.1	65:35
C_6H_5	23.7	62:38
$4\text{-}FC_6H_4$	35.4	62:38
$3\text{-}MeC_6H_4$	34.5	57:43

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, PR$_3$, 100°, CO/H$_2$ (1/1, 1MPa), 4 h	 I +  II	784

R[1]	R[2]	R[3]	R[4]	R[5]	R	Conv. (%)	I:II
H	H	H	Me	H	C_6H_5	43.5	56:44
H	H	H	Me	H	4-ClC_6H_4	46.4	68:32
H	H	H	Me	H	3-$CF_3C_6H_4$	45.1	79:21
H	H	H	Me	H	3,5-$Cl_2C_6H_3$	52.0	83:17
H	H	Me	Me	H	C_6H_5	64.1	56:44
H	H	Me	Me	H	4-ClC_6H_4	94.2	65:35
H	H	Me	Me	H	3-$CF_3C_6H_4$	59.7	75:25
Me	H	H	H	H	C_6H_5	23.7	62:38
Me	H	H	H	H	4-ClC_6H_4	81.9	74:26
Me	H	H	H	H	3-$CF_3C_6H_4$	29.4	80:20
Me	H	H	H	H	3,5-$Cl_2C_6H_3$	31.8	83:17
Me	Me	H	H	H	C_6H_5	64.4	63:37
Me	Me	H	H	H	4-ClC_6H_4	57.2	70:30
Me	Me	H	H	H	3-$CF_3C_6H_4$	44.6	75:25
Me	Me	H	H	Me	C_6H_5	64.9	73:27
Me	Me	H	H	Me	4-ClC_6H_4	92.6	77:23
Me	Me	H	H	Me	3-$CF_3C_6H_4$	75.0	85:15
Me	Me	H	H	Me	3,5-$Cl_2C_6H_3$	99.8	89:11

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, Ligand, P/Rh = 4, THF, H_2/CO (1/1, 800 psi)	 I +  II	785

R[1]	R[2]	Ligand	Temp.	Time (h)	Conv. (%)	I	I:II
H	*t*-Bu	PPh_3	75°	—	—	(81)	12:1
Me	*t*-Bu	PPh_3	75°	—	—	(72)	13:1
Me	Me	PPh_3	75°	—	—	(80)	14:1
i-Pr	*t*-Bu	PPh_3	85°	16	100	(60)	12:1
$(CH_2)_2$OBn	Me	P(OC_6H_4Bu-*t*-2)$_3$	75°	—	—	(71)	9:1
$(CH_2)_5$CH=CMe_2	Me	PPh_3	75°	—	—	(71)	11:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, Ligand, CO/H_2 (1/1, 800 psi), THF, 120°	 I +  II	786

R[1]	R[2]	Ligand	I	II	I (diastereoisomer ratio)
H	Me	PPh_3	(36)	(40)	7:1
H	Me	PCy_3	(68)	(20)	5:1
H	Bu	PCy_3	(37)	(—)	5:1
Me	Bu	PCy_3	(73)	(—)	10:1

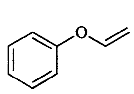
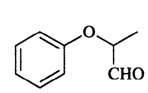
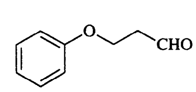
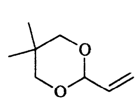
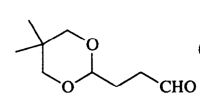
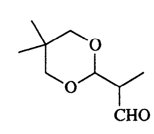
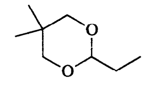
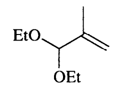
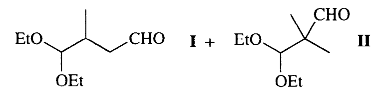
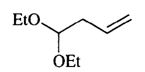
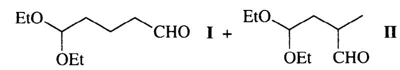
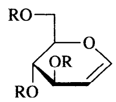
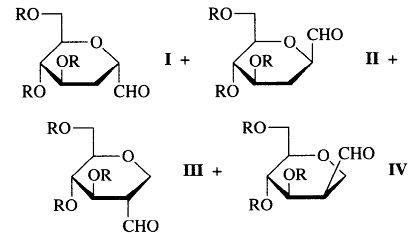
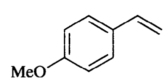
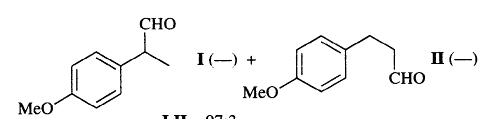
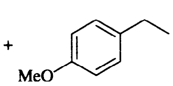
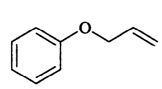
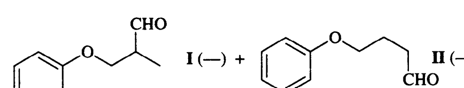
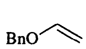
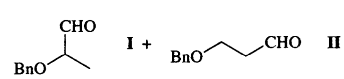
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	Rh(COD)BPh_4, CO/H_2 (1/2, 300 psi), $CHCl_3$, 60°, 22 h	 I (—) +  II (—) I:II = 97:3	251
	[Rh(COD)Cl]$_2$, CO/H_2 (1/1, 160 atm), C_6H_6, 100°, 10 h	II (83)	787, 699
	RhH(CO)(PPh_3)$_3$, P(OPh)$_3$, L/Rh = 50, CO/H_2 (1/1, 3 bar), 100°	 (84) +  (8) +  (8)	776

TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 80°, CO/H_2 (1/1, 100 atm), 2 h	 I + II (76) I:II = 98:2	373, 779
	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 I + II (75), I:II > 40:1	135
	Rh_2O_3, CO/H_2 (1/1, 110 atm), 100°	I + II (70), I:II = 44:56	373
	$Rh_2[\mu\text{-}S(CH_2)_3NMe_2]_2(COD)_2$, $(CH_2Cl)_2$, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, 120°, 24 h, CO/H_2 (1/1, 75 x 10^5 Pa)		335

R	Conv. (%)	I	II	III	IV
Me	94	(—)	(—)	(64)	(—)
TBDMS	35	(14)	(8)	(13)	(—)
Bn	88	(11)	(—)	(63)	(4)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	 I:II = 97:3	251
	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	I + II (76), I:II = 75:25	368
	$RhH_2(O_2COH)[P(Pr\text{-}i)_3]_2$, CO (15 atm), H_2O, THF, 115°, 20 h	I (30) + II (44) +  (18)	577
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 21 h	 I:II = 62:38	251
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 100 atm)		332

Temp.	Time (h)	I + II	I:II
100°	0.7	(97)	76:24
80°	1.0	(97)	79:21
50°	4.5	(97)	84:16
20°	15.0	(50)	88:12

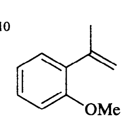
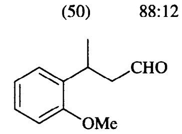
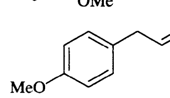
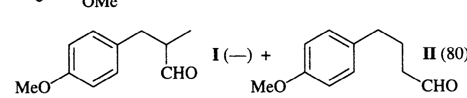
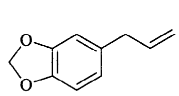
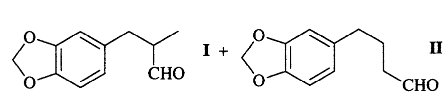
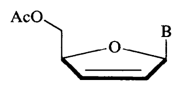
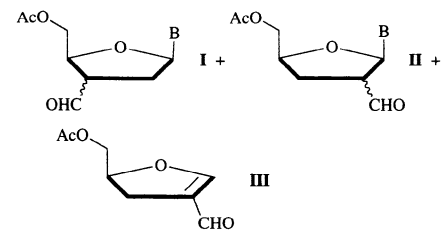
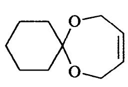
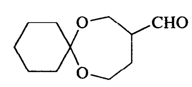
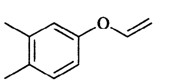
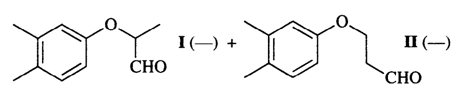
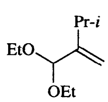
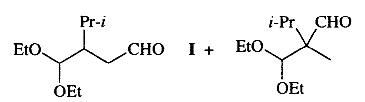
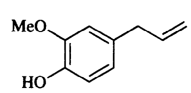
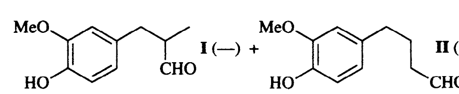
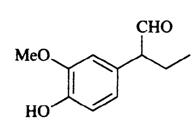
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 80°, 22 h	 (—) + starting material (27)	251
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2[P(OPh)_3]_2$, DMF, CO/H_2 (1/1, 5 bar), 80°, 90 min	 I (—) + II (80)	788
	$[Rh(COD)(OAc)]_2$, CO/H_2	I + II (57-80), I:II = 48:52	316
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(TPPTS)_2$, TPPTS, L/Rh = 4, CO/H_2 (1/1, 5 bar), H_2O, 80°, 18 h	I + II (21), I:II = 18:82	23
	$Rh_2(\mu\text{-}SBu\text{-}t)_2(CO)_2(TPPTS)_2$, TPPTS, L/Rh = 4, CO/H_2 (1/1, 5 bar), H_2O, 80°, 18 h	 I + II (16), I:II = 4:96	23

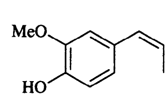
TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2(\mu\text{-SBu-}t)_2(CO)_2[P(OPh)_3]_2$, DMF, CO/H_2 (1/1, 5 bar), 80°, 90 min	I (—) + II (88)	788
	[Rh], CO/H (1/1, 5 atm), THF, 60°	 I + II + III	789

B	[Rh]	I	I:II	II + III
uracil	$RhCl(PPh_3)_3$	(<5)	—	(10)
uracil	Rh_2O_3	(12)	1:1	(—)
uracil	$Rh(acac)(CO)_2/4PPh_3$	(27)	3:1	(—)
cytocine	$Rh(acac)(CO)_2/4PPh_3$	(32)	3:1	(—)
N^4-acetylcytosine	$Rh(acac)(CO)_2/4PPh_3$	(32)	3:1	(—)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(TPP)_3$, CO/H_2 (130 bar), 100°, 4 h	 (93)	790
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 60°, 21 h	 I (—) + II (—) I:II = 90:10	251
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 105°, CO/H_2 (1/1, 100 atm), 5.5 h	 I + II I + II (75) I:II = 98:2	373, 779
	Rh/C (5%), $P(OPh)_3$, Et_3N, C_6H_6, 110°, CO/H_2 (1/1, 20 atm), 73 h	I + II (60), I:II = 98:2	373, 779
	$Rh_2(\mu\text{-SBu-}t)_2(CO)_2[P(OMe)_3]_2$, 80°, CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 90 min	 I (—) + II (96)	788
	$[RhCl(COD)]_2$, CO/H_2 (1/1, 600 bar)	I + II +  III	699, 791

Temp.	I : II : III
70°	48:52:0
80°	45:52:3
100°	37:52:11
130°	24:35:41

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[RhCl(COD)]_2$, CO/H_2 (1/1, 600 bar)	I + II + III	699, 791

Temp.	I : II : III
70°	5: 0:95
80°	10: 0:90
100°	45: 5:50
130°	50:10:40

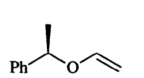
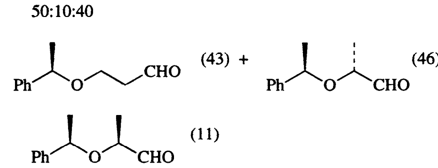
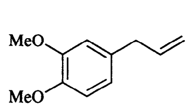
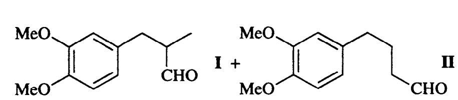
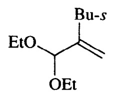
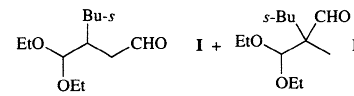
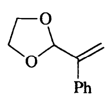
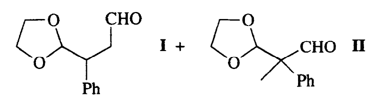
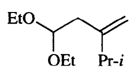
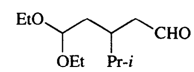
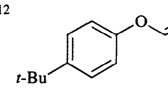
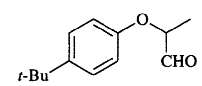
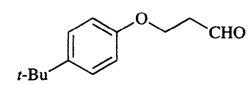
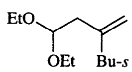
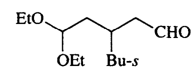
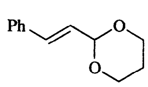
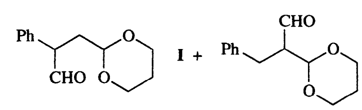
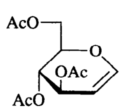
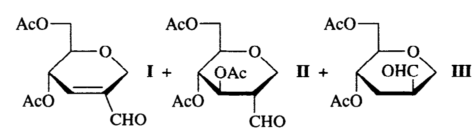
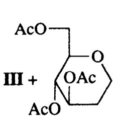
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[RhCl(CO)_2]_2/PPh_3$ (1/4), C_6H_6, 90°, CO/H_2 (120 atm), 4 h	 (43) + (46) + (11)	780
C_{11} 	$Rh_2(\mu\text{-SBu-}t)_2(CO)_2(TPPTS)_2$, TPPTS, L/Rh = 4, CO/H_2 (1/1, 5 bar), H_2O, 80°, 18 h	 I + II I + II (26), I:II = 3:97	23

TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2(\mu\text{-SBu-}t)_2(CO)_2[P(OPh)_3]_2$, 80°, CO/H_2 (1/1, 5 bar), $ClCH_2CH_2Cl$, 90 min	I (—) + II (86)	788
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 95°, CO/H_2 (1/1, 100 atm), 5 h	 I + II (85) I:II = 98:2	373, 779
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 90°, CO/H_2 (1/1, 100 atm), 5.5 h	 I + II (80) I:II = 98:2	373, 779
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 80°-100°, CO/H_2 (1/1, 100 atm), 36 h	 (70)	347
C_{12} 	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 55°, 22 h	 I (—) +  II (—) I:II = 90.2:9.8	374
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 80-100°, CO/H_2 (1/1, 100 atm), 36 h	 (70)	373, 374, 792
	$[Rh(OAc)_2]_2$, 2 PPh_3, EtOAc, 100°, CO/H_2 (500 psi), 22 h	 I + II (97) I:II = 85:15	367
		 I + II + III	335

Catalyst	CO/H_2 (1/1) Pressure (10^5 Pa)	Temp.	Solvent	Conv. (%)	I	II	III
$RhH(CO)(PPh_3)_3$	9	90°	$(CH_2Cl)_2$	6	(4)	(—)	(—)
$RhH(CO)(PPh_3)_3$	115	100°	$(CH_2Cl)_2$	10	(7)	(—)	(—)
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/PPh_3$	75	120°	$(CH_2Cl)_2$	—	(—)	(—)	(—)
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	35	120°	$(CH_2Cl)_2$	36	(7)	(8)	(11)
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	75	120°	$(CH_2Cl)_2$	82	(26)	(14)	(30)
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	75	120°	PhMe	71	(32)	(6)	(16)

I + II + III +  IV — 793

Catalyst	CO/H_2 (P, bar)	Temp.	Solvent	Conv. (%)	I	II	III	IV
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	3/2 (75)	120°	$(CH_2Cl)_2$	84	(34)	(6)	(27)	(15)
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	3/2 (60)	130°	$(CH_2Cl)_2$	94	(34)	(8)	(31)	(12)
$Rh_2[\mu\text{-S}(CH_2)_3NMe_2](COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	3/2 (60)	120°	PhMe	80	(40)	(3)	(tr)	(10)
$Rh_2(\mu\text{-OCH}_3)(COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	1/1 (55)	100°	$(CH_2Cl)_2$	90	(22)	(54)	(—)	(8)
$Rh_2(\mu\text{-OCH}_3)(COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	1/1 (70)	100°	$(CH_2Cl)_2$	91	(19)	(58)	(—)	(8)
$Rh_2(\mu\text{-OCH}_3)(COD)_2/P(OC_6H_4Bu\text{-}t\text{-}2)_3$	1/1 (55)	100°	PhMe	94	(37)	(5)	(tr)	(37)

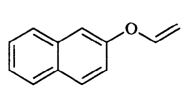
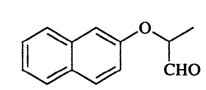
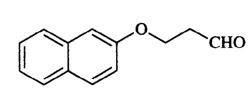
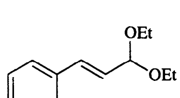
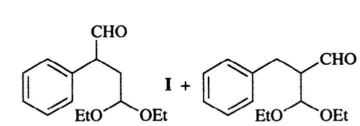
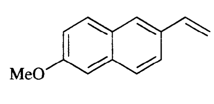
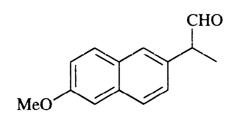
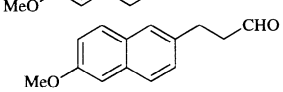
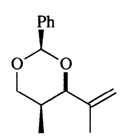
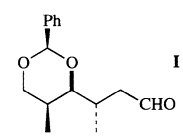
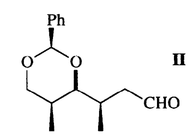
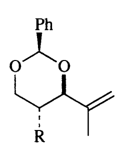
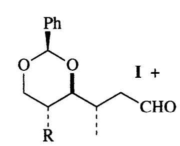
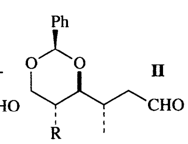
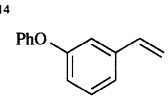
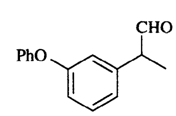
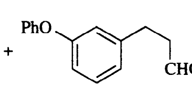
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 300 psi), $CHCl_3$, 55°, 22 h	 I (—) +  II (—) I:II = 96:4	251
	$RhH(PPh_3)_4$, CO/H_2 (1/1, 100 atm), C_6H_6, 80°, 3 h	 I + II (100) I:II = 97:3	769

TABLE VI. HYDROFORMYLATION OF UNSATURATED ETHERS AND ACETALS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, CO/H_2 (1/1, 100 atm), C_6H_6, 80°, 1.5 h	**I** + **II** (95), **I**:**II** = 98.4:1.6	769
	$RhCl(CO)(PPh_3)_2$, Et_3N, C_6H_6, 80°, CO/H_2 (1/1, 100 atm)	**I** + **II** (75), **I**:**II** = 90:10	373, 794
	[Rh(NBD)(2,5-bis(diphenylphosphino-methyl)bicyclo[2.2.1]heptane)ClO_4, CO/H_2 (1/1, 40 atm), C_6H_6, 50°, 13 h	 **I** (—) +  **II** (—) **I**:**II** = 95:5	247
	$Rh(acac)(CO)_2$, 4 $P(OPh)_3$, CO/H_2 (1/1, 20 bar), toluene, 70°, 48 h	 **I** (26) +  **II** (74)	795
	$Rh(acac)(CO)_2$, 4 $P(OPh)_3$, CO/H_2 (1/1, 20 bar), toluene, 70°, 48 h	 **I** +  **II**	795

R	I	I:II
Me	(80)	99:1
Et	(79)	99:1

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	$[RhCl(CO)_2]_2$, L/Rh = 5, Et_3N/Rh = 10, CO/H_2 (1/1, 20 bar), PhMe, 25°, 6 h	 **I** +  **II**	641

Ligand	Conv. (%)	I:II	I + II
TPP	95	91:9	(100)
PPPN	64	93:7	(100)
PPh_3	9	93:7	(100)

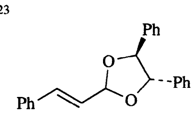
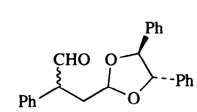
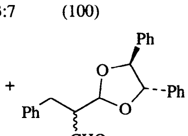
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23} 	$[Rh(OAc)_2]_2$, PPh_3, EtOAc, 100°, CO/H_2 (500 psi), 22 h	 **I** +  **II** **I** + **II** (74), **I**:**II** = 85:15	367

TABLE VII. HYDROFORMYLATION OF UNSATURATED HALOGEN COMPOUNDS

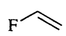
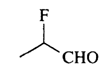
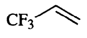
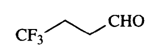
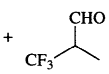
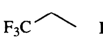
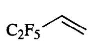
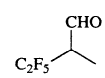
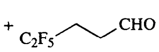
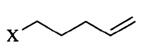
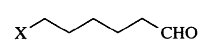
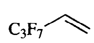
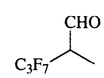
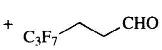
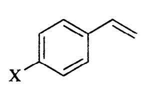
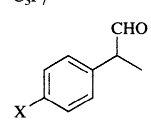
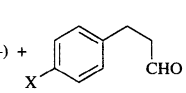
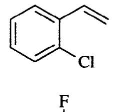
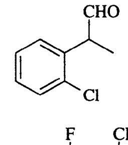
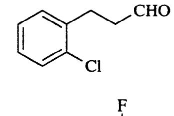
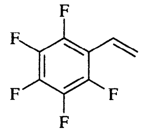
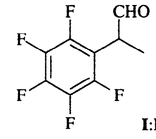
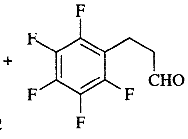
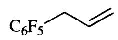
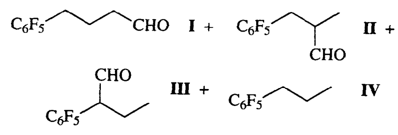
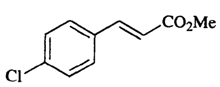
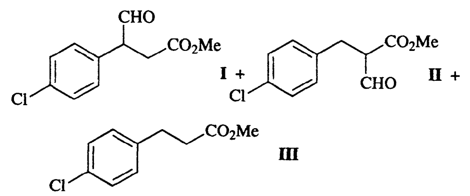
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2 	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 68 atm), 80°, PhMe, 18 h	 I (81)	357, 796
	$RhH(CO)(PPh_3)_3$, CO/H_2 (1/1, 68 atm), 80°, PhMe, 18 h	I (52)	357
	$Ru_3(CO)_{12}$, CO/H_2 (1/1, 68 atm), 80°, PhMe, 18 h	I (46)	357
	$Co_2(CO)_8$, CO/H_2 (1/1, 110 atm), 100°, PhMe, 18 h	I (30)	357
C_3 	$Co_2(CO)_8$, CO/H_2 (1/1, 130 atm), PhMe, 100°, 20 h	 I +  II I + II (95) I:II = 93:7	796, 354, 357
	$Rh_6(CO)_{16}$, CO/H_2 (1/1, 110 atm), PhMe, 80°, 5 h	I + II +  III (2) I + II (98) I:II = 4:96	357, 354
	Rh-C/$P(OPh)_3$, CO/H_2 (1/1, 110 atm), PhMe, 80°, 5 h	I + II + III (2) I + II (98) I:II = 4:96	357, 354
	$HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 110 atm), PhMe, 80°, 5 h	I + II + III (5) I + II (95) I:II = 5:95	357, 354
	$PtCl_2(DIOP)/SnCl_2$, CO/H_2 (1/1, 130 atm), PhMe, 100°, 4 h	I + II + III (25) I + II (75) I:II = 71:29	357, 354
C_4 	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 110 atm), 60°, PhMe, 6 h	 I (—) +  II (—) I:II = 95:5	357, 796
C_5 	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 X n:iso; Br >40:1 (71); I >40:1 (64)	135
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 110 atm), 60°, PhMe, 6 h	 I (—) +  II (—) I:II = 91:9	357, 796
C_8 	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 47°, 22 h	 I (—) +  II (—); X I:II; F 98:2; Cl 98.6:1.4; Br 98:2	251
	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	X I + II I:II; Cl (60) 93:7; Br (76) 92:8	368
	Rh/C (5%), DPPB, CO (8.5 atm), HCO_2H, DME, 110-120°, 24 h	Cl (67) 74:26; Br (73) 48:52	368
	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	 I +  II I + II (20) I:II = 85:15	368
	$Rh_6(CO)_{16}$, dioxane, CO/H_2 (1/1, 1200 psi), 90°, 3 h	 I (—) +  II (—) I:II = 98:2	359, 796
	$Co_2(CO)_8$, dioxane, CO/H_2 (1/1, 800 psi), 125°, 15 h	I + II + C_6F_5Et (22) I + II (60), I:II = 15:85	359
	$Rh_6(CO)_{16}$, C_6H_6, CO/H_2 (1/1, 80 atm), 90°, 3 h	I + II (100), I:II = 97:3	354, 357

TABLE VII. HYDROFORMYLATION OF UNSATURATED HALOGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhCl(PPh_3)_3$, C_6H_6, CO/H_2 (1/1, 90 atm), 90°, 20 h	**I** + **II** (100), **I**:**II** = 97:3	354, 357
	$HRh(CO)(PPh_3)_3$, C_6H_6, 90°, 8 h, CO/H_2 (1/1, 80 atm)	**I** + **II** (100), **I**:**II** = 98:2	354, 357
C_9 	$Co_2(CO)_8$, CO/H_2 (1/1, 80 atm), 100°, C_6H_6, 16 h	 **I** + **II** + **III** + **IV** (79), **I**:**II**:**III**:**IV** = 53:41:2:4	357, 796
	$Rh_6(CO)_{16}$, CO/H_2 (1/1, 80 atm), 95°, C_6H_6, 13 h	**I** + **II** (100), **I**:**II** = 41:59	357
	$RhH(CO)(PPh_3)_3$, CO/H_2 (1/1, 80 atm), C_6H_6, 95°, 3 h	**I** + **II** (94), **I**:**II** = 39:61	357
C_{10} 	CO/H_2 (1/1, 100 atm), C_6H_6, 80°		769

Catalyst	Time (h)	I:II	I + II	III
Rh(COD)(BPh_4)	22	100	(2)	(96)
Rh_2O_3/5 PPh_3	22	100	(3)	(93)
$RhH(CO)(PPh_3)_3$	7	100	(1)	(95)
$[Rh(COD)Cl]_2$	7	—	(0)	(5)
$RhH(PPh_3)_4$	6	95:5	(45)	(29)

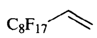
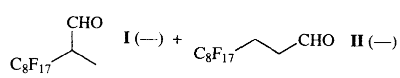
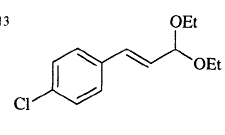
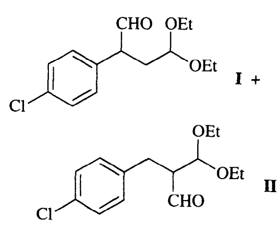
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 110 atm), 60°, PhMe, 6 h	 **I**:**II** = 92:8	796, 359
C_{13} 	$RhH(PPh_3)_4$, CO/H_2 (1/1, 100 atm), C_6H_6, 80°, 3 h	 **I** + **II** (98) **I**:**II** = 97:3	769
	$RhH(CO)(PPh_3)_3$, CO/H_2 (1/1, 100 atm), C_6H_6, 80°, 1.5 h	**I** + **II** (61), **I**:**II** = 98:2	769

TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS

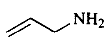
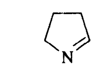
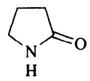
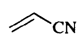
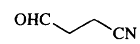
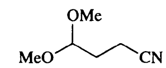
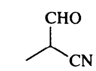
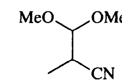
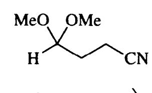
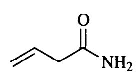
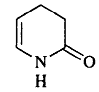
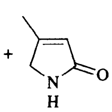
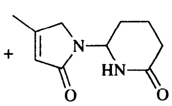
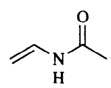
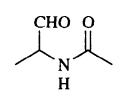
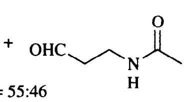
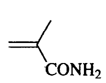
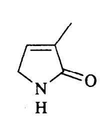
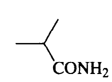
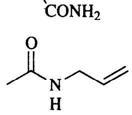
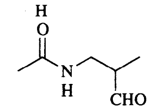
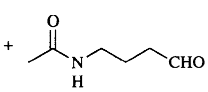
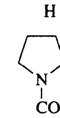
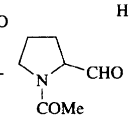
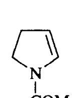
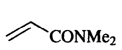
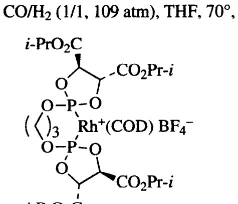
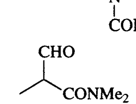
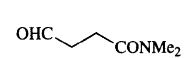
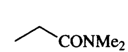
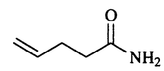
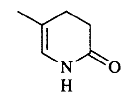
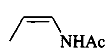
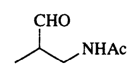
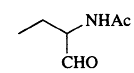
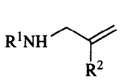
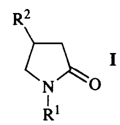
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	$HRh(CO)(PPh_3)_3$, PPh_3, 75-80°, dimethyl phthalate, CO/H_2 (1/1, 55 bar)	 I (92)	731
	$HRh(CO)(PPh_3)_3$, PPh_3, PhMe, CO/H_2 (1/1, 55 bar), 75-80°	I (—) +  II (—) I:II = 1:1	731
	$Co_2(CO)_8$, CO/H_2 (1/1, 250 kg/cm²), MeOH, 130°	 I (10) +  II (71) +  III (8) +  IV (tr)	797
	$[Pt(C_2H_4)(DPPB)]/CH_3SO_3H$ (1/1), CO/H_2 (1/1, 100 atm), PhMe, 100°, 22 h	I + III +  (5) I + III (69), I:III = 83:17	259
	$Co_2(CO)_8$, $CH(OCH_3)_3$, MeOH, CO/H_2 (1/1, 720 psi), 90°, 7h	 (82)	798
C_4			
	$RhCl(PPh_3)_3$, 10 $P(OPh)_3$, THF, 80°, CO/H_2 (3/1, 1200 psi), 40 h	 I +  II +  III I + II + III (90), I:II:III = 3:3:94	799, 800
	$RhCl(CO)(PPh_3)_2$, THF, 100°, CO/H_2 (1/1, 1200 psi), 5 h	I + II (87), I:II = 53:47	799
	$HRh(CO)(PPh_3)_3$, 2 DPPB, THF, 80°, CO/H_2 (3/1, 1200 psi), 40 h	I + II (88), I:II = 98:2	799
	$RhH(CO)(PPh_3)_3$, 40-45°, 40 h, CO/H_2 (500 psi)	 I (—) +  II (—) I:II = 55:46	801
	$[Rh(CO)_2Cl]_2$, PPh_3, Et_3N, PhMe, CO/H_2 (1/1, 50 atm), 120°, 17 h	 I +  II I:II = 45:55	762
C_5			
	$HRh(CO)(PPh_3)_3$, THF, 80°, 18 h, CO/H_2 (1/1, 1200 psi)	 I +  II +  III +  IV I + II + III + IV (76) I:II:III:IV = 63:11:13:13	363, 802
	$[Rh(DPPB)(NBD)][ClO_4]$, THF, 80°, 18 h, CO/H_2 (1/1, 1200 psi)	I + III + IV (78), I:III:IV = 71:5:24	363, 802
	$RhCl(PPh_3)_3$, THF, CO/H_2 (1/1, 1200 psi), 80°, 18 h	I + III + IV (80), I:III:IV = 65:7:28	363
	$Rh_4(CO)_{12}$, THF, CO/H_2 (1/1, 1200 psi), 80°, 18 h	I + II + III + IV (78), I:II:III:IV = 79:6:6:9	363
	$Co_2Rh_2(CO)_{12}$, CO/H_2 (1/1, 1200 psi), THF, 60°, 18 h	I + III (80), I:III = 82:18	363
	$RhH(CO)(PPh_3)_3$, C_6H_6, 40°, 30 h, CO/H_2 (1/1, 500 psi)	I (—) +  V (—) I:V = 54:46	801
	CO/H_2 (1/1, 109 atm), THF, 70°, 16 h 	 I (—) +  II (—) +  III (—) I:II:III = 49.5:0.5:50	248

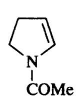
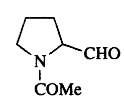
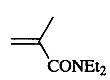
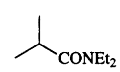
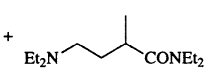
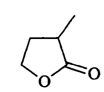
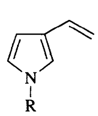
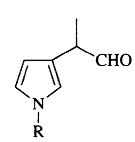
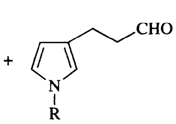
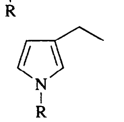
TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 1200 psi), THF, 100°, 18 h		799, 800

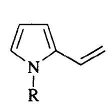
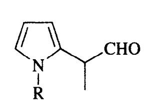
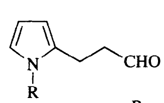
Catalyst	
$RhCl(PPh_3)_3$	(91)
$RhCl(CO)(PPh_3)_2$	(89)
$HRh(CO)(PPh_3)_3$	(88)
$Rh_4(CO)_{12}$	(92)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, 50-60°, 72 h, CO/H_2 (500 psi)	 I (—) +  II (—) I:II = 1:1	801
C_6 	(A) $HRh(CO)(PPh_3)_3$, CO (34.5 atm), $NaBH_4$, *i*-PrOH, CH_2Cl_2, 100°, 24 h (B) $Rh(COD)BPh_4$-$[Ru(CO)_3Cl_2]_2$, CH_2Cl_2, CO/H_2 (1/1, 48 atm), 100°, 24 h	 I	360

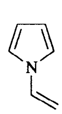
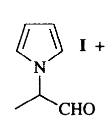
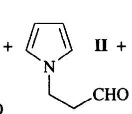
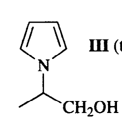
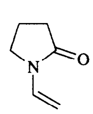
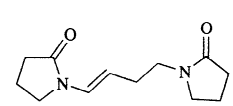
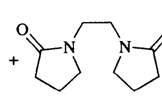
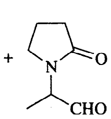
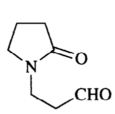
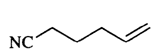
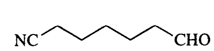
R^1	R^2	I (A)	I (B)
CH_2=$CHCH_2$	H	(20)	(25)
n-C_4H_9	H	(60)	(51)
C_6H_{11}	H	(78)	(59)
C_6H_{11}	Me	(46)	(35)
$PhCH_2$	H	(51)	(17)
$PhCH_2$	Me	(67)	(54)
$Ph(CH_2)_2$	H	(92)	(25)
C_8H_{15}	H	(79)	(72)

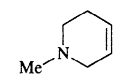
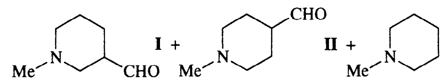
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, C_6H_6, 60°, 3 d, CO/H_2 (500 psi)	 (—)	801
	$Rh_4(CO)_{12}$, PhMe, CO/H_2 (1/1, 300 bar), 130°, 26 h	 (24) +  (29) +  (24)	803
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 120 atm), C_6H_6, 40°, 24 h	 I (—) +  II (—) +  III (tr) I:II = 94:6	804, 805

R	I + II	I:II
H	(98)	94:6
Ts	(92)	94:6

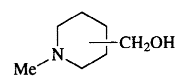
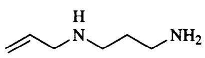
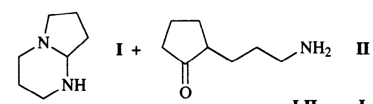
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 120 atm), C_6H_6, 40°, 44 h	 I +  II	804, 805

R	I + II	I:II
H	(—)	94:6
Ts	(92)	94:6

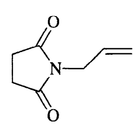
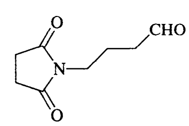
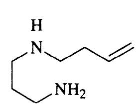
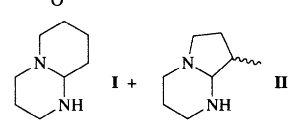
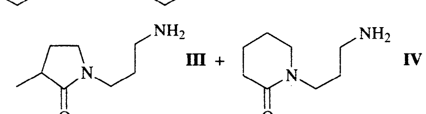
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 120 atm), C_6H_6, 40°, 36 h	 I +  II +  III (tr) I + II (—) I:II = 94:6	804
	$PtCl(SnCl_3)(DIOP)$, CO/H_2 (1/1, 80 bar), PhMe, 100°, 10 h	 I (89) +  (3)	806
	$[Rh(NBD)Cl]_2$, PPh_3, PhMe, 100°, CO/H_2 (1/1, 80 bar), 5 h	I (1) +  (60) +  (29)	806
	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 (84) *n:iso* > 40:1	135

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 80 bar), 100°, C_6H_6, 6 h		807

Catalyst	Conv. (%)	I:II:III
$HRh(CO)(PPh_3)_3$	64	39:59:2
$[Rh(NBD)Cl]_2$	64	0:0:100
$[Rh(NBD)Cl]_2 + PPh_3$	60	41:56:3
$[Rh(NBD)Cl]_2 + PBu_3$	50	20:72:8
$[Rh(NBD)Cl]_2 + PBu_3 + Et_3N$	59	38:58:4
$[Rh(NBD)Cl]_2 + P(C_6H_{11})_3$	8	17:42:41
$[Rh(NBD)Cl]_2$ + P(neomenthyl)Ph_2	60	11:18:71
$[Rh(NBD)Cl]_2 + P(C_6H_4Me\text{-}2)_3$	59	1:2:97

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, C_6H_6, 75-125°, 48 h, CO/H_2 (1/1, 200 psi)	II (42) + III (29) +  (1)	808
	[Rh (OAc)$_2$]$_2$, Ligand, CO/H_2		809, 810

Ligand	CO/H_2	I:II	I + II
PPh_3	1:1	40:60	(—)
PPh_3	9:1	95:5	(—)
BIPHEPHOS	1:1	100:0	(—)
PPh_3	1:9	10:90	(—)
P(tol-*o*)$_3$	1:1	15:85	(—)
P(tol-*o*)$_3$	1:9	15:85	(—)
$P(OPh)_3$	1:1	50:50	(—)
$P(OC_6H_4Me\text{-}o)_3$	1:1	25:75	(—)
$P(OCy)_3$	1:1	80:20	(—)
P(Bu-*n*)$_3$	1:1	95:5	(—)
$P(Cy)_3$	1:1	85:15	(—)

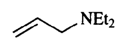
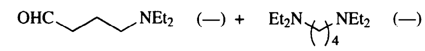
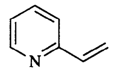
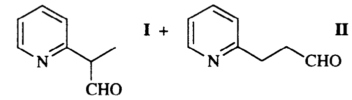
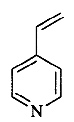
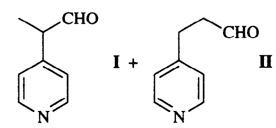
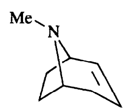
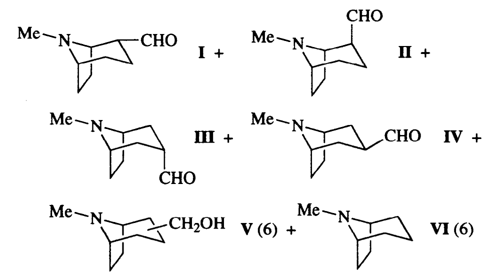
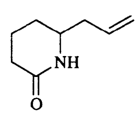
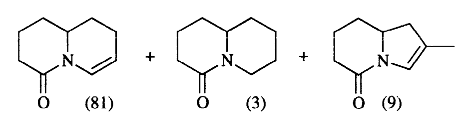
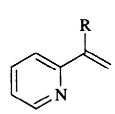
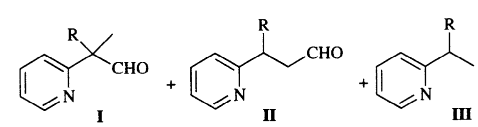
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	Rh $(CO)_2$(acac), BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 *n*:*iso* = 18:1, (95)	135
	$[Rh(OAc)_2]_2$, CO/H_2 (400 psi), C_6H_6	 	810

Ligand	H_2/CO	(I+II):(III+IV)	I:II	III/IV
BIPHEPHOS	9:1	100:0	>95:<5	—
BIPHEPHOS	1:1	100:0	100:0	—
$P(OPh)_3$	1:1	75:25	85:15	25:75
PPh_3	9:1	>95:<5	70:30	—
PPh_3	1:1	60:40	85:15	25/75
$P(C_6H_4Me\text{-}o)_3$	1:1	5:95	95:5	30:70
P(Bu-*n*)$_3$	1:1	>95:<5	75:25	—
$P(Cy)_3$	1:1	>95:<5	65:35	—

$[Rh(OAc)_2]_2$, Ligand, CO/H_2 — 809

Ligand	H_2/CO	(I+II):(III+IV)	I:II	III/IV
PPh_3	1:1	60:40	85:15	25:75
PPh_3	9:1	>95:<5	70:30	—
P(Bu-*n*)$_3$	1:1	>95:<5	75:25	—
$P(Cy)_3$	1:1	>95:<5	65:35	—
BIPHEPHOS	1:1	100:0	100:0	—
PPh_3	1:9	20:80	>95:<5	55:45
$P(C_6H_4Me\text{-}o)_3$	1:1	5:95	95:5	30:70
$P(C_6H_4Me\text{-}o)_3$	1:9	5:95	95:5	30:70

TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh complex, CO/H_2		811
	$[Rh(CO)_2Cl]_2$, $PPhMe_2$, P/Rh = 2, C_6H_6, CO/H_2 (1/1, 120 atm), 60°, 7 h	 I + II (90), I:II = 99:1	640
	$[Rh(CO)_2Cl]_2$, $PPhMe_2$, C_6H_6, CO/H_2, 60°	 I + II (—), I:II > 99:1	640
C_8 	$RhH(CO)(PPh_3)_3$, C_6H_6, 125°, 24 h, CO/H_2 (1/1, 200 psi)	 I + II + III + IV (86), I:II:III:IV = 2:2:9:87	808
	$RhCl(PPh_3)_3$, DPPB, L/Rh = 5, THF, 100°, 18 h, CO/H_2 (1/1, 1800 psi)	 (81) + (3) + (9)	363
	$HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 100 atm), C_6H_6	 I + II + III	812

R	Temp.	Time (h)	Conv.	I + II	I:II	III
Me	80°	48	81	(21)	100:0	(60)
Bu-*t*	120°	140	—	(—)	—	(—)
2-pyridyl	80°	48	20	(—)	—	(3)

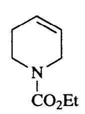
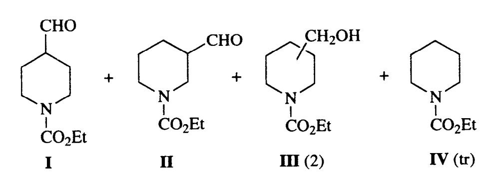
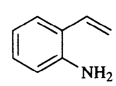
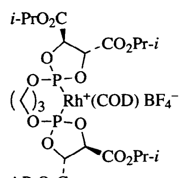
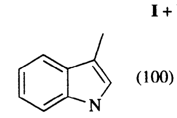
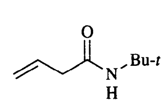
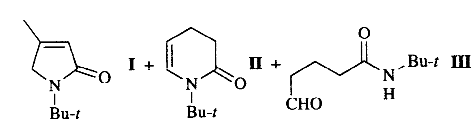
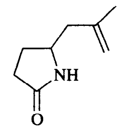
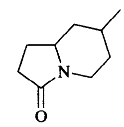
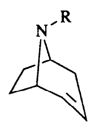
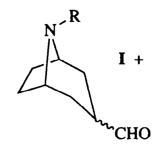
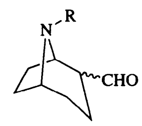
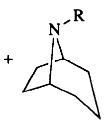
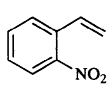
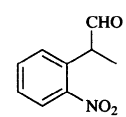
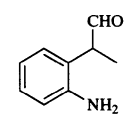
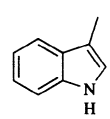
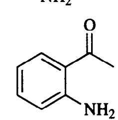
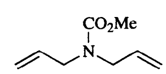
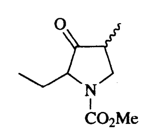
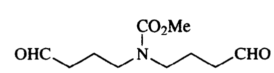
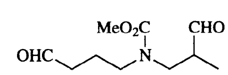
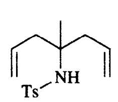
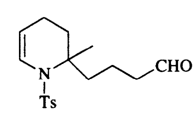
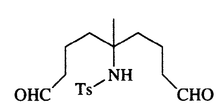
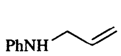
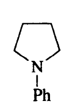
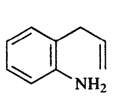
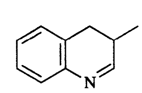
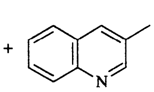
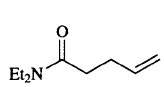
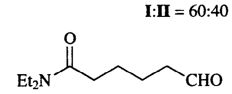
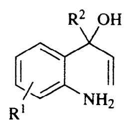
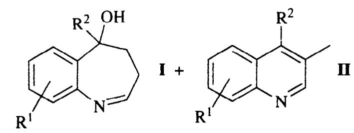
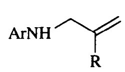
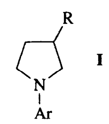
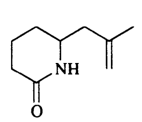
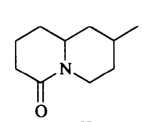
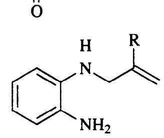
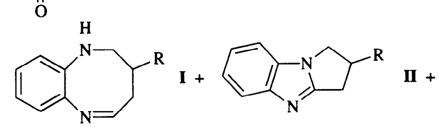
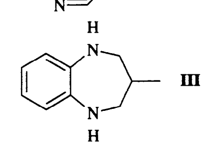
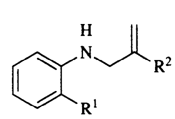
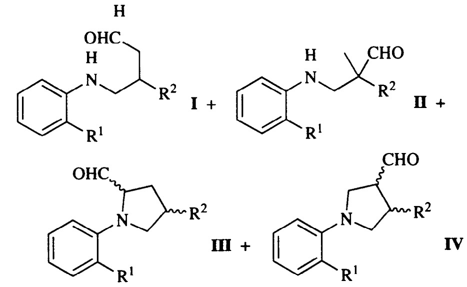
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_3$, PPh_3, L/Rh = 3, C_6H_6, CO/H_2 (1/1, 200 psi), 100°, 24 h	 I + II + III (2) + IV (tr); I + II (95), I:II = 25:75	808
	CO/H_2 (1/1, 100 atm), THF, 70°, 16 h, 	 (100)	248
	$HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 1200 psi), THF, 100°, 18 h	 I + II + III (90), I:II:III = 46:8:46	799

TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhCl(CO)(PPh_3)_2$, CO/H_2 (1/1, 1200 psi), THF, 100°, 18 h	**I** + **II** + **III** (78), **I**:**II**:**III** = 47:13:40	799
	$Co_2Rh_2(CO)_{12}$, CO/H_2 (1/2, 1800 psi), THF, 125°	 (78)	363
	$[Rh(NBD)Cl]_2$, L/Rh = 3, C_6H_6, 100°, CO/H_2 (1/1, 80 bar), 6 h	 **I** +  **II** +  **III**	807

Ligand	R	Conv. (%)	I:II:III
PPh_3	Me	94	87:11:1
PBu_3	Me	93	92:5:2
PPh_3	*i*-Pr	86	92:4:2
PBu_3	*i*-Pr	80	93:5:1
PPh_3	CH_2Ph	88	95:1:3
PBu_3	CH_2Ph	79	90:1:8

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh/C, C_6H_6, 80°, 1-2 h, CO/H_2 (1/1, 160 atm)	 (60) +  (5) +  (5) +  (28)	813
	$HCo(CO)_4$, CO/H_2 (1/1, 1 atm), hexane, rt, overnight	 (45)	814
	$Co_2(CO)_8$, CO/H_2 (1/1, 1300-1400 psi), C_6H_6, 120°	 **I** (28)	814
	$RhH(CO)(PPh_3)_3$, C_6H_6, CO/H_2	**I** +  **II** **I** + **II** (97) **I**:**II** = 1:3	814
	$Rh(acac)(CO)_2$, BIPHEPHOS, CO/H_2 (1/1, 4 atm), THF, 40°, 16 h	 (>98)	815
	$Rh(acac)(CO)_2$, BIPHEPHOS, CO/H_2 (1/1, 4 atm), THF, 40°, 16 h	 (>95)	815
C_9			
	$(DPPB)Rh(COD)BF_4$, CO/H_2 (1/1, 48 atm), CH_2Cl_2, 80°, 12 h	 **I** (75)	360
	$[Rh(COD)Cl]_2$, CO/H_2 (1/1, 48 atm), DPPB, CH_2Cl_2, 80°, 12 h	**I** (69)	360
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2, 60°, 20 h	 **I** (—) +  **II** (—) **I**:**II** = 60:40	313
	Rh $(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 (93) n:iso > 40:1	135

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 60°, 20 h		313, 361
	$Rh(COD)BPh_4$, CO (34.5 atm), $NaBH_4$, *i*-PrOH, CH_2Cl_2, 100°, 30 h		360
	$Co_2Rh_2(CO)_{12}$, CO/H_2 (1/2, 1800 psi), 125°, THF	 (77)	363
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 70°, 20 h		364
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 70-100°, 20 h		816

Ref. 313, 361:

R^1	R^2	I:II	I	II
H	H	75:25	(69)	(13)
H	Me	88:12	(85)	(12)
H	Ph	91:9	(79)	(9)
5-Cl	Ph	91:9	(86)	(7)
4-Me	Ph	87:13	(70)	(11)
H	C_6H_4Me-4	83:17	(80)	(15)

Ref. 360:

Ar	R	R	I
$2-C_5H_4N$	Me	Me	(26)
Ph	Me	Me	(84)
$4-MeOC_6H_4$	Me	Me	(68)
$2-MeOC_6H_4$	Me	Me	(49)
$2-MeC_6H_4$	Me	Me	(45) + *i*-$BuNHC_6H_4Me$ (30)
$4-ClC_6H_4$	Me	Me	(37)
$1-C_{10}H_7$	Me	Me	(57)
Ph	*n*-C_5H_{11}	*n*-C_5H_{11}	(83)
Ph	CH_2SO_2Ph	Me	(87)

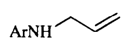
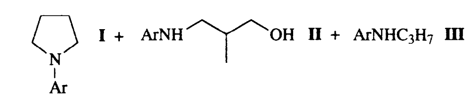
Ref. 364:

R	I	II	III
H	(40)	(29)	(17)
Me	(65)	(29)	(—)

Ref. 816:

R^1	R^2	I : II : III : IV	Yield
NO_2	H	20 : 80 : 0 : 0	(78)
CN	H	0 : 40 : 30 : 30	(75)
H	Me	0 : 0 : 67 : 33	(76)
CN	Me	0 : 0 : 67 : 33	(72)

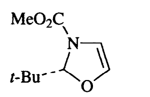
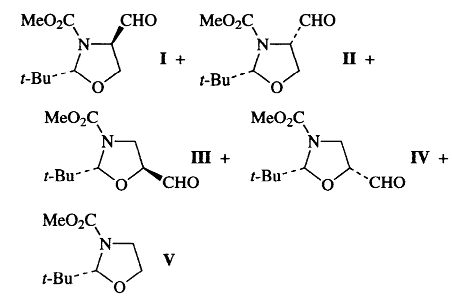
TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(COD)BPh_4, CO (34.5 atm), $NaBH_4$, *i*-PrOH, CH_2Cl_2, 100°, 30 h		360

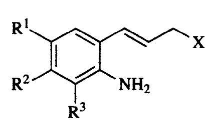
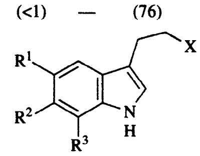
Ar	I	II	III
Ph	(31)	(33)	(10)
4-$MeOC_6H_4$	(30)	(30)	(0)
1-$C_{10}H_7$	(27)	(0)	(14)
2-$MeOC_6H_4$	(0)	(0)	(82)
2-MeC_6H_4	(0)	(0)	(72)

Rh(COD)BPh_4, CO/H_2 (1/1, 48 atm), DPPB, CH_2Cl_2, 80°, 12 h — 360

Ar	I
Ph	(68)
2-$MeOC_6H_4$	(55)
2-MeC_6H_4	(63)
1-$C_{10}H_7$	(59)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 80 bar), PhMe		817

Catalyst	Temp.	Time (h)	I + II	I:II	III + IV	III:IV	V
$[Rh(NBD)Cl]_2$/2.2 PPh_3	100°	12	(48)	97:3	(31)	96:4	(<1)
$[Rh(NBD)Cl]_2$/DPPB	100°	20	(28)	98:2	(54)	99:1	(<1)
$[Rh(NBD)Cl]_2$/DPPP	100°	20	(20)	99:1	(71)	99:1	(<1)
$[Rh(NBD)Cl]_2$/DPPE	100°	20	(22)	98:2	(43)	98:2	(<1)
$PtCl_2$((2*S*,4*S*)-BDPP)/2 $SnCl_2$	100°	6	(<1)	—	(36)	97:3	(15)
$PtCl_2$(DPPB)/2 $SnCl_2$	100°	15	(<1)	—	(30)	97:3	(22)
$PtCl_2$(DPPB)/2 $SnCl_2$	50°	75	(<1)	—	(76)	98:2	(3)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$HRh(CO)(PPh_3)_3$, PPh_3, PhMe, CO/H_2 (1/1, 20 atm), 70°, 70 h	 I	818

R^1	R^2	R^3	X	I
H	H	H	NHTs	(58)
H	H	H	$N(Boc)_2$	(69)
Me	H	H	$N(Boc)_2$	(60)
H	CF_3	H	$N(Boc)_2$	(58)
H	MeO	H	$N(Boc)_2$	(32)
H	H	Br	$N(Boc)_2$	(60)
Cl	H	Br	$N(Boc)_2$	(54)
Cl	H	F	$N(Boc)_2$	(56)
F	H	F	$N(Boc)_2$	(62)
H	H	H	OH	(73)

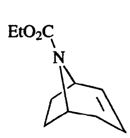
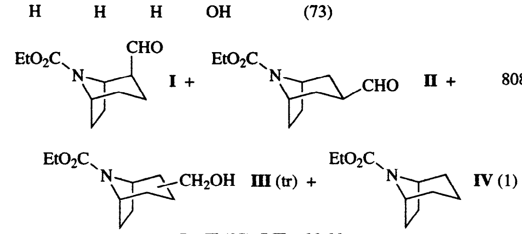
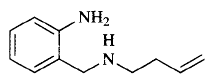
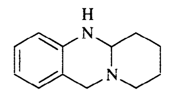
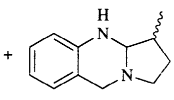
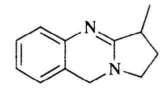
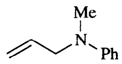
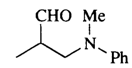
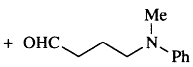
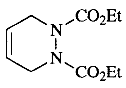
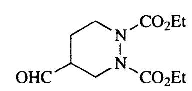
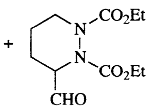
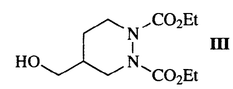
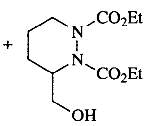
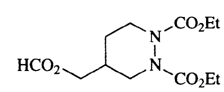
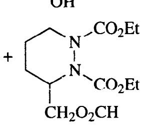
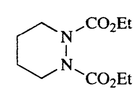
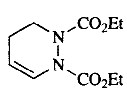
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$RhH(CO)(PPh_3)_3$, C_6H_6, 75°, 24 h, CO/H_2 (1/1, 200 psi)	 I + II (97), I:II = 20:80	808

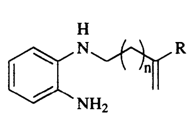
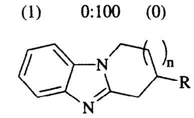
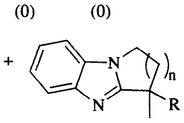
TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh_2(OAc)_4$, PPh_3, P/Rh=2, AcOEt, CO/H_2 (1/1, 27 atm), 80°, 20 h	 I +  II +  III I + II + III (93), I:II:III=48:32:20	819
	$Rh_2(OAc)_4$, PCy_3, P/Rh=2, AcOEt, CO/H_2 (1/1, 27 atm), 80°, 20 h	I + II (—), I:II=30:70	819
	$Rh(COD)BPh_4$, CO/H_2 (1/2, 200 psi), $CHCl_3$, 60°, 22 h	 I +  II I + II (—) I:II = 35:65	251
	CO/H_2 (1/1, 50 atm), C_6H_6, 20°	 I +  II +  III +  IV +  V +  VI +  VII	820

Catalyst precursor	Temp.	Time (h)	I + II	I:II	III + IV	V + VI	VII
$Co_2(CO)_8$	100°	6	(48)	53:47	(3)	(4)	(5)
$HRh(CO)(PPh_3)_3$	80 °	27	(52)	99:1	(tr)	(2)	(7)
$[Rh(COD)Cl]_2$/Bipy	80°	20	(95)	100:0	(0)	(0)	(0)
$Ru_3(CO)_{12}$	150°	24	(10)	100:0	(0)	(13)	(77)
$PtCl_2(PPh_3)_2/SnCl_2$	80°	8	(1)	100:0	(0)	(0)	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 50 atm), C_6H_6		820

Catalyst precursor	Temp.	Time (h)	I + II	I:II	III + IV	V + VI	VII
$Co_2(CO)_8$	100°	6	(75)	14:86	(8)	(4)	(13)
$HRh(CO)(PPh_3)_3$	80°	70	(11)	34:66	(0)	(0)	(0)
$[Rh(COD)Cl]_2$/Bipy	80°	20	(42)	23:77	(0)	(0)	(0)
$[Rh(COD)Cl]_2$/Bipy	120°	5	(68)	50:50	(0)	(0)	(0)
$Ru_3(CO)_{12}$	150°	24	(3)	47:53	(0)	(0)	(97)
$PtCl_2(PPh_3)_2/SnCl_2$	100°	45	(1)	0:100	(0)	(0)	(0)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 70-100°, 20-60 h	 I +  II	821, 364

n	R	I:II	Yield
1	H	60 : 40	(98)
1	Me	>97 : —	(78)
2	H	60 : 40	(72)
2	Me	>97 : —	(87)

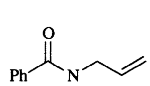
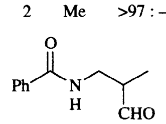
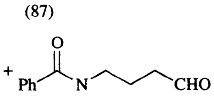
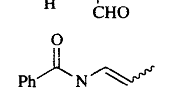
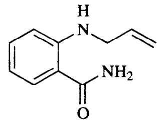
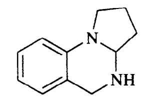
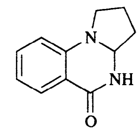
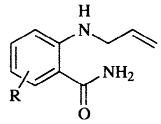
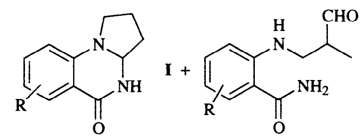
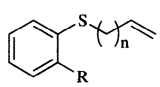
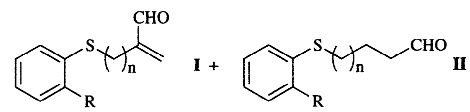
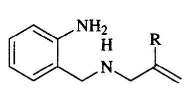
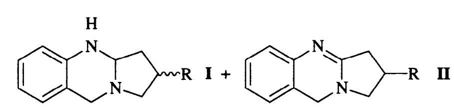
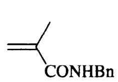
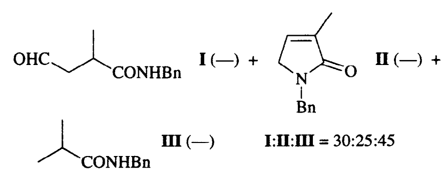
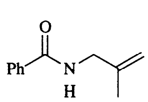
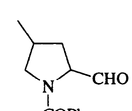
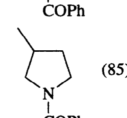
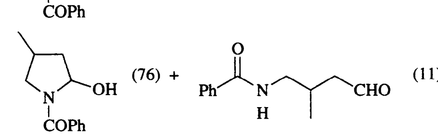
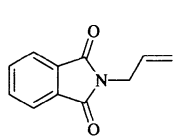
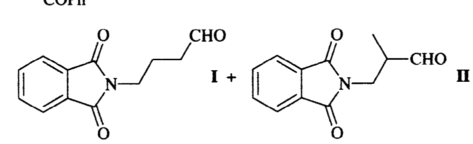
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ru_3(CO)_{12}$, CO/H_2, THF, 100°	 (40) +  (23) +  (11)	363

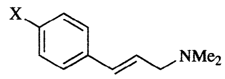
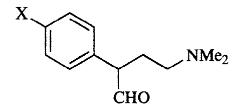
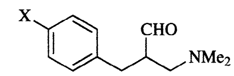
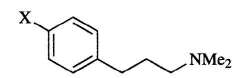
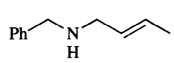
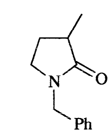
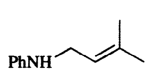
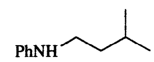
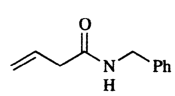
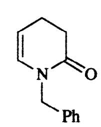
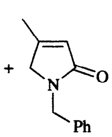
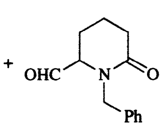
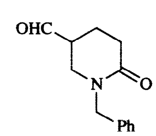
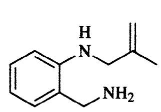
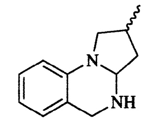
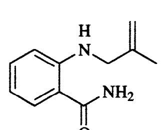
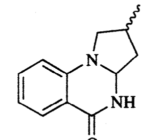
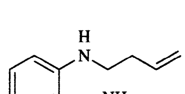
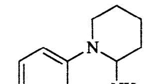
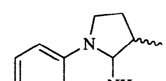
TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 (75)	822
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 (65)	822
	$[Rh(OAc)_2]_2$, PPh_3, P/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 R: 5-Me, I:II 100:0; R: 4-Cl, I:II 40:60	823
	$Rh(CO)H(PPh_3)_3$ or $[Rh(OAc)_2]_2/PPh_3$, CO/H_2 (1200 psi), C_6H_6, 40°, 65 h		824
	$Rh_2(OAc)_4$, PPh_3, P/Rh=2, AcOEt, CO/H_2 (1/1, 27 atm), 80°, 20 h		819
C_{11}			
	$Rh_4(CO)_{12}$, PhMe, 120°, 72 h, CO/H_2 (1/1, 80 atm)	 I:II:III = 30:25:45	762
	[Rh(DPPB)(NBD)][ClO_4], THF, 100°, 71 h, CO/H_2 (34/3, 1850 psi)	 (87)	363, 802
	$Co_2Rh_2(CO)_{12}$, THF, 100°, 18 h, CO/H_2 (1/3, 1200 psi)	 (85)	363, 802
	$Rh_4(CO)_{12}$, THF, CO/H_2 (2/1, 800 psi), 100°, 18 h		363, 802
	$RhCl(CO)(PPh_3)_2/PPh_3$ (1/50), C_6H_6, CO/H_2 (1/1, 100 atm), 70°, 15-20 h	 I + II (98), I:II = 0.7	825

n	R	I + II	I:II
1	CN	100	70:30
1	$CONH_2$	88	72:28
2	CN	91	43:57
2	$CONH_2$	91	30:70

R	Conv. (%)	I	II
H	100	(78)	(0)
Me	80	(50)	(30)

TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Co_2(CO)_8$, C_6H_6, CO/H_2 (1/1, 100 atm), 120°, 43 h	**I** + **II** (45), **I**:**II** = 4	825
	$PtCl_2(PPh_3)_2/SnCl_2$ (1/5), MEK, 70°, 15-20 h, CO/H_2 (1/1, 100 atm)	**I** + **II** (79), **I**:**II** = 1.5	825
	CO/H_2 (1/1, 100 atm), C_6H_6, 24 h	 **I** +  **II** +  **III**	826
	$HRh(CO)(PPh_3)_3$, CO (34.5 atm), $NaBH_4$, *i*-PrOH, CH_2Cl_2, 100°, 24 h	 (40)	360
	$Rh(COD)BPh_4$, CO (34.5 atm), $NaBH_4$, *i*-PrOH, CH_2Cl_2, 100°, 30 h	 (48)	360
	$RhCl(PPh_3)_3$, THF, 100°, CO/H_2 (1/1, 1200 psi), 18 h	 **I** +  **II** +  **III** +  **IV** **I** + **II** + **III** + **IV** (88) **I**:**II**:**III**:**IV** = 28:53:16:3	799
	$RhCl(CO)(PPh_3)_2$, THF, 100°, CO/H_2 (1/1, 1200 psi), 18 h	**I** + **II** + **III** + **IV** (92), **I**:**II**:**III**:**IV** = 35:49:14:2	799
	$RhCl(CO)(PPh_3)_2$, 20 PPh_3, THF, 100°, CO/H_2 (1/1, 1200 psi), 40 h	**I** + **II** (98), **I**:**II** = 91:9	799, 800
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 90°, 20 h	 (57) ratio 2:1 + starting material (25)	822
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 (60) ratio 3:1 + starting material (25)	822
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 **I** +  **I** + **II** (67) **II**, ratio 9:1 **I**:**II** = 70:30	822

Catalyst	Temp.	X	I:II	I + II	III
$HRh(CO)(PPh_3)_3$	80°	H	>99:1	(91)	(8)
Rh_2O_3	120°	H	>99:1	(14)	(81)
$(COD)Rh^+BPh_4^-$	120°	H	>99:1	(15)	(81)
$HRh(CO)(PPh_3)_3$	80°	Cl	99:1	(91)	(9)
Rh_2O_3	120°	Cl	>99:1	(6)	(92)
$(COD)Rh^+BPh_4^-$	120°	Cl	>99:1	(7)	(90)
$HRh(CO)(PPh_3)_3$	80°	Br	>99:1	(92)	(8)
Rh_2O_3	120°	Br	>99:1	(4)	(92)
$(COD)Rh^+BPh_4^-$	120°	Br	>99:1	(8)	(87)

TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

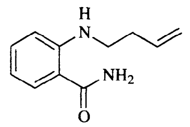
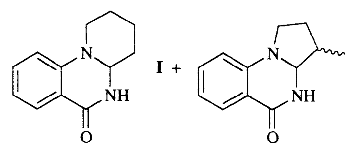
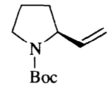
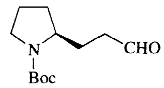
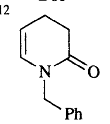
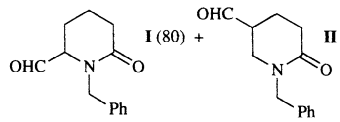
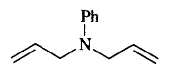
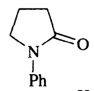
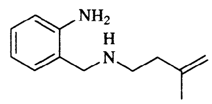
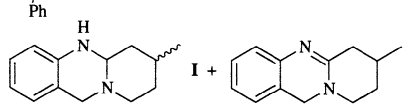
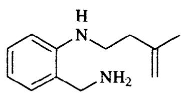
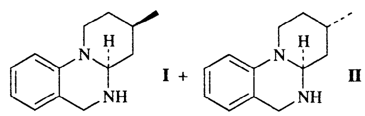
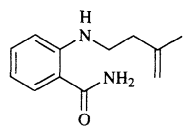
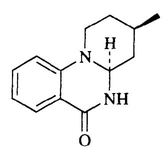
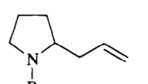
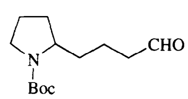
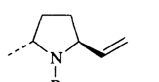
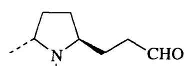
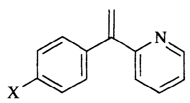
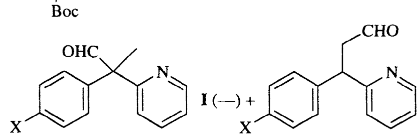
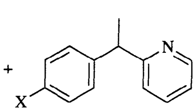
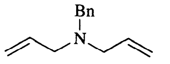
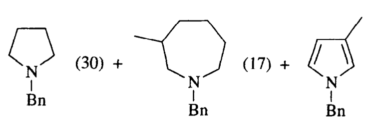
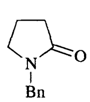
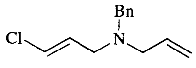
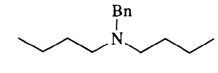
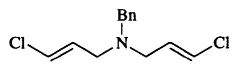
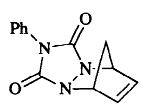
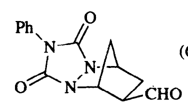
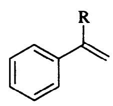
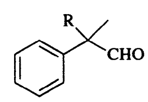
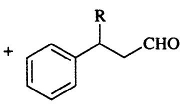
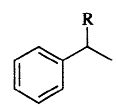
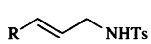
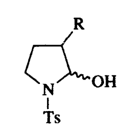
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 I + II (91) II, ratio 2:1 I:II = 70:30	822
	Rh(acac)$(CO)_2$, BIPHEPHOS, THF, L/Rh = 1.04, CO/H_2 (1/1, 70 psi), 60 °	 (77)	827
C_{12} 	$RhCl(PPh_3)_3$, CO/H_2 (13/3, 1600 psi), THF, 100°, 40 h	 I (80) + II (—) I:II = 87:13	799
	$Co_2(CO)_8$, CO/H_2 (1/1, 1300-1400 psi), C_6H_6, 90°, 4-5 h	 (50)	814
	$Rh_2(OAc)_4$, PPh_3, P/Rh = 2, AcOEt, CO/H_2 (1/1, 27 atm), 90°, 20 h	 I + II (*cis:trans*=75:25) I + II (—), I:II=85:15	819
	$Rh_2(OAc)_4$, PCy_3, P/Rh = 2, AcOEt, CO/H_2 (1/1, 27 atm), 80°, 20 h	I (—)	819
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 I + II I + II (75) I:II = 1:4	822
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 80°, 20 h	 (69)	822
	Rh(acac)$(CO)_2$, BIPHEPHOS, THF, L/Rh = 1.04, CO/H_2 (1/1, 70 psi), 60°	 (83)	827
	Rh(acac)$(CO)_2$, BIPHEPHOS, THF, L/Rh = 1.04, CO/H_2 (1/1, 70 psi), 60°	 (67)	827
C_{13}  X = H or Br	$HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 100 atm), C_6H_6, 90°	 I (—) + II (—) +  III (—) I:II > 95:5 (I + II):III > 80:20	826
	$RhH(CO)(PPh_3)_3$, CO/H_2	 (30) + (17) + (6)	814
	$Co_2(CO)_8$, CO/H_2 (1/1, 1300-1400 psi), C_6H_6, 90°, 4-5 h	 I (45) + starting material (45)	814
	$Co_2(CO)_8$, CO/H_2 (1/1, 1300-1400 psi), C_6H_6, 90°, 4-5 h	I (30) +  II (40)	814

TABLE VIII. HYDROFORMYLATION OF UNSATURATED NITROGEN COMPOUNDS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Co_2(CO)_8$, CO/H_2 (1/1, 1300-1400 psi), C_6H_6, 90°, 4-5 h	**I** (35) + **II** (37)	814
	$[RhCl(CO)_2]_2$, PPh_3, PhMe, 120-130°, CO/H_2 (1/1, 2000 psi)	 (62)	828
	[Rh], CO/H_2 (1/1, 100 atm), C_6H_6	 **I** +  **II** +  **III**	812

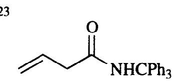
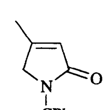
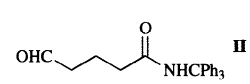
R	[Rh]	Temp.	Time (h)	Conv. (%)	I + II	I:II	III
2-pyridyl	$HRh(CO)(PPh_3)_3$	80°	96	41	(36)	32:68	(5)
2-pyridyl	$Rh(acac)(CO)_2$	80°	144	92	(38)	25:75	(51)
3-pyridyl	$HRh(CO)(PPh_3)_3$	100°	48	100	(20)	0:100	(80)
3-pyridyl	$[Rh(CO)_2Cl]_2$	100°	90	62	—	—	(62)
3-pyridyl	$[Rh(CO)_2Cl]_2/4PPhMe_2$	100°	90	95	(15)	0:100	(80)

C_{14}

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhH(CO)(PPh_3)_2/10PPh_3$, PhMe, 70°, CO/H_2 (1/1, 20 atm), 70 h		829

R	I
3-furyl	(70)
3-pyridyl	(80)
Ph	(83)
p-$MeOC_6H_4$	(58)
p-FC_6H_4	(61)
p-$CF_3C_6H_4$	(74)
o-NCC_6H_4	(52)
3-indanyl	(49)

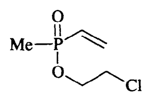
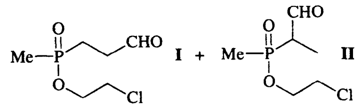
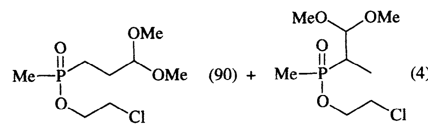
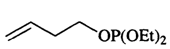
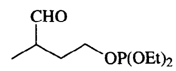
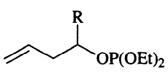
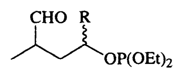
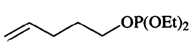
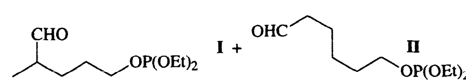
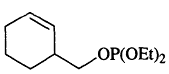
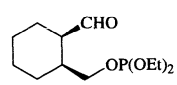
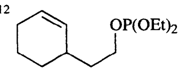
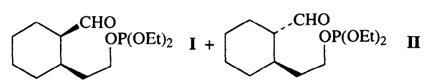
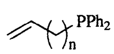
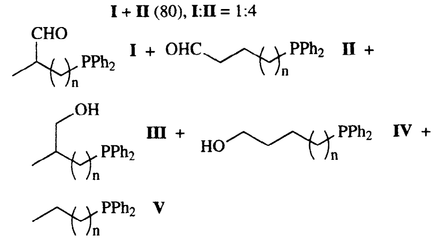
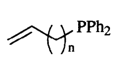
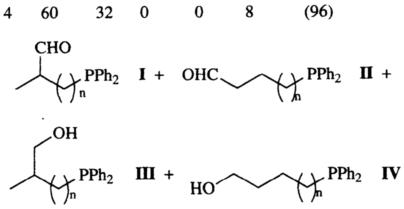
C_{23}

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$RhCl(CO)(PPh_3)_2$, CO/H_2 (1/1, 1200 psi), 100°, 18 h	 **I** +  **II**	799

Solvent	I:II	Yield
THF	47:53	(79)
PhMe	17:83	(83)
DMF	12:88	(80)
dioxane	0:100	(75)

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS

A. Phosphorus Compounds

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	$Co_2(CO)_8$, CO/H_2 (1/1, 100 atm), 120°, C_6H_6, 2 h	 I + II (42), I:II = 94:6	366
	$Rh(acac)[P(OPh)_3]_2$, CO/H_2 (1/1, 1 atm), 45°, C_6H_6, 2 h	I + II (53), I:II = 97:3	366
	$HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 100 atm), 100°, 5-19 h	I + II (80), I:II = 9:91	366
	$Co_2(CO)_8$, CO/H_2 (1/1, 100 atm), 120°, MeOH, 2 h	 (90) + (4)	366
C_8 	$Rh_4(CO)_{12}$, C_6H_6, CO/H_2 (1/1, 500 psi), 50°, 22 h	 I (100)	290
	$[Rh(OAc)_2]_2$, C_6H_6, CO/H_2 (1/1, 500 psi), 50°, 22 h	I (100)	290, 291
C_9 	$[Rh(OAc)_2]_2$, CO/H_2 (1/1, 500 psi), C_6H_6, 50°, 5-22 h	 R: Me (—) Ratio 60:40; Ph (—) Ratio 70:30	281, 291
	$[Rh(OAc)_2]_2$, CO/H_2 (1/1, 500 psi), C_6H_6, 90°, 22 h	 I + II (—), I:II = 87:13	290, 291
C_{11} 	$[Rh(OAc)_2]_2$, CO/H_2 (1/1, 500 psi), C_6H_6, 100°, 44 h	 (80)	290, 291
C_{12} 	—	 I + II (80), I:II = 1:4	290
C_{15} 	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 2, EtOAc, CO/H_2 (1/1, 400 psi), 100°, 20 h		288, 289
	$(CO)_4M(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, CO/H_2 (1/1, 400 psi), C_6H_6, 80°		830

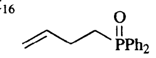
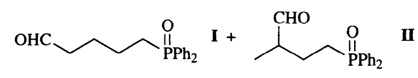
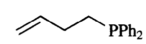
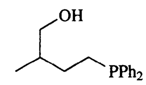
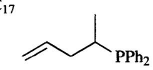
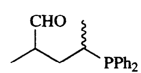
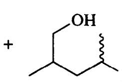
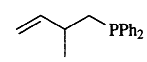
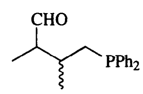
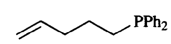
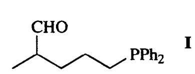
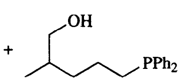
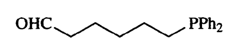
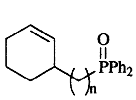
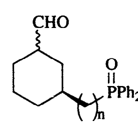
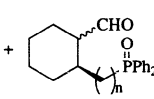
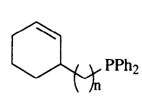
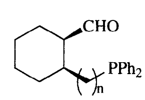
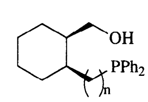
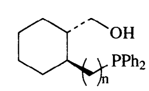
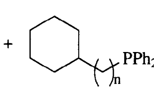
Ratio of Products (%)

n	I	II	III	IV	V	Yield
1	0	0	30	20	50	(68)
2	0	0	100	0	0	(86)
3	21-26	2-9	27-52	0	13-50	(64-95)
4	60	32	0	0	8	(96)

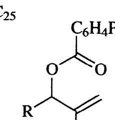
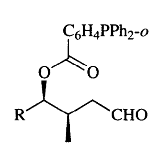
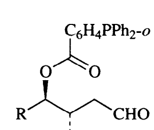
M	n	I	II	III	IV	Branched:Linear	Yield
W	1	—	—	36	18	67:33	(54)
Mo	1	—	—	35	21	62:38	(56)
Cr	1	—	—	24	10	71:29	(34)
W	2	—	—	100	—	100:0	(77)
Mo	2	—	—	100	—	100:0	(98)
Cr	2	17	—	83	—	100:0	(100)
W	3	77	6	17	—	83:17	(100)
Mo	3	92	—	8	—	100:0	(—)
Cr	3	90	—	10	—	100:0	(100)

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

A. Phosphorus Compounds (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 2, EtOAc, CO/H_2 (1/1, 400 psi), 100°, 5 h	 I + II (55), I:II = 64:36	288, 289
	$(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 380 psi), 80°, 22 h	 (77)	372
C_{17} 	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, 5 h, CO/H_2 (1/1, 400 psi), 45°	 I (90) +  II (—) I:II = 93:7; ratio 3:2	365. 289
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 50°, 17 h 365. 289	 (95) *syn:anti* = 1:1	365. 289
	$(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 380 psi), 80°, 22 h	 I +  II +  III I + II + III (100) I:II:III = 77:12:6	372
	$[Rh(OAc)_2]_2$, CO/H_2 (500 psi), C_6H_6, 100°, 22 h	I + II + III (80), I:II:III = 70:19:11	372
C_{19}  n = 1-2	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi)	 I (—) +  II (—); ratio 70:30; *trans:cis* = 80:20; I:II = 70:30	365
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 22 h	 I +  II +  III +  IV	289, 365

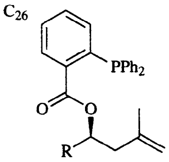
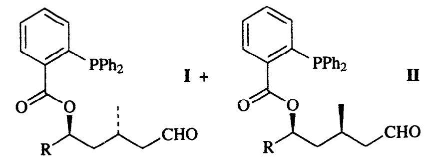
Temp.	n	I	II	III	IV	Ratio
55°	1	(—)	(—)	(0)	(—)	I:II:IV = 63:6:6
90°	1	(0)	(88)	(0)	(—)	II:IV = 88:12
90°	2	(0)	(—)	(—)	(0)	II:III = 80:20

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25} 	$Rh(acac)(CO)_2$, $P(OPh)_3$, P/Rh = 4, CO/H (1/1, 20 atm), PhMe, 70-90°, 24 h	 I +  II	743, 831

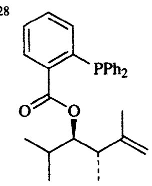
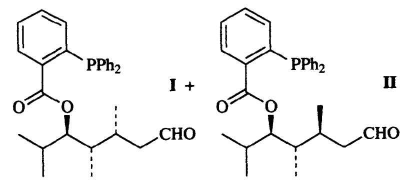
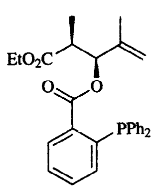
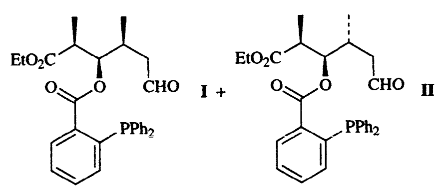
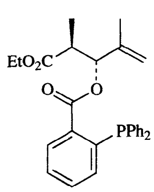
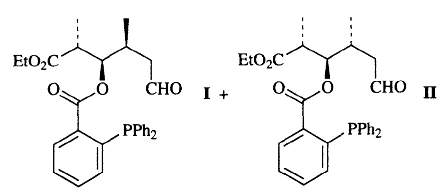
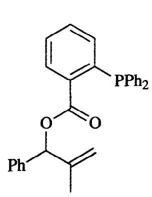
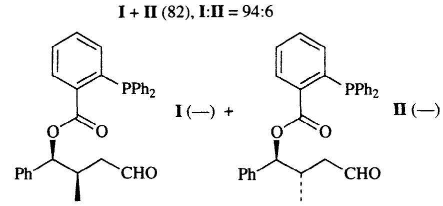
R	I:II	I
Et	73:27	(83)
i-Pr	96:4	(97)
Cy	95:5	(81)
CO_2Me	90:10	(80)
$CH_3(CH_2)C$	96:4	(36)
1-Furyl	93:7	(63)
Ph	92:8	(99)
Bn	80:20	(75)

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

A. Phosphorus Compounds (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26} 	Rh(acac)(CO)$_2$, P(OPh)$_3$, P/Rh = 4, H_2/CO (1/1, 20 bar), PhMe	 I + II	832

R	Temp.	Time (h)	I + II	I:II
i-Pr	50°	72	(93)	91:9
C_6H_{11}	50°	72	(90)	91:9
C_6H_{13}	30°	168	(81)	90:10
Ph	30°	120	(72)	90:10
o-MeOC_6H_4	30°	240	(78)	90:10
(*E*)-EtCH=CMe	30°	168	(85)	90:10

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28} 	Rh(acac)(CO)$_2$, P(OPh)$_3$, P/Rh = 4, PhMe, H_2/CO (1/1, 20 bar), 50°, 7 d	 I + II; I + II (91), I:II=96:4	832
 (±)	Rh(acac)(CO)$_2$, P(OPh)$_3$, P/Rh = 4, PhMe, CO/H_2 (1/1, 20 atm), 90°, 24 h	 I + II; I + II (98), I:II = 81:19	831
 (±)	Rh(acac)(CO)$_2$, P(OPh)$_3$, P/Rh = 4, PhMe, CO/H_2 (1/1, 20 atm), 90°, 24 h	 I + II; I + II (82), I:II = 94:6	831
C_{29} 	Rh(acac)(CO)$_2$, Ligand, L/Rh = 4, PhMe, H_2/CO (1/1, 20 atm), 90°, 24 h	 I (—) + II (—)	743

Ligand	Conv. (%)	I:II
—	35	81:19
PPh_3	100	88:12
P(OPh)$_3$	100	92:2
P[OC_6H_3(Bu-*t*)$_2$-2,6]$_3$	70	80:20
P(OEt)$_3$	62	86:14
P(pyrrolyl-*N*)$_3$	100	81:19

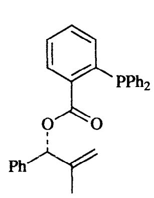
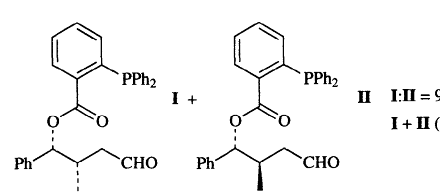
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Rh(acac)(CO)$_2$, P(OPh)$_3$, P/Rh = 4, PhMe, CO/H_2 (1/1, 20 atm), 90°, 24 h	 I + II I:II = 92:8 I + II (98)	743

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

A. Phosphorus Compounds (*Continued*)

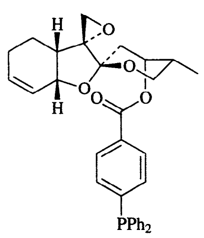
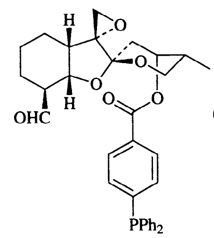
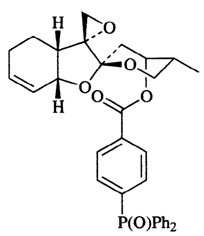
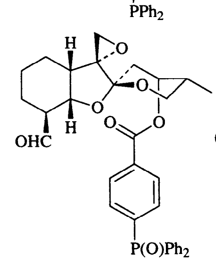
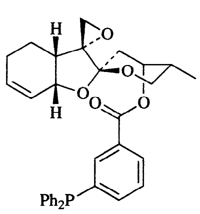
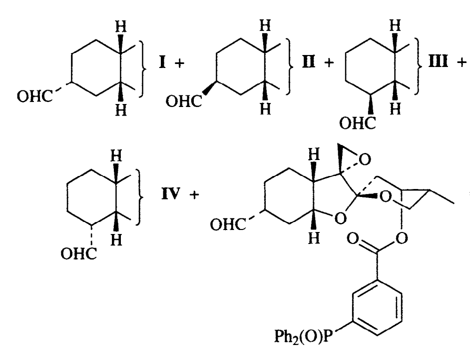
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{33} 	$[Rh(COD)(OAc)]_2$, C_6H_6, 85°, 3 h, CO/H_2 (1/1, 620 psi)	 (8) + starting material (84)	833, 292
	$[Rh(COD)(OAc)]_2$, C_6H_6, 85°, 3 h, CO/H_2 (1/1, 640 psi)	 (49)	833, 292
	$[Rh(COD)(OAc)]_2$, C_6H_6, 85°, 3 h, CO/H_2 (1/1, 660 psi)	 I:II:III:IV = 7.7:1:1:0.3, (74)	833, 292

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

B. Sulfur Compounds

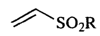
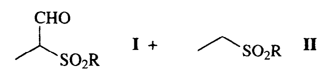
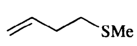
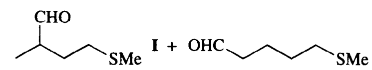
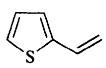
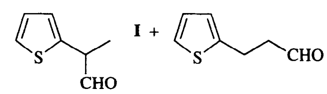
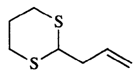
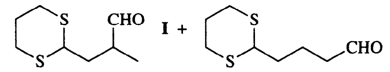
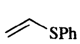
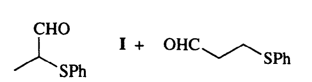
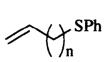
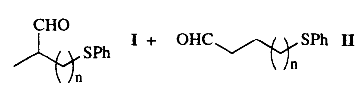
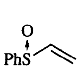
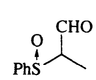
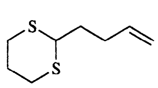
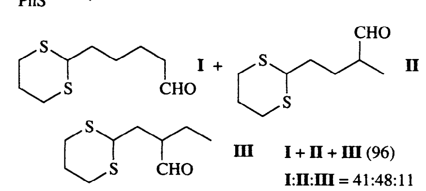
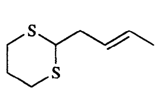
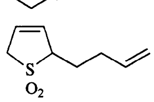
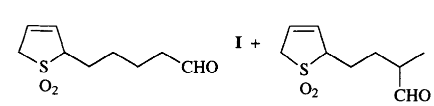
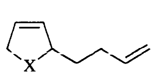
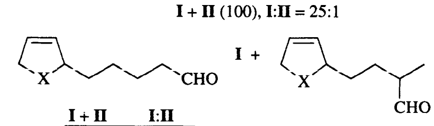
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	Rh(COD)BPh_4, DPPB, L/Rh = 2, CH_2Cl_2, CO/H_2 (1/1, 600 psi), 75°		371
R		I / II	
Me		(98) / (0)	
Et		(98) / (0)	
Ph		(83) / (17)	
$C_{10}H_7$-2		(83) / (17)	
C_5 	$Rh_4(CO)_{12}$, C_6H_6, 60°, 22 h, CO/H_2 (1/1, 500 psi)	 I + II (82) I:II = 76:24	367
	$[Rh(OAc)_2]_2$, PPh_3, 70°, 5 h, CO/H_2 (1/1, 400 psi)	I + II (51), I:II = 40:60	367
C_6 	$HRh(CO)(PPh_3)_3$, PhMe, 35°, 48 h, CO/H_2 (1/1, 80 bar)	 I + II (100) I:II = 19.5:1	370
C_7 	$Rh(CO)_2$(acac), BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 I + II (65), I:II = 1:1.8	135
	$Rh_4(CO)_{12}$, CO/H_2 (500 psi), C_6H_6, 50°, 22 h	I + II (100), I:II = 84:16	367
	$[Rh(OAc)_2]_2$, CO/H_2 (1000 psi), 100°, 22 h	I + II (88), I:II = 75:25	367
	$[Rh(OAc)_2]_2$, PPh_3, 100°, 5 h, CO/H_2 (400 psi)	I + II (92), I:II = 46:54	367
	$(CO)_4W(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)$, C_6H_6, CO/H_2 (1/1, 380 psi), 50°, 20 h	I + II (76), I:II = 53:47	372
C_8 	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	 I + II (71) I:II = 97:3	368
	$HRh(CO)(PPh_3)_3$, PhMe, 35°, 48 h, CO/H_2 (1/1, 80 bar)		370
		n / I + II / I:II	
		0 / (100) / 17:1	
		1 / (75) / 2:1	
		2 / (64) / 2:3	
		3 / (38) / 1:2	
	Rh(COD)BPh_4, DPPB, L/Rh = 4, CH_2Cl_2, CO/H_2 (1/1, 600 psi), 75°, 2 h	 (50)	371
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 500 psi), C_6H_6, 50°, 22 h	 I + II + III (96) I:II:III = 41:48:11	367
	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 800 psi), C_6H_6, 120°, 22 h	I + II + III (30), I:II:III = 2:29:69	367
	$RhH(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/2, 1 atm), rt, 4 d	 I + II (100), I:II = 25:1	369
	$RhH(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/2, 1 atm), rt, 4-5 d		369
X		I + II / I:II	
SO		(—) / 4:1	
S		(—) / 3:1	

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

B. Sulfur Compounds (*Continued*)

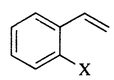
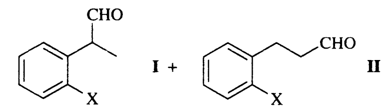
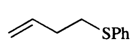
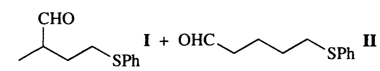
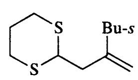
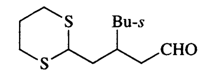
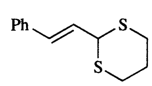
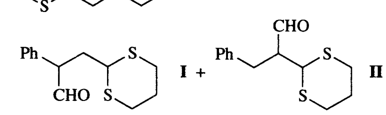
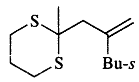
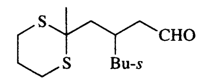
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	$HRh(CO)(PPh_3)_3$, PhMe, 35°, 48 h, CO/H_2 (1/1, 80 bar)	 I + II	370
X: SMe		I + II (100), I:II 19:1	
X: SBu-*t*		I + II (76), I:II 6:1	
X: H		I + II (90), I:II 12:1	
C_{10} 	$Rh_4(CO)_{12}$, CO/H_2 (1/1, 500 psi), 50°, 22 h	 I + II; **I + II** (86) **I:II** = 57:43	367
	$[Rh(OAc)_2]_2$, CO/H_2 (1/1, 800 psi), 100°, 22 h	**I + II** (29), **I:II** = 50:50	367
	$[Rh(OAc)_2]_2$, PPh_3, CO/H_2 (1/1, 400 psi), EtOAc, 70°, 5 h	**I + II** (100), **I:II** = 34:66	367
C_{11} 	$RhH(CO)(PPh_3)_3$, C_6H_6, 100°, CO/H_2 (1/1, 100 atm), 30 h	 (70)	373, 834
C_{12} 	$HRh(CO)(PPh_3)_3$, 5 PPh_3, C_6H_6, 100°, CO/H_2 (1/1, 1000 psi), 92 h	 I + II; **I + II** (70) **I:II** = 90:10	367
	$[Rh(OAc)_2]_2$, 2 PPh_3, 100°, 92 h, CO/H_2 (1/1, 1000 psi)	**I + II** (90), **I:II** = 90:10	367
	$HRh(CO)(PPh_3)_3$, C_6H_6, 130°, 48 h, CO/H_2 (1/1, 100 atm)	 (65)	374

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

C. Silicon Compounds

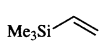
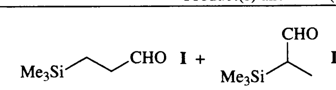
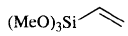
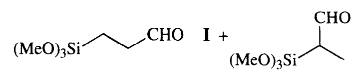
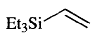
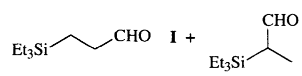
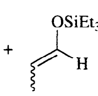
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	Rh(COD)BPh_4, C_6H_6, 100°, 1.5 h, CO (65 psi), H_2 (135 psi)	 I + II; **I + II** (20) **I:II** = 30:70	118
	$RhH(CO)(PPh_3)_3$, C_6H_6, 80°, 3 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (98), **I:II** = 54:46	375
	$RhH(PPh_3)_4$, C_6H_6, 80°, 2 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (99), **I:II** = 52:48	375
	$Rh_6(CO)_{16}$, C_6H_6, 100°, 8 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (85), **I:II** = 51:49	375
	$[Rh(CO)_2Cl]_2$, C_6H_6, 100°, 3 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (86), **I:II** = 50:50	375
	$RhCl(PPh_3)_3$, C_6H_6, 100°, 5 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (93), **I:II** = 56:44	375
	$RhH(CO)(PPh_3)_3$, PPh_3, L/Rh = 80, C_6H_6, 80°, 4 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (88), **I:II** = 95:5	375
	$Rh_6(CO)_{16}$, PPh_3, L/Rh = 50, C_6H_6, 80°, 3 h, CO/H_2 (1/1, 80 kg/cm^2)	**I + II** (85), **I:II** = 100:0	375
	$Co_2(CO)_8$, C_6H_6, 120°, 8 h, CO/H_2 (1/1, 120 kg/cm^2)	**I** (73) + $EtSiMe_3$ (1)	375
	$PtCl_2(PPh_3)_2$, C_6H_6, 100°, 6 h, CO/H_2 (1/1, 120 kg/cm^2)	**I** (73) + $EtSiMe_3$ (2)	375
	$Ru_3(CO)_{12}$, C_6H_6, 110°, 6 h, CO/H_2 (1/1, 100 kg/cm^2)	(**I + II**) (73) + $EtSiMe_3$ (4) **I:II** = 86:14	375
	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	**I + II** (42), **I:II** = 100:0	368

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

C. Silicon Compounds (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	CO/H_2 (1/1, 500 psi), 75°		377

Catalyst	Solvent	Time (h)	I:II:1,3-Si shifted	Yield
Rh-clay	C_6H_6	36	96:4:0	(95)
Rh-clay	PhMe	36	95:5:0	(88)
$[Rh(COD)Cl]_2$	C_6H_6	36	42:44:14	(76)
$[Rh(COD)Cl]_2$ Na^+-clay	C_6H_6	36	62:23:15	(91)
Na^+-clay	C_6H_6	48	—	(0)
Rh-clay calcined	C_6H_6	48	100:0:0	(11)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 $(MeO)_3Si$	$RhH(CO)(PPh_3)_3$, C_6H_6, 80°, 6 h, CO/H_2 (1/1, 80 kg/cm^2)	 I + II, I + II (83), I:II = 52:48	375
	$Co_2(CO)_8$, C_6H_6, 120°, 6 h, CO/H_2 (1/1, 100 kg/cm^2)	I + II (63), I:II = 62:38	375
	Rh-clay, CO/H_2 (1/1, 500 psi), C_6H_6, 75°, 24 h	I + II (89), I:II = 8:92	377
C_8  Et_3Si	$Ir(COD)BPh_4$, $CHCl_3$, 100°, 9 h, CO/H_2 (7/1, 800 psi)	 I + II, I + II (73), I:II = 94:6	118
	$[Ir(COD)_2]BF_4$, C_6H_6, 100°, 3 h, CO/H_2 (7/1, 800 psi)	I + II + $SiEt_4$ (III) I + II (60), I:II = 97:3; III (12)	118
	CO (65 psi), H_2 (135 psi), 100°	I + II +  IV	118

Catalyst	Additive (equiv)	Solvent	Time (h)	I:II	I + II	IV
$Rh(COD)BPh_4$	none	C_6H_6	1.5	65:35	(34)	(6)
$Rh(COD)BPh_4$	none	C_6H_6	4	65:35	(66)	(—)
$Rh(COD)BPh_4$	none	PhMe	1.5	66:34	(53)	(8)
$Rh(COD)BPh_4$	none	$PhCF_3$	1.5	72:28	(53)	(11)
$Rh(COD)BPh_4$	none	$CHCl_3$	1.5	95:5	(38)	(20)
$Rh(COD)BPh_4$	PPh_3 (1)	C_6H_6	1.5	80:20	(91)	(—)
$Rh(COD)BPh_4$	PPh_3 (2)	C_6H_6	1.5	93:7	(97)	(—)
$[Rh(COD)_2]BF_4$	none	C_6H_6	1.5	67:33	(40)	(6)
$[Rh(COD)_2]BF_4$	none	C_6H_6	3	65:35	(50)	(3)
$[Rh(COD)_2]BF_4$	none	PhMe	1.5	71:29	(31)	(6)
$[Rh(COD)_2]BF_4$	none	$PhCF_3$	1.5	81:19	(17)	(—)
$[Rh(COD)_2]BF_4$	none	$CHCl_3$	3	NR	(0)	(0)
$[Rh(COD)_2]BF_4$	PPh_3 (1)	C_6H_6	1.5	78:22	(93)	(—)

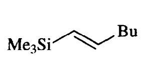
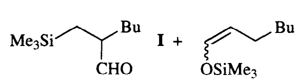
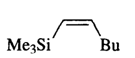
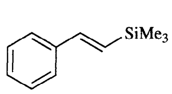
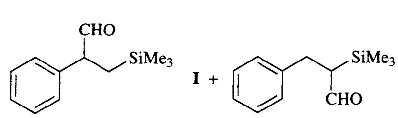
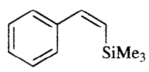
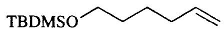
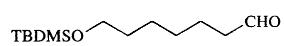
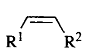
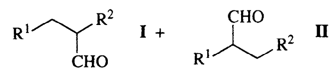
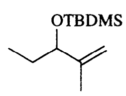
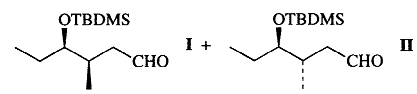
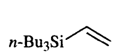
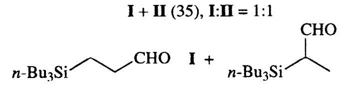
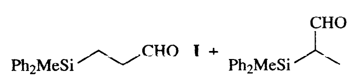
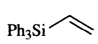
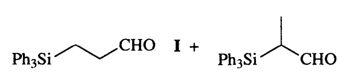
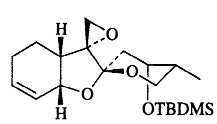
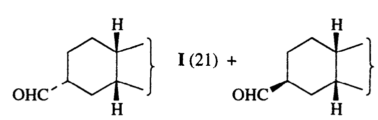
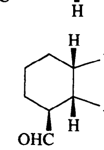
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$IrCl_3$, $AgBF_4$, $C_6H_6/CHCl_3$, 100°, 3 h, CO/H_2 (7/1, 800 psi)	I + II (59), I:II = 98:2; III (16)	118
	$[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]BPh_4$, 100°, 3 h	I + II + III (—), I:II:III = 59:18:23	118
	Rh-clay, CO/H_2 (1/1, 500 psi), C_6H_6, 75°, 36 h	I (98)	377
	Rh-clay, CO/H_2 (1/1, 500 psi), PhMe, 75°, 36 h	I (93)	377
C_9 	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, C_6H_6, CO/H_2 (1/1, 400 psi), 50°, 20 h	 I + II, I + II (79), I:II = 50:50	376
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, C_6H_6, CO/H_2 (1/1, 400 psi), 50°, 20 h	I + II (81), I:II = 50:50	376
C_{11} 	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, C_6H_6, CO/H_2 (1/1, 400 psi), 50°, 20 h	 I + II, I + II (86), I:II >98:2	315, 376

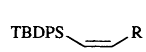
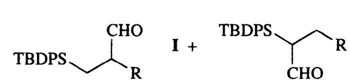
TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

C. Silicon Compounds (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, C_6H_6, CO/H_2 (1/1, 400 psi), 50°, 20 h	**I** + **II** (80), **I**:**II** >98:2	376
C_{12} 	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 (86) n:iso > 40:1	135
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, C_6H_6, CO/H_2 (1/1, 400 psi)	 **I** + **II**	376

Temp.	Time (h)	R^1	R^2	I + II	I:II
90°	20	TBDMS	Bu	(87)	70:30
65°	90	Ph_3Si	Bu	(69)	90:10
65°	90	Ph_3Si	Me	(82)	90:10
80°	90	TBDPS	Bu	(80)	96:4

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Rh(acac)(CO)_2$, $P(OPh)_3$, P/Rh = 4, PhMe, CO/H_2 (1/1, 20 bar), 80°, 48 h	 **I** + **II** **I** + **II** (35), **I**:**II** = 1:1	743
C_{14} 	$RhH(CO)(PPh_3)_3$, C_6H_6, 90°, CO/H_2 (1/1, 80 kg/cm^2)	 **I** + **II** **I** + **II** (100) **I**:**II** = 85:15	375
C_{15} 	$RhH(CO)(PPh_3)_3$, C_6H_6, 90°, CO/H_2 (1/1, 80 kg/cm^2)	 **I** + **II** **I** + **II** (91) **I**:**II** = 90:10	375
C_{20} 	$Rh(COD)BPh_4$, C_6H_6, 100°, CO (65 psi), H_2 (135 psi)	 **I** + **II** **I** + **II** (55) **I**:**II** = 95:5	118
	Rh/C (5%), DPPP, CO (8.5 atm), HCO_2H, DME, 100-105°, 18-24 h	**I** + **II** (92), **I**:**II** = 83:17	368
	Rh-clay, CO/H_2 (1/1, 500 psi), C_6H_6, 75°, 18 h	**I** (99)	377
	$[Rh(COD)(OAc)]_2$, CO/H_2 (1/1, 560 psi), C_6H_6, 76°, 3.25 h	 **I** (21) + **II** (20) +  **III** (12)	833, 292, 835
	$[Rh(COD)(OAc)]_2$, $P(OC_6H_4Bu\text{-}t\text{-}2)_3$, L/Rh = 20, CO/H_2 (1/1, 660 psi), C_6H_6, 77°, 75 min	**I** (5) + **II** (15) + **III** (54)	833

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, C_6H_6, CO/H_2 (1/1, 400 psi)	 **I** + **II**	315, 375

R	Time (h)	Temp.	I:II	I + II
CH(OH)Me	66	80°	>98:2	(83)
CH(OMe)Me	20	80°	>98:2	(17)
Bu	94	80°	94:4	(80)
CH_2OSiMe_3	20	70°	>98:2	(70)
CH(OH)Pr	90	80°	>98:2	(51)
CH(OH)Ph	66	80°	>98:2	(33)

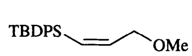
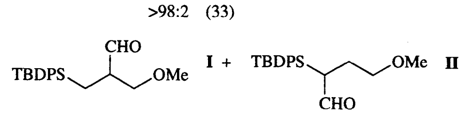
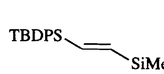
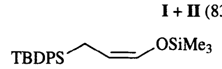
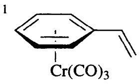
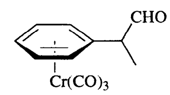
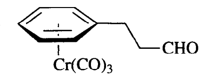
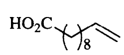
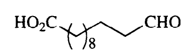
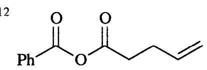
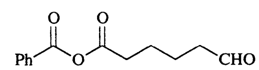
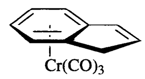
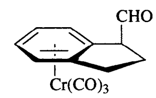
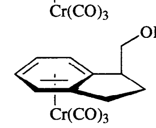
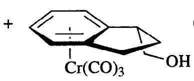
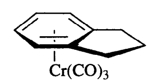
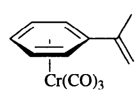
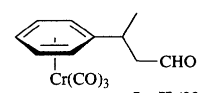
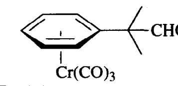
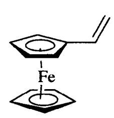
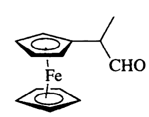
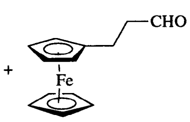
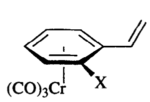
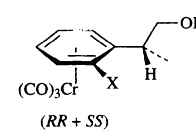
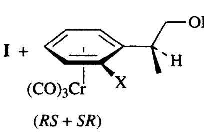
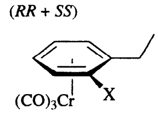
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, 50°, CO/H_2 (1/1, 400 psi), Et_3N, C_6H_6, 20 h	 **I** + **II** **I** + **II** (83), **I**:**II** = 97:3	315, 375
C_{21} 	$HRh(CO)(PPh_3)_3$, PPh_3, C_6H_6, CO/H_2 (1/1, 400 psi), 80°, 66 h	 (60)	315

TABLE IX. HYDROFORMYLATION OF OTHER FUNCTIONALLY SUBSTITUTED OLEFINS (*Continued*)

D. Other Compounds

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, CO/H_2 (400 psi), 40°, 20 h	 I +  II I + II (96), I:II > 98:2	387
	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 (68) n:iso > 40:1	135
C_{12} 	$Rh(CO)_2(acac)$, BIPHEPHOS, THF, CO/H_2 (1/1, 70 psi), 60°	 (73) n:iso > 40:1	135
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, CO/H_2 (400 psi), 50°	 (~ 100)	387
	1. $HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 28 bar), 50°, PhMe, 72 h 2. $LiAlH_4$, rt, 1 h	 (34) +  (20) +  (20)	388
	Catalyst, CO/H_2, 100°	 I +  II I + II (33), I:II = 1:1	387
	$Rh_4(CO)_{12}$, hexane, 100°, 4.5 h, CO/H_2 (1/1, 80 bar)	 (80) +  (20)	385
	1. $HRh(CO)(PPh_3)_3$, CO/H_2 (1/1, 28 bar), 50°, PhMe, 72 h 2. $LiAlH_4$, rt, 1 h	 I +  II +  III	388

X	I	II	III
Me	(69)	(8)	(20)
OMe	(72)	(8)	(16)
OPr-*i*	(56)	(8)	(19)

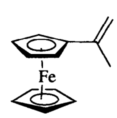
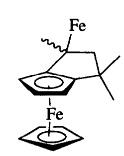
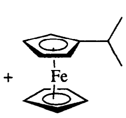
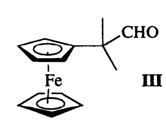
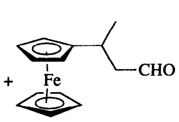
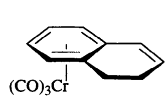
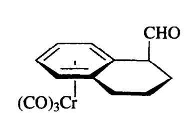
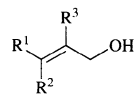
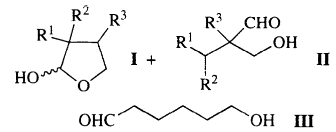
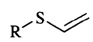
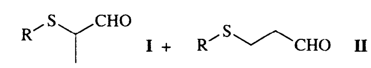
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	$[Rh(NBD)Cl]_2$, PPh_3, L/Rh = 2, CO/H_2 (1/1, 160 bar), PhMe, 100°, 7 h	 I (—) +  II (—) +  III (—) +  IV (—) I : II : III : IV = 1:32:6:62	386
	$HRh(CO)(PPh_3)_3$, PPh_3, L/Rh = 50, CO/H_2 (400 psi), 50°	 (ca. 100)	387

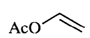
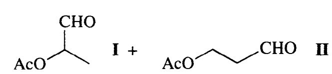
TABLE X. ASYMMETRIC HYDROFORMYLATION

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_3 	(*R*,*S*)-BINAPHOS	$Rh(acac)(CO)_2$, L/Rh = 4, CO/H_2 (1/1, 30 atm), PhH, 60 °, 30 h		836

R^1	R^2	R^3	Conv. (%)	I:II:III	I (%ee)	II (%ee)
H	H	H	>99	90:10:0	—	16
Me	H	H	51	26:74:0	27 (*R*)	ND
H	Et	H	>99	56:18:12	11 (–)	ND
H	H	Me	54	>99:<1:0	12 (*S*)	—

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_4 	(*R*,*S*)-BINAPHOS	$Rh(acac)(CO)_2$, PhH, CO/H_2 (1/1, 100 atm), L/Rh = 4-4.4		837

R	Temp.	Time (h)	Conv. (%)	I:II	I (%ee)
Et	50°	96	60	86:14	(66), —
Pr-*i*	50°	48	>99	92:8	(72), —
Bu-*t*	40°	27	70	96:4	(89), —
C_6H_{11}	40°	36	32	91:9	(72), —
Ph	40°	34	97	98:2	(76), —
p-MeC_6H_4	40°	20	96	96:4	(74), — *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, L/Rh = 4, CO/H_2 (1/1, 100 atm), C_6H_6		34, 113

Chiral Ligand	Temp.	Time (h)	Conv. (%)	I:II	I (%ee)
(*R*,*S*)-BINAPHOS	60°	36	>99	86:14	92 (*S*)
(*R*,*R*)-BINAPHOS	50°	37	46	92:8	73 (*S*)
(*R*,*S*)-3,5-Me_2-BINAPHOS	60°	36	72	85:15	90 (*S*)

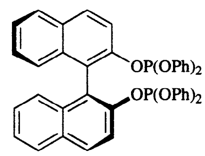
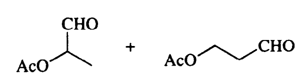
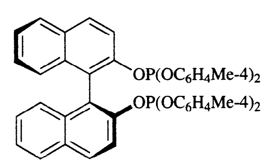
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), L/Rh = 1.0, 30°, 48 h	 I (77), 12 (*R*) + II (3)	35
	"	$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), L/Rh = 1.0, 30°, 40 h	I (27), 45 (*R*) + II (2)	35
	"	$[Rh(CO)_2Cl]_2$, C_6H_6, H_2/CO (1/1, 70 atm), L/Rh = 2.5, 60°, 40 h	I (86), 41 (*R*) + II (5)	35
	"	$[Rh(CO)_2Cl]_2$, C_6H_6, H_2/CO (1/1, 70 atm), L/Rh = 2.5, 60°, 40 h	I (75), 34 (*R*) + II (6)	35
	(*R*,*R*)-(–)-DIOP	$Rh_2(\mu\text{-}OMe)_2(COD)_2$, CO/H_2 (1/1, 20 bar), 20 h $(MeO)_2CMe_2$, 70°	I (80), 25 (*R*) + II (20)	663
	(*R*,*R*)-(–)-DIOP	$[RhCl(CO)_2]_2$, C_6H_6, CO/H_2 (49/51, 95.2 atm) 120°, 18 h	I (61), 16 (*S*) + II (—)	838
	(*R*)-$C_5Ph_4O_2CCH(OMe)Ph$	$Rh(\eta^5\text{-Chiral Ligand})(CO)_2$, CO/H_2 (1/1, 100 atm), 50°, 2 d	I (—), 3	839
		$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), L/Rh = 1.5, 40°, 40 h	I (76), 45 (*R*) + II (6)	35

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

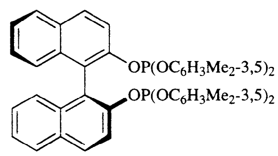
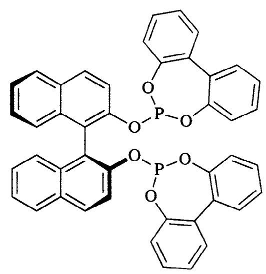
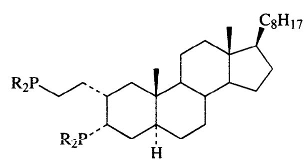
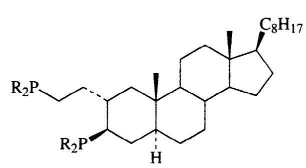
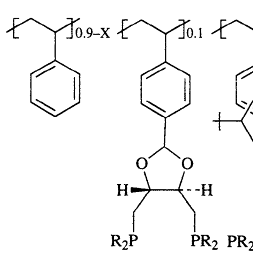
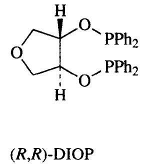
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), L/Rh = 2.5, 30°, 40 h	**I** (11), 45 (*R*) + **II** (1)	35
		$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), L/Rh = 2.5, 60°, 40 h	**I** (11), 14 (*R*) + **II** (1)	35
	(–)-BPPM	$PtCl_2(BPPM)/SnCl_2$, CO/H_2 (1/1, 2700 psi), C_6H_6, 60°, 40 h	**I** (—), 82 (*S*) + **II** (—), **I**:**II** = 3:7	406
		$[RhCl(CO)_2]_2$, C_6H_6, CO/H_2 (49/51, 95.2 atm) 120°, 18 h		
	R = Ph		**I** (29), 1 (*S*) + **II** (—)	838
	R = DBP		**I** (46), 6 (*R*) + **II** (—)	838
		$[RhCl(CO)_2]_2$, C_6H_6, CO/H_2 (49/51, 95.2 atm) 120°, 18 h		
	R = Ph		**I** (12), 6 (*R*) + **II** (—)	838
	R = DBP		**I** (58), 10 (*S*) + **II** (—)	838
	 PR_2 = DBP	Pt(Chiral ligand)Cl_2, $SnCl_2$, C_6H_6, 60°, CO/H_2 (1/1, 2700 psi) Time / X		
		42 h / 0	**I** (—), 58 (*S*) + **II** (—), **I**:**II** = 1:1	411, 412
		100 h / 0.1	**I** (—), 57 (*S*) + **II** (—), **I**:**II** = 1:1	411, 412
	(–)-DBP-DIOP	$Pt(DBP\text{-}DIOP)Cl_2$, $SnCl_2$, C_6H_6, 60°, 42 h, CO/H_2 (1/1, 2700 psi)	**I** (—), 61 (*S*) + **II** (—), **I**:**II** = 5.2:1	411, 412
	(–)-DIOP	$[RhCl(CO)_2]_2$, L/Rh = 2, CO/H_2 (1/1, 100 atm), 70°, 42 h	**I** (12), 23 + **II** (1)	840
		$[RhCl(CO)_2]_2$, L/Rh = 10, CO/H_2 (1/1, 9.6 MPa), C_6H_6, 120°, 19 h	**I** (71), 6 + **II** (<1)	841
	(*R*,*R*)-DIOP	Rh(COD)(acac), L/Rh = 4, 70°, CO/H_2 (44/56, 250 psi)	**I** (—), 40 (*S*) + **II** (—)	842

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

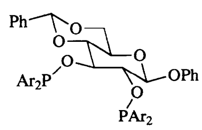
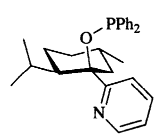
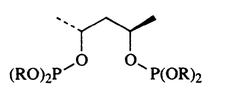
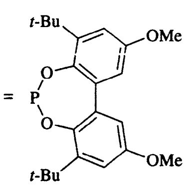
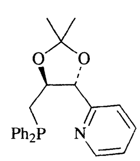
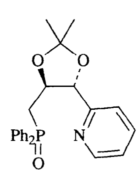
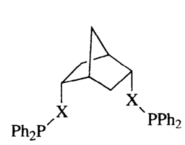
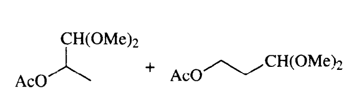
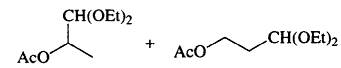
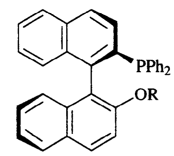
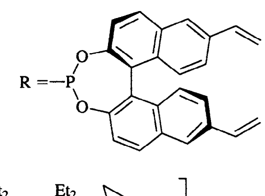
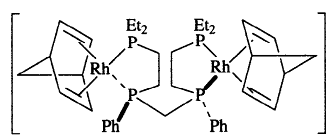
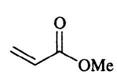
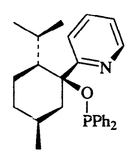
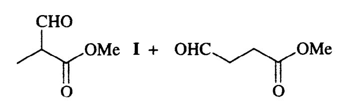
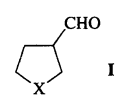
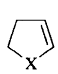
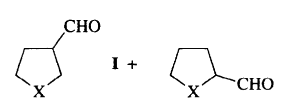
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*R*)-1-NA-DIOP	Rh(COD)(acac), L/Rh = 3, 80°, CO/H_2 (44/56, 250 psi)	**I** (—), 6 (*S*) + **II** (—)	842
	(*R*,*R*)-2-NA-DIOP	"	**I** (—), 39 (*S*) + **II** (—)	842
	(*R*,*R*)-*m*-CF_3DIOP	Rh(COD)(acac), L/Rh = 3, 50°, CO/H_2 (44/56, 150 psi)	**I** (—), 42 (*S*) + **II** (—)	842
	 Ar = 3,5-$(CF_3)_2C_6H_3$	Rh(COD)(chiral ligand)BF_4, CO/H_2 (1600 psi), hexane	**I** (—), 14 + **II** (—), **I**:**II** = 92:8	843
		[Rh(CO)(PPh_3)(L^*)]ClO_4, CO/H_2 (1/1, 60 atm), C_6H_6, 50°, 16 h	**I** (—), 12 (*R*)	844
	 $P(OR)_2$ = 	Rh(acac)$(CO)_2$, L^*/Rh = 4, PhMe, 50°, CO/H_2 (1/1, 130 psi)	**I** (—), 50 (*S*)	38
		Rh(acac)$(CO)_2$, C_6H_6, L^*/Rh = 2.5, 80°, 6 h, CO/H_2 (1/1, 80 atm)	**I** + **II** (90), —, **I**:**II** = 96:4	714
		Rh(acac)$(CO)_2$, C_6H_6, L^*/Rh = 2.5, 80°, 1 h, CO/H_2 (1/1, 80 atm)	**I** + **II** (95), —, **I**:**II** = 97:3	714
	(*R*,*R*)-DIPHOL	Rh(COD)(acac), L/Rh = 6, 80°, CO/H_2 (44/56, 500 psi)	**I** (—), 51 (*R*) + **II** (—)	842
	(*R*,*R*)-DMPP-DIOP	Rh(COD)(acac), L/Rh = 6, 70°, CO/H_2 (44/56, 250 psi)	**I** (—), 18 (*R*) + **II** (—)	842
	(*R*,*R*)-DIPH-DIOP	Rh(COD)(acac), L/Rh = 4, 80°, CO/H_2 (44/56, 250 psi)	**I** (—), 29 (*S*) + **II** (—)	842
		Rh$(CO)_2$(acac), C_6H_6, H_2/CO (50 atm), 40°, 20 h	X CH_2 **I** (—, —) O **I** (—, —)	845
	(−)-DIOP	$Rh_2(\mu\text{-}OMe)_2(COD)_2$, PPTS, $(MeO)_2CMe_2$, CO/H_2 (1/1, 20 bar), 24 h, 70°	 (96), 29 + (4)	663

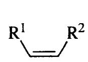
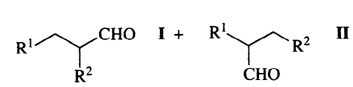
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(-)-BPPM	$PtCl_2(BPPM)/SnCl_2$, CO/H_2 (1/1, 2700 psi), $HC(OEt)_3$, 60°, 240 h	 I (—), >98 *S* I:II = 1.5:1 II (—)	406
	 	Rh(acac)L copolymerized with divinylbenzenes, CO/H_2 (1/1, 100 atm), C_6H_6, 60°, 12 h	I (—), 93 *S*, I:II = 90:10	416
	 $\cdot(BF_4)_2$	CO/H_2 (1/1, 6 atm), 90°	I (—) 84, I:II = 80:20, TOF = 125 h^{-1}	846, 847
		$[Rh(CO)(PPh_3)(-)L]ClO_4$, CO/H_2 (1/1, 60 atm), C_6H_6, 60°, 16 h	 I (—), 92 *R*, I:II = 97:3	848
		$Rh(acac)(CO)_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6		849

X		Temp.	Time (h)	I
O	(*R,S*)-BINAPHOS	40°	48	(63), 62 *R*
O	(*R,S*)-3,3'-Me_2-BINAPHOS	40°	41	(93), 63 *R*
NBoc	(*R,S*)-BINAPHOS	60°	72	(98), 47 *R*
NBoc	(*R,S*)-3,3'-Me_2-BINAPHOS	60°	72	(99), 73 *R*
NAc	(*R,S*)-BINAPHOS	60°	71	(92), 66 —
NAc	(*R,S*)-3,3'-Me_2-BINAPHOS	60°	72	(97), 65 —

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, L/Rh=4, H_2/CO (1/1, 100 atm), C_6H_6, 60°		849

X		Time (h)	I + II	I:II	I (%ee)	II (%ee)
O	(*R,S*)-3,3'-Me_2BINAPHOS	60	(77)	50:50	38 *S*	ND
NBoc	(*R,S*)-BINAPHOS	72	(>99)	33:67	71 *S*	97 *S*
NBoc	(*R,S*)-3,3'-Me_2BINAPHOS	72	(>99)	37:63	22 *S*	88 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm)		414

Chiral Ligand	Conditions	R^1	R^2	I	II
(*S, R*)-BIPHEMPHOS	60°, 40 h	H	OAc	(55), 90 *R*	(10)
"	60°, 40 h	Me	Me	(—), 85 *R*	
"	30°, 40 h	H	*n*-Bu	(12), 85 *S*	(39)
"	60°, 42 h	H	Ph	(90), 94 *S*	(10)
(*S, R*)-BINAPHOS	60°, 40 h	H	OAc	(56), 92 *R*	(9)
"	60°, 40 h	Me	Me	(—), 82 *R*	
"	30°, 40 h	H	*n*-Bu	(12), 75 *S*	(39)
"	60°, 42 h	H	Ph	(88), 94 *S*	(12)

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

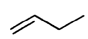
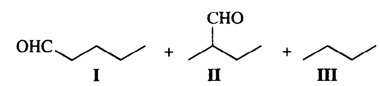
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		(Chiral Ligand)$PtCl_2$/ $SnCl_2$, C_6H_6, 80°, CO/H_2 (7/15, 220 atm)		407
		Time (h)	Conv. (%) I : II : III %ee	
	(*R,R*)-BCO-DPP	2.0 h	85 6 : 4 : 1 7.7 *S*	
	(*R,R*)-BCO-DBP	4.0 h	34 43 : 7 : 8 67.1 *S*	
	(*R,R*)-DIOP-DBP	5.5 h	95 17 : 3 : 20 39.0 *S*	
	(*R,R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 22 h	**I** (—) + **II** (—), 3.1 *R*, **I**:**II** = 71:29	850
	(*R,R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 4 h	**I** (—) + **II** (—), 3.5 *R*, **I**:**II** = 59:41	850
	(*S,S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, 6 h, CO/H_2 (1/1, 80 atm), 100°	**I** + **II** (35), 7.1 *R*, **I**:**II** = 54:46	130
	(*S,S*)-CHIRAPHOS	$Pt(CHIRAPHOS)(SnCl_3)Cl$, CO/H_2 (1/1, 80 atm), 100°	**I** (—) + **II** (—), 40 *S*, **I**:**II** = 91:9	130
	(*R,R*)-DIOP	$RhH(CO)(PPh_3)_3$, L/Rh = 4, 95°, 3 h, CO/H_2 (1/1, 80 atm)	**I** + **II** (70), 5.9 *R*, **I**:**II** = 92:8	130
	(*R,R*)-DIOP	$Pt(DIOP)(SnCl_3)Cl$, 100°, CO/H_2 (1/1, 80 atm)	**I** (—) + **II** (—), 24.8 *R*, **I**:**II** = 94:6	130
	(*R,R*)-DIOP	$Pt(DIOP)(SnCl_3)Cl$, 60°, CO/H_2 (1/1, 80 atm), 6.5 h	**I** + **II** (32), 46.7 *R*, **I**:**II** = 96:4	130
	(+)-DICOL	$HRh(CO)(PPh_3)_3$/DICOL (1/3), C_6H_6, 60°, 16 h, CO/H_2 (1/1, 80-90 atm)	**I** (54) + **II** (36), 1 *S*	851
	(–)-DIOCOL	$HRh(CO)(PPh_3)_3$/(–)-DIOCOL (1/1.5), C_6H_6, CO/H_2 (1/1, 80-90 atm), 60°, 65 h	**I** (79) + **II** (12), 3.8 *R*	851
	(–)-DIOP	Pt[(–)-DIOP]Cl_2, $SnCl_2{\cdot}2H_2O$, PhEt, CO/H_2 (1/1, 100 atm), 100°, 1 h	**I** (43) + **II** (7), 2.8 *R*	852
	BDP-DIOP	Pt(BDP-DIOP)Cl_2, $SnCl_2{\cdot}2H_2O$, PhEt, CO/H_2 (1/1, 100 atm), 100°, 3 h	**I** (33) + **II** (18), 12.1 *S*	852
		(Chiral Ligand)$PtCl_2$/ $SnCl_2$, C_6H_6, 80°, CO/H_2 (7/15, 220 atm)		407
		Time	Conv. (%) I : II : III % ee	
	(*R,R*)-BCO-DPP	5.3 h	68 31 : 69 : 1 3.7 *R*	
	(*R,R*)-BCO-DBP	21 h	67 13 : 87 : 2 30.4 *R*	
	(*R,R*)-DIOP-DBP	22 h	40 12 : 88 : — 12.2 *R*	
	(*R,R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 10 h	**I** (—) + **II** (—), 0.1 *S*, **I**:**II** = 5:95	850
	(*R,R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 8 h	**I** (—) + **II** (—), 1.4 *S*, **I**:**II** = 29:71	850
	(*S,S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 100°, 72 h	**II** (55, 18.4 (*S*))	130
	(*S,S*)-CHIRAPHOS	$Pt(CHIRAPHOS)(SnCl_3)Cl$, CO/H_2 (1/1, 80 atm), 100°	**I** (—) + **II** (—, 23.1 (*R*)), **I**:**II** = 28:72	130

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

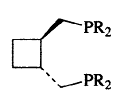
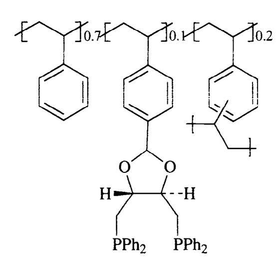
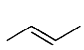
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,R*)-DIOP	$RhH(CO)(PPh_3)_3$, L/Rh = 4, 95°, 22 h, CO/H_2 (1/1, 80 atm)	**II** (30), 8.0 *S*	130
	(*R,R*)-DIOP	$Pt(DIOP)(SnCl_3)Cl$, 100°, CO/H_2 (1/1, 80 atm)	**I** (—) + **II** (—), 7.7 *S*, **I**:**II** = 45:55	130
	DIOP	$RhH(CO)(PPh_3)_3$, L/Rh = 4, 20°, 30 d, CO/H_2 (1/1, 16 psi)	**II** (—), 27	853
	BDP-DIOP	$Pt(BDP\text{-}DIOP)Cl_2$, $SnCl_2{\cdot}2H_2O$, PhEt, CO/H_2 (1/1, 100 atm), 100°, 8 h	**I** (17) + **II** (43), 0.6 *R*	852
	(*R,S*)-BINAPHOS	$Rh(acac)(CO)_2$, C_6H_6, (*R,S*)-BINAPHOS, CO/H_2 (1/1, 100 atm), 60°, 44 h	**II** (—), 82 *S*	36
	 PR_2 = DBP	$[Rh(CO)_3]_4$, L/Rh = 4, CO/H_2 (1/1, 100 atm), PhEt, 120°	**I** (—) + **II** (—), 16.8 *R*	854
	(+)-DICOL	$HRh(CO)(PPh_3)_3$/(+)-DICOL (1/3), C_6H_6, 80°, CO/H_2 (1/1, 80-90 atm)	**II** (91), 0	851
	(–)-DIOCOL	$HRh(CO)(PPh_3)_3$/(–)-DIOCOL (1/1.5), CO/H_2 (1/1, 80-90 atm), 90°, mesitylene	**II** (90), 1 *S*	851
	(–)-DIOP	$Pt[(–)\text{-}DIOP]Cl_2$, $SnCl_2{\cdot}2H_2O$, PhEt, CO/H_2 (1/1, 100 atm), 100°, 3 h	**I** (18) + **II** (22), 9.9 *S*	852
		$HRh(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/1, 45 psi), 25°, 26 d	**II** (—), 28.4	853
		(Chiral Ligand)$PtCl_2$/$SnCl_2$, C_6H_6, 80°, CO/H_2 (7/15, 220 atm)		407
		Time	Conv. (%) — **I** : **II** : **III** — % ee	
	(*R,R*)-BCO-DPP	9.8 h	50 — 25 : 75 : 1 — 1.6 *S*	
	(*R,R*)-BCO-DBP	30 h	65 — 13 : 87 : 3 — 28.9 *R*	
	(*R,R*)-DIOP-DBP	21 h	80 — 13 : 87 : 11 — 3.6 *R*	
	(*R,R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 46 h	**I** (—) + **II** (—), 2.4 *S*, **I**:**II** = 2:98	850
	(*R,R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 24 h	**I** (—) + **II** (—), 2.3 *S*, **I**:**II** = 3:97	850
	(*S,S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 100°, 97 h	**I** + **II** (40), 18.5 *S*, **I**:**II** = 1:99	130

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

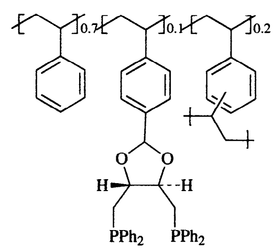
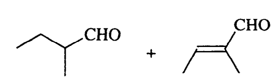
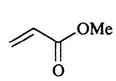
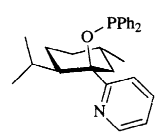
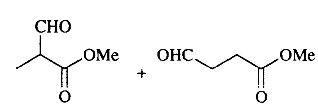
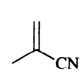
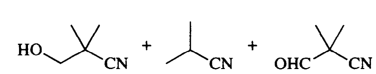
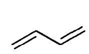
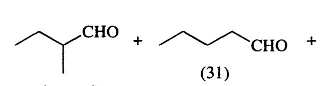
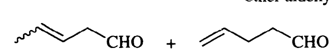
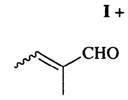
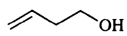
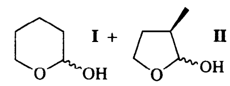
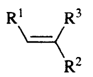
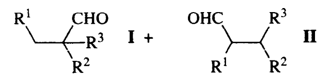
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-CHIRAPHOS	Pt(CHIRAPHOS)($SnCl_3$)Cl, CO/H_2 (1/1, 80 atm), 100°	I (—) + II (—), 8.8 *R*, I:II = 31:69	130
	(*R,R*)-DIOP	RhH(CO)(PPh_3)$_3$, L/Rh = 4, 95°, 22 h, CO/H_2 (1/1, 80 atm)	II (25), 3.2 *S*	130
	(*R,R*)-DIOP	Pt(DIOP)($SnCl_3$)Cl, 100°, CO/H_2 (1/1, 80 atm)	I (—) + II (—), 13.4 *S*, I:II = 49:51	130
		HRh(CO)(PPh_3)$_3$, C_6H_6, CO/H_2 (1/1, 45 psi), 25°, 21 d	II (—), 7.2	853
	(–)-DIOP	Pt[(–)-DIOP]Cl_2, $SnCl_2$·$2H_2O$, PhEt, CO/H_2 (1/1, 100 atm), 100°, 3.5 h	I (30) + II (35), 12.8 *S*	852
	BDP-DIOP	Pt(BDP-DIOP)Cl_2, $SnCl_2$·$2H_2O$, PhEt, CO/H_2 (1/1, 100 atm), 100°, 9 h	I (13) + II (32), 1.8 *R*	852
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, C_6H_6, (*R,S*)-BINAPHOS, CO/H_2 (1/1, 100 atm), 60°, 45 h	II (—), 48 *S*	36
	(–)-DIOP	RhH(CO)(PPh_3)$_3$, 80°, CO/H_2 (1/1, 100 psi), 24 h	 I (—), 0.2 *S* + II (—) I:II = 68:32	855
		[Rh(COD)(L*)]ClO_4, CO/H_2 (1/1, 60 atm), C_6H_6, 60°, 16 h	 I (—), 45 *R* + II (—) I:II = 99:1	844
	"	[Rh(CO)(PPh_3)(L*)]ClO_4, CO/H_2 (1/1, 60 atm), C_6H_6, 60°, 16 h	I (—), 92 *R* + II (—), I:II = 97:3	844
	"	[Rh(CO)(PPh_3)(L*)]ClO_4, CO/H_2 (1/1, 60 atm), C_6H_6, 100°, 16 h	I (—), 53 *R*	844
	(*S,S*)-Chiraphos	[Rh(CO)$_2$Cl]$_2$/(*S,S*)-Chiraphos/Et_3N (1/4/20), 130°, 63 h, CO/H_2 (1/1, 160 atm), PhMe	 (51) + (38) + (<1)	762
	(–)-DIOP	HRh(CO)(PPh_3)$_3$/(–)-DIOP (1/2), C_6H_6, 95°, CO/H_2 (1/1, 90 atm), 60 h	 (10), <1 *S* + (31) + other aldehydes (41)	856
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, C_6H_6, 30°, H_2/CO (1/1, 100 atm), L/Rh = 4	 I *E/Z* = 76/24 + II; I + II (—); I:II = 94:6	857
	(*R,S*)-BINAPHOS	Rh (acac)(CO)$_2$, C_6H_6, H_2/CO (1/1, 100 atm) L/Rh = 4, 30°	 (100)	413

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, C_6H_6, CO/H_2 (1/1, 30 atm), 60 °	 I + II I (—) + II (—), 73 I:II = 72:8	836
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6, 60°	 I + II	113

R[1]	R[2]	R[3]	I:II	I (%ee)
Et	H	Et	—	79 *S*
Et	Et	H	—	69 *S*
H	Et	H	21:79	83 *R*
H	Pr-*i*	H	8:92	83 *R*

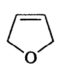
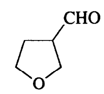
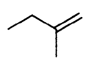
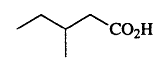
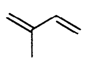
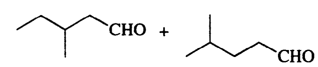
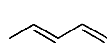
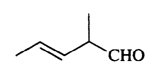
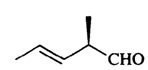
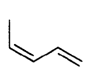
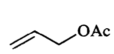
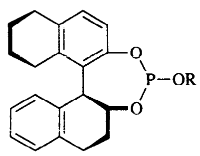
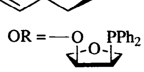
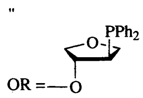
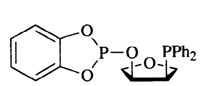
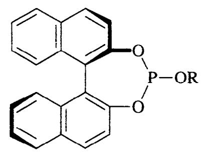
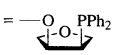
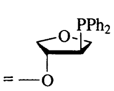
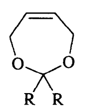
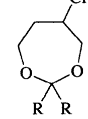
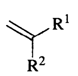
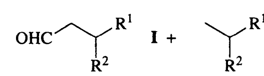
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(+)-DICOL	HRh(CO)(PPh$_3$)$_3$/DICOL (1/3), C_6H_6, 60°, 30 h, CO/H_2 (1/1, 80-90 atm)	 I (90), 0	851
	(–)-DIOCOL	HRh(CO)(PPh$_3$)$_3$/(–)-DIOCOL (1/1.5), C_6H_6, CO/H_2 (1/1, 80-90 atm), 60°, 44 h	I (93), 3.3 *R*	851
C_5 	(–)-DIOP	1. HRh(CO)(PPh$_3$)$_3$/(–)-DIOP (1/2), C_6H_6, 95°, CO/H_2 (1/1, 90 atm), 24 h 2. Ag_2O	 (40), <1 *R*	856
	(–)-DIOP	HRh(CO)(PPh$_3$)$_3$/(–)-DIOP (1/2), C_6H_6, 95°, CO/H_2 (1/1, 90 atm), 160 h	 I (—), 32.3 *S* II I + II (25) other aldehydes (27)	856
	(–)-DIOCOL	HRh(CO)(PPh$_3$)$_3$/(–)-DIOCOL (1/1.5), C_6H_6, CO/H_2 (1/1, 80-90 atm), 80°, 140 h	I (—), 34.2 *S* + II (—) + other aldehydes	851
	(*R,S*)-BINAPHOS	Rh (acac)(CO)$_2$, PhH, H_2/CO (1/1, 100 atm) L/Rh = 4, 30°	 (—), 24	413
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, C_6H_6, H_2/CO (1/1, 100 atm), 30 °, L/Rh = 4	 I (75), 22 *R*	857
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, C_6H_6, H_2/CO (1/1, 100 atm), 30 °, L/Rh = 4	I (88), 20 *R*	857
	 OR = 	Rh(acac)(CO)$_2$, THF CO/H_2 (1/1, 40 atm), L/Rh = 5, 80°	 I + II I (—), 32 (+), I:II = 76:24	858
	" OR = 	Rh(acac)(CO)$_2$, THF CO/H_2 (1/1, 40 atm), L/Rh = 5, 80°	I (—), 44 (+), I:II = 64:36	858
		Rh(acac)(CO)$_2$, THF, CO/H_2 (1/1, 40 atm), L/Rh = 5, 80°	I (—), 1 (+), I:II = 1:1	858

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	 OR = 	Rh(acac)(CO)$_2$, THF CO/H$_2$ (1/1, 40 atm), L/Rh = 5, 80°	I (—), 12 (–), I:II = 72:28	858
	" OR = 	Rh(acac)(CO)$_2$, THF CO/H$_2$ (1/1, 40 atm), L/Rh = 5, 80°	I (—), 14 (+), I:II = 60:40	858
		Rh(acac)(CO)$_2$, L/Rh = 4, H$_2$/CO (1/1, 100 atm), C$_6$H$_6$, 48 h	 I	849

Chiral Ligand	Temp.	R	I
(*R,S*)-BINAPHOS	40°	H	(95), 73 —
(*R,S*)-3,3'-Me$_2$-BINAPHOS	40°	H	(99), 56 —
(*R,S*)-BINAPHOS	60°	Me	(77), 73 *R*
(*R,S*)-3,3'-Me$_2$-BINAPHOS	60°	Me	(98), 69 *R*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,R*)-DIOP	PtCl(SnCl$_3$)(DIOP), CO/H$_2$ (1/1, 80 bar), PhMe, 100°	 I + II	859, 762

Time (h)	R^1	R^2	I	II
45	CO$_2$Me	Me	(83), 37.2 *S*	(16), —
24	Me	CH$_2$CO$_2$Me	(85), 10 *S*	(15), —
21.5	CO$_2$Me	CH$_2$CO$_2$Me	(51), 45.2 *R*	(44), 33.7 *R*
18	CO$_2$Ph	Me	(56), 23.8 *R*	(44), —
27	CO$_2$Me	Ph	(40), 16.3 *R*	(54), 27.2 *S*
15	CO$_2$Ph	CH$_2$CO$_2$Ph	(55), 42.5 *S*	(45), 35.5 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,R*)-DIOP	PtCl(SnCl$_3$)(DIOP), CO/H$_2$ (1/5, 240 bar), PhMe, 50°		859

Time (h)	R^1	R^2	I	II
110	CO$_2$Me	Me	(42), 55.5 *S*	(58)
45	CO$_2$Me	CH$_2$CO$_2$Me	(28), 81.9 *R*	(52), 52.8 *R*
145	CO$_2$Ph	Me	(21), 49.5 *R*	(65)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-BDPP	PtCl(SnCl$_3$)(DBPP), CO/H$_2$ (1/1, 80 bar), PhMe		109

Temp.	Time (h)	R^1	R^2	Conv.	I	II
100°	6.5	Me	CO$_2$Me	61%	(47), 8.2 *S*	(14), —
50°	18	Me	CO$_2$Me	21%	(17), 13.9 *S*	(4), —
100°	12	CH$_2$CO$_2$Me	CO$_2$Me	64%	(49), 26.7 *R*	(15), 44 *R*
50°	70	CH$_2$CO$_2$Me	CO$_2$Me	36%	(29), 39.1 *R*	(7), 58 *R*
100°	4.5	Me	Ph	64%	(51), 1.3 *R*	(13), —
50°	110	Me	Ph	35%	(33), 9.2	(2), —

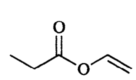
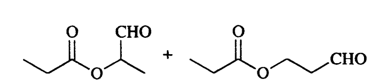
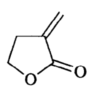
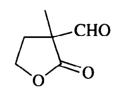
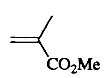
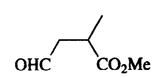
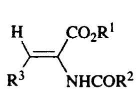
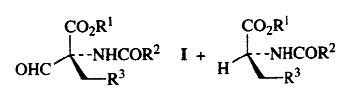
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-DIOP	Rh(NBD)(DIOP)·BPh$_4$, L/Rh = 3, 80°, C$_6$H$_6$, CO/H$_2$ (44/56, 250 psi)	 I (—), 29 *R* + II (—)	842
	(*R,R*)-2-NA-DIOP	Rh(COD)(acac), L/Rh = 3, C$_6$H$_6$, 80°, CO/H$_2$ (44/56, 250 psi)	I (—), 36 *S* + II (—)	842

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*R*)-*m*-CF_3DIOP	Rh(COD)(acac), L/Rh = 3, C_6H_6, 60°, CO/H_2 (44/56, 150 psi)	**I** (—), 33 *S* + **II** (—)	842
	(*R*,*R*)-DIPHOL	Rh(COD)(acac), L/Rh = 4, C_6H_6, 80°, CO/H_2 (44/56, 250 psi)	**I** (—), 32 *R* + **II** (—)	842
	(*R*,*R*)-DIPH-DIOP	Rh(COD)(acac), L/Rh = 3, C_6H_6, 80°, CO/H_2 (44/56, 250 psi)	**I** (—), 18 *S* + **II** (—)	842
	(*R*,*S*)-BINAPHOS	Rh(acac)$(CO)_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, PhH, 60°, 78 h	**I** (—), 90 *S* + **II** (>99), **I**:**II** = 85:15	113
		CO/H_2 (1/1, 600 psi)		756

Chiral Ligand (eq)	Catalyst	Solvent	Temp.	Time (h)	Conv. (%)	Yield (%) GC (Isolated)	%ee
(*R*)-BINAP (1)	Rh(COD)(η^6-$PhBPh_3$)	CH_2Cl_2	60°	42	100	13 (9)	2
(*R*)-BINAP (2)	Rh(COD)(η^6-$PhBPh_3$)	CH_2Cl_2	60°	42	5	5 (4)	17
(*R*)-BINAP (2)	Rh(COD)(η^6-$PhBPh_3$)	CH_2Cl_2	100°	48	73	69 (58)	18
(*S*,*S*)-CHIRAPHOS (2)	Rh(COD)(η^6-$PhBPh_3$)	CH_2Cl_2	100°	66	100	10 (9)	0
(*R*)-BINAP (2)	[Rh(COD)(DPPB)]BF_4	CH_2Cl_2	100°	66	95	80 (68)	4
(*R*)-BINAP (2)	[Rh(COD)(DPPB)]BF_4	CH_2Cl_2	100°	66	92	65 (60)	4
(*S*,*S*)-CHIRAPHOS (2)	$[Rh(COD)Cl]_2$	CH_2Cl_2	100°	66	9	6 (5)	20
(*R*)-BINAP (2)	[Rh(1,5-hd)(phen)]Cl	CH_2Cl_2	100°	66	37	32 (29)	21
(*R*)-BINAP (6)	[Rh(1,5-hd)(phen)]Cl	THF	80°	170	15	15 (12)	37
(*R*)-BINAP (6)	[Rh(1,5-hd)(phen)]Cl	THF	100°	66	37	36 (33)	35
(*R*)-BINAP (15)	[Rh(1,5-hd)(phen)]Cl	THF	100°	144	56	56 (50)	36
(*R*)-BINAP (6)	$[Rh(COD)Cl]_2$	THF	105°	66	22	22 (20)	35

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BPPM	$PtCl_2$(BPPM)/$SnCl_2$, CO/H_2 (1/3, 2650 psi), C_6H_6, 60°, 50 h	 (—), 60 *S*	406
C_6 		HRh(CO)$(PPh_3)_3$, C_6H_6, CO/H_2 (100 atm), 70 h		860, 861

Chiral Ligand	Conditions	R^1	R^2	R^3	I	II
(–)-DIOP	CO/H_2 (1/10), 60°	Me	Me	H	(90), 50 *R*	(—)
"	CO/H_2 (1/4), 60°	Bn	Me	H	(80-90), 36 *R*	(3-10)
(–)-DIOCOL	CO/H_2 (1/1), 80°	Bn	Me	H	(80-90), 33 *R*	(3-10)
(–)-DIOP	CO/H_2 (1/1), 80°	Me	*t*-BuO	H	(70-80), 32 *R*	(2-8)
"	CO/H_2 (1/3), 80°	Me	Me	Ph	no reaction	
"	CO/H_2 (1/1), 80°	H	Me	H	(0)	(—)

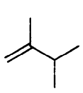
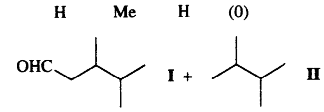
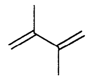
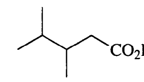
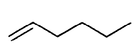
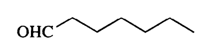
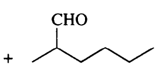
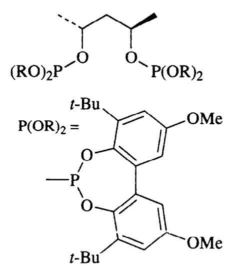
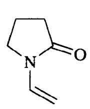
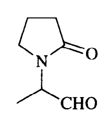
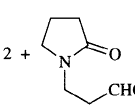
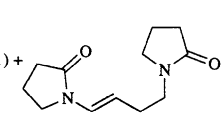
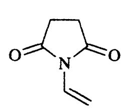
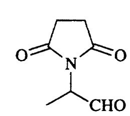
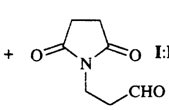
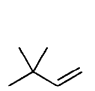
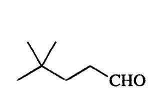
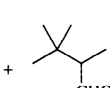
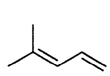
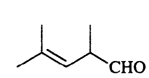
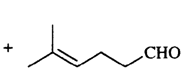
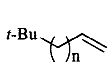
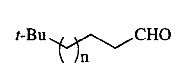
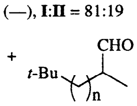
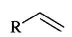
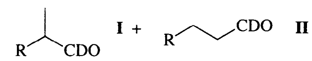
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*R*)-BCO-DPP	[(*R*,*R*)-Bco-dpp]$PtCl_2$/$SnCl_2$, C_6H_6, 80°, 12.5 h, CO/H_2 (7/15, 220 atm)	 **I** (—), 18.4 *S* + **II** (—), **I**:**II** = 90:10	407
	(*R*,*R*)-BCO-DBP	[(*R*,*R*)-Bco-dbp]$PtCl_2$/$SnCl_2$, C_6H_6, 80°, 17 h, CO/H_2 (7/15, 220 atm)	**I** (—), 46.1 *S* + **II** (—), **I**:**II** = 86:14	407
	(*R*,*R*)-DIOP-DBP	[(*R*,*R*)-Diop-dbp]$PtCl_2$/$SnCl_2$, C_6H_6, 80°, 116 h, CO/H_2 (7/15, 220 atm)	**I** (—), 36 *R* + **II** (—), **I**:**II** = 85:15	407
	(*R*,*R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 22 h	**I** (—), 0.1 *R*	850
	(*R*,*R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 23 h	**I** (—), 0.1 *R*	850
	(*S*,*S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 100°, 168 h	**I** (43), 21.8 *R*	130

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

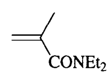
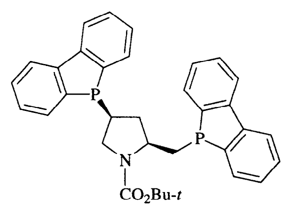
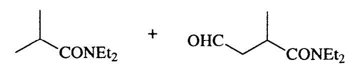
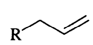
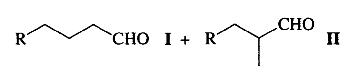
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-CHIRAPHOS	Pt(CHIRAPHOS)($SnCl_3$)Cl, CO/H_2 (1/1, 80 atm), 100°	I (—), 19.8 *S*	130
	(*R,R*)-DIOP	RhH(CO)(PPh_3)$_3$, L/Rh = 4, 100°, 96 h, CO/H_2 (1/1, 80 atm)	I (82), 3.5 *S*	130
	(*R,R*)-DIOP	Pt(DIOP)($SnCl_3$)Cl, 80°, CO/H_2 (1/1, 80 atm)	I (—), 15.0 *R*	130
	(–)-DIOP	1. HRh(CO)(PPh_3)$_3$/(–)-DIOP (1/2), C_6H_6, 95°, CO/H_2 (1/1, 90 atm), 160 h 2. Ag_2O	 (18), 5.7 *R* + aldehydes (22)	856
	(+)-DIOP	Pt(C_2H_4)((+)-DIOP)/ $PtCl_2$((+)-DIOP) (3/7), CO/H_2 (1/1, 50 atm), PhMe, 100°, 72 h	 I (74) +  II (12), 10.4 *R*	862
		Rh(acac)(CO)$_2$, L*/Rh = 4, Me_2CO, CO/H_2 (1/1, 600 psi)	I (—) + II (—), 20 *S*, I:II = 1:2	38
	(*R,R*)-DIOP	[Rh(NBD)Cl]$_2$, PhMe, CO/H_2 (1/1, 80 bar), 100°, 15 h	 I (42), 2 +  II (13)	806
	(*S,S*)-BDPP	[Rh(NBD)Cl]$_2$, PhMe, CO/H_2 (1/1, 80 bar), 40°, 425 h	I (20), 5 + II (1) +  (1)	806
	16	RhH(CO)(PPh_3)$_3$, C_6H_6, L/Rh = 2, 6 d, 57°, CO/H_2 (1/1, 500 psi)	 +  I:II = 83:17 I (—), 19.8 *R* II (—)	801
	(+)-DIPHOL	RhH(CO)(PPh_3)$_3$, C_6H_6, L/Rh = 4, 8 d, 54°, CO/H_2 (1/1, 500 psi)	I (—), 27.4 *S*	801
	(–)-DIPHOL	RhH(CO)(PPh_3)$_3$, C_6H_6, L/Rh = 4, 7 d, 46°, CO/H_2 (1/1, 500 psi)	I (—), 41 *R*	801
	(+)-DICOL	HRh(CO)(PPh_3)$_3$/DICOL (1/3), C_6H_6, 60°, 24 h, CO/H_2 (1/1, 80-90 atm)	 (75) +  (6), 1 *S*	851
	(*R,S*)-BINAPHOS	Rh (acac)(CO)$_2$, C_6H_6, H_2/CO (1/1, 100 atm) L/Rh = 4, 30°, 96 h	 +  I (—), 84 *R* + II (—), I:II = 81:19	413
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 50°	 I +  II	863

n	Time (h)	Conv. (%)	I:II	II (%ee)
0	49	49	100:0	—
1	87	87	57:43	92 (—)
2	68	68	74:26	77 (—)

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

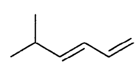
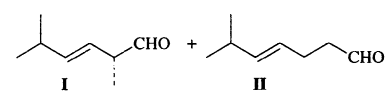
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(R,S)-BINAPHOS	Rh(acac)(CO)$_2$, ligand, D_2/CO (1/1), C_6H_6, L/Rh = 4		51

R	Temp.	H_2/CO	Time (h)	Conv. (%)	I:II	I (% ee)
Bu	30°	100	48	18	18:82	77 (*R*)
Bu	30°	20	24	19	21:79	77 (*R*)
Bu	30°	1	24	22	19:81	77 (*R*)

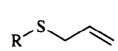
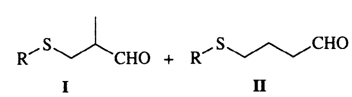
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh_4(CO)_{12}$/(–)-DIOP, CO/H_2 (1/1, 300 bar), PhMe, 130°, 32 h	 (33) + (44), —	803
	(*R*,*S*)-BINAPHOS	Rh(acac)(CO)$_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 50°		863

R	Temp.	Time (h)	Conv. (%)	I:II	II (%ee)
Pr-*i*	50°	68	54	74:26	83 (–)
Ph_3C	50°	20	>99	40:60	>99 (+)
TMS_3C	60°	69	51	93:7	—

C_7

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*S*)-BINAPHOS	Rh(acac)(CO)$_2$, L/Rh = 4, H_2/CO (1/1), C_6H_6		857

Temp.	Press. (atm.)	Time (h)	Conv. (%)	I:II	I
60°	100	18	92	78:22	(—), 80 *R*
30°	100	96	67	81:19	(—), 84 *R*
30°	20	76	79	83:17	(—), 84 *R*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*S*)-BINAPHOS	Rh(acac)(CO)$_2$, C_6H_6, CO/H_2 (1/1, 100 atm), L/Rh = 4-4.4, 50°		837

R	Time (h)	Conv. (%)	I:II	I (%ee)
Bu-*t*	47	76	56:44	(64), —
Ph	48	100	67:33	(80), —

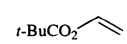
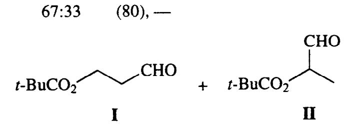
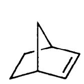
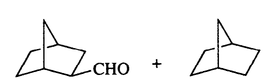
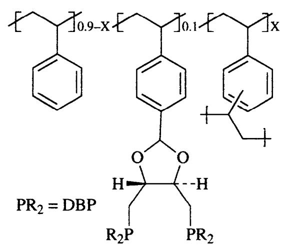
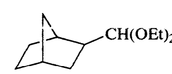
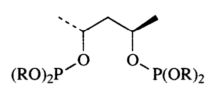
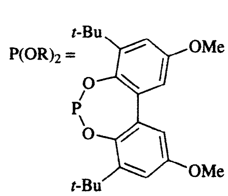
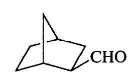
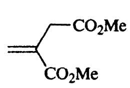
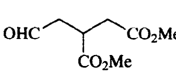
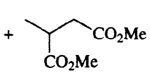
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*S*)-BINAPHOS	Rh(acac)(CO)$_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh=4, C_6H_6, 40 °, 47 h	 I:II = 88:12, I (—), 98 *S* + II (38)	113
	(*R*,*R*)-BCO-DPP	[(*R*,*R*)-BCO-DPP]$PtCl_2$/$SnCl_2$, C_6H_6, 80°, 0.5 h, CO/H_2 (7/15, 220 atm)	 I (79), 29.8 1*R*,2*R*,4*S* II (—)	407
	(*R*,*R*)-BCO-DPP	[(*R*,*R*)-BCO-DBP]$PtCl_2$/$SnCl_2$, C_6H_6, 80°, 0.5 h, CO/H_2 (7/15, 220 atm)	I (63), 7.3 1*R*,2*R*,4*S* + II (—)	407
	(*R*,*R*)-DIOP-DBP	[(*R*,*R*)-DIOP-DBP]$PtCl_2$/$SnCl_2$, C_6H_6, 80°, 15 h, CO/H_2 (7/15, 220 atm)	I (—), 0.6 1*R*,2*R*,4*S* + II (21)	407
	(*R*,*R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 0.6 h	I (—), 2.3 1*R*,2*R*,4*S*	850
	(*R*,*R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 0.75 h	I (—), 4.8 1*R*,2*R*,4*S*	850
	(–)-BPPM	$PtCl_2$(BPPM)/$SnCl_2$, CO/H_2 (1/1, 2700 psi), C_6H_6, 30°, 20 h	I (—), 60 1*S*, 2*S*,4*R*	406

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-DBP-DIOP	$Pt(DBP\text{-}DIOP)Cl_2$, $SnCl_2$, C_6H_6, 60°, 3 h CO/H_2 (1/1, 2650 psi)	I (—), 26 1*R*,2*R*,4*S* + II (—), I:II = 88:12	411, 412
	(*R*,*R*)-DIOP	$Pt(DIOP)(SnCl_3)Cl$, 80°, CO/H_2 (1/1, 80 atm)	I (—), 29.2 1*R*,2*R*,4*S*	130
	(*R*,*R*)-DIOP	$RhH(CO)(PPh_3)_3$, L/Rh = 4, 100°, 1 h, CO/H_2 (1/1, 80 atm)	I (100), 3.3 1*S*,2*S*,4*R*	130
	(*S*,*S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 100°, 3 h	I (100), 16.4 1*R*,2*R*,4*S*	130
	(*S*,*S*)-CHIRAPHOS	$Pt(CHIRAPHOS)(SnCl_3)Cl$, CO/H_2 (1/1, 80 atm), 100°	I (—), 8.3 1*R*,2*R*,4*S*	130
	 PR$_2$ = DBP	Pt(Chiral ligand)Cl_2, $SnCl_2$, C_6H_6, 60°, CO/H_2 (1/1, 2650 psi)		411, 412
		Time: 3 h	X = 0, I (—), 20 1*R*,2*R*,4*S* + II (—), I:II = 86:14	
		Time: 4 h	X = 0.1, I (—), 20 1*R*,2*R*,4*S* + II (—), I:II = 87:13	
	(–)-BPPM	$PtCl_2(BPPM)/SnCl_2$, CO/H_2 (1/1, 2700 psi), $HC(OEt)_3$, 30°, 140 h	 (—), 60 1*S*, 2*S*,4*R*	406
	 	$Rh(acac)(CO)_2$, L*/Rh = 4, Me_2CO, 50°, CO/H_2 (1/1, 130 psi)	 (—), 60 1*R*,2*R*,4*S*	38
	(*R*,*R*)-DIOP	$PtCl(SnCl_3)(DIOP)$, PhMe	 I +  II	859

CO/H_2 (bar)	Temp.	Time (h)	Conv. (%)	I	II
40/40	100°	21.5	95	(51), 45.2	(44), 33.7
80/40	100°	67	97	(66), 34.5	(31), 17.7
40/80	100°	15	100	(40), 58.7	(60), 31.0
40/200	100°	15	100	(26), 64.0	(74), 40.1
120/120	100°	15	99	(55), 56.6	(45), 30.3
40/40	50°	174	86	(66), 70.6	(20), 45.0

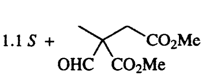
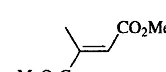
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*R*)-DIOP	$Rh_4(CO)_{12}$, 8 DIOP, PhMe, 100°, 6 h, CO/H_2 (1/1, 80 bar)	I (3), — + II (40), 1.1 *S* +  + III (43), 8.3 *S*  IV (6)	767
	(*R*,*R*)-DIOP	$RhH(CO)(PPh_3)_3$, 2 DIOP, PhMe, 100°, CO/H_2 (1/1, 80 bar), 6 h	I (4), — + II (10), 0 + III (73), 9.1 *S* + IV (6)	767
	(*R*,*R*)-DIOP	$[Rh(CO)_2Cl]_2$, 4 DIOP, PhMe, 100°, Et_3N, 17 h, CO/H_2 (1/1, 80 bar)	I (5), — + II (44), 0 + III (43), 7.2 *S* + IV (6)	767

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

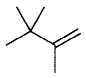
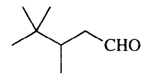
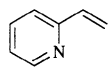
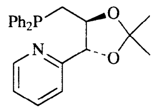
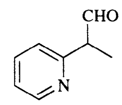
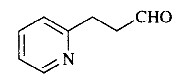
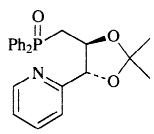
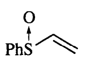
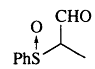
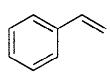
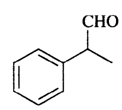
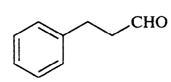
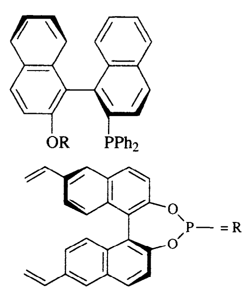
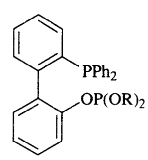
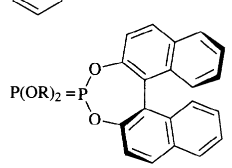
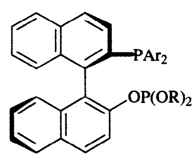
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-DIOCOL	$HRh(CO)(PPh_3)_3$/(–)-DIOCOL (1/1.5), C_6H_6, CO/H_2 (1/1, 80-90 atm), 100°	 (50), 1.1 *R*	851
		$Rh(acac)(CO)_2$, C_6H_6, L^*/Rh = 2.5, 80°, 3 h, CO/H_2 (1/1, 80 atm)	 **I** +  **II** **I** + **II** (95), —, **I**:**II** = 99:1	714
		$Rh(acac)(CO)_2$, C_6H_6, L^*/Rh = 2.5, 80°, 16 h, CO/H_2 (1/1, 80 atm)	**I** + **II** (67), —, **I**:**II** = 99:1	714
C_8 		$Rh(COD)BPh_4$, CH_2Cl_2, CO/H_2 (600 psi), 75°	 Yield / % de / % ee	371
	(*R*)-(+)-BINAP		(27) / 40 / 18	
	(*S*)-(–)-BINAP		(22) / 50 / 21	
	(*S*/*R*)-(±)-BINAP		(43) / 46 / 0	
		$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm)	 **I** +  **II** CO/H_2 (atm) / **I**, %ee / **II**	34 113
	(*S*,*R*)-BINAPHOS	60°, 43 h	50/50 / (88), 94 *S* / (12)	
	(*R*,*S*)-BINAPHOS	rt, 39 h	50/50 / (92), 95 *R* / (8)	
	(*R*, *S*)-BINAPHOS	60°, 40 h	63/8 / (88), 92 *R* / (12)	
	(*R*,*S*)-BINAPHOS + (*R*,*R*)-BINAPHOS (1/1)	$Rh(acac)(CO)_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6, 25°, 42 h	**I** (—), 85 *R* + **II** (—), **I**:**II** = 90:10	113
		Rh(acac)L copolymerized with divinylbenzenes, CO/H_2 (1/1, 100 atm), C_6H_6, 60°, 12 h	**I**:**II** = 85:15, **I** (—), 90 *R*	416
	 	$Rh(acac)(CO)_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 60°, 40 h	**I**:**II** = 89:11, **I** + **II** (>98), 69 *S*	113
	(*R*,*R*)-BIPHEMPHOS	$Rh(acac)(CO)_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 60°, 40 h	**I**:**II** = 92:8, **I** + **II** (95), 16 *R*	113

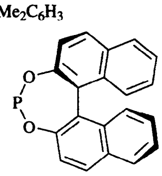
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(+)-BDPP	[Rh(μ-OMe)(COD)]$_2$, ligand, H_2/CO, THF		865

P/Rh	Temp.	H_2/CO (bar)	Time (h)	Conv. (%)	I:II	I (% ee)
2	65°	1/1 (5)	7	88	77:23	<1 (*R*)
2	65°	1/1 (10)	12	100	84:16	2 (*S*)
2	65°	1/1 (30)	12	100	90:10	5 (*R*)
2	65°	4/1 (10)	1.5	90	84:16	17 (*S*)
4	65°	1/1 (10)	7	92	94:6	56 (*S*)
4	40°	1/1 (30)	24	12	96:4	60 (*S*)
8	65°	1/1 (10)	7	76	95:5	45 (*S*)
8	65°	1/1 (30)	24	92	94:6	48 (*S*)



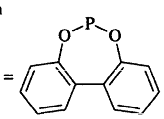
Ar = 3,5-$Me_2C_6H_3$

P(OR)$_2$ = 

Rh(acac)(CO)$_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 60°, 37 h — I:II=90:10, I (—), 85 *R* + II (>99) — 113

"

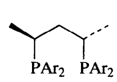
Ar = Ph

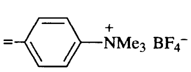
P(OR)$_2$ = 

Rh(acac)(CO)$_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 60°, 43 h — I:II = 91:9, I (—), 83 *R* + II (>99) — 113

Pt(chiral ligand)(P-P)$_2$, $SnCl_2$, Sn/Rh = 20, H_2/CO (1/2, 100 atm), 125°, 24 h, THF — 661

Ligand	P-P	I + II	I:II	I (%ee)	PhEt	Alcohol
(–)-DIOS	$(PPh_3)_2$	(19)	54:46	2 (S)	(4)	—
(*R*)-BINAS	$(PPh_3)_2$	(58)	14:86	2 (S)	(4)	(1)
(–)-DIOS	DPPB	(59)	39:61	7 (S)	(22)	—
(*R*)-BINAS	DPPB	(79)	44:56	4 (S)	(18)	—
(–)-DIOS	DPPB	(80)	32:68	7 (S)	(17)	—
(*R*)-BINAS	DPPB	(76)	42:58	14 (S)	(24)	—



Ar = 

$PtCl_2$(Chiral Ligand), PhMe/H_2O, 100°, CO/H_2 (1/1, 1000 psi) — I:II = 0.5 I + II (29), 0 + EtPh (3) — 601

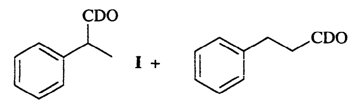
"

$PtCl_2$(Chiral Ligand), $SnCl_2$ on glass, PhMe, H_2O, CO/H_2 (1/1, 1000 psi) — 601

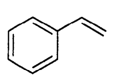
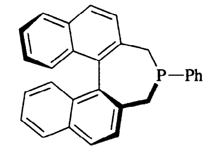
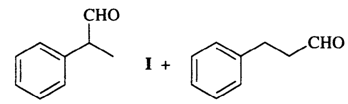
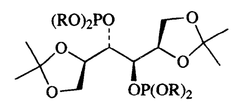
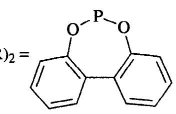
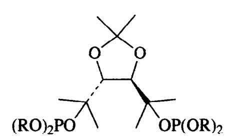
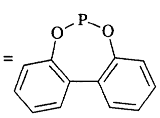
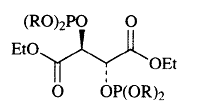
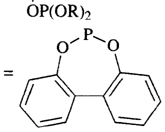
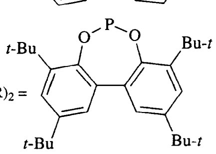
Temp.	Time (h)	TOF	I + II	I:II	I (%ee)	PhEt
100°	24	1.6	(28)	0.7	10.7 (*R*)	(12)
60°	48	0.8	(36)	0.5	14.1 (*S*)	(28)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, CO/H_2 (40 atm), CO_2 (d= 0.48 g/ml)	I + II; I (66), *R*	866

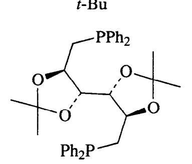
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

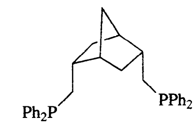
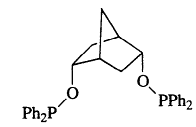
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	Rh(acac)$(CO)_2$, ligand, D_2/CO (1/1), C_6H_6, L/Rh = 4	 I + II	51

Temp.	H_2/CO	Time (h)	Conv. (%)	I:II	I (% ee)
40°	100	13	12	88:12	92 (*R*)
40°	20	5	15	88:12	93 (*R*)
40°	1	5	6.4	82:18	90 (*R*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(CO)_2$(acac), C_6H_6, CO/H_2 (1/1, 50 bar)	 I + II	867
		60°	I (89), 12 *R* + II (7), I:II = 93:7	
		30°	I (—), 20 *R* + II (—), I:II = 95:5	
	 P$(OR)_2$ = 	$Rh(CO)_2$(acac), L/Rh = 10, CO/H_2 (40 bar), C_6H_6, 40°, 4 h	No reaction	868
	 P$(OR)_2$ = 	$Rh(CO)_2$(acac), L/Rh = 10, CO/H_2 (40 bar), C_6H_6, 40°, 16 h	I (—), 7.3 *R* + II (—), I:II = 5.4:1	868
	 P$(OR)_2$ = 	$Rh(CO)_2$(acac), L/Rh = 2.2, CO/H_2 (40 bar), C_6H_6, 80°, 16 h	I (—), 0 + II (—), I:II = 1.9:1	868
	P$(OR)_2$ = 	$Rh(CO)_2$(acac), C_6H_6, CO/H_2 (40 bar)	see below	868

L/Rh	Time (h)	Temp.	Conv. (%)	I:II	I %ee)
2.2	15	80°	42.3	1.6:1	1.4 *R*
10	23	25°	19.7	26.1:1	19.3 *R*
10	5	40°	16.2	17.8:1	19.9 *R*
20	16	80°	99.7	10.2:1	6.6 *R*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(CH_2CH{=}CH_2)_3$, 20°, CH_2Cl_2, CO/H_2 (1/1)	I + II (100), —, I:II = 11.2:1	250
	αα-TREDIP	$[Rh(NBD)_2]BF_4$, Et_3N, CH_2Cl_2, CO/H_2 (1/1), 20°, 20 h	I + II (100), —, I:II = 61.5:1	869, 250
	ββ-TREDIP	$[Rh(NBD)_2]BF_4$, Et_3N, CH_2Cl_2, CO/H_2 (1/2), 20°, 20 h	I + II (85), —, I:II = 15.9:1	250
	(–)-DIOP	$Rh(CH_2CHCH_2)_3$, 20°, CH_2Cl_2, CO/H_2 (1/2)	I + II (71), —, I:II = 4:1	250

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(CO)_2(acac)$, H_2/CO (1/1, 40 atm), C_6H_6, 30°, 30 h	**I** (—),— + **II** (—), **I**:**II** = 97:3	845
		$Rh(CO)_2(acac)$, H_2/CO (1/1, 40 atm), C_6H_6, 30°, 30 h	**I** (—),— + **II** (—), **I**:**II** = 97:3	845

Catalyst	Pressure (bar)	Temp.	Time (h)	Conv. (%)	I:II	I (%ee)	Refs.
$Rh_2(COD)_2(BINAS)$	30	80°	24	77	56:44	11	870
$Rh_2(COD)_2(BINAS)/2\ PPh_3$	30	60°	4	100	92:8	7	
$[Rh(COD)(Me_2BINAS)]BF_4$	30	80°	24	98	51:49	6	
$[Rh(COD)(Me_2BINAS)]BF_4/3\ Me_2BINAS$	80	80°	24	100	84:16	15	
$[Rh(COD)(Me_2BINAS)]BF_4/3\ Me_2BINAS$	80	40°	24	100	94:6	6	
$[Rh(COD)(Me_2BINAS)]BF_4/3\ Me_2BINAS$	80	25°	24	81	96:4	2	

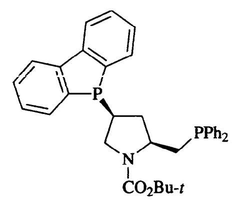
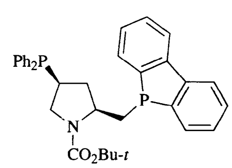
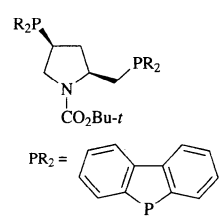
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BPPM	Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, 60°, 4 h, CO/H_2 (1/1, 2400 psi)	**I** (—), 77 + **II** (—), **I**:**II** = 1.1:2	871, 409
		Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, 60°, 4 h, CO/H_2 (1/1, 2400 psi)	**I** (—), 12 + **II** (—), **I**:**II** = 1.35:1	409
		Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, 60°, 4 h, CO/H_2 (1/1, 2400 psi)	**I** (—), 74 + **II** (—), **I**:**II** = 1.0:1	409
		Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, 60°, 4 h, CO/H_2 (1/1, 2400 psi)	**I** (—), 40 + **II** (—), **I**:**II** = 3.2:1	409
	(*R*,*R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 2.5 h	**I** (—), 0.2 *S*	850
	(*R*,*R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, 80°, CO/H_2 (1/1, 80 atm), 4 h	**I** (—), 0.4 *R* + **II** (—), **I**:**II** = 90:10	850
	(*S*,*S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 100°, 3 h	**I** + **II** (80), 24.2 *R*, **I**:**II** = 94:6	130
	(*S*,*S*)-CHIRAPHOS	$Pt(L^*)(SnCl_3)Cl$, 100°, CO/H_2 (1/1, 80 atm)	**I** (—), 45.0 *R* + **II** (—), **I**:**II** = 62:38	130
	(*R*,*R*)-DIOP	$RhH(CO)(PPh_3)_3$, L/Rh = 4, 100°, 1 h, CO/H_2 (1/1, 80 atm)	**I** + **II** (94), 10.0 *R*, **I**:**II** = 71:29	130
	(*R*,*R*)-DIOP	$Pt(DIOP)(SnCl_3)Cl$, 100°, CO/H_2 (1/1, 80 atm)	**I** (—), 4.4 *S* + **II** (—), **I**:**II** = 38:62	130
	(*S*,*S*)-BDPP	$PtCl(SnCl_3)(BDPP)$, CO/H_2 (1/1, 80 bar), PhMe, 40°, 55 h	**I** (31), 64.5 *S* + **II** (42) + PhEt (3)	109

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-BDPP	$PtCl(SnCl_3)(BDPP)$, 2 $SnCl_2$, PhMe, 40°, CO/H_2 (1/1, 80 bar), 115 h	**I** (23), 75.5 *S* + **II** (32) + PhEt (1)	109
		CO/H_2 (1/1, 80 bar), PhMe	**I** + **II** + PhEt (**III**)	110

Catalyst	Temp.	Time (h)	Conv. (%)	I:II:III	%ee
$PtCl_2(BDPP)+SnF_2$	40°	240	72	31:66:2	76.0 *S*
$PtCl_2(BDPP)+SnF_2$	140°	5	86	17:57:25	16.6 *R*
$PtCl_2(VALPHOS)+SnF_2$	160°	50	70	40:27:33	23.7 *S*
$PtCl_2(BDPP)+SnCl_2$	20°	72	36	50:49:1	45.0 *S*
$PtCl_2(BDPP)+SnCl_2$	100°	10	79	31:62:7	28.0 *R*
$PtCl_2(BDPP)+2\text{-}PPh_2C_5H_4N+2SnCl_2$	40°	160	30	31:67:2	86.7 *S*
$PtCl_2(BDPP)+PBu_3+2SnCl_2$	25°	240	69	35:56:9	72.5 *S*

(Chiral Ligand)$PtCl_2/SnCl_2$, CO/H_2 (7/15, 220 atm), C_6H_6 — Refs. 407, 872

Chiral Ligand	Temp.	Time (h)	Conv. (%)	I:II:III	%ee
(*R,R*)-BCO-DPP	80°	1.0	100	21:29:10	23.4 *S*
(*R,R*)-BCO-DBP	80°	0.5	100	77:23:49	68.1 *S*
(*R,R*)-BCO-DBP	40°	10	98	80:20:—	86.3 *S*
(*R,R*)-DIOP-DBP	80°	5.5	80	35:15:21	55.8 *S*

$PtCl(SnCl_3)$(Chiral Ligand), CO/H_2 (1/1, 70 bar), PhMe — Ref. 112

Chiral Ligand	Temp.	Time (h)	I + II	I:II	I (%ee)	III
(*S,S*)-BDPP-$(pNMe_2)_4$	30°	550	17	1:1.52	60.6 *S*	0
(*S,S*)-BDPP-$(pNMe_2)_4$	100°	3	32	1:3.32	41.4 *R*	4
(*S,S*)-DIOP-$(pNMe_2)_4$	25°	480	20	1:1.3	20.0 *R*	0
(*S,S*)-DIOP-$(pNMe_2)_4$	100°	2	18	1:1.84	6.4 *S*	5
(*S,S*)-CHIRAPHOS-$(pNMe_2)_4$	25°	300	12	1:0.62	46.0 *R*	<1
(*S,S*)-CHIRAPHOS-$(pNMe_2)_4$	100°	12	20	1:1.46	12.4 *R*	2

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S*)-PROLOPHOS	$Pt(PROLOPHOS)Cl_2/SnCl_2$, Sn/Pt = 2.5, 40°, 40 h, CO/H_2 (1/2, 130 atm), C_6H_6	**I** (50), 29 *R* + **II** (42) + **III** (5) **I**:**II** = 1.2:1	873
	(–)-(2*S*,4*S*)-BDPP	$PtCl_2(PPh_3)_2$, BDPP, $SnCl_2$, Pt/L/Sn = 2/1/4, PhMe, 20°, 210 h, CO/H_2 (1/2, 120 bar)	**I** (4), 88.8 *S* + **II** (10) + **III** (tr) + starting material (86)	874
		PhMe, CO/H_2 (1/1, 80 bar)		874

Catalyst	Temp.	Time (h)	Conv. (%)	I	II	III
$PtCl_2(PPh_3)_2$ + 1/2 (–)-DIOP + 2 $SnCl_2$	120°	1.5	70	(19), 5.1 *S*	(31)	(20)
$PtCl_2(PPh_3)_2$ + (–)-DIOP + 2 $SnCl_2$	120°	2	76	(24), 5.0 *S*	(42)	(10)
$PtCl(SnCl_3)$((–)-DIOP)	120°	2	82	(25), 2.6 *S*	(42)	(15)
$PtCl_2(PPh_3)_2$ + 1/2 (–)-BDPP + 2 $SnCl_2$	40°	88	37	(14), 79.4 *S*	(22)	(1)
$PtCl_2(PPh_3)_2$ + (–)-BDPP + 2 $SnCl_2$	25°	168	14	(4), 85.9 *S*	(10)	(0.2)
$PtCl_2(PPh_3)_2$ + 1/2 (–)-BDPP + 2 $SnCl_2$	125°	3	34	(8), 9.0 *R*	(22)	(4)
$PtCl_2$((–)-BDPP) + 2 PPh_3 + $SnCl_2$	125°	6	63	(14), 9.8 *R*	(40)	(9)
$PtCl(SnCl_3)$((–)-BDPP)	40°	55	76	(31), 64.5 *S*	(42)	(3)
$PtCl_2$((–)-BDPP) + 2 $SnCl_4$	80°	6	59	(17), 14.6 *S*	(39)	(3)
$PtCl_2$((–)-BDPP) + 2 $SnCl_4$	110°	1.5	76	(22), 13.5 *R*	(46)	(8)
$PtCl_2$((–)-DIOP) + $CuCl_2$	100°	6.5	32	(11), 10.6 *S*	(17)	(4)
$PtCl_2$((–)-DIOP) + CuCl	100°	3	22	(7), 8.9 *S*	(12)	(3)
$PtCl_2$((–)-BDPP) + $CuCl_2$	100°	10	17	(4), 12.3 *R*	(12)	(1)
$PtCl_2$((–)-BDPP) + CuCl	120°	8.5	14	(3), 14.5 *R*	(10)	(1)

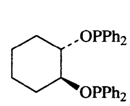
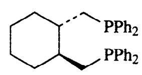
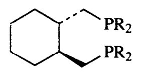
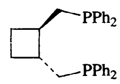
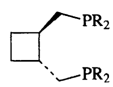
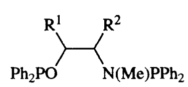
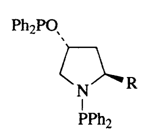
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BDP-DIOP	$Pt(DBP\text{-}DIOP)Cl_2/SnCl_2$, CO/H_2 (1/1, 2600 psi), 60°, 16 h	**I** (—), 64 *S* + **II** (—) + **III** (—) **I**:**II** = 3.4:1	404
		$[RhCl(CO)_2]_2$, L/Rh = 2, CO/H_2 (1/1, 100 atm), C_6H_6, 110°	**I** (—), 0.8 *S* + **II** (—)	854

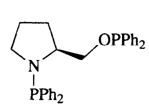
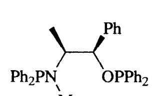
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$[RhCl(CO)_2]_2$, L/Rh = 2, CO/H_2 (1/1, 100 atm), C_6H_6, 90°	**I** (—, 15.1 (*S*)) + **II** (—)	854
	 PR_2 = dbp	$[RhCl(CO)_2]_2$, L/Rh = 2, CO/H_2 (1/1, 100 atm), C_6H_6, 80°	**I** (—), 0.6 *R* + **II** (—)	854
		$[Rh(CO)_3]_4$, L/Rh = 2, CO/H_2 (1/1, 100 atm), C_6H_6, 80°	**I** (—), 4.2 *R* + **II** (—)	854
	 PR_2 = dbp	$[Rh(CO)_3]_4$, L/Rh = 2, CO/H_2 (1/1, 100 atm), C_6H_6, 80°	**I** (—), 40.3 *S* + **II** (—)	854
	(+)-DIOP	$Pt(C_2H_4)((+)\text{-DIOP})/PtCl_2((+)\text{-DIOP})$ (1/1), CO/H_2 (1/1, 50 atm), PhMe, 100°, 72 h	**I** (40), 27.6 *R* + **II** (22) + PhEt (2)	862
		$PtL^*_2Cl_2$, $SnCl_2 \cdot H_2O$, CO/H_2 (1/1, 130 bar), C_6H_6, 80°, 4 h		875

R^1	R^2	Conv. (%)	(I + II):III	I/II	I (%ee)
H	Me	68	95 : 5	0.75	24 *S*
H	Pr-*i*	80	96 : 4	1.06	14 *S*
H	Bu-*i*	85	96 : 4	0.96	4 *S*
H	Ph	72	97 : 3	0.99	2 *S*
H	Bn	57	95 : 5	0.89	<1 *S*
Ph	Me	54	92.5 : 7.5	0.70	36 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$PtL^*_2Cl_2$, $SnCl_2 \cdot H_2O$, CO/H_2 (1/1, 130 bar), C_6H_6, 80°, 4 h		875

R	Conv. (%)	(I + II):III	I/II	I (%ee)
CO_2Et	57	92 : 8	0.86	16.5 *R*
COBu-*n*	75	93 : 7	1.01	11.8 *R*
$COCH_2CH_2OEt$	25	95 : 5	1.06	0.35 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$PtL^*_2Cl_2$, $SnCl_2 \cdot H_2O$, CO/H_2 (2/3, 162.5 bar), C_6H_6, 50°, 36 h	**I** + **II** (68), 48.1 *S*, **I**:**II** = 0.7	875
		$RhCl(CO)L^*/2e^-$, L^*/Rh = 2, 40°, 111 h, CO/H_2 (1/1, 1 atm)	**I** (—), 30.9 *R* + **II** (—); **I**:**II** = 9.1	53
	(*S*)-BINAP	$PtCl_2[(S)\text{-BINAP}]/SnCl_2$, CO/H_2 (1/1, 80 bar), PhMe		54

Temp.	Time (h)	Conv. (%)	I	II	PhEt
50°	52	37	(12), 68.8 *S*	(24)	(1)
70°	26	38	(14), 11.2 *S*	(22)	(2)
90°	12	45	(17), 1.5 *R*	(25)	(3)
100°	7	40	(15), 11.3 *R*	(22)	(3)
115°	5	95	(28), 19.2 *R*	(42)	(15)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(+) DICOL	$HRh(CO)(PPh_3)_3$/DICOL (1/3), C_6H_6, 80°, 4 h, CO/H_2 (1/1, 80-90 atm)	**I** (27), 1 *R* + **II** (3)	851

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

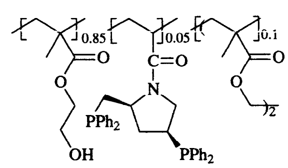
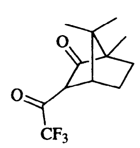
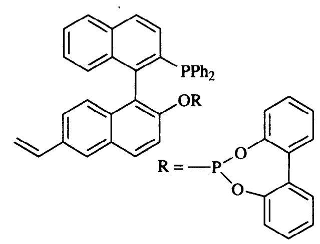
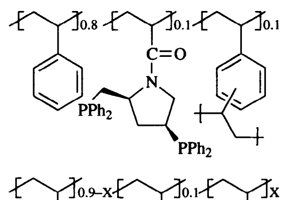
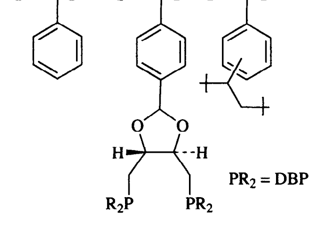
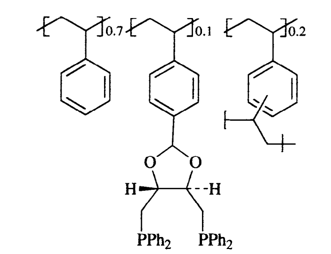
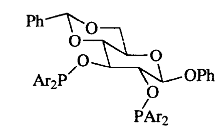
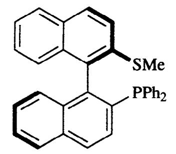
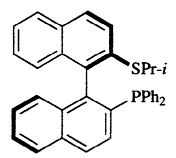
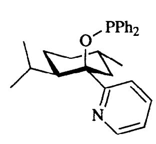
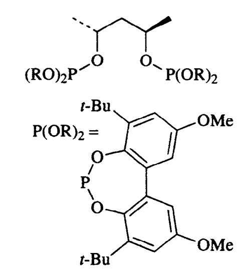
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-DIOCOL	HRh(CO)(PPh_3)$_3$/(–)-DIOCOL (1/1.5), C_6H_6, CO/H_2 (1/1, 80-90 atm), 80°, 16 h	**I** (58), 6.3 *R* + **II** (27)	851
	(–)-DBP-DIOP	(–)-DBP-DIOP-$PtCl_2$/$SnCl_2$·H_2O (1/2.5), CO/H_2 (1/2.9, 314 kg/cm^2), C_6H_6, 36°, 55 h	**I** (52), 79.8 *S* + **II** (12) + PhEt (36)	404, 405
	(–)-DIOP	Pt[(–)-DIOP]Cl_2, $SnCl_2$·$2H_2O$, C_6H_6, CO/H_2 (1/1, 250 atm), 100°, 1 h	**I** (34), 18.1 *S* + **II** (26)	852
	BDP-DIOP	Pt(BDP-DIOP)Cl_2, $SnCl_2$·$2H_2O$, C_6H_6, CO/H_2 (1/1, 235 atm), 100°, 1 h	**I** (39), 22.1 *S* + **II** (12)	852
	Polystyrene-divinylbenzene (1%), 10.5% ring substitution with (–)-DIOP	Polymer-bound (–)-DIOP-$PtCl_2$-$SnCl_2$, $SnCl_2$/Pt = 2.1, C_6H_6, CO/H_2 (1/1, 87 kg/cm^2), 60°, 12 h	**I** + **II** (94), 28, **I**:**II** = 0.57	404
		$PtCl_2$, $SnCl_2$, C_6H_6, CO/H_2 (1/1, 2200 psi), 60°, 24 h	**I** (14, 70) + **II** (31)	871
		Rh(CO)$_2$(Chiral Ligand), CO/H_2 (65 bar), 85°, 4 h	**I** + **II** (—), —, **I**:**II** = 4:1	876
	Polystyrene-divinylbenzene copolymerized with: 	Rh(acac)(CO)$_2$, CO/H_2, 50atm, C_6H_6, 60°, 40 h	**I** (94), 82	877
		Pt(Chiral ligand)Cl_2, $SnCl_2$, 60°, 90 h CO/H_2 (1/1, 2600 psi)	**I** (—), 73 *S* + **II** (—) + **III** (—); **I**:**II** = 0.53:1	412, 871
		Pt(Chiral ligand)Cl_2, $SnCl_2$, 60°, 24 h CO/H_2 (1/1, 2600 psi)	X = 0, **I** (—), 65 *S* + **II** (—) + **III** (—), **I**:**II** = 1.6:1 X = 0.1, **I** (—), 56 *S* + **II** (—) + **III** (—), **I**:**II** = 1:1	411, 412

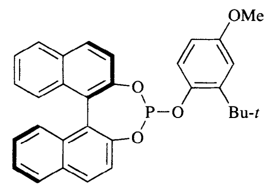
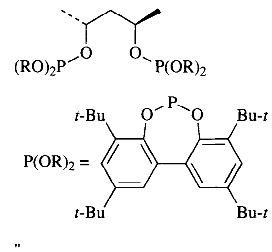
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$HRh(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/1, 45 psi), 25°, 72 h	**I** (—),11.4 + **II** (—) + **III** (—), **I**:**II** = 2:1	853
	 Ar = 3,5-$(CF_3)_2C_6H_3$	$Rh(COD)(L^*)BF_4$, CO/H_2 (1600 psi), hexane	**I** (—), 24 + **II** (—), **I**:**II** = 96:4	843
		$[Rh(COD)(L^*)]CF_3SO_3$, CO/H_2 (1/1, 60 bar), C_6H_6, 60°, 4 h	**I** (—), 2.5 + **II** (—), **I**:**II** = 88:12	878
		$Rh(acac)(CO)_2$, L^*, L^*/Rh = 4, C_6H_6, 40°, CO/H_2 (1/1, 120 bar)	**I** (—), 14 + **II** (—), **I**:**II** = 96:4	878
		$[Rh(COD)(L^*)]ClO_4$, CO/H_2 (1/1, 50 atm), C_6H_6, 70°, 4 h	**I** (—), 6 *R* + **II** (—), **I**:**II** = 88:12	844
	"	$[Rh(CO)(PPh_3)(L^*)]ClO_4$, CO/H_2 (1/1, 30 atm), C_6H_6, 70°, 4 h	**I** (—), 6 *R* + **II** (—), **I**:**II** = 78:22	844
		$Rh(acac)(CO)_2$		38

L*/Rh	Solvent	Temp.	H_2/CO	Pressure (psi)	I:II	%ee
4:1	PhMe	70°	1:1	130	12.4:1	60
4:1	PhMe	70°	1:1	75	6.9:1	45
4:1	PhMe	70°	2:1	130	13.2:1	61
4:1	PhMe	50°	1:1	200	18.5:1	71
8:1	PhMe	50°	1:1	130	27.0:1	71
8:1	PhMe	50°	1:1	130	28.9:1	72
8:1	PhMe	25°	1:1	130	45.3:1	81
4:1	PhMe	25°	1:1	500	49.2:1	90
4:1	EtOAc	70°	1:1	130	14.4:1	61
4:1	Et_2CO	70°	1:1	130	14.2:1	66
4:1	Me_2CO	70°	1:1	130	12.9:1	66
2:1	$PhNO_2$	25°	1:2.7	130	91.0:1	85

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	"	$Rh(acac)(CO)_2$, L^*, P/Rh = 2.5, PhMe, CO/H_2 (1/1, 9 bar), 40°, 5 h	**I** (—), 67 *S* + **II** (—), **I**:**II** = 94:6	56
	"	$Ru(acac)_3$, L^*/Ru = 2, 70°, CO/H_2 (1/1, 500 psi), Me_2CO	**I** (—), 54 *S* + **II** (—), **I**:**II** = 17:1	38

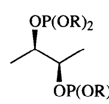
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

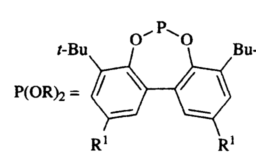
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, $L^*/Rh = 2$, PhMe, 45°, CO/H_2 (1/1, 130 psi)	**I** (—), 10 *S* + **II** (—), **I**:**II** = 6:1	38
		$Rh(acac)(CO)_2$		38

L*/Rh	Solvent	Temp.	H_2/CO	Pressure (psi)	I:II	%ee
4:1	PhMe	70°	1:1	130	21:1	44
4:1	PhMe	50°	1:1	130	55:1	61
8:1	PhMe	50°	1:1	130	54:1	67
8:1	PhMe	40°	1:1	130	58:1	66
2:1	Me_2CO	25°	4:1	130	190:1	77

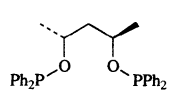
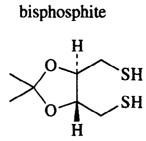
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	"	$Rh(acac)(CO)_2$, L^*, PhMe		56

P/Rh	Temp.	H_2/CO	Pressure (bar)	Time (h)	Conv. (%)	I:II	% ee
8	40°	1:1	9	5	99	95:5	40 *S*
8	25°	1:1	9	5	21	96:4	68 *S*
2.5	40°	1:1	9	5	89	96:4	50 *S*
2.5	40°	1:3	18	5	45	96:4	57 *S*
2.5	40°	3:1	18	5	78	80:20	8 *S*
2.5	40°	1:1	45	5	63	96:4	63 *S*

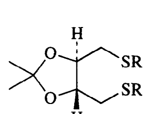
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, L^*, P/Rh = 2.5, PhMe, 5 h, CO/H_2		56



R^1	Temp.	Conv. (%)	I:II	% ee
Bu-*t*	40°	74	93:7	19 *S*
Bu-*t*	25°	18	95:5	30 *S*
OMe	40°	99	92:8	25 *S*
OMe	25°	40	93:7	34 *S*

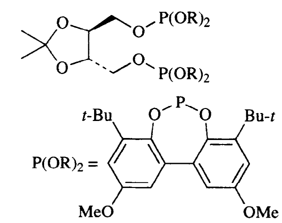
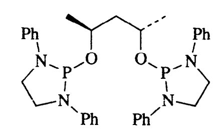
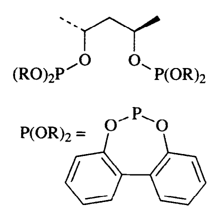
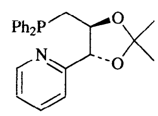
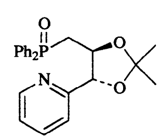
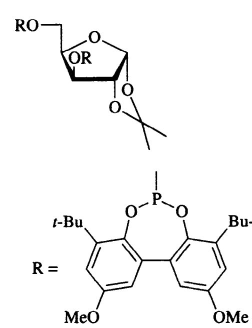
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, $L^*/Rh = 4$, PhMe, 70°, CO/H_2 (1/1, 130 psi)	**I** (—), 5 *S* + **II** (—), **I**:**II** = 3.4:1	38
	tris[(*S*)-1,1'-bi-2-Naphthol] bisphosphite	$Rh(acac)(CO)_2$, $L^*/Rh = 4$, PhMe, 70°, CO/H_2 (1/1, 130 psi)	**I** (—), 25 *S* + **II** (—), **I**:**II** = 3:1	38
		CO/H_2 (1/1, 30 bar), THF, 65°		879

Catalyst	Time (h)	Conv. (%)	I:II	% ee
$[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]_2$	22	100	64:36	5 *S*
$[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]_2$/4 PPh_3	3	97	91:9	4 *S*
$Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2$/4 PPh_3	3	100	91:9	3 *S*
$[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]_2$/4 (+)-DIOP	23	99	59:41	17 *S*
$[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]_2$/4 (–)-DIOP	17	84	66:34	3 *S*

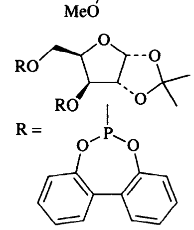
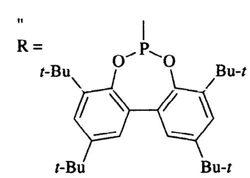
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$[Rh(COD)L]ClO_4$, CO/H_2 (1/1, 30 bar), THF, 65°		880

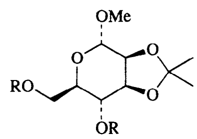
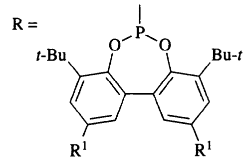
R	Time (h)	Conv. (%)	I:II	%ee
Me	14	57	69:31	3(*S*)
i-Pr	22	74	72:28	6(*S*)

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

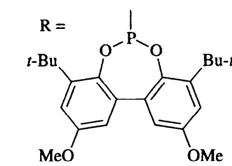
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, L^*/Rh = 4, PhMe, 70°, CO/H_2 (1/1, 130 psi)	**I** (—), 4 *S* + **II** (—), **I**:**II** = 8.8:1	38
		$Rh(acac)(CO)_2$, L^*/Rh = 1, PhMe, 70°, CO/H_2 (1/1, 130 psi)	**I** (—), 6 *R* + **II** (—), **I**:**II** = 7.25:1	38
		$Rh(acac)(CO)_2$, 70°, L^*/Rh = 1.2, Me_2CO, CO/H_2 (1/1, 130 psi)	**I** (—), 14 *R* + **II** (—), **I**:**II** = 4.6:1	38
	"	Rh $(acac)(CO)_2$, L^*, P/Rh = 2.5, PhMe, 40°, CO/H_2 (1/1, 9 bar), 5 h	**I** (—, 11 (*R*)) + **II** (—), **I**:**II** = 80:20	56
		$Rh(acac)(CO)_2$, C_6H_6, L^*/Rh = 2.5, 30°, 20 h, CO/H_2 (1/1, 90 atm)	**I** + **II** (70), <1, **I**:**II** = 95:5	714
		$Rh(acac)(CO)_2$, C_6H_6, L^*/Rh = 2.5, 30°, 5 h, CO/H_2 (1/1, 90 atm)	**I** + **II** (97), <1, **I**:**II** = 95:5	714
		$Rh(acac)(CO)_2$, L^*, P/Rh = 2.5, PhMe	(see below)	55

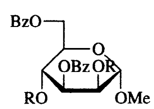
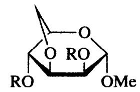
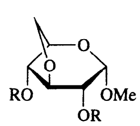
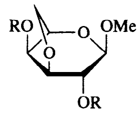
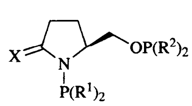
Temp.	Pressure (bar)	CO/H_2	Time (h)	Conv. (%)	**I**:**II**	% ee
40°	9	1	5	51	92:8	51 *S*
25°	9	1	5	3	91:9	62 *S*
40°	18	3	5	23	92:8	53 *S*
40°	45	9	70	99	92:8	43 *S*
40°	18	0.33	5	98	51:13	48 *S*
40°	45	1	5	21	91:9	53 *S*
40°	25	4	5	38	94:6	50 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, L^*, 40°, CO/H_2 (4/1, 25 bar), PhMe, 5 h	**I** (—), 3 *S* + **II** (—), **I**:**II** = 83:17	55
	" 	"	**I** (—), 40 *S* + **II** (—), **I**:**II** = 95:5	55

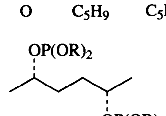
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		$Rh(acac)(CO)_2$, L*, P/Rh = 2.5, PhMe		55
	R = 			

R^1	Temp.	*P* (bar)	CO/H_2	Time (h)	Conv. (%)	I:II	% ee
Bu-*t*	40°	40	1	5	67	97:3	31 *R*
Bu-*t*	25°	40	1	5	3	97:3	50 *R*
Bu-*t*	40°	25	4	5	38	96:4	45 *R*
OMe	40°	25	4	5	42	95:5	53 *R*
OMe	25°	25	4	110	14	93:7	64 *R*

R = 

Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	$Rh(acac)(CO)_2$, L*, P/Rh = 2.5, PhMe, 40°, CO/H_2 (1/1, 40 bar), 5 h	Conversion >99%, **I** (—), 0 + **II** (—), **I**:**II** = 94:6	55
	"	Conversion >99%, **I** (—), 7 *S* + **II** (—), **I**:**II** = 93:7	55
	"	Conversion 49%, **I** (—), 8 *S* + **II** (—), **I**:**II** = 92:8	55
	"	Conversion 94%, **I** (—), 2 *S* + **II** (—), **I**:**II** = 93:7	55
	$PtCl_2(L^*)/SnCl_2$, PhMe, CO/H_2 (2/3, 130 atm), 50°		59

X	R^1	R^2	Time (h)	Conv. (%)	I : II : PhEt	% ee
H_2	Ph	Ph	36	100	39 : 59 : 2	42 *S*
H_2	C_6H_{11}	Ph	70	100	40 : 52 : 8	40 *S*
H_2	Ph	C_6H_{11}	38	100	37 : 62 : 1	55 *S*
H_2	C_6H_{11}	C_6H_{11}	200	10	38 : 54 : 8	not determined
O	Ph	Ph	15	100	29 : 68 : 3	40 *S*
O	C_6H_{11}	C_6H_{11}	160	70	33 : 62 : 4	56 *S*
O	C_5H_9	C_5H_9	70	90	22 : 47 : 30	47 *S*

Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	Rh $(acac)(CO)_2$, L*, P/Rh = 2.5, PhMe, 40°, CO/H_2 (1/1, 9 bar), 5 h	R^1 = *t*-Bu: **I** (—), 1 *R* + **II** (—), **I**:**II** = 93:7 R^1 = OMe: **I** (—), 7 *R* + **II** (—), **I**:**II** = 92:8	56

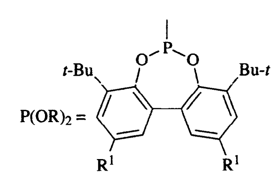
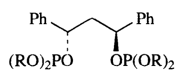
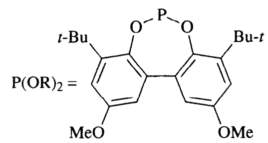


TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

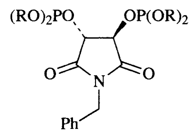
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.

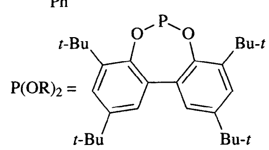




Rh (acac)$(CO)_2$, L*, P/Rh = 2.5, PhMe, CO/H_2 (1/1, 9 bar), 5 h — Refs. 56

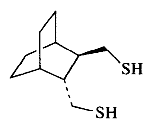
Temp.	Conv. (%)	I:II	% ee
40°	99	90:10	47 *S*
25°	45	95:5	62 *S*





Rh (acac)$(CO)_2$, L*, P/Rh = 2.5, PhMe, CO/H_2 (1/1, 9 bar), 5 h — Refs. 56

Temp.	Conv. (%)	I:II	% ee
40°	81	92:8	3 *S*
25°	27	95:5	10 *S*



$[Rh_2(\mu\text{-BCOS})(COD)_2]_2$, PPh_3, THF, CO/H_2 (1/1) — Refs. 808

P/Rh	*P* (bar)	Temp.	Time (h)	Conv. (%)	I:II	I + II
0	30	80°	24	99	54:46	(—)
2	5	80°	24	47	66:34	(—)
2	10	80°	12	86	86:14	(—)
4	10	80°	8	86	86:14	(—)
8	10	80°	8	81	85:15	(—)
8	10	65°	24	81	90:10	(—)

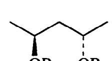
$[Rh_2(\mu\text{-BCOS})(COD)_2]_2$, ligand, THF, CO/H_2 (1/1) — Refs. 881

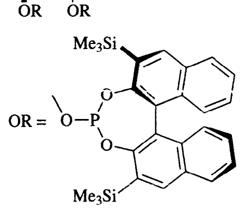
Ligand	P/Rh	*P* (bar)	Temp.	Time (h)	Conv. (%)	I:II	I (% ee)
—	—	30	65°	24	81	49:51	8 *S*
PPh_3	4	5	80°	24	50	73:27	7 *S*
PPh_3	4	10	65°	24	93	90:10	5 *S*
BPPP	2	10	65°	12	88	92:8	10 *S*
(+)-DIOP	4	10	65°	23	98	60:40	16 *S*
(–)-DIOP	4	10	65°	23	98	57:43	8 *R*
(+)-BDPP	4	10	65°	23	99	95:5	55 *S*
(–)-BDPP	4	10	65°	23	99	94:6	43 *R*
(+)-BDPP	2	10	65°	12	94	94:6	52 *S*
(–)-BDPP	2	10	65°	12	96	94:6	48 *R*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(+)-DIOP	$[Rh(\mu\text{-OMe})(COD)]_2$, CO/H_2 (1/1, 10 atm), P/Rh = 4, THF, 65°, 7 h	I (57), 12 *S* + II (37), I:II = 61:39	865

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-DIOP	$Pt(CH_3)Cl$(chiral ligand), $SnCl_2$, Pt/Sn = 1, PhMe, H_2/CO (1/1, 100 atm)		882

Temp.	Time (h)	Conv. (%)	I + II	I:II	I (% ee)	III	Polymer
30°	66	46.8	(67)	0.29	29.2 *R*	(4)	(29)
50°	22	52.6	(70)	0.41	27.2 *R*	(5)	(25)
80°	2	56.6	(67)	0.59	20.7 *R*	(9)	(24)





Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(structures above)	$Rh(acac)(CO)_2$, ligand, toluene-d_8, L/Rh = 1.1, H_2/CO (1/1, 20 bar), 25°, 5 h	I (20), 40 *R* + II (1) + PhEt (<1); I:II = 94:5	883

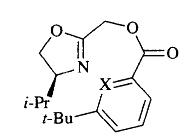
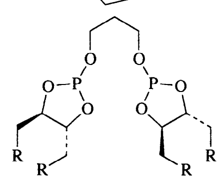
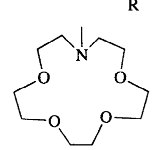
TAIBLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral ILigand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	"	$Pt(PhCN)_2Cl_2$, $SnCl_2$, P/Pt = 2.05, Sn/Pt = 1, H_2/CO (1/1, 100 atm), CH_2Cl_2, 17°, 70 h	**I** (—), 91 *R* + **II** (—) + PhEt (54); **I**:**II** = 60:40	408
	(*R*)-BINAP	$Pt(CH_3)Cl$(chiral ligand), $SnCl_2$, Pt/Sn = 1, PhMe, H_2/CO (atm)		882

H_2/CO	Temp.	Time (h)	Conv. (%)	I + II	I:II	I (% ee)	III	Polymer
50/50	30°	688	33.5	(63)	0.50	58.4 *R*	(3)	(34)
50/50	50°	118	79.8	(84)	0.58	41.6 *R*	(4)	(12)
50/50	80°	40	93.4	(67)	0.64	3.9 *R*	(5)	(29)
50/20	50°	132	75.5	(80)	0.50	23.1 *R*	(8)	(12)
50/80	50°	104	81.9	(87)	0.63	55.2 *R*	(2)	(11)
50/110	50°	88	77.7	(85)	0.72	66.8 *R*	(2)	(13)
110/50	50°	88	82.7	(75)	0.75	48.4 *R*	(12)	(13)

Reactant	Chiral ILigand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S*)-MOBIPH	$Pt(CH_3)Cl$(chiral ligand), $SnCl_2$, Pt/Sn = 1, PhMe, H_2/CO (atm)		882

H_2/CO	Temp.	Time (h)	Conv. (%)	I + II	I:II	I (% ee)	III	Polymer
50/50	30°	240	52.7	(85)	1.09	75.8 *S*	(3)	13
50/50	50°	164	86.7	(75)	0.73	56.3 *S*	(4)	22
50/50	80°	17	97.8	(77)	0.77	0.1 *S*	(7)	17
50/20	50°	148	70.0	(68)	0.79	28.8 *S*	(9)	23
50/80	50°	65	60.7	(70)	0.86	67.1 *S*	(2)	28
50/110	50°	74	74.5	(71)	0.96	72.1 *S*	(2)	28
110/50	50°	87	100	(73)	0.92	58.5 *S*	(7)	20

Reactant	Chiral ILigand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(+)-BINAP	[Rh(μ-OMe)(COD)]$_2$, CO/H_2 (1/1, 10 atm), P/Rh = 4, THF, 65°, 7 h	**I** (57), 25 *S* + **II** (6), **I**:**II** = 91:9	865
		Rh (acac)(CO)$_2$, ligand, L/Rh = 2, CO/H_2 (1/1, 50 atm), 20°, 22 h	see below	664
	 R = 	Rh(acac)(CO)$_2$, L/Rh = 1, CO/H_2 (1/1, 6 atm), CH_2Cl_2, 35°	**I** (—),<10 + **II** (—), **I**:**II** = 6.7	884
	(*S*,*S*)-BDPP	$PtCl_2$((*S*,*S*)BDPP), SnX_2, H_2/CO (1/1, 80 bar), AgY, PhMe		60

Ref. 664:

X	I	II	I:II
P	(94), —	(4)	24.8
CH	(28), —	(<1)	46.7

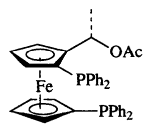
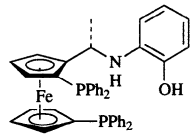
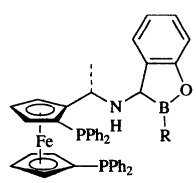
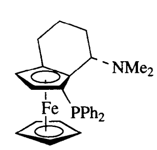
Ref. 60:

X	Y	Sn/Ag/Pt	Temp.	Time (h)	Conv. (%)	I + II	I:II	I (% ee)
Cl	—	2/0/1	100°	3	50	(88)	32:68	9.9 *R*
Cl	TfO	2/2/1	100°	25	75	(88)	37:63	1.6 *R*
Cl	—	2/0/1	60°	30	60	(90)	38:62	63.0 *S*
Cl	TfO	2/2/1	60°	100	98	(69)	44:56	0.9 *S*
Cl	—	2/0/1	40°	115	58	(98)	42:58	75.5 *S*
F	—	2/0/1	100°	5	26	(95)	31:69	15.1 *S*
F	—	2/0/1	40°	240	72	(98)	32:68	76.0 *S*
F	F	1/5/1	40°	180	65	(97)	33:67	71.3 *S*

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-BDBPP	*cis*-PtCl((*S,S*)-BDBPP)($SnCl_3$), PhMe, H_2/CO (1/1, 70 bar)		885

Temp.	Time (h)	Conv. (%)	I:II	I (%ee)	III
70°	27	90	6.14	19 (*S*)	(27)
100°	8	27	3.84	12 (*S*)	(47)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*S,S*)-BDPP	$PtCl_2$((*S,S*)BDPP), H_2/CO (1/1, 80 bar), Pt/$SnCl_2$/Sn(OTf)$_2$ = 1/2/2, PhMe, 100°, 35 h	**I** (39), 29.3 *S* + **II** (57) + **III** (5)	60
		Rh(acac)(CO)$_2$, THF, 80°, chiral ligand, L/Rh = 4, CO/H_2 (1/1, 6 atm)	**I** (—),— + **II** (—), **I**:**II** = 2	886
		Rh(acac)(CO)$_2$, THF, 80°, chiral ligand, L/Rh = 4, CO/H_2 (1/1, 6 atm)	**I** (—),— + **II** (—), **I**:**II** = 4	886
		Rh(acac)(CO)$_2$, THF, 80°, chiral ligand, L/Rh = 4, CO/H_2 (1/1, 6 atm)	**I** (—),— + **II** (—), **I**:**II** = 4-5	886
		$PtCl_2$, $SnCl_2$, CO/H_2 (1/1, 80 bar), PhMe	**I** + **II** + **III**	887

Additional Ligand	Time (h)	Temp	Conv. (%)	(I+II)/(I+II+III)	(I)/(I+II)	I(%ee)
—	100	80°	89	74	58	—
BDPP	30	80°	79	93	32	21(*S*)
BDPP	15	100°	90	83	60	7(*S*)

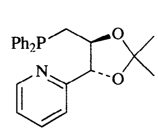
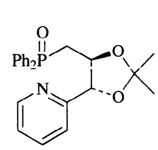
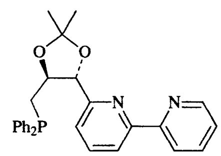
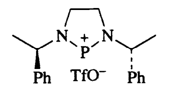
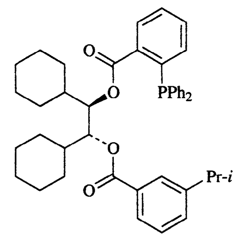
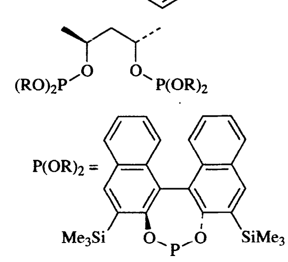
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	Ala-Xaa$_1$-Ala-ala-Xaa$_2$-Val-Ala-Ala-Xaa$_2$-Ala-Xaa$_1$-Ala Xaa$_1$ = aminoisobutyric acid Xaa$_2$ = diphenylphosphinoserine	Chiral Ligand/Rhcomplex, CO/H_2	**I** (85), 40 *S*	888
		Rh(acac)(CO)$_2$, C_6H_6, L*/Rh = 2.5, 30°, 20 h, CO/H_2 (1/1, 90 atm)	**I** (—, 1 (*R*)), **I** + **II** (70), **I**:**II** = 95:5	889
	"	Rh(CO)(L*)Cl, C_6H_6, 30°, 21 h, CO/H_2 (1/1, 85 atm)	**I** (—), 28 *R*, **I** + **II** (15), **I**:**II** = 90:10	889
	"	PtCl(ligand)($SnCl_3$), C_6H_6, 60 °, 18 h, CO/H_2 (1/1, 90 atm)	**I** (—), 31 *R*, **I** + **II** (12), **I**:**II** = 70:30	889
		Rh(acac)(CO)$_2$, C_6H_6, L*/Rh = 2.5, 30°, 5 h, CO/H_2 (1/1, 90 atm)	**I** + **II** (95), 1 *R*, **I**:**II** = 95:5	889

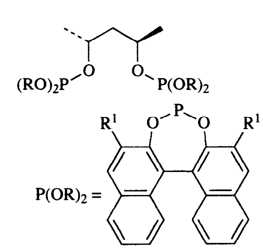
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs
		Rh(acac)(CO)$_2$, C_6H_6, L*/Rh = 2.5, 30°, 1 h, CO/H_2 (1/1, 90 atm)	I + II (95), 1 *R*, I:II = 97:3	889
		Rh (acac)(CO)$_2$, P/Rh = 2, CO/H_2 (1/1, 50 atm), 20°, 22 h	I (10), <5 + II (<1), I:II = 29.8	664
		Rh (acac)(CO)$_2$, P/Rh = 2, CO/H_2 (1/1, 50 atm), 20°, 22 h	I (5), —, I:II = 100:0	664
		Rh(acac)(CO)$_2$, ligand, L/Rh = 1.1, toluene-d_8, CO/H_2 (1/1, 20 atm)		883

Temp.	Conv. (%)	TOF	I	II	III	I (% ee)
50°	98	281	(89)	(10)	(1)	8 *R*
40°	89	259	(91)	(8)	(1)	18 *R*
25°	21	45	(94)	(5)	(1)	40 *R*

Rh(acac)(CO)$_2$, ligand, H_2/CO (1/1) — 890

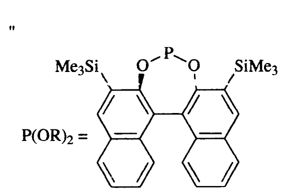
Ligand	L/Rh	Solvent	*P* (atm)	Temp.	Time (h)	Conv. (%)	I	I (% ee)
(*S*)-NAPHOS	3	toluene	100	40°	24	53	(83)	34 *S*
(*S*)-NAPHOS	3	toluene	70	40°	40	89	(96)	32 *S*
(*S*)-BINAS	4	MeOH-H_2O/toluene	100	40°	25	92	(95)	18 *S*
(*R*)-BDPAP	3	toluene	80	50°	24	98	(97)	0
(*R*)-BDPAP	3	toluene	100	25°	18	52	(98)	0



Rh(acac)(CO)$_2$, ligand, toluene-d_8, CO/H_2 (1/1, 20 atm) — 883

R^1	P/Rh	Temp.	Time (h)	Conv. (%)	TOF	I	II	III	I (% ee)
Me_3Si	2.2	50°	15	38	104	(86)	(13)	(1)	21 *S*
Me_3Si	2.2	25°	23	20	14	(91)	(7)	(2)	47 *S*
Me_3Si	8.8	25°	15	26	11	(94)	(6)	(0)	57 *S*
Et_3Si	2.2	50°	15	94	256	(90)	(9)	(1)	20 *S*
Et_3Si	2.2	25°	24	51	17	(94)	(6)	(0)	28 *S*
TBDMS	2.2	50°	15	47	163	(85)	(14)	(1)	7 *S*
TBDMS	2.2	25°	24	36	16	(93)	(6)	(1)	15 *S*

"



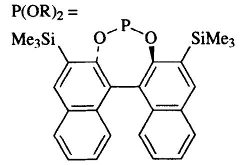
Rh(acac)(CO)$_2$, ligand, L/Rh = 1.1, toluene-d_8, CO/H_2 (1/1, 20 atm) — 883

Temp.	Conv. (%)	TOF	I	II	III	I (% ee)
50°	99	386	(87)	(10)	(3)	12 *S*
40°	99	186	(92)	(6)	(2)	30 *S*
25°	18	28	(95)	(4)	(1)	38 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.

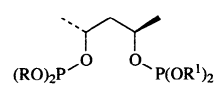
"

$P(OR)_2$ =

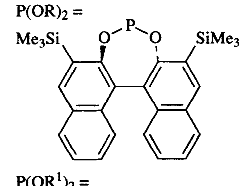


Rh(acac)(CO)$_2$, ligand, L/Rh = 1.1, toluene-d_8, CO/H$_2$ (1/1, 20 atm) — Refs. 883

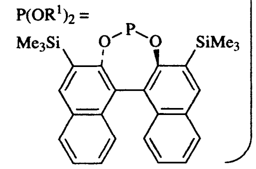
Temp.	Time (h)	Conv. (%)	TOF	I	II	III	I (% ee)
50°	5	43	133	(83)	(13)	(4)	58 *S*
25°	24	38	17	(88)	(8)	(4)	69 *S*
15°	24	12	11	(92)	(6)	(2)	86 *S*



$P(OR)_2$ =

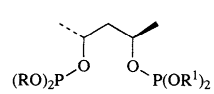


$P(OR^1)_2$ =

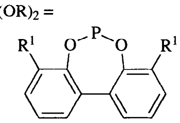


Rh(acac)(CO)$_2$, ligand, L/Rh = 1.1, toluene-d_8, CO/H$_2$ (1/1, 20 atm) — Refs. 883

Temp.	Conv. (%)	TOF	I	II	III	I (% ee)
50°	36	12	(87)	(11)	(2)	16 *S*
40°	25	6	(88)	(11)	(1)	18 *S*
25°	2	4	(91)	(8)	(1)	23 *S*

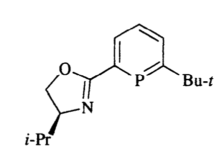


$P(OR)_2$ =



Rh(acac)(CO)$_2$, ligand, L/Rh = 1, toluene-d_8, CO/H$_2$ — Refs. 883

R^1	H$_2$/CO (atm/atm)	Temp.	Time (h)	Conv. (%)	I	II	III	I (% ee)
Me$_3$Si	10:10	50°	15	52	(84)	(13)	(3)	60 *S*
Me$_3$Si	10:10	40°	15	21	(89)	(8)	(3)	67 *S*
Me$_3$Si	10:10	25°	23	26	(93)	(5)	(2)	87 *S*
Me$_3$Si	10:20	25°	110	69	(95)	(4)	(1)	53 *S*
Et$_3$Si	10:10	50°	15	14	(85)	(12)	(3)	25 *S*
Et$_3$Si	10:10	40°	15	7	(93)	(3)	(4)	34 *S*
Et$_3$Si	10:10	25°	24	7	(89)	(8)	(3)	29 *S*
TBDMS	10:10	50°	15	30	(67)	(29)	(4)	11 *S*
TBDMS	10:20	50°	15	53	(81)	(17)	(2)	14 *S*
TBDMS	5:10	50°	15	72	(71)	(23)	(6)	20 *S*
TBDMS	10:10	25°	72	8	(78)	(20)	(2)	4 *S*



Rh (acac)(CO)$_2$, P/Rh = 2, CO/H$_2$ (1/1, 50 atm), 20 °, 22 h — **I** (40, —) + **II** (2), **I**:**II** = 21.4 — Refs. 664

Pt/SnCl$_2$ = 1/2, PhMe — Refs. 891

Catalyst	CO/H$_2$ (atm)	Time (h)	Temp.	Conv. (%)	Aldehydes:PhEt	I:II	%ee
[PtCl$_2$(DPE-BNP)]$_n$/SnCl$_2$	40/40	24	90°	6	48:52	72:28	—
PtCl$_2$(DIOP-BNP)/SnCl$_2$	40/40	20	85°	97	64:36	63:37	20 (*S*)
PtCl$_2$(DIOP-BNP)/SnCl$_2$	40/40	20	58°	50	74:26	68:32	44 (*S*)
PtCl$_2$(DIOP-BNP)/SnCl$_2$	40/40	40	38°	22	73:27	66:34	39 (*S*)
PtCl$_2$(DIOP-BNP)/SnCl$_2$	40/55	380	32°	77	78:22	63:37	43 (*S*)
PtCl$_2$(SKEWPHOS-BNP)/SnCl$_2$	40/40	22	58°	45	76:24	68:32	17 (*S*)
PtCl$_2$(SKEWPHOS-BNP)/SnCl$_2$	40/40	22	34°	10	71:29	65:35	18 (*S*)
PtCl$_2$(SKEWPHOS-BNP)/SnCl$_2$	40/55	93	32°	97	73:27	78:22	24 (*S*)
PtCl$_2$(SKEWPHOS-BNP)/SnCl$_2$	40/80	70	32°	89	68:32	80:20	24 (*S*)
PtCl$_2$(SKEWPHOS-BNP)/SnCl$_2$	20/100	70	32°	95	55:45	85:15	20 (*S*)

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

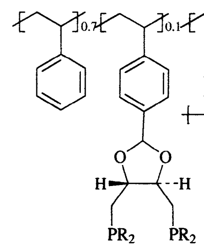
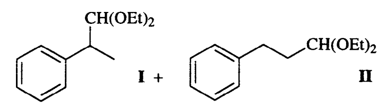
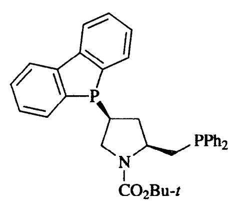
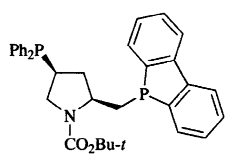
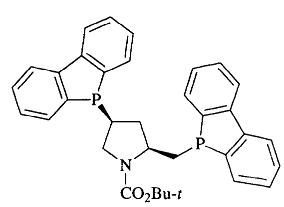
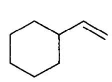
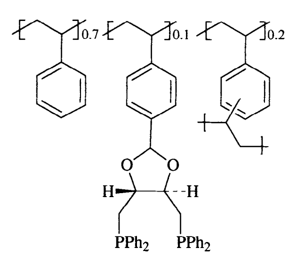
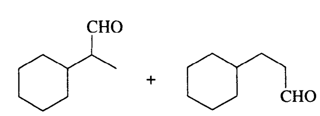
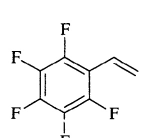
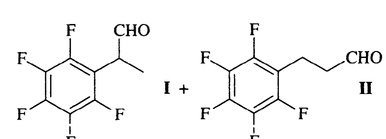
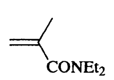
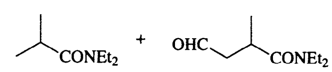
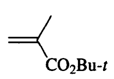
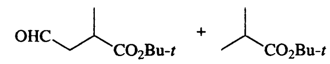
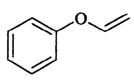
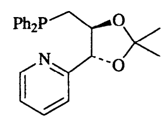
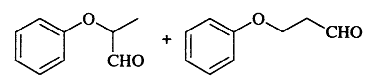
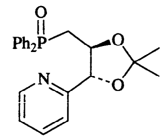
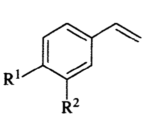
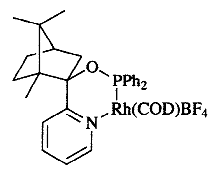
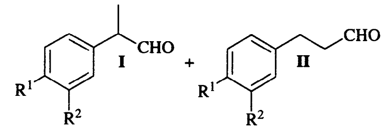
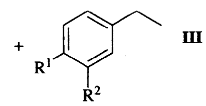
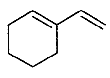
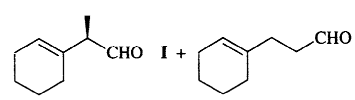
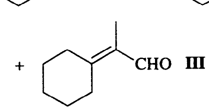
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	 PR_2 = DBP	$HRh(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/1, 1400 psi), 80°, 12 h	**I** (—), 6.1 + **II** (—) + **III** (—), **I**:**II** = 17:1	853
	(–)-BPPM	Pt(Chiral Ligand)Cl_2/ $SnCl_2$, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), C_6H_6, 60°, 150 h	 **I** + **II** **I** (—), >96 + **II** (—), **I**:**II** = 1:2	409
		Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 114 h	**I** (—), >96 + **II** (—), **I**:**II** = 1.2:1	409
		Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 115 h	**I** (—), >96 + **II** (—), **I**:**II** = 0.9:1	409
		Pt(Chiral Ligand)Cl_2/ $SnCl_2$, C_6H_6, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 95 h	**I** (—), >96 + **II** (—), **I**:**II** = 3.3:1	409
		$HRh(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/1, 400 psi), 40°, 96 h	 **I** (—), — **II** (—) **I**:**II** = 0.31	853
	DIOP	$HRh(CO)(PPh_3)_3$, C_6H_6, CO/H_2 (1/1, 16 psi), 50°, 168 h	**I** (—, —) + **II** (—), **I**:**II** = 0.025	853
	(*R,S*)-BINAPHOS	Rh (acac)$(CO)_2$, C_6H_6, H_2/CO (1/1, 100 atm) L/Rh = 4, 60°, 18 h	**I** (—, 96 (*R*)) + **II** (—), **I**:**II** = 86:14	413
	(*R,S*)-BINAPHOS	Rh(acac)$(CO)_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6	 **I** + **II** **I**+**II** = 72, **I**:**II** = 96:4, **I** (98) *R*	113

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	"	$Rh_4(CO)_{12}$/(–)-DIOP, CO/H_2 (1/1, 300 bar), PhMe, 130°, 32 h	 I (33) + II (44, —)	803
	"	$PtCl(SnCl_3)$[(–)-DIOP], CO/H_2 (1/1, 300 bar), PhMe, 130°, 50 h	II (10), — + starting material (90)	803
	"	Pt((–)-DIOP)($SnCl_3$)Cl, CO/H_2 (1/1, 80 atm), PhMe, 100°, 25 h	 I (32), 20 *S* + II (8)	762
		$Rh(acac)(CO)_2$, C_6H_6, L^*/Rh = 2.5, 80°, 5 h, CO/H_2 (1/1, 80 atm)	 I + II; I + II (70), ca. 10, I:II = 80:20	714
		$Rh(acac)(CO)_2$, C_6H_6, L^*/Rh = 2.5, 80°, 2 h, CO/H_2 (1/1, 80 atm)	I + II (97), —, I:II = 87:13	714
		CO/H_2 (1/1), C_6H_6, 80°, 24 h	 I + II +  III	892, 256

R^1	R^2	Conv. (%)	I + II	I:II	I (% ee)	III
H	H	95	(95)	80:20	8.7 *S*	0
i-Bu	H	98	(96)	60:40	18.8 *S*	2
H	PhO	97	(70)	54:46	6.6 *S*	7

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	$Rh(acac)(CO)_2$, L/Rh = 4, H_2/CO (1/1), C_6H_6	 I + II +  III	857

Temp.	*P* (atm)	Time (h)	Conv. (%)	I:II:III	I (% ee)
60°	100	18	85	86:14:0	96 *R*
40°	100	96	78	88:12:0	96 *R*
30°	100	108	60	88:12:0	97 *R*
40°	100	144	96	70:11:19	88 *R*
40°	40	48	84	88:12:0	95 *R*
40°	40	96	95	84:12:4	96 *R*
40°	20	49	94	87:13:0	96 *R*

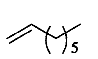
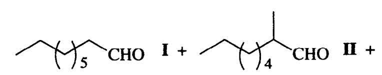
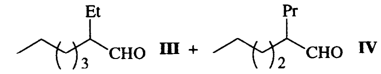
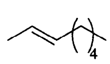
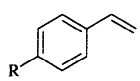
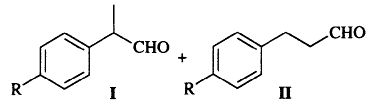
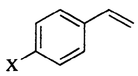
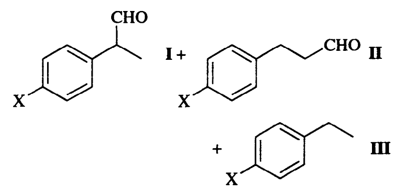
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	BPNAP	Rh_4(μ-BPNAP)$(CO)_{10}$, CO/H_2 (1/1, 7 atm), PhMe, 110°	 I + II +  III + IV; I + II + III + IV (—), I:II:III:IV = 11.9:3.5:1.1:1	893
	BPNAP	$Rh(acac)(CO)_2$, BPNAP, L/Rh = 1.1, C_6H_6, CO/H_2 (1/1, 13 atm), 80°, overnight	I + II + III + IV (—), I:II:III:IV = 2.9:3.3:1.4:1	893

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	$Rh(acac)(CO)_2$, L/Rh = 4, H_2/CO (1/1, 100 atm), C_6H_6, 60°		34, 113

Time (h)	R	I + II	I:II	I (% ee)
20	Me	(97)	86:14	95 (+)
34	OMe	(>99)	87:13	88 (+)
34	Cl	(>99)	87:13	93 (+)
66	Bu-*i*	(>99)	88:12	92 *S*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BPPM	$PtCl_2(BPPM)/SnCl_2$, CO/H_2 (1/1, 2650 psi), C_6H_6, 60°, 8 h		406

X	Conv. (%)	I/II	% ee
H	89	0.47	70
Br	49	0.53	75
Ac	47	0.87	85
NO_2	14	1.40	58
Me	77	0.57	72
OMe	65	0.60	73

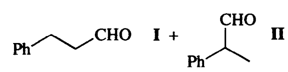
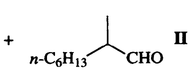
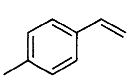
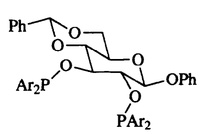
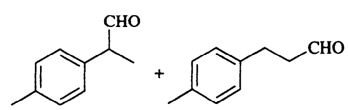
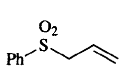
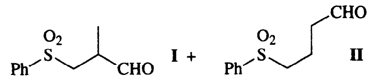
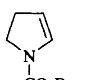
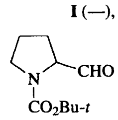
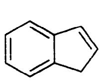
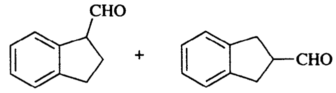
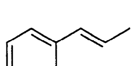
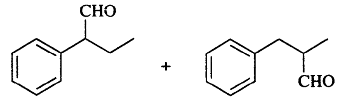
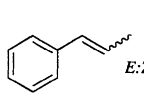
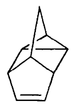
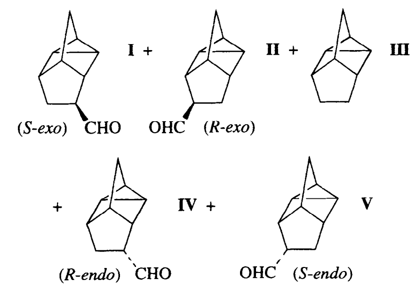
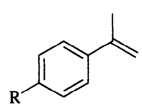
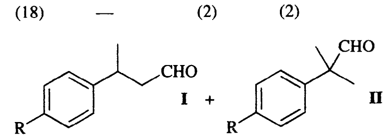
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
Ph—≡	(–)-DIOP	$RhH(CO)(PPh_3)_3$, 95°, CO/H_2 (1/1, 85 psi), 28 h	 I (—) + II (—), 0.9 *R*, I:II = 62:38	855
n-C_6H_{13}—≡	(–)-DIOP	$RhH(CO)(PPh_3)_3$, 95°, CO/H_2 (1/1, 80 psi), 24 h	*n*-C_8H_{17}CHO I +  II; I (—) + II (—), 0.2 *S*, I:II = 74:26	855
C_9 	 Ar = 3,5-$(CF_3)_2C_6H_3$	$Rh(COD)(L^*)BF_4$, CO/H_2 (1600 psi), hexane	 I (—), 30 + II (—) I:II = 94:6	843
	(*R,S*)-BINAPHOS	$Rh(acac)(CO)_2$, PhH, 40°, CO/H_2 (1/1, 100 atm), L/Rh = 4-4.4, 46 h	 I (—), 65 (+) + II (—), I:II = 86:14	837
	(–)-DIPHOL	$RhH(CO)(PPh_3)_3$, L/Rh = 4, C_6H_6, 52°, CO/H_2 (500 psi), 8 d	 (—), 0.35 *R*	801
	(*S, R*)-BIPHEMPHOS	$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), 60°, 20 h	 I (57), 88 (+) + II (5)	414
	(*S, R*)-BINAPHOS	"	I (57), 83 (+) + II (5)	414
	(*R,S*)-BINAPHOS	"	I (—), 83 (–) + II (—), I:II = 92:8	36
	(*R,R*)-BCO-DBP	$Pt(BCO\text{-}DBP)Cl_2/SnCl_2$, CO/H_2 (7/15, 220 atm), C_6H_6, 80°, 7 h	I (21), 45 + starting material (78)	872
	(*R,S*)-BINAPHOS	$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), 60°, 50 h	 I (—), 92 *R* + II (—), I:II = 97:3	36
 *E:Z* = 1:1	(*R,S*)-BINAPHOS	$Rh(acac)(CO)_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6, 60°	I (—), 79 *R* + II (—), I:II = 78:22	113

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		CO/H_2 (1/1, 80 bar), PhMe		894

Catalyst	Temp.	Time (h)	I + II	I:II	III	IV + V
$[Rh(NBD)Cl]_2$ + 6 PPh_3	100°	8	(93)	—	(0)	(7)
$[Rh(NBD)Cl]_2$ + 3 (2*S*, 3*S*)-CHIRAPHOS	100°	8	(96)	61.0:39.0	(0)	(4)
$[Rh(NBD)Cl]_2$ + 3 (2*S*, 3*S*)-CHIRAPHOS	50°	8	(59)	—	(0)	(2)
$[Rh(NBD)Cl]_2$ + 3 (2*S*, 3*S*)-CHIRAPHOS	50°	15	(98)	48.3:51.7	(0)	(2)
$[Rh(NBD)Cl]_2$ + 3 (4*S*, 5*S*)-DIOP	100°	8	(98)	48.5:51.5	(0)	(2)
$PtCl(SnCl_3)$[(*S*, *S*)-BDPP]	100°	4	(96)	46.2:53.8	(0)	(3)
$PtCl(SnCl_3)$[(*S*, *S*)-BDPP]	25°	60	(96)	41.9:58.1	(0)	(2)
$PtCl_2$[(*S*, *S*)-BPPM] + $SnCl_2$	100°	10	(55)	40.7:59.3	(tr)	(2)
$PtCl_2$[(*R*)-PROPHOS] + $SnCl_2$	100°	10	(93)	50.6:49.4	(4)	(3)
$PtCl_2$[(*R*)-PROPHOS] + $SnCl_2$	25°	115	(89)	49.6:50.4	(2)	(2)
$PtCl_2$[(*R*)-PROPHOS] + $SnCl_2$	25°	20	(18)	—	(2)	(2)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*, *R*)-DIOP	[(*R*,*R*)-DIOP]$PtCl(SnCl_3)$, C_6H_6, hydroquinone, 80°, CO/H_2 (180 bar)		895

R	I:II	Yield	% ee
OMe	97:3	(16)	(17)
H	>99:1	(62)	(15) *S*
Cl	>99:1	(30)	(12)
CF_3	>99:1	(55)	(13)
NO_2	—	(0)	(—)

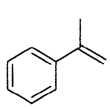
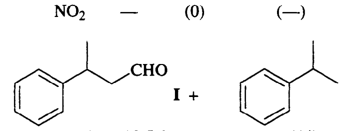
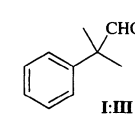
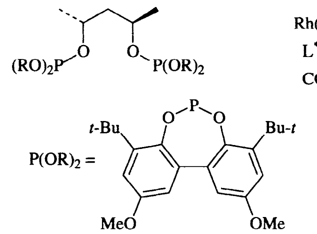
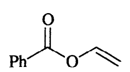
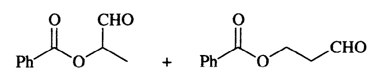
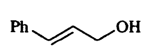
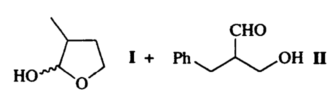
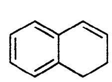
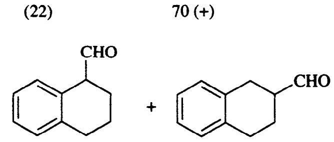
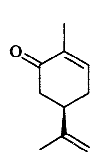
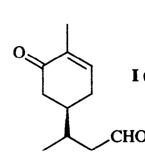
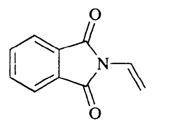
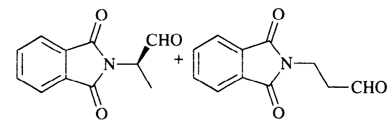
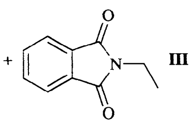
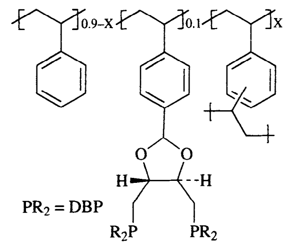
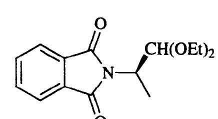
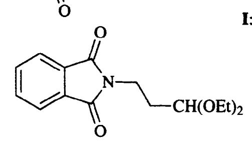
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R*,*R*)-BCO-DPP	[(*R*,*R*)-BCO-DPP]$PtCl_2$/ $SnCl_2$, C_6H_6, 80°, 8.5 h, CO/H_2 (7/15, 220 atm)		407
	(*R*,*R*)-BCO-DBP	[(*R*,*R*)-BCO-DBP]$PtCl_2$/ $SnCl_2$, C_6H_6, 80°, 9 h, CO/H_2 (7/15, 220 atm)	I (—), 15.9 *R* + II (74)	407
	(*R*,*R*)-EtDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 80°, 165 h	I (—), 0.9 *S* +  III (—) I:III = 86:14	850
	(*R*,*R*)-CyDIOP	$Rh_4(CO)_{12}$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 80°, 66 h	I (—), 1.5 *S* + III (—), I:III = 91:9	850
	(*S*,*S*)-CHIRAPHOS	$[Rh(NBD)Cl]_2$, L/Rh = 4, CO/H_2 (1/1, 80 atm), 100°, 70 h	I + III (30), 21.4 *R*, I:III = 99:1	130
	"	Pt(CHIRAPHOS)$(SnCl_3)$Cl, CO/H_2 (1/1, 80 atm), 100°	I (—), 3.0 *S* + III (—), I:III = 99:1	130
	(*R*,*R*)-DIOP	$RhH(CO)(PPh_3)_3$, L/Rh = 4, 100°, 46 h, CO/H_2 (1/1, 80 atm)	I (77), 1.4 *R*	130
	"	Pt(DIOP)$(SnCl_3)$Cl, 100°, CO/H_2 (1/1, 80 atm)	I (—), 7.2 *S*	130

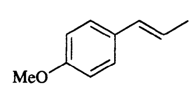
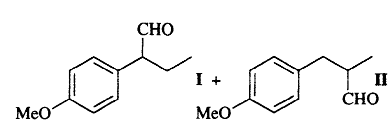
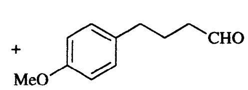
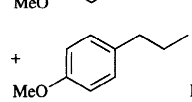
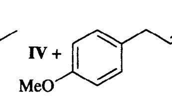
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(+)-DICOL	$HRh(CO)(PPh_3)_3$/DICOL (1/3), C_6H_6, 90°, 110 h, CO/H_2 (1/1, 80-90 atm)	I (49), 1 *R* + III (2.6)	851
		$Rh(acac)(CO)_2$, L^*/Rh = 4, Me_2CO, 50°, CO/H_2 (1/1, 600 psi)	I (—), 26 *S*	38
	(*R*)-BPNAP	$Rh(acac)(CO)_2$, (*R*)-BPNAP, L/Rh = 1.7, PhMe, CO/H_2 (1/1, 7 atm), 110°, 20 h	I (96), 0	893
	(–)-DIOCOL	$HRh(CO)(PPh_3)_3$/(–)-DIOCOL (1/1.5), C_6H_6, CO/H_2 (1/1, 80-90 atm), 90°, 240 h	I (48), 1 *S* + III (3)	851
	(*S,S*)-DIOP	Rh(NBD)(DIOP)·BPh_4, L/Rh = 3, 80°, C_6H_6, CO/H_2 (44/56, 250 psi)	 I (—), 30 *R* + II (—)	842
	(*R,R*)-DIPHOL	Rh(COD)(acac), L/Rh = 4, C_6H_6, 80°, CO/H_2 (44/56, 1000 psi)	I (—), 12 *R* + II (—)	842
	(*R,S*)-BINAPHOS	$Rh(acac)(CO)_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6, 60°, 71 h	I (—), 89 *S* + II (>99), I:II=91:9	113
		$Rh(acac)(CO)_2$, ligand, L/Rh = 4, C_6H_6, CO/H_2 (1/1), 60°	 I + II	836

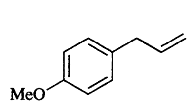
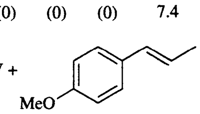
Ligand	H_2/CO (atm/atm)	Time (h)	I	I (% ee)
PPh_3	50/50	72	(>99)	—
(*R,S*)-BINAPHOS	15/15	30	(>99)	88 (+)
(*S*)-BINAP	15/15	30	(0)	—
(*R*)-2-Nap-BIPNITE	15/15	30	(>99)	5 (+)
(*R,S*)-BINAPHOS	50/50	57	(>99)	6 (+)
(*R,S*)-BINAPHOS	50/50	20	(53)	12 (+)
(*R,S*)-BINAPHOS	25/25	30	(65)	15 (+)
(*R,S*)-BINAPHOS	20/20	30	(73)	40 (+)
(*R,S*)-BINAPHOS	5/5	30	(64)	75 (+)
(*R,S*)-BINAPHOS	0.5/0.5	30	(22)	70 (+)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R, S*)-BIPHEMPHOS	$Rh(CO)_2(acac)$, C_6H_6, H_2/CO (1/1, 100 atm), 60°, 12 h	 I (70), 96 (–) + II (4), —	414
	(*R, S*)-BINAPHOS	"	I (71), 97 (–) + II (3), —	414, 36
	(+)-BDPP	$PtCl_2(BDPP)/SnCl_2$, CO/H_2 (1/1, 80 bar), PhMe, 100°, 7 h	 I (—), (5*R*,8*R*):(5*R*,8*S*) = 70:30	896
	(–)-BDPP	"	I (—), (5*R*,8*R*):(5*R*,8*S*) = 44:56	896

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BPPM	$PtCl_2$(BPPM)/$SnCl_2$, CO/H_2 (1/1, 2650 psi), C_6H_6, 60°, 46 h	 I (—), 73 *R* + II (—), I:II = 1:2	406
	(–)-BDP-DIOP	Pt(BDP-DIOP)($SnCl_3$)Cl, C_6H_6, 60°, 60 h, CO/H_2 (1/1, 2700 psi)	I (—), 70 *S* + II (—) +  III (—) I:II = 6:1	411
	 PR_2 = DBP	Pt(Chiral ligand)Cl_2, $SnCl_2$, C_6H_6, 60°, CO/H_2 (1/1, 2700 psi)		411, 412
		Time (h)		
		70	X = 0, I (—), 62 *S* + II (—) + III (—), I:II = 3.5:1	
		100	X = 0.1, I (—), 60 *S* + II (—) + III (—), I:II = 2.4:1	
	(–)-DIPHOL	$RhH(CO)(PPh_3)_3$, 50-56°, L/Rh = 4, C_6H_6, 6 d, CO/H_2 (1/1, 500 psi)	I (—), 34.1 *R*	801
	"	$RhH(CO)(PPh_3)_3$, 48°, L/Rh = 3, MEK, 4 d, CO/H_2 (1/1, 500 psi)	I (—), 38.3 *R*	801
	(+)-DIPHOL	$RhH(CO)(PPh_3)_3$, 40-50°, L/Rh = 4, C_6H_6, 12 d, CO/H_2 (1/1, 500 psi)	I (—), 31.3 *S*	801
	(–)-BPPM	$PtCl_2$(BPPM)/$SnCl_2$, CO/H_2 (1/1, 2700 psi), $HC(OEt)_3$, 60°, 240 h	 I (—), >96 *R* +  II (—) I:II = 1:2	406

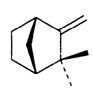
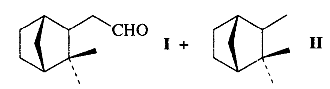
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Catalyst, CO/H_2 (1/1, 80 atm), PhMe, 100 °	 I + II +  III +  IV +  V	898

Catalyst	Time (h)	Conv. (%)	I	II	III	IV	V	I (% ee)
$PtCl_2$((*S,S*)BDPP)/$SnCl_2$	21	44.5	(22)	(14)	(6)	(2)	(1)	27.5
[Rh(NBD)Cl]$_2$/4.4PPh_3	7	84	(71)	(12)	(0)	(1)	(1)	—
[Rh(NBD)Cl]$_2$/2.2(*R,R*)DIOP	14	51	(44)	(7)	(0)	(0)	(0)	7.4

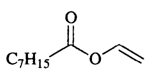
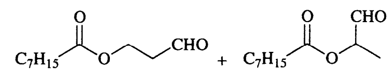
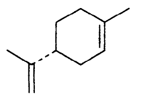
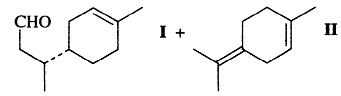
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Catalyst, CO/H_2 (1/1, 80 atm), PhMe, 100 °	I + II + III + IV +  VI	898

Catalyst	Time (h)	Conv. (%)	I	II	III	IV	VI	I (% ee)
$PtCl_2$((*S,S*)BDPP)/$SnCl_2$	27	8.5	(2)	(3)	(2)	(1)	(1)	—
[Rh(NBD)Cl]$_2$/4.4PPh_3	7	97	(21)	(30)	(35)	(1)	(10)	—
[Rh(NBD)Cl]$_2$/2.2(*R,R*)diop	7	99.5	(23)	(32)	(39)	(1)	(5)	3.6

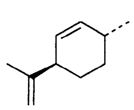
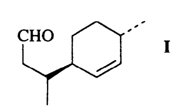
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		CO/H_2 (1/1, 80 bar), PhMe, 100°	 I + II	897

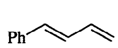
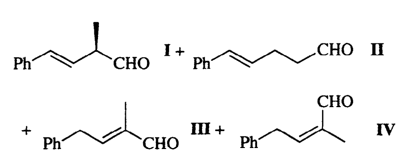
Catalyst	Time (h)	Conv. (%)	I/(I + II) (%)	I [(1*R*,3*S*,4*S*):(1*R*,3*R*,4*S*)]
$[Rh(NBD)Cl]_2/PPh_3$	10	> 99	93	60:40
$[Rh(NBD)Cl]_2$/DPPE	20	85	87	65:35
$[Rh(NBD)Cl]_2$/DPPB	20	91	88	66:34
$[Rh(NBD)Cl]_2$/(*S,S*)-DIOP	20	90	90	69:31
$[Rh(NBD)Cl]_2$/(*R,R*)-DIOP	20	91	91	52:48
$PtCl_2$(DPPE)/$SnCl_2$	13	2	—	—
$PtCl_2$((+)-BDPP)/$SnCl_2$	20	68	93	67:33
$PtCl_2$(DPPB)/$SnCl_2$	20	17	83	62:38

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	Rh(acac)$(CO)_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6, 60°, 72 h	 I (—), 80 *S* + II (>99), I:II = 88:12	113
		CO/H_2 (1/1, 80 bar), PhMe, 100°	 I + II	897, 896

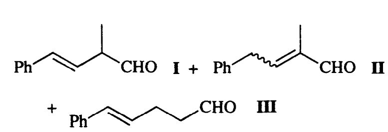
Catalyst	Time (h)	Conv. (%)	I/(I + II) (%)	I [(4*R*,8*S*):(4*R*,8*R*)]
$[Rh(NBD)Cl]_2/PPh_3$	22	98	97.8	45:55
$[Rh(NBD)Cl]_2$/DPPP	20	91	93.5	49:51
$[Rh(NBD)Cl]_2$/DPPB	38	96	94.4	50:50
$[Rh(NBD)Cl]_2$/(*S,S*)-DIOP	20	96	95.5	49:51
$[Rh(NBD)Cl]_2$/(*R,R*)-DIOP	16	87	95.0	49:51
$PtCl_2$(DPPP)/$SnCl_2$	35	20	> 99	52:48
$PtCl_2$((+)-BDPP)/$SnCl_2$	35	28	> 99	38:62
$PtCl_2$((–)-BDPP)/$SnCl_2$	25	27	> 99	60:40

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		CO/H_2 (1/1, 80 bar), PhMe, 100°	 I	897

Catalyst	Time (h)	Conv. (%)	I [(3*R*,6*R*,8*S*):(3*R*,6*R*,8*R*)]
$[Rh(NBD)Cl]_2/PPh_3$	10	97	43:57
$[Rh(NBD)Cl]_2$/DPPB	20	90	48:52
$[Rh(NBD)Cl]_2$/(*R,R*)-DIOP	20	88	49:51
$[Rh(NBD)Cl]_2$/(*S,S*)-DIOP	20	86	53:47
$PtCl_2$(BDPP)/$SnCl_2$	11	95	41:59
$PtCl_2$(DPPB)/$SnCl_2$	24	7	45:55
$PtCl_2$(DPPE)/$SnCl_2$	26	9	48:52

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	Rh(acac)$(CO)_2$, L/Rh = 4, H_2/CO (1/1), PhH	 I + II + III + IV	857

Temp.	Press. (atm)	Time (h)	Conv. (%)	I:II:III:IV	I (% ee)
60°	100	18	>99	57:2:28:13	64 *R*
30°	100	48	62	91:5:2:2	89 *R*
30°	100	72	90	42:1:56:1	56 *R*
30°	40	24	88	92:5:2:1	90 *R*
30°	20	12	47	94:6:0:0	92 *R*

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(*R,S*)-BINAPHOS	Rh (acac)$(CO)_2$, C_6H_6, H_2/CO (1/1, 100 atm) L/Rh = 4, 30°	 I + II + III	413

Time (h)	Conv. (%)	I:II:III	I (% ee)
72	90	42:57:1	56
48	62	91:4:5	89

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

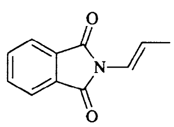
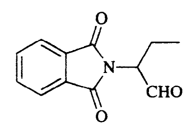
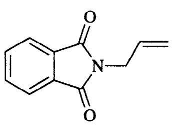
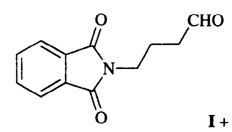
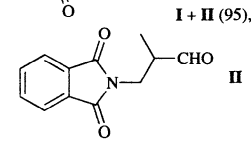
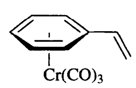
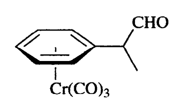
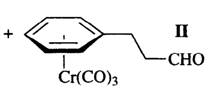
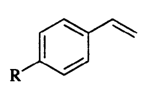
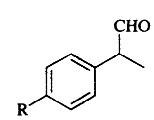
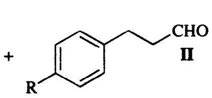
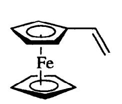
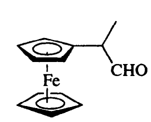
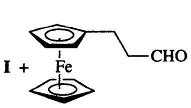
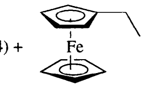
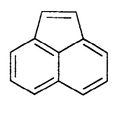
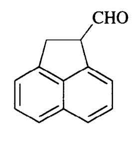
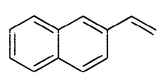
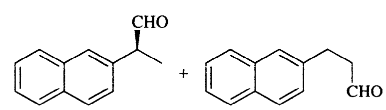
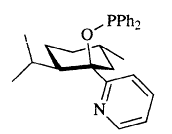
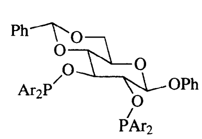
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_{11}				
	(–)-DIOP	$HRh(CO)(PPh_3)_3$/DIOP (1/2), C_6H_6, 100°, 24 h, CO/H_2 (1/1, 100 atm)	 I (98), 0	825
	(–)-DIOCOL	$HRh(CO)(PPh_3)_3$/DIOCOL (1/2), C_6H_6, 100°, 24 h, CO/H_2 (1/1, 100 atm)	I (90), 0	825
	(–)-DIOP	$HRh(CO)(PPh_3)_3$/Chiral Ligand (1/2), C_6H_6, 70°, CO/H_2 (1/1, 100 atm), 15-20 h	 I +  II; I + II (95), 1 *R*, I:II = 1.3	825
	(–)-DIOCOL	"	I + II (90), 1.5 *R*, I:II = 1.7	825
	(–)-DIOP	$[RhCl(CO)_2]_2$, L/Rh = 2, CO/H_2 (400 psi), 50°, 66 h	 I +  II; I + II (82), 20 *R*, I:II = 90:10	387
	(–)-BPPM	"	I + II (70), 14 *S*, I:II = 95:5	387
	(–)-BINAP	"	I + II (89), 7 *R*, I:II = 93:7	387
	(–)-DIOP	$Pt(DIOP)Cl_2/SnCl_2$, 50°, CO/H_2 (400 psi), 48 h	I + II (73), 46 *R*, I:II = 73:27	387
	(–)-BPPM	$Pt(BPPM)Cl_2/SnCl_2$, 50°, CO/H_2 (400 psi), 88 h	I + II (84), 40 *S*, I:II = 24:76	387
	(–)-BINAP	$Pt(BINAP)Cl_2/SnCl_2$, 65°, CO/H_2 (400 psi), 66 h	I + II (36), 0, I:II = 32:68	387
	(–)-CHIRAPHOS	$Pt(CHIRAPHOS)Cl_2/SnCl_2$, CO/H_2 (400 psi), 80°, 20 h	I + II (19), 6 *R*, I:II = 65:35	387
C_{12}				
		Rh(CO)$_2$(acac), C_6H_6, H_2/CO (1/1, 100 atm)	 I +  II	34, 113
			R — I — II	
	(*S,R*)-BINAPHOS	60°, 34 h	$4\text{-}ClC_6H_4$ — (87), 93 (+) — (13)	
	"	60°, 20 h	$4\text{-}MeC_6H_4$ — (86), 95 (+) — (14)	
	"	60°, 34 h	$4\text{-}MeOC_6H_4$ — (87), 88 (+) — (13)	
	"	60°, 66 h	4-(*i*-C_4H_9)C_6H_4 — (88), 92 *S* — (12)	
	(*R,S*)-BINAPHOS	Rh(acac)(CO)$_2$, ligand, H_2/CO (1/1, 100 atm), L/Rh = 4, C_6H_6	R: *p*-FC_6H_4; Temp.: 40°; Time: 39 h; I + II: (43); I:II: 89:11; I (% ee): 92 (—)	113
	(R,R)-DIOP	$Rh_4(CO)_{12}$, L/Rh = 2, CO/H_2 (1/1, 80 bar), hexane, 100°	 I +  II; (81), — ; (19)	385

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(R,R)-DIOP	$HRh(CO)(PPh_3)_3$, 240 h, L/Rh = 4, rt, PhMe, CO/H_2 (1/1, 1 bar)	**I** (71), 11.9 (–) + **II** (29)	385
	(R,R)-DIOP	$PtCl(SnCl_3)(DIOP)$, CO/H_2 (1/1, 80 bar), PhMe, 50°	**I** (18), — + **II** (64) +  (19)	385
	(*R,R*)-BCO-DPP	$Pt(BCO\text{-}DPP)Cl_2/SnCl_2$, CO/H_2 (7/15, 220 atm), C_6H_6, 50°, 48 h	 **I** (81), 20 + Starting Material (15)	872
	(*R,R*)-BCO-DBP	$Pt(BCO\text{-}DBP)Cl_2/SnCl_2$, CO/H_2 (7/15, 220 atm), C_6H_6, 50°, 7 h	**I** (31), 48 + Starting material (65)	872
	BPPM	$Pt(BPPM)Cl_2/SnCl_2$, CO/H_2 (7/15, 220 atm), C_6H_6, 50°, 70 h	**I** (32), 43 + Starting material (67)	872
	(–)-BPPM	$Pt(BPPM)Cl_2/SnCl_2$, CO/H_2 (1/1, 2400 psi), C_6H_6, 60°, 18 h	 **I** (22), 78 *S* + **II** (—) **I/II** = 0.53	406
		$[Rh(CO)(PPh_3)(L^*)]ClO_4$, CO/H_2 (1/1, 80 atm), C_6H_6, 100°, 16 h	**I** (—), 78 *R*	844
	 Ar = 3,5-$(CF_3)_2C_6H_3$	Rh(COD)(chiral ligand)BF_4, CO/H_2, rt, 18 h	(see below)	843

Solvent	Pressure (psi)	Conv. (%)	I	II	I:II
C_6H_6	1600	43	(—), 38	(—)	97:3
C_6H_{14}	1600	53	(—), 51	(—)	96:4
C_6H_{14}	500	100	(—), 49	(—)	95:5
C_6H_{14}	2400	80	(—), 31	(—)	96:4
THF	1600	71	(—), 12	(—)	97:3
$C_6H_{14}/HC(OEt)_3$	1600	85	(—), 17	(—)	95:5
Et_3SiH	1600	20	(—), 72	(—)	95:5

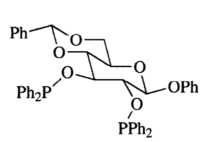
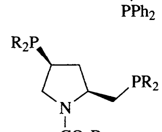
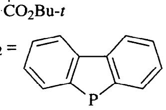
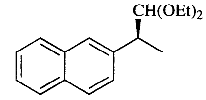
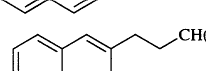
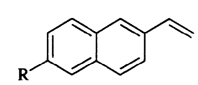
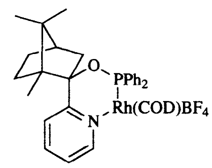
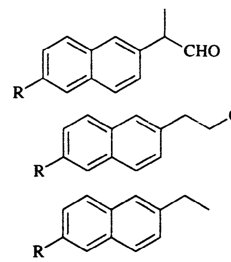
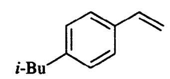
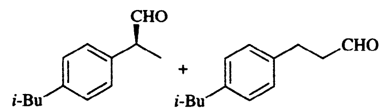
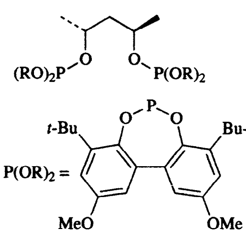
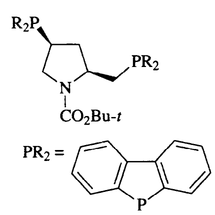
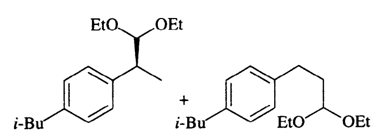
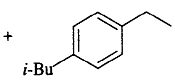
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Rh(COD)(chiral ligand)BF_4, CO/H_2 (1600 psi), rt, C_6H_6, 18 h	**I** (—), 10 + **II** (—); **I:II** = 95:5	843
	 PR_2 = 	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 38 h CO/H_2 (1/1, 2400 psi)	**I** (—), 39 *S* + **II** (—), **I:II** = 10:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $CH(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 145 h	 **I** (—), 96 *S* +  **II** (—) **I:II** = 3.4:1	409

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		CO/H_2 (1/1), C_6H_6, 80°, 24 h	 I + II + III	892

R	Conv. (%)	I + II	I:II	I (% ee)	III
H	98	(96)	72:28	45 *S*	2
MeO	93	(88)	78:22	14 *S*	5

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BPPM	$PtCl_2$(BPPM)/$SnCl_2$, CO/H_2 (1/1, 2400 psi), C_6H_6, 60°, 9 h	 I (—), 78 *S* + II (—) I:II = 1:2	406
		Rh(acac)$(CO)_2$, L^*/Rh = 4, Me_2CO, CO/H_2 (2/1, 200 psi)	I (—), 82 *S* + II (—), I:II = 66:1	38
		Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 37 h, CO/H_2 (1/1, 2400 psi)	I (—), 39 *S* + II (—), I:II = 2:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 215 h	 I (—), 96 *S* + II (—) I:II = 2:1	409
	(*S*,*S*)-BDBPP	Chiral Catalyst, H_2/CO (1/1, 70 bar)	I + II +  III	885

Chiral Catalyst	Solvent	Temp.	Time (h)	Conv. (%)	I/II	I (% ee)	III
PtCl((*S*,*S*)-BDBPP)$(SnCl_3)$	PhMe	20°	336	53.2	0.42	74.8 *S*	(<1)
PtCl((*S*,*S*)-BDBPP)$(SnCl_3)$	PhMe	100°	2	51.7	0.29	8.2 *R*	(2)
PtCl((*S*,*S*)-BDBPP)$(SnCl_3)$	CH_2Cl_2	100°	2	54.0	0.50	13.8 *R*	(10)
cis-PtCl((*S*,*S*)-BDBPP)$(SnCl_3)$	PhMe	20°	336	25.6	8.2	25.7 *S*	(6)
cis-PtCl((*S*,*S*)-BDBPP)$(SnCl_3)$	PhMe	100°	3	32.5	2.4	3.9 *S*	(15)
[*trans*-PtCl((*S*,*S*)-BDBPP)$(SnCl_3)$]$_n$	PhMe	100°	3	7.7	2.5	1.8 *S*	(4)

C_{13}

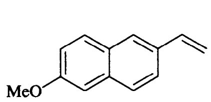
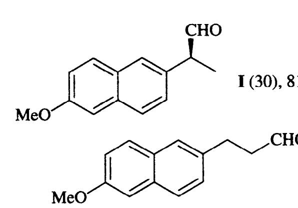
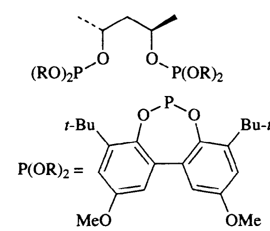
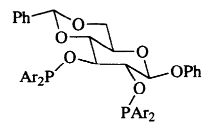
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	(–)-BPPM	$PtCl_2$(BPPM)/$SnCl_2$, CO/H_2 (1/1, 2700 psi), C_6H_6, 60°, 9 h	 I (30), 81 *S* + II (—) I:II = 7:10	406

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Rh(acac)(CO)$_2$, L*/Rh = 4, Me$_2$CO, CO/H$_2$ (4/1, 200 psi)	I (—), 85 *S* + II (—), I:II = 80:1	38
		Rh(COD)(chiral ligand)BF$_4$, CO/H$_2$, rt, 18 h		843

Ar	Solvent	Pressure (psi)	Conv. (%)	I:II	I	II
3,5-Me$_2$C$_6$H$_3$	C$_6$H$_{14}$	500	<5	—	(—), <1	(—)
C$_6$H$_5$	C$_6$H$_{14}$	500	<5	—	(—), —	(—)
3,5-F$_2$C$_6$H$_3$	C$_6$H$_{14}$	500	<5	—	(—), 24	(—)
3,5-(CF$_3$)$_2$C$_6$H$_3$	C$_6$H$_{14}$	500	73	90:10	(—), 12	(—)
3,5-Me$_2$C$_6$H$_3$	C$_6$H$_{14}$	1600	<5	—	(—), <2	(—)
C$_6$H$_5$	C$_6$H$_{14}$	1600	<5	—	(—), 10	(—)
3,5-F$_2$C$_6$H$_3$	C$_6$H$_{14}$	1600	<5	—	(—), 25	(—)
3,5-(CF$_3$)$_2$C$_6$H$_3$	C$_6$H$_{14}$	1600	73	94:6	(—), 39	(—)
3,5-Me$_2$C$_6$H$_3$	C$_6$H$_{14}$	2400	<5	—	(—),<1	(—)
C$_6$H$_5$	C$_6$H$_{14}$	2400	<5	—	(—), 7	(—)
3,5-F$_2$C$_6$H$_3$	C$_6$H$_{14}$	2400	<5	—	(—), 16	(—)
3,5-(CF$_3$)$_2$C$_6$H$_3$	C$_6$H$_{14}$	2400	31	95:5	(—), 12	(—)
3,5-Me$_2$C$_6$H$_3$	THF	500	<5	—	(—), <3	(—)
C$_6$H$_5$	THF	500	18	94:6	(—), 8	(—)
3,5-F$_2$C$_6$H$_3$	THF	500	38	95:5	(—), <1	(—)
3,5-(CF$_3$)$_2$C$_6$H$_3$	THF	500	35	95:5	(—), 24	(—)

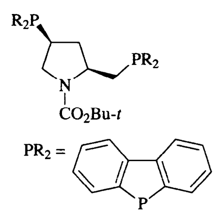
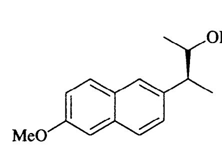
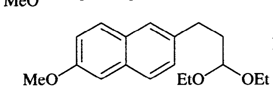
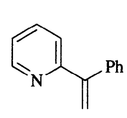
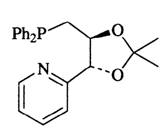
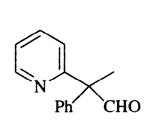
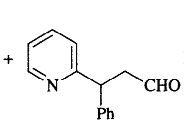
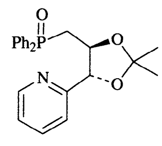
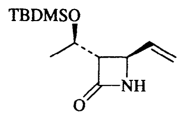
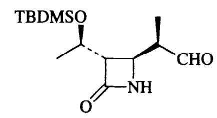
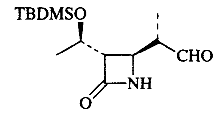
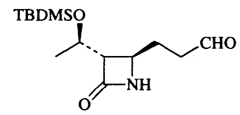
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	α,α-TREDIP	Rh(CH$_2$CH=CH$_2$)$_3$, 48 h, CH$_2$Cl$_2$, CO/H$_2$ (1/1)	I + II (95), 0, I:II = 95:5	250
		Pt(Chiral Ligand)Cl$_2$, SnCl$_2$, PhCl, 60°, 40 h, CO/H$_2$ (1/1, 2400 psi)	I (—), 37 *S* + II (—), I:II = 3.3:1	409
	"	Pt(Chiral Ligand)Cl$_2$, SnCl$_2$, PhCl, CH(OEt)$_3$, CO/H$_2$ (1/1, 2400 psi), 60°, 182 h	 I (—), 96 *S* +  II (—) I:II = 3.4:1	409
	(-)-BPPM	PtCl$_2$(BPPM)/SnCl$_2$, CO/H$_2$ (1/1, 2700 psi), HC(OEt)$_3$, 60°, 200 h	I (—), >96 *S* + II (—), I:II = 7:10	406
		Rh(acac)(CO)$_2$, C$_6$H$_6$, L*/Rh = 2.5, 80°, 21 h, CO/H$_2$ (1/1, 80 atm)	 I +  II I + II (13), —, I:II = 99:1	714
		Rh(acac)(CO)$_2$, C$_6$H$_6$, L*/Rh = 2.5, 80°, 69 h, CO/H$_2$ (1/1, 80 atm)	I + II (60), ~10, I:II = 99:1	714

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Rh(acac)(CO)$_2$, L/Rh = 2, CO/H$_2$ (1/1, 50 atm), C$_{10}$H$_{22}$, 60°	 I +  II +  III	418

Ligand	Time (h)	I + II + III	(I+II):III	I:II
PPh$_3$	48	(86)	51:46	45:55
(*R*)-BINAP	17	(24)	52:48	67:33
(*R,S*)-BINAPHOS	6	(95)	55:45	93:7
(*R*)-BIPPHOS	6	(92)	71:29	60:40
(*R*)-BIPNITE	6	(58)	64:36	95:5
(*R*)-2-Nap-BIPNITE	6	(76)	74:26	95:5
(*R*)-2-Nap-BIPNITE-F-*p*	6	(95)	74:26	96:4

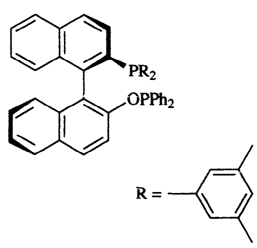
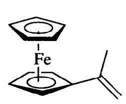
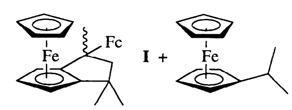
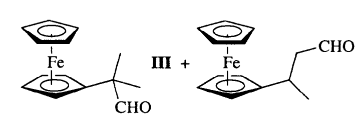
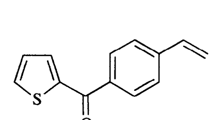
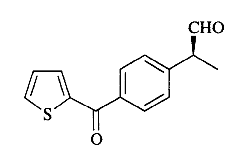
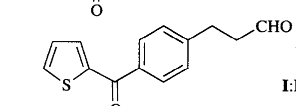
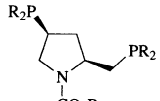
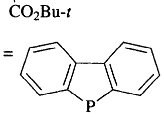
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		[Rh(COD)Cl]$_2$, CO/H$_2$	I + II (68), I:II:III = 68:4:28	724
	(–)-DIOP	[Rh(NBD)Cl]$_2$, 100°, CO/H$_2$ (1/1, 150 bar), PhMe, 22 h	 I + II +  III + IV I : II : III : IV = 1:26:4:70	386
	(–)-CHIRAPH	[Rh(NBD)Cl]$_2$, 100°, CO/H$_2$ (1/1, 140 bar), PhMe, 22 h	II + III + VI (—, —), II : III : IV = 8:9:83	386
	(–)-BPPM	PtCl$_2$(BPPM)/SnCl$_2$, CO/H$_2$ (1/1, 2600 psi), C$_6$H$_6$, 60°, 9 h	 I (—), 78 *S* +  II (—) I:II = 1:2	406
	 PR$_2$ = 	Pt(Chiral Ligand)Cl$_2$, SnCl$_2$, PhCl, 60°, 64 h, CO/H$_2$ (1/1, 2400 psi)	I (—), 9 *S* + II (—), I:II = 4:1	409

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

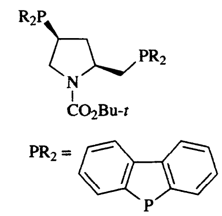
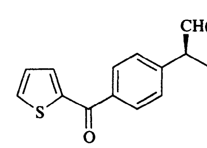
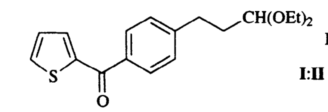
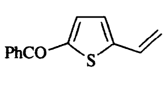
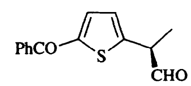
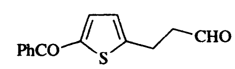
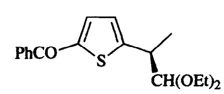
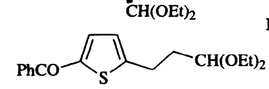
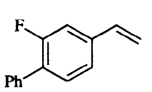
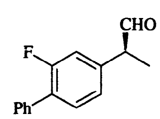
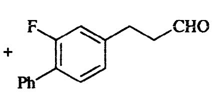
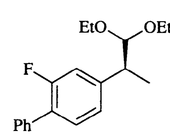
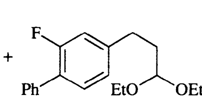
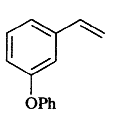
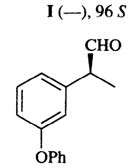
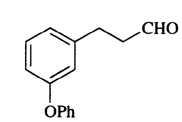
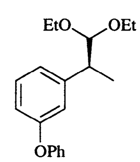
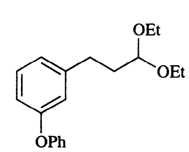
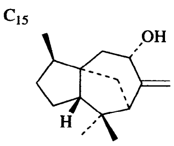
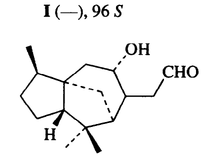
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 143 h	 I (—), 96 *S* +  II (—) I:II = 3.4:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 38 h, CO/H_2 (1/1, 2400 psi)	 I (—), 96 *S* +  II (—) I:II = 5:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $CH(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 210 h	 I (—), 96 *S* + I:II = 25:1  II (—)	409
C_{14} 	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 70 h, CO/H_2 (1/1, 2400 psi)	 +  I (—), 19 *S* II (—) I:II = 3.8:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 138 h	 +  I (—), 96 *S* II (—) I:II = 3.4:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 44 h, CO/H_2 (1/1, 2400 psi)	 +  I (—), 25 *S* II (—) I:II = 0.8:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 163 h	 +  I (—), 96 *S* II (—) I:II = 1.3:1	409
C_{15} 	—	$PtCl_2(DPPP)/SnCl_2$, CO/H_2 (1/1, 80 bar), PhMe, 100°, 21 h	 I (—), —	897
	"	$[Rh(NBD)Cl]_2/PPh_3$, CO/H_2 (1/1, 80 bar), PhMe, 100°, 19 h	I (—) (1*R*,2*R*,5*S*,7*R*,8*R*,9*S*):(1*R*,2*R*,5*S*,7*R*,8*S*,9*S*) = 20:80	897

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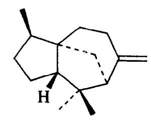
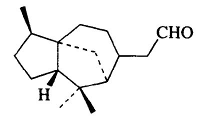
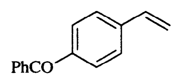
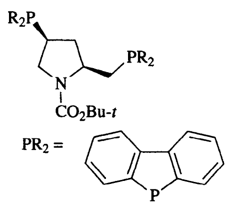
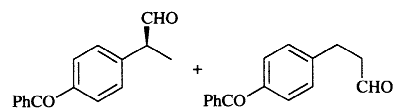
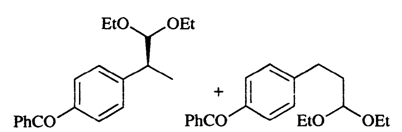
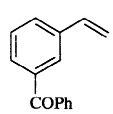
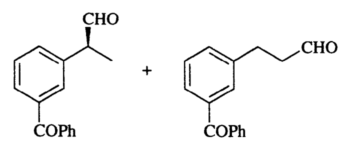
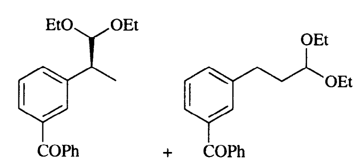
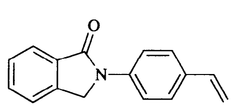
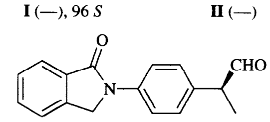
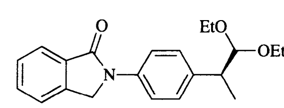
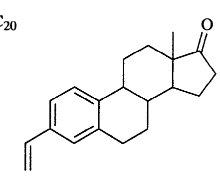
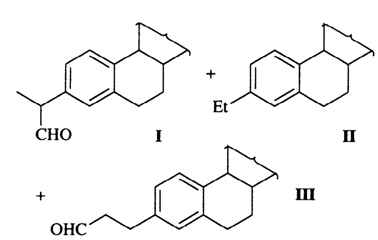
TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		CO/H_2 (1/1, 80 bar), PhMe, 100°	 I	897

Catalyst	Time (h)	Conv. (%)	I [(1*S*,2*R*,5*S*,7*R*,8*R*):(1*S*,2*R*,5*S*,7*R*,8*S*)]
$PtCl_2$((*S*,*S*)-BDPP)/$SnCl_2$	8	32	20:80
$PtCl_2$(DPPP)/$SnCl_2$	21	50	21:79
$PtCl_2$((*S*,*S*)-DIOP)/$SnCl_2$	20	9	—
$[Rh(NBD)Cl]_2/PPh_3$	22	100	27:73

Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 48 h, CO/H_2 (1/1, 2400 psi)	 I (—), 37 *S* + II (—) I:II = 3.2:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 170 h	 I (—), 96 *S* + II (—) I:II = 3.0:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 44 h, CO/H_2 (1/1, 2400 psi)	 I (—), 27 *S* + II (—) I:II = 3.3:1	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 135 h	 I (—), 96 *S* + II (—) I:II = 3.3:1	409
C_{16} 	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, 60°, 50 h, CO/H_2 (1/1, 2400 psi)	 (—), 0	409
	"	Pt(Chiral Ligand)Cl_2, $SnCl_2$, PhCl, $HC(OEt)_3$, CO/H_2 (1/1, 2400 psi), 60°, 180 h	 (—), 60 *S*	409
C_{20} 		CO/H_2 (1/1, 80 bar), Toluene, 100°	 I + II + III	899

Catalyst/Ligand	Time (h)	I, % de	II	III
$[Rh(NBD)Cl]_2/PPh_3$	10	(66), 96	(21)	(12)
$[Rh(NBD)Cl]_2$/(*R*)-PROPHOS	12	(81), 80	(8)	(7)
$[Rh(NBD)Cl]_2$/(2*S*, 3*S*)-CHIRAPHOS	10	(77), 96	(10)	(9)
$PtCl(SnCl_3)$[(*R*)-PROPHOS]	20	(64), 96	(19)	(15)
$PtCl(SnCl_3)$[(2*S*, 3*S*)-CHIRAPHOS]	20	(68), 96	(14)	(14)

TABLE X. ASYMMETRIC HYDROFORMYLATION (*Continued*)

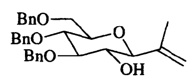
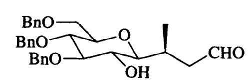
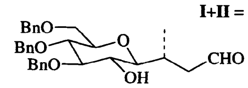
Reactant	Chiral Ligand	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
		Rh(acac)$(CO)_2$, CO/H_2 (1/1, 80 atm), toluene, 80°, 48 h	 **I** + **I+II** = 81, **I:II** = 83:17  **II**	900

TABLE XI. HYDROFORMYLATION OF ALKYNES

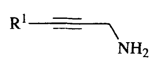
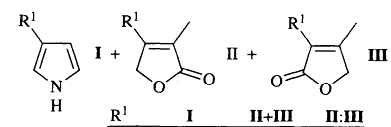
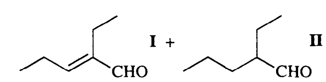
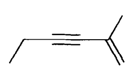
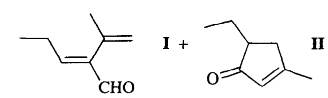
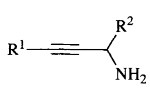
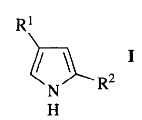
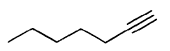
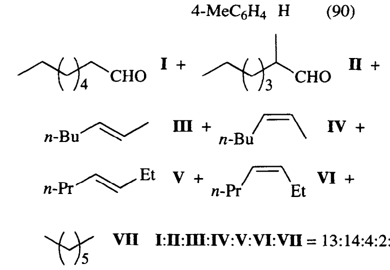
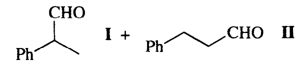
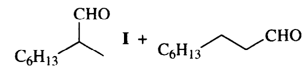
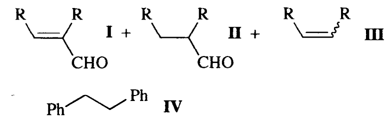
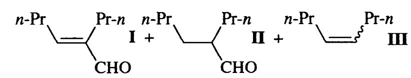
Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_4			
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 90°, 20 h	 I + II + III R^1 / I / II+III / II:III Me / (10) / (23) / 9:1 n-Bu / (31) / (23) / 100:0 t-Bu / (2) / (—) / —	380
C_6			
	$RhH(CO)(PPh_3)_3$, PPh_3, C_6H_6, CO/H_2 (1/1, 400 psi), 80°, 20 h	 I + II I + II (25) I:II = 1:1	378
C_7			
	$RhH(CO)(PPh_3)_3$, PPh_3, C_6H_6, CO/H_2 (1/1, 400 psi), 80°, 20 h	 I + II I + II (60) I:II = 70:30	378
	$[Rh(OAc)_2]_2$, PPh_3, CO/H_2 (400 psi), 70°, 20 h	 I R^1 / R^2 / I n-Bu / H / (50) Ph / H / (85) Ph / Ph / (96) Ph / Me / (78) 4-MeC_6H_4 / H / (90)	384, 380
	[Ir(pyrazolate)(COD)]$_2$, $2PPh_3$, Me_2CO, CO/H_2 (1/1, 50 atm), 140°	 I + II + III + IV + V + VI + VII I:II:III:IV:V:VI:VII = 13:14:4:2:4:1:62	379

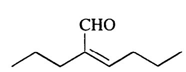
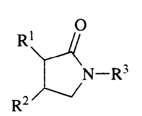
TABLE XI. HYDROFORMYLATION OF ALKYNES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_8			
Ph—≡	Rh/C (5%), DPPP, HCO_2H, CO (8.5 atm), THF, 105°, 27 h	 I + II (55) I:II = 60:40	368
C_6H_{13}—≡	Rh/C (5%), DPPP, HCO_2H, CO (8.5 atm), THF, 130°, 26 h	 I + II (52) I:II = 40:60	368
R—≡—R	Catalyst, C_6H_6, Et_3N, 150°, CO/H_2 (1/1, 70 atm)		266

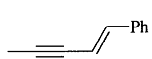
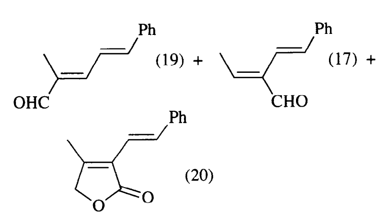
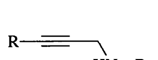
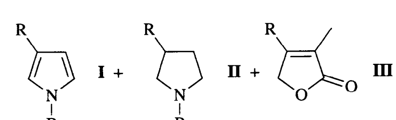
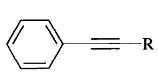
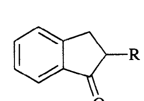
R	Catalyst	Time (h)	Conv. (%)	I	II	III	IV
Et	$PdCl_2(PCy_3)_2$-$Co_2(CO)_8$	1	96	(88)	(3)	(3)	(—)
n-Bu	$PdCl_2(PCy_3)_2$-$Co_2(CO)_8$	1	97	(90)	(2)	(5)	(—)
n-C_5H_{11}	$PdCl_2(PCy_3)_2$-$Co_2(CO)_8$	1	95	(95)	(2)	(2)	(—)
Ph	$PdCl_2(PCy_3)_2$-$Co_2(CO)_8$	1	99	(53)	(0)	(30)	(16)
Ph	$PdCl_2(PCy_3)_2$	5	94	(77)	(0)	(15)	(2)

Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
n-Pr—≡—Pr-*n*	Catalyst, C_6H_6, Et_3N, 150 °, CO/H_2 (1/1, 70 atm)		266

Catalyst	Time (h)	Conv. (%)	I	II	III
$PdCl_2(PCy_3)_2$	1	20	(16)	(<1)	(0)
$PdCl_2(PCy_3)_2$	6	84	(83)	(<1)	(<1)
$Co_2(CO)_8$	1	12	(0)	(<1)	(1)
$Co_2(CO)_8$-$2PCy_3$	1	25	(21)	(2)	(2)
$Co_2(CO)_8$-$2PCy_3$	6	89	(50)	(24)	(15)
$PdCl_2(PCy_3)_2$-$Co_2(CO)_8$	1	100	(95)	(2)	(3)
$PdCl_2(PCy_3)_2$-$W(CO)_6$	1	92	(85)	(tr)	(tr)
$PdCl_2(PCy_3)_2$-$Fe_3(CO)_{12}$	1	76	(68)	(tr)	(tr)
$PdCl_2(PCy_3)_2$ $Rh_4(CO)_{12}$	1	65	(46)	(16)	(3)

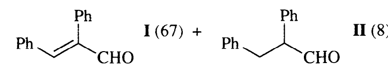
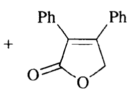
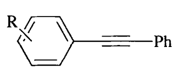
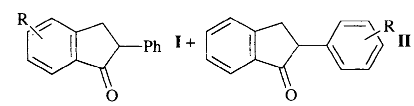
Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
	$(Cy_3P)_2PdCl_2$, $C0_2(CO)_8$, CO/H_2, 150°	 (95)	901
R^1—≡—R^2	Rh(COD)BPh_4, CO/H_2 (1/1, 100 bar), dioxane, R^3NH_2, 100°	 I	902

R^1	R^2	R^3	I
H	Ph	Bu	(21)
H	Ph	C_6H_{13}	(37)
H	Ph	Bn	(25)
Pr	Pr	Bn	(14)

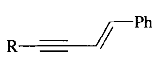
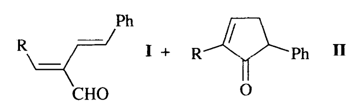
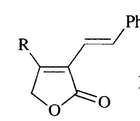
Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_{11}			
	$Rh_4(CO)_{12}$, C_6H_6, CO/H_2 (1/1, 200 atm), 60°, 6 h	 (19) + (17) + (20)	381
	$[Rh(OAc)_2]_2$, PPh_3, L/Rh = 4, EtOAc, CO/H_2 (1/1, 400 psi), 90°, 18-20 h	 R = Me, I + II + III (—), I:II:III = 1:3:3 R = Ph, I + II + III (—), I:II:III = 70:20:5	380
C_{12}			
	$[Co(CO)_3(PBu_3)]_2$, H_2O, CO (100 atm), 220°, 4 h	 I	382

R	I
n-Bu	(18)
CH=CHPh (*E*)	(41)

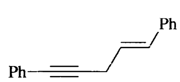
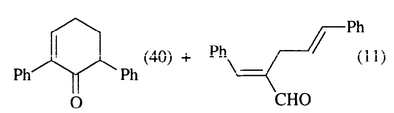
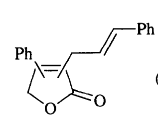
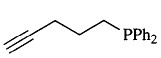
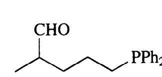
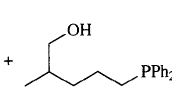
TABLE XI. HYDROFORMYLATION OF ALKYNES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_{14}	RhH(CO)(PPh$_3$)$_3$, PPh$_3$, C$_6$H$_6$, CO/H$_2$ (1/1, 400 psi), 80°, 20 h		378
	Rh$_4$(CO)$_{12}$, CO/H$_2$, 60°	I (31) +  (44)	383, 381
	[Co(CO)$_3$(PBu$_3$)]$_2$, H$_2$O, CO (100 atm), 220°, 4 h		382

R	I + II	
H	(77)	—
2-Me	(65)	50:50
4-Me	(74)	52:48
4-Cl	(63)	41:59

Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_{16} 	Rh$_4$(CO)$_{12}$, C$_6$H$_6$, CO/H$_2$ (1/1, 200 atm), 60°, 6 h	  III	383, 381

R	I	II	III
Ph	(31)	(23)	(9)
4-MeOC$_6$H$_4$	(20)	(15)	(12)
4-NCC$_6$H$_4$	(23)	(17)	(6)

Reactant	Conditions	Product(s) and Yield(s) (%), %ee	Refs.
C_{17} 	Rh$_4$(CO)$_{12}$, CO/H$_2$ (1/1, 200 atm), C$_6$H$_6$, 60°, 6 h	  (18)	383, 381
	(CO)$_4$W(μ-PPh$_2$)$_2$RhH(CO)(PPh$_3$), C$_6$H$_6$, CO/H$_2$ (1/1, 380 psi), 80°, 22 h	 I (39) + starting material (61)	372
	[Rh(OAc)$_2$]$_2$, CO/H$_2$ (1/1, 500 psi), C$_6$H$_6$, 100°, 22 h	I (55) + starting material (45)	372
	[Rh(OAc)$_2$]$_2$, CO/H$_2$ (1/1, 500 psi), C$_6$H$_6$, 100°, 48 h	I +  II I + II (87) I:II = 75:25	372

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The Vilsmeier Reaction of Non-Aromatic Compounds

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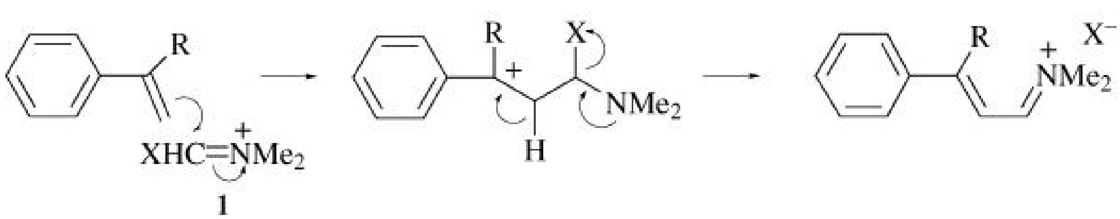
1. Introduction

In a previous chapter (1) we described the reactions of the Vilsmeier-Haack reagent with conjugated cyclic systems. In this chapter we extend the discussion to reactions between the Vilsmeier-Haack reagent (subsequently referred to as the Vilsmeier reagent for brevity) and any other compounds in which a carbon-carbon bond is formed. The discussion thus excludes reactions in which the Vilsmeier reagent acts as a chlorinating agent (for example in the preparation of acid chlorides), or in which it forms carbon-oxygen or carbon-nitrogen bonds, unless these are accompanied by formation of a carbon-carbon bond. For a discussion of the nature of the reagent and of the mechanism of the reaction, the earlier chapter should be consulted. There are also a number of reviews that deal at length with mechanisms of reactions involving the Vilsmeier reagent, notably those by Jutz (2) and Marson, (3) and hence this chapter will concentrate on applications, with brief mention of mechanisms when necessary. Smaller reviews of the Vilsmeier reaction have been published by Balbi (3a) and Seybold. (3b)

The Vilsmeier reagent is regarded as the cation **1** where X is chlorine or dichlorophosphonyl. Wizinger pointed out (4) that alkenes could react with the Vilsmeier reagent, but his only examples were styrenes (Eq. 1) where the intermediate carbocation has considerable stability.



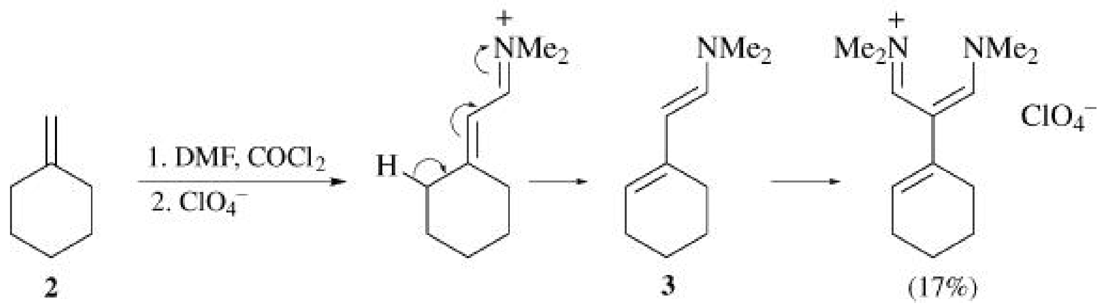
(1)

Hydrolysis gives the cinnamaldehyde. In principle, any alkene which is not too sterically hindered can undergo this reaction, but the Vilsmeier reagent has low reactivity as an electrophile, and in practice activation is often necessary. The addition depends on the HOMO of the alkene, and anything increasing the HOMO energy will aid reaction, as for example further conjugation (dienes, trienes, etc.) or the presence of an electron-donating substituent. Hence aldehydes and ketones are active in their enol forms, and enol ethers and enamines are good substrates. Indeed, all additions covered by this chapter can be regarded as alkene additions, even those on active methyl groups attached to electron-deficient rings. As with any reaction involving carbocation intermediates, rearrangements are possible; the initial products are sometimes enamines, and this can give rise to polysubstitution. In the section which follows the substrates are grouped into eleven major subsections; references to reviews of particular relevance will be found in the appropriate subsection.

2. Scope and Limitations

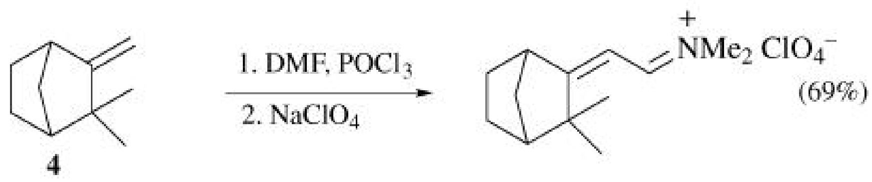
2.1. Alkenes, Dienes, and Polyenes

Simple aliphatic alkenes are normally unreactive unless one end of the double bond has two alkyl substituents, as in methylenecyclohexane (**2**) (5) (Eq. 2), or the



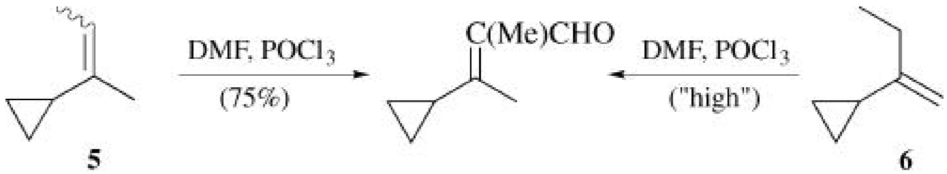
(2)

more powerful stabilization of a conjugated aryl group (Eq. 1). The methylene group in compound **2** is still relatively unreactive, and the initial product, by elimination of a proton, can form a more reactive substrate **3** so that further substitution takes place. Further reaction reaches an extreme in methylenebornane (5) and isobutene (6) which give, respectively, products with three and five aminomethylene substituents by successive shifts and secondary reactions. Camphene (**4**), (7, 5) where double bond migration cannot occur, reacts normally (Eq. 3).



(3)

The short lifetime of the intermediate carbocation is indicated by the formation of formyl derivatives from vinylcyclopropane (**5**) (8) with no evidence of the opening of the cyclopropane ring that would normally be expected on formation of a carbocationic site α to the cyclopropane ring. The same paper illustrates an example of double bond migration prior to formylation: the major product from Vilsmeier reaction of the vinylcyclopropane **6** is the same as that from isomer **5** (Eq. 4); conversely, increasing the size of the substituent β to the cyclopropane ring can cause formylation of the thermodynamically unfavored isomer, as shown for compound **7** (Eq. 5). (8)



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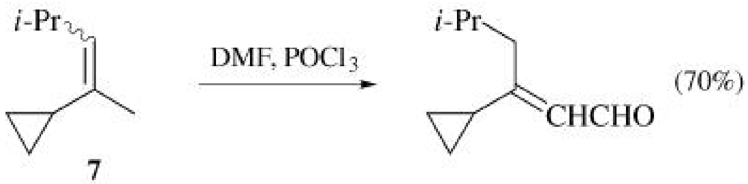
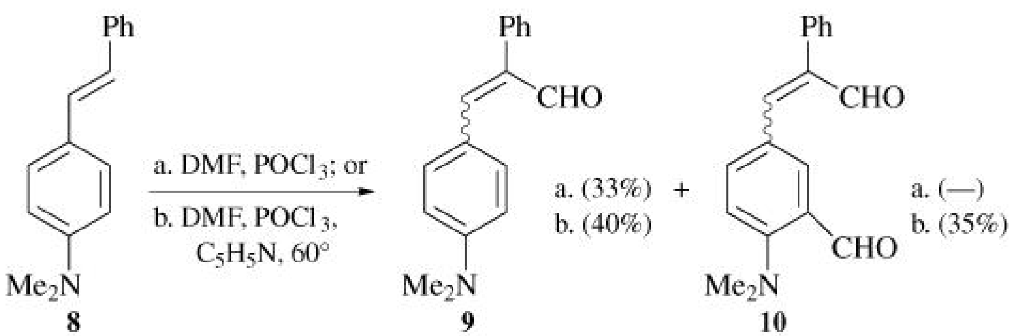


(5)

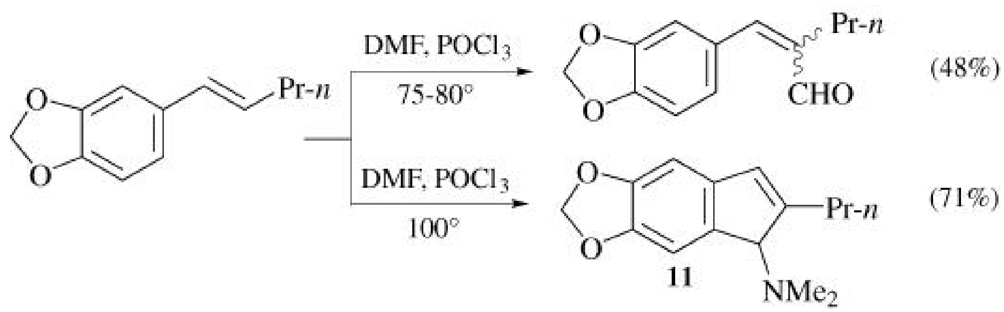
An indication of the relative activity of the aromatic ring vs. the alkene can be obtained from substituted stilbenes. Stilbene itself does not react, but 4-dimethyl-aminostilbene (**8**) forms aldehyde **9** (Eq. 6); (9) at higher temperature or when a



(6)

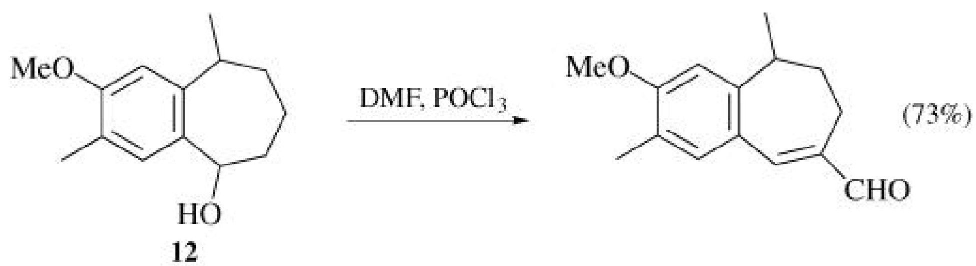
large excess of Vilsmeier reagent is used, substitution also occurs on position 3 of the ring, giving compound **10**. These results are compared with Hückel calculations which show the reactivity as 3 = 5 > α > 4. (10)

Styrenes react with the Vilsmeier reagent to give cinnamaldehydes, often in excellent yields. In some cases, when the benzene ring is electron rich, the product at higher temperatures may be an indene, such as compound **11**, (11) formed by cyclization of the intermediate cation (Eq. 7). Polymerization of styrenes (and



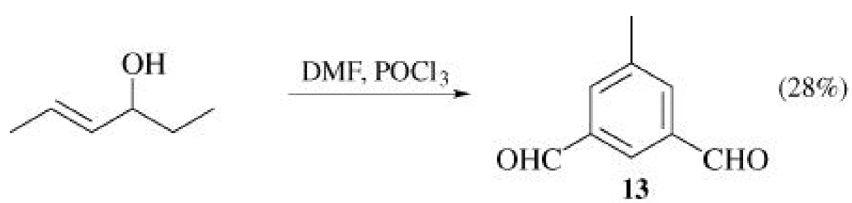
(7)

dienes or polyenes) under electrophilic attack can be prevented by using a precursor alcohol, such as compound **12**, and relying on the known dehydrating ability of the Vilsmeier reagent to generate the alkene in situ (Eq. 8). (12)



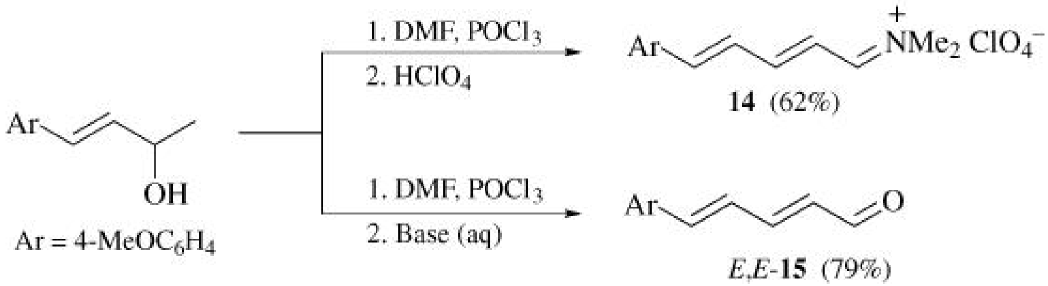
(8)

Simple aliphatic dienes do not react satisfactorily to give dienals. A series of allylic alcohols has been treated with the Vilsmeier reagent to give benzene-1,3-dicarboxaldehydes, such as compound **13**, presumably via the diene and disubstitution of the terminal methyl group (Eq. 9). (13) Successful preparation of



(9)

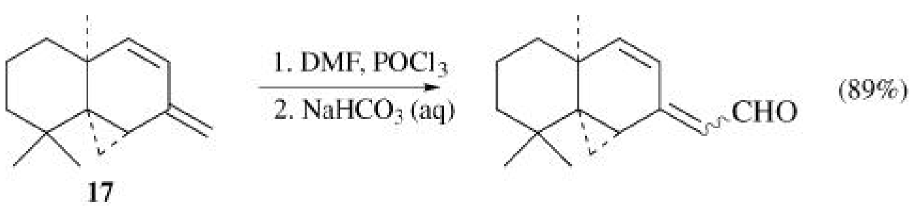
ω -arylpentadienals **15** (14) or the dimethyliminium precursors such as **14** (15) has been reported (Eq. 10), starting generally from an allylic alcohol, although there is one report of the use of diarylbutadienes such as **16** to give hydroxyfulvenecarboxaldehydes (Eq. 11). (16)



(10)

(11)

Formylation of dienes is much more successful when the double bonds are constrained in a ring, as with the bicyclic compound **17** (Eq. 12) (8) or steroid **18** (Eq. 13). (17) In the latter case, higher reaction temperature results in elimination of



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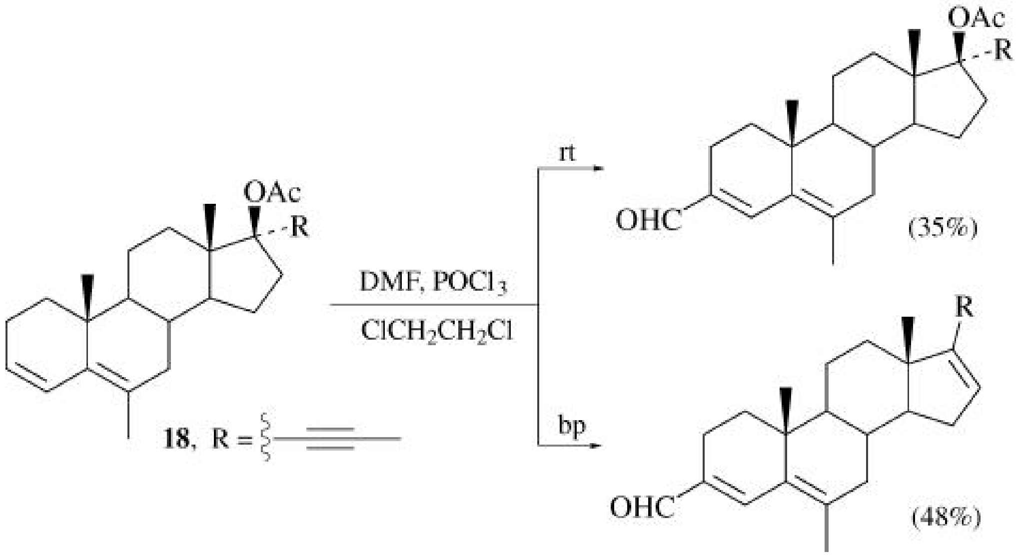
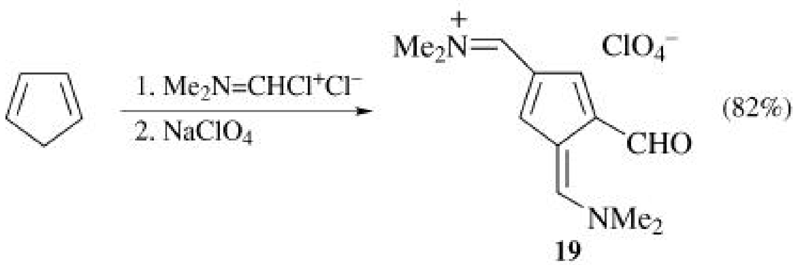


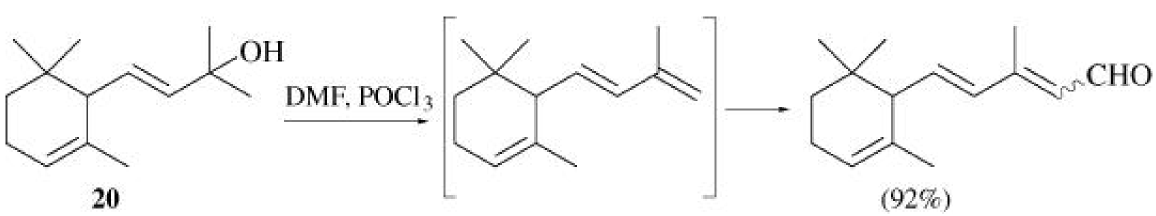
(13)

acetic acid to give a 16,17-dehydro derivative. Cyclopentadienes give dimethylaminofulvenes, with further mono- or disubstitution, as illustrated by the preparation of compound **19** (Eq. 14). (18) Two examples of the high yields which can be



(14)

obtained with acyclic dienes are those from alcohol **20** (Eq. 15) (19) and the camphane derivatives **21** and **22** (Eq. 16). (20) All have terminal methylene groups and are hindered at the other terminus.



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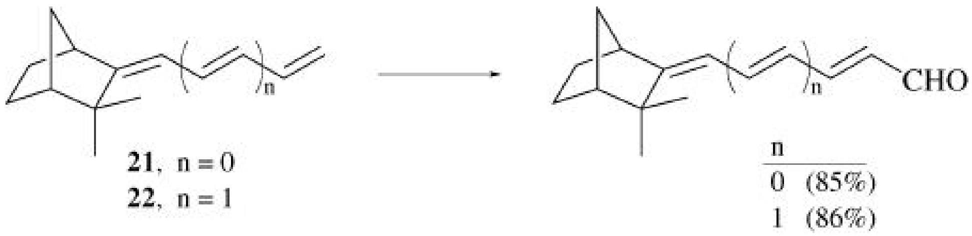
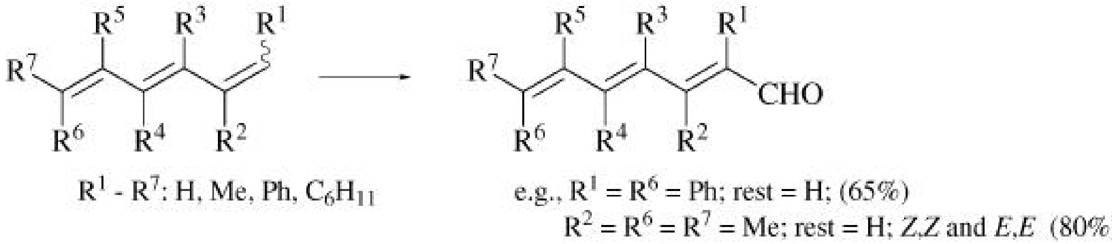


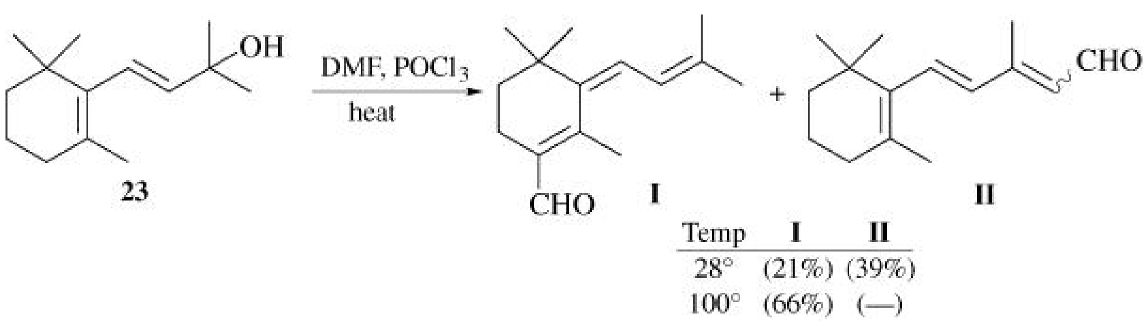
(16)

A range of acyclic trienes reacts at the end of the conjugated system (Eq. 17). (16, 21) The reaction with alcohol **23** illustrates the problems arising from double bond



(17)

migration (only product **I** is obtained at 100°; Eq. 18). (19) Single products are obtained in good yields from steroidal trienes of type **24** (Eq. 19). (22) Cycloheptatrienes (23) and the iron tricarbonyl derivative **25** (24) (Eq. 20) are formylated under normal conditions.



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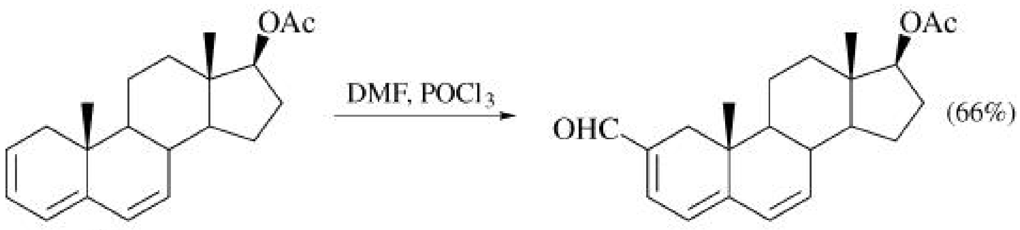

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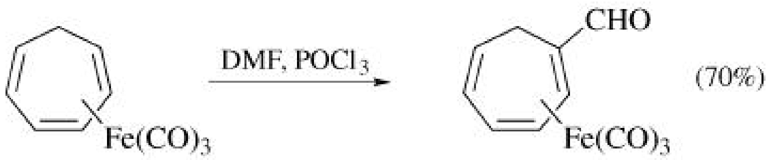
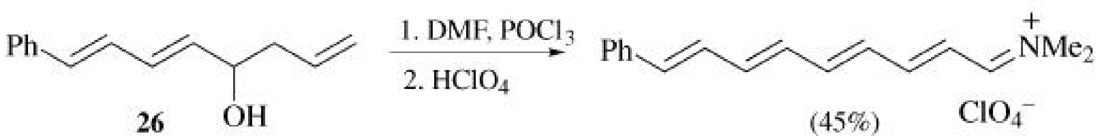
(19)



25

(20)

Two examples of tetraenes reacting with Vilsmeier reagents are the acyclic example derived from alcohol **26** (Eq. 21) (15) and the sesquiterpene **27** (Eq. 22). (25) In general, there seems to be no rule that predicts the stereochemistry engendered in the double bond which carries the formyl group for acyclic compounds.



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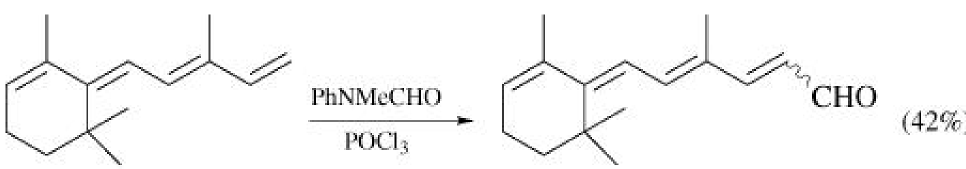

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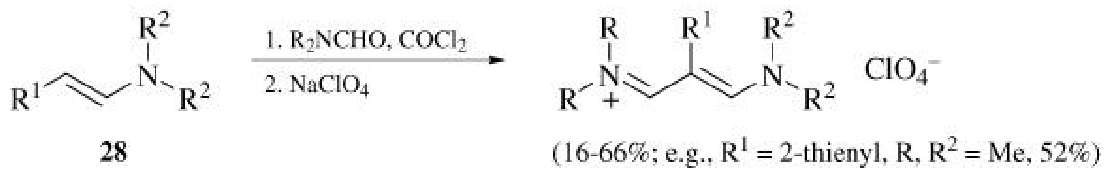
(22)

2.2. Alkenes with Heteroatom Substituents

2.2.1. Enamines and Enamides

The electron-donating nitrogen atom in enamines and to a lesser extent in enamides makes for considerable reactivity toward the Vilsmeier reagent.

Simple enamines **28** provide a route to methinium salts (Eq. 23), and hence simple malonaldehydes. (26) It is necessary to be wary of the reactivity of the intermediate; the malonaldehyde synthon which is formed from a styrylenamine can be converted into a heterocycle, as in the formation of isoxazoles **29**, pyrazoles **30**, and pyrimidines **31** (Eq. 24). (27)



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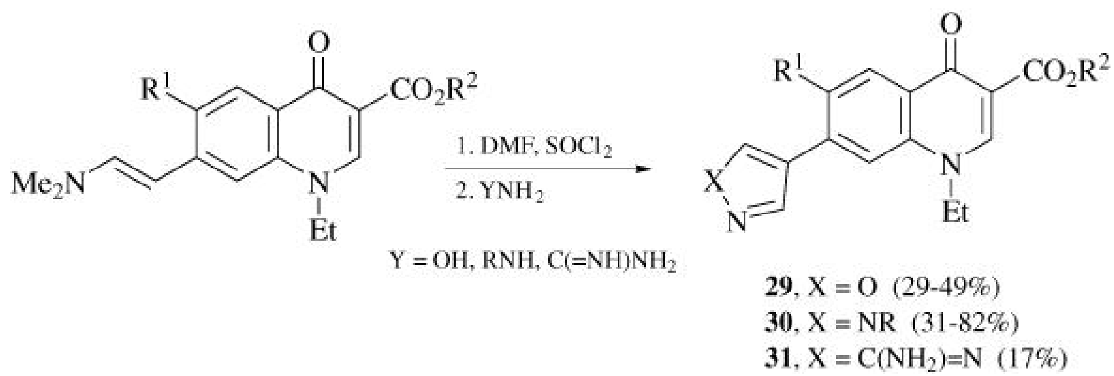
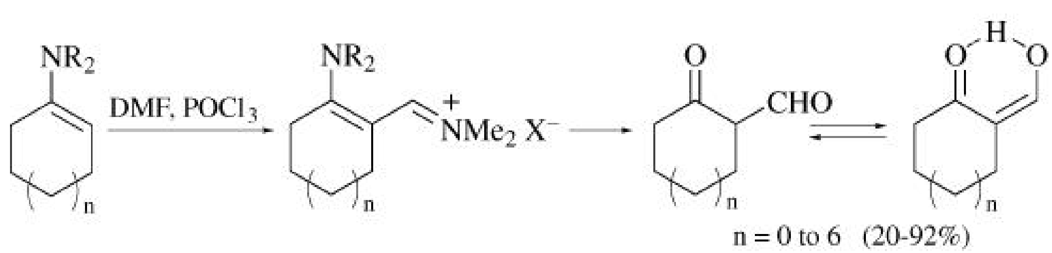


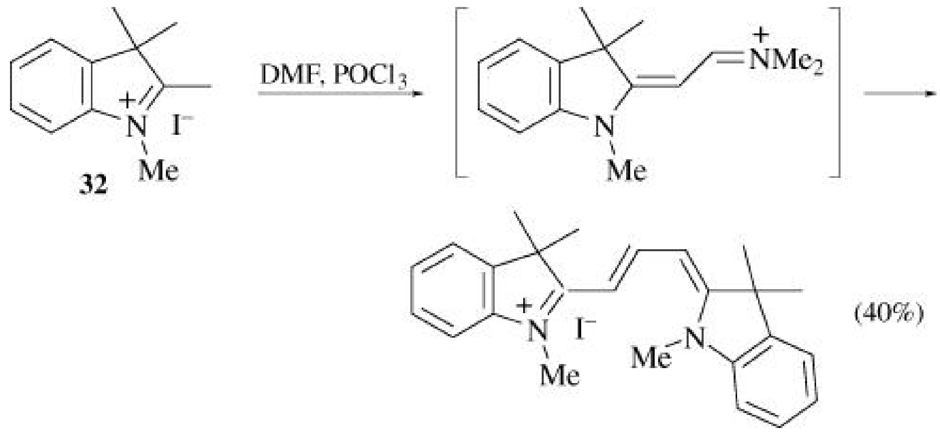
(24)

Simple enamines of cyclic ketones were among the earliest examples to be studied, and allow the synthesis of cyclic β -ketoaldehydes (Eq. 25). (28) An example of



(25)

reaction from an iminium salt **32** leads by bond migration to a pentamethinium salt (Eq. 26). (29) An enamine can still react even when there is an electron-withdrawing group at the β position (Eq. 27). (30) This equation shows the production of thioaldehydes.



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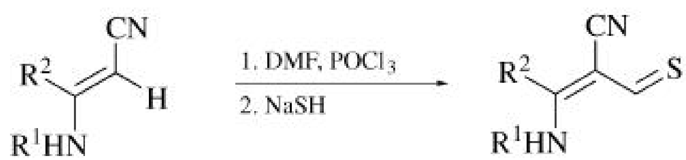
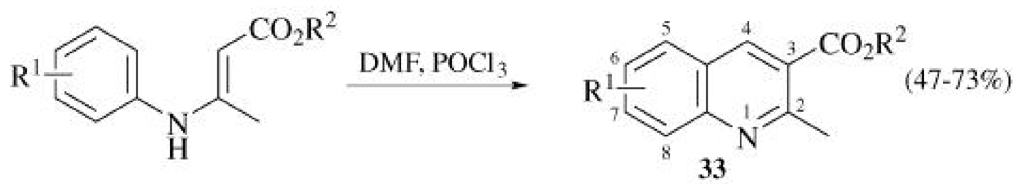


R^1 = H, Me, Et; R^2 = Me, aryl; (52-88%)

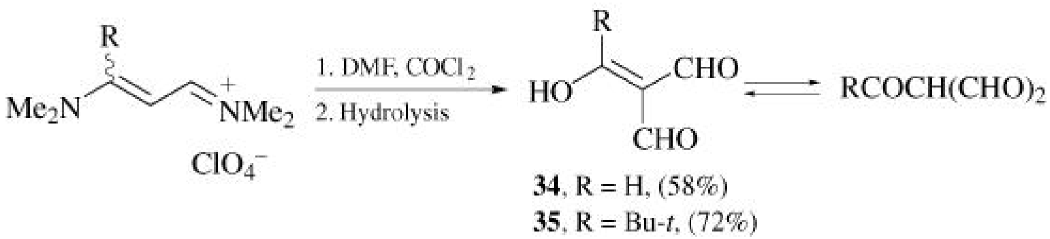
(27)

Cyclization can occur as is seen in the production of quinolines **33** (Eq. 28). (31) An enamine with a strongly electron-withdrawing substituent can still be converted into a polycarbonyl compound, as shown in the synthesis of compounds **34** and **35** (Eq. 29). (32, 33)



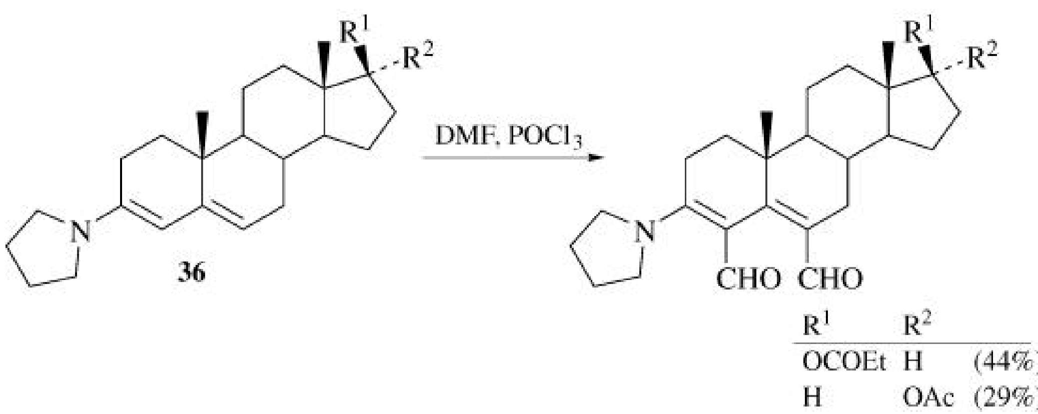
(28)

R^1 = 6,7,8-MeO; 6,7-$(MeO)_2$; 6-NO_2 (numbering as in **33**)
R^2 = Me, Et



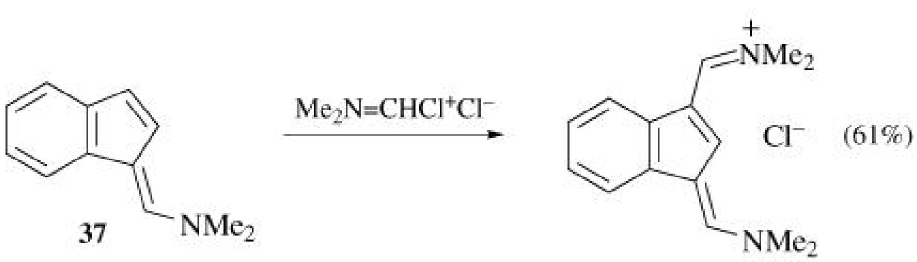
(29)

With dienamines which are constrained in a ring as in the steroids **36** simple diformylation occurs (Eq. 30). (34, 35) The benzfulvene **37** and similar fulvenes may react as dienamines, or may, in their extreme resonance forms be considered



(30)

aromatic (Eq. 31). (36) From the iminium salt **38**, a monoformylated derivative is obtained, which is converted in good yield into pyridine-3-carboxaldehyde by treatment with ammonium chloride (Eq. 32). (37) A notable contrast is provided by the methyl derivatives of compound **38**; the first, **39**, gives *N,N* -dimethylaniline-2,4-dicarboxaldehyde (Eq. 33) (38) whereas the second, **40**, reacts with three moles of Vilsmeier reagent to give the polyiminium salt **41** and hence the naphthyridine **42** (Eq. 34). (39) In both cases the active methyl group becomes doubly substituted. With increasing numbers of conjugated double bonds in acyclic systems,



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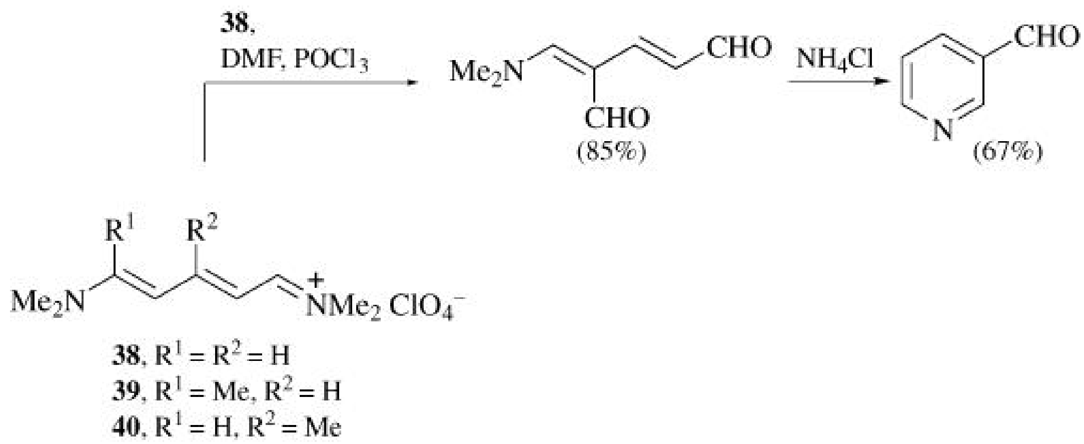

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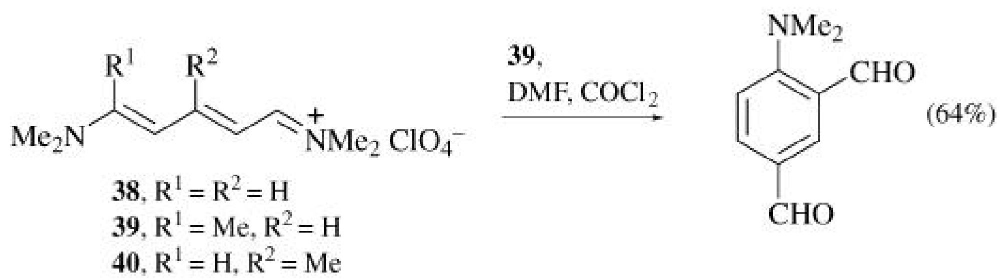

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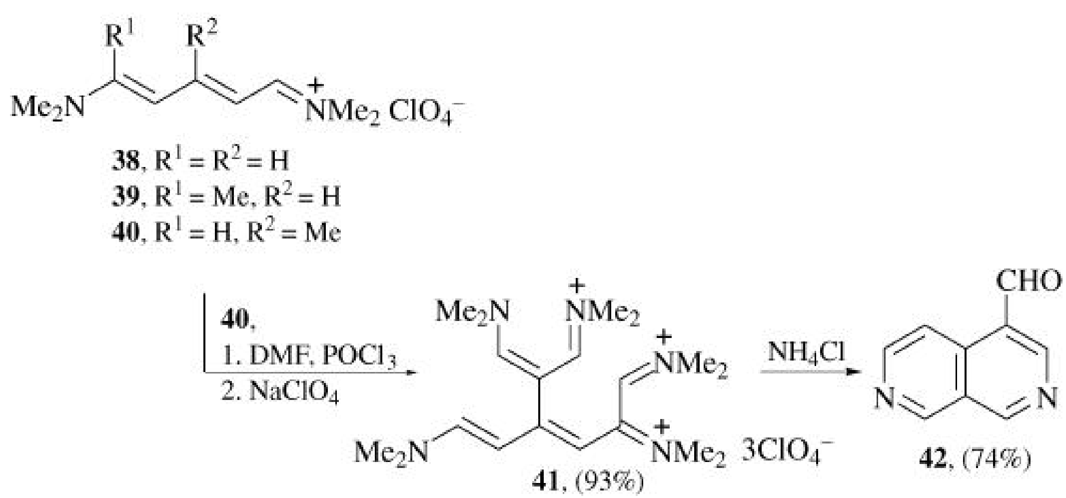
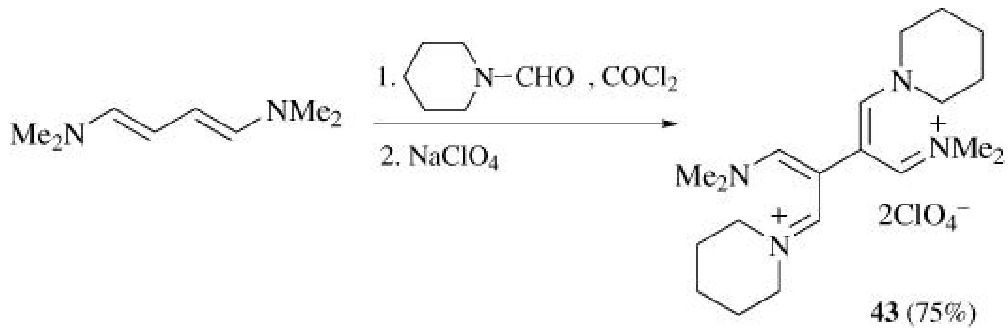


(34)

the complexity of products increases. By isolating the primary product as the diperchlorate, the masked tetraaldehyde **43** is obtained from 1,4-bis(dimethylamino)-1,3-butadiene in quite high yield (Eq. 35). (40)

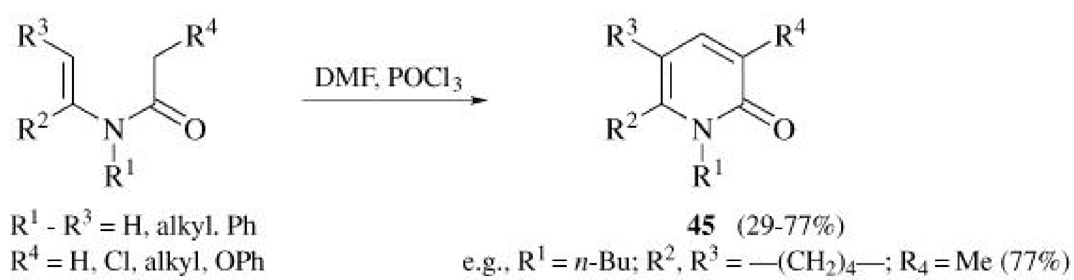


(35)

Enamides are excellent substrates for Vilsmeier reactions, possibly because of their lower reactivity. The acyclic carbamate **44** gives the acrylaldehyde in high yield, but stereochemical integrity is lost (Eq. 36). (41) As in many Vilsmeier reactions,

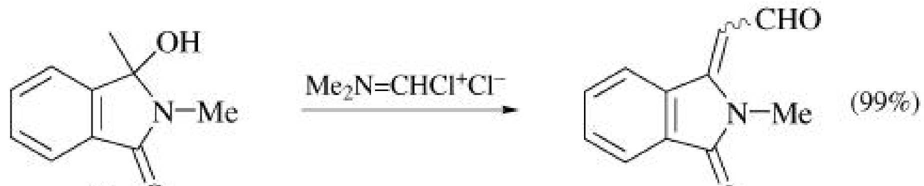
(36)

a suitably placed neighboring group can react with the initial adduct to give a new ring; 2-pyridones **45** have thus been prepared (Eq. 37). (42) With an alcohol

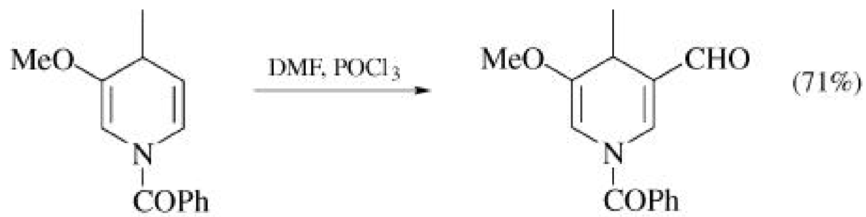


(37)

46 as starting material, dehydration by the reagent and subsequent Vilsmeier reaction gives an unsaturated aldehyde in excellent yield (Eq. 38). (43) A range of 3-formyl-1,4-dihydropyridines, such as compound **47**, can be obtained from a cyclic enamide (Eq. 39). (41, 44) As noted for enamines, dienes constrained in a ring provide uncomplicated reactions, as in the formation of the pyridine-3-carboxaldehydes produced from carbamate **48** (Eq. 40). (44, 45)


46

(38)


47

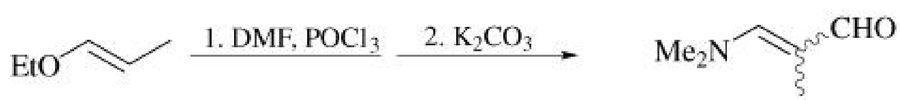
(39)


48 R = H, Br, Cl, MeO, Me, Ph, c-C_6H_{11} R = H (81%)

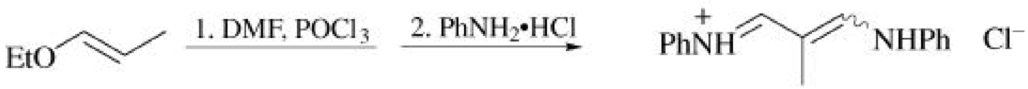
(40)

2.2.2. Enol Ethers and Enol Thioethers: Acetals and Ketals as Precursors of Enol Ethers

Reactivity of enol ethers is considerably lower than that of enamines so that product mixtures are less complex. Acetals or ketals react with the Vilsmeier reagent to generate enol ethers which can subsequently undergo formylation, although ambiguity is possible if the preliminary elimination is not regiospecific. The simplest vinyl ethers react to give malonaldehydes, or more usually their dimethylamino derivatives such as **49** (Eq. 41), (46, 47) although the anils **50** can be isolated after treatment with aniline (Eq. 42). (46) By adding *N*-ethyl-4-methylquinolinium iodide, compound **51** is isolated as its perchlorate (Eq. 43). (48)

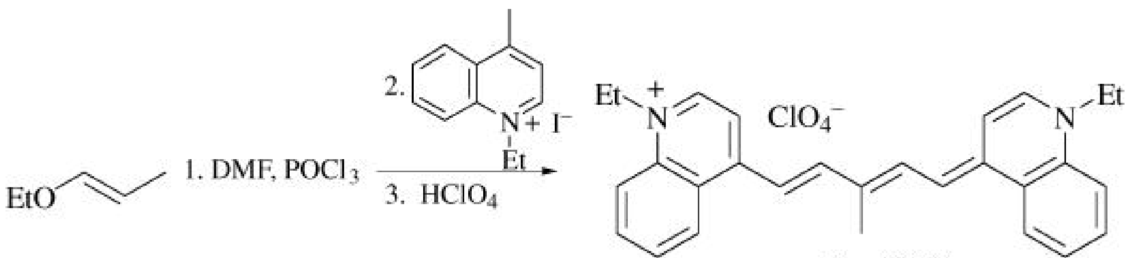

49 (68%)

(41)



50 (83%)

(42)



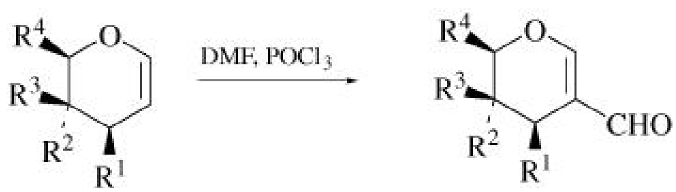
51 (60%)

(43)

Reaction with derivatives of 1,1-dialkoxyalkenes such as compound **52** gives α -formyl esters in reasonable yield (Eq. 44). (49) Cyclic vinyl ethers and enol ethers give generally cleaner reactions with good yields. Examples of the former are the dihydropyrans **53** (Eq. 45) (50) and of the latter the morphine derivative **54**

52

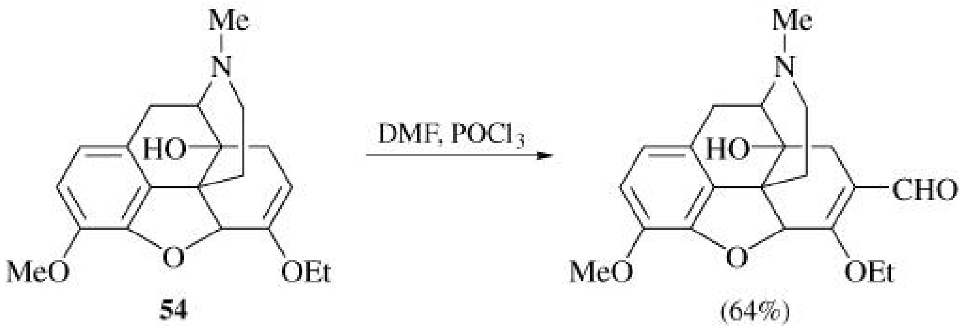
(44)



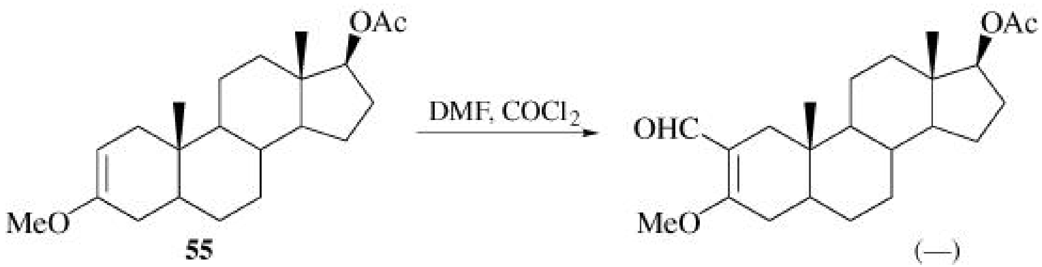
53, R^1-R^4 = H, various alkoxy (55-85%)

(45)

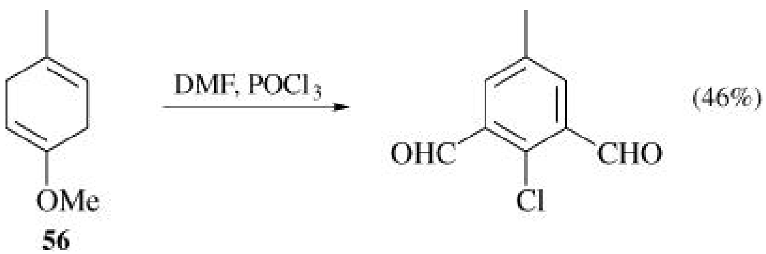
(Eq. 46) (51) and the steroid **55** (Eq. 47). (52) With additional unconjugated cyclic unsaturation, as in compound **56**, the products can be benzenedi- or tricarboxalde-hydes although the yields are only fair (Eq. 48). (53)



(46)

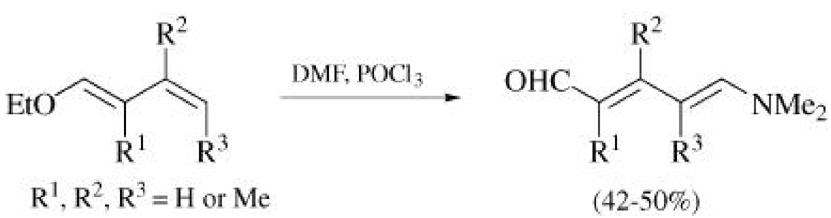


(47)

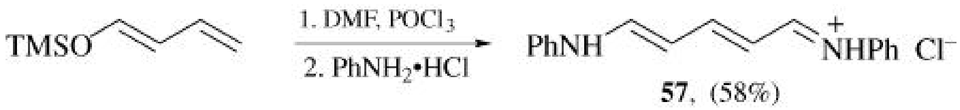


(48)

There are a few alkoxy (54) or trimethylsilyloxy (55) butadienes which react with the Vilsmeier reagent to give formylated products in moderate yields (Eqs. 49 and 50). In the latter case the products are isolated as aniline derivatives **57**.

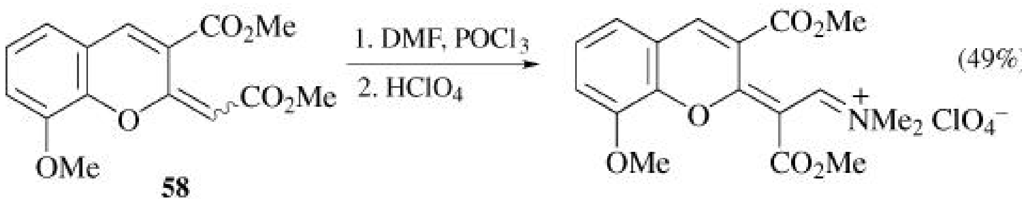


(49)

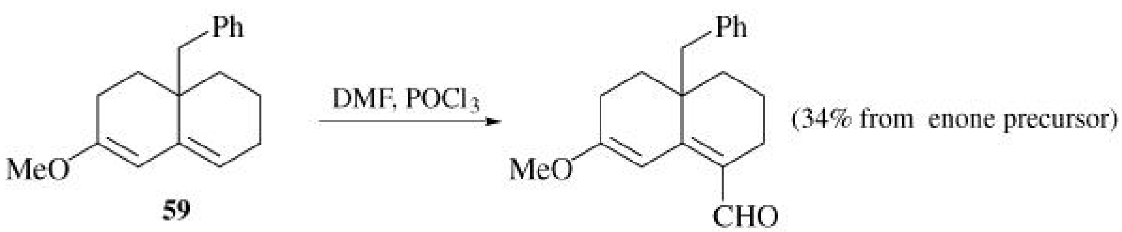


(50)

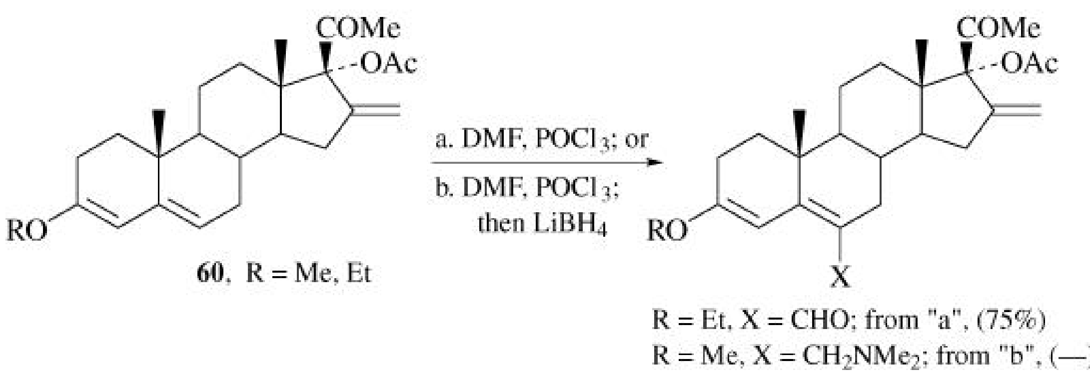
Some simple cyclic diene ethers such as the benzopyran derivative **58** (Eq. 51) (56) and hexahydronaphthalene **59** (Eq. 52) (57) react normally; the majority of cyclic dienes used as substrates are steroids. The example given (**60**; Eq. 53) (58) is one of the few with a recorded yield, but it and other examples in Table VI show that a wide range of substituents can be tolerated.



(51)



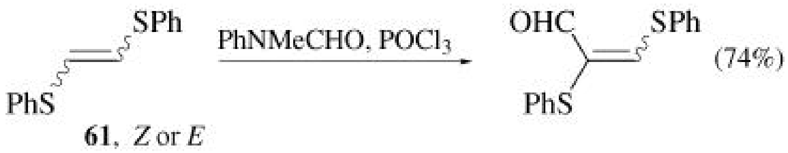
(52)



(53)

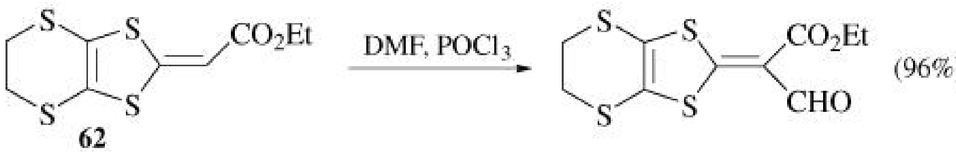
In a number of cases the intermediate dimethylammonium salt has been reduced in situ by lithium borohydride to give a dimethylaminomethyl derivative (Eq. 53). (59) There is a report of the isolation of chloroformyl derivatives when an enol acetate was used. (60)

There are a few examples of Vilsmeier reactions on vinyl sulfides, and yields can be good, as with the acyclic example **61** (Eq. 54) (61) or the exocyclic olefin **62**

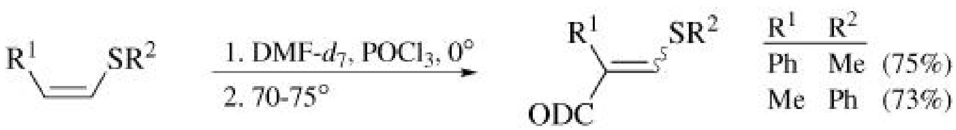


(54)

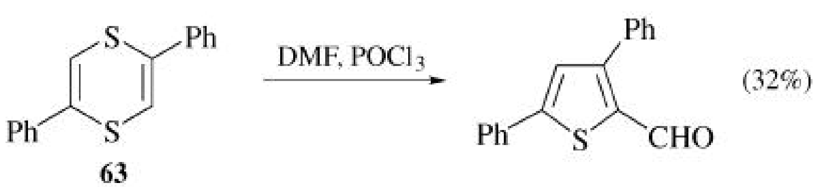
(Eq. 55). (62) The vinyl thioethers shown in Eq. 55a demonstrate the use of deuterated DMF to produce deuteroaldehydes. (62a) Reaction of 1,4-dithiine **63** gives a thiophene (Eq. 56). (62b)



(55)



(55a)



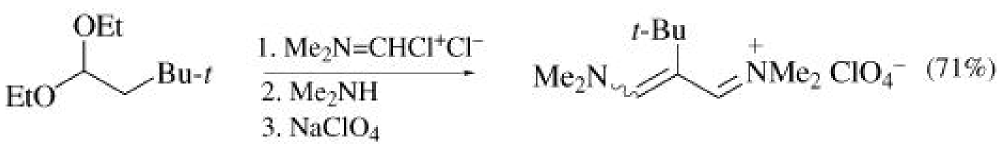
(56)

There is now general agreement that Vilsmeier reactions with acetals, ketals, and the corresponding thio derivatives proceed by loss of a molecule of alcohol or thiol to give the reactive unsaturated ether or thioether; with cyclic ketals the alcohol remains tethered, and may be chlorinated. The acetals and ketals are often more readily available than the unsaturated ethers, and yields of products are similar. A wide range of aliphatic and alicyclic acetals and ketals has been formylated; the reaction can tolerate bulky groups at either end of the double bond, as is shown for compound **64** (Eq. 57). (63, 64) Products are isolated as iminium salts

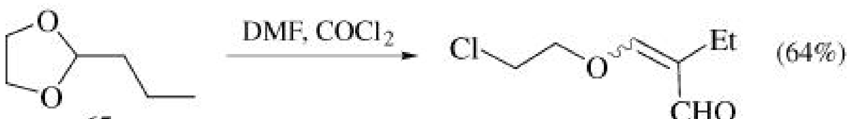
64

(57)

if dimethylamine is added during workup (Eq. 58) (65) or as dianils if an arylamine hydrochloride is added. (66) Reaction with 2-alkyl-1,3-dioxolanes such as **65** causes ring opening (Eq. 59). (67) Oxathiolanes react similarly, but 1,3-dithiolanes give products such as **66**, which must be formed by recyclization in a Michael fashion (Eq. 60). (67)



(58)



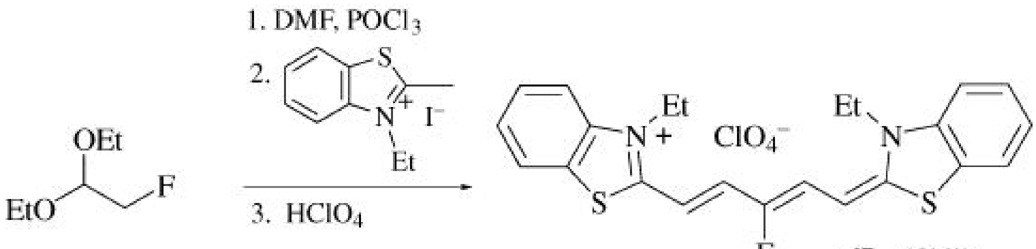
65

(59)

66

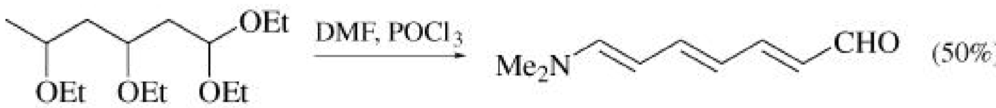
(60)

A large number of polymethinium salts of type **67** have been prepared from acetals in 26 to 84% yields (Eq. 61). (48) Compound **51** can also be prepared in this

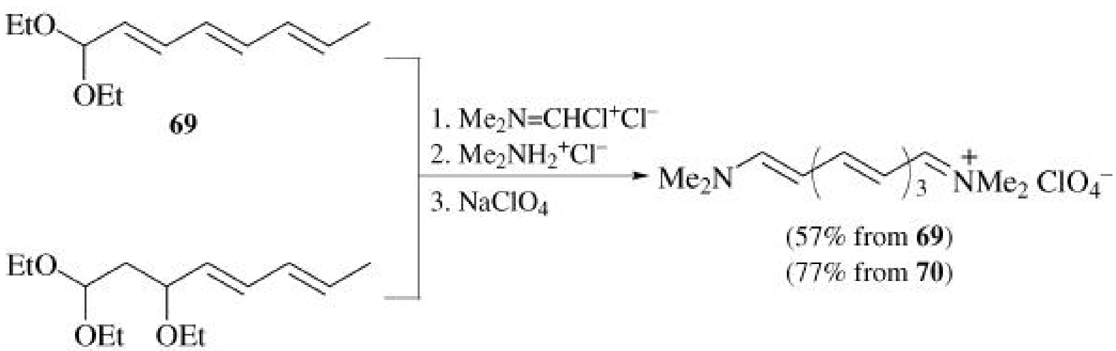


67 (61%) (61)

way (Eq. 43). Aldehydes with extended unsaturated chains can be obtained in two ways. In the first a polyether **68** is treated with the Vilsmeier reagent (Eq. 62) (68) and in the second, unsaturated acetals **69** or **70** are used (Eq. 63) (69) producing aldehydes up to nonatetraenedial.

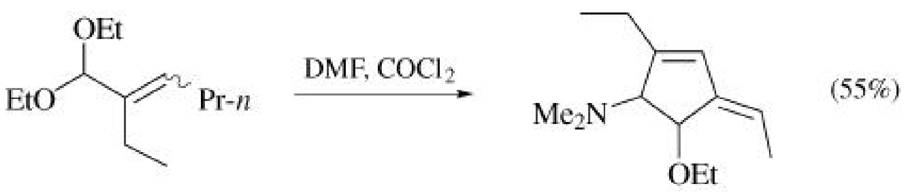


68 (62)



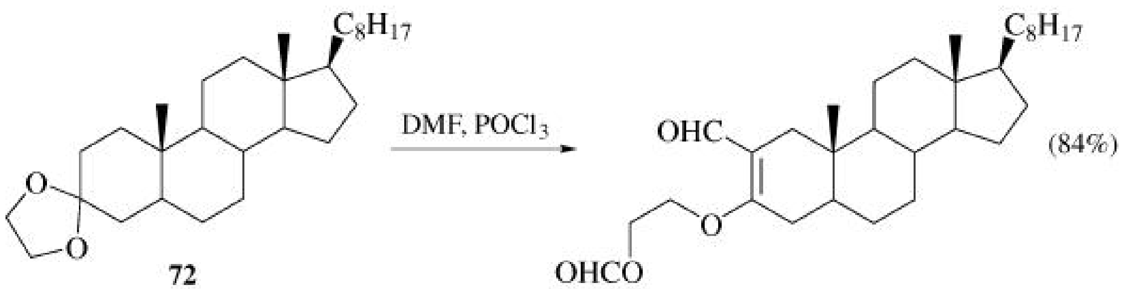
69, 70 (63)

Interesting secondary products are pyridine, obtained in 55% yield after ammonium acetate is added to the Vilsmeier product from 1,1,3-triethoxybutane, (37, 70) and the cyclopentene **71** (Eq. 64). (71)

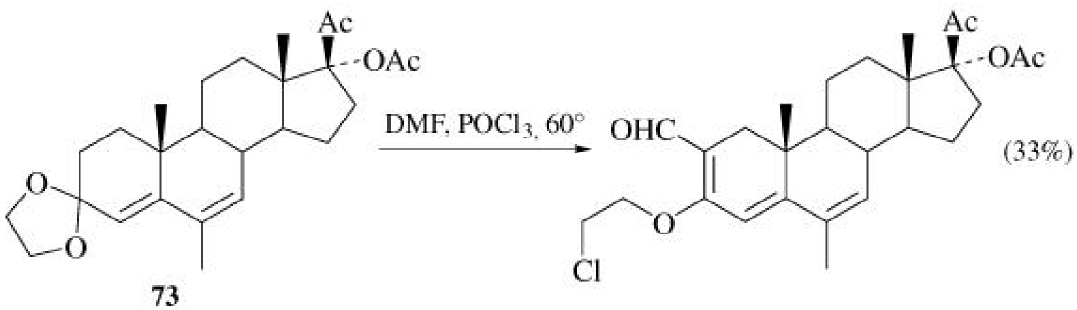


71 (64)

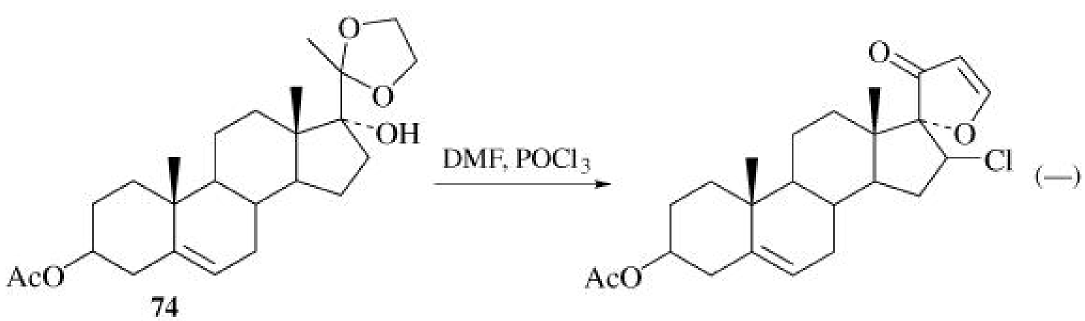
Many examples use steroids as substrates. The simple 3-ketal **72** shows the generally preferred substitution in position 2 (Eq. 65). (72) The diene **73** illustrates the successful use of a Vilsmeier reagent in the presence of a second reactive group (a methyl ketone; Eq. 66). (73) Steroid **74** with an exocyclic ketal shows that cyclization can occur to a suitable adjacent substituent (Eq. 67). (35)



(65)



(66)



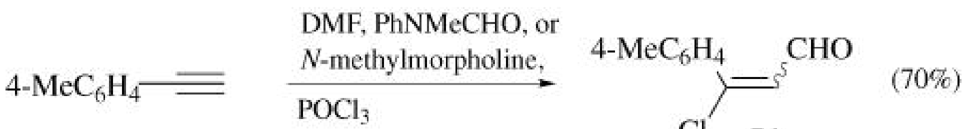
(67)

2.3. Alkynes

There are not many Vilsmeier reactions reported for alkynes. Ethoxyacetylene gives the malonaldehyde derivative **75** (Eq. 68), (74) and arylalkynes give chlorocinnamaldehydes such as **76** (Eq. 69). (75) The use of the unusual reagent $Ph_3P{\cdot}Br_2$ with

75

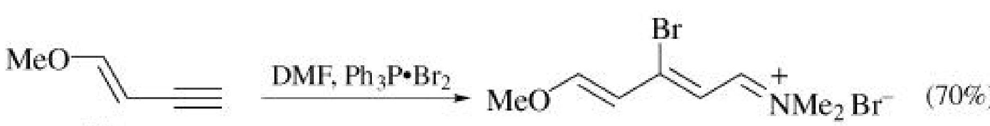
(68)



76

(69)

DMF gives a bromocinnamaldehyde. (76) From a number of 1-buten-3-ynes such as **77** a range of pentadienal derivatives can be prepared (Eq. 70) (77) and again $Ph_3P{\cdot}Br_2$ gives a 3-bromo derivative; addition of iodine and triphenylphosphine to the reaction mixture gives the 3-iodo derivative. The methoxy group in the product can be replaced using ethyl sulfide, phenyl sulfide, or dimethylamine.

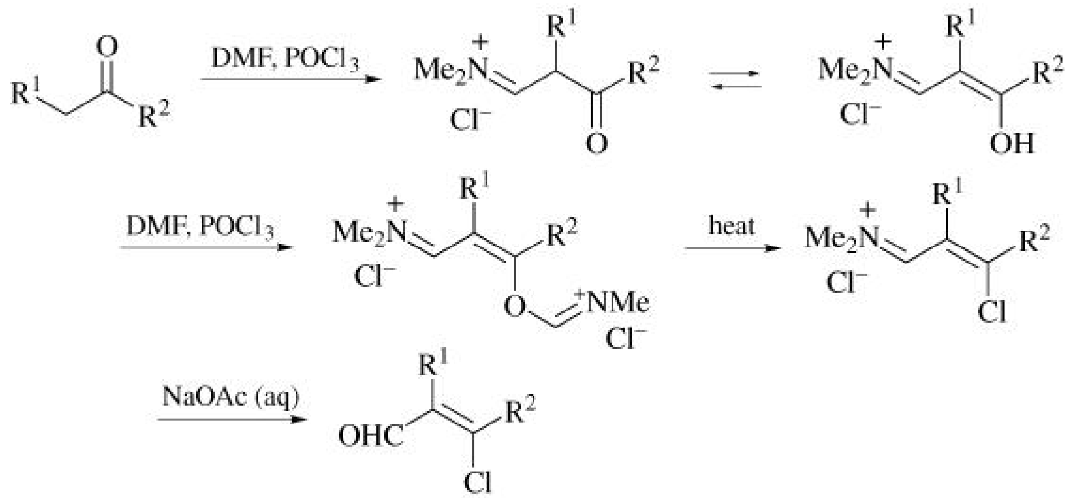


77

(70)

2.4. Aldehydes and Ketones

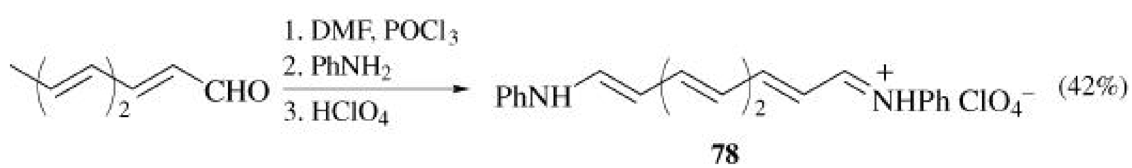
The reactions between carbonyl compounds and Vilsmeier reagents have been thoroughly reviewed. (3) It seems generally accepted that the enols are involved, with initial attack occurring on the double bond, and a final displacement of a derivative of the enolic hydroxy group by chloride or other halide (Eq. 71). There are few examples of reactions with aldehydes; one of the simple reactions is shown by butanal (Eq. 72). (78, 79) Conjugated aldehydes can give chloroiminium salts, but these are commonly treated with an amine (dimethylamine (80) or an aromatic amine (68)) to give more easily handled products such as compound **78**



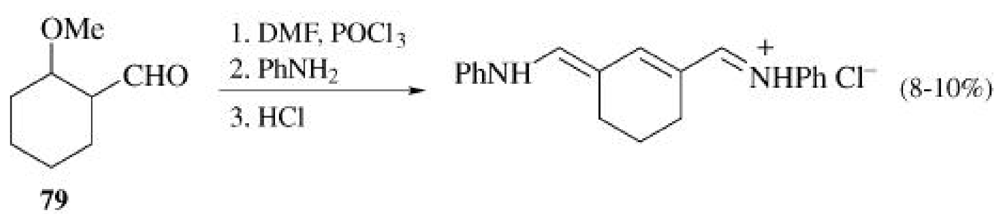
(71)

(72)

(Eq. 73). The use of an ether as the precursor to a conjugated aldehyde substrate is shown by the reaction of 2-methoxycyclohexanecarboxaldehyde (**79**; Eq. 74). (81)

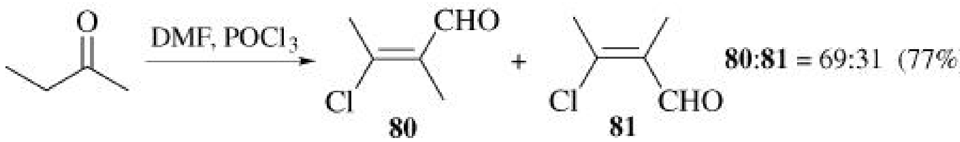


(73)



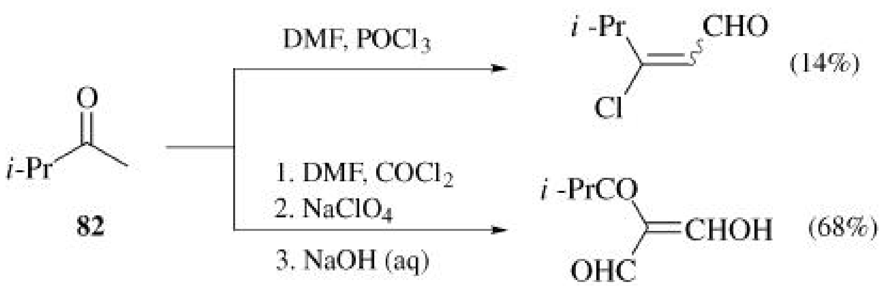
(74)

With acyclic and alicyclic ketones regiochemical complications can arise from alternative modes of enolization. With acyclic compounds there is the additional complication of geometrical isomers. Direction of enolization is usually in accord with thermodynamic stability; thus butan-2-one gives (*E*)-**80** and (*Z*)-**81** forms of 3-chloro-2-methyl-2-butenal (Eq. 75). (82) Chain branching at the α or β carbon

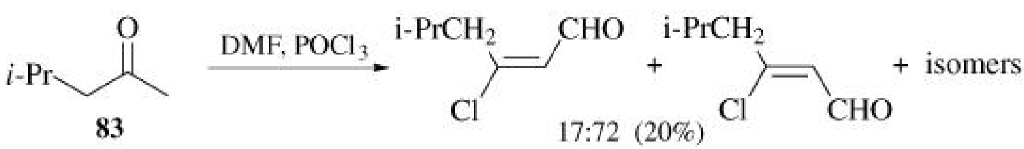


(75)

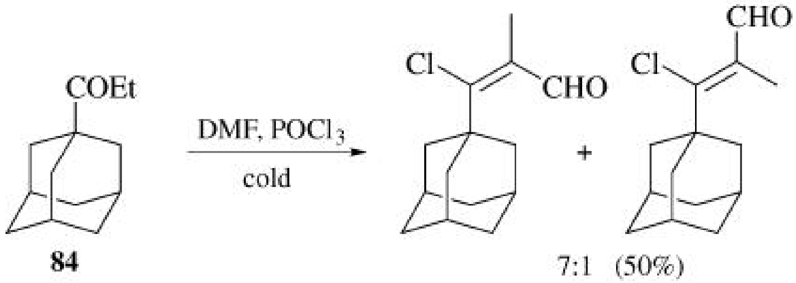
can inhibit attack on the more stable enol such that ketones **82** (Eq. 76) (68, 83) and **83** (Eq. 77) (84) are formylated on the methyl group rather than on the methine or methylene groups, while **84**, with a tertiaryα-carbon, shows a high *E*:*Z* ratio (Eq. 78). (85) The first of these three examples involves diformylation.



(76)



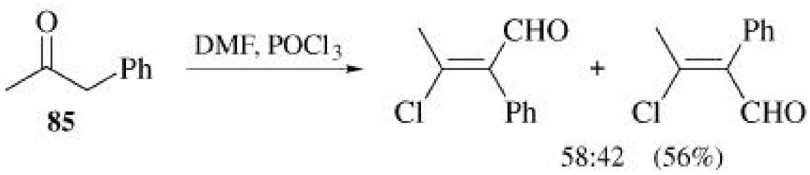
(77)



(78)

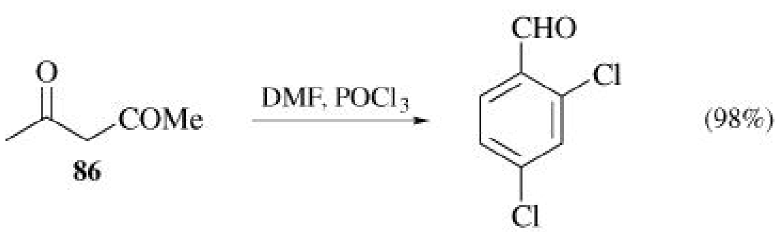
The expected direction of enolization is shown by β -ketoesters, such as methyl acetoacetate (Eq. 79) (82) and the benzyl ketone **85** (Eq. 80). (82) *Z*:*E* ratios have been recorded in detail by several groups. (82, 86, 87)

(79)



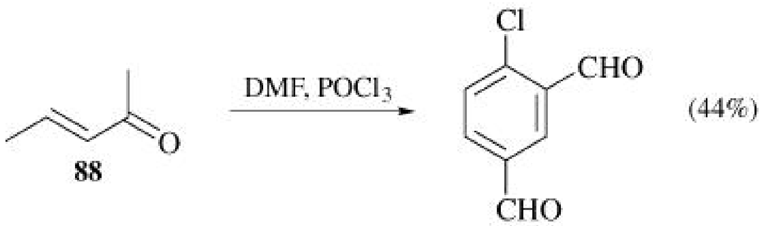
(80)

Vilsmeier reactions on 1,3-diketones, 1,4-diketones, and conjugated enones give cyclic products as shown by the reactions of compounds **86** (Eq. 81), (88) **87** (Eq. 82), (89) and **88** (Eq. 83). (38) The reaction of the Vilsmeier reagent with α , β-epoxy ketones also gives benzaldehydes or 1,3-phthalaldehydes (Eq. 83a);

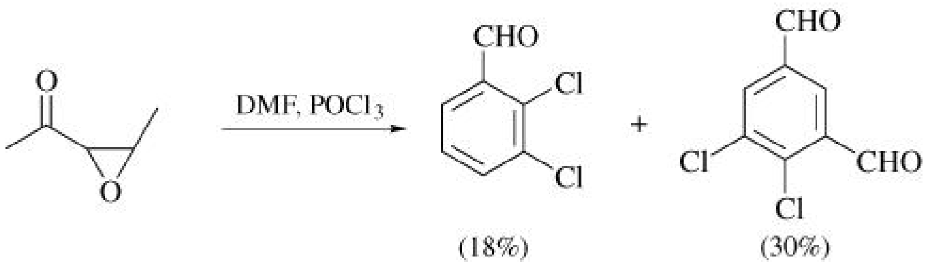


(81)

(82)

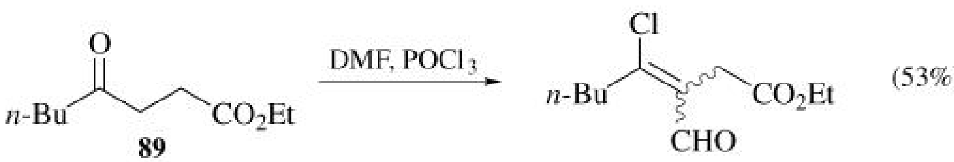


(83)



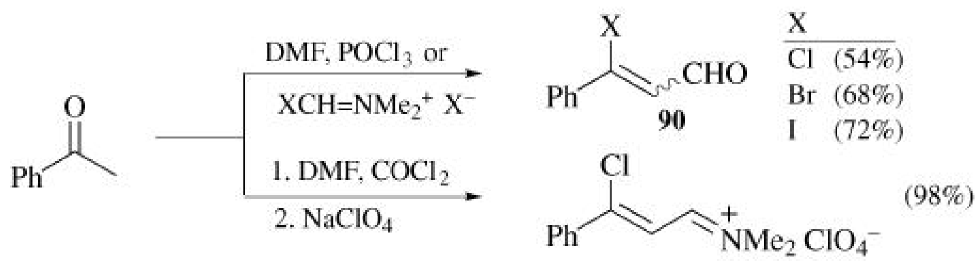
(83a)

cyclohexenone epoxides also give simple benzaldeydes. (89a) The reaction of γ -ketoesters such as compound **89** is normal (Eq. 84). (90)

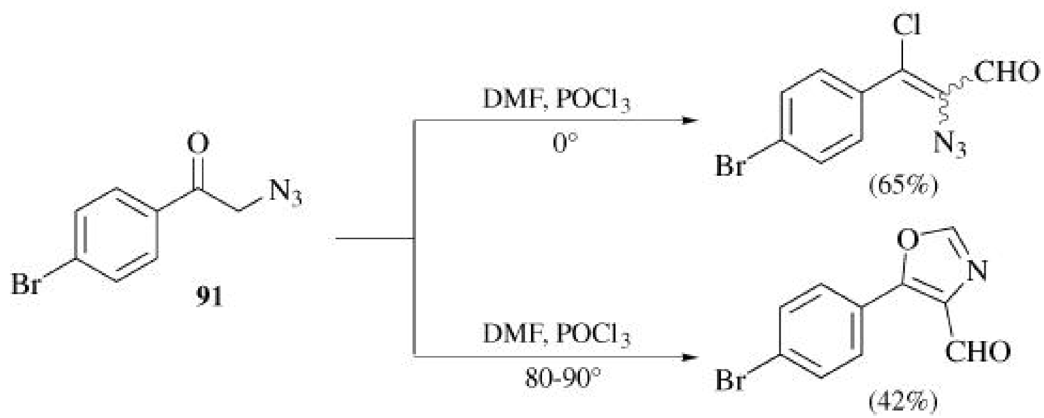


(84)

A large number of reactions have been reported between Vilsmeier reagents and acetophenones, their vinylogs, and polycyclic and heterocyclic analogs. Acetophenone itself illustrates the production of β -halocinnamaldehydes **90**, (91-93) although higher yields can be obtained if the dimethylamino intermediates are isolated and subsequently hydrolyzed (Eq. 85). (71) There is normal reaction with ω -azidoacetophenones such as **91** and the Vilsmeier reagent at room temperature giving chloroenals, but at higher temperatures loss of nitrogen occurs, producing oxazoles (Eq. 85a). (93a), (93b) In the latter reaction, the ω ,4-bromoacetophenone can be used in a one-pot reaction where sodium azide in DMF is added first, then the phosphoryl chloride. A route to quinolines has been found from 2-azidoacetophenones

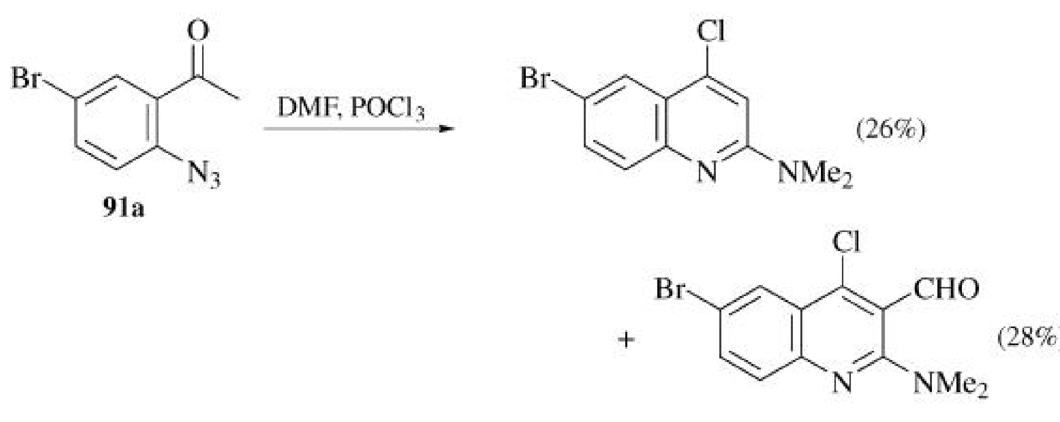


(85)



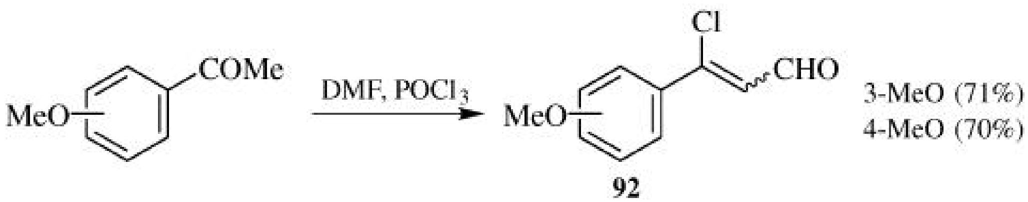
(85a)

and homologs. In the example shown azidoketone **91a** reacts to give a mixture of a 2-dimethylamino-4-chloroquinoline and the 3-formyl derivative (Eq. 85b). (93c), (93d) Other 2-amino groups are obtained from other Vilsmeier amides. An α -methyl substituent (as in propiophenones) has little inhibitory effect on yield. (94)

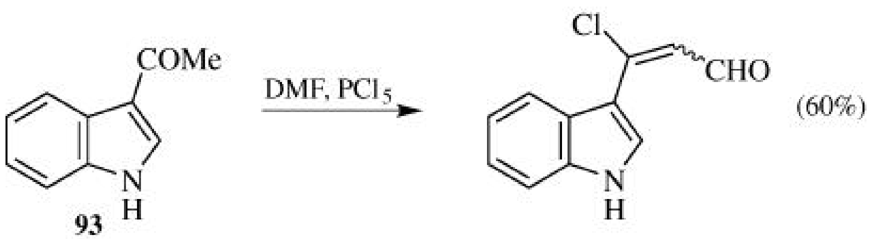


(85b)

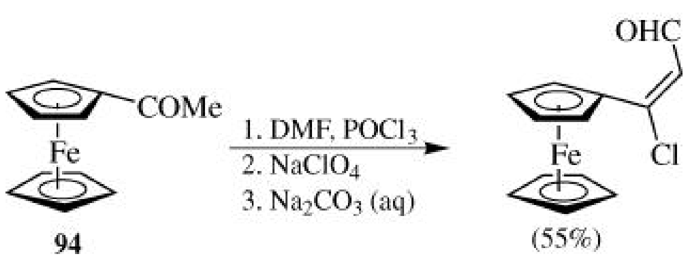
In view of the ability of the Vilsmeier reagent to attack aromatic rings, especially those activated by electron-donating groups, it is instructive to note the formation in high yield of the cinnamaldehydes **92** when *meta*-, or *para*-methoxyacetophenones (Eq. 86), (95) or even *para*-dimethylaminoacetophenone are used. (33) Similarly, an acetylpyrazole, (96) 3-acetylindole (**93**, Eq. 87), (97) and acetylferrocene (**94**, Eq. 88) (98) react to give chloroenals without nuclear substitution.



(86)

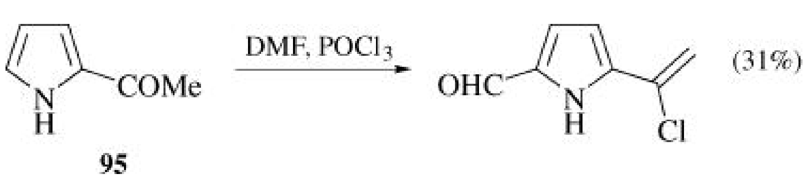


(87)



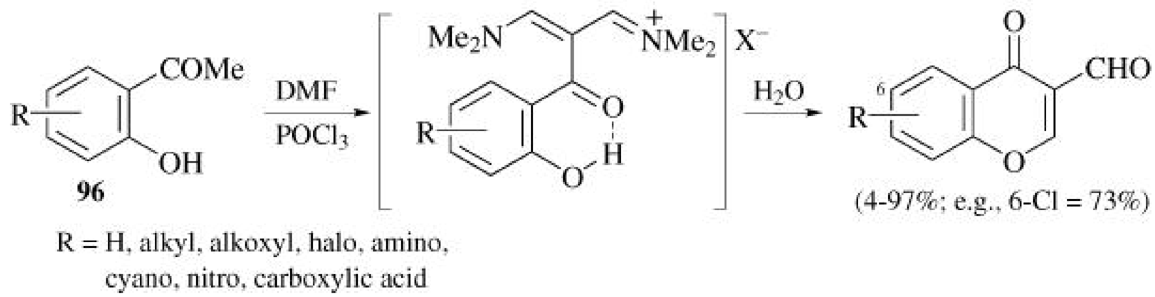
(88)

By contrast, pyrroles are sufficiently reactive that formylation normally proceeds both on nucleus and side chain. An unusual result is shown in the reaction of compound **95** (Eq. 89). (99)

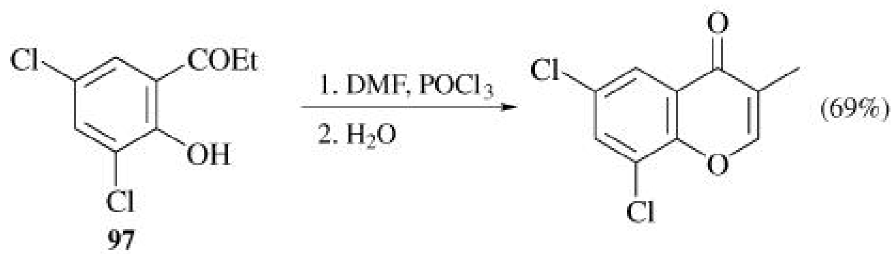


(89)

With a suitably reactive ortho substituent, cyclization can follow Vilsmeier reaction to give chromones. From 2-hydroxyacetophenones **96** the products are 3-formylchromones (Eq. 90), (100-102) and from the propiophenone **97** a 3-methylchromone is formed (Eq. 91). (103) The reaction is equally successful with

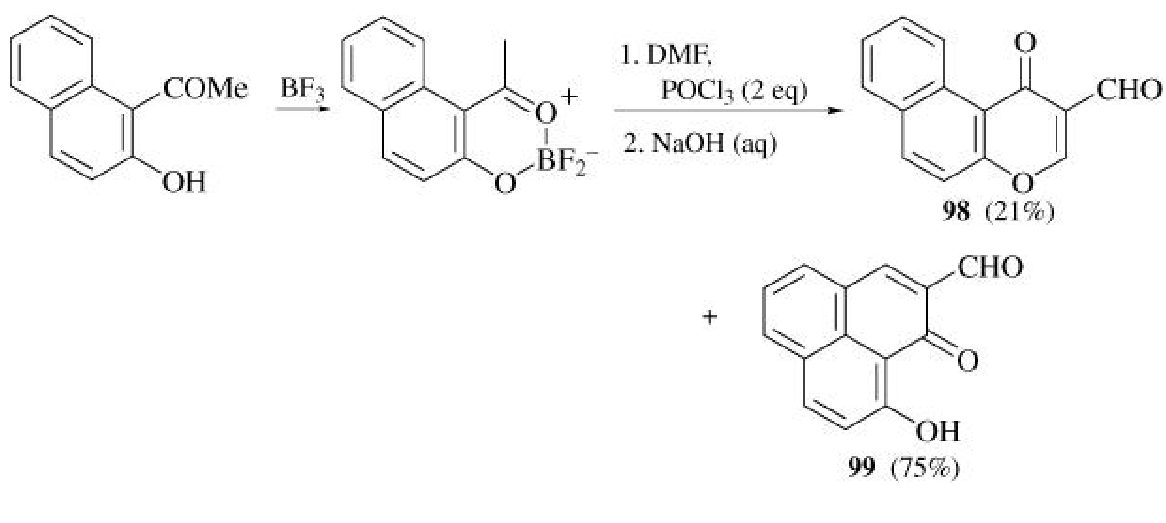


(90)



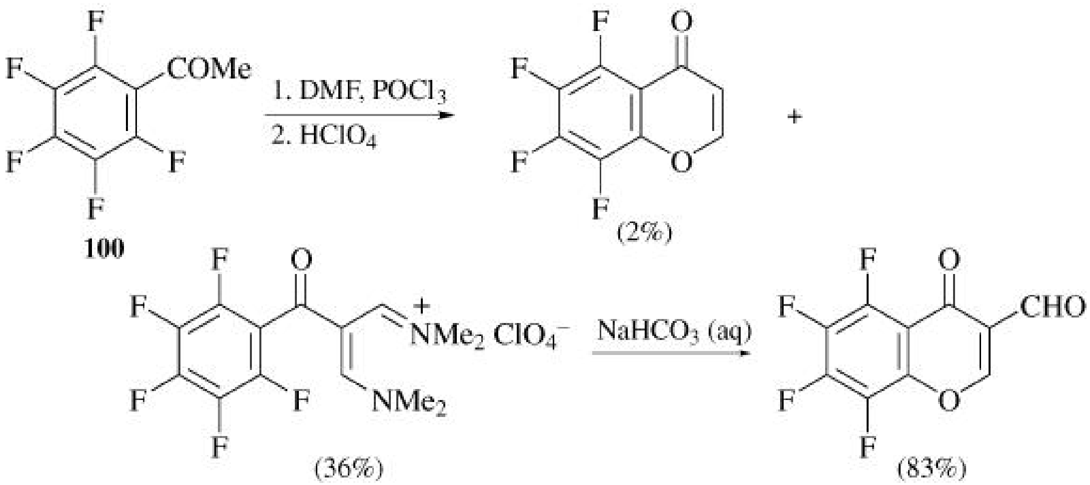
(91)

the three isomeric *o*-hydroxyacetylnaphthalenes. (100, 104) A variant uses the BF_3 complex of *o*-hydroxyacetophenones. (105) There are numerous examples of this modification in the patent literature. (106-112) In the example shown (Eq. 92), the



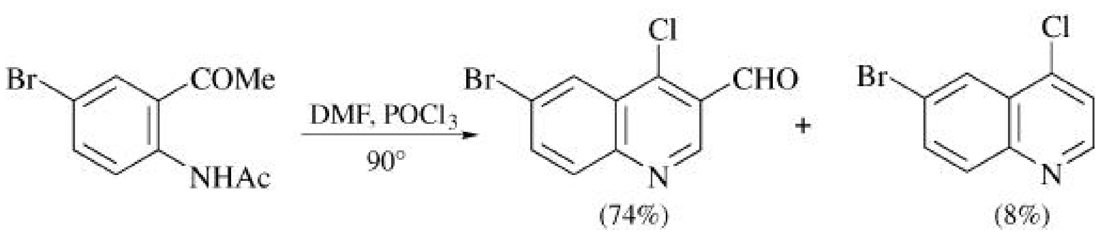
(92)

normal product **98** is accompanied by a second, **99**, derived from an alternative cyclization. (105) An adjacent fluorine atom has also been reported to be involved in the cyclization during Vilsmeier reaction of pentafluoroacetophenone (**100**); here the intermediate malonaldehyde derivative was isolated and subsequently cyclized (Eq. 93). (112a) A synthesis of quinolines makes use of an adjacent amine or



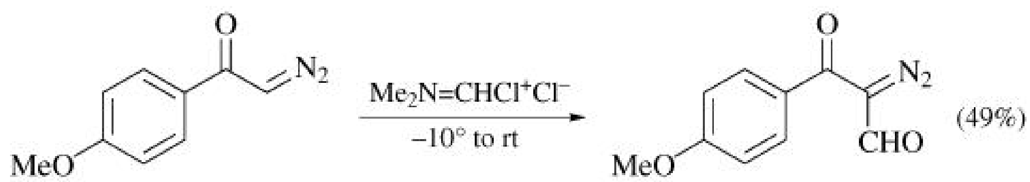
(93)

acetylamine to give a 4-chloroquinoline-3-carboxaldehyde (Eq. 93a). (112b), (112c) Acetylation of the starting material improves the yields, but some 4-chloroquinoline is also formed, and this becomes the major product when the ketone side chain is extended.



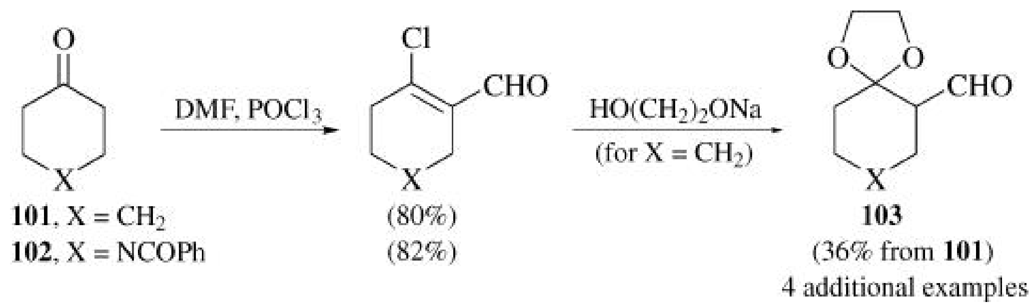
(93a)

It is possible to formylate α -diazoketones, albeit in usually poor yield, by keeping the reaction mixture between –10° and room temperature; one of the better yields is shown in Eq. 93b. (112d)



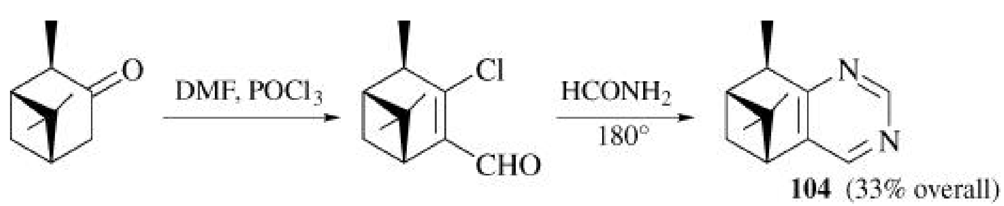
(93b)

Alicyclic ketones, even cyclobutanone, (71) react well with Vilsmeier reagents without the ambiguity of stereochemistry observed in acyclic examples. Thus cyclohexanone **101** gives a chloroenal (113) as does *N*-benzoylpiperidone (**102**; Eq. 94). (114) The products may be converted into the synthetically useful ketal

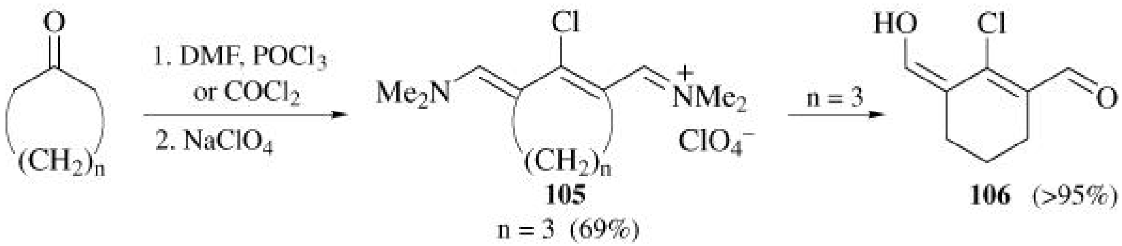


(94)

103. (115)In a number of cases (116, 117) the crude chloroenal has been converted into a pyrimidine **104** (Eq. 95). (116) With a higher ratio of Vilsmeier reagent to substrate, reaction occurs twice via intermediates of type **105** to give compounds of type **106** (Eq. 96). (118) Earlier workers (71) had reported a dimethylamino derivative, but the later authors could not repeat this.

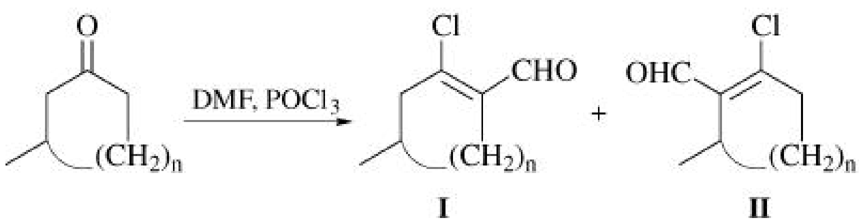


(95)



(96)

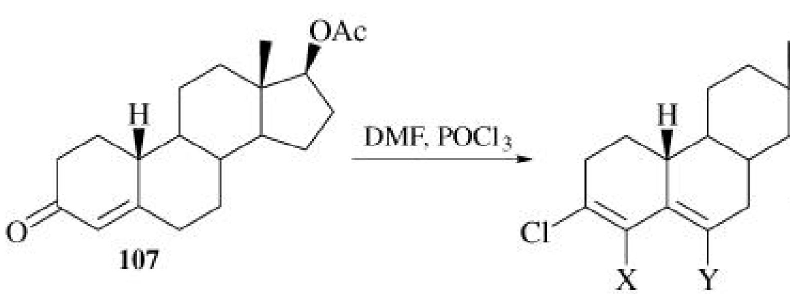
The introduction of substituents into the ring of cyclic ketones produces problems of regiochemistry. A number of methylcycloalkanones have been used in Vilsmeier reactions, and there is a tendency for the double bonds to be formed preferentially away from the substituent if it is in the β position to the carbonyl group, as shown for a number of cycloalkanones (Eq. 97). (119) The effect is negligible if the substituent is further away. Introduction of additional unsaturation



n	I	II
1	(26%)	(17%)
2	(47%)	(5%)
3	(40%)	(2%)
4	(56%)	(0%)

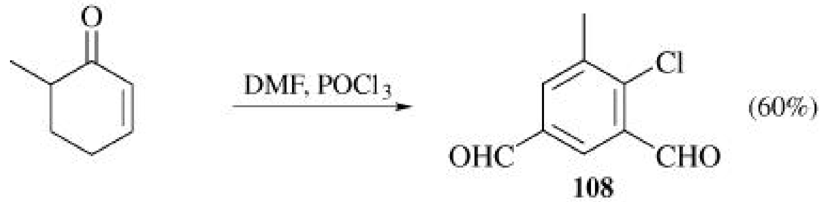
(97)

gives varying results in steroid systems such as the enone **107** (Eq. 98), (120) whereas from simple cyclohexenones benzene derivatives such as compound **108** are formed (Eq. 99). (121) Cyclohexane-1,3-dione has been reported to give benzene derivative **109**, (122) as well as non-benzenoid derivatives **110** (122) and **111** (123, 124) (Eq. 100).

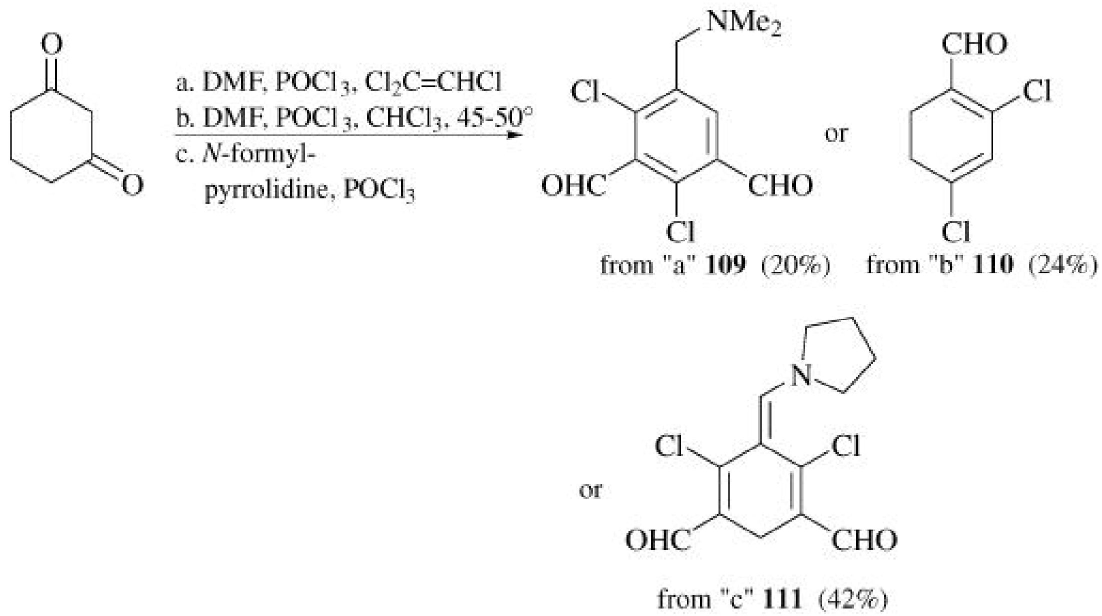


X	Y	
H	H	(13%)
CHO	H	(15%)
H	CHO	(18%)

(98)



(99)



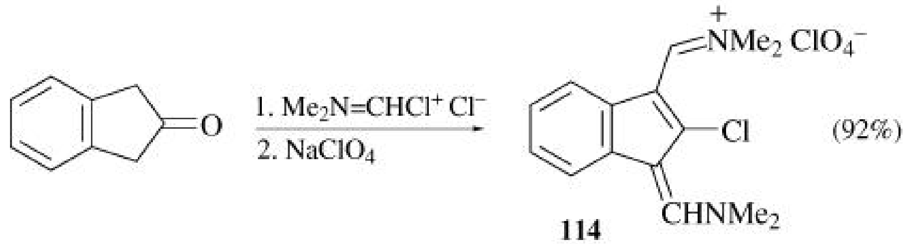
(100)

Cyclic ketones with a fused aromatic ring usually form chloroenals without side reaction, as in the case of compounds **112** (125, 126) and heteroatom-substituted analogs such as compounds **113** (Eq. 101); (127, 128) 2-indanone gives the iminium compound **114** (Eq. 102). (36)

X	n		n	
CH_2	1	(88%)	2	(75%)
O	1	(36%)	2	(70%)
S	1	(68%)	2	(54%)
Se	1	(—)		

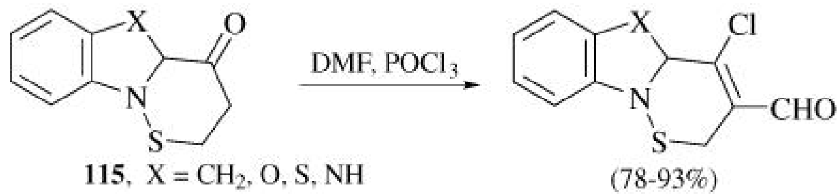
(101)

112, X = CH_2; n = 1, 2
113, X = O, S; n = 1, 2; X = Se; n = 1

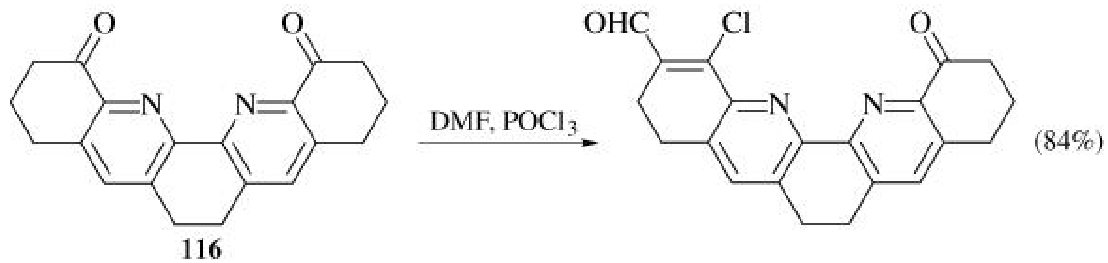


(102)

A number of examples involving cyclic ketones with fused heteroaromatic rings are reported. Among the few that react normally are the heterocycles **115** (Eq. 103) (129) and the pyridine derivative **116** (Eq. 104), (130) where monofunctionalization

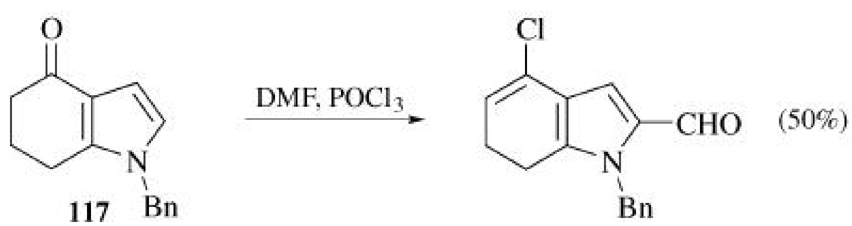


(103)

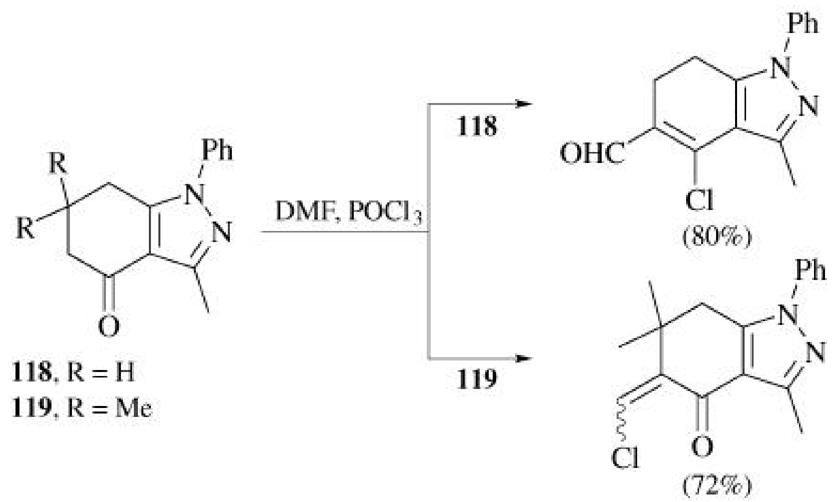


(104)

is reported. When the fused heterocycle is π -excessive, formylation can occur on the heterocyclic ring as in the dihydroindole **117** (Eq. 105). (131) While the pyrazole **118** gives a normal product (Eq. 106), the closely related compound **119** gives an abnormal reaction; (132) other compounds are reported to react normally. (133)

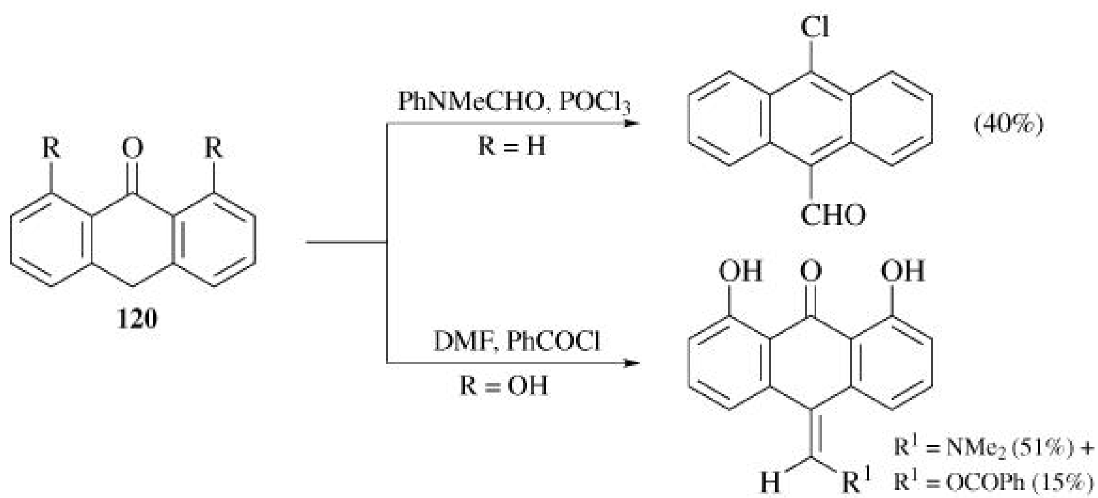


(105)

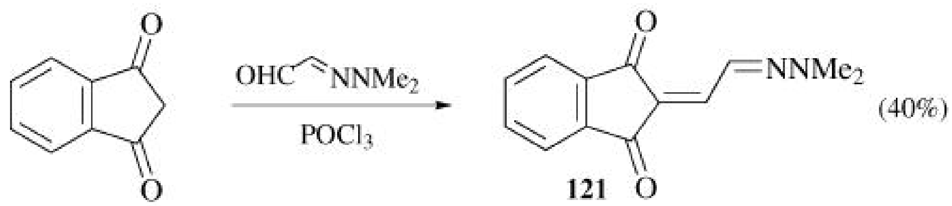


(106)

Anthrone **120** (R = H) reacts like an enone giving an anthracene derivative, (134) but 1,8-dihydroxyanthrone **120** (R = OH), with the unusual combination of benzoyl chloride and DMF, gives a mixture of methylene derivatives (Eq. 107). (134a) Other Vilsmeier reagents using phosphoryl chloride give only aminomethylene derivatives. (134b) The reaction of indane-1,3-dione with the vinylogous aza-Vilsmeier reagent gives compound **121** (Eq. 108). (135)



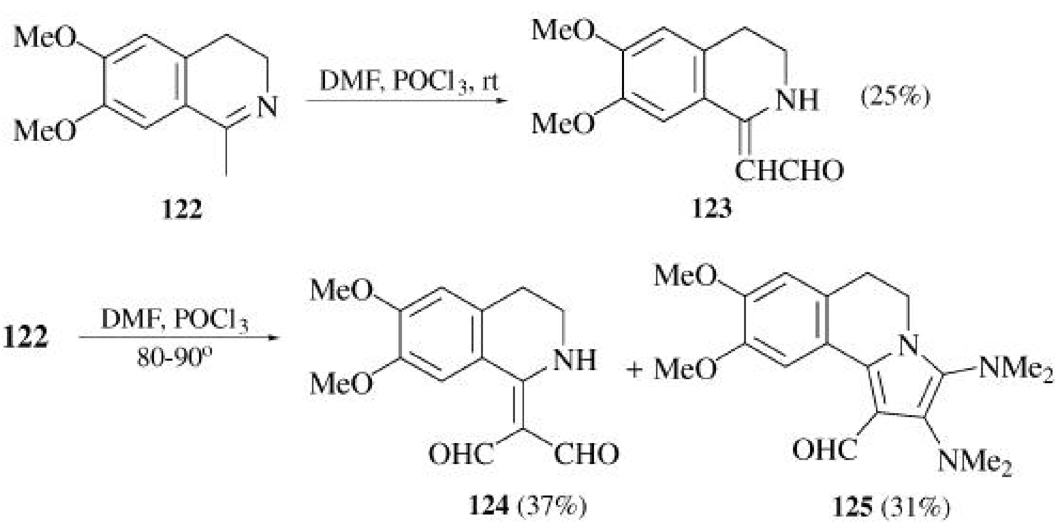
(107)



(108)

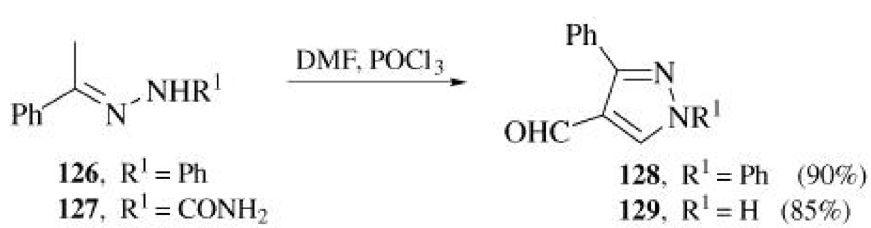
2.5. Imines, Hydrazones, Semicarbazones, and Oximes

In most of the examples of this type the C = N bond provides activation for an adjacent methyl or methylene group; three products can be obtained from the cyclic imine **122**. The least substituted product **123** is only obtained at low temperatures; at higher temperatures products **124** and **125** are obtained, the proportion of the latter increasing as the $POCl_3$ proportion is raised (Eq. 109). (136, 137) From



(109)

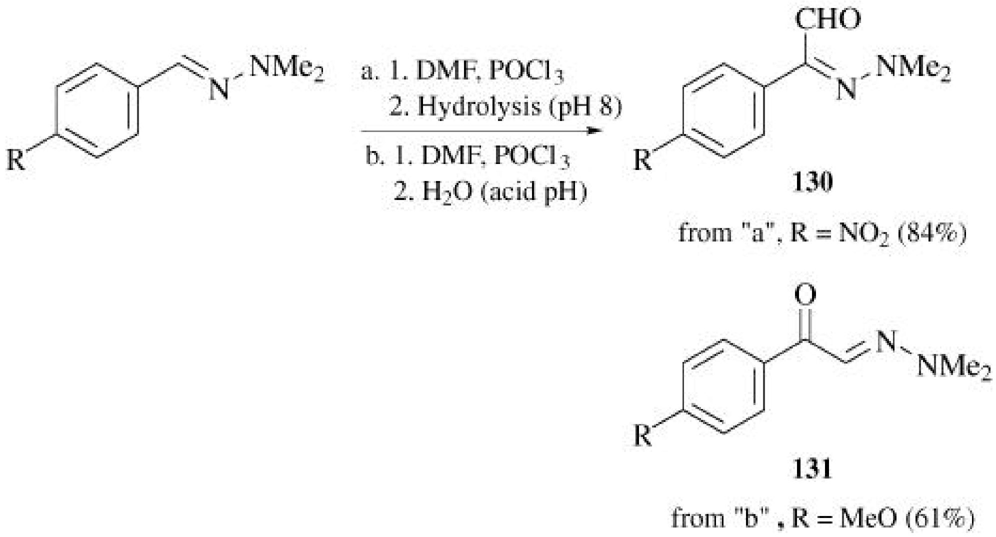
hydrazones and semicarbazones cyclization of the first-formed product gives a pyrazole. Thus the phenylhydrazone **126**, (138) or semicarbazone **127**, (139) give pyrazoles **128** and **129**, in the latter case with loss of the amide group (Eq. 110), often



(110)

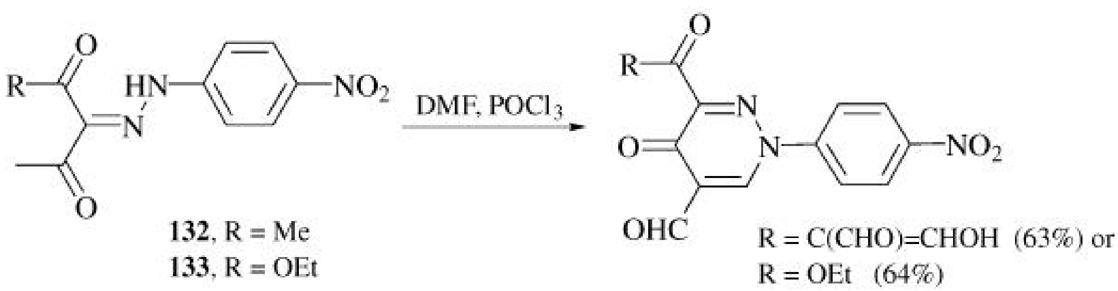
in excellent yields, presumably via a malonaldehyde derivative.

N,N-Disubstituted hydrazones without methylene groups adjacent to the imine bond are mainly formylated to give compounds **130** (140) but have also been reported to give isomeric ketones **131** such as (Eq. 111). (141, 140)



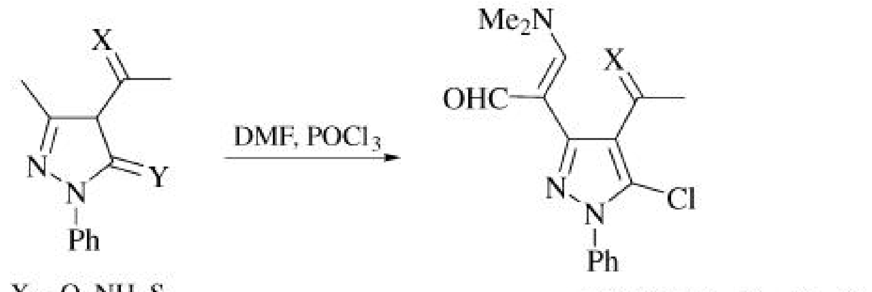
(111)

Cyclization to give pyridazinones is observed when the hydrazones **132** and **133** are treated with the Vilsmeier reagent (Eq. 112). (142) Methyl substituents on a



(112)

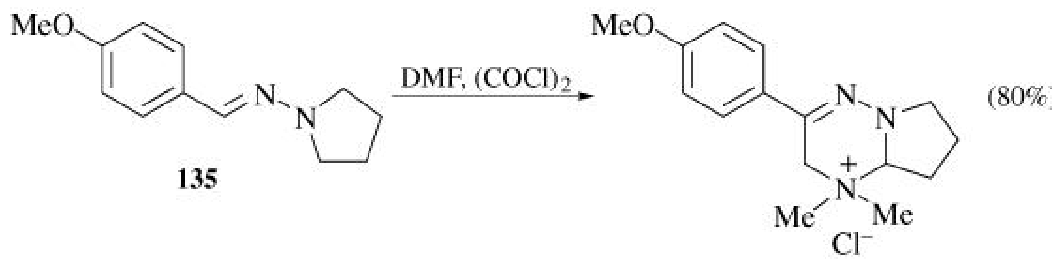
number of dihydropyrazoles are converted into malonaldehyde derivatives **134** (Eq. 113). (143, 144) Chlorination at C5 also occurs if the oxo derivative is used. The



134 (75% for X = Y = O)

(113)

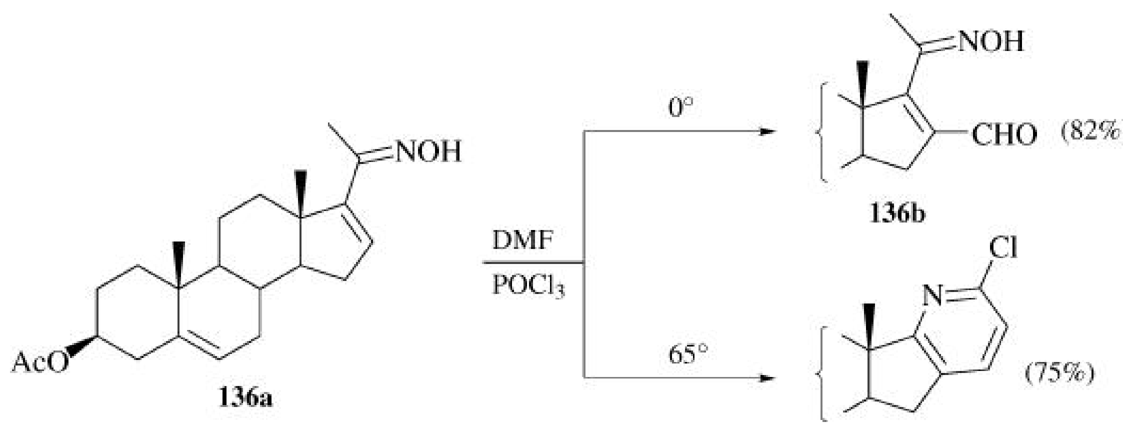
unusual cyclization of hydrazone **135** gives the quaternary salt **136** in high yield (Eq. 114). (138) There is an example where an oxime has survived the normal Beckman rearrangement, or, in the case of aldoximes, dehydration to give cyanides. From the steroid **136a** the unsaturated aldehyde **136b** is obtained at 0°, with more normal formation of a 2-chloropyridine via the Beckman rearrangement product at 65° (Eq. 114a). (144a)



135

136

(114)



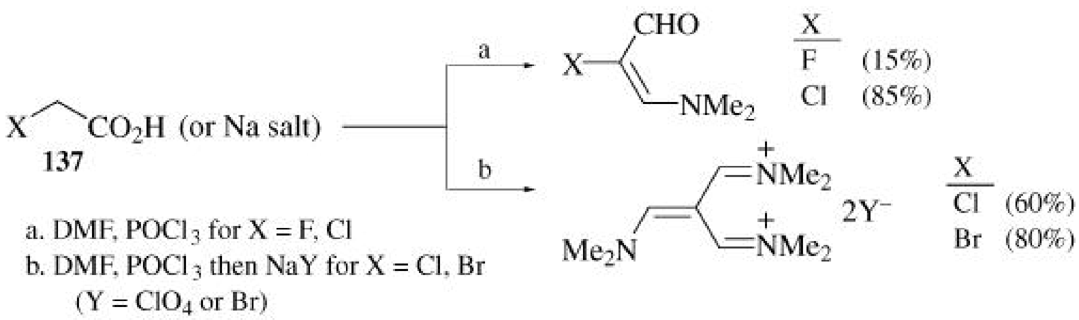
136a

136b

(114a)

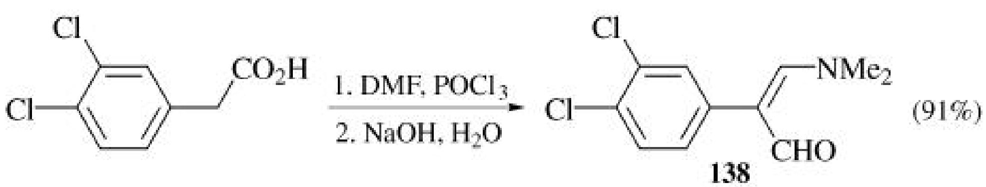
2.6. Carboxylic Acids, Anhydrides, and Acid Chlorides

The reaction of derivatives of acetic acid (or its salts) with the Vilsmeier reagent is widely used to prepare malonaldehydes or their derivatives. The simple haloacetic acids **137** (or their salts) give fluoro- (145) or chloromalonaldehyde derivatives (74, 146) or chloro- or bromotriformylmethane derivatives (Eq. 115). (74, 146)

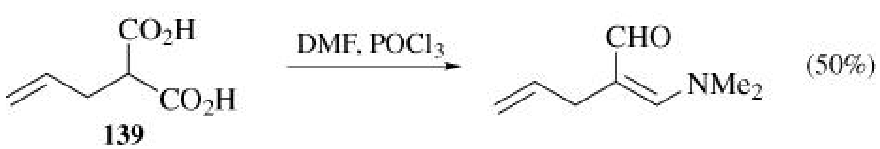


(115)

This reaction has been exploited using arylacetic acids; yields are excellent when the products are isolated as dimethylamino derivatives as shown for compound **138** (Eq. 116). (147) Malonic acids such as **139** are thus converted into derivatives of malonaldehyde in moderate yields (Eq. 117) (148). Cyanoacetyl chloride gives derivatives

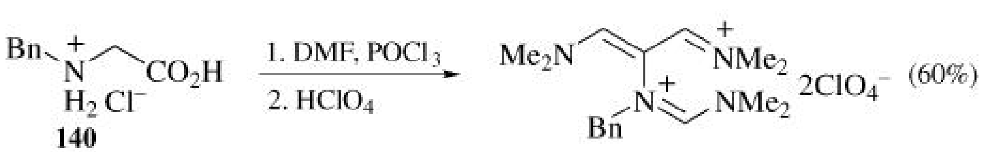


(116)



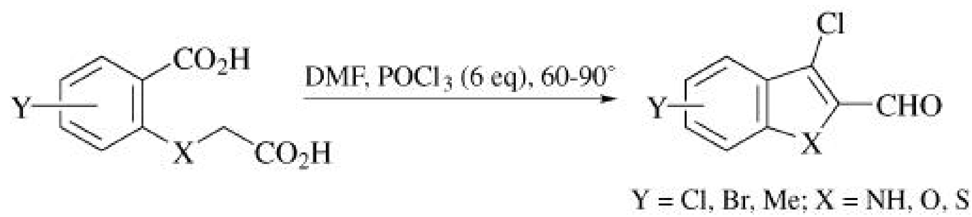
(117)

of acrylonitrile (145) or acrylic acid. (74) Reactions with *N*-substituted glycines produce derivatives of aminomalonaldehyde, as shown for compound **140** (Eq. 118). (149)



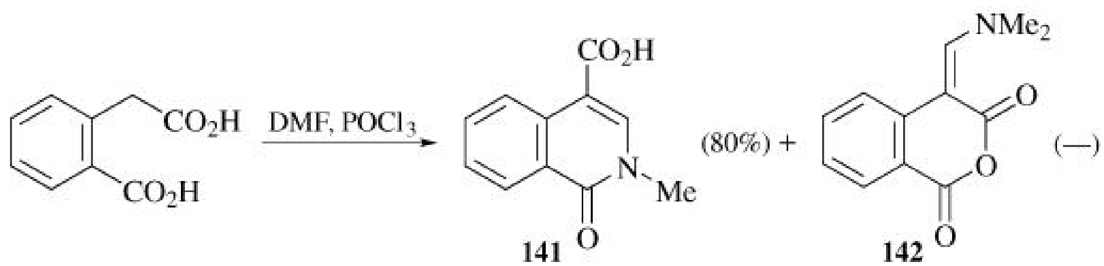
(118)

The only notable side reactions are the formation of substituted indoles, benzofurans, and benzthiophenes from diacids (Eq. 118a), (149a) the isoquinoline **141**



(118a)

from 2-carboxyphenylacetic acid (Eq. 119) (150) (some of the benzpyranedione **142** may also be formed), the indenone **143** from 1,2-bis(carboxymethyl)benzene (Eq. 120), (36) and the lactones **144** and **145** from 2-hydroxyphenylacetic acid (Eq. 121). (151)



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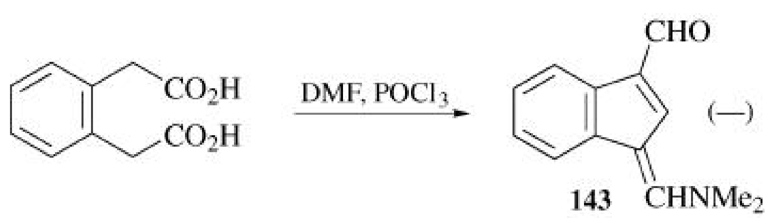

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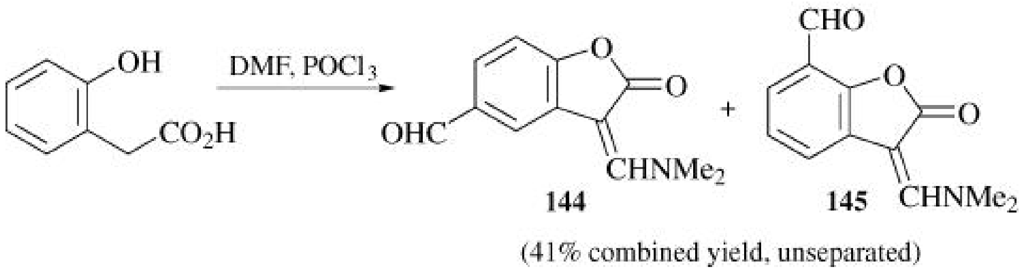
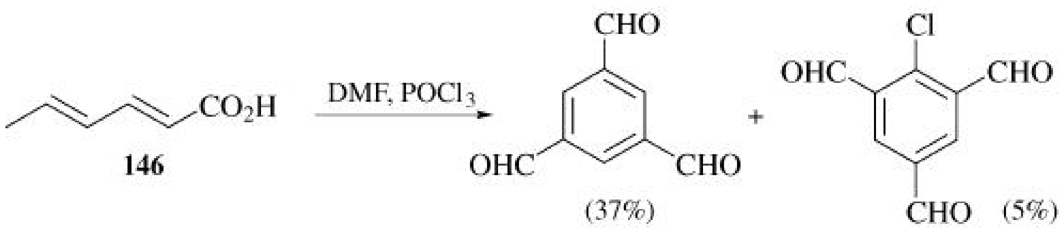
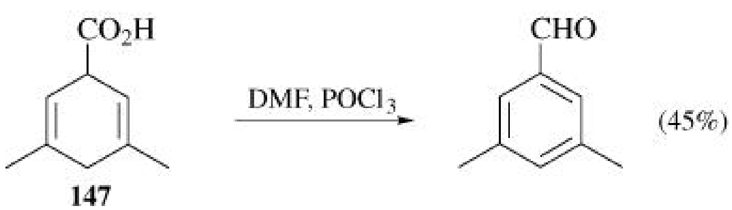


(121)

Acyclic dienoic acids and cyclohexa-2,5-dienecarboxylic acids give a variety of benzaldehydes. An example of the former class is acid **146** (Eq. 122) (152) and of the latter, acid **147** (Eq. 123). (153) A few examples exist of the preparation of malonaldehyde

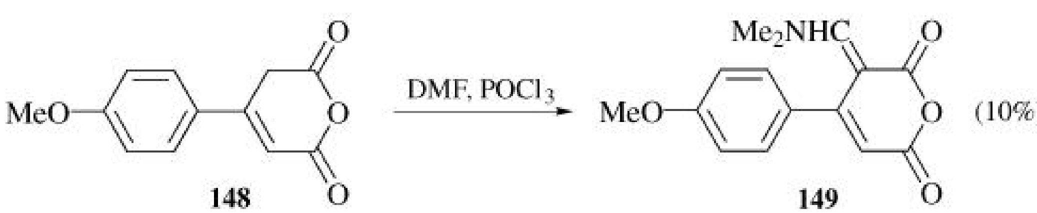


(122)



(123)

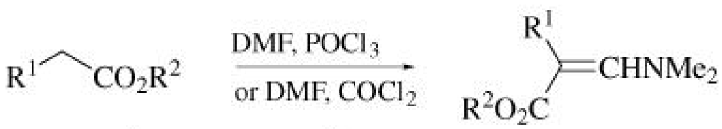
derivatives from acid chlorides; (154) it should be noted that the Vilsmeier reagent is often used as a mild reagent to prepare acid chlorides at low temperatures. The anhydride **148** reacts in a manner similar to lactams to give compound **149** in low yield (Eq. 124). (155)



(124)

2.7. Esters and Lactones

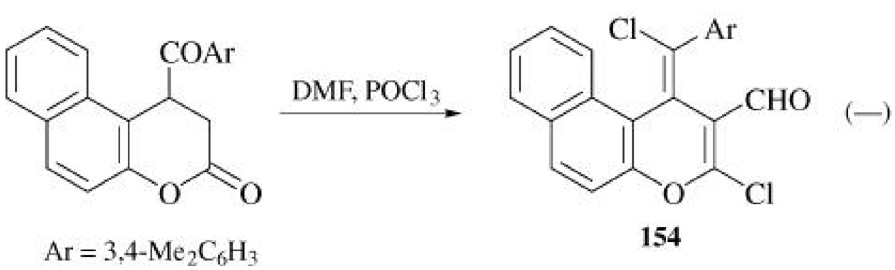
Almost all examples of Vilsmeier reactions on esters use activated acetic esters bearing a second electron-withdrawing group, as in diethyl malonate **150** and ethyl cyanoacetate **151** (Eq. 125), (156) or an electron-deficient heterocyclic ring as



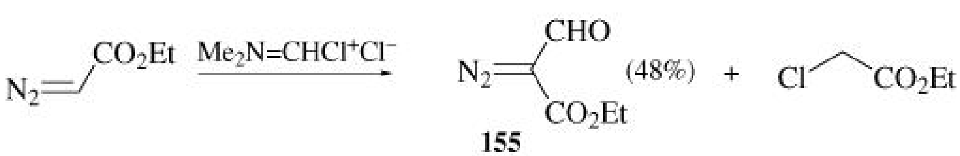
	R^1	R^2	
150,	CO_2Et	Et	(81%)
151,	CN	Et	(75%)
152,	2-quinolyl	Et	(82%)
153,	3-Me-2-indolyl	Me	(59%)

(125)

in quinoline-2-acetate **152**, (157) but the electron-rich 2-indolylacetate **153** has also been reported (158) to react in good yield (Eq. 125). One lactone has been converted into a dichloro enal **154** (Eq. 126). (159) The most remarkable reaction gives a formyl derivative **155** from ethyl diazoacetate, although some decomposition occurs (Eq. 127). (160)



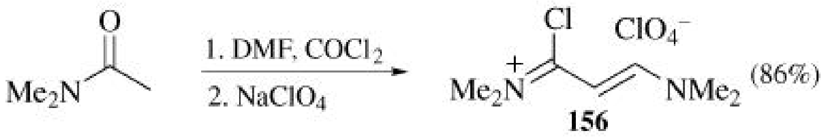
(126)



(127)

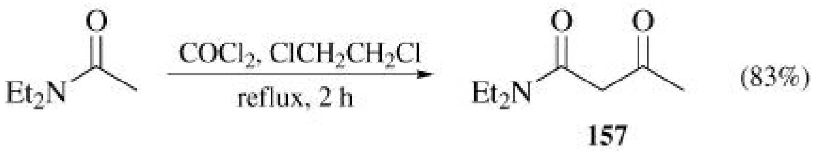
2.8. Amides and Lactams

Lactams that may be regarded as tautomers of hydroxyheteroaromatics were included in the chapter in volume 49. (1) Simple amides react with the Vilsmeier reagent like other carbonyl compounds to form mono- or diformyl derivatives, but such simple cases are rare; an example is provided by the synthesis of compound **156** (Eq. 128). (74) An amide with an α hydrogen can function both as Vilsmeier reagent



(128)

precursor and as substrate with phosgene to give compounds such as **157** (Eq. 129). (161) The modified Vilsmeier conditions, using formamide and

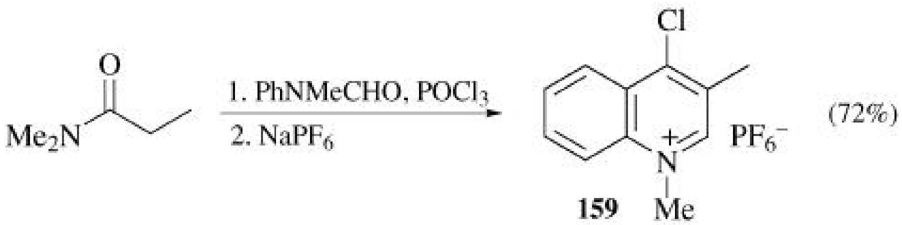


(129)

phosphoryl chloride, can be used to form pyrimidine **158** from dimethylacetamide, although yields of such reactions are usually lower than that shown (Eq. 130). (162)

(130)

From acetanilides or *N*-acetylaminothiophenes a range of fused pyridines can be formed. Variants shown are compounds **159** (Eq. 131), (163) **160** and **161** (Eq. 132), (164, 165) **162** (Eq. 133), (166, 167) and **163** (Eq. 134). (168) Compounds of type **162** (Eq. 133) can also be obtained from an acetophenone oxime via an initial Beckmann rearrangement. (169) 2,5-Dimethyl-3-acetamidothiophene gives thieno[3,4-*b*]pyridines. (164, 165) Acetamidopyrazoles have also been used in reactions analogous to that shown in (Eq. 132). (170)



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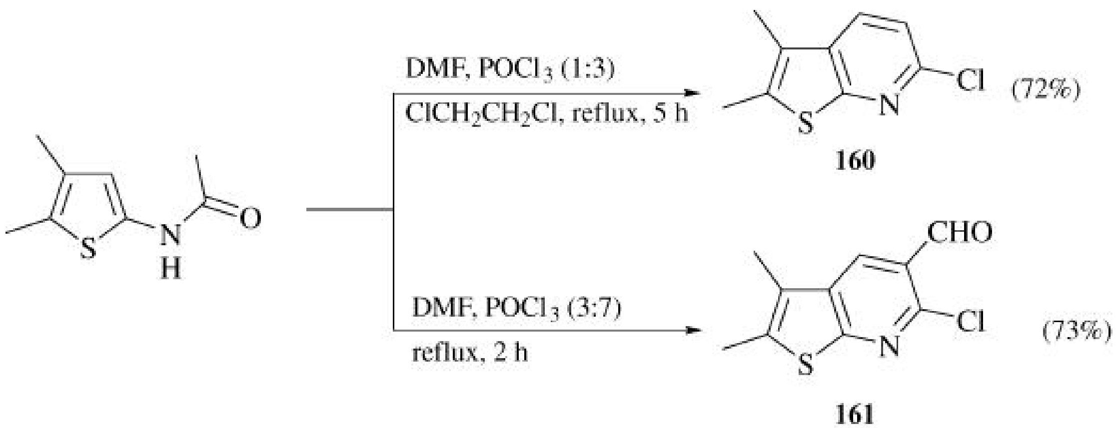

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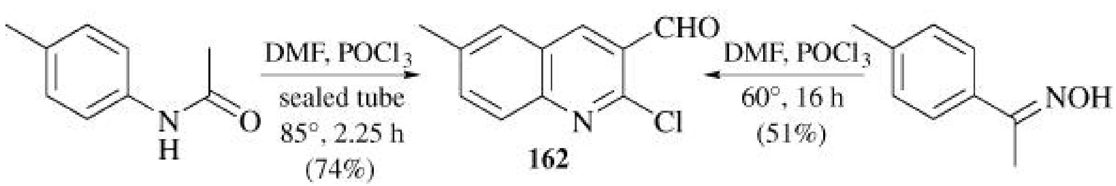

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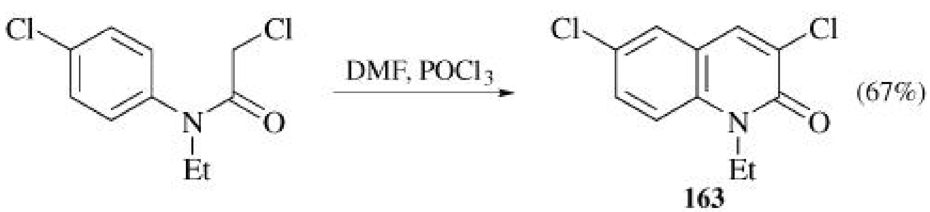


(134)

When the alkyl chain is extended (171) or is an arylacetyl group, (172) a 3-alkyl- or 3-aryl-2-chloroquinoline **164** is the product (Eq. 135). With 3-substituted

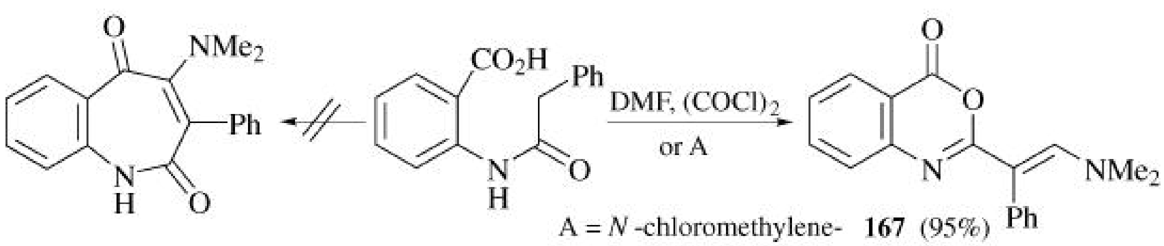
164 (95%) (135)

anilides there is the possibility for formation of two isomeric products, but in the cases recorded the products are always 7-substituted quinolines. The oximes of 4-arylbut-3-en-2-ones, which are vinylogs of acetophenones, give 2-chloro-5-arylpyridine-3-carboxaldehydes under Vilsmeier conditions. (144a) Only one example of the use of phosphoryl bromide with acetanilides is recorded, giving the 2,5-dibromoquinoline **165** in poor yield (Eq. 136). (171) Cyclohexenes such as compound **166** give 2-pyridones in poor to moderate yields (Eq. 137). (168) Cyclization

165 (13%) (136)

166 (43%) (137)

has been reported to occur to an adjacent carboxy group to produce an azepinedione, (173) where the aromatic ring can be benzene, pyridine, or thiophene, but a later report of this reaction shows that the products are benzo[*d*]oxazinones such as **167** (Eq. 138). (173a), (174)

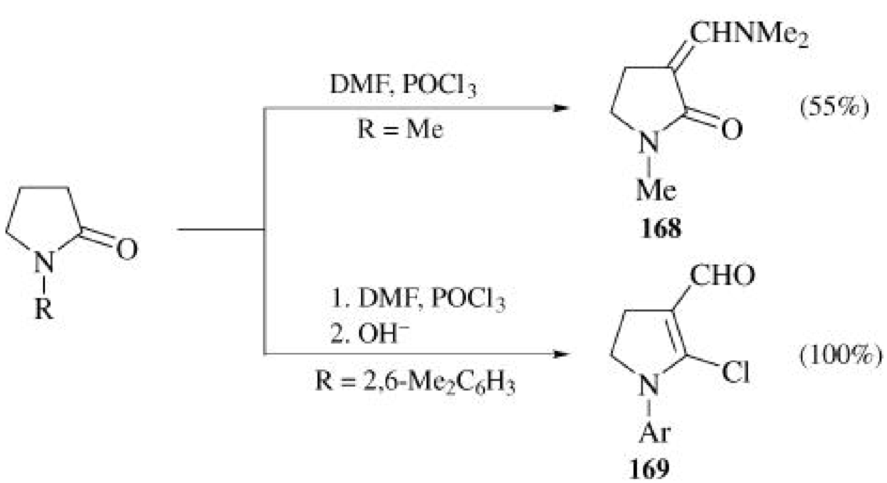


A = *N*-chloromethylene-morpholinium chloride **167** (95%) (138)

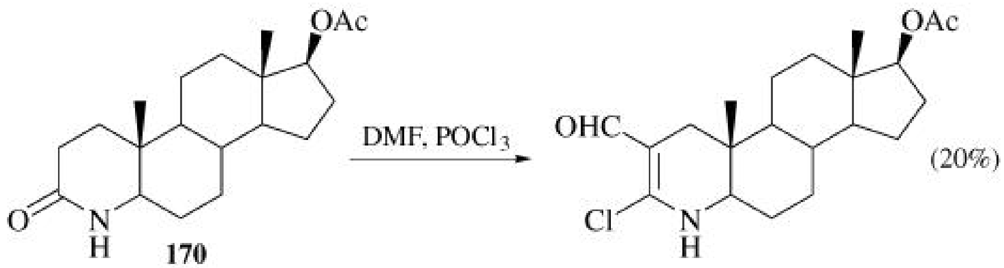
N-Acylureas or thioureas such as **167a** react with elimination of the urea and formation of malonaldehyde derivatives, isolated as perchlorates (Eq. 138a). (174a) *N*-Acetylurea does not react.

(138a)

As mentioned earlier, lactams that are potentially aromatic by tautomerism are dealt with elsewhere. (1) Simple lactams normally react to give compounds such as **168** (175) although a quantitative yield of chloroaldehyde **169** is reported in one case (Eq. 139). (176) A few examples of reactions with azasteroids are reported, as exemplified by compound **170** (Eq. 140), (177) although yields are generally poor.

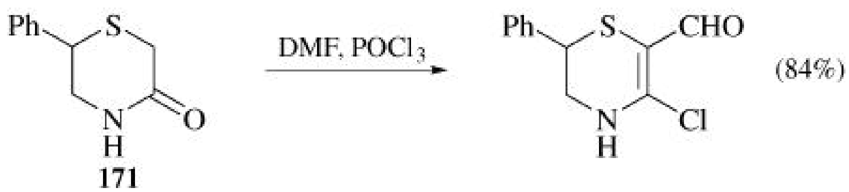


(139)

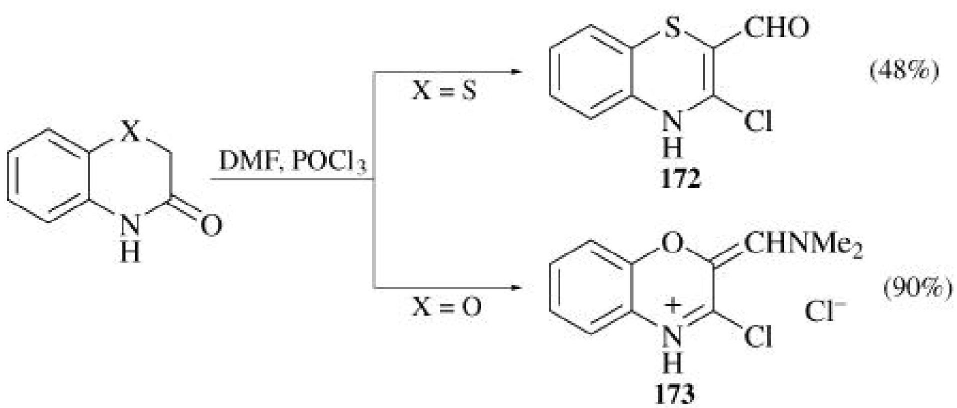


(140)

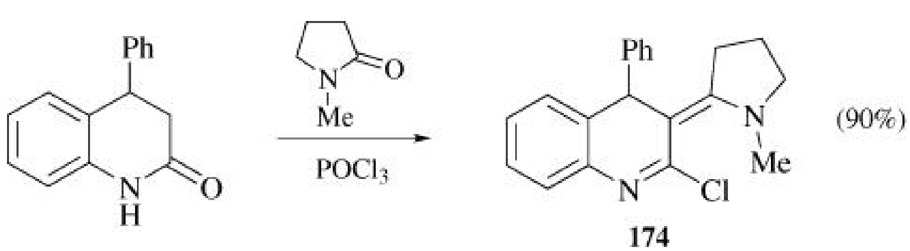
Monocyclic lactams containing other heteroatoms, such as compound **171**, give chloroenals (Eq. 141). (178, 179) There are numerous examples of Vilsmeier reactions with lactams fused to benzene rings; representative products are **172** (178, 179) and **173** (180) (Eq. 142), **174** (Eq. 143), (181) **175** (Eq. 144), (182) and **176** (Eq. 145). (181)



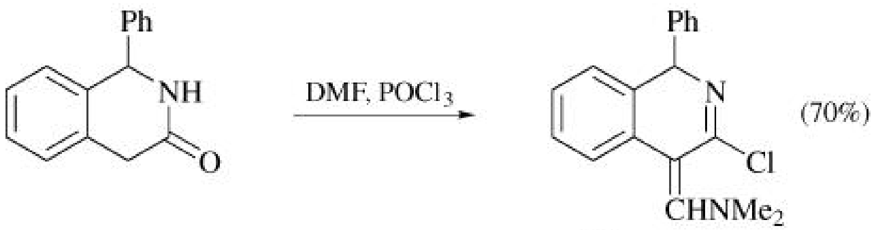
(141)



(142)

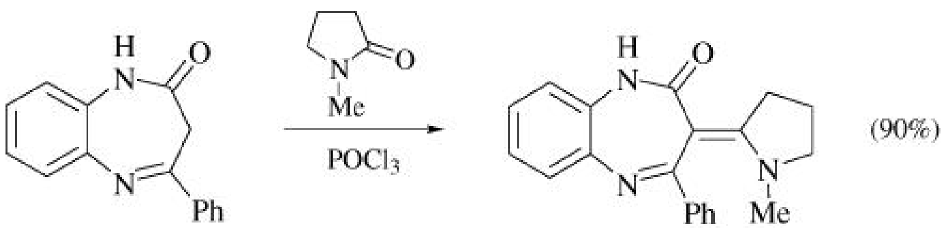


(143)



175

(144)

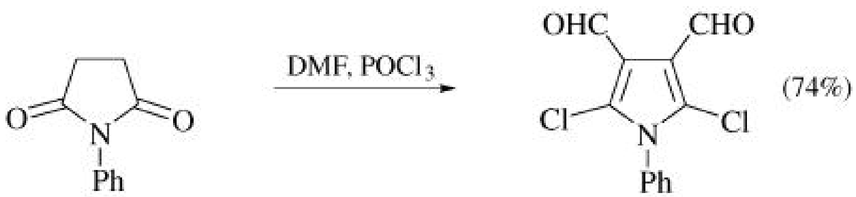


176

(145)

2.9. Imides

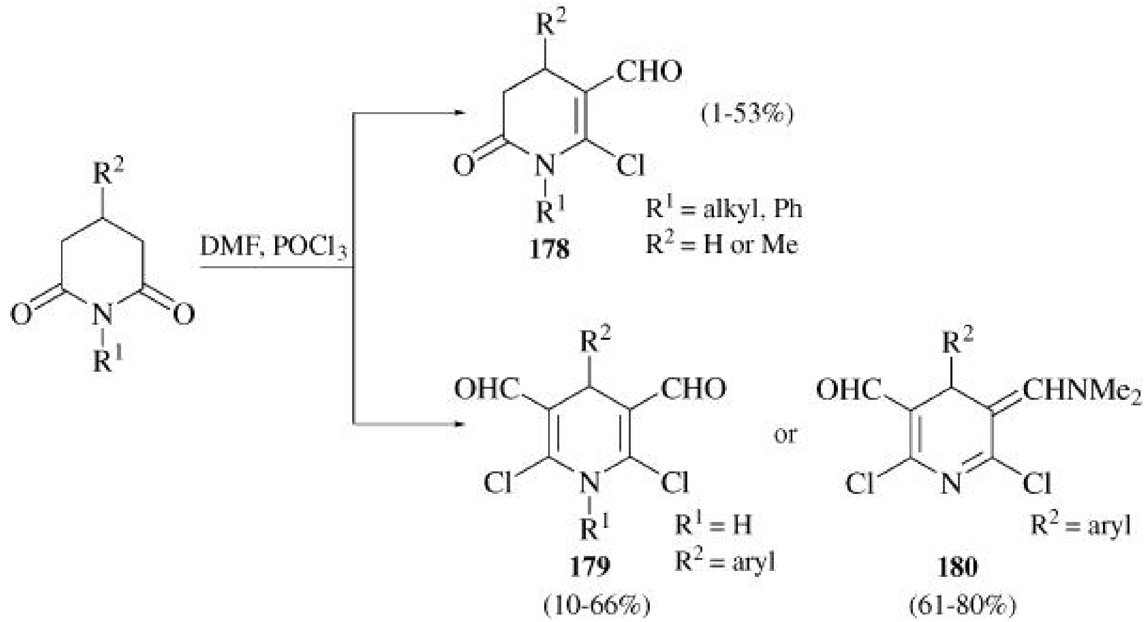
Vilsmeier reagents react with *N*-substituted succinimides to give pyrroles **177** (Eq. 146). (183) Glutarimides can give monoformyl derivatives **178** or diformyl



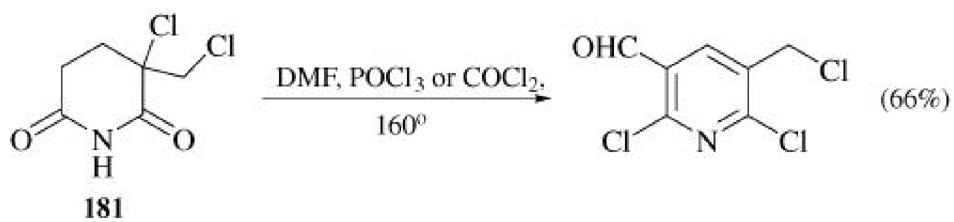
177

(146)

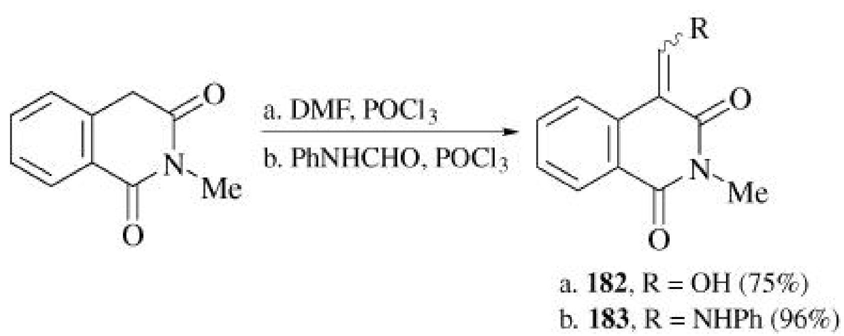
derivatives **179** (Eq. 147). (184, 185) In the latter case, yields are higher when the dimethylaminomethyl compounds **180** are isolated. (186) The α , α -disubstituted glutarimide **181** gives a pyridine when treated with the Vilsmeier reagent at high temperature (Eq. 148). (187) Monoformylation of an isoquinolinedione proceeds in high yield with DMF to give compound **182**; an anilinomethylene derivative **183** is obtained when the Vilsmeier reagent from formanilide is used (Eq. 149). (188)



(147)



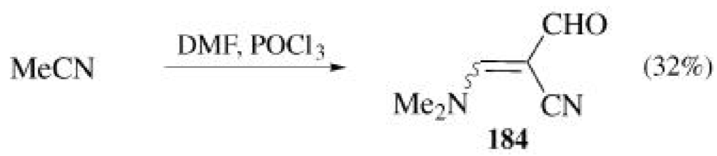
(148)



(149)

2.10. Nitriles

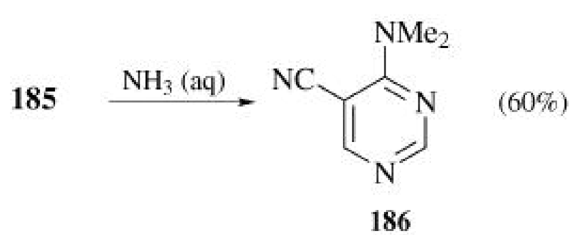
Acetonitrile gives the cyanomalonaldehyde derivative **184** (Eq. 150). (145) Malononitrile provides an example of a Vilsmeier reaction at both nitrogen and



(150)

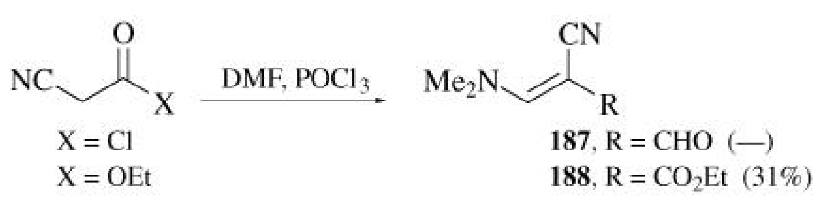
carbon to give the iminium salt **185** (Eq. 151), which with ammonia gives pyrimidine **186** (Eq. 152); (189) aniline or *N*-methylaniline convert the intermediate into the 4-phenylamino- and the 4-[phenyl(methyl)amino]pyrimidines. Cyanoacetyl chloride (145)

(151)



(152)

and ethyl cyanoacetate (190) form the corresponding dimethylaminomethylene derivatives **187** and **188** by condensation with the activated methylene group (Eq. 153). Cyanoacetamides, depending on the pattern of substitution, can react with phosphoryl chloride to give pyridines such as **189** (Eq. 154) or **190** (Eq. 155) (191) or 4,6-dichloropyrimidines **191** (192) alone (Eq. 156) or, as with



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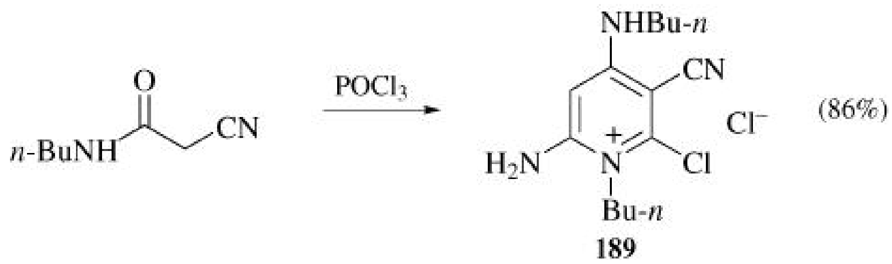

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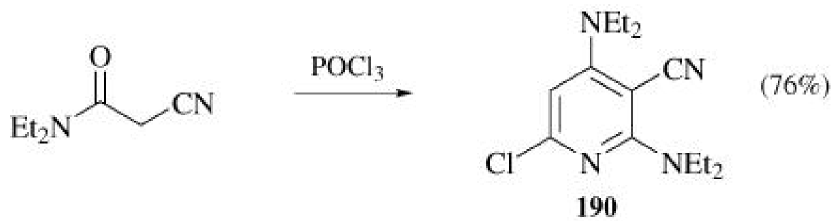

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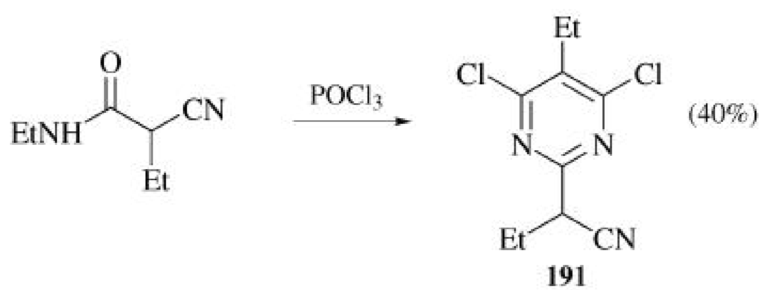
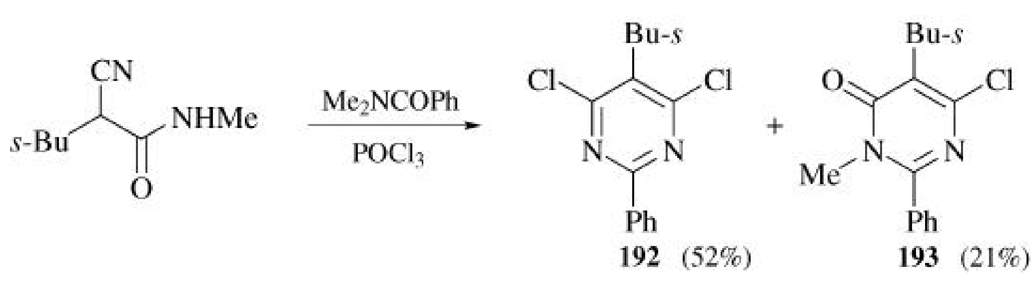


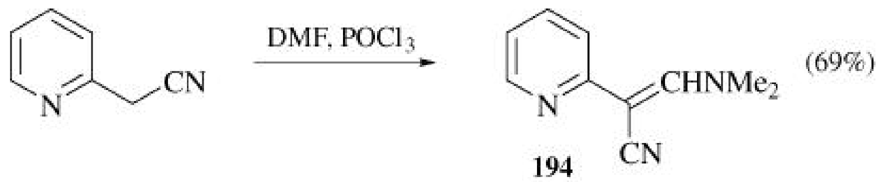
(156)

192, mixed with 6-chloro-4-pyrimidinones **193** (Eq. 157). (193) In these reactions, the cyanoacetamides act as precursors and substrates for the Vilsmeier reaction.



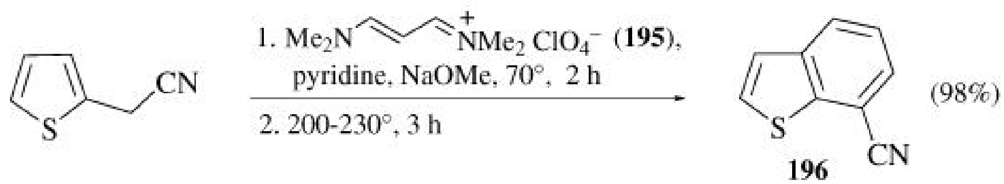
(157)

Aryl- and heteroarylacetonitriles give compounds of type **194** (Eq. 158). (157) When the aryl group is π -excessive (azulene or heteroaryl) and vinamidinium



(158)

salts **195** are used, cyclization to the aromatic ring producing benzannulated compounds such as **196** (Eq. 159) can occur. (194) A similar reaction with *N*-unsubstituted pyrrole **197** gives an indolizine **198**, whereas the azavinamidinium salt **199** gives an azaindolizine (Eq. 160). (194)



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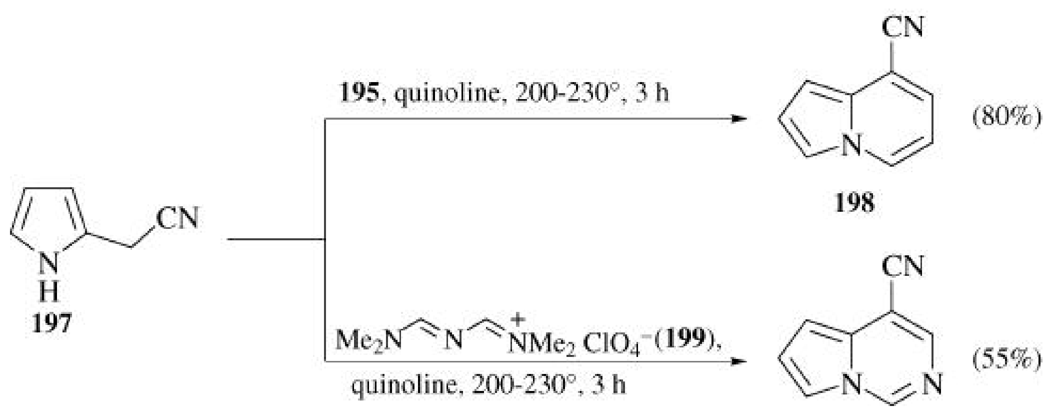
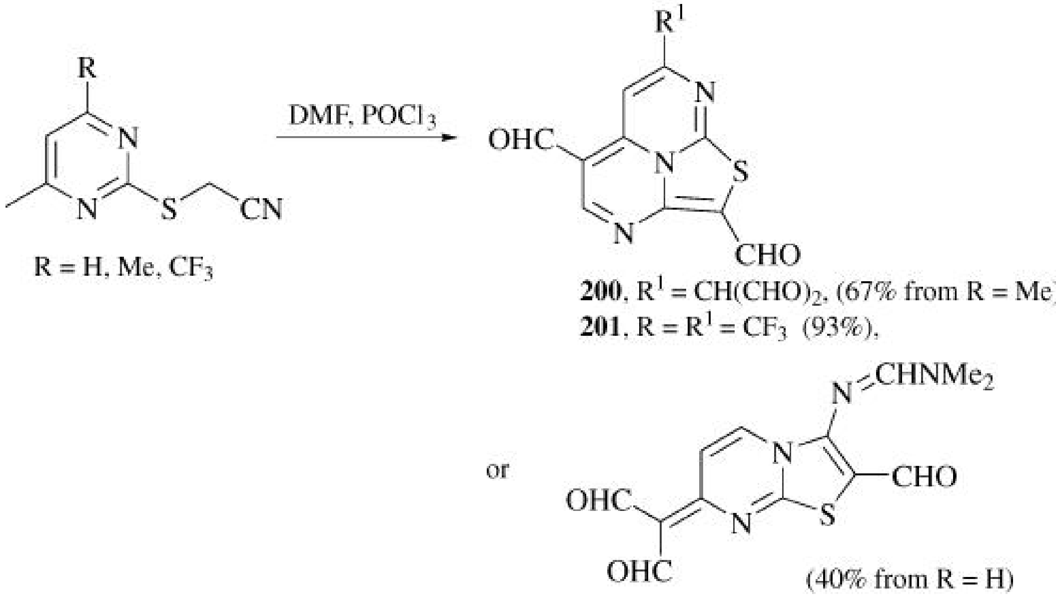


(160)

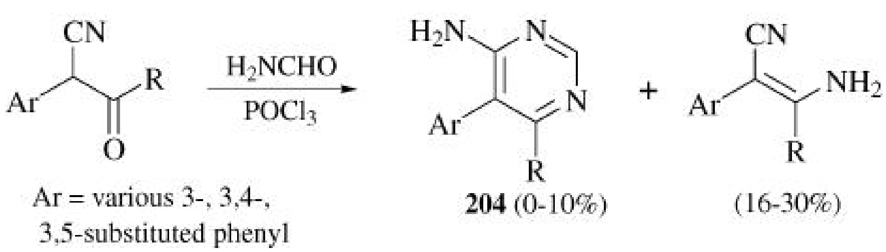
2-Cyanomethylthiopyrimidines react with the Vilsmeier reagent giving thiazolopyrimidinopyrimidines **200** and **201** if the substituent at position 4 in the pyrimidine is methyl or trifluoromethyl; if the substituent is hydrogen a bicyclic product is formed (Eq. 161). (195)



(161)

In α , β -unsaturated nitriles, reaction can occur at a vinylogous methylene group, as in example **202**, to give a 2-chloro-3-cyanopyridine (Eq. 162). (196) Yields are poor, but are much better with the vinylogous cyanoacetates such as compound **203**. (197) Aminopyrimidines **204** can be obtained from arylcyanocarbonyl compounds, using formamide and phosphoryl chloride (Eq. 163). (198) Yields, when quoted, are very poor.

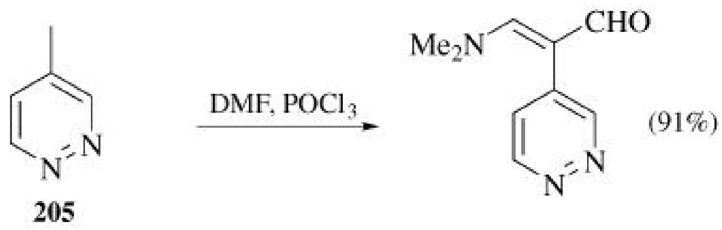
(162)



(163)

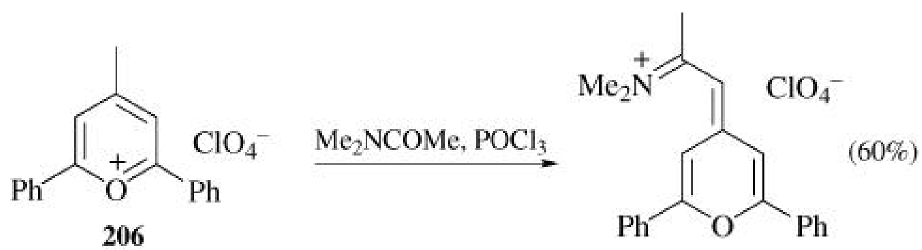
2.11. Methyl and Methylene Groups Activated by Adjacent Aromatic and Heteroaromatic Rings

In most of the examples in this section, the aromatic ring is π-deficient or positively charged. The products are mono- or diformylated, and are often isolated as the aminomethylene derivatives. A typical reaction is that of 4-methylpyridazine (**205**; Eq. 164). (199) Other neutral monocyclic activating rings



(164)

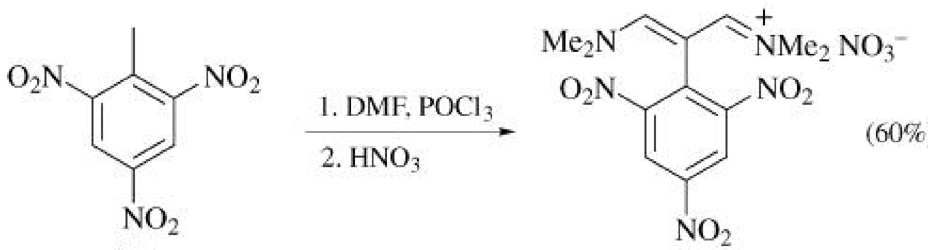
are isoxazole, (200) 1,3,5-triazine, (201, 202) pyrimidine (2- (203) or 4-substituted (204)), pyrazine, (205) pyridine (4-substituted), (206) and benzene. (207) Bicyclic neutral activating rings are 1,2-dithiolo-[1,5-*b*]dithiole, (208) imidazo[4,5-*e*]pyrimidines, (209) benzimidazoles, (210) benzoxazole, (211) benzthiazole, (212) benzisothiazoles, (212) benzselenazoles, (211) pyrrolo[2,3-*a*]pyrimidine, (209) indole, (213) azulene, (214) benzpyrimidinone, (215) benzpyrazinethione, (216) quinoline (2- and 4-substituted), (211) benzpyranone, (217) and naphthalene. (218) Charged monocyclic rings which activate methyl groups are exemplified by the pyrylium salt **206** (Eq. 165). (219) Other activating rings are dithiolium, (220)



(165)

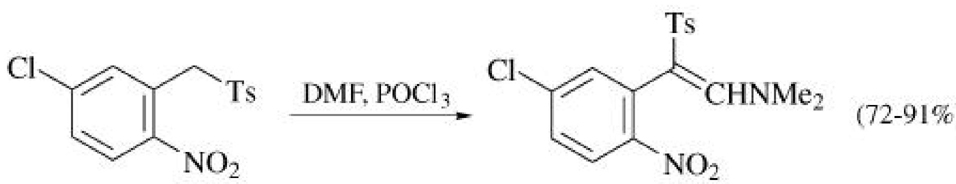
pyrimidinium, (221) oxazinium, (222) and cycloheptatrienylium. (223) Bicyclic charged ring systems used are thiazolo[3,2-*a*]pyrimidinium, (224) benzoxazolium, (211) benzthiazolium, (225) benzselenazolium, (211) benzpyrimidinium, (215) quinolinium (2- and 4-substituted), (211) benzpyrylium, (219) benzthiopyrylium, (219) and a naphthopyrylium. (219)

Some comment on benzene activation may be useful. Several activating groups are required, which may be on the benzene nucleus as shown in example **207** (Eq. 166), (207) or on the side chain, as in compound **208** (Eq. 167). (218) Naphthalenes



207

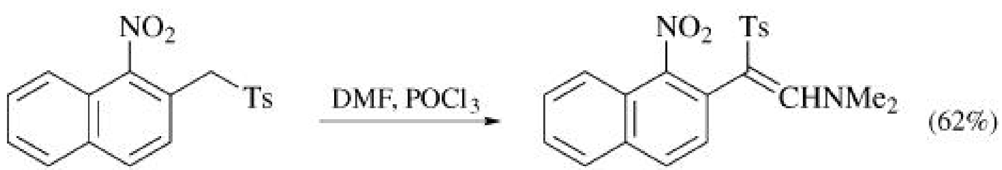
(166)



208

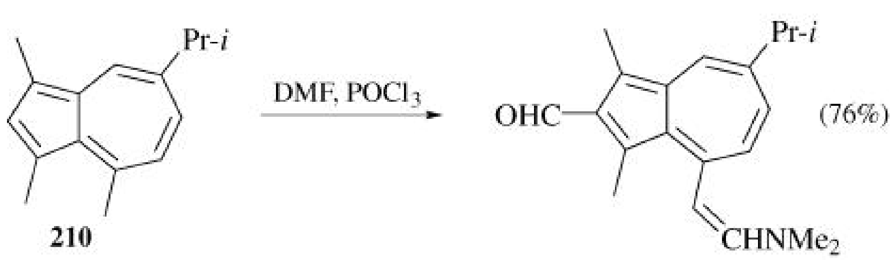
(167)

behave similarly, as shown by compound **209** (Eq. 168). (218) Azulenes require no additional activation for substituents on the seven-membered ring, as shown by the reaction of compound **210** (Eq. 169); (226) formylation also occurs on the electron-rich five-membered ring.



209

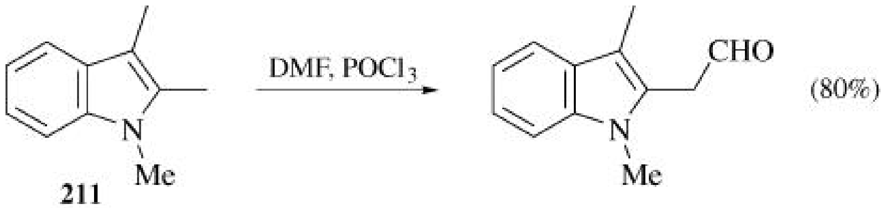
(168)



210

(169)

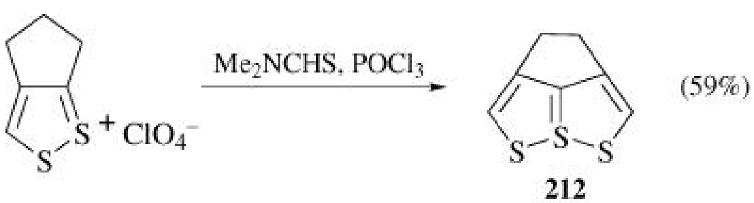
It is surprising to see reaction in a methylindole **211**; the product is also unusual (Eq. 170). (213) Many products are described for the reaction between



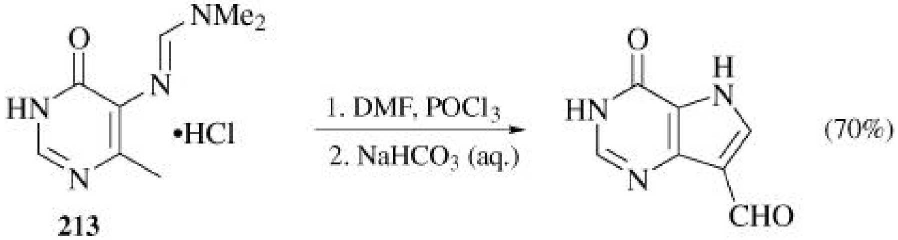
(170)

N-methyl-1,2,3,4-tetrahydrocarbazole and the Vilsmeier reagent, with formylation on saturated and aromatic rings, dehydrogenation, and even introduction of a carbonyl group. (227)

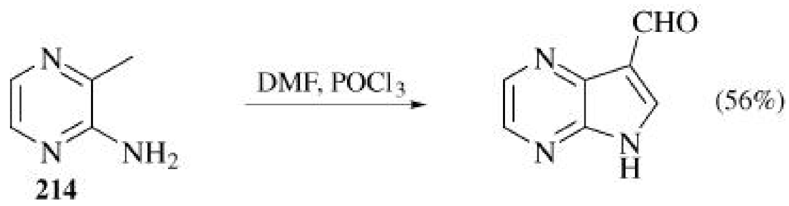
Secondary products are obtained when adjacent active sites or groups are present, such as the tricyclic compound **212**, which is formed when the Vilsmeier reagent from dimethylthioformamide reacts with a dithiolium salt (Eq. 171). (220) Reaction at the pyrimidinyl methyl group in compound **213** results in formation of a pyrrolopyrimidinecarboxaldehyde (Eq. 172), (228) and a similar reaction is seen with pyrazine **214** (Eq. 173). (229) Vilsmeier reaction of tetrahydroisoquinoline **215** gives a mixture of three products, two arising from cyclization (Eq. 174). (230)



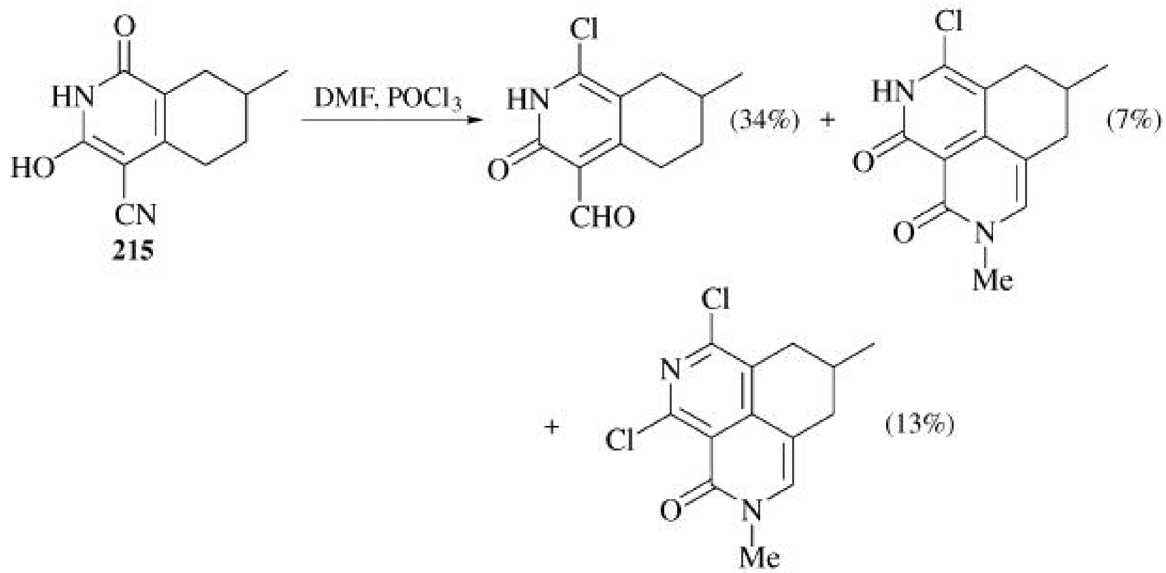
(171)



(172)

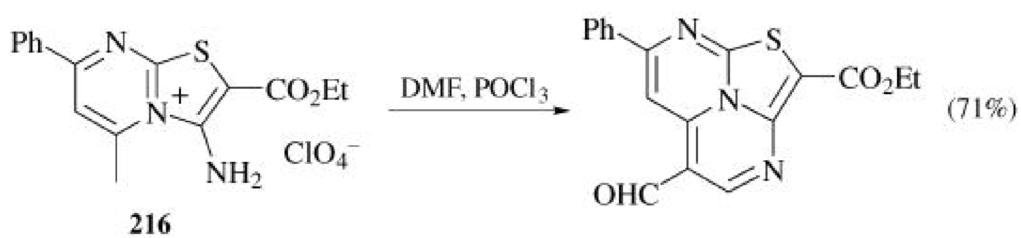


(173)



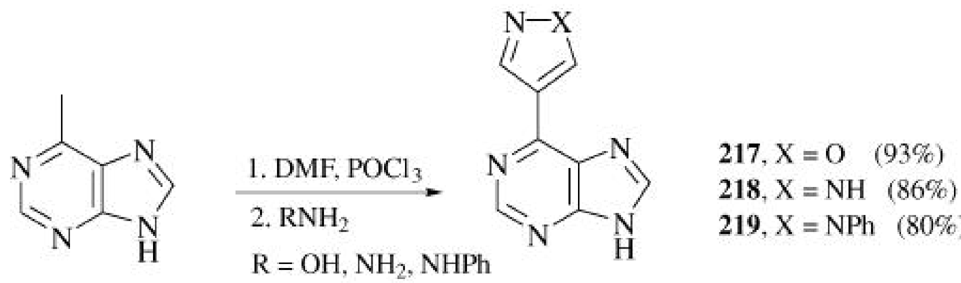
(174)

Cyclization to a more remote amino group is observed in the reaction of salt **216** (Eq. 175). (224) It should be noted that since the primary products are malonaldehyde derivatives, the addition of a suitable reagent can be used to generate a new

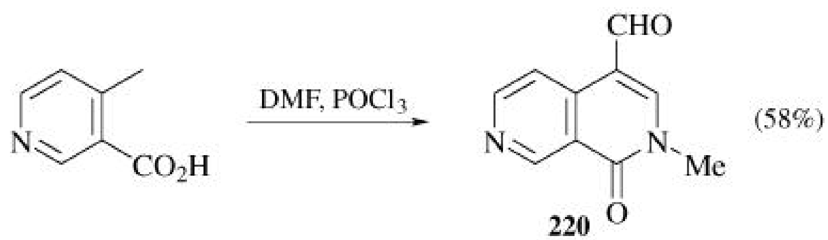


(175)

five-membered aromatic ring as shown by the synthesis of compounds **217** to **219** (Eq. 176). (209) Cyclization to an adjacent carboxy group gives a pyridinone **220** (Eq. 177) (231)


1. DMF, POCl3
2. RNH2
R = OH, NH2, NHPh
217, X = O (93%)
218, X = NH (86%)
219, X = NPh (80%)

(176)


DMF, POCl3
CHO
N
Me
O
CO2H
(58%)

220

(177)

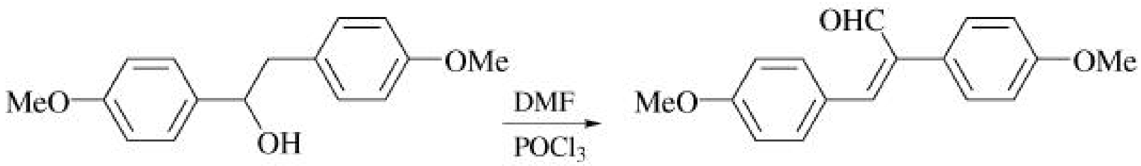
3. Comparison with Other Methods

Because of the wide variation in reaction between the Vilsmeier reagent and these different non-aromatic substrates, ranging from the production of β-chloroenals via malonaldehydes to quinolines and chromans, the usual comparison with other methods cannot be made. Each separate class of product would require its own set of comparisons, and this would tax the patience of authors, editors, and readers.

4. Experimental Conditions

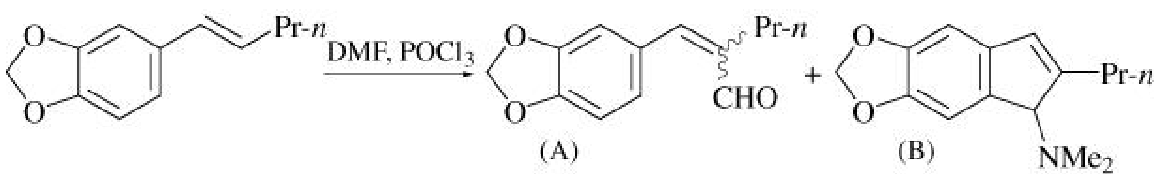
By far the most common experimental procedure for the Vilsmeier reaction involves DMF, usually in excess and acting as the solvent, and $POCl_3$ (**Note**; the formation of the reagent is exothermic and cooling in ice water is necessary). The coreagent is added and the reaction often proceeds at room temperature. In the Tables, the temperature of reaction is specified only when the products vary with variation in the temperature. Solvents (usually chlorinated hydrocarbons) are occasionally used. It is possible to prepare the solid Vilsmeier salt and use this in the reaction, but there is usually no obvious advantage. Acid chlorides other than $POCl_3$ have been used, notably oxalyl chloride and carbonyl chloride (phosgene); the latter seems to offer little advantage, particularly in view of its toxicity. It would be interesting to see more use of pyrophosphoryl chloride (an example is given in *Procedures*), which has been claimed to offer enhanced activity in the formylation of aromatic systems. (1) Bromide can be introduced into Vilsmeier products by using $POBr_3$ although PBr_3 is said to be as efficient. (92) The most commonly used amide after DMF is *N*-methylformanilide, which was used in Vilsmeier's first experiments. The most common workup procedure is with an aqueous base (sodium acetate, sodium or potassium hydroxide), but in many cases better yields are obtained if the intermediate iminium salt is isolated (perchlorate or hexafluorophosphate) and hydrolyzed in a subsequent step.

5. Experimental Procedures



5.1.1. 4-Methoxy- α -(4-Methoxyphenyl)Cinnamaldehyde (Formylation of an Alcohol as a Precursor of an Alkene) (232)

To a solution of deoxydihydroanisoin (2.6 g, 10.1 mmol) in DMF (20 mL) was added $POCl_3$ (9 g, 58.63 mmol) dropwise with stirring and the reaction mixture was heated at 100° for 14 hours. The iminium complex was decomposed with sodium acetate (27 g) in water (70 mL) and the product was extracted with ether (3 × 30 mL). Removal of the solvent afforded the aldehyde (2.65 g, 98%), which was recrystallized from benzene-hexane: mp 120°; IR (Nujol) 2850, 1675 cm^{-1}; UV(EtOH) 233 (log ε = 4.25), 323 (4.27) nm; ^1H NMR ($CDCl_3$) δ 3.73 (s, 3 H), 3.80 (s, 3 H), 6.63–7.23 (m, 9 H), and 9.63 (s, 1 H). Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.0; H, 6.0. Found: C, 75.9; H, 6.2.



5.1.2. α -(n-Propyl)-3,4-Methylenedioxycinnamaldehyde(A) or 1-Dimethylamino-5,6-Methylenedioxy-2-(n-Propyl)indene (B) (Reaction with a Styrene) (11)

a) To a mixture of $POCl_3$ (3.85 g, 0.025 mol) and DMF (7.3 g, 0.061 mol) was added at 20°,α -(*n*-propyl)-3,4-methylenedioxystyrene (4.75 g, 0.03 mol), and the mixture was heated to 55°, maintained at this temperature during the exothermic reaction, and then heated at 75–80° for 1 hour. The reaction mixture was poured into aqueous sodium acetate and heated at 70–75° for 1 hour. The cooled mixture was extracted with ether, the organic extracts were dried, and then concentrated. The cinnamaldehyde (A) was obtained (2.6 g, 48%): bp 115–117° (0.1 mm); Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.55; H, 6.42. Found: C, 71.24; H, 6.35.

b) To a cooled (ice bath), round bottom flask containing DMF (45 g, 0.61 mol) was added dropwise with stirring $POCl_3$ (18.4 g, 0.12 mol). The mixture was stirred in an ice bath for 15–20 minutes and the α -(*n*-propyl)-3,4-methylenedioxystyrene (19.1 g, 0.10 mol) was added dropwise. After the addition, the reaction mixture was immediately heated on a steam bath for 3 hours. The resulting black mixture was poured into 400 mL of ice-H_2O and unreacted olefin was removed by extraction with two 175 mL portions of Et_2O. The aqueous layer was made basic by the addition of 10% aqueous NaOH solution and extracted with three 150 mL portions of Et_2O. The combined ether extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The aminoindene (B) was distilled, bp 125–127.5° (0.25 mm), converted into the stable HCl salt, then recrystallized (19.98 g, 71%): mp (from EtOH-Et_2O) 177–178°; ^{1}H NMR ($CDCl_3$) δ 4.82 (1 H), 6.01 (2 H), 6.61 (1 H), 6.77 (1 H), 7.50 (1 H) among others.

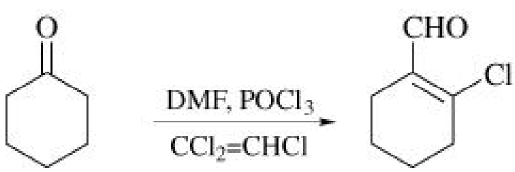
5.1.3. Methyl 3-Amino-2-Thioformylcrotonate (Thioformylation of an Enamine) (30)

A solution of $POCl_3$ (0.5 mL, 5.5 mmol) in DMF (1.5 mL) was added dropwise during 10 minutes to a stirred solution of methyl 3-aminocrotonate (0.575 g, 5 mmol) in THF (10 mL) with the temperature maintained at 0°. The resulting mixture was stirred for a further 1 hour at room temperature and then for 4 hours at 30°; it was then allowed to stand overnight in a refrigerator. Addition of ether in portions at 0° precipitated a highly hygroscopic yellowish white to yellow solid from which ether was removed by decantation. The remaining solid was washed several times with ether until the ether layer became clear. The solid was then dissolved in dichloromethane (250 mL) in a separating funnel (1 L) and to the solution was added aqueous sodium hydrogen sulfide (2 M; 25 mL). The mixture was shaken vigorously, separated, and the water layer extracted with further dichloromethane (30 mL). The combined organic extracts were washed six times with water, dried ($MgSO_4$), and concentrated to give orange crystals. The thioformyl derivative was crystallized from benzene-hexane, mp 110.5–111° (0.66 g, 83%): IR(KBr) 3300, 1643, 1442, 1361, 1279, 1248, and 1030 cm^{-1}; UV (EtOH) 216 (log ε = 4.17), 256 (4.09), and 354.5 nm (4.32); ^{1}H NMR ($CDCl_3$) δ 13.94 and 6.83 (1 H, each br s, NH_2), 10.97 (1 H, s, CHS), 3.79 (3 H, s, OCH_3), and 2.58 (3 H, s, CH_3). Anal. Calcd.

for $C_6H_9NO_2S$: C, 45.3; H, 5.7; N, 8.8; S, 20.1. Found: C, 45.5; H, 5.9; N, 8.9; S, 20.0.

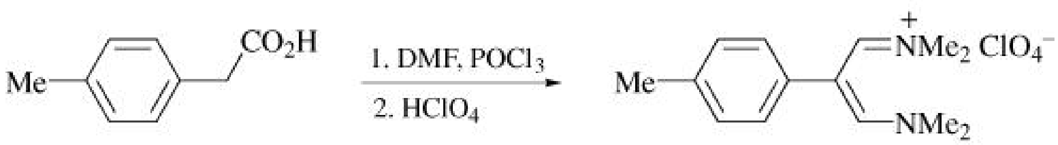
5.1.4. 2,4-Diphenyl-3-Formyl-4H-Chromene (Formylation of an Unsaturated Ether) (233)

To a solution of 2,4-diphenyl-4*H*-chromene (2.84 g, 0.01 mol) in 10 mL of anhydrous DMF was added $POCl_3$ (1.1 mL). The mixture was kept on a boiling water bath for 3 hours and then added to 150 mL of a 5% aqueous solution of sodium hydroxide. The separated reaction product was extracted with ether. The organic layer was dried with sodium sulfate, and the solvent was distilled on a water bath. The residue was crystallized from propyl alcohol (10 mL) to give the title product, mp 144–145° (2.93 g, 94%). IR (Nujol) 1665, 1620, 1600, 1590, 1220 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.10 (s, 1 H), 6.82–7.73 (m, 14 H), 9.48 (s, 1 H). Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.78; H, 5.26.



5.1.5. 2-Chlorocyclohex-1-ene-1-Carboxaldehyde (Formylation of a Cyclic Ketone)

A detailed procedure for this reaction is described in *Organic Syntheses*. (113) The yield of the chlorocyclohexenecarboxaldehyde was 53–74%.

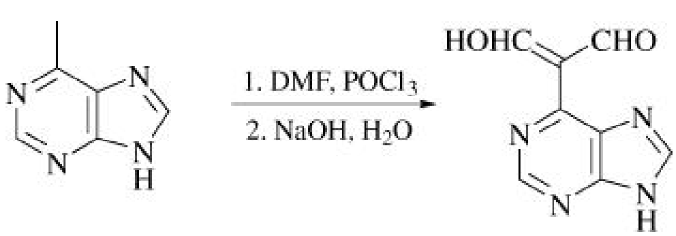


5.1.6. 3-Dimethylamino-2-(4-Methylphenyl)prop-2-En-1-Dimethyliminium Perchlorate (Diformylation of 4-Methylphenylacetic Acid; Isolation as Dimethyliminium Perchlorate) (234)

$POCl_3$ (27 mL, 0.3 mol) was dropped slowly into DMF (36.5 g, 0.5 mol) with cooling and stirring. The solution was cooled to –10° and 4-methylphenylacetic acid (15 g, 0.1 mol) was added in small portions. The syrupy slurry was stirred for 1 hour at room temperature, and then 2 hours at 60° and finally 5 hours at 80°. After removing excess solvent under vacuum on a water bath, the dark brown syrup was decomposed cautiously with cooling in a beaker with water (20 mL), cooled to –10°, and 30 mL of 70% perchloric acid and 400 mL of ether were added. After cooling in solid CO_2 the precipitate was quickly collected by filtration and washed with ether. The iminium perchlorate was crystallized from methanol/ether, mp 164° (28.8 g, 91%).

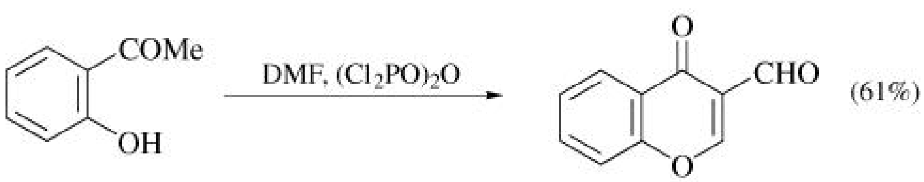
5.1.7. 2-Chloro-7-Methoxyquinoline-3-Carboxaldehyde (Formylation of an Amide with Cyclization to a Quinoline) (166)

DMF (9.13 g, 9.6 mL, 0.125 mol) was cooled to 0° in a flask fitted with a drying tube and $POCl_3$ (53.7 g, 32.2 mL, 0.35 mol) was added dropwise with stirring. To this solution was added 3-methoxyacetanilide (8.25 g, 0.05 mol) and after 5 minutes the solution was heated under reflux for 4 hours. The reaction mixture was poured into ice-water (300 mL) and stirred for 30 minutes at 0–10°. The aldehyde was filtered off, washed well with water, and recrystallized from ethyl acetate, mp 197–198° (9.85 g, 89%). Anal. Calcd. for $C_{11}H_8ClNO_2$: C, 59.6; H, 3.6; N, 6.3. Found: C, 59.9; H, 3.6; N, 6.2.



5.1.8. 2-(6-Purinyl)Malonaldehyde (Diformylation of a Reactive Methyl Group) (209)

DMF (30 mL) was cooled to 0° and $POCl_3$ (50 mL) was slowly added with stirring. 6-Methylpurine (13.4 g, 0.1 mol) was added slowly at 5° with stirring to this previously prepared reagent. The mixture was maintained at 5° for 15 minutes with continuous stirring, then at 25° (1 hour). The mixture was then heated slowly to 120° (oil bath) and kept at this temperature for 1 hour. The thick syrup that resulted was cooled to 60° and poured onto crushed ice with vigorous stirring. Solid sodium carbonate was added to adjust the pH to 3 and the volume brought up to 500 mL by addition of cold water. This solution (50 mL, equivalent to 0.01 mol of 6-methylpurine) was cooled to 5° and sodium hydroxide (2 g) was added slowly with stirring. Charcoal was added, the solution was filtered, and the filtrate was acidified with glacial acetic acid to pH 5. The crystalline precipitate was collected, washed with water, and dried, to yield the title product as thin needles (1.55 g, 82%), mp 330° (dec.). The malonaldehyde could be further purified by repeated treatment with alkali followed by glacial acetic acid precipitation, mp 330° (dec.). IR 1667 cm^{-1}; ^1H NMR (CF_3CO_2H) δ 9.7 (s, 2 H), 9.48 (s, 1 H), 9.25 (s, 1 H). Anal. Calcd. for $C_8H_6N_4O_2$: C, 50.5; H, 3.2; N, 29.5. Found: C, 50.4; H, 3.3; N, 29.3.



5.1.9. 4-Oxo-4H-1-Benzopyran-3-Carboxaldehyde (Use of Pyrophosphoryl Chloride) (101)

To a stirred solution of *o*-hydroxyacetophenone (25 g, 0.184 mol) in 80 mL of DMF, 80 mL of $(Cl_2PO)_2O$ was added dropwise at –20° during about 10 minutes. The mixture was stirred at room temperature for 13 hours, and decomposed by ice-water. The resulting precipitate was collected by filtration, washed with H_2O and then EtOH, and recrystallized from acetone to afford the benzopyrancarboxaldehyde (19.6 g, 61%) as colorless crystals, mp 152–153° (lit. 152°). From the ethanol washings a small amount (430 mg) of *trans*-1-(2-hydroxybenzoyl)-2-(4-oxo-4*H*-1-benzopyran-3-yl)ethylene, mp 177–179° (from acetone) was isolated.

5.1.10. 2-Bromocyclohex-1-Ene-1-Carboxaldehyde (Use of PBr_3 to Produce a 2-Bromoenal) (92)

A solution of DMF (10.97 g, 0.15 mol) in anhydrous $CHCl_3$ (40 mL) was cooled with ice and stirred while distilled PBr_3 (34.0 g, 0.125 mol) was added dropwise. After a while the white crystalline adduct precipitated. Then a solution of cyclohexanone (4.2 g, 0.05 mol) in $CHCl_3$ (20 mL) was added to the reaction mixture with stirring. The mixture was stirred at 20° (12 hours), then the $CHCl_3$ was evaporated in vacuo and the oily residue was decomposed with ice (ca 100 g) taking care that the mixture did not warm up excessively. The cold mixture was then neutralized with solid sodium hydrogen carbonate and left standing to reach room temperature. The product was then extracted with ether, the extract washed well with water and with a saturated solution of K_2CO_3 to a negative reaction with $FeCl_3$, and dried over anhydrous $MgSO_4$. Ether was removed by distillation through a Widmer column (30 cm in length), and the product was isolated by vacuum distillation b.p. 51°/0.7 mm, (4.73 g, 54%): IR (CCl_4) 3343, 2740, 1683, 1620, 1386 cm^{-1}; UV (cyclohexane) 262 nm (log ε = 4.023); UV (EtOH) 260 nm (log ε = 3.961).

6. Tabular Survey

We have attempted to cover thoroughly the literature until the end of 1998. Only carbon-carbon bond formation reactions are included in the Tables. Where a reaction has been reported by different workers, the yield in the Table corresponds to that reported in the first reference.

Some oximes appear in Table XV when they clearly undergo Beckmann rearrangement prior to formylation; non-rearranged oximes appear in Table XII.

Table XVIII has been subdivided according to the number of component rings, with monocyclic systems first (XVIIIA), and polycyclic systems second (XVIIIB). Within each ring classification, rings are arranged by size, and within each group by the increasing number of component carbon atoms.

Compounds with multiple functionality, for example ketoesters, are listed in only one Table. Such compounds are assigned to the Table which best appears to reflect their chemistry, but readers are advised to search both Tables in such cases.

List of Abbreviations

DMF	*N,N*-dimethylformamide
MFA	*N*-methylformanilide
DMA	*N,N*-dimethylacetamide
TMS	trimethylsilyl
Ts	tosyl; *p*-toluenesulfonyl

Table I. Alkenes

View PDF

Table II. Dienes, Trienes and Tetraenes with Carbon Substituents

View PDF

Table III. Alkenes with Nitrogen Substituents

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Table IV. Dienes, Trienes and Tetraenes with Nitrogen Substituents

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Table V. Alkenes with Oxygen Substituents

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Table VI. Dienes with Oxygen Substituents

View PDF

Table VII. Alkenes, Dienes and Trienes with Sulfur Substituents

View PDF

Table VIII. Acetals, Ketals and Their Thio Analogs

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Table IX. Alkynes

View PDF

Table X. Aldehydes

View PDF

Table XI. Ketones

View PDF

Table XII. Imines, Hydrazones, Semicarbazones, and Oximes

View PDF

Table XIII. Carboxylic Acids, Anhydrides, and Acid Chlorides

View PDF

Table XIV. Esters and Lactones

View PDF

Table XV. Amides and Lactams

View PDF

Table XVI. Imides

View PDF

Table XVII. Nitriles

View PDF

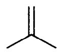
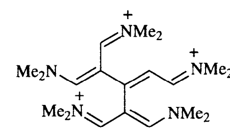
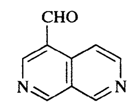
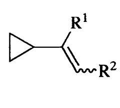
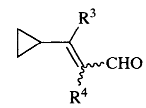
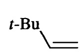
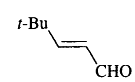
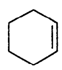
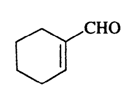
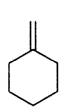
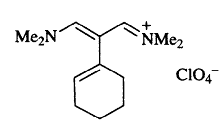
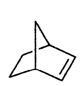
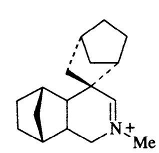
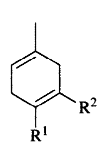
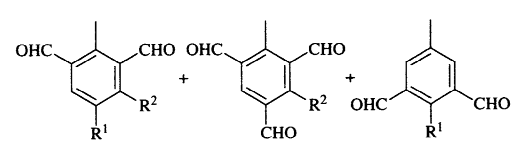
Table XVIIIA. Methyl and Methylene Groups Activated by a Fully Conjugated Monocyclic Ring

View PDF

Table XVIIIB. Methyl and Methylene Groups Activated by a Fully Conjugated Polycyclic Ring

View PDF

TABLE I. ALKENES

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	1. DMF, $(COCl)_2$ 2. $NaClO_4$	 $3ClO_4^-$ (73)	235, 6
	1. DMF, $COCl_2$ 2. $NaClO_4$ 3. NH_4Cl	 (49)	235
C_5-C_{11}			
	DMF, $POCl_3$	 (see table below)	8
C_6			
	*N*-Formylmorpholine, $POCl_3$	 (80)	236
	*N*-formylmorpholine, $POCl_3$	 (35)	236
C_7			
	1. DMF, $(COCl)_2$ 2. $NaClO_4$	 ClO_4^- (17)	5
	1. DMF, $POCl_3$ 2. $HClO_4$	 ClO_4^- (85)	236
C_7-C_{10}			
	DMF, $POCl_3$	 I + II + III (see table below)	237

R^1	R^2	R^3	R^4	
H	H	H	H	(65)
Me	H	Me	H	(75)
Me	Me	Me	Me	(75)
Et	H	Me	Me	and
Et	H	Et	H	(81)
c-C_3H_5	H	c-C_3H_5	H	(80)
c-C_3H_5	Me	c-C_3H_5	Me	(82)
Me	c-C_3H_5	Me	c-C_3H_5	(25)
Me	*i*-Pr	*i*-Bu	H	(70)
c-C_3H_5	c-C_3H_5	c-C_3H_5	c-C_3H_5	(30)
Me	*t*-Bu	CH_2Bu-*t*	H	(71)
Ph	H	Ph	H	(92)

R^1	R^2	I	II	III
H	H	(3)	(9)	(0)
H	Me	(0)	(9)	(0)
Me	H	(10)	(0)	(0)
Et	H	(6)	(0)	(3)
i-Pr	H	(10)	(0)	(0)

TABLE I. ALKENES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
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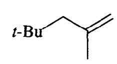
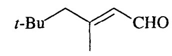
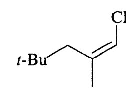
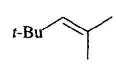
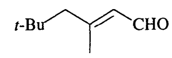
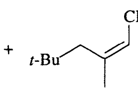
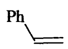
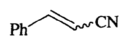
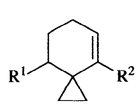
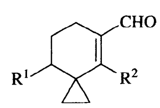
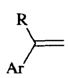
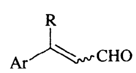
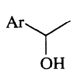
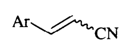
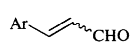
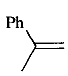
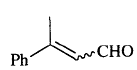
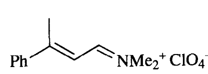
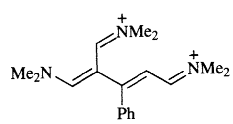
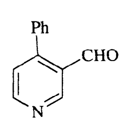
	*N*-formylmorpholine, $POCl_3$	 (57) +  (28)	236
	*N*-formylmorpholine, $POCl_3$	 (57) +  (28)	236
	DMF, $POCl_3$	 (38-42)	238, 11
	DMF, BCl_3	" (70)	239
	DMF, $Ph_3P{\cdot}Br_2$	" (42)	76
	MFA, $POCl_3$	" (48)	240, 241
	1. DMF, $POCl_3$ 2. NH_2OH	 (42)	242
C_8-C_9			
	DMF, $POCl_3$	 R^1 / R^2 H / H (15) Me / H (—) H / Me (85)	8
	MFA, $POCl_3$	 Ar / R Ph / Cl (39) 4-BrC_6H_4 / Cl (41) 4-$MeOC_6H_4$ / Cl (67) 4-MeC_6H_4 / H (46) 4-$MeOC_6H_4$ / H (70)	243 243 243 238 241, 244
	1. DMF, $POCl_3$ 2. H_2NOH	 Ar Ph (30) 4-MeC_6H_4 (45) 4-$MeOC_6H_4$ (46)	242
	1. DMF, $POCl_3$ 2. $HClO_4$	 ClO_4^- Ar Ph (52) 4-$MeOC_6H_4$ (76) 4-$MeSC_6H_4$ (60)	15
	DMF, $POCl_3$	 Ar 4-$MeOC_6H_4$ (93)	14
C_9			
	DMF, $POCl_3$	 (74)	245, 238
	1. DMF, $COCl_2$ 2. $NaClO_4$ 3. Hydrolysis	" (75)	235, 6
	1. DMF, $COCl_2$ 2. ClO_4^-	 (—)	6
	1. DMF, $(COCl)_2$ 2. $NaClO_4$	 $2ClO_4^-$ (98)	235, 6
	1. DMF, $COCl_2$ 2. $NaClO_4$ 3. NH_4Cl	 (—)	6, 235

TABLE I. ALKENES (*Continued*)

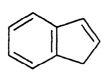
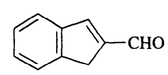
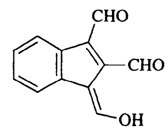
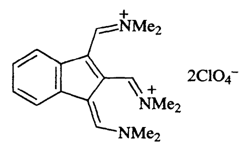
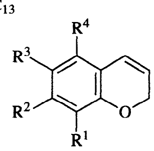
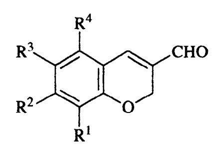
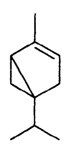
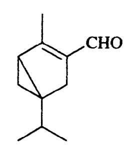
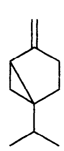
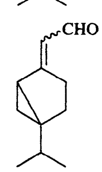
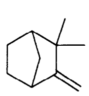
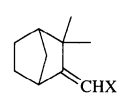
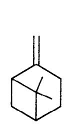
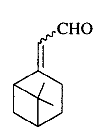
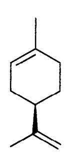
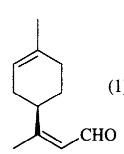
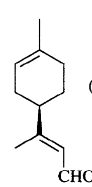
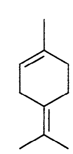
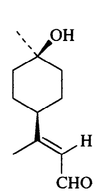
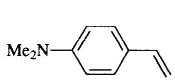
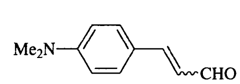
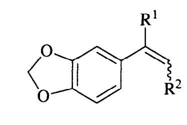
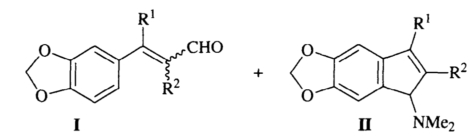
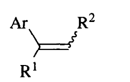
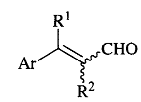
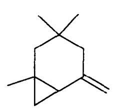
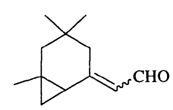
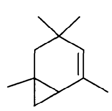
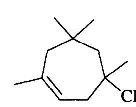
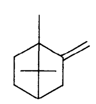
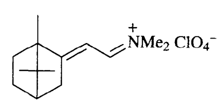
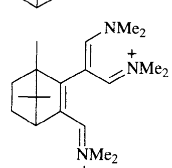
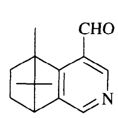
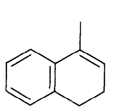
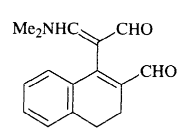
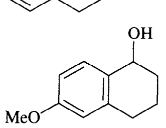
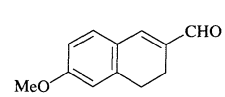
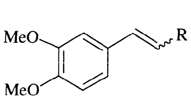
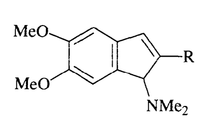
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[Me_2N{=}CHCl]^+Cl^-$ (1 eq), rt	 (20)	36
	$[Me_2N{=}CHCl]^+Cl^-$ (3 eq), 90°	 (55)	36
	1. $[Me_2N{=}CHCl]^+Cl^-$ (5 eq), 80° 2. $HClO_4$	 $2ClO_4^-$ (66)	36
C_9-C_{13}			
	DMF, $POCl_3$	 R[1] R[2] R[3] R[4]: H H H H (41); H H Me H (58); H H benzo (82); benzo H H (62)	246
C_{10}			
	DMF, $POCl_3$	 (30)	8
	DMF, $POCl_3$	 (70)	8
	1. DMF, $POCl_3$ 2. $NaClO_4$	 I (69) $X = CH{=}NMe_2^+ ClO_4^-$	5,7
	DMF, $POCl_3$	I (56-74) X = CHO	20, 5, 7
	DMF, $POCl_3$	 (41)	7
	1. DMF, $POCl_3$ (1 eq) 2. NaOH, H_2O	 (1) +  (40) +  (37)	247
	1. DMF, $POCl_3$ (10 eq) 2. NaOH, H_2O	 (35)	247
	MFA, $POCl_3$	 (—)	241

TABLE I. ALKENES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}-C_{12}			
	DMF, $POCl_3$	 I + II	

Conditions	R^1	R^2	Temp	I	II	Refs.
DMF, $POCl_3$	H	Me	—	(27)	(0)	238
	H	Me	100°	(23)	(47)	11
	H	Me	75-80°	(48)	(0)	11
	Me	H	—	(70)	(0)	245
	H	*n*-Pr	100°	(0)	(71)	11
	H	*n*-Pr	75-80°	(48)	(0)	11
MFA, $POCl_3$	Me	H	—	(46)	(0)	245

Substrate	Conditions	Product	Ar	R^1	R^2	Yield	Refs.
	DMF, $POCl_3$		4-MeC_6H_4	Me	H	(62)	238
			4-$MeOC_6H_4$	H	Me	(54-68)	238
			4-$MeOC_6H_4$	Me	H	(62)	245
			4-*i*-PrC_6H_4	Me	H	(34)	238

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMF, $POCl_3$	 (81)	8
	DMF, $POCl_3$	 (100)	8
	1. DMF, $(COCl)_2$ 2. $NaClO_4$	 (45)	5
	1. DMF, $POCl_3$ 2. $NaClO_4$	 $2ClO_4^-$ (30)	5
	1. DMF, $POCl_3$ 2. NH_4Cl	 (—)	5
	DMF, $POCl_3$	 (18)	123
	—	 (—)	248
C_{11}-C_{14}			
	DMF, $POCl_3$, 100°		11

R	Yield
Me	(45)
Et	(62)
n-Pr	(66)
n-Bu	(62)

TABLE I. ALKENES (*Continued*)

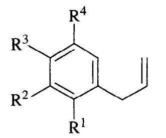
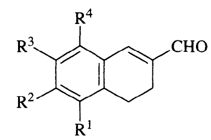
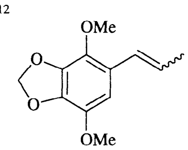
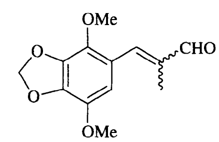
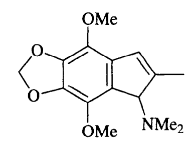
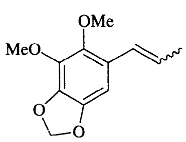
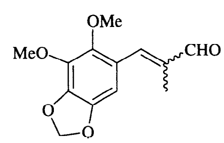
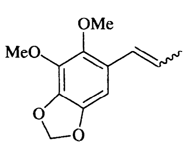
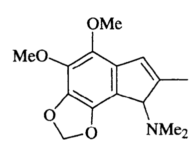
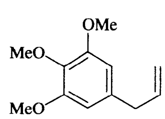
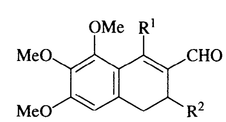
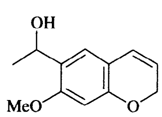
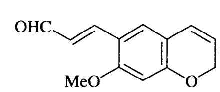
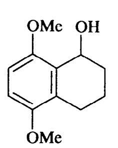
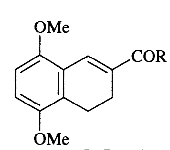
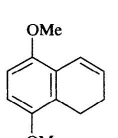
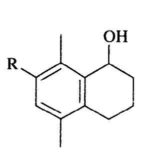
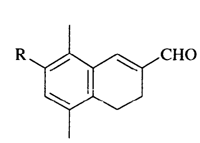
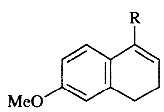
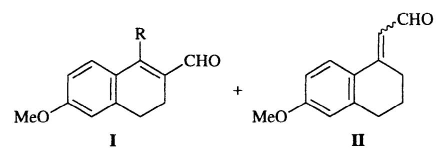
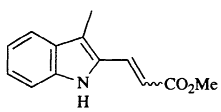
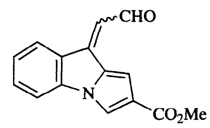
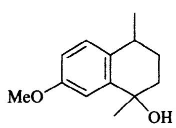
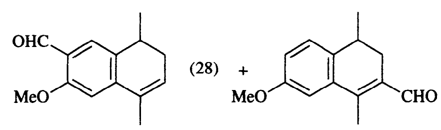
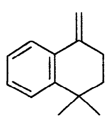
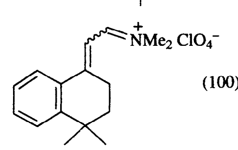
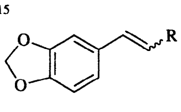
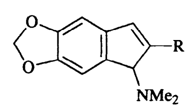
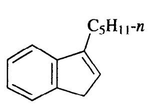
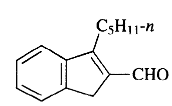
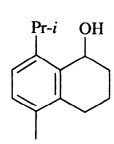
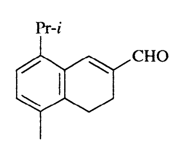
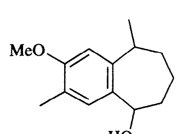
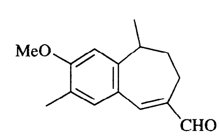
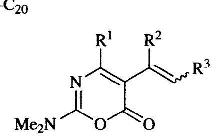
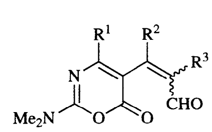
Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
	MFA, $POCl_3$		R^1	R^2	R^3	R^4	
			H	—OCH_2O—		OMe (33)	249
			—OCH_2O—		—OCH_2O—	(52)	249
			OMe	—OCH_2O—		OMe (55)	249
			H	OMe	OMe	OMe (58)	249, 250
			OMe	OMe	—OCH_2O—	(37)	249
			—OCH_2O—		OMe	OMe (49)	249
			OEt	OEt	—OCH_2O—	(32)	249
C_{12}							
	DMF, $POCl_3$, <50°	 (56)					249
	DMF, $POCl_3$, 100°	 (29)					249
	DMF, $POCl_3$, <50°	 (46)					249
	DMF, $POCl_3$, 100°	 (10)					249
	Reagent, $POCl_3$	 (—) Reagent / R^1 / R^2: PhN(Me)CDO, D, H; PhN(CD_3)CHO, H, D					250
	DMF, $POCl_3$	 (64)					251
	—	 **I**, R = H (92-95)					252, 253
	DMF, $POCl_3$	**I**, R = H (90)					253a
	Ph_2NCOMe, $POCl_3$, $CHCl_3$, boil	**I**, R = Me (10)					254
C_{12}-C_{13}							
	DMF, $POCl_3$	 R: H (68)					255
		R: OMe (60)					256

TABLE I. ALKENES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}-C_{18}			
	DMF, $POCl_3$		
		R / I / II: Me (57) (2)	257
		n-Bu (100) (0)	258
		4-$MeOC_6H_4$ (99-100) (0)	258, 259
C_{13}			
	DMF, $POCl_3$	 (67)	260
	DMF, $POCl_3$	 (28) + (28)	261
	1. DMF, $POCl_3$ 2. ClO_4^-	 (100)	6
C_{13}-C_{15}			
	DMF, $POCl_3$, 100°	 R: *n*-Bu (70); Ph (25)	11
C_{14}			
	DMF, $POCl_3$	 (36)	258
	DMF, $POCl_3$	 (—)	226
	DMF, $POCl_3$	 (73)	12
C_{14}-C_{20}			
	DMF, $POCl_3$		262

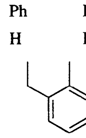
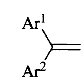
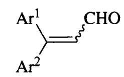
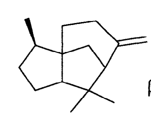
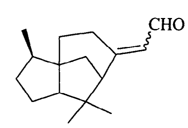
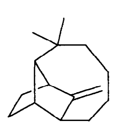
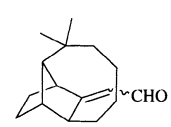
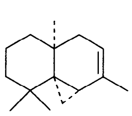
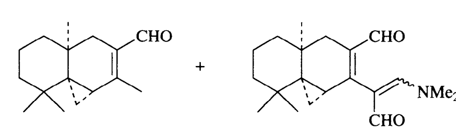
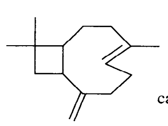
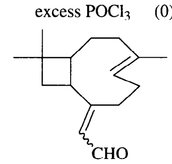
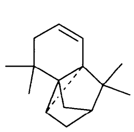
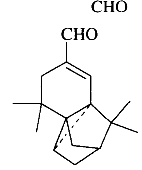
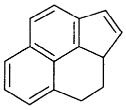
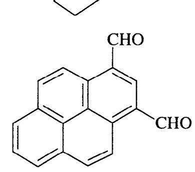
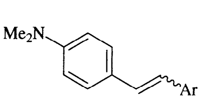
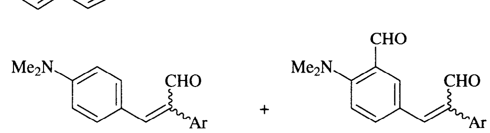
R^1	R^2	R^3	Yield
n-Pr	—$(CH_2)_3$—		(50)
Ph	Me	H	*E* (18) + *Z* (27)
Ph	—$(CH_2)_3$—		(69)
Ph	—$(CH_2)_4$—		(25)
Ph	Ph	H	*E* (23) + *Z* (67)
Ph	H	Ph (*E*)	*E* (40)
Me			(80)

TABLE I. ALKENES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
C_{14}-C_{22}						
	MFA, $POCl_3$		Ar^1	Ar^2		
			4-ClC_6H_4	4-ClC_6H_4	(—)	241
			4-HOC_6H_4	4-HOC_6H_4	(—)	241
			Ph	Ph	(50-60)	263, 240, 241
	DMF, $POCl_3$		Ph	Ph	(70)	11
	DMF, $Ph_3P\cdot Br_2$		Ph	Ph	(61)	76
	MFA, $POCl_3$		Ph	4-$MeOC_6H_4$	(90)	263
			Ph	4-$Me_2NC_6H_4$	(—)	240, 263
			4-$MeOC_6H_4$	4-$MeOC_6H_4$	(90)	263
			4-$Me_2NC_6H_4$	4-$Me_2NC_6H_4$	(—)	240, 263, 241
			4-$Et_2NC_6H_4$	4-$Et_2NC_6H_4$	(—)	241
C_{15}						
 β-cedrene	DMF, $POCl_3$	 (—)				7
 longifolene	DMF, $POCl_3$	 (31)				7
	DMF, $POCl_3$	 I + II				264
			I	II		
			(80)	(0)		
	excess $POCl_3$		(0)	(76)		
 caryophyllene	DMF, $POCl_3$	 (34)				7
	DMF, $POCl_3$	 (90)				8
	DMF, $POCl_3$	 (57)				265
C_{16}						
	DMF, $POCl_3$, additional conditions (See table)	 I + II				9, 10

Ar	Add. Cond.	I	II
Ph	—	(33)	(0)
Ph	pyridine, 60°	(40)	(35)
4-$O_2NC_6H_4$	$POCl_3$ (2 eq)	(25)	(0)

TABLE I. ALKENES (*Continued*)

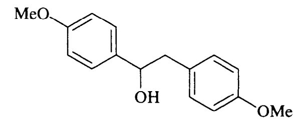
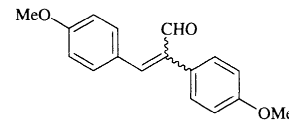
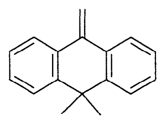
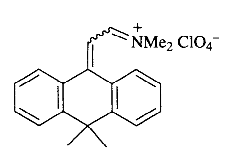
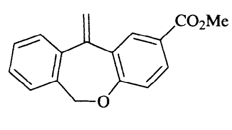
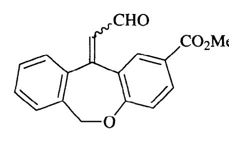
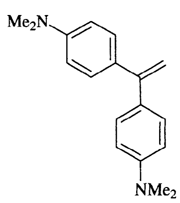
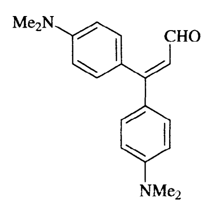
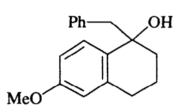
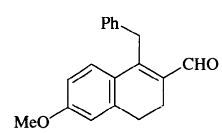
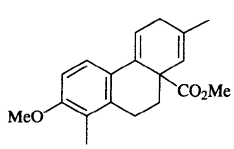
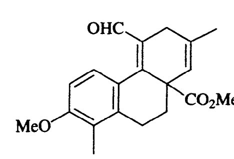
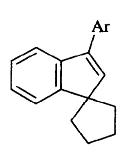
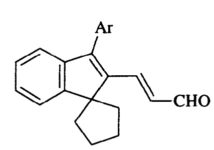
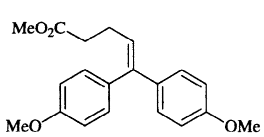
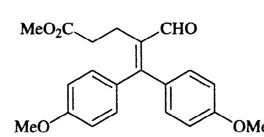
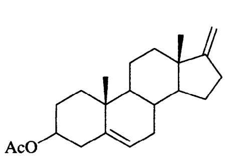
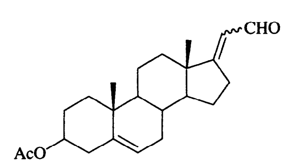
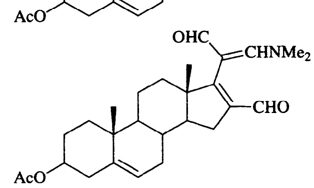
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (98)	232
C_{17}			
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (74)	6, 235
	MFA, $POCl_3$	 (86)	267
C_{18}			
	MFA, $POCl_3$	 (—)	268
	DMF, $POCl_3$	 (81)	259
C_{19}			
	DMF, $POCl_3$	 (94)	269
 Ar = 4-FC_6H_4	Ph(Me)NCH=CHCHO, $POCl_3$	 (97)	270
C_{20}			
	—	 (80)	271
C_{22}			
	DMF, $POCl_3$, 24 h	 (40)	272
	DMF, $POCl_3$, 15 d	 (50)	272

TABLE I. ALKENES (*Continued*)

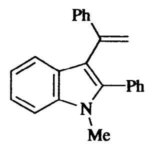
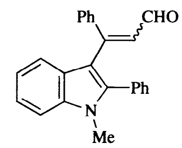
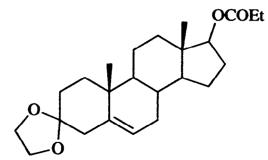
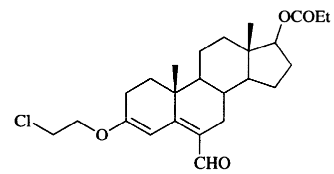
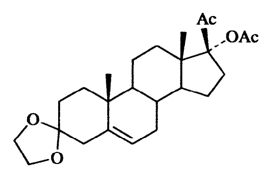
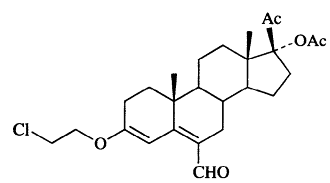
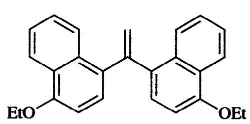
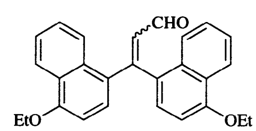
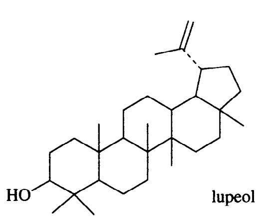
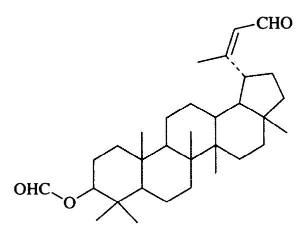
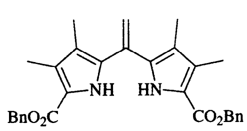
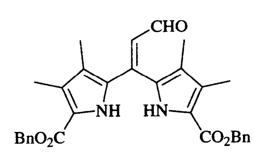
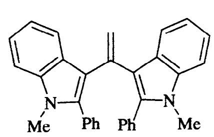
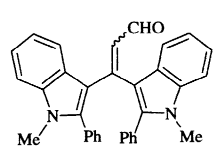
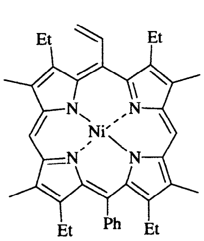
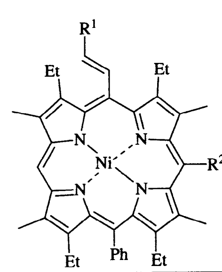
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{23} 	MFA, $POCl_3$	 (—)	241
C_{24} 	DMF, $POCl_3$	 (80)	273
C_{25} 	DMF, $POCl_3$	 (30)	273
C_{26} 	MFA, $POCl_3$	 (—)	241
C_{30}  lupeol	DMF, $POCl_3$	 (42)	274
	DMF, $POCl_3$, 50°	 (90)	275
C_{32} 	MFA, $POCl_3$	 (—)	241
C_{40} 	DMF, $POCl_3$	 R^1 / R^2: CHO / H (41) H / CHO (15) CHO / CHO (33)	276

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS

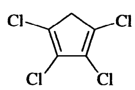
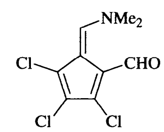
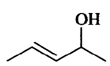
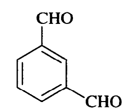
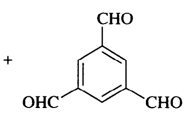
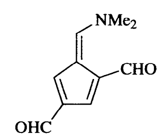
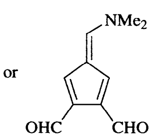
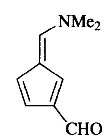
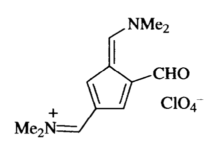
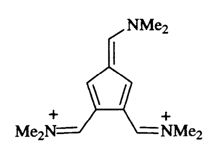
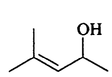
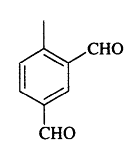
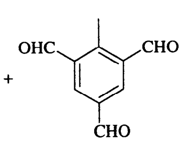
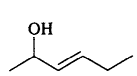
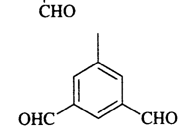
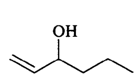
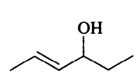
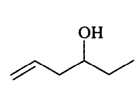
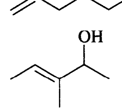
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	1. DMF, $POCl_3$ 2. NaOH (aq)	 (33)	277
	DMF, $POCl_3$	 (26) +  (6)	278
	DMF, $COCl_2$	 or  (60) I	18
	DMF, $POCl_3$	I (40)	279
	DMF, $POCl_3$, rt	I (90)	280
	DMF, $POCl_3$, −10°	 (—)	280
	1. DMF, $COCl_2$ 2. $NaClO_4$	 (82)	18
	1. DMF, $POCl_3$ 2. $HClO_4$	 $2ClO_4^-$ (69)	281, 282
	1. DMF, $POCl_3$ 2. $HClO_4$ 3. NaOH (aq)	I (90)	282
C_6			
	DMF, $POCl_3$	 (24) +  (6)	283
	DMF, $POCl_3$	 (25)	13
	DMF, $POCl_3$	" (24)	13
	DMF, $POCl_3$	" (28)	13
	DMF, $POCl_3$	" (22)	13
	DMF, $POCl_3$	" (35)	13

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS (*Continued*)

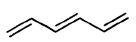
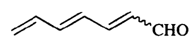
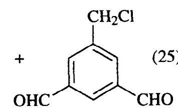
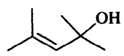
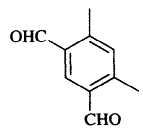
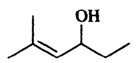
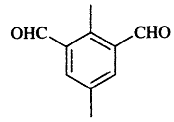
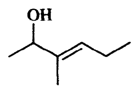
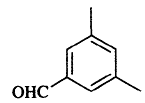
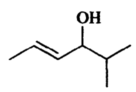
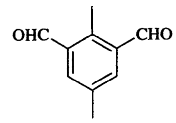
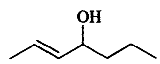
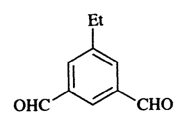
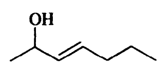
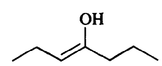
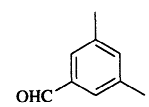
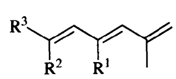
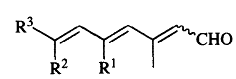
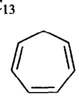
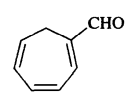
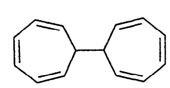
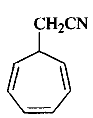
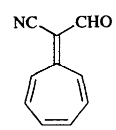
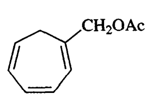
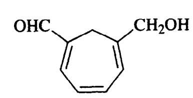
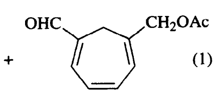
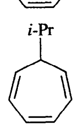
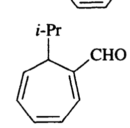
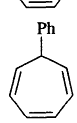
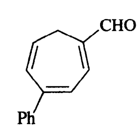
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	—	 (25) +  (25)	21
C_7			
	DMF, $POCl_3$	 (12)	278
	DMF, $POCl_3$	 (20-22)	278
	DMF, $POCl_3$	 (14-18)	278
	DMF, $POCl_3$	 (20-22)	278
	DMF, $POCl_3$	 (15-18)	278
	DMF, $POCl_3$	" (15-18)	278
	DMF, $POCl_3$	 (14-18)	278
C_7-C_9			
	—	 R¹ R² R³: H H H (65); Me H H (70); H Me Me (80)*; * *Z,Z* + *Z,E*	21
C_7-C_{13}			
	DMF, $POCl_3$	 (18-30) +  (1-2.5)	23
	DMF, $POCl_3$	 (16)	23
	DMF, $POCl_3$	 (1.5) +  (1)	23
	DMF, $POCl_3$	 (4)	23
	DMF, $POCl_3$	 (40)	23

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS (*Continued*)

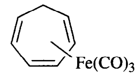
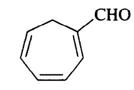
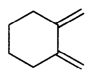
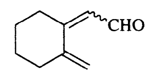
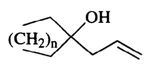
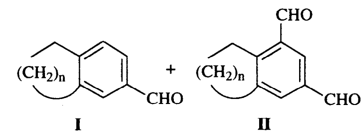
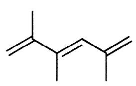
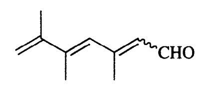
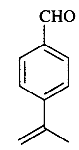
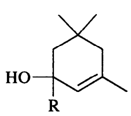
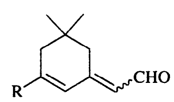
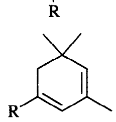
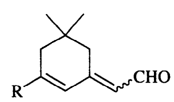
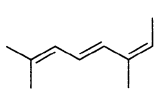
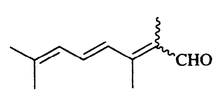
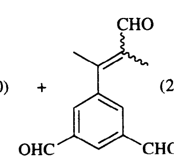
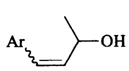
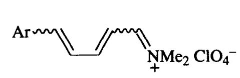
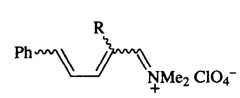
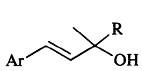
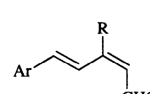
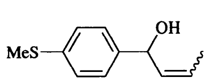
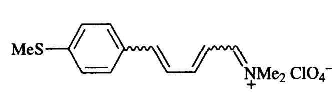
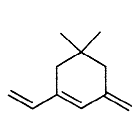
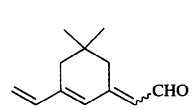
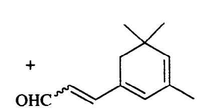
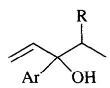
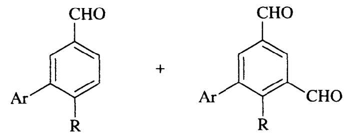
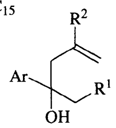
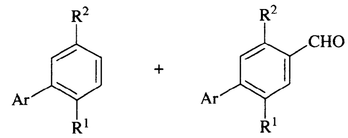
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (70)	24
C_8			
	DMF, $POCl_3$	 (20)	7
C_8-C_{10}			
	DMF, $POCl_3$	 n / I / II: 2 (—) (23); 3 (11) (25); 4 (13) (22)	284
C_9			
	—	 (67) +  (—)	21
C_9-C_{10}			
	1. Al_2O_3, 300° 2. DMF, $POCl_3$	 R: H (75); Me (85)	285
	DMF, $POCl_3$	 R: H (75); Me (85)	8
C_{10}			
	—	 (30) +  (20)	21
C_{10}-C_{11}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 Ar: Ph (35); 4-$MeOC_6H_4$ (62)	15
	1. DMF, $POCl_3$ 2. $HClO_4$	 R: H (92); Me (91)	16
C_{10}-C_{12}			
	DMF, $POCl_3$	 Ar / R: 4-ClC_6H_4 H (68); 4-$MeOC_6H_4$ H (79); 4-ClC_6H_4 Me (92); 4-MeC_6H_4 Me (94); 4-$MeOC_6H_4$ Me (94)	14
C_{11}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 (70)	15
 and isomers	—	 (53) +  (30)	21

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}-C_{13} 	DMF, $POCl_3$	 I + II	286

Ar	R	I	II
Ph	H	(30)	(35)
4-MeC_6H_4	H	(40)	(30)
4-MeC_6H_4	Me	(8)	(55)
4-MeOC_6H_4	Me	(10)	(58)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}-C_{15} 	DMF, $POCl_3$	 I + II	287

Ar	R^1	R^2	I	II
Ph	H	H	(42)	(—)
4-MeC_6H_4	H	H	(51)	(—)
4-MeOC_6H_4	H	H	(55)	(—)
Ph	H	Me	(80)	(—)
4-MeC_6H_4	H	Me	(98)	(—)
4-MeOC_6H_4	H	Me	(97)	(—)
4-EtOC_6H_4	H	H	(52)	(—)
2,5-(MeO)MeC_6H_3	H	H	(30)	(—)
Ph	Me	Me	(30)	(25)
2-MeO-5-MeC_6H_3	H	Me	(85)	(—)
4-MeC_6H_4	Me	Me	(35)	(20)
2-naphthyl	H	H	(40)	(—)

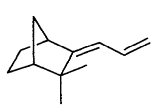
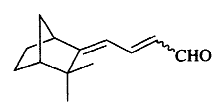
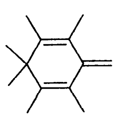
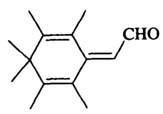
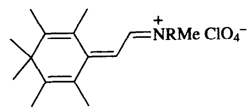
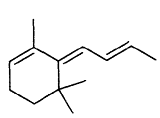
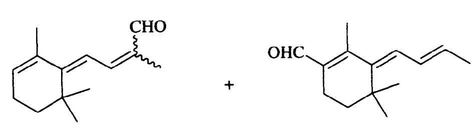
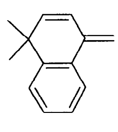
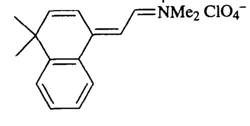
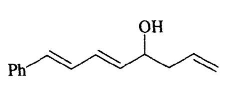
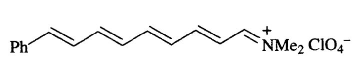
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	—	 (85)	20
C_{13} 	1. DMF, $POCl_3$ 2. $NaClO_4$ 3. NaOH	 (82)	235
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (92) I R = Me	235
	1. MFA, $POCl_3$ 2. $NaClO_4$	I, R = Ph (—)	235
	MFA, $POCl_3$	 (E = 20; Z = 20) + (40)	25
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (94)	235
C_{14} 	1. DMF, $POCl_3$ 2. $HClO_4$	 (45)	15

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS (*Continued*)

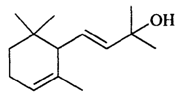
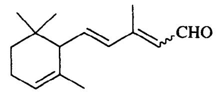
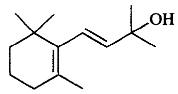
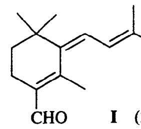
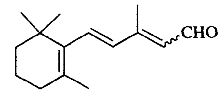
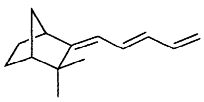
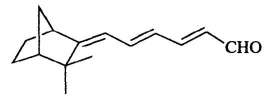
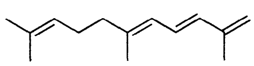
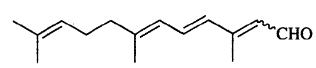
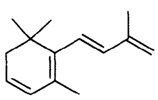
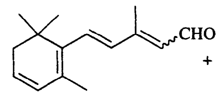
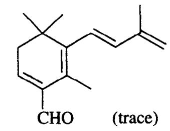
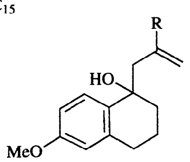
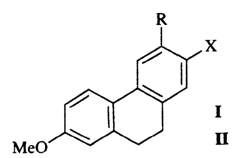
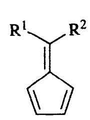
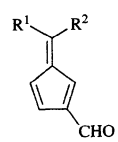
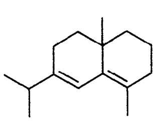
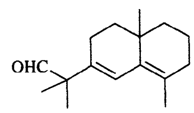
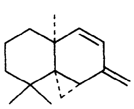
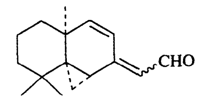
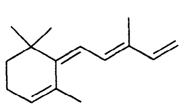
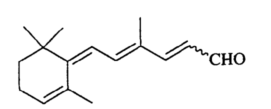
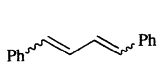
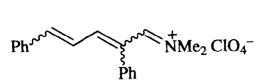
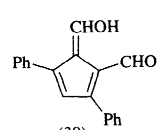
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (92)	19
	DMF, $POCl_3$, 28°	 I (21) +  (39)	19
	DMF, $POCl_3$, 100°	I (66)	19
	—	 (86)	20
	MFA, $POCl_3$	 (16)	25
	MFA, $POCl_3$	 (33) +  (trace)	25
C_{14}-C_{15}			
	DMF, $POCl_3$	 I X = H; II X = CHO R: H, I (43), II (15) R: Me, I (80), II (—)	287
C_{14}-C_{18}			
	DMF, $POCl_3$	 R^1 = 4-$Me_2NC_6H_4$, R^2 = H (—) R^1 = Ph, R^2 = Ph (—)	280
C_{15}			
 δ-selinene	DMF, $POCl_3$	 (60)	288
	DMF, $POCl_3$	 (89)	8
	MFA, $POCl_3$	 (42)	25
C_{16}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 (18) +  (39)	15

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS (*Continued*)

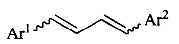
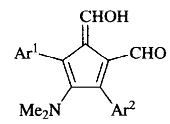
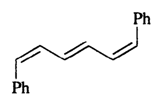
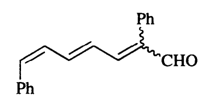
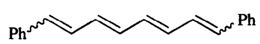
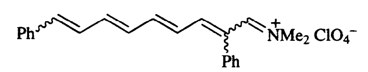
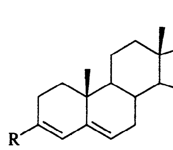
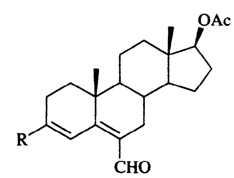
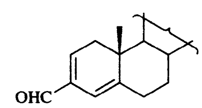
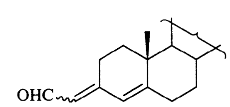
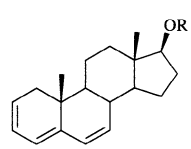
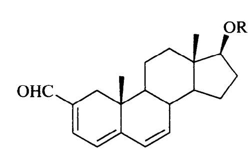
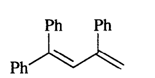
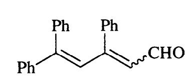
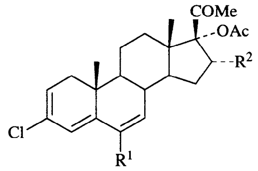
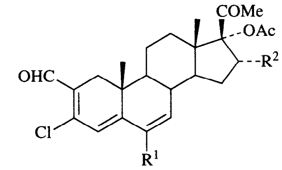
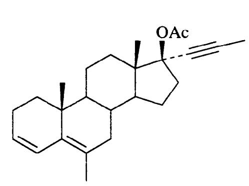
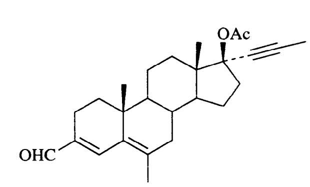
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}-C_{18}			
	DMF, $POCl_3$	 Ar[1] / Ar[2]: $4\text{-}MeOC_6H_4$ / Ph (14); $4\text{-}MeOC_6H_4$ / $4\text{-}MeOC_6H_4$ (82)	16
C_{18}			
	DMF, $POCl_3$	 (65)	16
C_{20}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 (49)	16
C_{21}-C_{22}			
 R = H	DMF, $POCl_3$	 (20)	17
	DMF, $POCl_3$, $ClCH_2CH_2Cl$, boil	" (35)	17
	DMF, $POCl_3$, $ClCH_2CH_2Cl$, rt	 (15)	17
R = Me	DMF, $POCl_3$, $ClCH_2CH_2Cl$, rt	 (48)	17
C_{21}-C_{26}			
	DMF, $POCl_3$	 R: Ac (66); Bn (29)	22
C_{22}			
	MFA, $POCl_3$	 (96) *E*:*Z*, 5:1	289
C_{23}-C_{25}			
	DMF, $POCl_3$	 R[1] / R[2]: H / Cl (43); Me / Me (14)	22
C_{25}			
	DMF, $POCl_3$, $ClCH_2CH_2Cl$, rt	 (35)	17

TABLE II. DIENES, TRIENES AND TETRAENES WITH CARBON SUBSTITUENTS (*Continued*)

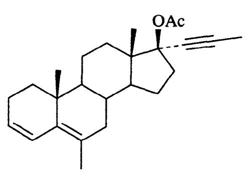
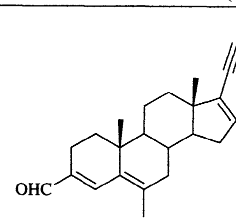
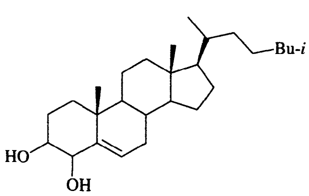
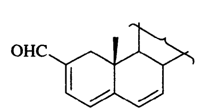
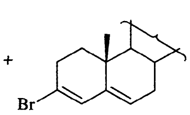
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$, $ClCH_2CH_2Cl$, boil	 (—)	17
C_{27}			
	DMF, $Ph_3P \cdot Br_2$	 (12) +  (13-26)	290

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS

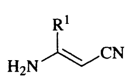
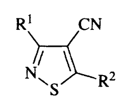
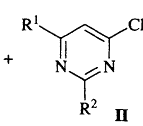
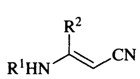
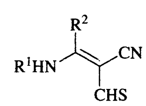
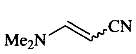
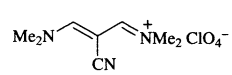
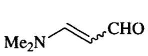
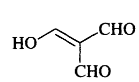
Substrate	Conditions	Product(s) and Yield(s) (%)	R^1	R^2	I	II	Refs.
C_4-C_9							
	1. R^2CONMe_2, $POCl_3$ 2. NaSH 3. I_2	 I +  II	Me	Me	(56)	(0)	291
			Ph	H	(60)	(0)	
			Me	Ph	(11)	(27)	
			Ph	Me	(38)	(0)	
			Ph	Ph	(7)	(62)	
C_4-C_{14}							
	1. DMF, $POCl_3$ 2. NaSH		H	Me	(60)		30
			Me	Me	(61)		
			Et	Me	(73)		
			H	Ph	(53)		
			Me	Ph	(81)		
			H	3-MeC_6H_4	(69)		
			H	4-MeC_6H_4	(83)		
			H	4-$MeOC_6H_4$	(88)		
			Et	Ph	(70)		
			Me	3-MeC_6H_4	(75)		
			Me	4-MeC_6H_4	(62)		
			H	2-naphthyl	(70)		
			Me	2-naphthyl	(52)		
C_5							
	1. DMF, $POCl_3$ 2. ClO_4^-	 (80)					292
	1. $[ClCH{=}NMe_2]^+Cl^-$ 2. $Me_2NH_2^+$ ClO_4^-	" (40)					293
	1. DMF, $COCl_2$ 2. Hydrolysis	 (84)					32

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

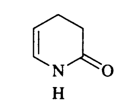
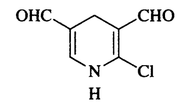
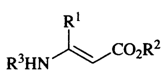
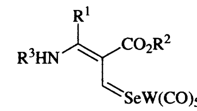
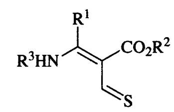
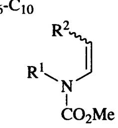
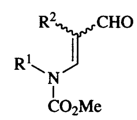
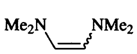
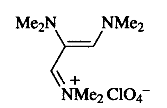
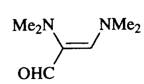
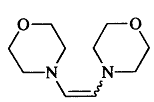
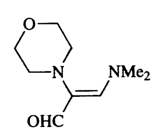
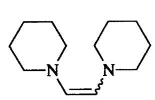
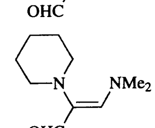
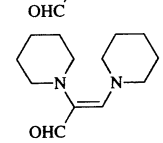
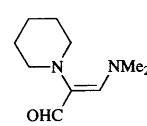
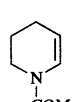
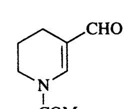
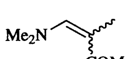
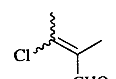
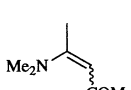
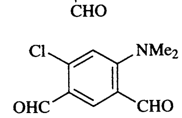
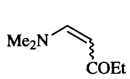
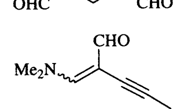
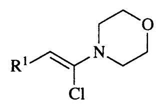
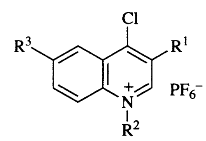
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $(COCl)_2$	 (75)	186
C_5-C_{17}			
	1. DMF, $POCl_3$ 2. NaSeH 3. $Et_4N^+ WI(CO)_5^-$	 R^1 / R^2 / R^3: Me / Me / H (8); Ph / Et / H (13); Ph / Et / Ph (23)	30
	1. DMF, $POCl_3$ 2. NaSH	 R^1 / R^2 / R^3: Me / Me / H (83); Et / Me / H (48); *n*-Pr / Et / H (71); Ph / Et / H (69); 3-MeC_6H_4 / Et / H (80); 4-MeC_6H_4 / Et / H (83); 1-naphthyl / Et / H (35)	30
C_6-C_{10}			
	DMF, $POCl_3$	 R^1 / R^2: —$(CH_2)_2$— (66); —CH=CHCH$_2$— (75); —$(CH_2)_3$— (94); *n*-Bu / Et (*E*) (91)* *(*Z* + *E*)	41, 294 41 41, 294 41, 294
C_6-C_{12}			
	1. DMF, $POCl_3$ 2. ClO_4^-	 (67)	292, 295
	DMF, $(COCl)_2$	 (29)	296, 297
	DMF, $(COCl)_2$	 (24)	296, 297, 298
	DMF, $(COCl)_2$	 (20)	296, 297
	DMF, $(COCl)_2$	 (35) +  (15)	298
C_7			
	DMF, $POCl_3$	 (26)	41
	DMF, $POCl_3$	 (68)	79
	DMF, $POCl_3$	 (48)	38
	DMF, $POCl_3$	 (11)	299

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7-C_{13}			
	1. $ArR^2N{=}CHCl^+\ Cl^-$ 2. $NH_4^+\ PF_6^-$		300

Ar	R^1	R^2	R^3	
$4\text{-}ClC_6H_4$	Me	Me	Cl	(37)
$4\text{-}MeOC_6H_4$	Me	Me	OMe	(56)
$4\text{-}MeC_6H_4$	Me	Me	Me	(55)
Ph	Me	Me	H	(79)
Ph	Me	Bn	H	(93)
Ph	Me	Me	H	(87)
Ph	Et	Me	H	(73)
Ph	Cl	Me	H	(76)
Ph	*i*-Pr	Me	H	(78)
Ph	Bn	Me	H	(93)
Ph	CH_2Cl	Me	H	(61)
Ph	$(CH_2)_2Cl$	Me	H	(63)
Ph	Ph	Bn	H	(70)
Ph	*t*-Bu	Me	H	(70)
Ph	$(CH_2)_2Cl$	Me	H	(63)

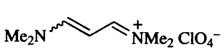
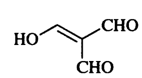
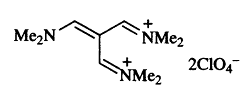
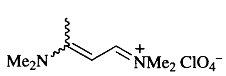
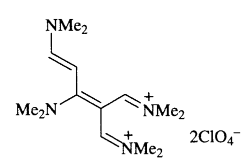
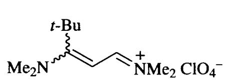
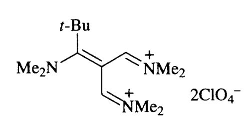
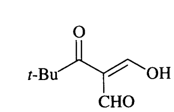
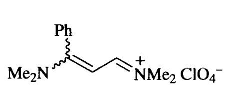
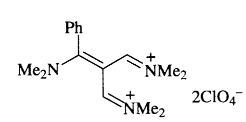
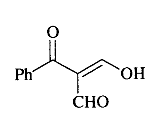
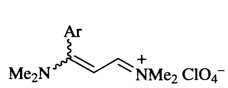
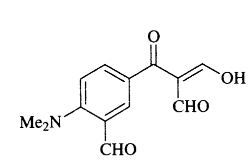
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7-C_{15}			
	1. DMF, $COCl_2$ 2. Hydrolysis	 (58)	32
	1. DMF, $POCl_3$ 2. $HClO_4$	 (86)	281
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (83)	33
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (90)	33
	1. DMF, $POCl_3$ 2. $NaClO_4$ 3. Hydrolysis	 (72)	33
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (91)	33
	1. DMF, $POCl_3$ 2. $NaClO_4$ 3. Hydrolysis	 (77)	33
 Ar = $4\text{-}Me_2NC_6H_4$	1. DMF, $POCl_3$ 2. NaOH	 (73)	33

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

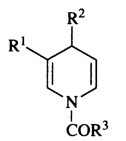
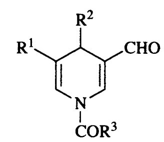
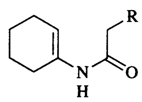
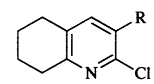
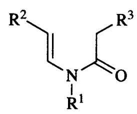
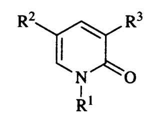
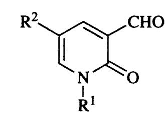
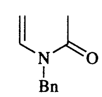
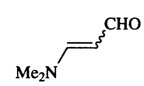
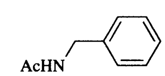
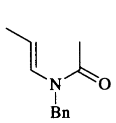
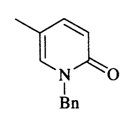
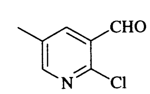
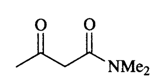
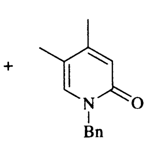
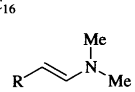
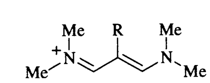
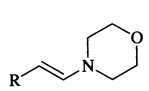
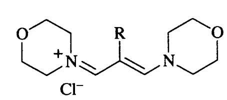
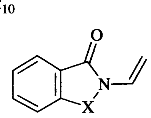
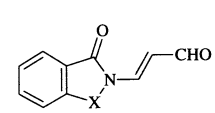
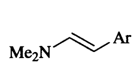
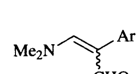
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7-C_{18}			
	DMF, $POCl_3$		
		R[1] R[2] R[3]	
		H H Me (75)	41
		H Me Ph (61)	44
		OMe Me Ph (71)	44
		H Ph Ph (43)	44
C_8-C_9			
	DMF, $POCl_3$		42
		R	
		H (62)	
		Me (45)	
C_8-C_{12}			
	DMF, $POCl_3$	 I +  II	42
		R[1] R[2] R[3] I II	
		n-Pr Me H (52) (14)	
		n-Bu Me H (55) (17)	
		n-Bu Me Me (62) (0)	
		n-Pr Et H (58) (13)	
		n-Pr Et Me (69) (0)	
	DMF, $POCl_3$	 (17) +  (30)	42
	DMF, $POCl_3$	 (44) +  (12)	42
	DMA, $POCl_3$	 (24) +  (18)	42
C_8-C_{16}			
	DMF, $(COCl)_2$		26
		R	
		t-Bu (24)	
		2-thienyl (52)	
		1-adamantyl (16)	
	*N*-formylmorpholine, $(COCl)_2$		26
		R	
		t-Bu (56)	
		2-thienyl (45)	
		Ph (47)	
		3,5-$Me_2C_6H_3$ (63)	
		3,4,5-$Me_3C_6H_2$ (66)	
		1-adamantyl (42)	
C_9-C_{10}			
	—		301
		X	
		CO (68)	
		SO_2 (45)	
	DMF, acid chloride		
		Ar / Acid chloride	
		4-pyridyl $COCl_2$ (79)	206
		2-Cl-6-$O_2NC_6H_3$ $POCl_3$ (74)	302

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

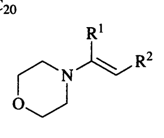
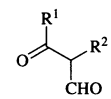
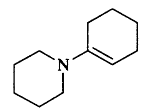
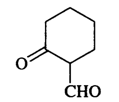
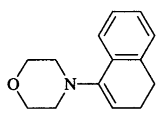
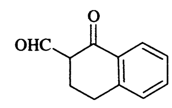
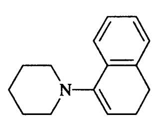
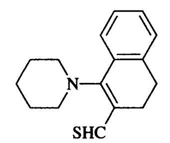
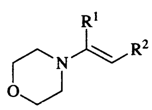
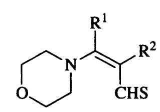
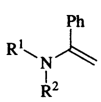
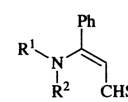
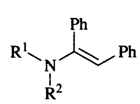
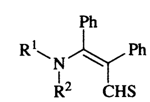
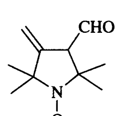
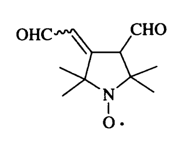
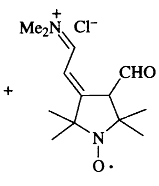
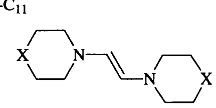
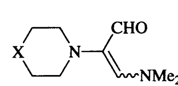
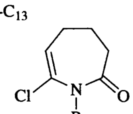
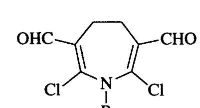
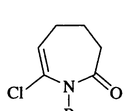
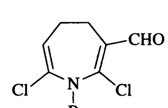
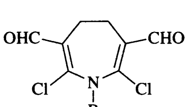
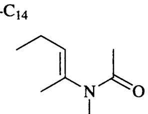
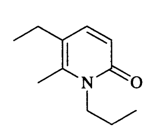
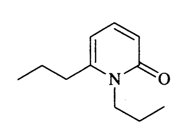
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9-C_{20}			
	DMF, $COCl_2$	 R[1] R[2] —$(CH_2)_3$— (20) —$(CH_2)_4$— (52) —$(CH_2)_5$— (48) —$(CH_2)_{10}$— (59)	28
	DMF, $COCl_2$	 (50)	28
	DMF, $COCl_2$	 (92)	28
	1. MFA, $POCl_3$ 2. NaSH	 (56)	30
	1. DMF, $POCl_3$ 2. NaSH	 R[1] R[2] —$(CH_2)_3$— (50) Ph H (42)	30, 303
	1. DMF, $POCl_3$ 2. NaSH	 R[1] R[2] —$(CH_2)_5$— (37) c-C_6H_{11} c-C_6H_{11} (38)	30
	1. MFA, $POCl_3$ 2. NaSH	 R[1] R[2] n-Pr n-Pr (44) —$(CH_2)_4$— (43) —$(CH_2)_2O(CH_2)_2$— (71) c-C_6H_{11} c-C_6H_{11} (87) n-C_6H_{13} n-C_6H_{13} (51)	30 30, 303 30, 303 30 30
C_{10}			
	DMF, $POCl_3$	 (52) +  (15)	304
C_{10}-C_{11}			
	DMF, $(COCl)_2$	 X O (—) CH_2 (20)	297
C_{10}-C_{13}			
	DMF, $POCl_3$ (11 eq)	 R CH_2CO_2Et (65) Ph (66) Bn (62)	305
	DMF, $POCl_3$ (4 eq)	 (35) +  (10)	305
C_{10}-C_{14}			
	DMF, $POCl_3$	 (29) +  (13)	42

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

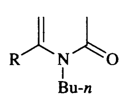
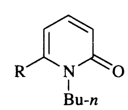
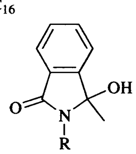
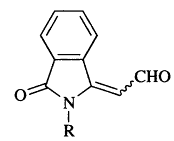
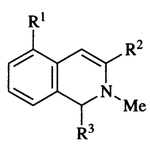
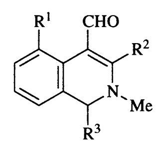
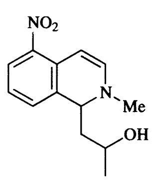
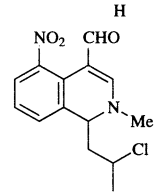
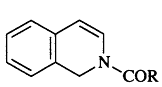
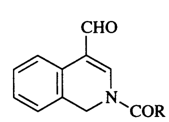
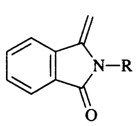
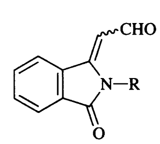
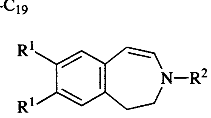
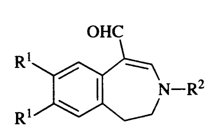
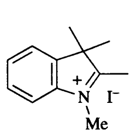
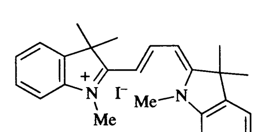
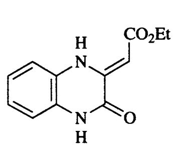
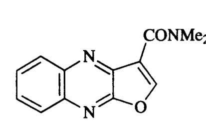
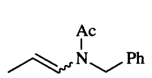
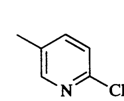
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 R: *i*-Bu (19); Ph (68)	42
C_{10}-C_{16}			
	DMF, —	 R: Me (99); Et (80); Pr (84); 4-ClC_6H_4 (94); *c*-C_6H_{11} (82); Bn (81)	43
C_{10}-C_{18}			
	DMF, $POCl_3$		
		R^1 = NO_2, R^2 = H, R^3 = H (48)	306
		R^1 = NO_2, R^2 = H, R^3 = $CH_2CH(Me)OAc$ (39)	307
		R^1 = H, R^2 = 3,4-$(MeO)_2C_6H_3$, R^3 = H (83)	308
	DMF, $POCl_3$	 (57)	307
C_{11}-C_{12}			
	"Vilsmeier-Haack reagent"	 R: Me (31)[a]; OEt (41)[a]	309
C_{11}-C_{15}			
	DMF, $POCl_3$		
		R = Et (—)	310
		R = CH_2CO_2H (—)	310
		R = *i*-Pr (—)	310
		R = 2,4-$Cl_2C_6H_3$ (—)	310
		R = 4-ClC_6H_4 (—)	310
		R = 4-$NO_2C_6H_4$ (90)	310, 43
		R = Ph (96)	43
C_{11}-C_{19}			
	DMF, $POCl_3$		311, 312
		R^1 = H, R^2 = SO_2Me (73)	
		R^1 = OMe, R^2 = SO_2Me (87)	
		R^1 = OMe, R^2 = 4-$MeC_6H_4SO_2$ (83)	
C_{12}			
	DMF, $POCl_3$	 (40)	29
	DMF, $POCl_3$	 (83-88)	313, 314
	DMF, $POCl_3$	 (68)	315

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

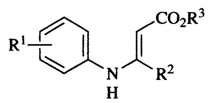
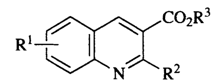
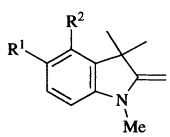
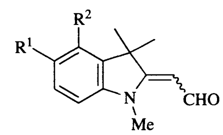
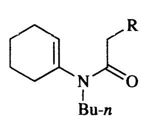
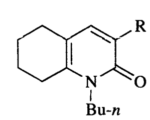
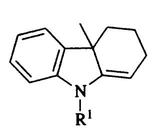
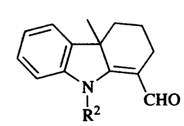
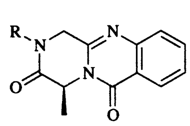
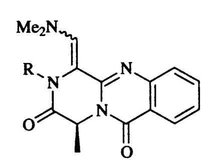
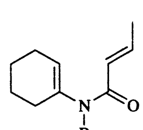
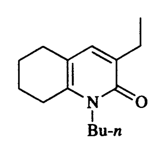
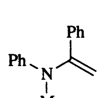
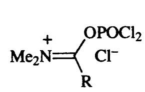
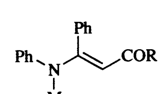
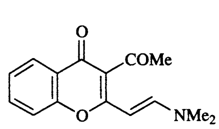
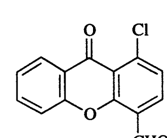
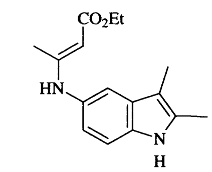
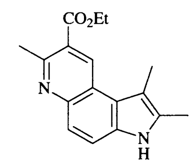
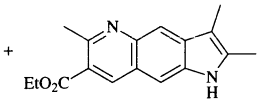
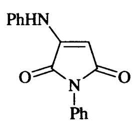
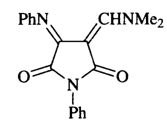
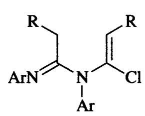
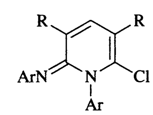
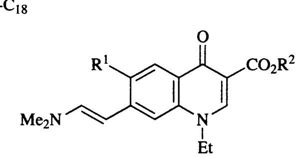
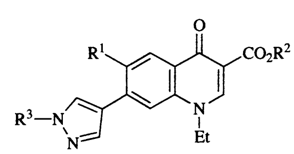
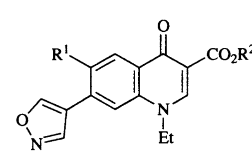
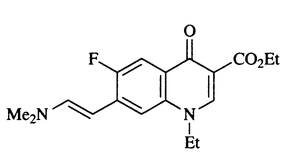
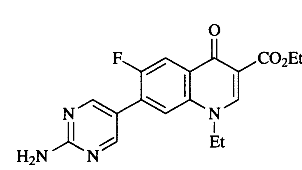
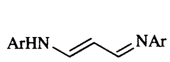
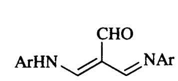
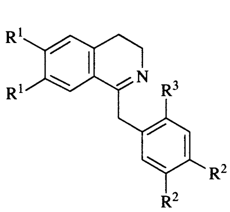
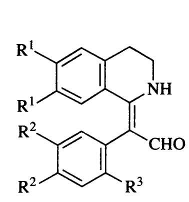
Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
C_{12}-C_{14}							
	DMF, $POCl_3$		R^1	R^2	R^3		
			2-MeO	Me	Me	(47)	31
			4-MeO	Me	Me	(60)	31
			3-O_2N	Me	Et	(61)	31
			4-O_2N	Me	Et	(60)	31
			3-MeO	Me	Et	(73)	31
			4-MeO	Me	Et	(69)	31
			3,4-$(MeO)_2$	Me	Et	(71)	31
			H	CO_2Et	Et	(—)	316
C_{12}-C_{16}							
	See table		R^1	R^2	Reagents		
			Cl	H	—, $COCl_2$	(—)	317
			H	H	MFA, $POCl_3$	(—)	318
			H	H	—, $COCl_2$	(—)	317
			H	H	DMF, $POCl_3$	(39)	319
			MeO	H	MFA, $POCl_3$	(—)	318
			CO_2Et	H	—, $COCl_2$	(—)	317
			benzo		—, $COCl_2$	(—)	317
C_{12}-C_{18}							
	DMF, $POCl_3$		R				
			Cl	(53)			
			H	(32)			42
			Me	(77)			
			Et	(52)			
			OPh	(60)			
C_{13}-C_{14}							
	DMF, $POCl_3$		R^1	R^2			
			H	CHO	(74)		319
			CHO	CHO	(52)		320
			Me	Me	(65)		319
C_{13}-C_{20}							
	$ClCH{=}NMe_2^+\ Cl^-$		R				321
			Me	(96) *Z*			
			Bn	(—)			
			4-MeOBn (PMB)	(95) *E*			
C_{14}							
	DMF, $POCl_3$	 (31)					42
C_{15}							
		 (—) R = H, Me, Ph					322
	DMF, $POCl_3$	 (40)					323

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}			
	DMF, $POCl_3$	 (34) +  (5)	324
	DMF, $POCl_3$	 (25)	325
C_{16}-C_{20}			
	DMF, $POCl_3$		326
C_{17}-C_{18}			
	1. DMF, $SOCl_2$ 2. H_2NNHR^3		27
	1. DMF, $SOCl_2$ 2. H_2NOH		27
C_{18}			
	1. DMF, $SOCl_2$ 2. $H_2NC(=NH)NH_2$	 (17)	27
C_{19}			
 Ar = 3,5-$Me_2C_6H_3$	DMF, $POCl_3$	 (31)	327
C_{20}			
	—, rt		328

Ref. 326:

Ar	R	
Ph	H	(49)
2-$MeOC_6H_4$	Cl	(28)
2-MeC_6H_4	H	(31)
3-MeC_6H_4	H	(47)
4-MeC_6H_4	H	(42)
2-$MeOC_6H_4$	H	(68)
3-$MeOC_6H_4$	H	(29)
4-$MeOC_6H_4$	H	(75)
2-$MeOC_6H_4$	Me	(51)
2,4-$Me_2C_6H_3$	H	(31)

Ref. 27 (H_2NNHR^3):

R^1	R^2	R^3	
H	Me	H	(82)
H	Me	$(CH_2)_2OH$	(62)
H	Me	2-pyridyl	(62)
F	Et	H	(57)
F	Et	Me	(31)

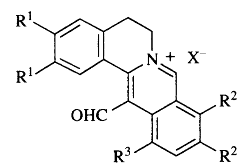
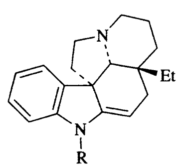
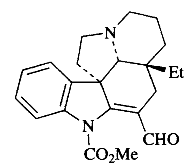
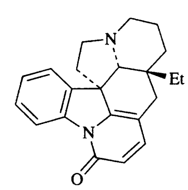
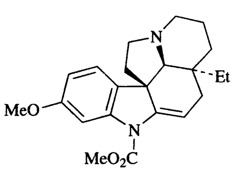
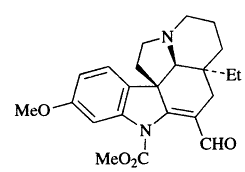
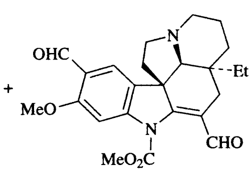
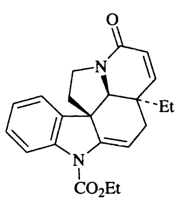
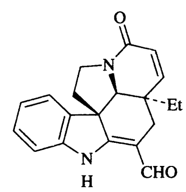
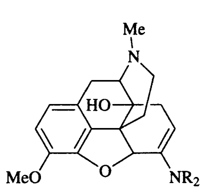
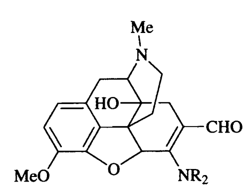
Ref. 27 (H_2NOH):

R^1	R^2	
H	Me	(49)
F	Et	(29)

Ref. 328:

R^1	R^2	R^3	
MeO	MeO	Br	(70)
EtO	H	H	(45)

TABLE III. ALKENES WITH NITROGEN SUBSTITUENTS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	—, heat	 R¹ / R² / R³: MeO / MeO / Br (—); EtO / H / H (—)	329
C_{21}  R = Ac, CO_2Me	DMF, $POCl_3$, R = CO_2Me	 (94)	330
	DMF, $POCl_3$, rt, R = Ac	 (49)	330
C_{22} 	DMF, $POCl_3$, rt	 (58) +  (15)	331
	1. DMF, $POCl_3$ 2. NaOH (aq)	 (76)	332
	DMF, $POCl_3$	 R_2: —$(CH_2)_4$— (54); —$(CH_2)_2O(CH_2)_2$— (50)	51

[a] The reported yields are based on isoquinoline as the starting material.

TABLE IV. DIENES, TRIENES AND TETRAENES WITH NITROGEN SUBSTITUENTS

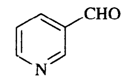
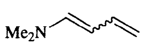
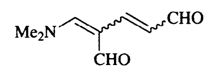
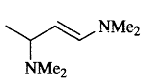
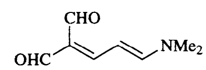
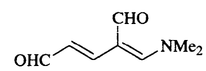
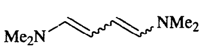
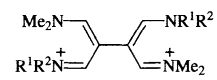
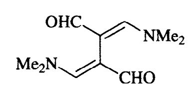
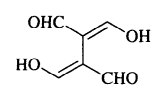
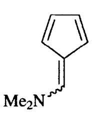
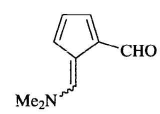
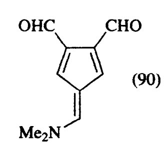
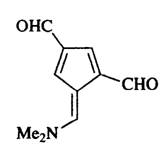
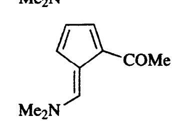
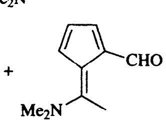
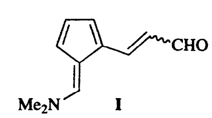
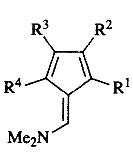
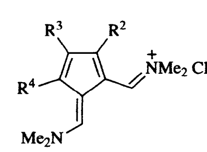
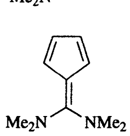
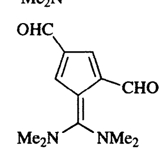
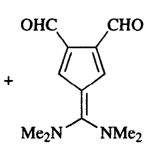
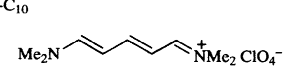
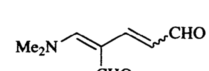
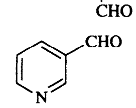
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	1. $HNMe_2$ 2. DMF, $POCl_3$ 3. NH_4Cl	 (30)	37
C_6			
	DMF, $COCl_2$	 (35)	70
C_8			
	—	 (—)	333
	DMF, $COCl_2$	 (65)	70
	1. R^1R^2NCHO, $COCl_2$ 2. $NaClO_4$	 $2ClO_4^-$ R^1 = Me, R^2 = Me (65); R^1R^2 = —$(CH_2)_5$— (75)	40
	1. DMF, $COCl_2$ 2. $NaClO_4$ 3. K_2CO_3	 (73)	40
	1. *N*-formylmorpholine, $COCl_2$ 2. $NaClO_4$ 3. KOH	 (—)	40
C_8-C_{10}			
	DMF, $COCl_2$, -10°	 (90)	278
	DMF, $COCl_2$, rt	 (90) or  (trace)	278, 18
	Me_2NCOMe, $POCl_3$	 (—) +  (—)	334
	Bu_2NCH=CHCHO, $(COCl)_2$	 I (77)	335
	R_2NCH=CHCHO, $COCl_2$ (R not specified)	I (—)	334
	1. DMF, $POCl_3$ 2. $NaClO_4$	 R^1 R^2 R^3 R^4: D H H D (—); H D D H (—)	336
	1. DMF, $POCl_3$ 2. NaOH	 (26) +  (37)	337
C_9-C_{10}			
	DMF, $COCl_2$	 (85)	70
	1. DMF, $COCl_2$ 2. NH_4Cl	 (67)	70

TABLE IV. DIENES, TRIENES AND TETRAENES WITH NITROGEN SUBSTITUENTS (*Continued*)

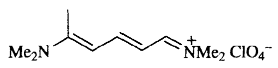
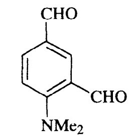
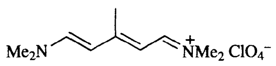
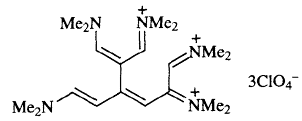
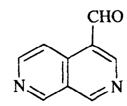
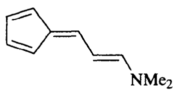
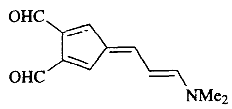
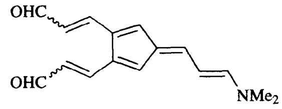
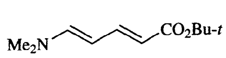
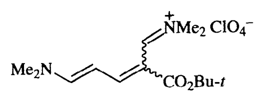
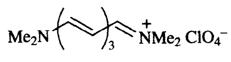
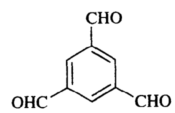
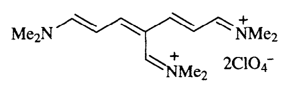
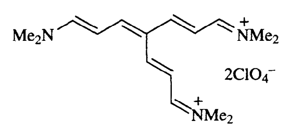
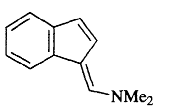
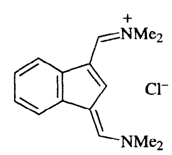
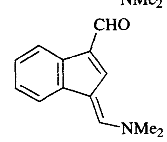
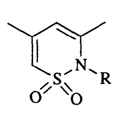
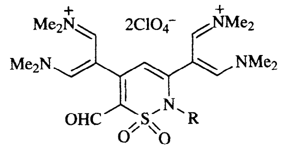
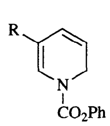
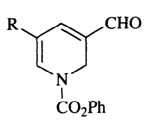
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (64)	38
	1. $[ClCH{=}NMe_2]^+Cl^-$ 2. $NaClO_4$	 (93)	39
	1. $[ClCH{=}NMe_2]^+Cl^-$ 2. $NaClO_4$ 3. NH_4Cl	 (74)	39
C_{10}			
	DMF, $POCl_3$	 (—)	334
	$R_2NCH{=}CHCHO$, $COCl_2$ (R not specified)	 (—)	334
C_{11}			
	1. $[ClCH{=}NMe_2]^+Cl^-$ 2. $NaClO_4$	 (68)	338
	DMF, $COCl_2$	 (40)	38
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (32)	339
	1. $Me_2NCH{=}CHCHO$, $POCl_3$ 2. $NaClO_4$	 (75)	339
C_{12}			
	$[ClCH{=}NMe_2]^+Cl^-$	 (61)	36
	1. $[ClCH{=}NMe_2]^+Cl^-$ 2. K_2CO_3, H_2O	 (—)	36
C_{12}-C_{13}			
	1. DMF, $POCl_3$ 2. $NaClO_4$	 R: Ph (65); 4-ClC_6H_4 (55); 4-MeC_6H_4 (60); 4-$MeOC_6H_4$ (62)	340
C_{12}-C_{18}			
	DMF, $POCl_3$	 R = Cl (64)	44
		R = Br (57)	44
		R = H (81)	45
		R = Me (71)	44
		R = MeO (71)	44
		R = Ph (73)	44
		R = c-C_6H_{11} (65)	44

TABLE IV. DIENES, TRIENES AND TETRAENES WITH NITROGEN SUBSTITUENTS (*Continued*)

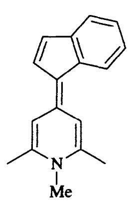
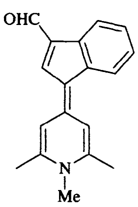
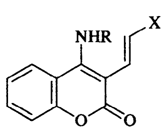
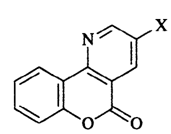
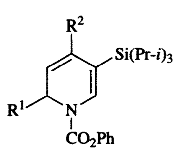
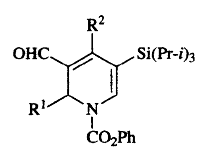
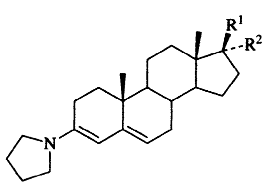
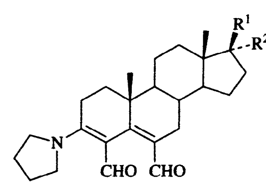
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	DMF, $POCl_3$	 (—)	341
C_{19}-C_{22} 	DMF, $POCl_3$	 R / X: Bn, CO_2Me (85); 4-MeOBn, CO_2Et (90); 4-O_2NBn, CO_2Et (90); Bn, CN (74)	342
C_{22}-C_{27} 	DMF, $POCl_3$	 R^1 / R^2: Me, Cl (50); *n*-Bu, Cl (88); Ph, H (97)	343
C_{26}-C_{27} 	DMF, $POCl_3$	 R^1 / R^2: OCOEt, H (44); Ac, OAc (29)	34, 35; 34

TABLE V. ALKENES WITH OXYGEN SUBSTITUENTS

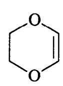
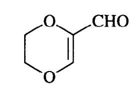
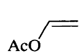
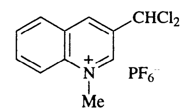
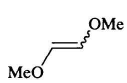
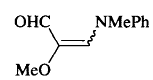
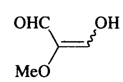
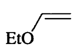
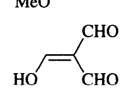
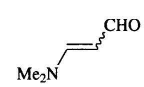
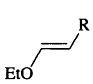
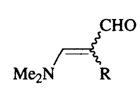
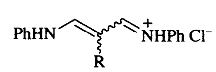
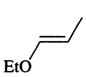
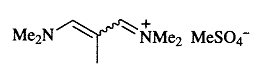
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	"Vilsmeier reagent"	 (45)	344
	1. MFA, $POCl_3$ 2. $NH_4^+PF_6^-$	 (79)	300
	MFA, $POCl_3$	 (35)	345
	1. MFA, $POCl_3$ 2. Hydrolysis	 (20)	345
	1. DMF, $COCl_2$ 2. Hydrolysis	 (—) +  (10)	32
C_4-C_6			
	1. DMF, $POCl_3$ 2. K_2CO_3	 R: H (57), Me (68), Et (77)	46
	1. DMF, $POCl_3$ 2. $PhNH_2$•HCl	 R: H (14), Me (83), Et (62)	46
C_5			
	1. DMF, $POCl_3$ 2. Me_2SO_4	 (67)	292

TABLE V. ALKENES WITH OXYGEN SUBSTITUENTS (*Continued*)

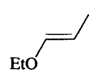
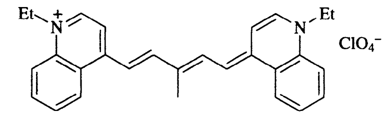
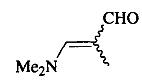
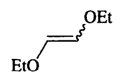
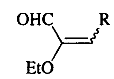
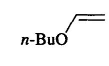
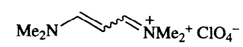
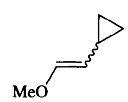
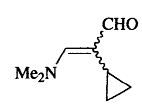
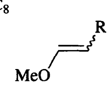
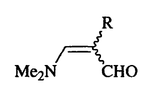
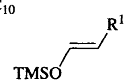
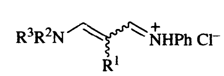
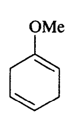
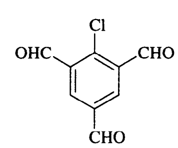
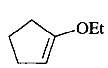
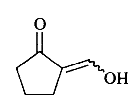
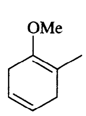
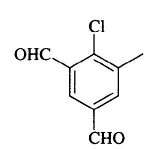
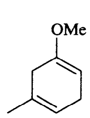
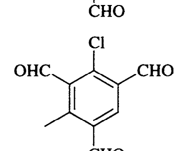
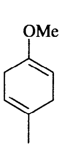
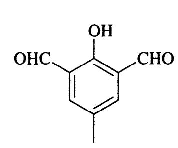
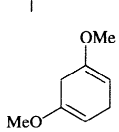
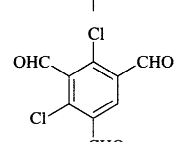
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. *N*-ethyl-4-methylquinolinium iodide, Ac_2O, Et_3N, pyridine 3. $HClO_4$	 (60)	48
	DMF, $POCl_3$	 (72)	346
C_6 	MFA, $POCl_3$	 (—) **I** R = NMePh	345
	1. MFA, $POCl_3$ 2. Hydrolysis	**I** R = OH (—)	345
	DMF, $POCl_3$	**I** R = OEt (36)	347
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (70)	292
	DMF, $COCl_2$	 (70)	348
C_6-C_8 	1. DMF, $(COCl)_2$ or $POCl_3$ 2. K_2CO_3	 R: *c*-C_3H_5 (66-71); *c*-C_4H_7 (60); *c*-C_5H_9 (54)	47
C_7-C_{10} 	1. DMF, $POCl_3$ 2. $PhNH_2$	 R^1 = Et, R^2 = H, R^3 = Ph (55) R^1 = C_5H_{11}, R^2 = Me, R^3 = Me (47)	55
C_7 	DMF, $POCl_3$	 (44)	53
	DMF, $POCl_3$	 (20)	349
C_8 	DMF, $POCl_3$	 (39)	53
	DMF, $POCl_3$	 (17)	53
	DMF, $POCl_3$	 (46)	53
	DMF, $POCl_3$	 (42)	53

TABLE V. ALKENES WITH OXYGEN SUBSTITUENTS (*Continued*)

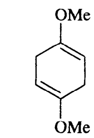
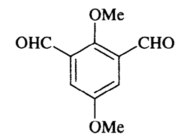
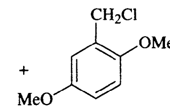
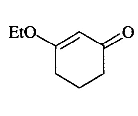
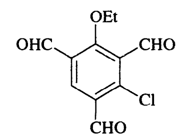
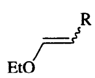
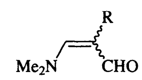
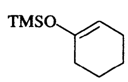
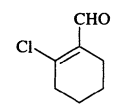
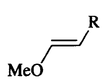
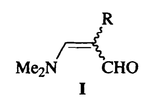
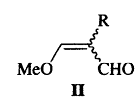
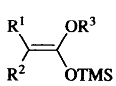
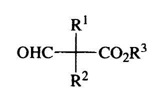
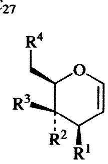
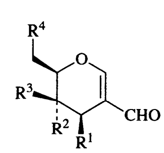
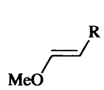
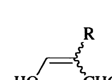
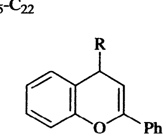
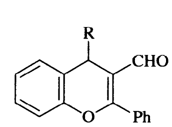
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (14) +  (13)	53
	*N*-formylmorpholine, $POCl_3$	 (31)	350
C_8-C_{10}			
	DMF, $(COCl)_2$ or $POCl_3$	 R: *c*-C_4H_7 (50-60) *c*-C_5H_9 (50-60) *c*-C_6H_{11} (50-60)	348
C_9			
	DMF, $POCl_3$	 (60)	49
C_9-C_{10}			
	1. DMF, $(COCl)_2$ 2. K_2CO_3	 I +  II R — I — II *c*-C_6H_{11} (57) (0) *n*-C_7H_{13} (18) (43)	47
C_9-C_{11}			
	DMF, $POCl_3$	 R^1 — R^2 — R^3 H Et Et (53) Me Me Et (52) Me Et Me (52) H *i*-Pr Et (56) Et Et Et (62) —$(CH_2)_4$— Me (51) —$(CH_2)_5$— Me (53)	49
C_9-C_{27}			
	DMF, $POCl_3$	 R^1 — R^2 — R^3 — R^4 OMe OMe H OMe (60) OMe H OMe OMe (80) OMe † H † (—) OBn OBn H OBn (55) OBn H OBn OBn (85) OMe H OC(Ph)$_3$ OMe (72) † R^2,R^4 = —OC(Me)$_2$O—	50
C_{13}			
	DMF, $(COCl)_2$	 R: 1-adamantyl (20) 2-adamantyl (6)	351
C_{15}-C_{22}			
	DMF, $POCl_3$	 R: H (56) Ph (94) 4-MeC$_6$H$_4$ (77)	233

TABLE V. ALKENES WITH OXYGEN SUBSTITUENTS (*Continued*)

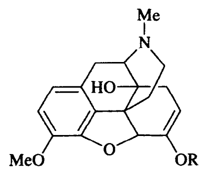
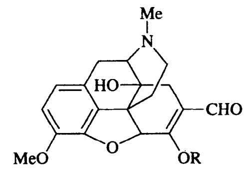
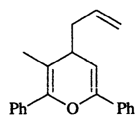
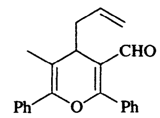
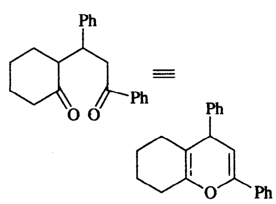
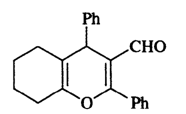
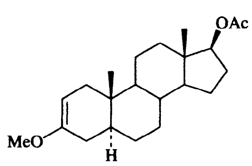
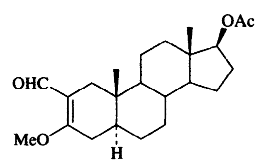
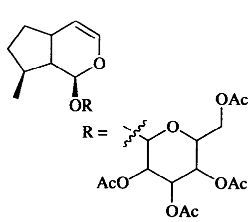
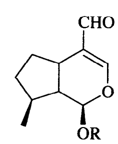
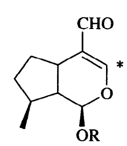
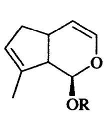
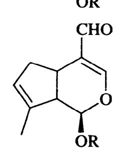
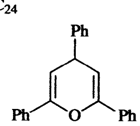
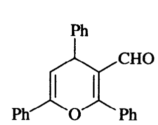
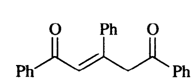
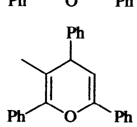
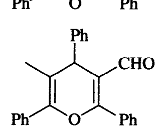
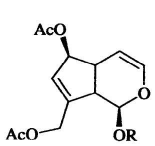
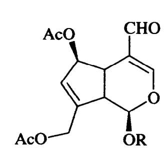
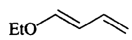
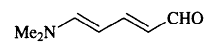
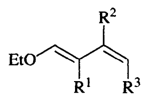
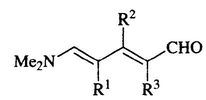
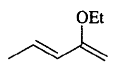
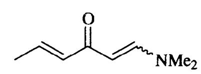
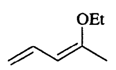
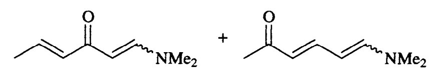
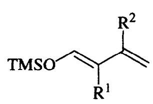
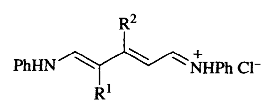
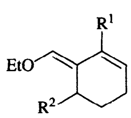
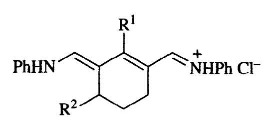
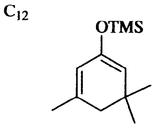
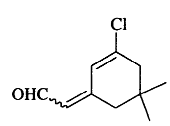
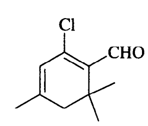
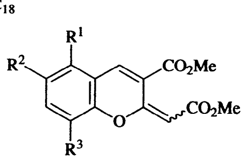
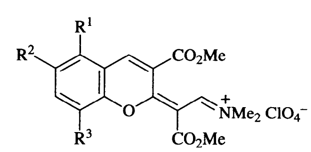
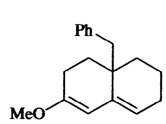
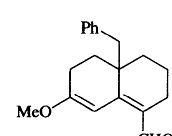
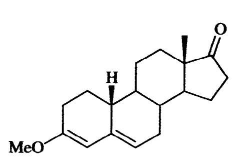
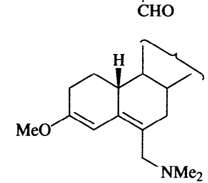
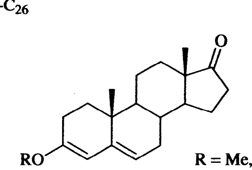
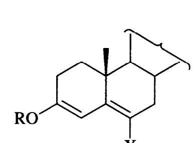
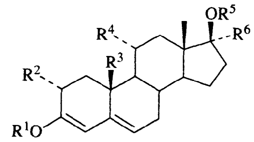
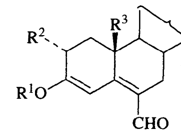
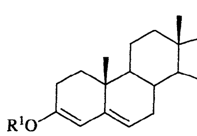
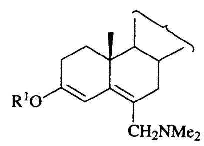
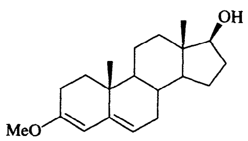
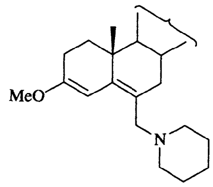
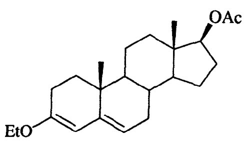
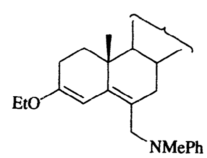
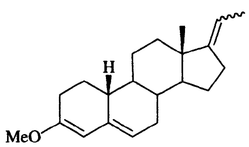
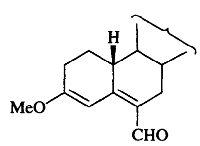
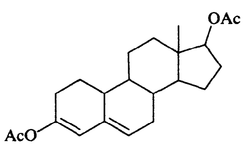
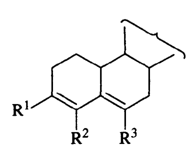
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20-22}			
	DMF, $POCl_3$	 R: Et (64); *n*-Bu (46)	51
C_{21}			
	DMF, $POCl_3$	 (68)	352
	DMF, $POCl_3$	 (45)	353
C_{22}			
	DMF, $COCl_2$	 (—)	52
C_{23}			
	DMF, $POCl_3$	 (26)	354
	$Me_2N^{13}CHO$, $POCl_3$	 (5% of ^{13}C label incorporated)	354
 R = as above	DMF, $POCl_3$	 (89)	354
C_{23}-C_{24}			
	—	 (78) +  (10)	355, 352
	DMF, $POCl_3$	 (60)	352
C_{27}			
 R = as above	DMF, $POCl_3$	 (63)	354, 356

TABLE VI. DIENES WITH OXYGEN SUBSTITUENTS

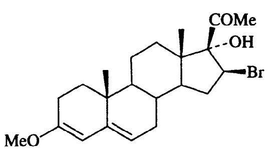
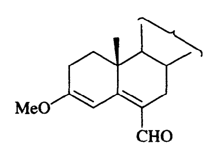
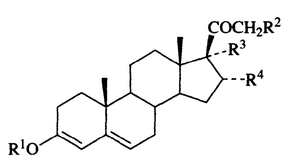
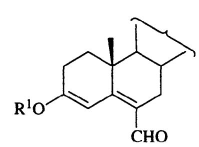
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	DMF, $COCl_2$	 (35)	70
C_6-C_8			
	DMF, $POCl_3$	 R^1 R^2 R^3: H H H (42); Me H H (45); H H Me (50); Me Me H (48)	54
C_7			
	DMF, $POCl_3$	 (—)	357
	DMF, $POCl_3$	 (—) 1:1	357
C_7-C_{13}			
	1. DMF, $POCl_3$ 2. $PhNH_2$	 R^1 R^2: H H (58); H Me (45); Ph H (51)	55
C_9-C_{15}			
 R^1, R^2 = H, H; Me, H; H, Me; Me, Me; Ph, H	1. DMF, $POCl_3$ 2. $PhNH_2$	 (30-50)	358
C_{12}			
	*N*-formylmorpholine, $POCl_3$	 (87) +  (8)	350
C_{14}-C_{18}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 R^1 R^2 R^3: H H H (28); H H OMe (49); benzo H (39)	56
C_{18}			
	DMF, $POCl_3$	 (34)[a]	57
C_{19}			
	1. DMF, $COCl_2$ 2. $LiBH_4$ [b]	 (—)	59
C_{20}-C_{26}			
 R = Me, Et, Bn	1. DMF, $COCl_2$ 2. $LiBH_4$[b]	 **I**, X = CH_2NMe_2	59, 57
R = Me, Bn	DMF, $COCl_2$	**I**, X = CHO (—)	359, 360

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}-C_{28}			
	DMF, $COCl_2$	 (—)	359

R^1	R^2	R^3	R^4	R^5	R^6
Me	H	Me	H	H	H
Me	H	H	H	Ac	H
Me	H	Me	H	Ac	H
Me	H	Me	H	Ac	Me
Et	H	Me	H	Ac	H
Me	H	Me	OAc	Ac	H
Et	Me	Me	H	Ac	H
Bn	H	Me	H	Ac	H

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1, R^2 = Me, H; Me, Ac; Et, Ac	1. DMF, $COCl_2$ 2. $LiBH_4$ [b]	 (—)	59
	1. *N*-formylpiperidine, $COCl_2$ 2. $LiBH_4$	 (—)	59
	1. MFA, $COCl_2$ 2. $LiBH_4$	 (—)	59
C_{21}			
	—	 (—)	361
C_{22}			
	DMF, $POCl_3$	 I + II + III + IV (—)	60

	R^1	R^2	R^3
I	Cl	H	H
II	Cl	CHO	H
III	Cl	H	CHO
IV	OAc	H	CHO

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $COCl_2$	 (—)	359
C_{22}-C_{26}			
	DMF, $COCl_2$	 (—)	

R^1	R^2	R^3	R^4	Refs.
Me	H	—O—		359
Me	OH	H	H	359
Me	F	OAc	H	359
Me	H	OAc	H	359
Me	H	—OCH_2O—		359
Me	H	OAc	Me	359
Et	F	OAc	H	362
Et	H	—$OC(Me)_2O$—		359

TABLE VI. DIENES WITH OXYGEN SUBSTITUENTS (*Continued*)

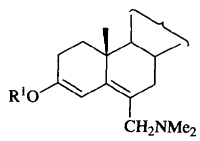
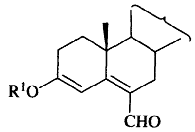
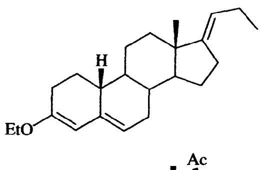
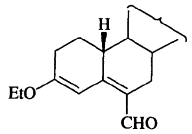
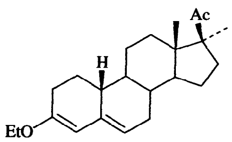
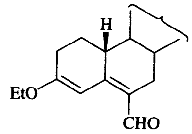
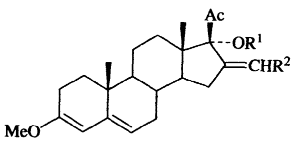
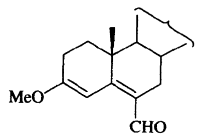
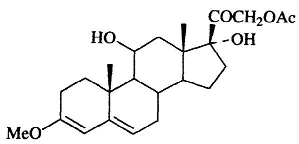
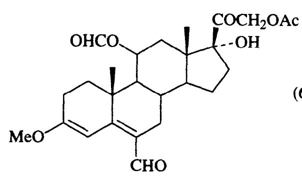
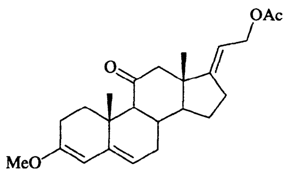
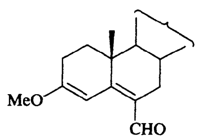
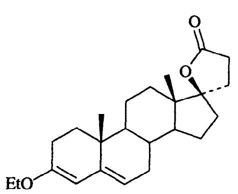
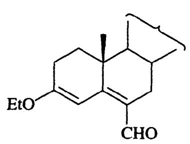
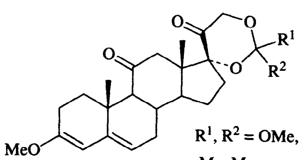
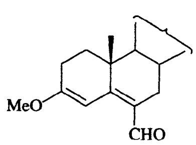
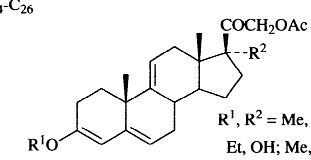
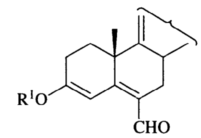
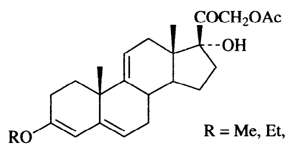
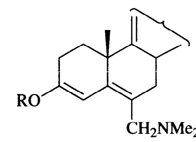
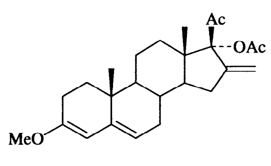
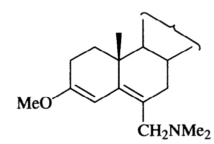
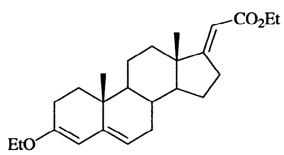
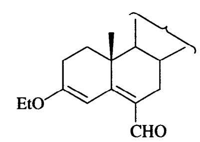
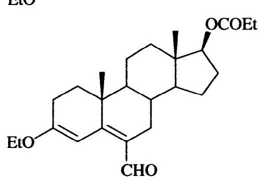
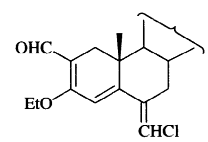
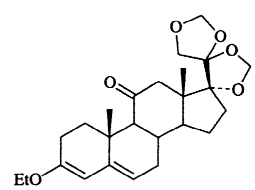
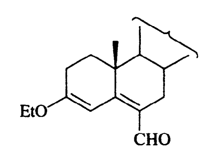
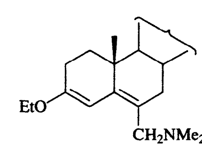
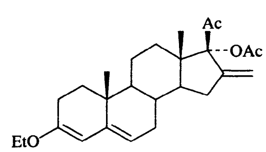
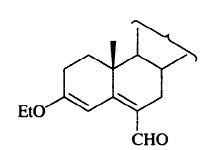
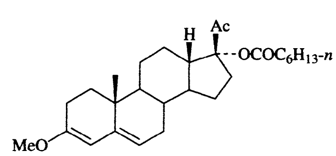
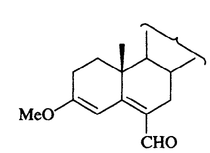
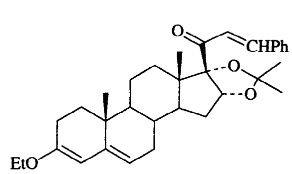
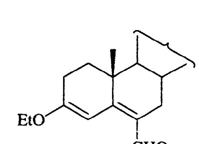
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $COCl_2$ 2. $LiBH_4$, rt[b]	 (—) R^1 R^2 R^3 R^4 Me H —O— Et H OH OH Me H OAc H Et H OAc H	59
	DMF, $POCl_3$	 (—) R^1 R^2 R^3 R^4 Me H OAc H	360, 363
C_{23}			
	—	 (—)	364
	—	 (95)	364a
C_{23}-C_{26}			
	DMF, $COCl_2$	 (—) R^1 R^2 H H Ac H Ac Me	359
C_{24}			
	DMF, $POCl_3$	 (60-70)	365
	DMF, $COCl_2$	 (—)	359
	DMF, $COCl_2$	 (—)	359
C_{24}-C_{25}			
 R^1, R^2 = OMe, H; Me, Me	DMF, $COCl_2$	 (—)	359

TABLE VI. DIENES WITH OXYGEN SUBSTITUENTS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{24}-C_{26}  R^1, R^2 = Me, OH; Et, OH; Me, OAc	DMF, $COCl_2$		(—)	359
 R = Me, Et, *n*-Pr	1. DMF, $COCl_2$ 2. $LiBH_4$ [b]		(—)	59
C_{25} 	1. DMF, $COCl_2$ 2. $LiBH_4$, rt [b]		(—)	59
	DMF, $COCl_2$		(—)	359
	DMF, $POCl_3$		(45)	73
	DMF, $COCl_2$		(—)	359
	1. DMF, $COCl_2$ 2. $LiBH_4$, rt, [b]		(—)	59
C_{26} 	DMF, $POCl_3$		(75)	58
C_{28} 	DMF, $POCl_3$		(—)	366, 367
C_{33} 	DMF, $COCl_2$		(—)	359

[a] The yield is that of the corresponding enone.

[b] Phenazone is added to suppress reduction of the carbonyl group.

TABLE VII. ALKENES, DIENES AND TRIENES WITH SULFUR SUBSTITUENTS

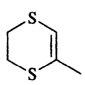
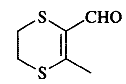
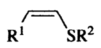
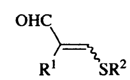
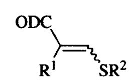
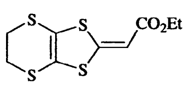
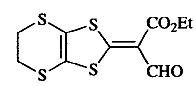
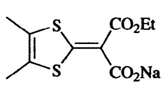
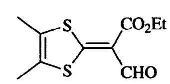
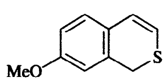
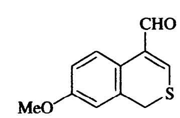
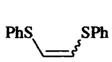
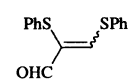
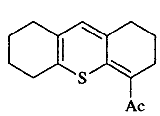
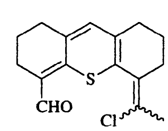
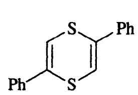
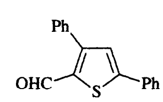
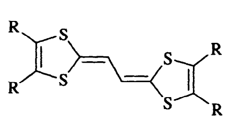
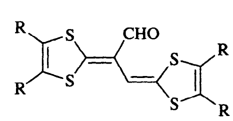
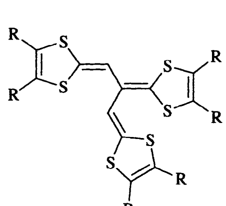
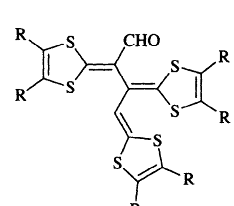
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	DMF, $POCl_3$	 (—)	368
C_9			
	1. DMF, $POCl_3$, 0° 2. 90°, 3 h	 R^1 R^2: Ph Me (72); Me Ph (64)	62a
	1. DMF-d_7, $POCl_3$, 0° 2. 90°, 3 h	 R^1 R^2: Ph Me (75); Me Ph (73)	62a
	DMF, $POCl_3$	 (96)	62
C_{10}			
	DMF, $POCl_3$	 (76)	62
	—	 (—)	369
C_{14}			
 *E* or *Z*	MFA, $POCl_3$	 (74)	61
C_{15}			
	"Vilsmeier reagent"	 (75)	370
C_{16}			
	DMF, $POCl_3$	 (32)	61a
	DMF, $(COCl)_2$	 R: CO_2Me (75); benzo (74)	371
C_{24}			
	DMF, $(COCl)_2$	 R: CO_2Me (86); benzo (85)	371

TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS

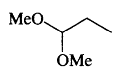
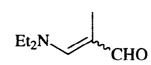
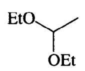
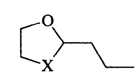
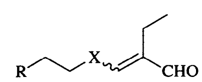
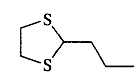
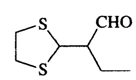
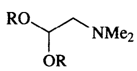
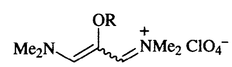
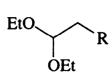
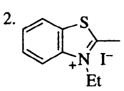
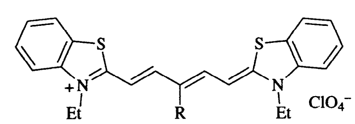
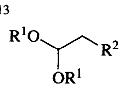
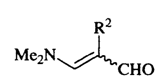
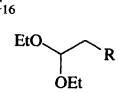
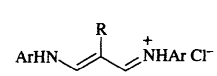
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	Et_2NCHO, $POCl_3$	 (79)	372
C_6			
	1. DMF, $COCl_2$ 2. $Me_2NH_2^+ Cl^-$ 3. $NaClO_4$	 (64)	69
	DMF, $COCl_2$	 X R O Cl (64) S OH (52)	67
	1. DMF, $COCl_2$ 2. 4-$MeC_6H_4SO_3H$	 (77)	67
C_6-C_8			
	1. DMF, $POCl_3$ 2. ClO_4^-	 R Me (20-39) Et (78)	295
C_6-C_{12}			
	1. DMF, $POCl_3$ 2.  3. $HClO_4$	 R F (61) Cl (58) Br (26) H (26) CCl_3 (45) Me (84) Et (80) OEt (65) *i*-Pr (40) Ph (46)	48
C_6-C_{13}			
	DMF, $COCl_2$		
		R^1 R^2	
		Et H (69)	373
		Me Et (89)	372
		Et Me (81)	373
		Me *i*-Pr (31)	372
		Et Et (75)	373
		Et *n*-Pr (70)	373
		Et *i*-Pr (48)	373
		Et *n*-Bu (60)	373
		Et *n*-C_5H_{11} (89)	373
		Et Ph (87)	373
		Et Bn (70)	373
C_6-C_{16}			
	1. DMF, $POCl_3$ 2. $ArNH_2$		
		R Ar	
		Cl Ph (48-81)	66
		H Ph (14)	46
		Me Ph (66-81)	66, 46
		Et Ph (75)	66, 46
		Et 4-BrC_6H_4 (31)	66
		Et 2-HOC_6H_4 (79)	66
		Et 2-MeC_6H_4 (1)	66
		Et 3-MeC_6H_4 (32)	66
		Et 4-$MeOC_6H_4$ (51)	66
		n-Pr Ph (71)	66
		n-Pr 4-ClC_6H_4 (80)	66
		n-Pr 3-MeC_6H_4 (70)	66
		n-Pr 4-MeC_6H_4 (68)	66
		n-Pr 4-$MeOC_6H_4$ (21)	66
		n-C_6H_{13} Ph (61)	66
		n-C_7H_{15} Ph (62)	66
		n-C_8H_{17} Ph (50)	66
		n-$C_{10}H_{21}$ Ph (29)	66
		n-$C_{10}H_{21}$ 4-MeC_6H_4 (35)	66

TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS (*Continued*)

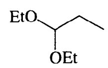
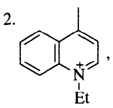
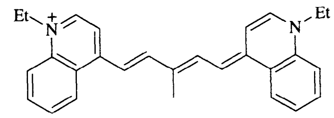
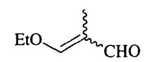
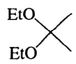
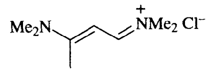
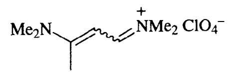
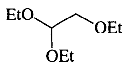
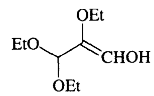
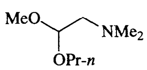
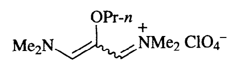
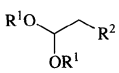
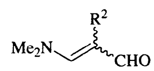
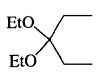
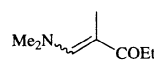
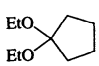
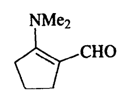
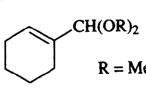
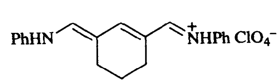
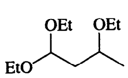
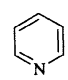
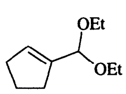
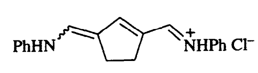
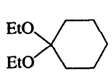
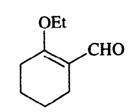
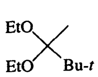
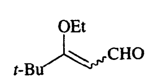
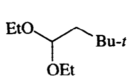
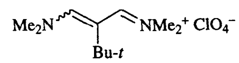
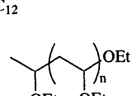
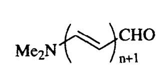
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	1. DMF, $POCl_3$ 2.  , Ac_2O, Et_3N, pyridine 3. $HClO_4$	 ClO_4^- (73)	48
	DMF, $POCl_3$	 (73)	375
	DMF, $COCl_2$	 (56)	63, 64
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $NaClO_4$	 (37)	33
C_8			
	DMF, $COCl_2$	 (—)	376
	1. DMF, $POCl_3$ 2. ClO_4^-	 (55)	378
C_8-C_{10}			
	DMF, $POCl_3$	 R^1 R^2: Et Et (51); Me Ph (—)	67
C_9			
	DMF, $POCl_3$	 (—)	67
	DMF, $COCl_2$	 (48)	63, 64
C_9-C_{11}			
 R = Me or Et	1. DMF, $POCl_3$ 2. $PhNH_2$ 3. $HClO_4$	 (60)	81
C_{10}			
	1. DMF, $COCl_2$ 2. NH_4OAc	 (55)	70, 37
	1. DMF, $POCl_3$ 2. $PhNH_2$	 (64)	81
	DMF, $COCl_2$	 (59)	64
	DMF, $COCl_2$	 (82)	63, 64
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. Me_2NH 3. $NaClO_4$	 (71)	65
C_{10}-C_{12}			
	DMF, $POCl_3$	 n: 1 (43-50); 2 (50)	68

TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS (*Continued*)

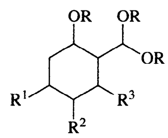
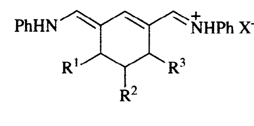
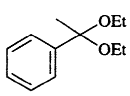
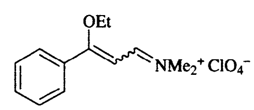
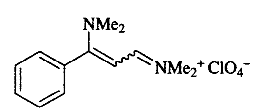
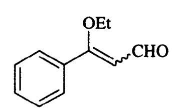
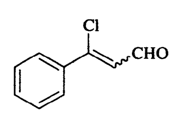
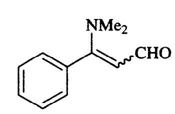
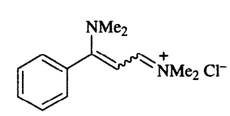
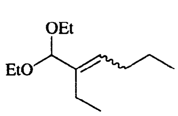
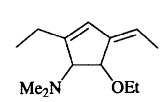
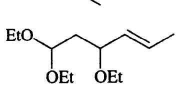
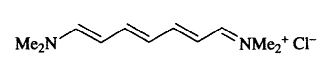
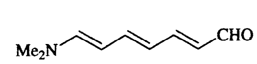
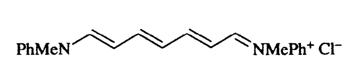
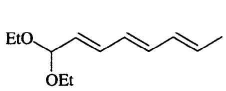
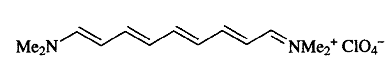
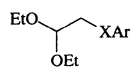
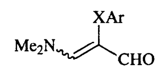
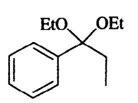
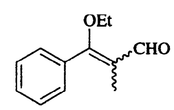
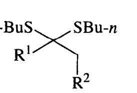
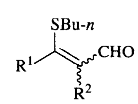
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}-C_{15}			
 R = Me or Et	1. DMF, $POCl_3$ 2. $PhNH_2$ 3. HX	 R^1 R^2 R^3 X H H H Cl (60) H H H Br (75) H H H I (31) H H H OTs (69) H H H ClO_4 (61) H H Me ClO_4 (61) H Me H ClO_4 (50) Me H Me ClO_4 (42)	81
C_{12}			
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $NaClO_4$	 (82)	33
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $NaClO_4$ 3. Me_2NH	 (41)	33
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $NaClO_4$ 3. NaOAc, H_2O	 (32)	33
	DMF, $COCl_2$	 (6) +  (26) +  (45)	63, 64
	DMF, $COCl_2$	 (55)	71
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $Me_2NH_2^+ Cl^-$	 (62)	69
	DMF, $POCl_3$	 (43-50)	68
	1. DMF, $POCl_3$ 2. PhNHMe	 (—)	68
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $Me_2NH_2^+ Cl^-$ 3. $NaClO_4$	 (57)	69

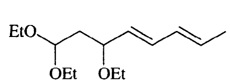
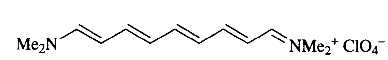
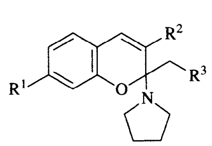
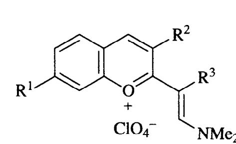
TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}-C_{15}			
	DMF, $POCl_3$	 (see below)	379

X	Ar	
S	4-ClC_6H_4	(23)
S	Ph	(36)
S	4-BrC_6H_4	(29)
O	4-FC_6H_4	(59)
O	3-ClC_6H_4	(42)
O	4-ClC_6H_4	(48)
O	4-BrC_6H_4	(70)
O	Ph	(81)
O	3-$CF_3C_6H_4$	(44)
O	3,4-$MeClC_6H_3$	(53)
O	2-MeC_6H_4	(33)
O	3-MeC_6H_4	(61)
O	4-MeC_6H_4	(22)
O	3-$MeOC_6H_4$	(4)
O	4-$MeOC_6H_4$	(26)
O	4-$MeSC_6H_4$	(15)
O	2,4-$Me_2C_6H_3$	(69)
O	3,4-$Me_2C_6H_3$	(48)
O	3,5-$Me_2C_6H_3$	(34)
O	3-EtC_6H_4	(44)
O	4-EtC_6H_4	(15)
O	4-*i*-PrC_6H_4	(36)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}			
	DMF, $COCl_2$	 (92)	63, 64
C_{13}-C_{17}			
	DMF, $POCl_3$	 (see below)	380

R^1	R^2		*E*:*Z*
Et	Me	(67)	100
2-thienyl	H	(72)	80:20
—$(CH_2)_4$—		(65)	—
Ph	H	(69)	95:5
Me	Ph	(70)	30:70

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. $[ClHC{=}NMe_2]^+ Cl^-$ 2. $Me_2NH_2^+ Cl^-$ 3. $NaClO_4$	 (77)	69
C_{15}-C_{22}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 (see below)	381

R^1	R^2	R^3	
H	Me	H	(16)
H	Me	Me	(48)
H	—$(CH_2)_2$—		(60)
H	—$(CH_2)_3$—		(66)
H	—$(CH_2)_4$—		(63)
OMe	—$(CH_2)_2$—		(60)
OMe	—$(CH_2)_3$—		(51)
OMe	—$(CH_2)_4$—		(45)
NEt_2	—$(CH_2)_2$—		(56)
NEt_2	—$(CH_2)_3$—		(41)
NEt_2	—$(CH_2)_4$—		(20)

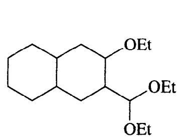
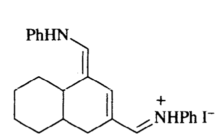
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	1. DMF, $POCl_3$ 2. $PhNH_2$•HI	 (42)	81

TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS (*Continued*)

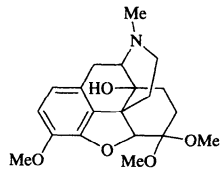
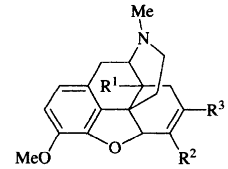
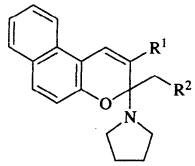
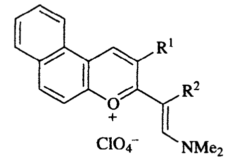
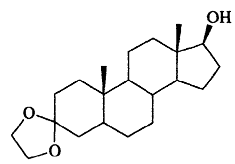
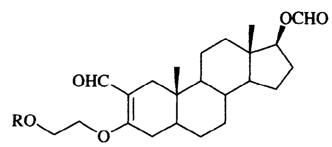
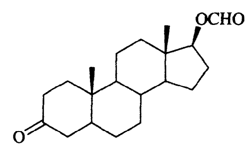
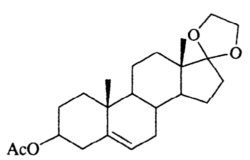
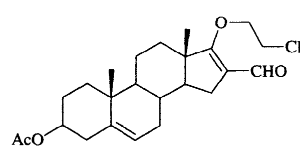
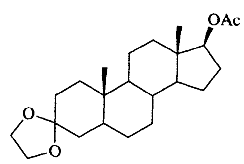
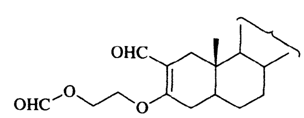
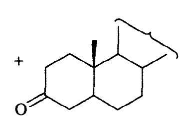
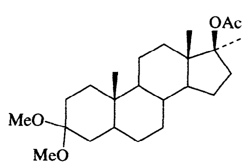
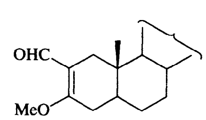
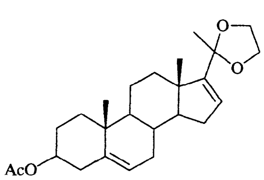
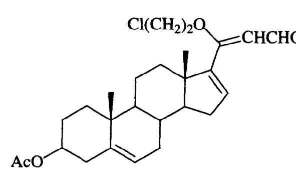
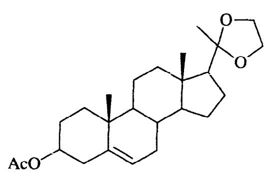
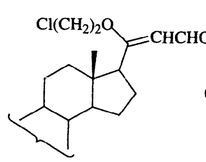
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	DMF, $POCl_3$, heat	 (—) Temp / R^1 / R^2 / R^3 rt / OH / OMe / H 50° / OCHO / OMe / H 60-70° / OCHO / OMe / CHO + Cl / OMe / H + OH / Cl / CHO + thebaine	51
C_{20}–C_{22}			
	1. DMF, $POCl_3$ 2. $HClO_4$	 R^1 R^2 —$(CH_2)_2$— (56) —$(CH_2)_3$— (52) —$(CH_2)_4$— (26)	381
C_{21}			
	DMF, $POCl_3$	 + **I** R = H **II** R = CHO  **III** **I** (4) + **II** (67) + **III** (22)	72
C_{23}			
	DMF, $POCl_3$	 (5)	273, 35
	DMF, $POCl_3$	 (92) +  (3)	72
C_{24}			
	DMF, $COCl_2$	 (—)	52
C_{25}			
	DMF, $POCl_3$	 (—)	35
	DMF, $POCl_3$	 (—)	35, 382

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TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS (*Continued*)

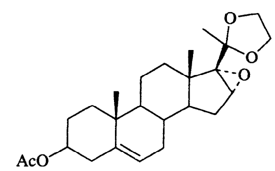
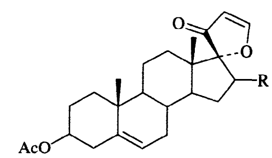
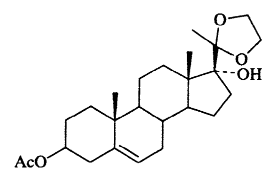
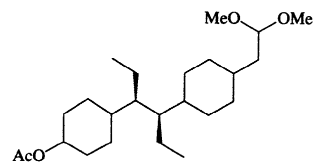
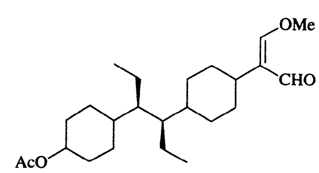
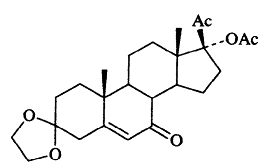
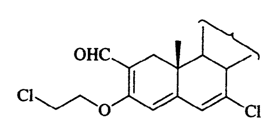
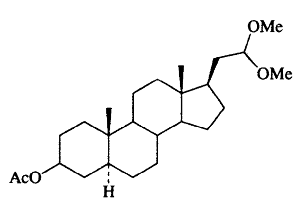
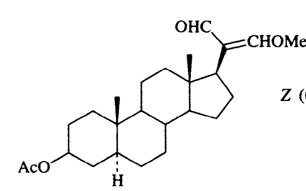
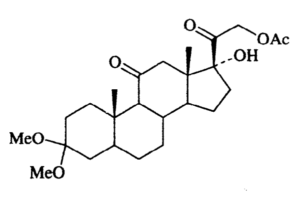
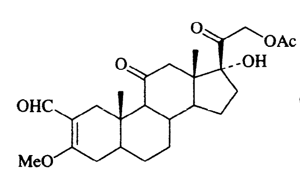
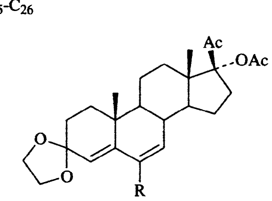
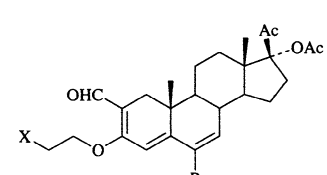
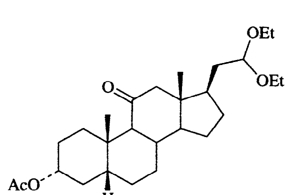
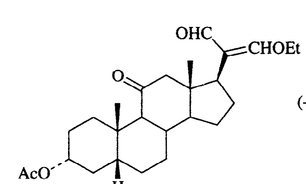
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (—) I, R = Cl	35
	DMF, $POCl_3$	I, R = H (—)	35
	DMF, $POCl_3$	 (78)	383
	DMF, $POCl_3$	 (53)	73
	DMF, $POCl_3$	 *Z* (64) + *E* (15)	384
	DMF, $COCl_2$	 (—)	52
C_{25}-C_{26}			
	DMF, $POCl_3$, heat	 R X Temp Cl Cl 60° (28) H OCHO rt (—) H Cl 60° (—) Me Cl 60° (33)	73
C_{27}			
	DMF, $POCl_3$	 (—)	385

TABLE VIII. ACETALS, KETALS AND THEIR THIO ANALOGS (*Continued*)

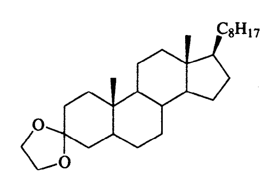
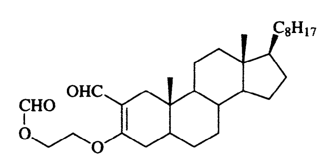
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29}			
	DMF, $POCl_3$	 (84)	72

TABLE IX. ALKYNES

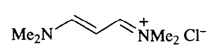
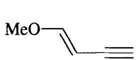
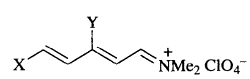
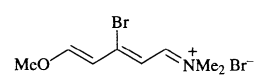
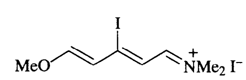
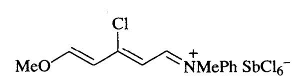
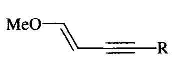
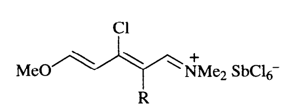
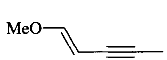
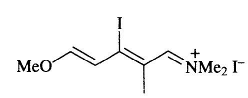
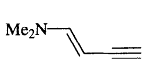
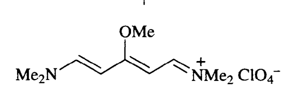
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	DMF, $COCl_2$	 (66)	74
C_5			
	1. DMF, $(COCl)_2$ 2. (See table) 3. $NaClO_4$	 Cond. 2 / X / Y: None / MeO / Cl (60) EtSH / EtS / Cl (30) PhSH / PhS / Cl (40) Me_2NH / Me_2N / Me_2N (51)	77
	DMF, $Ph_3P{\bullet}Br_2$	 (70)	77
	DMF, $POCl_3$, I_2	 (64)	77
	MFA, $COCl_2$, $SbCl_5$	 (66)	77
C_5-C_6			
	$[Me_2N{=}CHCl]^+ SbCl_6^-$	 R: D (48) Me (—)	77
C_6			
	DMF, $Ph_3P{\bullet}I_2$	 (—)	77
	1. $[Me_2N{=}CHOMe]^+ MeSO_4^-$ 2. $NaClO_4$	 (81)	77

TABLE IX. ALKYNES (*Continued*)

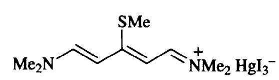
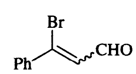
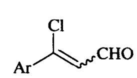
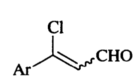
Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
	$[Me_2N{=}CHSMe]^+ HgI_3^-$		(83)	77
C_8 Ph—≡	DMF, $Ph_3P{\cdot}Br_2$		(60)	76
C_8-C_{10} Ar—≡	MFA, $POCl_3$		Ar: Ph (45); 4-BrC_6H_4 (24); 4-$MeOC_6H_4$ (51)	243
	DMF, MFA or *N*-formylmorpholine, $POCl_3$		Ar: Ph (67); 3-MeC_6H_4 (70); 4-MeC_6H_4 (70); 4-$MeOC_6H_4$ (70); 4-Ethynyl-C_6H_4 (—)	75

TABLE X. ALDEHYDES

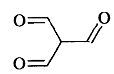
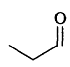
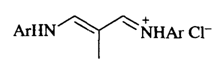
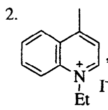
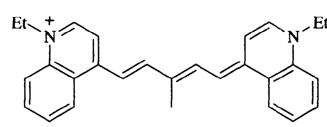
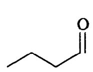
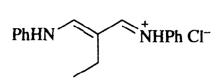
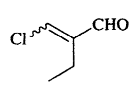
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
	DMF, $COCl_2$	 (—)	32
C_3			
	1. DMF, $POCl_3$ 2. $ArNH_2$•HCl	 Ar Ph (55)	46
		$2\text{-}HOC_6H_4$ (42)	66
		$4\text{-}BrC_6H_4$ (31)	66
		$2\text{-}MeC_6H_4$ (30)	66
		$3\text{-}MeC_6H_4$ (30)	66
		$4\text{-}MeC_6H_4$ (29)	66
		$4\text{-}MeOC_6H_4$ (29)	66
	1. DMF, $POCl_3$ 2. , Ac_2O, Et_3N, pyridine 3. $HClO_4$	 ClO_4^- (30)	48
C_4			
	1. DMF, $POCl_3$ 2. $PhNH_2$•HCl	 (18)	46
	DMF, $POCl_3$	 (40)	78, 79

TABLE X. ALDEHYDES (*Continued*)

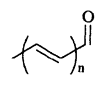
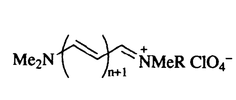
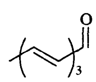
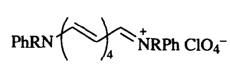
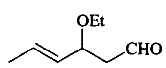
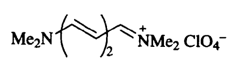
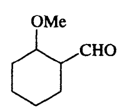
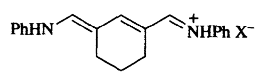
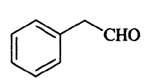
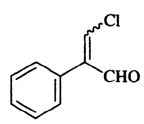
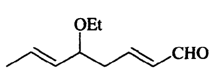
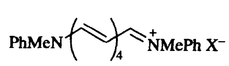
Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4-C_{10}				
	1. DMF, $POCl_3$ 2. MeRNH, $NaClO_4$		n R 1 Me (28) 2 Me (11) 3 Me (60) 4 Ph (33)	80
C_8				
	1. DMF, $POCl_3$ 2. PhRNH 3. $HClO_4$		R H (42) Me (40)	68
	1. DMF, $POCl_3$ 2. Me_2NH 3. $HClO_4$		(60)	68
	1. DMF, $POCl_3$ 2. $PhNH_2$		(8-10)	81
	DMF, $POCl_3$	 (54)		94
C_{10}				
	1. DMF, $POCl_3$ 2. PhMeNH 3. HX		X Cl (15) Br (17) ClO_4 (15)	68

TABLE XI. KETONES

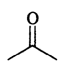
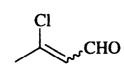
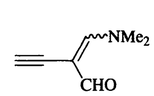
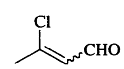
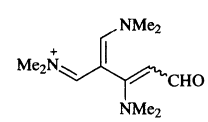
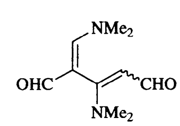
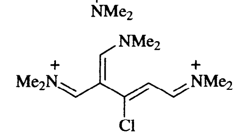
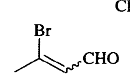
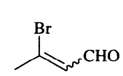
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3			
	DMF, $POCl_3$	 (39)	79, 386, 83
	1. DMF, $POCl_3$ 2. K_2CO_3	 (14)	299
	DMF, $COCl_2$	 (—)	78
	DMF, $COCl_2$	 Cl^- (31)	299
	1. DMF, $COCl_2$ 2. K_2CO_3	 (25)	299
	1. DMF, $COCl_2$ 2. $NaClO_4$	 $2ClO_4^-$ (87)	299
	DMF, PBr_3	 (20)	92
	$[BrHC{=}NMe_2]^+Br^-$	 (27)	92

TABLE XI. KETONES (*Continued*)

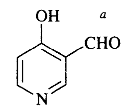
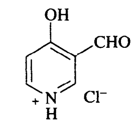
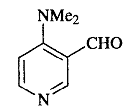
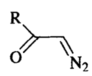
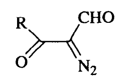
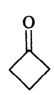
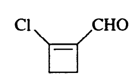
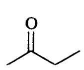
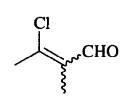
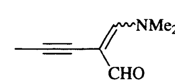
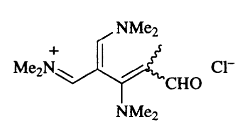
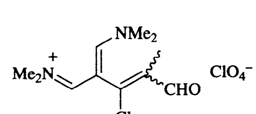
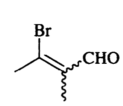
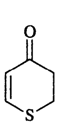
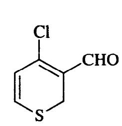
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $COCl_2$ 2. NH_3 3. $Cu(OAc)_2$	 [a] (66)	299
	1. DMF, $COCl_2$ 2. NH_3 3. HCl	 (39)	299
	1. DMF, $COCl_2$ 2. K_2CO_3 3. NH_4Cl, H_2O, NH_3	 (15)	299
C_3-C_{12}			
	1. $[Me_2N{=}CHCl]^+Cl^-$, −10° 2. rt, 1h	 R: Me (14); *i*-Pr (27); *i*-Bu (21); *t*-Bu (44); 2-furyl (30); 2-thienyl (21); 1-Me-2-pyrrolyl (12); 1-Me-3-pyrrolyl (15); 3,5-Me_2-3-furyl (19); 2,5-Me_2-3-furyl (17); 4-MeC_6H_4 (66); 4-$MeOC_6H_4$ (49); 2,4-$(MeO)_2C_6H_3$ (20); 1-naphthyl (41); 2-naphthyl (35)	112d
C_4			
	DMF, $POCl_3$	 (46)	71
	DMF, $POCl_3$	 Z:E (77) — (31) 1:2 (18) 1:69	79, 386, 83 387 82
	1. DMF, $POCl_3$ 2. K_2CO_3	 (18)	299
	1. DMF, $POCl_3$ 2. K_2CO_3	 (31)	299
	1. DMF, $POCl_3$ or $COCl_2$ 2. $NaClO_4$	 (67)	299
	DMF, PBr_3	 (36)	92
C_5			
	DMF, $POCl_3$	 (30)	388, 389

TABLE XI. KETONES (*Continued*)

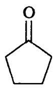
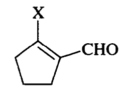
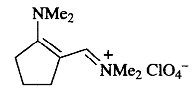
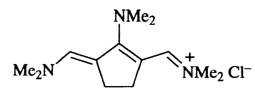
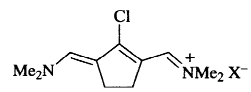
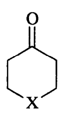
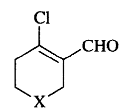
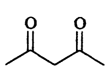
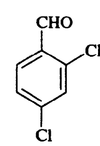
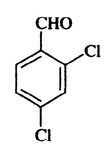
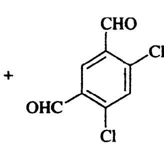
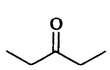
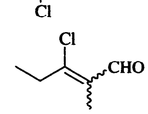
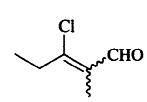
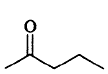
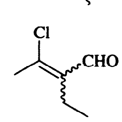
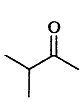
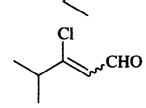
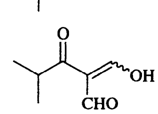
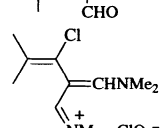
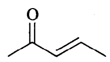
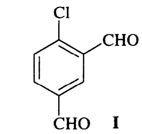
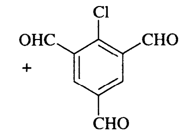
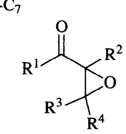
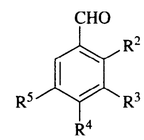
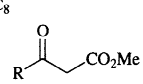
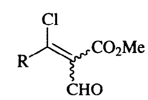
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
		 X	
	DMF, $POCl_3$	Cl (82)	126, 79, 386
	DMF, $COCl_2$	Cl (—)	78
	DMF, PBr_3	Br (45)	92
	$[BrHC{=}NMe_2]^+Br^-$	Br (31)	92
	1. DMF, $POCl_3$ 2. $HNMe_2$ 3. $NaClO_4$	 (34)	390
	1. DMF, $COCl_2$ 2. K_2CO_3	 (20)	71
		 X	
	1. DMF, $COCl_2$ 2. $HClO_4$	ClO_4 (100)	71
	DMF, $POCl_3$	PO_2Cl_2 (—)	48
	DMF, $POCl_3$	 X: O (44); S (52)	388, 389
	DMF, $POCl_3$	 (98)	88, 38, 123, 124, 391
	N-formylmorpholine, $POCl_3$	 (17) +  (29)	123
	DMF, $POCl_3$	 (77)	386, 43, 48
	DMF, $COCl_2$	 (—)	78
	DMF, $POCl_3$	 (59)	83
	DMF, $POCl_3$	 (14)	83
	1. DMF, $COCl_2$ 2. $NaClO_4$ 3. NaOH	 (68)	68
	1. DMF, $COCl_2$ 2. $NaClO_4$	 (16)	48

TABLE XI. KETONES (*Continued*)

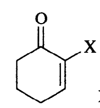
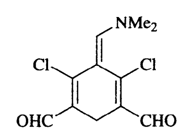
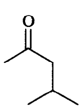
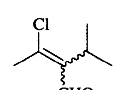
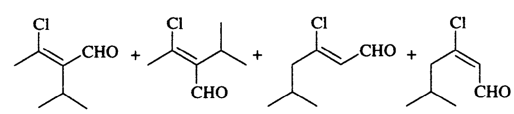
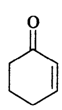
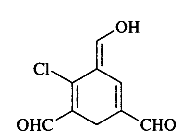
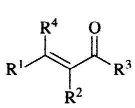
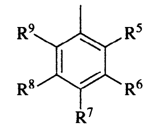
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 I (18) +  (10)	392
	DMF, $POCl_3$	I (44)	38
C_5-C_7 	DMF, $POCl_3$		89a

R^1	R^3	R^2	R^4
Me	H	H	Me
Me	Me	H	Me
Me	H	H	Me
Me	H	Me	Me
—$(CH_2)_3$—		H	H
—$(CH_2)_3$—		H	Me

R^2	R^3	R^4	R^5			R^2	R^3	R^4	R^5	
Cl	Cl	H	H	(18)	+	H	CHO	Cl	Cl	(30)
Cl	Cl	Me	H	(45)	+	—	—	—	—	(0)
H	Cl	Cl	Me	(38)		—	—	—	—	(0)
H	CHO	Cl	Me	(29)		—	—	—	—	(0)
Cl	CHO	H	H	(24)	+	Cl	Cl	H	H	(13)
Cl	H	Me	CHO	(19)	+	Cl	Cl	Me	H	(11)

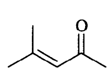
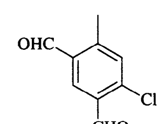
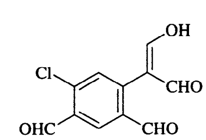
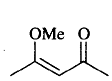
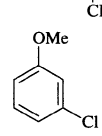
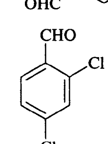
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5-C_8 	DMF, $POCl_3$		393

R	
CF_3	(—)
HCF_2	(—)
$H(CF_2)_2$	(—)
C_4F_9	(—)
$H(CF_2)_4$	(—)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6  X = Cl, Br	DMF, $POCl_3$	 From X = Cl (43) From X = Br (59)	123
	DMF, $POCl_3$	 (20)	83
	DMF, $POCl_3$	 1 : 10 : 72 : 17	84[b]
	*N*-formylmorpholine, $POCl_3$	 (45)	123
	DMF, $POCl_3$		392

R^1	R^2	R^3	R^4
Me	H	Et	H
Et	H	Me	H
Me	H	Me	Me
Me	Me	Me	H

	R^5	R^6	R^7	R^8	R^9	
	Cl	CHO	H	CHO	H	(20)
	H	CHO	Cl	CHO	H	(19)
	H	Cl	CHO	H	H	(11)
and	H	Cl	CHO	H	CHO	(23)
	Cl	CHO	H	CHO	H	(42)
and	Cl	CHO	H	H	H	(15)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (33) +  (15)	38
	DMF, $POCl_3$	 (42) +  (23)	38

500

501

TABLE XI. KETONES (*Continued*)

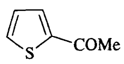
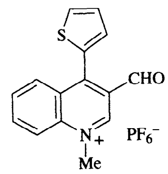
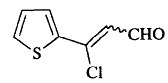
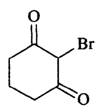
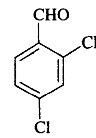
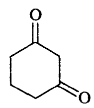
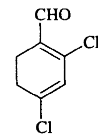
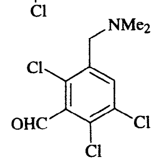
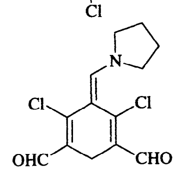
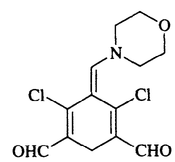
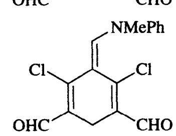
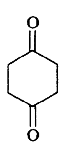
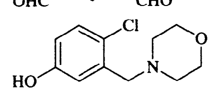
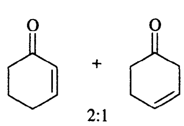
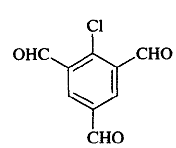
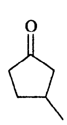
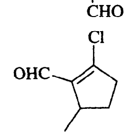
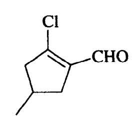
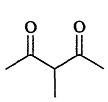
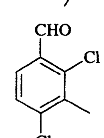
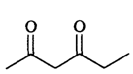
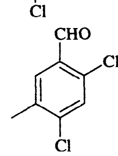
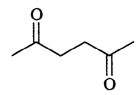
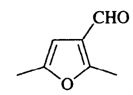
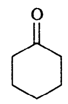
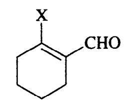
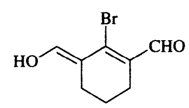
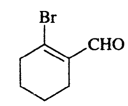
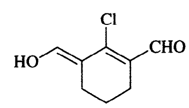
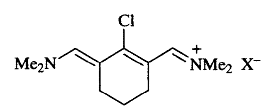
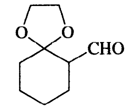
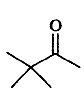
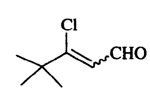
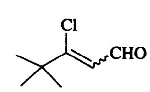
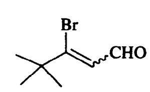
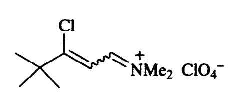
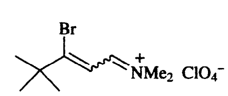
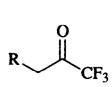
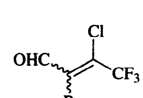
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. MFA, $POCl_3$ 2. $NH_4^+PF_6^-$	 (63)	300
	DMF, $POCl_3$	 (11)	83
	*N*-formylmorpholine, $POCl_3$	 (20)	123
	DMF, $POCl_3$	 (24)	123, 124
	DMF, $POCl_3$, Cl_2C=CHCl, boil	 (20)	122
	N-formylpyrrolidine, $POCl_3$	 (42)	122
	N-formylmorpholine, $POCl_3$	 (30)	123, 122
	MFA	 (10)	122
	*N*-formylmorpholine, $POCl_3$	 (16)	123
	DMF, $POCl_3$	 (61)	121
	DMF, $POCl_3$	 (17) +  (26)	119
	DMF, $POCl_3$	 (51)	391
	DMF, $POCl_3$	 (25)	391

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (60)	89
	DMF, $POCl_3$	 **I**, X = Cl (80)	126, 79, 386, 113
	DMF, $COCl_2$	**I**, X = Cl (—)	78
	DMF, PBr_3	**I**, X = Br (54)	92
	1. DMF, PBr_3 2. NaOAc	 (—) +  (—)	92
	1. DMF, $COCl_2$ 2. NaOAc	 (>95)	118, 71
	1. DMF, $COCl_2$ 2. NaOAc 3. $HClO_4$	 **I**, X = ClO_4 (69)	71
	DMF, $POCl_3$	**I**, X = PO_2Cl_2 (—)	48
	1. DMF, $POCl_3$ 2. $NaOCH_2CH_2OH$	 (36)	115
	DMF, $POCl_3$	 (80)	386, 78, 83
	DMF, $COCl_2$	 (80)	79
	DMF, PBr_3	 (75)	92
	1. DMF, $POCl_3$ 2. $NaClO_4$	 (47)	33
	1. DMF, PBr_3 2. $NaClO_4$	 (84)	92
C_6-C_{10}			
	DMF, $POCl_3$		

Conditions	R	Yield	Z:E	Refs.
DMF, $POCl_3$	CO_2Et	(76)	30:70	86, 394
	3-thienyl	(70)	30:70	86
	$4\text{-}ClC_6H_4$	(78)	60:40	86
	$4\text{-}BrC_6H_4$	(77)	50:50	87
	Ph	(91)	60:40	86
	Ph	(50)	50:50	394
	Ph	(75)	40:60	87
	$3\text{-}CF_3C_6H_4$	(79)	55:45	87
	$4\text{-}MeC_6H_4$	(81)	—	395
	$4\text{-}MeOC_6H_4$	(75)	45:55	87
DMF, $COCl_2$	CO_2Et	(—)	—	395

TABLE XI. KETONES (*Continued*)

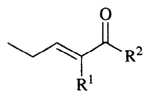
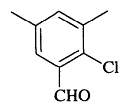
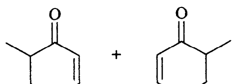
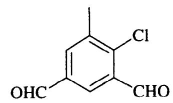
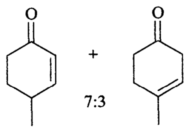
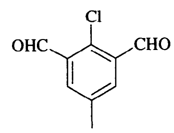
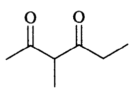
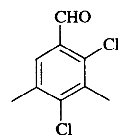
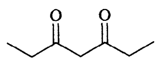
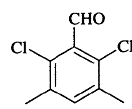
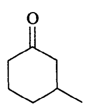
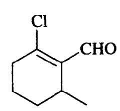
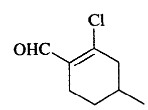
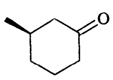
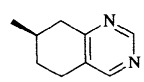
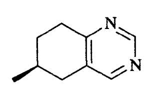
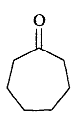
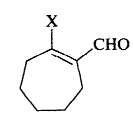
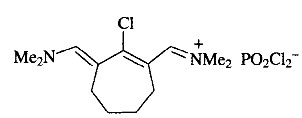
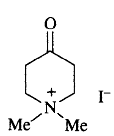
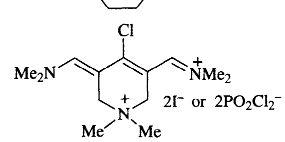
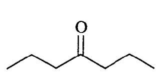
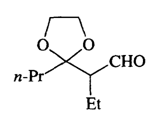
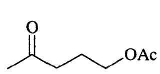
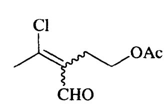
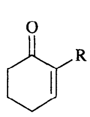
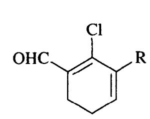
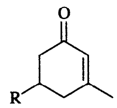
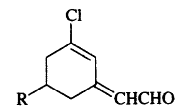
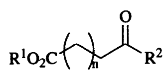
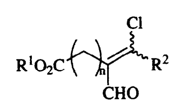
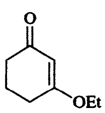
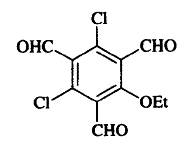
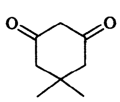
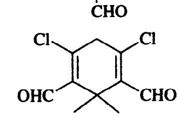
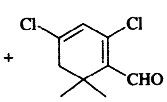
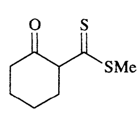
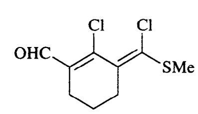
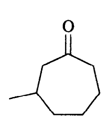
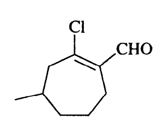
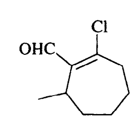
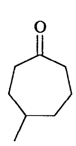
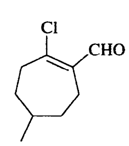
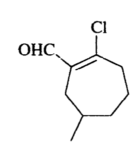
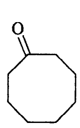
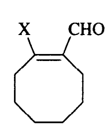
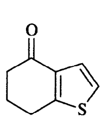
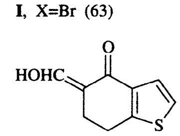
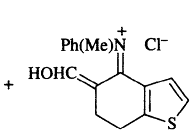
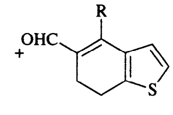
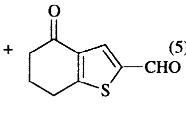
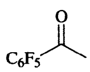
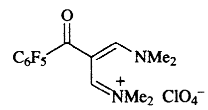
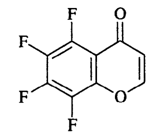
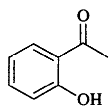
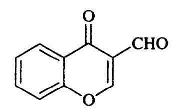
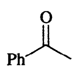
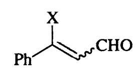
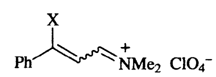
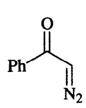
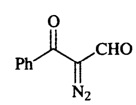
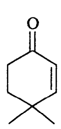
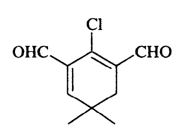
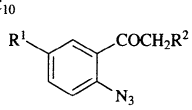
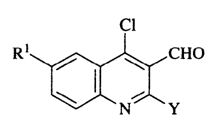
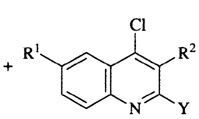
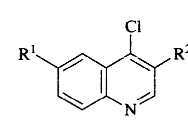
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	DMF, $POCl_3$	 R^1 R^2: Me Me (12); H Et (8)	392
 20:1	DMF, $POCl_3$	 (60)	121
 7:3	DMF, $POCl_3$	 (63)	121
	DMF, $POCl_3$	 (24)	391
	DMF, $POCl_3$	 (7.5)	391
	DMF, $POCl_3$	 (5) +  (47)	119
	1. DMF, $POCl_3$ 2. $HCONH_2$	 (17) +  (17)	117
	DMF, $POCl_3$	 **I**, X=Cl (65)	79, 386
	DMF, $COCl_2$	**I**, X = Cl (88)	126
	DMF, PBr_3	**I**, X = Br (45)	92
	$[BrHC{=}NMe_2]^+ Br^-$	**I**, X = Br (67)	92
	DMF, $POCl_3$	 (—)	48
	DMF, $POCl_3$	 (—)	48
	1. DMF, $POCl_3$ 2. $NaOCH_2CH_2OH$	 (50)	115
	DMF, $POCl_3$	 (30)	396
C_7-C_8			
	*N*-formylmorpholine, $POCl_3$	 R: Me (33); Et (12)	397, 350

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	N-formylmorpholine, $POCl_3$	 R: H (66); Me (73)	350
C_7-C_{18} 	DMF, $POCl_3$		90
C_8 	N-formylmorpholine, $POCl_3$	 (31)	350
	DMF, $POCl_3$	 I (30) +  (33)	398
	N-formylmorpholine, $POCl_3$	I (22)	123
	1. DMF, $POCl_3$, 0–5° 2. rt, 20 h	 (38)	399
	DMF, $POCl_3$	 (40) +  (2)	119
	DMF, $POCl_3$	 (24) +  (24)	119
	DMF, $POCl_3$	 I, X=Cl (77)	126, 386
	DMF, $COCl_2$	I, X=Cl (—)	78
	DMF, PBr_3	I, X=Br (37)	92
	$[BrHC{=}NMe_2]^+ Br^-$	I, X=Br (63)	92
	1. MFA, $POCl_3$ 2. NaOAc	 (29) +  (19) +  R: Cl (5); NMePh (38) +  (5)	220

R^1	R^2	n	
Et	Me	1	(—)
Et	n-C_4H_9	1	(53)
Et	2-thienyl	1	(77)
Me	4-$MeOC_6H_4$	1	(65)
Et	Ph	1	(80)
Et	4-ClC_6H_4	1	(72)
Et	4-MeC_6H_4	1	(77)
Et	4-$MeOC_6H_4$	1	(81)
Et	$3,4$-$(MeO)_2C_6H_3$	1	(77)
Et	4-MeC_6H_4	2	(83)
Et	Ph	3	(77)
Et	4-$(i$-$Pr)C_6H_4$	1	(67)
Et	4-$(c$-$C_6H_{11})C_6H_4$	1	(60)

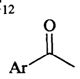
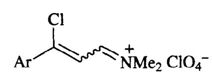
TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. $HClO_4$	 (36) +  (3)	112a
	DMF, $POCl_3$	 (—)	400
	DMF, PBr_3	 I, X = Br (45)	92
	$[BrHC{=}NMe_2]^+ Br^-$	I, X = Br (68)	92
	1. $[IHC{=}NMe_2]^+ I^-$ 2. $NaClO_4$ 3. NaOAc	I, X = I (72)	345
	1. $[IHC{=}NMe_2]^+ I^-$ 2. $NaClO_4$	 II, X = I (90)	345
	1. DMF, $COCl_2$ 2. $NaClO_4$	II, X = Cl (98)	71
	1. DMF, $PhOP(O)Cl_2$ 2. $NaClO_4$	II, X = Cl (62)	345
	1. DMF, PBr_3 2. $NaClO_4$	II, X = Br (50)	92
	1. $[BrHC{=}NMe_2]^+ Br^-$ 2. $NaClO_4$	II, X = Br (76)	92
	$[ClHC{=}NMe_2]^+ Cl^-$	 (50)	160
	*N*-formylmorpholine, $POCl_3$	 (29)	350
C_8-C_{10} 	XCHO, $POCl_3$	 I +  II +  III	93c, 93d

R^1	R^2	X	Y	I	II	III
H	H	Me_2N	Me_2N	(35)	(50)	(0)
H	H	PhMeN	PhMeN	(0)	(41)	(0)
H	H	Morpholino	Morpholino	(30)	(12)	(0)
Br	H	Me_2N	Me_2N	(28)	(26)	(0)
Cl	H	Me_2N	Me_2N	(44)	(44)	(0)
H	Me	Me_2N	Me_2N	(0)	(53)	(19)
Br	Me	Me_2N	Me_2N	(0)	(80)	(0)
Cl	Me	Me_2N	Me_2N	(0)	(78)	(0)
H	Me	PhMeN	PhMeN	(0)	(46)	(2)*
H	Me	Morpholino	Morpholino	(0)	(53)	(18)
H	Me	Piperidino	Piperidino	(0)	(53)	(20)
H	Et	PhMeN	PhMeN	(0)	(29)	(3)*
H	Et	Morpholino	Morpholino	(0)	(29)	(33)
H	Et	Piperidino	Piperidino	(0)	(19)	(51)
Br	Et	Me_2N	Me_2N	(0)	(30)	(36)

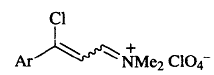
*In these compounds Y = $(4\text{-}OHCC_6H_4)MeN$

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8-C_{12}			
	1. DMF, $POCl_3$ 2. $HClO_4$		

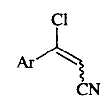
Ar		Refs.
3-$O_2NC_6H_4$	(87)	401
4-$O_2NC_6H_4$	(66)	
3-$CF_3C_6H_4$	(74)	
4-$CF_3C_6H_4$	(70)	

Conditions: 1. $[ClHC{=}NMe_2]^+ Cl^-$, $CHCl_3$, boiling point 2. $NaClO_4$

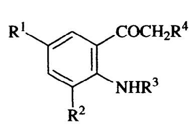


Ar		Refs.
4-ClC_6H_4	(76)	402
4-$O_2NC_6H_4$	(64)	402
4-MeC_6H_4	(76)	402
4-$MeOC_6H_4$	(82)	402
4-$Me_2NC_6H_4$	(82) [c]	33

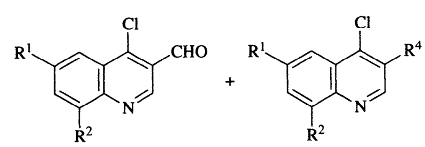
Conditions: 1. DMF, $POCl_3$ 2. NH_2OH



Ar		Refs.
4-ClC_6H_4	(74)	403
4-BrC_6H_4	(54)	
4-$O_2NC_6H_4$	(61)	
Ph	(50)	
4-MeC_6H_4	(46)	
4-$MeOC_6H_4$	(47)	
2-naphthyl	(44)	



Conditions: 1. DMF, $POCl_3$, 0° 2. 90°, time



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R^1	R^2	R^3	R^4	Time	I	II	Refs.
Cl	H	H	H	4.5 h	(60)	(0)	112c
Br	H	H	H	3-6 h	(66)	(0)	112c
H	H	H	H	3-6 h	(43)	(0)	112c
Cl	H	H	Me	4-6 h	(0)	(56)	112b
Br	H	H	Me	4-6 h	(0)	(68)	112b
H	H	H	Me	4-6 h	(0)	(36)	112b
Br	H	Ac	H	3-6 h	(74)	(8)	112c
NO_2	H	Ac	H	3-6 h	(87)	(0)	112c
H	NO_2	Ac	H	3-6 h	(24)	(17)	112c
H	H	Ac	H	3-6 h	(60)	(14)	112c
H	H	H	Et	5 h	(0)	(38)	112c
Br	H	Ac	Me	4-6 h	(0)	(90)	112b
NO_2	H	Ac	Me	4-6 h	(0)	(75)	112b
H	H	Ac	Me	4 h	(0)	(89)	112b
Br	H	Ac	Et	3-6 h	(0)	(79)	112c
NO_2	H	Ac	Et	3-6 h	(0)	(86)	112c
H	H	Ac	Et	3-6 h	(0)	(81)	112c

C_8-C_{14}

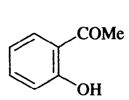
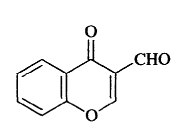
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $(Cl_2PO)_2O$, 0°	 (61)	102

TABLE XI. KETONES (*Continued*)

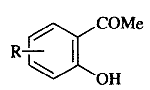
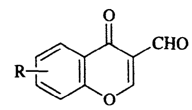
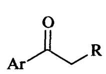
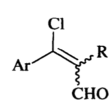
Substrate	Conditions	Product(s) and Yield(s) (%)			Refs.
	DMF, $POCl_3$		R		
			3,5-Br_2	(60)	103
			3,5-Cl_2	(77)	103
			5-Cl	(53)	103
			H	(71)	100
			5-Cl-7-Me	(58)	103
			4-Me	(86)	100
			4,5-Me_2	(55)	103
			3,5-Br_2	(40)	101, 102
			5-Cl	(73)	101, 102
			5-O_2N	(54)	101, 102
			5-Me	(65)	101, 102
			5-CN	(55)	101, 102
			4-MeO	(6)	101, 102
			5-MeO	(62)	101, 102
			6-MeO	(61)	101, 102
			5-HO_2C	(14)	101, 102
			3,5-Me_2	(25)	101, 102
			5-Et	(76)	101, 102
			5-Me_2N	(49)	101, 102
			4,5-$(MeO)_2$	(4)	101, 102
			4-AcO	(67)	101, 102
			6-AcO	(97)	101, 102
			5-*n*-Pr	(53)	101, 102
			5-*i*-Pr	(42)	101, 102
			5-*n*-Bu	(32)	101, 102
			4,5-$(AcO)_2$	(66)	101, 102
			4,6-$(AcO)_2$	(80)	101, 102
			5-*n*-C_6H_{13}	(60)	101, 102
			5-*c*-C_6H_{11}	(43)	101, 102
	DMF, $POCl_3$	 Ar	R		
		4-ClC_6H_4	H	(30)	127
		4-BrC_6H_4	H	(24)	127
		4-$O_2NC_6H_4$	H	(71)	387
		Ph	H	(54)	91, 79, 94, 386, 387, 404
					386
		Ph	CF_3	(—)	394
		2-$MeOC_6H_4$	H	(40)	387
		3-$MeOC_6H_4$	H	(71)	95
		4-$MeOC_6H_4$	H	(70)	95, 127, 404
		2-BrC_6H_4	Me	(85)	94
		4-BrC_6H_4	Me	(79)	94
		2-$O_2NC_6H_4$	Me	(69)	94
		3-$O_2NC_6H_4$	Me	(58)	94
		4-$O_2NC_6H_4$	Me	(80)	94
		Ph	Me	(98)	372, 79, 94, 386, 387
		2-MeC_6H_4	Me	(63)	94
		3,4-$(MeO)_2C_6H_3$	H	(60)	404, 83
		2-(3-methylindolyl)	H	(50)	260
		2-naphthyl	H	(56)	83, 387
		6-MeO-2-naphthyl	H	(30)	387
		4-PhC_6H_4	H	(36)	127
		Ph	Ph	(50)	127
		Ph	Ph	(24)[d]	405

TABLE XI. KETONES (*Continued*)

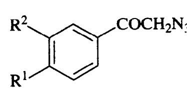
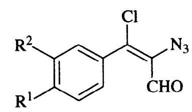
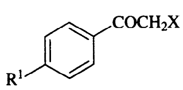
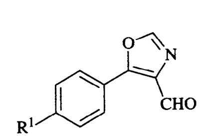
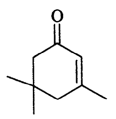
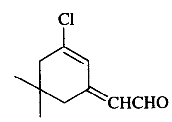
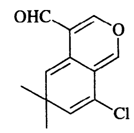
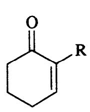
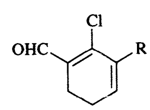
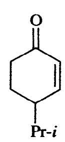
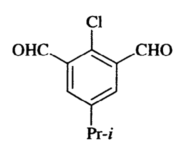
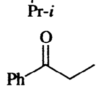
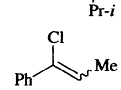
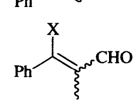
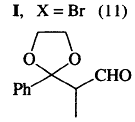
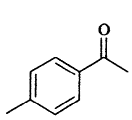
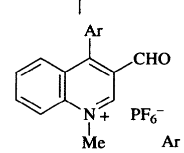
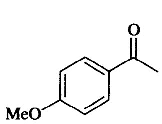
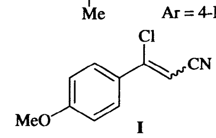
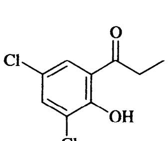
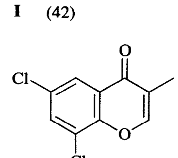
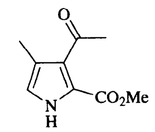
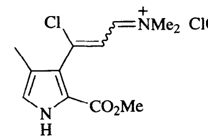
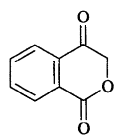
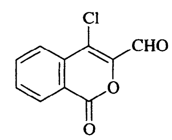
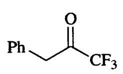
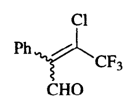
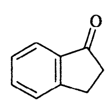
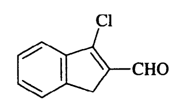
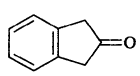
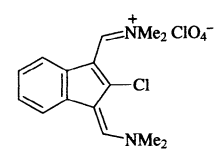
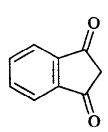
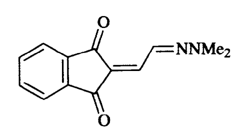
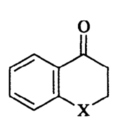
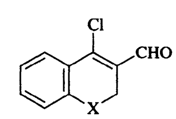
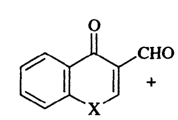
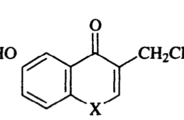
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$ (6 eq), rt	 R^1 R^2 Me H (70) Cl H (62) Br H (65) Ph H (80) H Me (64)	93a, 93b
	DMF, $POCl_3$, 80-90° ($X = N_3$); or 1. DMF, NaN_3 2. $POCl_3$, heat (X = Br)	 R^1 ($X = N_3$) (X = Br) Me (36) (45) Cl (36) (48) Br (42) (56) Ph (45) (61)	93a, 93b
C_9			
		 I +  II	
	DMF, $POCl_3$	I (80) Z:E = 2:1 + II (—)	406
	DMF, $POCl_3$ (3 eq)	I (—) + II (51)	406
	N-formylmorpholine, $POCl_3$	I (87) + II (—)	350
	*N*-formylmorpholine, $POCl_3$	 R *n*-Pr (3) *i*-Pr (5)	397
	*N*-formylmorpholine, $POCl_3$	 (31)	350
	1. DMF, $POCl_3$ 2. NaOAc, H_2O	 (92)	94
	DMF, $COCl_2$	 I, X=Cl (60)	79, 78
	DMF, PBr_3	I, X = Br (71)	92
	$[BrHC{=}NMe_2]^+ Br^-$	I, X = Br (11)	92
	1. DMF, $POCl_3$ 2. $NaOCH_2CH_2OH$	 (59)	115
	1. MFA, $POCl_3$ 2. $NH_4^+ PF_6^-$	 (32) Ar = 4-MeC_6H_4	300
	1. DMF, PCl_5 2. NH_2OH	 I (50)	403
	1. DMF, $POCl_3$ 2. NH_2OH	I (42)	403
	DMF, $POCl_3$	 (69)	103

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. ClO_4^-	 (33)	407
	DMF, $POCl_3$	 (80)	408
	DMF, $POCl_3$	 (80) *E*:*Z* = 4:6	394, 409
	DMF, $POCl_3$	 (—)	74
	1. $[ClHC{=}NMe_2]^+Cl^-$ 2. $NaClO_4$	 (92)	36
	$Me_2NN{=}CHCHO$, $POCl_3$	 (42)	135
	DMF, $POCl_3$	 I X: O (36); S (68)	127
	DMF, $POCl_3$ (n eq)	I +  II +  III	388, 389

X	n	Temp.	I	II	III
O	1.3	65°	(—)	(0)	(0)
O	5	100°	(0)	(0)	(48)
S	1.3	20°	(—)	(0)	(0)
S	5	100°	(40)	(29)	(0)

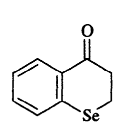
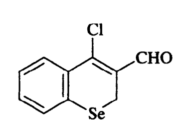
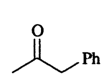
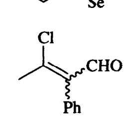
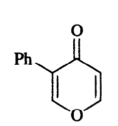
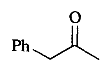
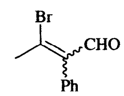
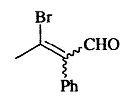
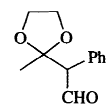
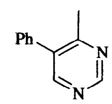
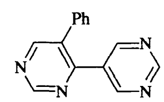
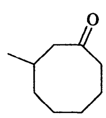
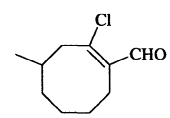
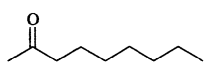
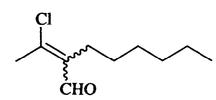
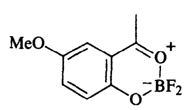
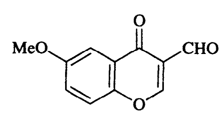
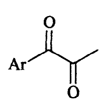
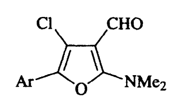
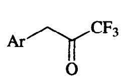
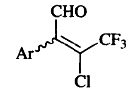
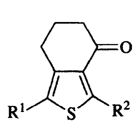
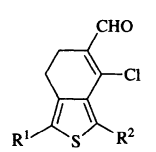
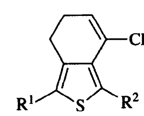
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	—	 (—)	128
	DMF, $POCl_3$	 I (67)	94, 387
	DMF, $POCl_3$	I (—) *E*:*Z* = 58:42	82
	—	I (—)	394
	DMF, $POCl_3$, (4 eq)	 (60)	410

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, PBr_3	 (25)	92
	$[BrHC{=}NMe_2]^+Br^-$	 (56)	92
	1. DMF, $POCl_3$ 2. $NaOCH_2CH_2OH$	 (32)	115
	$HCONH_2$, $POCl_3$	 (13) +  (3)	411
	DMF, $POCl_3$	 (56)	119
	DMF, $POCl_3$	 (65)	83
	DMF, $POCl_3$	 (97)	412
C_9-C_{10}			
	1. DMF, $POCl_3$ 2. $NaClO_4$ 3. NaOH	 Ar Ph (36) 4-ClC_6H_4 (28) 4-HOC_6H_4 (15) 4-$MeOC_6H_4$ (36)	413
	1. DMF, $POCl_3$, rt 2. 65°, 6 h	 Ar — *E*:*Z* Ph (75) 63:37 4-BrC_6H_4 (77) 50:50 3-$CF_3C_6H_4$ (79) 46:54 4-$MeOC_6H_4$ (75) 55:45	87
C_9-C_{12}			
	1.DMF, $POCl_3$, 0° 2. 60°, 3 h	 I +  II	414

R^1	R^2	I	II
H	SMe	(56)	(30)
H	SO_2Me	(46)	(0)
CO_2Et	SMe	(61)	(25)
CO_2Et	SO_2Me	(0)	(0)

TABLE XI. KETONES (*Continued*)

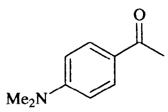
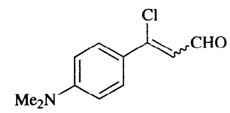
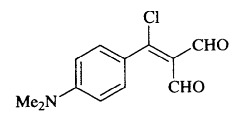
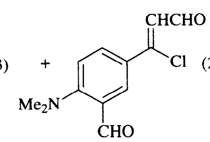
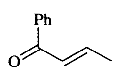
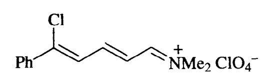
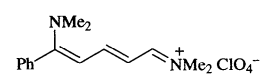
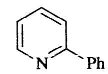
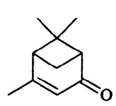
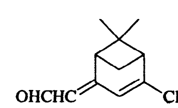
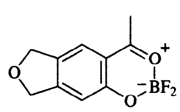
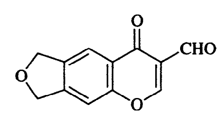
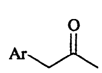
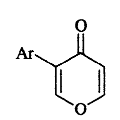
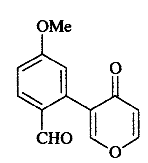
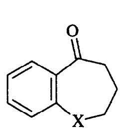
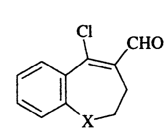
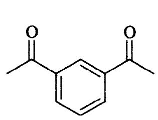
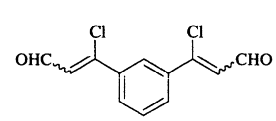
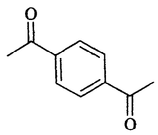
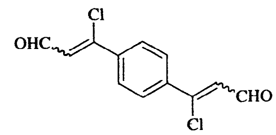
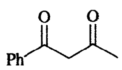
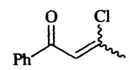
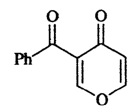
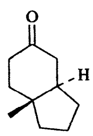
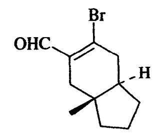
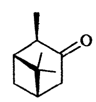
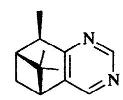
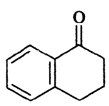
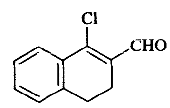
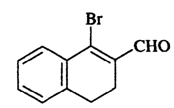
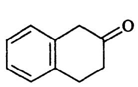
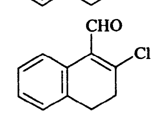
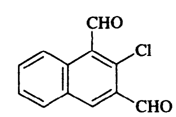
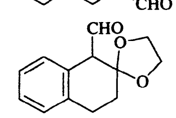
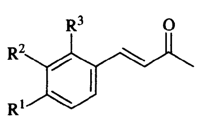
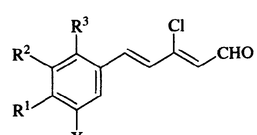
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	1. $[ClHC{=}NMe_2]^+Cl^-$, rt 2. $NaClO_4$ 3. $NaHCO_3$	 (66)	33
	1. $[ClHC{=}NMe_2]^+Cl^-$, 75° 2. H_2O	 (23) +  (25)	33
	1. $[ClHC{=}NMe_2]^+Cl^-$ 2. $NaClO_4$	 (65)	69
	1. $[ClHC{=}NMe_2]^+Cl^-$ 2. $NaClO_4$ 3. Me_2NH	 (29)	69
	1. $[ClHC{=}NMe_2]^+Cl^-$ 2. $NaClO_4$ 3. Me_2NH 4. NH_3, NH_4Cl	 (20)	69
	*N*-formylmorpholine, $POCl_3$	 (95)	350
	DMF, $POCl_3$	 (7)	412
	DMF, $POCl_3$ (4 eq)	 Ar: 2-$MeOC_6H_4$ (63); 4-$MeOC_6H_4$ (70)	410
	DMF, $POCl_3$ (4 eq)	 Ar: 3-$MeOC_6H_4$ (72)	410
	DMF, $POCl_3$	 X: O (70); S (54)	127
	DMF, $POCl_3$	 (58)	415

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (55)	391, 415
	DMF, $POCl_3$, 50°	 (50)	391
	DMF, $POCl_3$, 80°	 (18.5)	391
	DMF, PBr_3	 (47)	416
	1. DMF, $POCl_3$ 2. $HCONH_2$	 (33)	116
	DMF, $POCl_3$	 (88)	125, 126, 417, 418, 419
	DMF, PBr_3	 (—)	420
	DMF, $POCl_3$, 27°, 8 h	 (84)	418
	1. DMF, $POCl_3$, 100°, 5 min 2. rt, overnight	 (54)	421
	1. DMF, $POCl_3$ 2. $NaOCH_2CH_2OH$	 (36)	115
C_{10}-C_{11} 	DMF, $POCl_3$	 I, X = H; or II, X = CHO	422

R^1	R^2	R^3	Temp	I	II
H	H	Cl	40°	(0)	(68)
Cl	H	H	90°	(65)	(0)
H	H	H	0°	(65)	(0)
H	H	H	90°	(0)	(60)
Me	H	H	90°	(65)	(0)
H	H	Me	40°	(0)	(69)
OMe	H	H	90°	(62)	(0)
H	OMe	H	90°	(0)	(65)
H	H	OMe	40°	(0)	(65)

TABLE XI. KETONES (*Continued*)

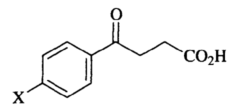
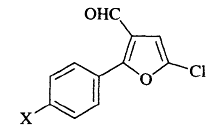
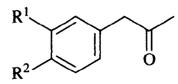
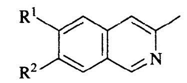
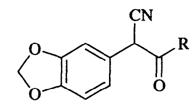
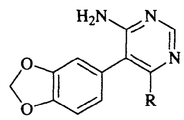
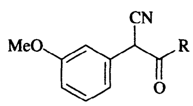
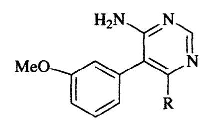
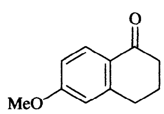
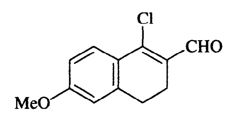
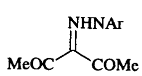
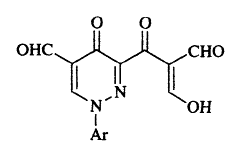
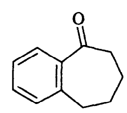
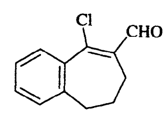
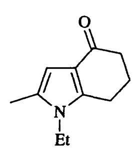
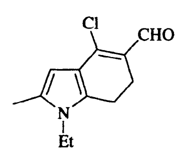
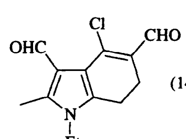
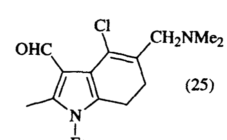
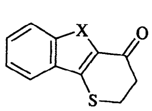
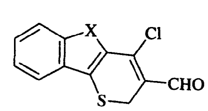
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 X: Cl (75); H (80); Me (85); OMe (70)	89
	$HCONH_2$, $POCl_3$	 R^1, R^2: —OCH_2O— (—)	423
		MeO, H (6)	411
		MeO, MeO (—)	423
C_{10}-C_{16}			
 R = H, Me, Ph	$HCONH_2$, $POCl_3$	 (—)	424
 R = H, Me, Et, Ph	$HCONH_2$, $POCl_3$	 (—)	425
C_{11}			
	DMF, $POCl_3$	 (84)	125, 417
	DMF, $POCl_3$	 Ar: 2,4,6-$(Br)_3C_6H_2$ (61); 4-$O_2NC_6H_4$ (63); Ph (54)	142
	DMF, $POCl_3$	 (75)	126, 426
	DMF, $POCl_3$ (1 eq)	 (6)	131
	DMF, $POCl_3$ (2 eq)	 (14) +  (25)	131
C_{11}-C_{12}			
	DMF, PCl_3	 X: NH (78); O (89); S (91); CH_2 (93)	129

TABLE XI. KETONES (*Continued*)

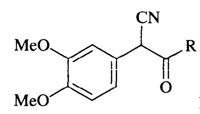
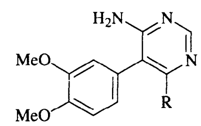
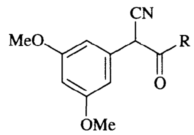
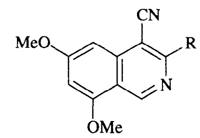
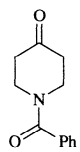
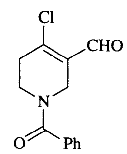
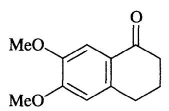
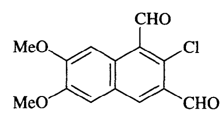
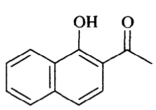
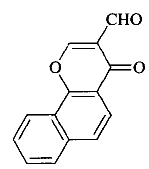
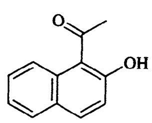
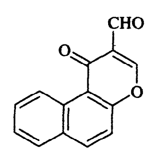
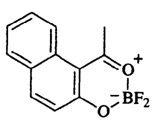
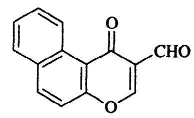
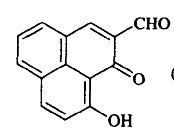
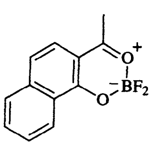
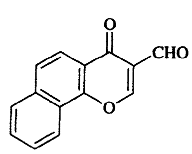
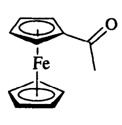
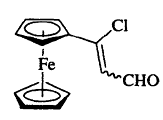
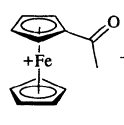
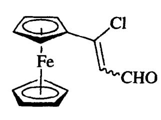
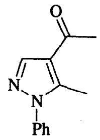
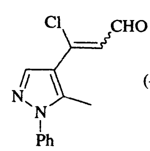
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}-C_{17}			
 R = H, Me, Ph	$HCONH_2$, $POCl_3$	 (—)	427
	$HCONH_2$, $POCl_3$	 R: H (28); Me (35); Et (30); Ph (26)	428
C_{12}			
	DMF, $POCl_3$	 (82)	114
	DMF, $POCl_3$	 (30)	421
	DMF, $POCl_3$	 (64)	429
	DMF, $POCl_3$	 (90)	429
	DMF, $POCl_3$ (2 eq)	 (25) +  (71)	429, 105
	DMF, $POCl_3$ (2 eq)	 (91)	429
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (55)	98
 $^{-}OSO_3H$	DMF, $POCl_3$	 (—)	403a
	"Vilsmeier complex"	 (—)	96

TABLE XI. KETONES (*Continued*)

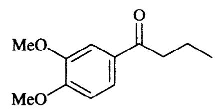
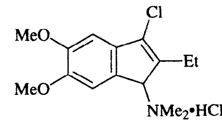
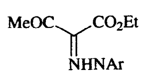
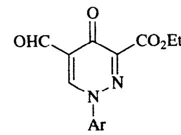
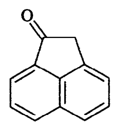
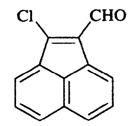
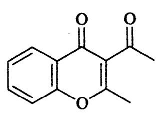
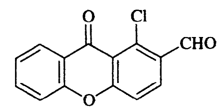
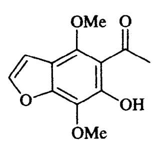
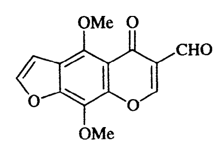
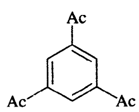
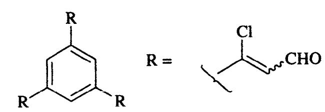
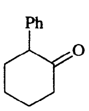
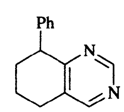
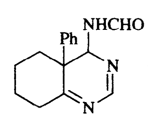
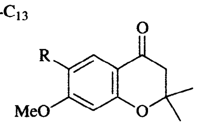
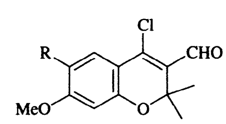
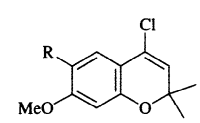
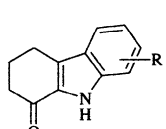
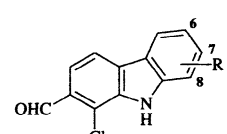
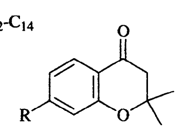
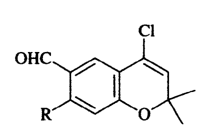
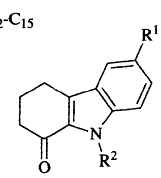
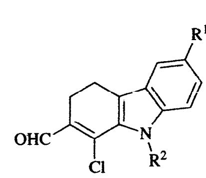
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (75)	430
	DMF, $POCl_3$	 Ar: 2,4,6-$(Br)_3C_6H_2$ (63); 4-$O_2NC_6H_4$ (64); Ph (59)	142
	DMF, $POCl_3$	 (80)	127, 431
	DMF, $POCl_3$	 (41)	323
	DMF, $POCl_3$	 (89)	432
	DMF, $POCl_3$	 (41)	391, 415
	$HCONH_2$, $POCl_3$	 (17) +  (3)	411
C_{12}-C_{13}			
	DMF, $POCl_3$	 I +  II	433
		R / I / II: Br (12) (88); H (8) (92); MeO (2) (98)	
	1. DMF, $POCl_3$, 0° 2. 80°, 5-6 h	 R: 6-Cl (78); 6-Br (79); H (77); 6-Me (77); 7-Me (71); 8-Me (78)	434
C_{12}-C_{14}			
	DMF, $POCl_3$	 R: MeO (78); EtO (80); PrO (78)	434a
C_{12}-C_{15}			
 R^1 = H, Cl, Br, CO_2Et R^2 = H, Me	"Vilsmeier reagent"	 (60-80)	435

TABLE XI. KETONES (*Continued*)

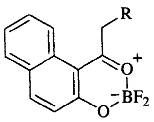
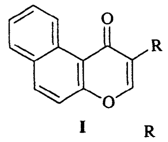
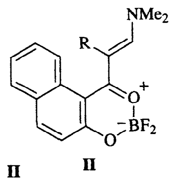
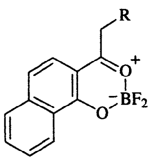
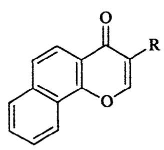
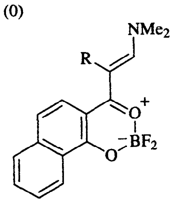
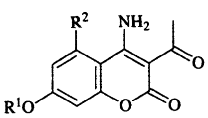
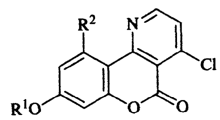
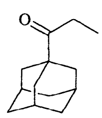
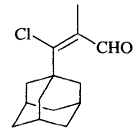
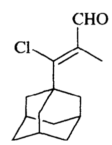
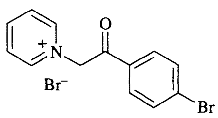
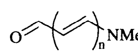
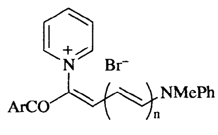
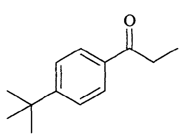
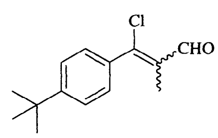
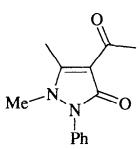
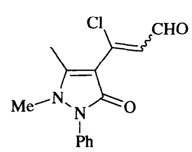
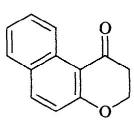
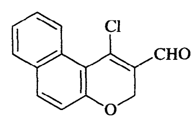
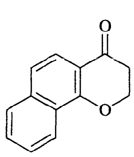
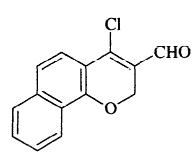
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}-C_{19}			
	DMF, $POCl_3$ (1 eq)	 I or  II R / I / II H (0) (85) Me (85) (0) Ph (98) (0) Bn (96) (0)	429
	DMF, $POCl_3$ (1 eq)	 I or  II R / I / II H (0) (91) Me (78) (0) Ph (0) (81) Bn (97) (0)	429
C_{12}-C_{20}			
	DMF, $POCl_3$	 R^1 / R^2 Me / H (62) n-C_5H_{11} / AcO (78) $CH(CH_3)C_5H_{11}$-n / AcO (23)	436
C_{13}			
	DMF, $POCl_3$, cold	 I +  II Temp / I:II cold 7:1 (50) 70° 14:1 (25)	85
	 NMePh, MeCOBr or PhCOBr	 (—) n = 1 or 2 Ar = 4-BrC_6H_4	437
	—	 (68)	438, 439
	DMF, $POCl_3$	 (73)	83
	DMF, $POCl_3$	 (84)	440
	DMF, $POCl_3$	 (86)	440

TABLE XI. KETONES (*Continued*)

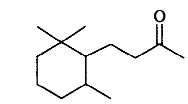
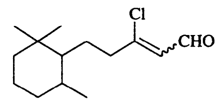
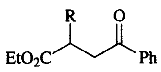
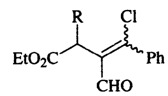
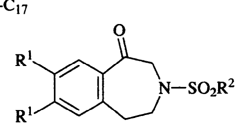
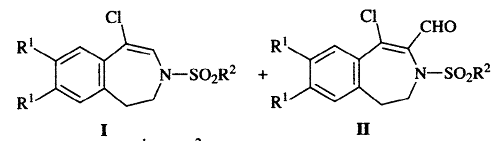
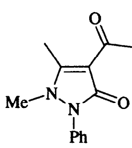
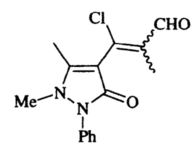
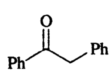
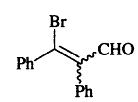
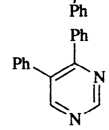
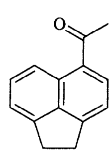
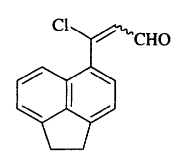
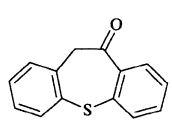
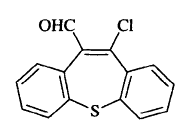
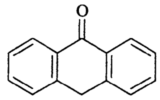
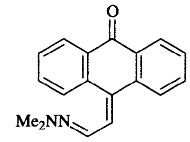
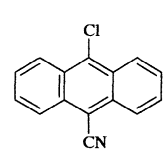
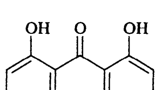
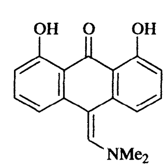
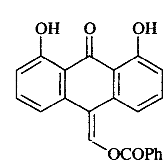
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (25) Z:E = 1:2	387
C_{13}-C_{14}			
	DMF, $POCl_3$	 R: Me (57); Et (71)	90
C_{13}-C_{17}			
	DMF, $POCl_3$	 I + II	311, 312
		R^1 = MeO, R^2 = Me: I (29), II (30)	
		R^1 = H, R^2 = 4-MeC_6H_4: I (19), II (36)	
C_{14}			
	DMF, $POCl_3$	 (75)	83
	DMF, PBr_3	 (75)	92
	H_2NCHO, $POCl_3$	 (—)	423, 441
	DMF, $POCl_3$	 (71)	442
	DMF, $POCl_3$	 (52)	443
	Me_2NN=CHCHO, $POCl_3$ or $COCl_2$	 (70)	135
	1. MFA, $POCl_3$ 2. NH_2OH	 (40)	242
	DMF, PhCOCl	 (51) +  (15)	134a

TABLE XI. KETONES (*Continued*)

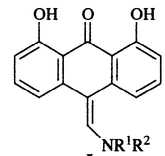
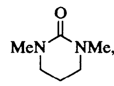
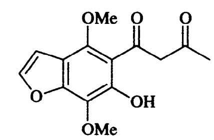
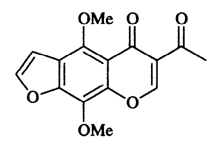
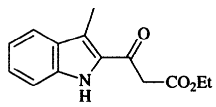
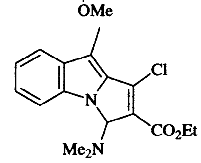
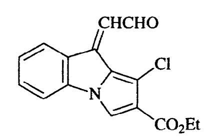
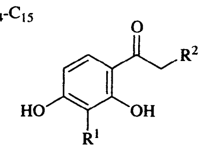
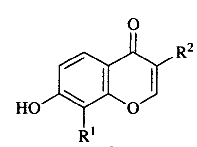
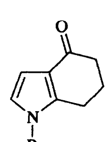
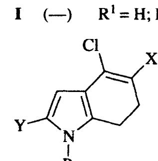
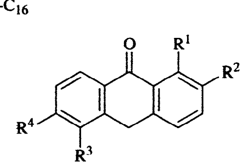
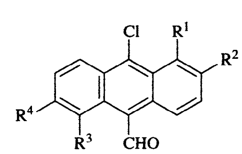
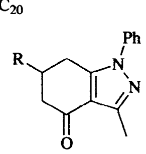
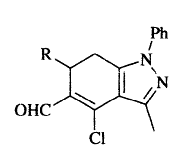
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$R^1MeNCHO$, $POCl_3$	 I R^1 / R^2: H, Me (25); Ph, Me (11)	134b
	$[R^1R^2N{=}CHCl^+]Cl^-$, , pyridine	I R^1 / R^2: Me, H (25); Ph, Me (11); 4-FC_6H_4, H (20); 4-ClC_6H_4, H (28); 4-BrC_6H_4, H (17); 4-$O_2NC_6H_4$, H (6); Ph, H (33); 3,4-$OCH_2OC_6H_3$, H (17); Bn, H (10); 2-$MeOC_6H_4$, H (24); 4-$MeOC_6H_4$, H (16); 2,4-$(MeO)_2C_6H_3$, H (8); 3,4-$(MeO)_2C_6H_3$, H (5)	134b
	DMF, $POCl_3$	 (46)	432
	DMF, $POCl_3$, rt	 (34)	260
	DMF, $POCl_3$, 70°	 (73)	260
C_{14}-C_{15} 	DMF, $POCl_3$	 I R^1 / R^2: H, Ph (100)	444, 445
		OH, Ph (—)	444
		H, 4-$MeOC_6H_4$ (—)	444
	—	I (—) R^1 = H; R^2 = 4-FC_6H_4O or PhO	445
	DMF, $POCl_3$	 R / X / Y: SO_2Ph, CHO, H (45); Bn, H, CHO (50)	131
C_{14}-C_{16} 	MFA, $POCl_3$	 (—) R^1 / R^2 / R^3 / R^4: Cl, H, Cl, H; H, H, H, H; MeO, MeO, H, H; H, MeO, H, MeO	134
C_{14}-C_{20} 	DMF, $POCl_3$	 R: H (80); Ph (67)	132

TABLE XI. KETONES (*Continued*)

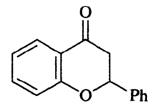
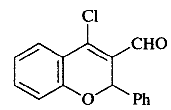
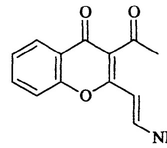
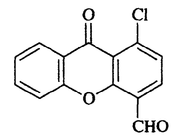
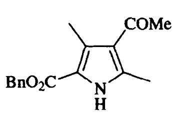
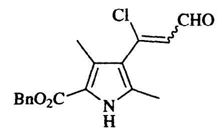
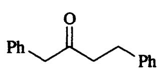
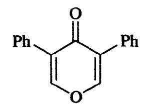
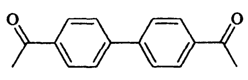
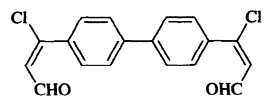
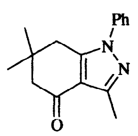
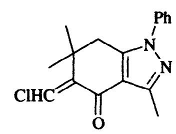
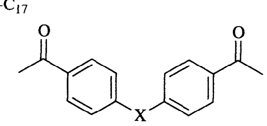
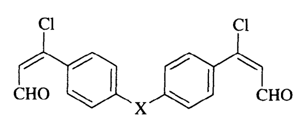
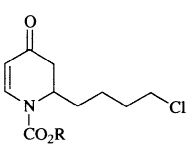
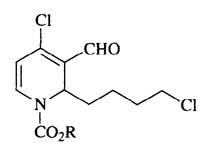
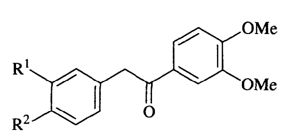
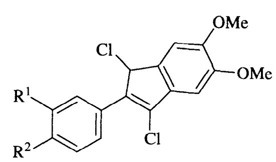
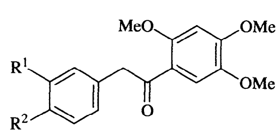
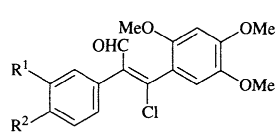
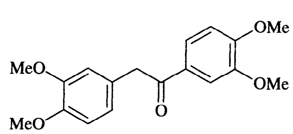
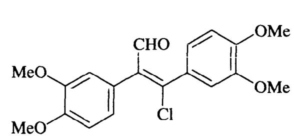
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	DMF, $POCl_3$	 (—)	447
	DMF, $POCl_3$	 (40)	323
C_{16}			
	DMF, $POCl_3$	 (69)	446
	DMF, $POCl_3$	 (35)[e]	448
	DMF, $POCl_3$	 (68)	415
	DMF, $POCl_3$	 (72)	132
C_{16}-C_{17}			
	DMF, $POCl_3$	 X O (53) S (73) SO_2 (68) CO (69) CH_2 (73)	415
	DMF, $POCl_3$	 R Ph (73) Bn (87)	449
C_{16}-C_{18}			
	DMF, $POCl_3$, 80-100°	 R^1 R^2 H F (24) H Cl (20) H Br (22) H MeO (37) MeO MeO (35)	450
C_{17}-C_{19}			
	DMF, $POCl_3$	 R^1 R^2 H H (65) H MeO (50) MeO H (48) MeO MeO (47)	451
C_{18}			
	DMF, $POCl_3$, 0-60°	 (35)	447

TABLE XI. KETONES (*Continued*)

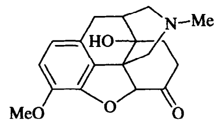
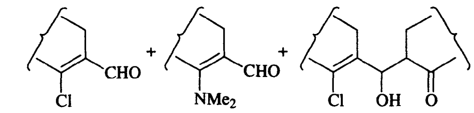
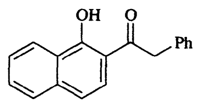
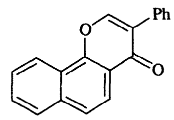
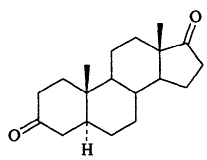
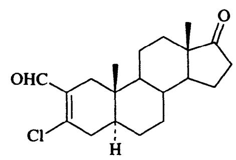
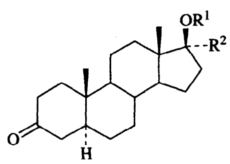
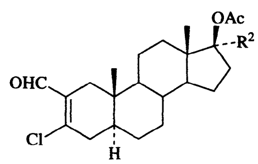
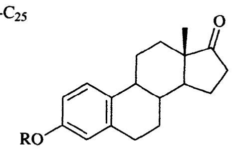
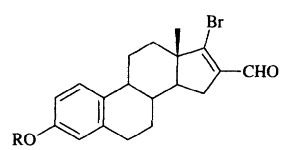
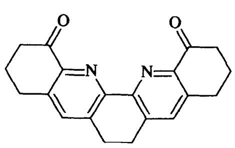
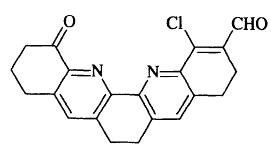
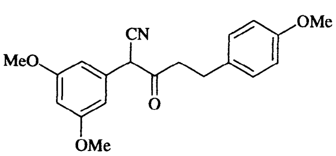
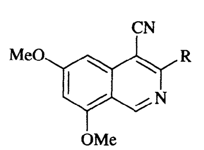
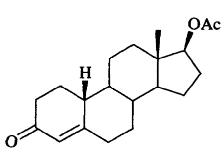
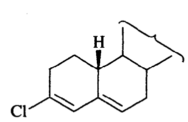
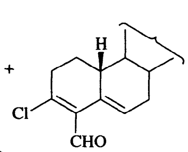
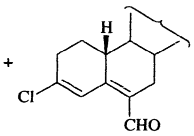
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (17) + (13) + (9)	51
	DMF, $POCl_3$	 (—)	444
C_{19}			
	DMF, $POCl_3$, AcCl, rt	 (39)	452
C_{19}-C_{22}			
			
		R^1 R^2	
	DMF, $POCl_3$, AcCl	H H (13)	452
	DMF, $POCl_3$	Ac H (55)	120a, 35
	DMF, $POCl_3$, AcCl	EtCO H (56)	453
	DMF, $POCl_3$	Ac Me (27)	454
C_{19}-C_{25}			
	DMF, PBr_3, $CHCl_3$	 R: Me (34); COPh (38)	455
C_{20}			
	DMF, $POCl_3$	 (84)	130
	$HCONH_2$, $POCl_3$	 R: H (8) + $(CH_2)_2C_6H_4OMe$-4 (24)	456
	DMF, $POCl_3$	 (13) +  (15) +  (18)	120

TABLE XI. KETONES (*Continued*)

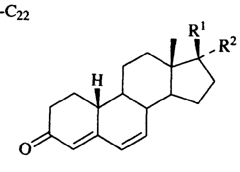
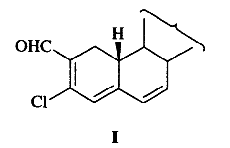
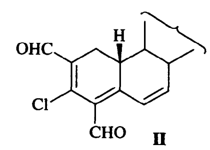
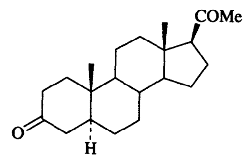
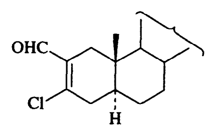
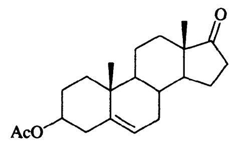
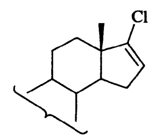
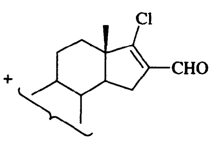
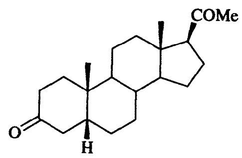
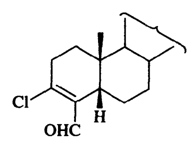
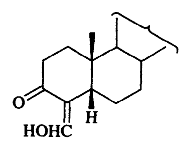
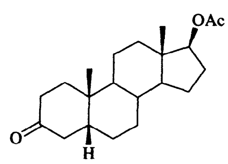
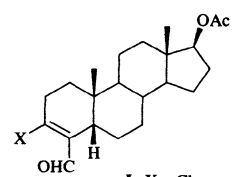
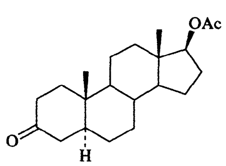
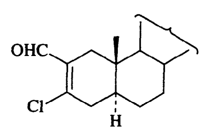
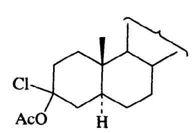
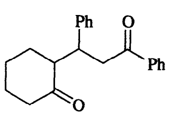
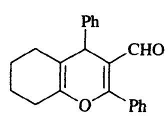
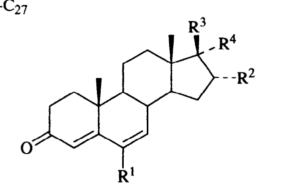
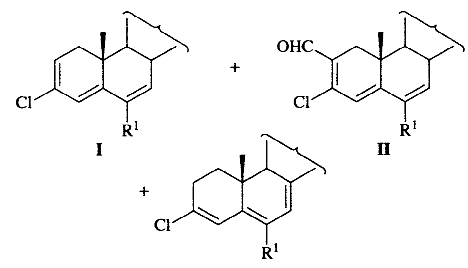
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}-C_{22}			
	DMF, $POCl_3$	 I +  II R¹ / R² / I / II OAc / H / (11) / (6) COMe / OAc / (10) / (7)	22
C_{21}			
	DMF, $POCl_3$, AcCl	 (47)	452
	DMF, $POCl_3$	 I +  II I / II (0) / (69) (—) / (—) (3) / (41)	454, 458 35 120a
	DMF, $POCl_3$, AcCl, boiling point	 (5)	453
	1. DMF, $POCl_3$, rt 2. Boil 3. NaAc (aq), boiling point	 (20 crude)	453
	DMF, $POCl_3$, AcCl	 (22) I, X = Cl	453
	DMF, PBr_3, $Cl_2C{=}CCl_2$, reflux	I, X = Br (32 crude)	453
	DMF, $POCl_3$	I, X = Cl (20)	120a, 35
	DMF, $POCl_3$, AcCl	 (45) +  (3)	452
	DMF, $POCl_3$	 (45)	353

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}-C_{27} 	DMF, $POCl_3$		

R^1	R^2	R^3	R^4	I	II	III	Refs.
H	H	OAc	H	(25)	(21)	(—)	22
H	H	OAc	Me	(—)	(23)	(—)	22
H	H	COEt	H	(—)	(10)	(40)	73
Cl	H	COMe	OAc	(—)	(28)	(—)	22, 73
H	H	COMe	OAc	(43)	(18)	(—)	22
H	H	COMe	OAc	(—)	(8)	(14)	73
Me	H	COMe	OAc	(—)	(50)	(10)	73
Me	Me	COMe	OAc	(32)	(13)	(—)	22
H	H	$COCH_2OAc$	OAc	(—)	(28)	(—)	22
H	H	C_8H_{17}	H	(45)	(12)	(—)	22

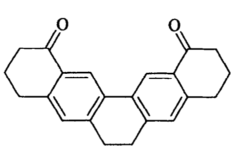
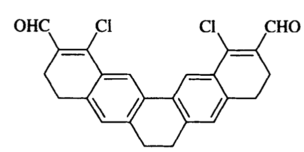
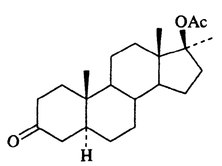
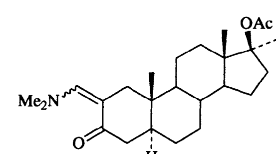
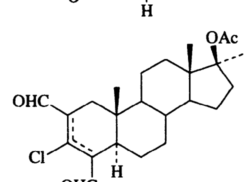
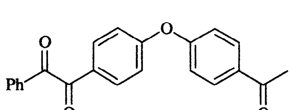
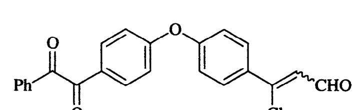
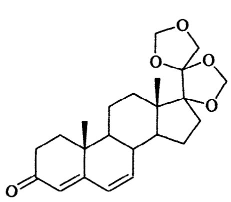
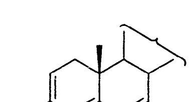
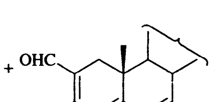
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	DMF, $POCl_3$	 (56)	459
	DMF, $POCl_3$	 (34)	454
	DMF, $POCl_3$, excess	 (12)	454
	—	 (29)	460
C_{23} 	DMF, $POCl_3$	 (39) +  (22)	22

TABLE XI. KETONES (*Continued*)

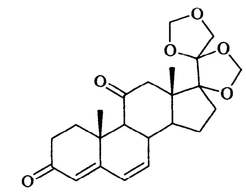
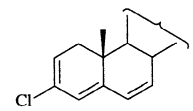
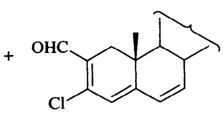
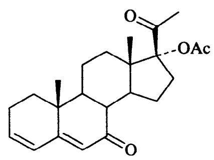
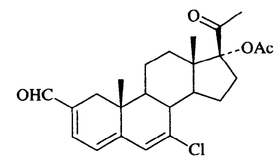
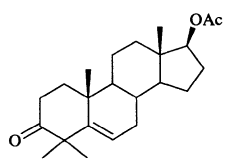
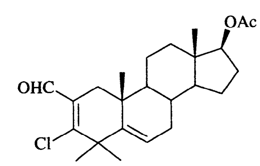
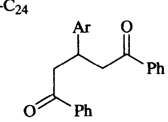
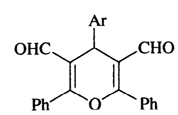
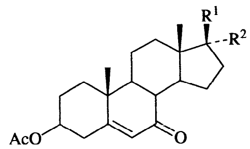
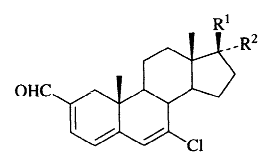
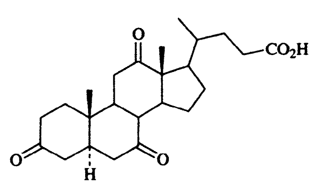
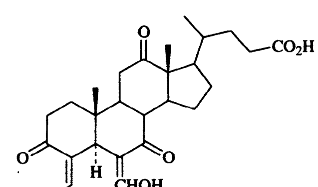
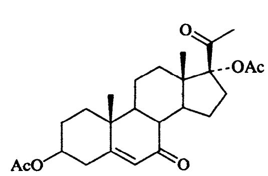
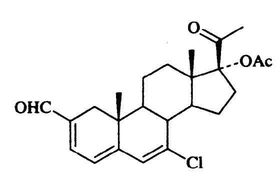
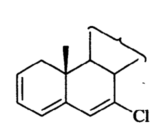
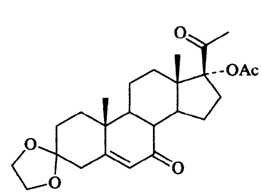
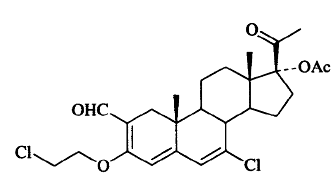
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (9) +  (10)	22
	DMF, $POCl_3$	 (—)	73
	DMF, $POCl_3$	 (62)	454
C_{23}-C_{24} 	DMF, $POCl_3$	 Ar Ph (52) 4-ClC_6H_4 (55) 4-MeC_6H_4 (53) 4-$MeOC_6H_4$ (45)	353
	DMF, $POCl_3$	 R^1 R^2 OAc H (43) OAc Me (37)	461
C_{24} 	1. DMF, $POCl_3$ 2. $NaHCO_3$ (aq)	 (92)	462
C_{25} 	DMF, $POCl_3$, forcing conditions	 (34)	461, 73
	DMF, $POCl_3$, mild conditions	 (30)	461
	DMF, $POCl_3$	 (52)	73

TABLE XI. KETONES (*Continued*)

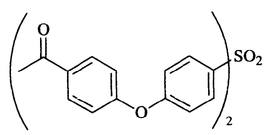
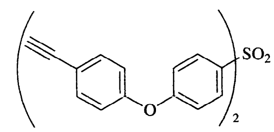
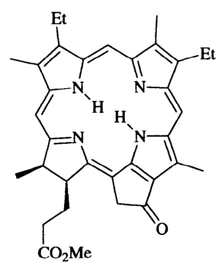
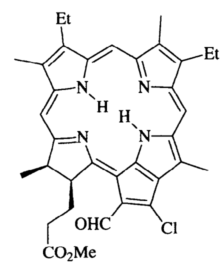
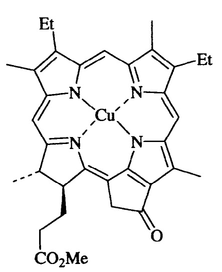
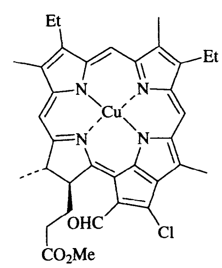
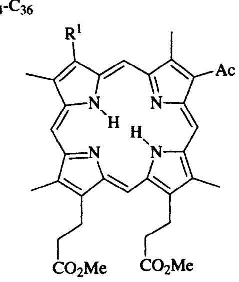
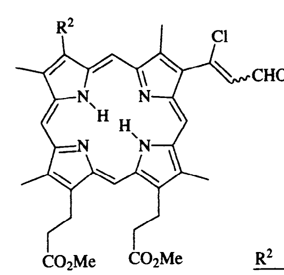
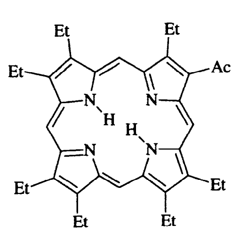
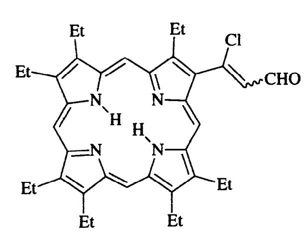
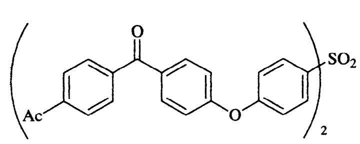
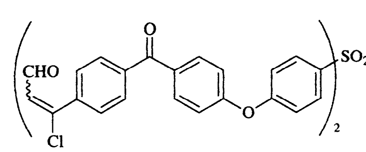
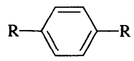
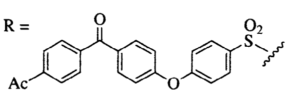
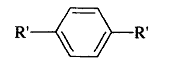
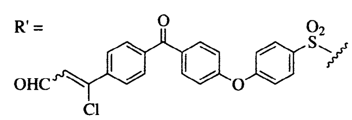
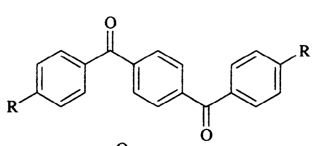
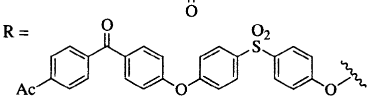
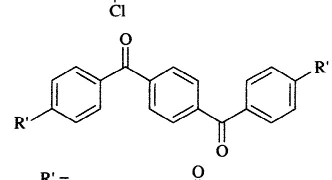
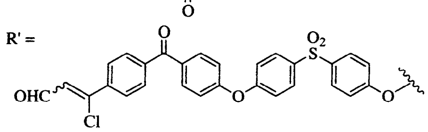
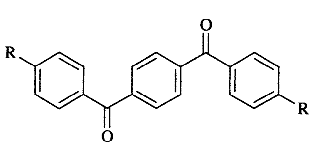
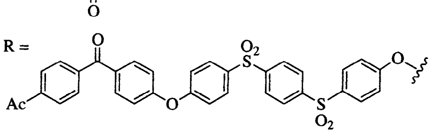
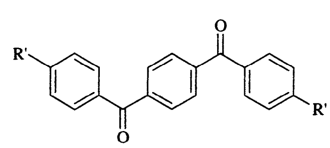
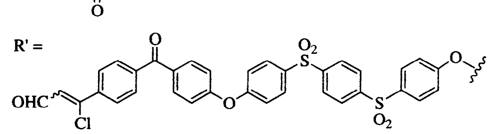
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}			
	1. "Vilsmeier reagent" 2. KOH, EtOH, DMF	 (—)	463
C_{34}			
	DMF, $POCl_3$	 (—)	464
	DMF, $POCl_3$, $ClCH_2CH_2Cl$, 50°, 1 h	 (—)	465
C_{34}-C_{36}			
			446
R^1		R^2	
H	DMF, $POCl_3$	H (69)	
Ac	DMF, $POCl_3$ (16 eq)	C(Cl)=CHCHO (30)	
C_{36}			
	DMF, $POCl_3$	 (67)	446
C_{42}			
	DMF, $POCl_3$, 0°	 (80)	466

TABLE XI. KETONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{48}  R = 	DMF, $POCl_3$, 0°	 (62) R' = 	467
C_{74}  R = 	DMF, $POCl_3$, 0°	 (93) R' = 	466
C_{86}  R = 	DMF, $POCl_3$, 0°	 (86) R' = 	467

[a] The yield given is that of the product isolated as the cupric salt.

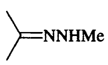
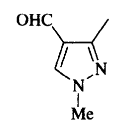
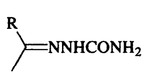
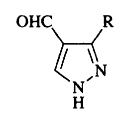
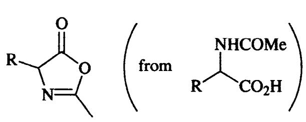
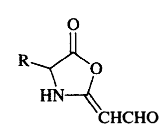
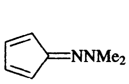
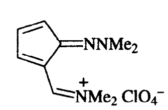
[b] The authors repeated the work detailed in reference #83 where the yield was reported as 20%. They did not report a yield for this reaction in reference #84.

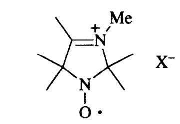
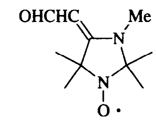
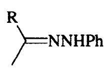
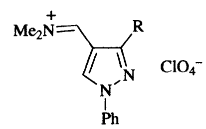
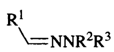
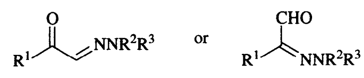
[c] This reaction was carried out at rt.

[d] The ratio of *E* to *Z* isomers in the crude mixture is 6:4.

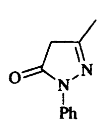
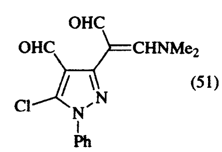
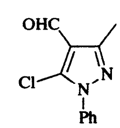
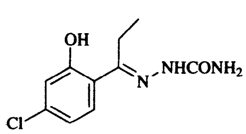
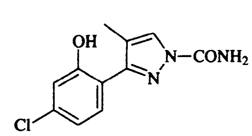
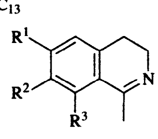
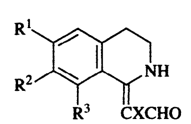
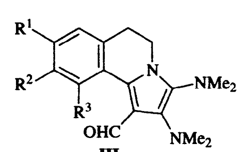
[e] Sixty percent of the starting ketone was recovered.

TABLE XII. IMINES, HYDRAZONES, SEMICARBAZONES, AND OXIMES

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4				
	DMF, $POCl_3$	 **I**	(94)	468
	DMF, $COCl_2$	**I** (98)		469, 470
	DMF, $SOCl_2$	**I** (7)		469, 470
	MFA, $POCl_3$	**I** (11)		468
C_4-C_{10}				
	DMF, $POCl_3$		R	
			Me (—)	139
			2-thienyl (83)	139
			2-(5-O_2N)-furyl (21)	471
			Ph (85)	139
			3-$O_2NC_6H_4$ (54)	139
			4-$O_2NC_6H_4$ (63)	139
			2-$MeOC_6H_4$ (95)	139
C_5-C_8				
 R = Me, *i*-Pr, $(CH_2)_2CO_2H$, CH_2Pr-*i*	DMF, $POCl_3$		(30-38)	472
C_7				
	1. DMF, $POCl_3$ 2. $NaClO_4$, MeOH		(74)	473

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	DMF, $POCl_3$	 (—)	474
C_9-C_{14}			
	1. DMF, $POCl_3$ 2. $HClO_4$		
		R: Me (77)	475
		R: Ph (96)	475, 476
C_9-C_{20}			
	DMF, $POCl_3$ or 1. DMF, $POCl_3$ 2. H_2O (pH 8)	 I or II	

R^1	R^2	R^3	I	II	Refs.
4-$O_2NC_6H_4$	Me	Me	(99)	(0)	140
4-$O_2NC_6H_4$	Me	Me	(—) or	(—)	477
4-$O_2NC_6H_4$	Me	Me	(0)	(67)	141
Ph	Me	Me	(0)	(57)	141
4-$MeOC_6H_4$	Me	Me	(61)	(0)	140, 141
4-$MeOC_6H_4$	Me	Me	(0)	(72)	140
4-$O_2NC_6H_4$	—$(CH_2)_4$—		(73)	(0)	140
4-$O_2NC_6H_4$	*i*-Pr	*i*-Pr	(0)	(—)	140
4-$O_2NC_6H_4$	*c*-C_6H_{11}	*c*-C_6H_{11}	(0)	(76)	140
Ph	*c*-C_6H_{11}	*c*-C_6H_{11}	(0)	(90)	140
4-$MeOC_6H_4$	*c*-C_6H_{11}	*c*-C_6H_{11}	(0)	(25)	140

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMF, $POCl_3$	 (51) +  (8)	478
	DMF, $POCl_3$	 (18)	479
C_{10}-C_{13}			
	DMF (x eq), $POCl_3$ (y eq), heat	 +  I, X = H II, X = CHO III	136, 137

R^1	R^2	R^3	x	y	Temp	I	II	III
H	H	H	—	—	rt	(34)	(—)	(—)
H	H	H	5	3	80-90°	(—)	(55)	(—)
H	H	H	5	5	80-90°	(—)	(14)	(46)
—OCH_2O—		H	—	—	rt	(14)	(—)	(—)
—OCH_2O—		H	5	3	80-90°	(—)	(48)	(—)
—OCH_2O—		H	5	5	80-90°	(—)	(37)	(31)
OMe	OMe	NO_2	5	5	80-90°	(—)	(—)	(48)
OMe	OMe	H	—	—	rt	(25)	(—)	(—)
OMe	OMe	H	5	3	80-90°	(—)	(63)	(—)
OMe	OMe	H	5	5	80-90°	(—)	(31)	(24)
OMe	OMe	OMe	—	—	rt	(11)	(—)	(—)
OMe	OMe	OMe	5	3	80-90°	(—)	(45)	(—)
OMe	OMe	OMe	5	5	80-90°	(—)	(4)	(43)

TABLE XII. IMINES, HYDRAZONES, SEMICARBAZONES, AND OXIMES (*Continued*)

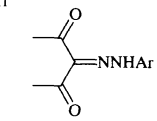
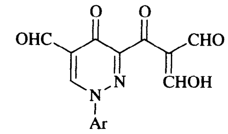
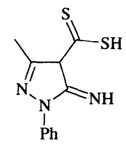
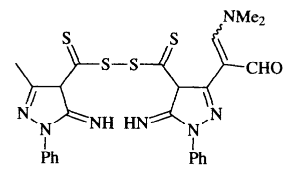
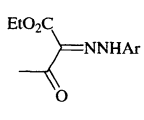
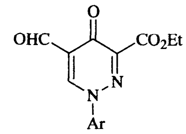
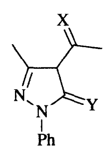
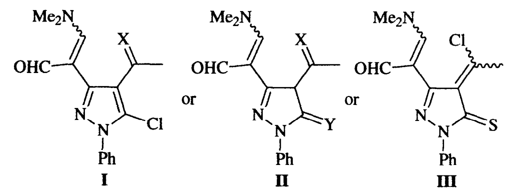
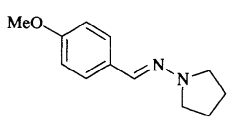
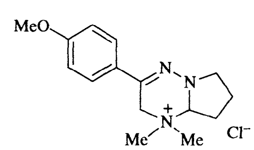
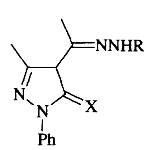
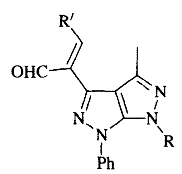
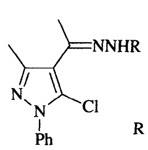
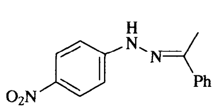
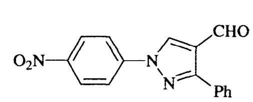
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	DMF, $POCl_3$	 Ar: 2,4,6-$Br_3C_6H_2$ (61); 4-$NO_2C_6H_4$ (63); Ph (54)	142
	DMF, $POCl_3$	 (86)	479a
C_{12}			
	DMF, $POCl_3$	 Ar: 2,4,6-$Br_3C_6H_2$ (63); 4-$NO_2C_6H_4$ (64); Ph (59)	142
	DMF, $POCl_3$		
		X = O, Y = O: I (75), II (0), III (0)	143
		X = NH, Y = O: I (35), II (0), III (0)	143
		X = NH, Y = S: I (0), II (55), III (0)	144
		X = S, Y = S: I (0), II (53), III (0)	144
		X = O, Y = S: I (0), II (0), III (55)	144
	DMF, $(COCl)_2$	 (80)	140
C_{12}-C_{18}			
	DMF, $POCl_3$	 I, R′ = NMe_2; X = O, R = H (68); X = S, R = H (65); X = O, R = Ph (68); X = S, R = Ph (65)	480
	1. DMF, $POCl_3$ 2. NaOH, H_2O	I, R′ = OH; X = O or S, R = H (76); X = O or S, R = Ph (73)	480
 R = H, Ph	DMF, $POCl_3$	I, R = NMe_2 (—)	480
C_{14}			
	DMF, $POCl_3$	 (90)	475

TABLE XII. IMINES, HYDRAZONES, SEMICARBAZONES, AND OXIMES (*Continued*)

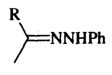
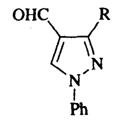
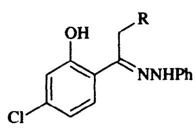
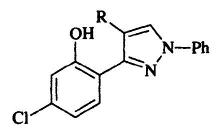
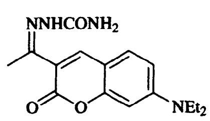
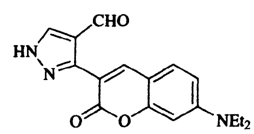
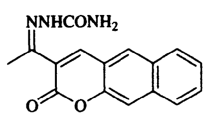
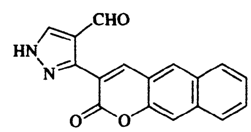
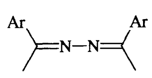
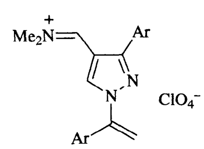
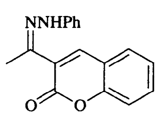
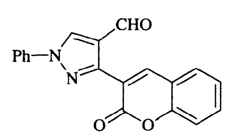
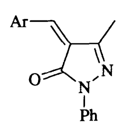
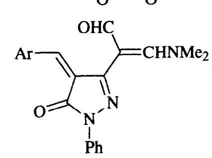
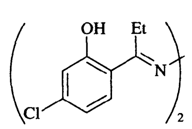
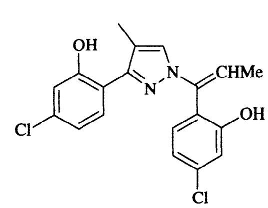
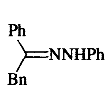
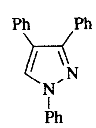
Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{14}-C_{20}				
	DMF, $POCl_3$		R	
			$4\text{-}FC_6H_4$ (70)	138
			$4\text{-}ClC_6H_4$ (90)	138
			$4\text{-}BrC_6H_4$ (88)	138
			$4\text{-}O_2NC_6H_4$ (72)	475, 476
			Ph (96)	475, 138
			$4\text{-}MeC_6H_4$ (50)	138
			$4\text{-}MeOC_6H_4$ (92)	138
			$4\text{-}PhC_6H_4$ (85)	138
C_{15}-C_{18}				
	DMF, $POCl_3$		R	479
			Me (30)	
			Et (26)	
			n-Pr (20)	
			n-Bu (20)	
C_{16}				
	DMF, $POCl_3$		(95)	481
	DMF, $POCl_3$		(90)	481
C_{16}-C_{18}				
	1. DMF, $POCl_3$ 2. $HClO_4$		Ar	476
			$4\text{-}O_2NC_6H_4$ (40)	
			Ph (100)	
			$4\text{-}MeC_6H_4$ (95)	
			$4\text{-}MeOC_6H_4$ (90)	
C_{17}				
	DMF, $POCl_3$		(90)	481
 Ar = $4\text{-}ClC_6H_4$, Ph	DMF, $POCl_3$		(—)	482
C_{18}				
	DMF, $POCl_3$		(8)	479
C_{20}				
	—		(45)	475

TABLE XII. IMINES, HYDRAZONES, SEMICARBAZONES, AND OXIMES *(Continued)*

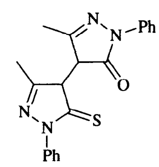
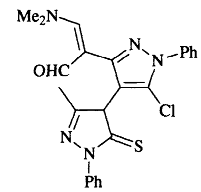
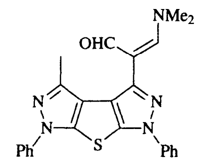
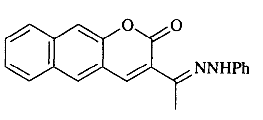
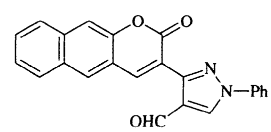
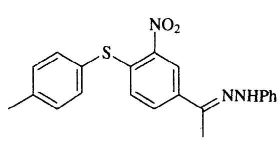
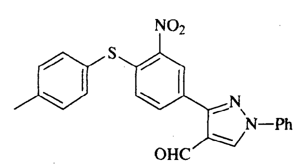
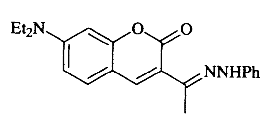
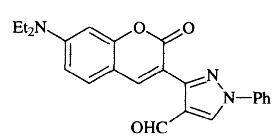
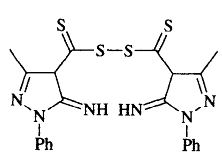
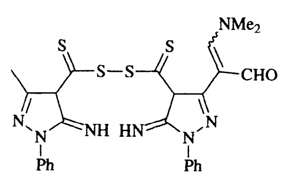
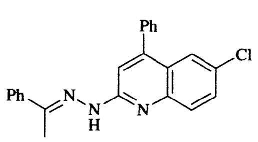
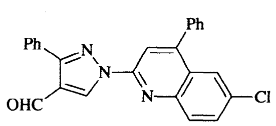
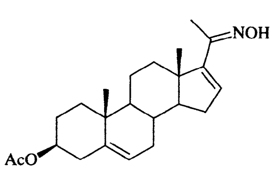
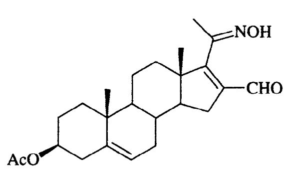
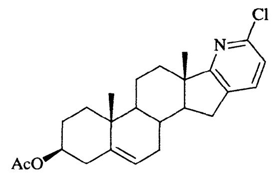
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$, 5-10°	 (72)	482a
	DMF, $POCl_3$, 70°	 (78)	482a
C_{21}			
	DMF, $POCl_3$	 (98)	481
	DMF, $POCl_3$	 (76)	483
	DMF, $POCl_3$	 (95)	481
C_{22}			
	DMF, $POCl_3$	 (—)	479a
C_{23}			
	DMF, $POCl_3$	 (93)	484
	DMF, $POCl_3$ (10 eq), 0°	 (82)	144a
	DMF, $POCl_3$ (10 eq), 65°	 (75)	144a

TABLE XII. IMINES, HYDRAZONES, SEMICARBAZONES, AND OXIMES (*Continued*)

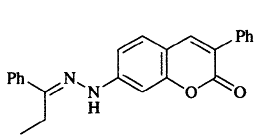
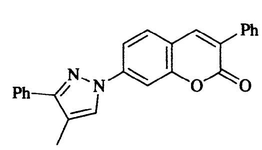
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{24}			
	"Vilsmeier reagent"	 (—)	485

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES

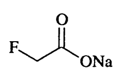
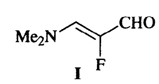
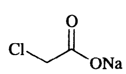
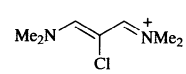
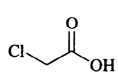
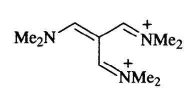
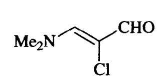
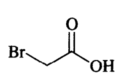
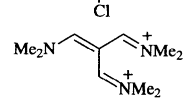
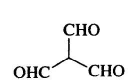
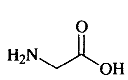
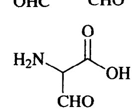
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
	DMF, $POCl_3$	 **I** (15)	74
	DMF, $(COCl)_2$, Et_3N	**I** (40-50)	145, 486, 292
	1. DMF, $POCl_3$ 2. $HClO_4$	 ClO_4^- (40) **II**	292
	1. DMF (2 eq), $POCl_3$ 2. $NaClO_4$	**II** (70)	146
	1. DMF (3 eq), $POCl_3$ 2. $NaClO_4$	 $2ClO_4^-$ (60)	146
	DMF, $POCl_3$	 (85)	74
	1. DMF, $POCl_3$ 2. Br_2, NaBr	 $2Br_3^-$ (80)	146
	1. DMF, $POCl_3$ 2. K_2CO_3 3. H^+/H_2O	 (65)	74
 [as a $Co(en)_2$ complex]	DMF, $POCl_3$	 (90) [as a $Co(en)_2$ complex]	487

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES (*Continued*)

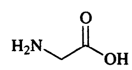
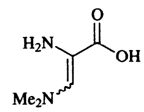
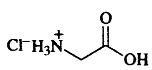
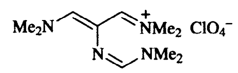
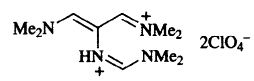
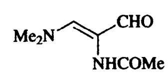
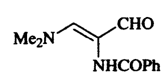
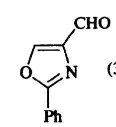
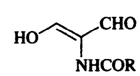
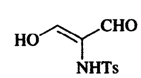
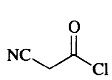
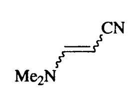
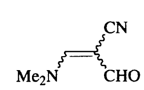
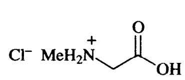
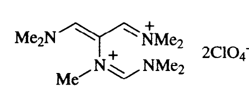
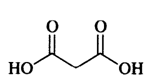
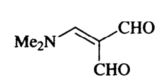
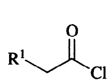
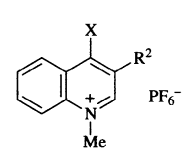
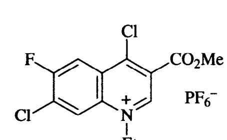
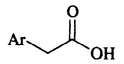
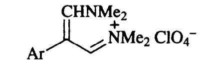
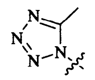
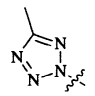
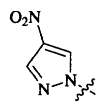
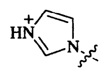
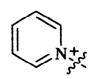
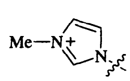
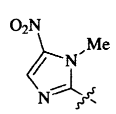
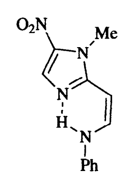
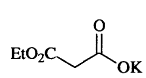
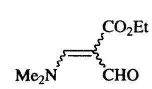
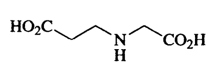
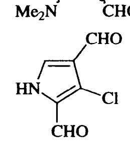
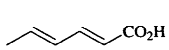
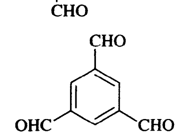
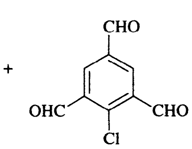
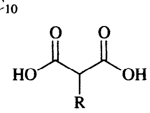
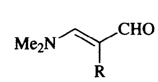
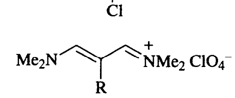
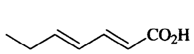
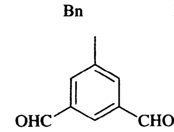
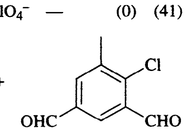
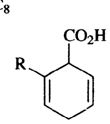
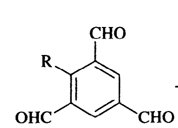
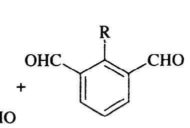
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 [as a Co(trien) complex]	DMF, $POCl_3$	 (81) [as a Co(trien) complex]	488
	1. DMF, $POCl_3$ 2. $HClO_4$ 3. Et_3N	 (59)	149
	1. DMF, $POCl_3$ 2. $HClO_4$	 (74)	149
	1. DMF, $POCl_3$ 2. $HClO_4$ 3. Et_3N 4. Ac_2O 5. K_2CO_3 (aq)	 (51)	149
	1. DMF, $POCl_3$ 2. $HClO_4$ 3. Et_3N 4. $(PhCO)_2O$ 5. K_2CO_3 (aq)	 (—) +  (31)	149
	1. DMF, $POCl_3$ 2. $HClO_4$ 3. NaOH 4. See table	 Cond. 4 / R: Ac_2O Me (66) $(CF_3CO)_2O$ CF_3 (19) PhCOCl Ph (39)	149
	1. DMF, $POCl_3$ 2. $HClO_4$ 3. NaOH 4. $4\text{-}MeC_6H_4SO_2Cl$	 (13)	149
C_3 	DMF, $(COCl)_2$, Et_3N	 (—) or  (—)	145
	1. DMF, $POCl_3$ 2. $HClO_4$	 (56)	149
	1. DMF, $POCl_3$ 2. $NaHCO_3$	 (40)	74
C_3-C_8 	1. MFA, $POCl_3$ 2. $NH_4^+PF_6^-$	 R^1 / R^2 / X: CN CONHCHO OH (68) CO_2Me CO_2Me Cl (87) Ph Ph Cl (75)	489
$R^1 = CO_2Me$	1. 3-Cl-4-F-*N*-ethylformanilide, $POCl_3$ 2. $NH_4^+PF_6^-$	 (40)	490

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4-C_7			
 (or carboxylic acid salt)	1. DMF, $POCl_3$ 2. $HClO_4$	 I	
Ar =			
		I (60-70)	491
		I (76)	492
		I (60-70)	491
		I (54)	492
		I (60-70)	491
		I (99)	492, 491
		I (60-70) Counterion = $2ClO_4^-$	491, 492, 493
		I (—)	492
	1. DMF, $(COCl)_2$ 2. $PhNH_2$, C_5H_5N 3. $NaHCO_3$ (aq)	 (56)	494
C_5			
	DMF, $POCl_3$	 (58)	74
	DMF, $POCl_3$ (6 eq), 90°	 (30)	149a
C_6			
	DMF, $POCl_3$	 (37) +  (5)	152
C_6-C_{10}			
	1. DMF, $POCl_3$ 2. See table 3. See table	 I or  II	148
C_7			
	DMF, $POCl_3$	 (13) +  (5)	152
C_7-C_8			
	DMF, $POCl_3$	 + 	153

Sub-table for ref. 148:

R	Cond. 2	Cond. 3	I	II
$CH_2CH{=}CH_2$	OH^-	—	(50)	(0)
n-Bu	$Me_2NH_2^+ClO_4^-$	OH^-	(—)	(0)
n-Bu	$Me_2NH_2^+ClO_4^-$	—	(0)	(31)
Bn	OH^-	—	(47)	(0)
Bn	$Me_2NH_2^+ClO_4^-$	—	(0)	(41)

Sub-table for ref. 153:

R		
H	(62)	(0)
Me	(34)	(6)

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES (*Continued*)

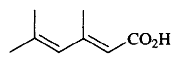
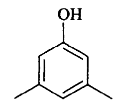
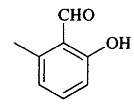
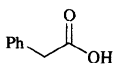
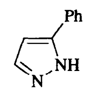
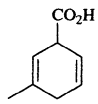
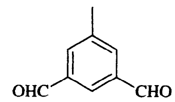
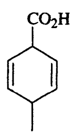
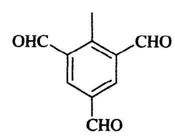
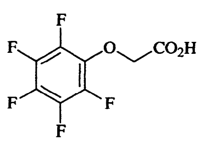
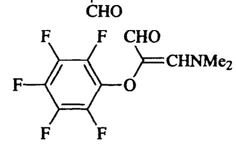
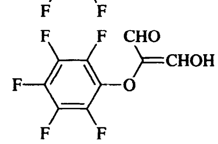
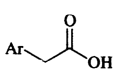
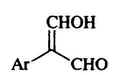
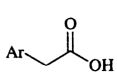
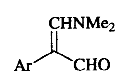
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	DMF, $POCl_3$	 (45) +  (6)	152
	1. DMF, $POCl_3$ 2. NH_2NH_2	 (—)	495
	DMF, $POCl_3$	 (14)	153
	DMF, $POCl_3$	 (17)	153
	DMF, $POCl_3$	 (16)	496
	1. DMF, $POCl_3$ 2. OH^-	 (—)	496
C_8-C_{12}			
	1. DMF, $POCl_3$ 2. OH^-	 Ar: C_6F_5 (73)	496
		1-naphthyl (56)	497
 (or carboxylic acid salt)	DMF, $POCl_3$		
		Ar	
		C_6F_5 (36)	496
		2,4-$Cl_2C_6H_3O$ (3)	379
		3,4-$Cl_2C_6H_3$ (91)	147
		4-ClC_6H_4 (65)	147
		2-$O_2NC_6H_4$ (58)	147
		4-$O_2NC_6H_4$ (—)	498
		Ph (52)	147, 499
			74
		Ph [a] (73)	151
		3-HOC_6H_4 (72)	151
		4-HOC_6H_4 (92)	147
		3-MeC_6H_4 (68)	147
		4-MeC_6H_4 (80)	147
		4-$MeOC_6H_4$ (37)	147
		3,4-$OCH_2OC_6H_3$ (40)	498
		4-$MeSC_6H_4$ (—)	498
		4-$MeSOC_6H_4$ (—)	498
		4-$MeSO_2C_6H_4$ (—)	147,
		3,4-$(MeO)_2C_6H_3$ (53)	500, 501
		3,4,5-$(MeO)_3C_6H_2$ (75)	147, 500,
			501
		1-naphthyl (66)	497
	MFA, $POCl_3$	3,4-$(MeO)_2C_6H_3$ (—)	501

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES (*Continued*)

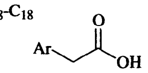
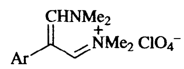
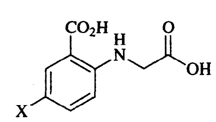
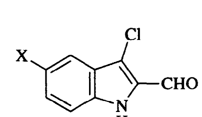
Substrate	Conditions	Product(s) and Yield(s) (%)				Refs.
C_8-C_{18}  (or carboxylic acid salt)	1. DMF, $POCl_3$ 2. See table					
			Ar	Cond. 2		
			4-ClC_6H_4	$NaClO_4$	(77)	402
			4-BrC_6H_4	$HClO_4$	(60)	493
			4-$O_2NC_6H_4$	$HClO_4$	(90)	74, 493, 502
			Ph	$NaClO_4$ or $HClO_4$	(92)	74, 151, 292, 493, 502
			3-HOC_6H_4	$HClO_4$	(47)	151
			4-HOC_6H_4	$HClO_4$	(96)	234, 151
			4-HOC_6H_4	$NaPF_6$ [b]	(86)	503
			4-NCC_6H_4	$HClO_4$	(—)	502
			2-MeC_6H_4	$HClO_4$	(48)	493
			4-MeC_6H_4	$HClO_4$	(91)	234, 493, 502
			4-MeC_6H_4	$NaClO_4$	(70)	402
			4-$MeOC_6H_4$	$HClO_4$	(70)	234, 493
			4-$MeOC_6H_4$	$NaClO_4$	(99)	402
			3,4-$(MeO)_2C_6H_3$	$NaClO_4$	(69)	74
			4-EtC_6H_4	$HClO_4$	(78)	234
			4-$EtOC_6H_4$	$HClO_4$	(94)	234
			3-indolyl	$NaClO_4$	(90)	74
			4-*n*-PrC_6H_4	$HClO_4$	(75)	234
			4-*n*-$PrOC_6H_4$	$HClO_4$	(83)	234
			4-*n*-BuC_6H_4	$HClO_4$	(69)	234
			4-*n*-$BuOC_6H_4$	$HClO_4$	(81)	234
			4-*n*-$BuSC_6H_4$	$HClO_4$	(84)	234
			1-naphthyl	$NaClO_4$	(39)	74
			2-naphthyl	$HClO_4$	(85)	493
			4-*n*-$C_5H_{11}C_6H_4$	$HClO_4$	(75)	234
			4-*n*-$C_5H_{11}C_6H_4$	$Mg(ClO_4)_2$ [c]	(—)	504, 505
			4-*n*-$C_5H_{11}OC_6H_4$	$HClO_4$	(79)	234
			4-*n*-$C_5H_{11}OC_6H_4$	$Mg(ClO_4)_2$ [c]	(—)	506
			4-PhC_6H_4	$HClO_4$	(—)	493
			4-*n*-$C_6H_{13}C_6H_4$	$HClO_4$	(88)	234
			4-*n*-$C_6H_{13}OC_6H_4$	$HClO_4$	(85)	234
			4-*n*-$C_6H_{13}SC_6H_4$	$HClO_4$	(64)	234
			4-*n*-$C_7H_{15}C_6H_4$	$HClO_4$	(95)	234
			4-*n*-$C_7H_{15}OC_6H_4$	$HClO_4$	(78)	234, 154
			4-*n*-$C_8H_{17}C_6H_4$	$HClO_4$	(83)	234
			4-*n*-$C_8H_{17}C_6H_4$	$Mg(ClO_4)_2$	(—)	507
			4-*n*-$C_8H_{17}OC_6H_4$	$HClO_4$	(96)	234
			4-*n*-$C_9H_{19}C_6H_4$	$HClO_4$	(81)	234
			4-*n*-$C_9H_{19}OC_6H_4$	$HClO_4$	(81)	234
			4-*n*-$C_{10}H_{21}C_6H_4$	$HClO_4$	(76)	234
			4-*n*-$C_{10}H_{21}OC_6H_4$	$HClO_4$	(95)	234
C_9 	DMF, $POCl_3$, (6 eq), 90°		X			149a
			Cl		(75)	
			Br		(61)	
			H		(75)	

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES (*Continued*)

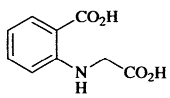
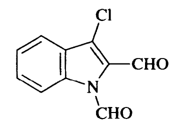
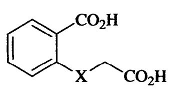
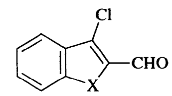
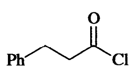
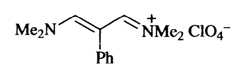
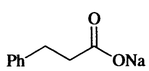
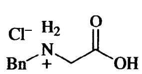
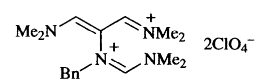
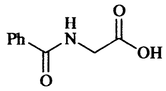
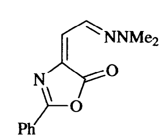
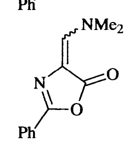
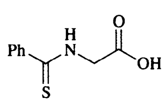
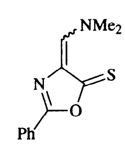
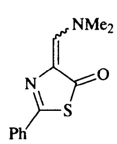
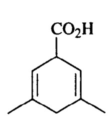
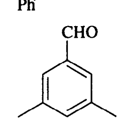
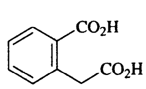
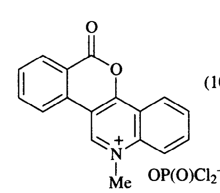
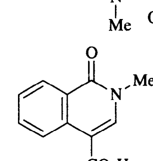
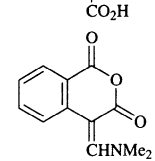
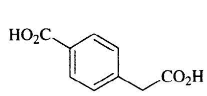
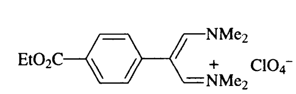
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$, (6 eq), 0°-rt	 (53)	149a
	DMF, $POCl_3$, (6 eq), 90°	 X: O (21); S (51)	149a
	1. DMF, $POCl_3$ 2. $HClO_4$	 I (90)	74
	1. DMF, $POCl_3$ 2. $HClO_4$	I (74)	74
	1. DMF, $POCl_3$ 2. $HClO_4$	 (62)	149
	Me_2NN=CHCHO, $POCl_3$ or $COCl_2$	 (41)	135
	DMF, $POCl_3$	 (93)	508
	DMF, $POCl_3$	 (30) +  (35)	508
	DMF, $POCl_3$	 (45)	153
	MFA, $POCl_3$	 (100)	489
	DMF, $POCl_3$	 (80)	150
	DMF, $POCl_3$	 (—)	509, 150
	1. DMF, $POCl_3$ 2. EtOH 3. $NaClO_4$	 (—)	402

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES *(Continued)*

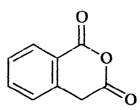
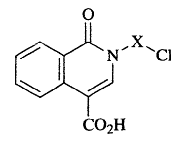
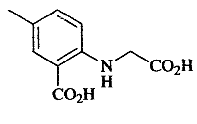
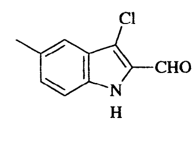
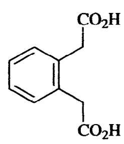
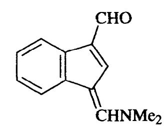
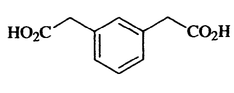
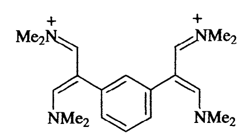
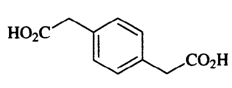
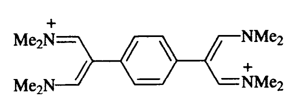
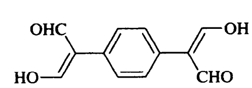
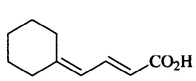
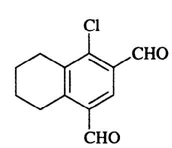
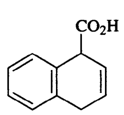
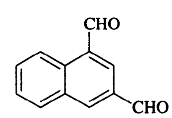
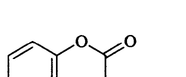
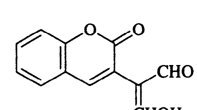
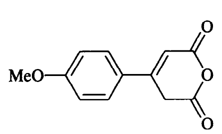
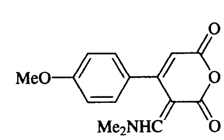
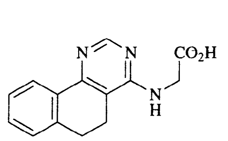
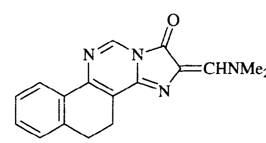
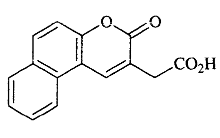
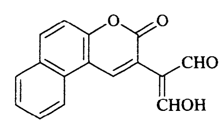
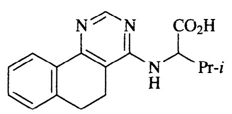
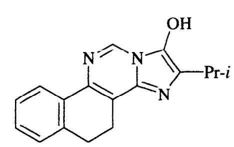
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Amide, $POCl_3$	 Amide / X: *N*-formylpyrrolidine, $(CH_2)_4$ (70); *N*-formylmorpholine, $(CH_2)_2O(CH_2)_2$ (100); *N*-formylpiperidine, $(CH_2)_5$ (60)	510
C_{10}			
	DMF, $POCl_3$, (6 eq), 90°	 (45)	149a
	1. DMF, $POCl_3$ 2. K_2CO_3 (aq)	 (—)	36
	1. DMF, $POCl_3$ 2. $NaClO_4$	 $2ClO_4^-$ (65)	36
	1. DMF, $POCl_3$ 2. $NaClO_4$	 $2ClO_4^-$ (82)	36
	1. DMF, $POCl_3$ 2. $NaClO_4$ 3. K_2CO_3 (aq)	 (49)	36
	DMF, $POCl_3$	 (15)	152
C_{11}			
	DMF, $POCl_3$	 (91)	153
	DMF, $POCl_3$	 (87)	511
C_{12}			
	DMF, $POCl_3$	 (10)	155

TABLE XIII. CARBOXYLIC ACIDS, ANHYDRIDES, AND ACID CHLORIDES *(Continued)*

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	1. DMF, $POCl_3$ 2. $NaHCO_3$ (aq)	 (35)	512
C_{15}			
	DMF, $POCl_3$	 (70)	511
C_{17}			
	1. DMF, $POCl_3$ 2. $NaHCO_3$ (aq)	 (20)	512

[a] In this example, reaction with DMF, $POCl_3$ was followed by treatment with K_2CO_3.

[b] The counterion in this reaction was PF_6^-.

[c] The first condition was not reported.

TABLE XIV. ESTERS AND LACTONES

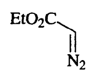
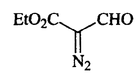
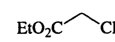
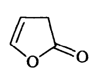
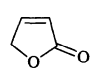
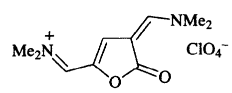
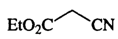
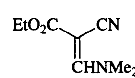
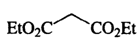
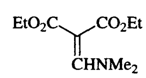
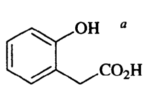
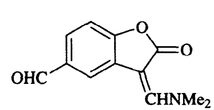
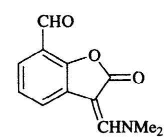
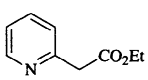
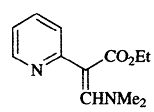
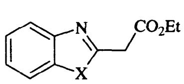
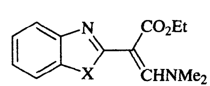
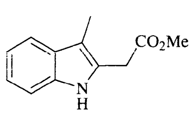
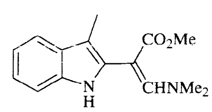
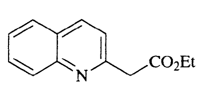
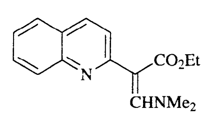
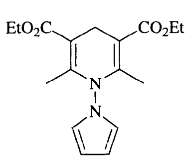
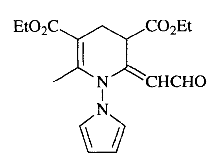
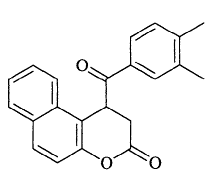
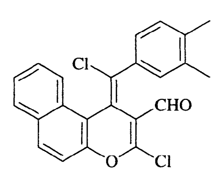
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	$[Me_2N{=}CHCl]^+ Cl^-$	 (48) +  (55)	160
 and/or 	1. DMF, $POCl_3$, 0° 2. 60-70°, 3 h 3. $HClO_4$	 (80-84)	513, 514
C_5			
	DMF, $COCl_2$	 (75)	156
C_7			
	DMF, $COCl_2$	 (81)	156
C_8			
 [a]	DMF, $POCl_3$	 +  (41)	151
C_9			
	DMF, $POCl_3$	 (50)	157
C_{11}			
	DMF, $POCl_3$	 X: O (69); S (78); NH (66)	515

TABLE XIV. ESTERS AND LACTONES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}				
	DMF, $POCl_3$		(59)	158
C_{13}				
	DMF, $POCl_3$		(82)	157
C_{17}				
	DMF, $POCl_3$		(32)	516, 517, 518
C_{22}				
	DMF, $POCl_3$		(—)	159

[a] The starting material is as shown, however, the author states that it reacts as the cyclic lactone.

TABLE XV. AMIDES AND LACTAMS

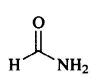
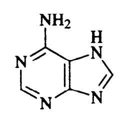
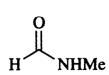
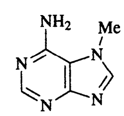
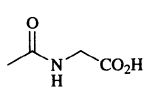
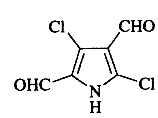
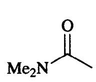
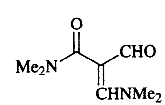
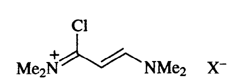
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1			
	$POCl_3$	 (40-50)	519, 520
C_2			
	$HCONH_2$, $POCl_3$	 (—)	162
C_4			
	DMF, $POCl_3$	 (82)	472
	DMF, $POCl_3$	 (76)	74
	1. DMF, $COCl_2$ 2. $NaClO_4$	 (86) **I**, $X = ClO_4^-$	74
	1. $[Me_2N{=}CHCl]^+ Cl^-$ 2. $HClO_4$	**I**, $X = ClO_4^-$ (54)	521
	$[Me_2N{=}CHCl]^+ Cl^-$	**I**, $X = Cl^-$ (—)	522

TABLE XV. AMIDES AND LACTAMS (*Continued*)

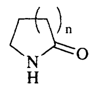
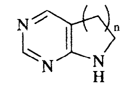
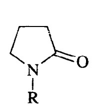
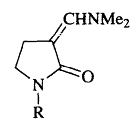
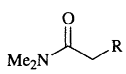
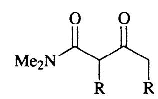
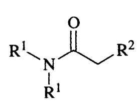
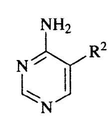
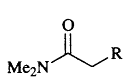
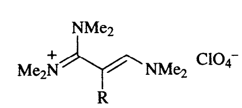
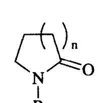
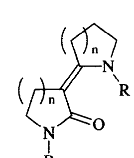
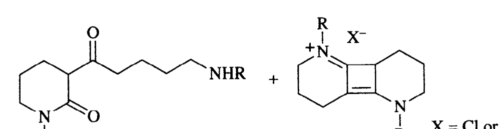
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4-C_6			
	$HCONH_2$, $POCl_3$	 n 1 (9) 2 (15) 3 (7)	162
C_4-C_{10}			
	DMF, $POCl_3$	 R H (9) Me (55) *n*-Bu (—) Ph (35)	523 175 175 523
C_4-C_{12}			
	$POCl_3$	 R H (74) Me (52) Et (61) *i*-Pr (60) *n*-Pr (61) *n*-C_8H_{17} (57)	524 524, 525 524 524 525 524
C_4-C_{18}			
	H_2NCHO, $POCl_3$	 R^1 R^2 Me H (32) Me Me (28) H Et (16) H *n*-Pr (17) H *n*-Bu (17) Me *n*-Pr (18) H *n*-C_8H_{17} (16) H *n*-$C_{14}H_{29}$ (27) H *n*-$C_{16}H_{33}$ (21)	162
C_5-C_7			
	1. $[Me_2N{=}CHCl]^+ Cl^-$ 2. Me_2NH 3. $NaClO_4$	 R CN (86) CO_2Et (40)	521
C_5-C_{13}			
	$COCl_2$	 R n Me 1 (90) Et 3 (61) Ph 1 (68) *c*-C_6H_{11} 1 (83)	161
	$POCl_3$	 I + II, X = Cl or I R n I II Me 2 (—) (—) Bn 2 (—) (—) $(CH_2)_2Ph$ 2 (—) (—)	526, 527

TABLE XV. AMIDES AND LACTAMS (*Continued*)

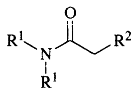
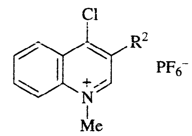
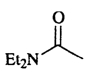
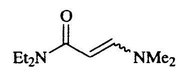
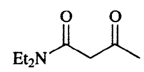
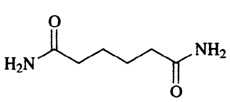
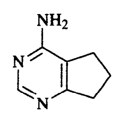
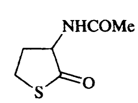
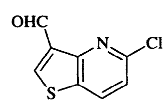
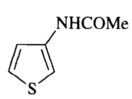
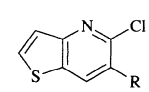
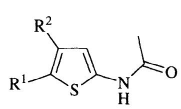
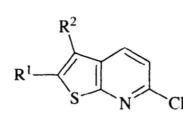
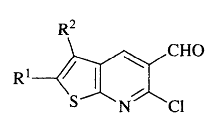
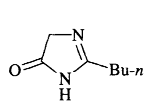
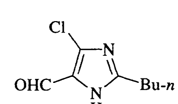
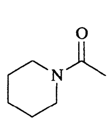
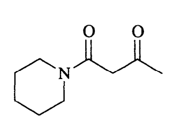
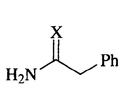
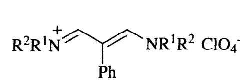
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. MFA, $POCl_3$ 2. $NaPF_6$	 R¹, R¹ / R² Me, Me / Me (72) —$(CH_2)_2O(CH_2)_2$— / Cl (76) —$(CH_2)_2O(CH_2)_2$— / CH_2Cl (60) —$(CH_2)_4$— / Me (56) —$(CH_2)_2O(CH_2)_2$— / Me (79) —$(CH_2)_2O(CH_2)_2$— / $(CH_2)_2OH$ (60)* —$(CH_2)_2O(CH_2)_2$— / Et (73) —$(CH_2)_2O(CH_2)_2$— / *i*-Pr (78) —$(CH_2)_2O(CH_2)_2$— / *t*-Bu (30) —$(CH_2)_2O(CH_2)_2$— / Bn (93) *R^2 = $(CH_2)_2Cl$ in product	163
C_6			
	DMF, $COCl_2$	 (23)	161
	$COCl_2$	 (83)	161
	$HCONH_2$, $POCl_3$	 (14)	162
	DMF, $POCl_3$	 (60)	472
	DMF, $POCl_3$	 DMF:$POCl_3$ / R 1:3 / H (77) 3:7 / CHO (72)	164, 165
C_6-C_{10}			
	DMF, $POCl_3$ (1:3)	 R¹ / R² Br / H (66) Me / H (79) Me / Me (72) —$(CH_2)_4$— (79)	164, 165
	DMF, $POCl_3$ (3:7)	 R¹ / R² Br / H (66) Me / H (62) Me / Me (73) —$(CH_2)_4$— (88)	164, 165
C_7			
	1. $POCl_3$, toluene or ClC_6H_5, 0-20° 2. 80°, then DMF 3. 100°, 2-3 h 4. NaOH	 (55)	528
	$COCl_2$	 (80)	161
C_8			
	1. R^1R^2NCHO, $POCl_3$ 2. $HClO_4$	 X / R¹ / R² O / Me / Me (36) S / Me / Me (61) S / —$(CH_2)_4$— (96) S / —$(CH_2)_2O(CH_2)_2$— (82)	529

TABLE XV. AMIDES AND LACTAMS (*Continued*)

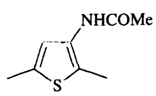
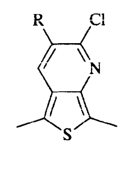
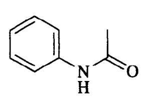
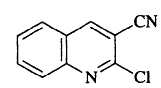
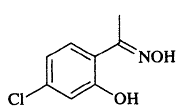
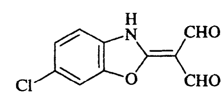
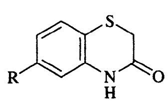
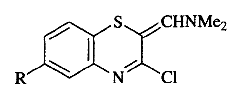
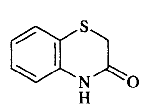
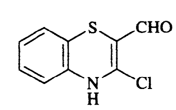
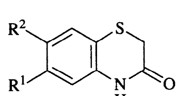
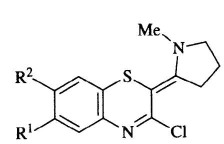
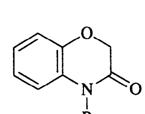
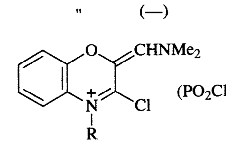
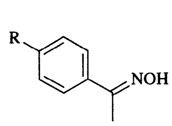
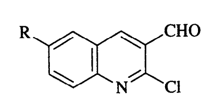
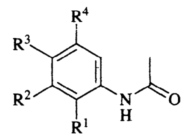
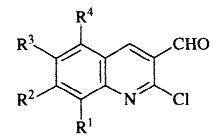
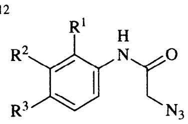
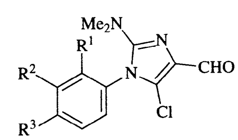
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 DMF:$POCl_3$ / R: 1:3, H (52); 3:7, CHO (39)	164, 165
	1. DMF, $POCl_3$ 2. H_2NOH	 (70)	530, 531
	DMF, $POCl_3$	 (60)	532
 R = H, Cl, NO_2	DMF, $POCl_3$	 (—)	533
	DMF, $POCl_3$	 (48)	178, 179, 533
C_8-C_9			
 R^1 = Cl, R^2 = H	1-Me-2-pyrrolidone, $POCl_3$	 (20)	181
R^1 = H, R^2 = OMe	DMF, $POCl_3$	" (—)	533
	DMF, $POCl_3$	 $(PO_2Cl_2)^-$ R: H (90); Me (85)	180
	DMF, $POCl_3$	 R: Br (10); H (57); Me (51); OMe (13)	169

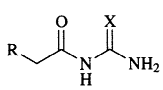
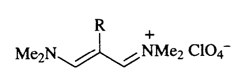
TABLE XV. AMIDES AND LACTAMS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8-C_{11}			
	DMF, $POCl_3$		

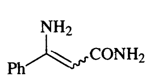
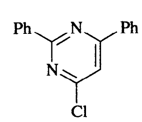
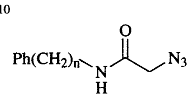
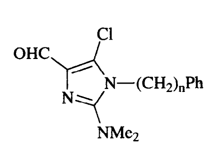
R^1	R^2	R^3	R^4		Refs.
H	H	H	H	(78)	166, 167
H	Cl	H	H	(25)	166, 167
H	H	Cl	H	(2)	166
H	H	Br	H	(23)	166, 167
Me	H	H	H	(67)	166, 167
H	Me	H	H	(66)	166, 167
H	H	Me	H	(70)	166, 167
OMe	H	H	H	(5)	166
H	OMe	H	H	(89)	166, 167, 534
H	H	OMe	H	(56)	166, 167
H	SMe	H	H	(92)	167
H	N_3	H	H	(—)	535
Me	H	Me	H	(32)	167
H	OMe	OMe	H	(72)	166, 167, 534
OMe	H	H	OMe	(50)	536
H	OMe	OMe	OMe	(92)	166, 167, 544

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8-C_{12}			
	DMF, $POCl_3$, 80-90°		93a

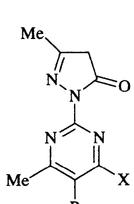
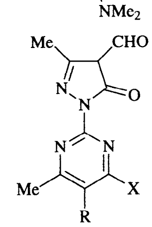
R^1	R^2	R^3	
H	H	H	(45)
H	H	Cl	(48)
H	H	OMe	(58)
H	Cl	H	(39)
H	H	Me	(62)
Et	H	H	(36)
H	—$(CH=CH)_2$—		(51)
Me	H	H	(41)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	1. DMF, $POCl_3$ 2. $NaClO_4$		174a

R	X	
Ph	O	(80)
$4\text{-}BrC_6H_4$	O	(78)
$4\text{-}O_2NC_6H_4$	O	(76)
Ph	S	(85)
$4\text{-}O_2NC_6H_4$	S	(69)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Me_2NCOPh, $POCl_3$	 (89)	536a
C_9-C_{10}			
	DMF, $POCl_3$, 80-90°		93a

n	
1	(11)
2	(20)

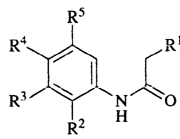
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = H, Me	1. DMF, $POCl_3$, 0° 2. 70°, 3 h		537

X	
OH	(60-64)
Cl	(—)

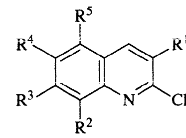
TABLE XV. AMIDES AND LACTAMS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.

C_9-C_{11}

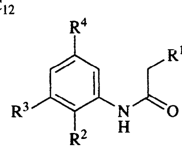


Conditions: DMF, $POCl_3$

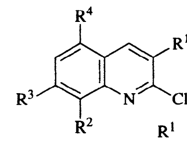


R^1	R^2	R^3	R^4	R^5	Yield (%)	Refs.
Me	H	H	H	H	(62)	171
H	H	Me	H	H	(64)	164
H	H	OMe	H	H	(73)	164
Me	H	Me	H	H	(78)	171
H	H	OMe	OMe	H	(69)	164
H	H	OMe	H	OMe	(55)	165
H	H	OMe	OMe	OMe	(71)	164, 165

C_9-C_{12}



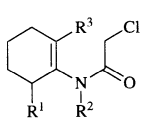
Conditions: DMF, $POCl_3$



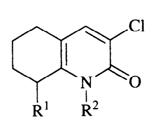
R^1	R^2	R^3	R^4	Yield (%)	Refs.
Cl	H	Me	H	(28)	171
CN	H	Me	H	(13)	171
CN	H	OMe	H	(40)	538
CH_2Cl	H	OMe	H	(76)	171
$(CH_2)_3Cl$	H	N_3	H	(—)	535
$(CH_2)_2Cl$	H	Me	H	(90)	171
$(CH_2)_2Cl$	H	OMe	H	(76)	171
CH_2Cl	OMe	H	OMe	(22)	536
Me	H*	H	NMe_2	(76)	539
Me	OMe	H	OMe	(70)	536
Et	OMe	H	OMe	(75)	536
n-Bu	H	H	H	(75)	171
CH_2CO_2Me	H	OMe	H	(56)	171
CO_2Et	OMe	H	OMe	(64)	536

*R^2 = CHO in the product.

C_9-C_{14}

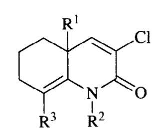


Conditions: DMF, $POCl_3$



I

or

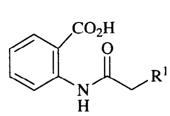


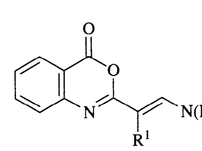
II

Refs. 168

R^1	R^2	R^3	I	II
Cl	Me	H	(43)	(0)
H	Me	H	(43)	(0)
H	$(CH_2)_2OEt$	H	(43)	(0)
H	Ph	H	(43)	(0)
Me	Me	H	(0)	(19)
Me	Me	Me	(0)	(44)

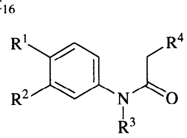
C_9-C_{15}



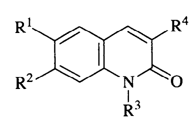


Conditions	R^1	R^2	Yield (%)	Refs.
$[(R^2)_2N{=}CHCl]^+Cl^-$	H	$(CH)_2O(CH_2)_2$	(77)	173a
$[(R^2)_2N{=}CHCl]^+Cl^-$	Me	$(CH)_2O(CH_2)_2$	(75)	173a
$[(R^2)_2N{=}CHCl]^+Cl^-$	Ph	Me	(95)	173a
$COCl_2$, DMF	Ph	Me	(50)	173, 173a, 174

C_9-C_{16}

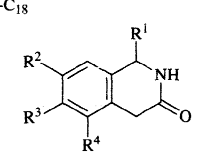
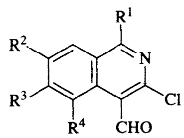


Conditions: DMF, $POCl_3$



R^1	R^2	R^3	R^4	Yield (%)	Refs.
H	H	Mc	Cl	(46)	168
Cl	H	Et	Cl	(67)	168
H	H	Et	Cl	(55)	168
Me	H	Me	Cl	(28)	168
OMe	H	Me	Cl	(22)	168
H	Me	Mc	Cl	(43)	168
H	H	Me	OMe	(6)	168
H	H	Me	SMe	(23)	168
H	H	Ph	Cl	(—)	540
H	H	Me	Ph	(40)	168
H	H	Me	$PhN(Me)SO_2$	(2)	168

TABLE XV. AMIDES AND LACTAMS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9-C_{18}			
	1. DMF, $POCl_3$ 2. $KMnO_4$	 (see below)	182

R^1	R^2	R^3	R^4	Yield (%)
H	H	H	H	(72)
2,4-$Cl_2C_6H_3$	H	H	H	(32)
2-FC_6H_4	H	F	H	(30)
2-FC_6H_4	H	H	H	(58)
Ph	H	Cl	H	(48)
Ph	H	H	H	(54)
2-MeC_6H_4	H	Cl	H	(32)
2-MeC_6H_4	H	H	H	(37)
Ph	H	Me	H	(37)
Ph	H	H	Me	(36)
Ph	OMe	OMe	H	(33)
4-ClC_6H_4	OMe	OMe	H	(27)
Ph	—$(CH_2)_3$—		H	(15)

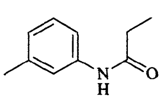
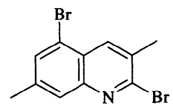
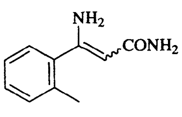
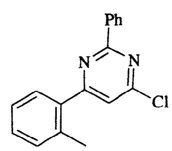
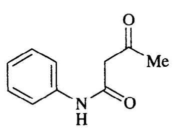
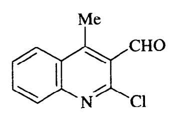
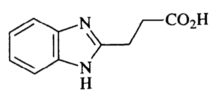
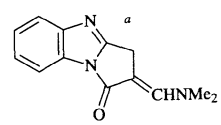
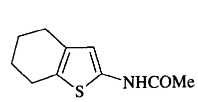
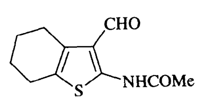
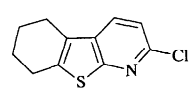
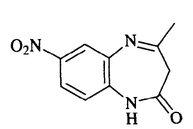
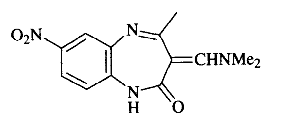
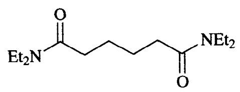
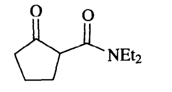
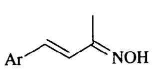
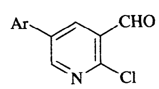
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMF, $POBr_3$	 (13)	171
	Me_2NCOPh, $POCl_3$	 (82)	536a
	1. DMF, $POCl_3$ 2. 105°, 2 h	 (56)	541
	DMF, $POCl_3$	 [a] (68)	210
	DMF, $POCl_3$ (3:1), reflux, 1 h	 I (8) +  II (80)	165
	DMF, $POCl_3$ (3:1), reflux, 15 min	I (76) + II (12)	165
	DMF, —	 (—)	542
	$COCl_2$	 (75)	161
C_{10}-C_{11}			
	DMF, $POCl_3$	 Ar: Ph (75); 4-MeC_6H_4 (—); 4-ClC_6H_4 (—); 4-$MeOC_6H_4$ (—)	144a

TABLE XV. AMIDES AND LACTAMS (*Continued*)

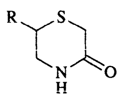
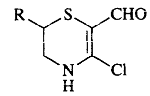
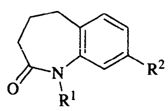
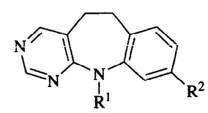
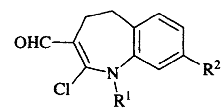
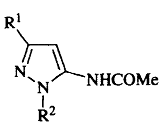
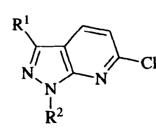
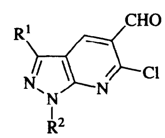
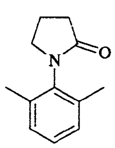
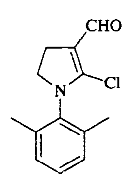
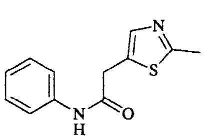
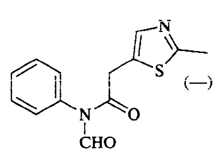
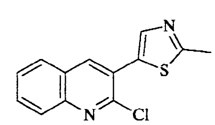
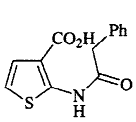
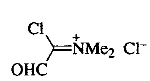
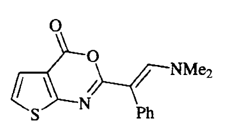
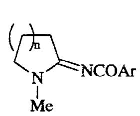
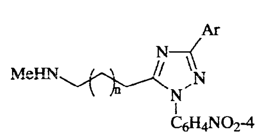
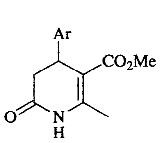
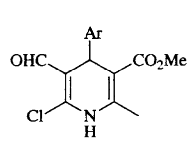
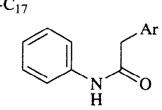
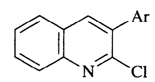
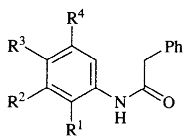
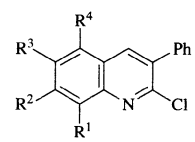
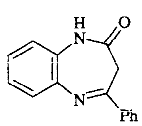
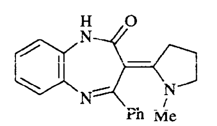
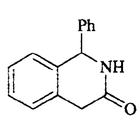
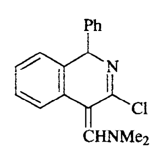
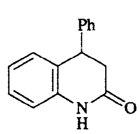
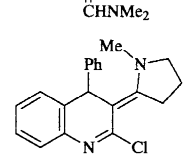
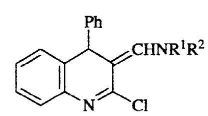
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 R Ph (84) 4-$MeOC_6H_4$ (41)	178, 179
C_{10}-C_{15}			
	$HCONH_2$, $POCl_3$	 R^1 R^2 H Cl (42) H H (29) $Me_2N(CH_2)_3$ H (5) $Me_2N(CH_2)_3$ Cl (18)	162
	DMF, $POCl_3$	 R^1 R^2 H Cl (23)	178
C_{11}-C_{17}			
	DMF, $POCl_3$	 I +  II R^1 R^2 I II H 4-ClC_6H_4 (13) (53) H 4-$O_2NC_6H_4$ (8) (35) H Ph (14) (53) Me Ph (23) (47) Ph Ph (25) (49)	170
C_{12}			
	1. DMF, $POCl_3$ 2. NaOH	 (100)	176
	DMF, $POCl_3$	 (—) +  (—)	173
C_{13}			
		 (90)	173, 173a
C_{13}-C_{15}			
	1. DMF, $POCl_3$ 2. $H_2NNHC_6H_4NO_2$-4	 Ar n 4-$MeOC_6H_4$ 1 (68) 3-MeC_6H_4 3 (51)	543
C_{14}-C_{16}			
	DMF, $POCl_3$	 Ar Ph (80) 2-ClC_6H_4 (82) 3-$O_2NC_6H_4$ (75) 4-NCC_6H_4 (73) 4-$MeO_2CC_6H_4$ (75)	544

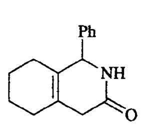
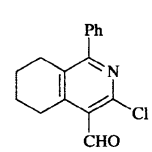
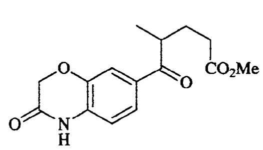
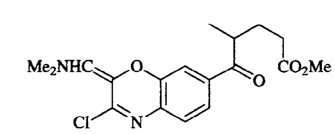
TABLE XV. AMIDES AND LACTAMS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}-C_{17}			
	DMF, $POCl_3$	 (—)	172
		Ar = 2-FC_6H_4, 3-FC_6H_4, 4-FC_6H_4, 2-ClC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-HOC_6H_4, 4-NCC_6H_4, 4-$CF_3C_6H_4$, 2-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-$MeSC_6H_4$, 4-*i*-$PrOC_6H_4$, 2,5-$(MeO)_2C_6H_3$	
	DMF, $POCl_3$		

R^1	R^2	R^3	R^4	Yield	Refs.
H	H	H	H	(42)	171, 172
H	Me	H	H	(95)	171
OMe	H	H	H	(—)	172
H	OMe	H	H	(—)	172
H	SMe	H	H	(—)	172
H	H	OMe	H	(—)	172
H	H	SMe	H	(—)	172
OMe	H	H	OMe	(61)	536
H	NMe_2	H	H	(—)	172
H	H	*n*-PrO	H	(—)	172

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	1-Me-2-pyrrolidone, $POCl_3$	 (90)	181
	DMF, $POCl_3$	 (70)	182
	1-Me-2-pyrrolidone, $POCl_3$	 (90)	181
	R^1R^2NCHO, $POCl_3$		545

R^1	R^2	Yield
Me	Me	(90)
—$(CH_2)_5$—		(90)
—$(CH_2)_2O(CH_2)_2$—		(90)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. DMF, $POCl_3$ 2. $KMnO_4$	 (80)	182
	DMF, $POCl_3$	 (—)	546

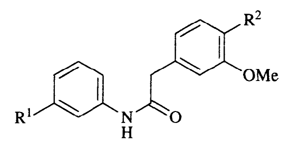
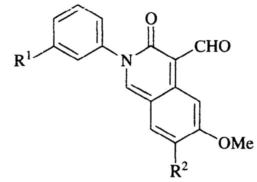
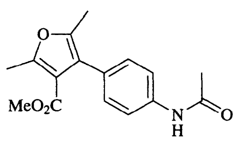
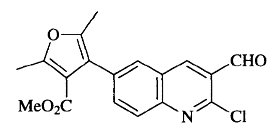
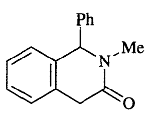
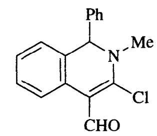
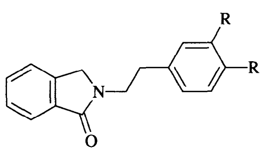
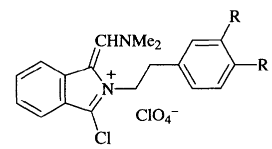
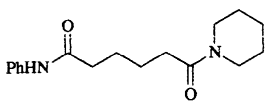
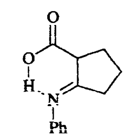
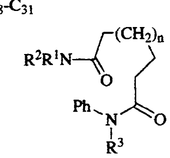
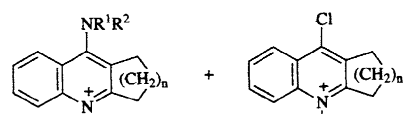
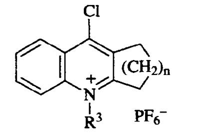
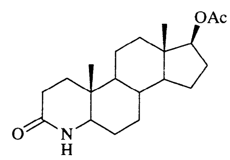
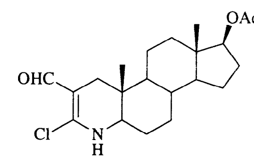
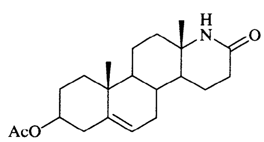
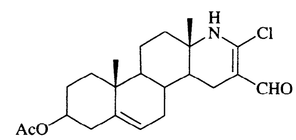
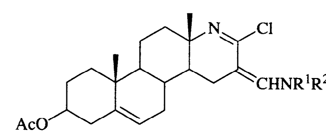
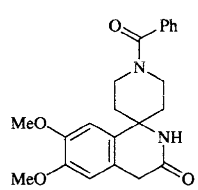
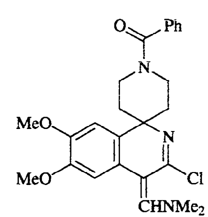
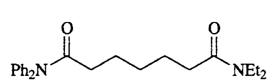
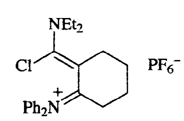
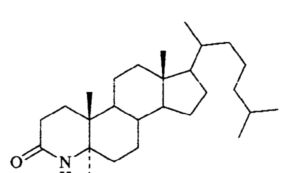
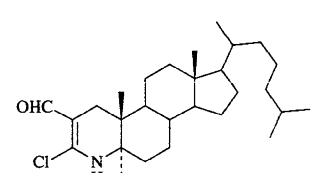
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}-C_{16}			
	DMF, $POCl_3$	 R^1 R^2 Cl H (66) CF_3 H (60) Cl OMe (66)	173
C_{16}			
	DMF, $POCl_3$	 (50)	547
	1. DMF, $POCl_3$ 2. $KMnO_4$	 (25)	182
C_{16}-C_{18}			
	1. DMF, $POCl_3$ 2. $NaClO_4$	 R H (80) MeO (80)	548
C_{17}			
	$POCl_3$	 (60)	549
C_{18}-C_{31}			
	1. $POCl_3$ 2. $NH_4^+ PF_6^-$	 I + II n R^1 R^2 R^3 I II 1 H Ph H (0) (55) 2 H Ph H (0) (97) 1 Ph Me Me (74) (18) 2 Ph Me Me (90) (0) 1 Ph Ph Ph (98) (0) 2 Ph Ph Ph (39) (—) 2 Me Ph Ph (6) (trace)	549
	1. $POCl_3$, PCl_5 2. $NH_4^+ PF_6^-$	 (30) n R^1 R^2 R^3 2 —$(CH_2)_5$— Me	549

TABLE XV. AMIDES AND LACTAMS (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}			
	DMF, $POCl_3$	 (20)	177
C_{21}			
	DMF, $POCl_3$, $CHCl_3$, reflux	 (18)	550
	R^1R^2NCHO, $POCl_3$		
		R^1 R^2	
		Me Me (—)	550
		—$(CH_2)_5$— (90)	545
		—$(CH_2)_2O(CH_2)_2$— (95)	545
C_{22}			
	DMF, $POCl_3$	 (94)	182
C_{23}			
	1. $POCl_3$ 2. $NH_4^+PF_6^-$	 PF_6^- (48)	549
C_{27}			
	DMF, $POCl_3$	 (20)	550

[a] The acid cyclizes to the lactam before reacting with the Vilsmeier reagent.

TABLE XVI. IMIDES

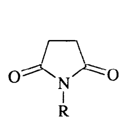
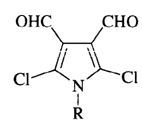
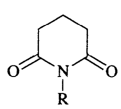
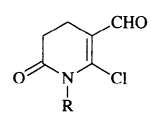
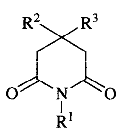
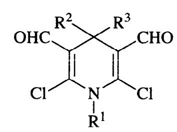
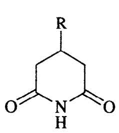
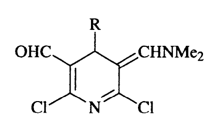
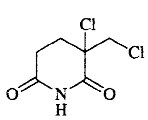
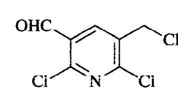
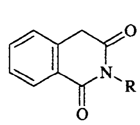
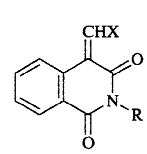
Substrate	Conditions	Product(s) and Yield(s) (%)					Refs.
C_5-C_{10}							
	DMF, $POCl_3$		R				183
			Me	(72)			
			Et	(40)			
			i-Pr	(41)			
			Ph	(74)			
C_5-C_{11}							
	DMF, $POCl_3$		R				185
			H	(1)			
			Me	(21)			
			Et	(53)			
			n-Pr	(85)			
			Ph	(41)			
C_5-C_{12}							
	DMF, $POCl_3$		R^1	R^2	R^3		
			H	H	H	(66)	184
			Me	Me	Me	(—)	551
			4-ClC_6H_4	H	H	(30)	184
			3-$O_2NC_6H_4$	H	H	(10)	184
			Ph	H	H	(61)	184
			4-MeC_6H_4	H	H	(10)	184
	DMF, $POCl_3$		R				186
			3-ClC_6H_4	(80)			
			3-$O_2NC_6H_4$	(61)			
			Ph	(72)			
			3-$CF_3C_6H_4$	(75)			
	DMF, $(COCl)_2$		H	(65)			
C_6							
	DMF, $POCl_3$ or $COCl_2$		(66)				187
C_9-C_{10}							
			R	X			188
	DMF, $POCl_3$		H	OH	(96)		
	DMF, $POCl_3$		Me	OH	(75)		
	PhNHCHO, $POCl_3$		Me	NHPh	(96)		
	MFA, $POCl_3$		Me	N(Me)Ph	(84)		

TABLE XVII. NITRILES

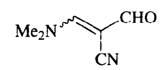
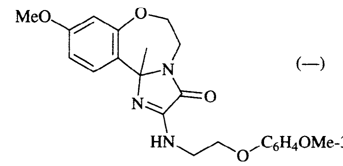
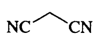
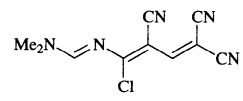
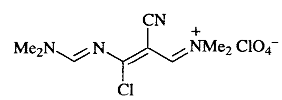
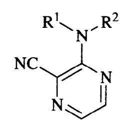
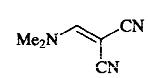
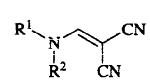
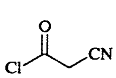
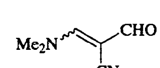
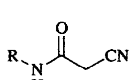
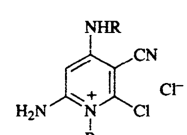
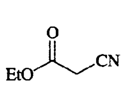
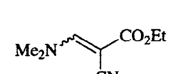
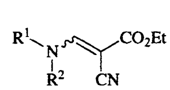
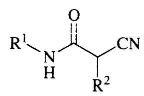
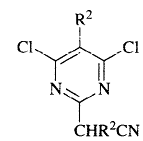
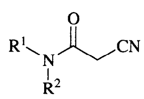
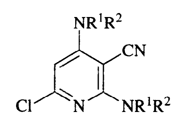
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
Me—CN	DMF, $POCl_3$	 (32)	145
	$(3\text{-}MeOC_6H_4OCH_2CH_2NHCO)_2$, $(Cl_2PO)_2O$	 (—)	552
C_3			
	DMF, $POCl_3$	 (17)	553
	1. DMF, $POCl_3$, $COCl_2$, or $(COCl)_2$ 2. $HClO_4$	 I (81)	189
	1. $[Me_2N{=}CHCl]^+ Cl^-$ 2. $HClO_4$	I (81)	189
	1. DMF, $POCl_3$ or $[Me_2N{=}CHCl]^+ Cl^-$ 2. $HClO_4$ 3. NH_3 (aq)	 II R^1, R^2 = Me (60)	189
	1. DMF, $POCl_3$ or $[Me_2N{=}CHCl]^+ Cl^-$ 2. $HClO_4$ 3. aniline 4. NH_3 (aq)	II R^1 = H, R^2 = Ph (90)	189
	1. DMF, $POCl_3$ or $[Me_2N{=}CHCl]^+ Cl^-$ 2. $HClO_4$ 3. *N*-methylaniline 4. NH_3 (aq)	II R^1 = Me, R^2 = Ph (90)	189
	DMF, $POCl_3$ or $ClCO_2Et$	 (10)	190
	R^1R^2NCHO, $POCl_3$	 R^1 R^2: Me Me (33); Me Ph (42)	554
	DMF, $POCl_3$	 (—)	145
C_4-C_{11}			
	$POCl_3$	 R: Me (80)	191, 555
		Bu (86)	191, 555
		i-Pr (39)	191
		c-C_5H_9 (67)	191
		c-C_6H_{11} (57)	191
		n-C_6H_{13} (75)	191
		n-C_8H_{17} (75)	191, 555
C_5			
	DMF, $POCl_3$ or $ClCO_2Et$	 (31)	190
	R^1R^2NCHO, $POCl_3$	 R^1 R^2: Me Me (48); Me Ph (71)	554

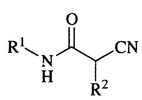
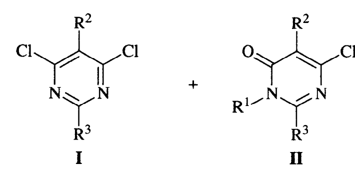
TABLE XVII. NITRILES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5-C_7 	$POCl_3$		192

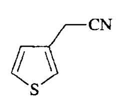
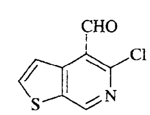
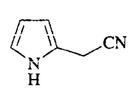
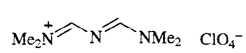
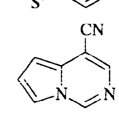
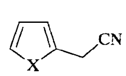
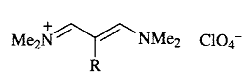
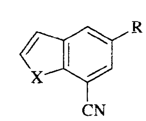
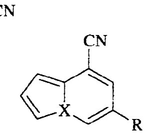
R^1	R^2	
Me	Me	(26)
Me	Et	(23)
Et	Me	(37)
Et	Et	(40)
i-Pr	Me	(44)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5-C_{10} 	$POCl_3$		556, 191

R^1	R^2	
Me	Me	(84)
Et	Et	(76)[a]
—$(CH_2)_4$—		(86)
—$(CH_2)_2O(CH_2)_2$—		(81)
Me	Ph	(76)

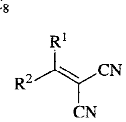
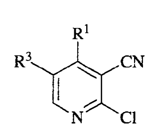
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5-C_{16} 	Me_2NCOR^3, $POCl_3$		

R^1	R^2	R^3	I	II	Refs.
Me	Me	Ph	(21)	(14)	193
Me	*s*-Bu	Ph	(52)	(21)	193
i-Pr	Et	Ph	(53)	(0)	193
c-C_6H_{11}	Et	Ph	(55)	(0)	193
c-C_6H_{11}	*n*-Pr	H	(37)	(19)	193
c-C_6H_{11}	*n*-Pr	Me	(25)	(0)	193
c-C_6H_{11}	*n*-Pr	Ph	(60)	(0)	193
c-C_6H_{11}	Ph	Ph	(80)	(0)	536a
c-C_6H_{11}	2-MeC_6H_4	Ph	(69)	(0)	536a

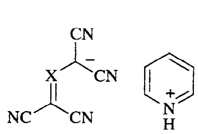
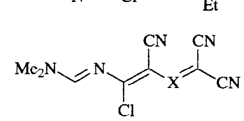
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	DMF, $POCl_3$	 (34)	558
		 (—)	194
C_6-C_7 		 I or  II	194

X	R	I	II
O	H	(81)	(0)
O	OMe	(93)	(0)
O	Bn	(82)	(0)
S	H	(98)	(0)
S	OMe	(83)	(0)
S	Bn	(88)	(0)
NH*	H	(0)	(80)
NH*	OMe	(0)	(83)
NH*	Bn	(0)	(79)
NMe	H	(94)	(0)
NMe	Me	(85)	(0)
NMe	OMe	(91)	(0)
NMe	Bn	(95)	(0)

*X = N in products **II**

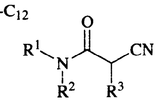
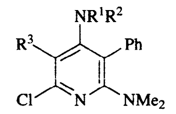
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6-C_8 	DMF, $POCl_3$		196

R^1	R^2	R^3	
H	Et	Me	(15)
H	*n*-Pr	Et	(19)
Me	Et	Me	(22)
Et	Et	Me	(23)

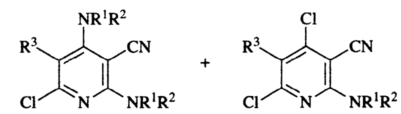
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$		553

X	
N	(71)
CH	(87)
C(Me)	(95)

TABLE XVII. NITRILES (*Continued*)

Substrate		Conditions	Product(s) and Yield(s) (%)	Refs.
C_6-C_{12} 		Me_2NCOCH_2Ph, $POCl_3$		559

R^1	R^2	R^3	
Me	Me	Me	(16)
Me	Me	Et	(17)
—$(CH_2)_4$—		Me	(35)
—$(CH_2)_4$—		Et	(40)

Substrate		Conditions	Product(s) and Yield(s) (%)	Refs.
		$POCl_3$	 I + II	559

R^1	R^2	R^3	Time	I	II
Me	Me	*i*-Pr	2 h	(9)	(10)
Me	Me	*i*-Pr	16 h	(0)	(75)
—$(CH_2)_4$—		*i*-Pr	2 h	(31)	(23)
—$(CH_2)_4$—		*i*-Pr	16 h	(0)	(88)
Et	Et	*i*-Pr	16 h	(62)	(0)
Me	Me	CH_2Ph	16 h	(0)	(60)

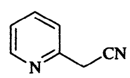
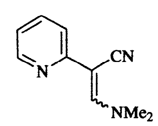
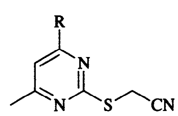
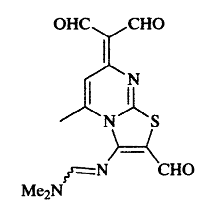
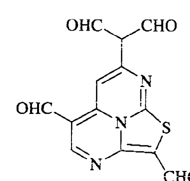
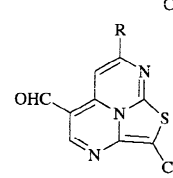
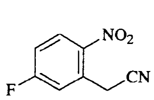
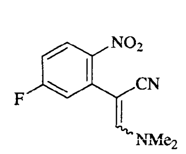
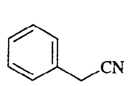
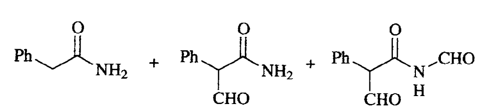
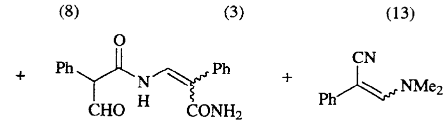
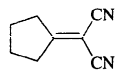
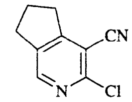
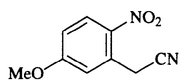
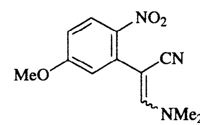
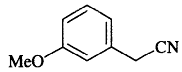
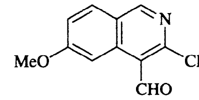
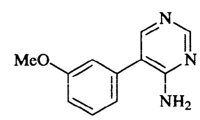
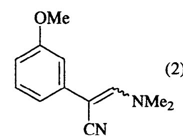
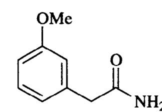
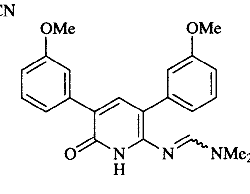
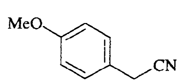
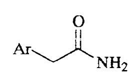
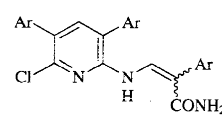
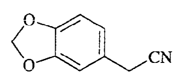
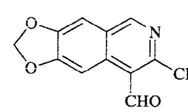
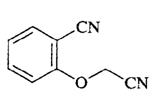
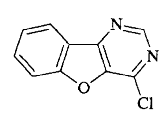
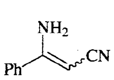
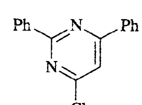
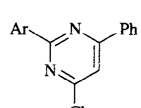
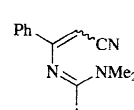
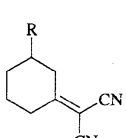
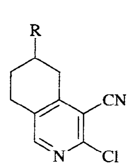
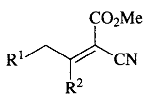
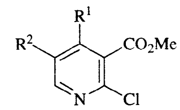
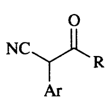
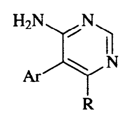
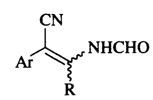
Substrate		Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		DMF, $POCl_3$	 (69)	157
C_7-C_{14} 	R = H	DMF, $POCl_3$	 (40)	195
	R = Me	DMF, $POCl_3$	 (67)	195
	R = CF_3	DMF, $POCl_3$	 (93) I, R = CF_3	195
	R = Ph	DMF, $POCl_3$	I, R = Ph (75)	195
	R = 4-$MeOC_6H_4$	DMF, $POCl_3$	I, R = 4-$MeOC_6H_4$ (51)	195
C_8 		DMF, $POCl_3$	 (81)	218
		1. DMF, $POCl_3$, 10-12° 2. 60-70°	 (8) + (3) + (13)  + (1) + (1)	560

TABLE XVII. NITRILES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 (9)	196
C_9			
	DMF, $POCl_3$	 (87)	218
	DMF, $POCl_3$, 110-120°, 2 h	 (4)	561
	H_2NCHO, $POCl_3$	 (—)	425
	1. DMF, $POCl_3$, 10-12° 2. 60-70°	 (2) +  (10) +  (11)	560
	1. DMF, $POCl_3$, 10-12° 2. 60-70°	 (7) +  (1.5) Ar = 4-$MeOC_6H_4$	560
	DMF, $POCl_3$, 100-110°, 3 h	 (6)	561
	DMF, $POCl_3$	 (5)	562
	Me_2NCOPh, $POCl_3$	 (85) I	536a
	$Me_2NCOC_6H_4Me$-2, $POCl_3$	 (50) +  (13) Ar = 2-MeC_6H_4	536a
C_9-C_{10}			
	DMF, $POCl_3$	 R: H (11); Me (10)	196

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9-C_{14}			
	DMF, $POCl_3$	 (see below)	197

R^1	R^2	
Me	Me	(65)
—$(CH_2)_3$—		(35)
—$(CH_2)_4$—		(50)
—$CH_2C_6H_4$—		(20)
Ph	Me	(35)
—$(CH_2)_2C_6H_4$—		(40)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9-C_{17}			
	H_2NCHO, $POCl_3$	 I +  II	

Ar	R	I	II	Refs.
3-ClC_6H_4	H	(6)	(23)	198
3-ClC_6H_4	Me	(10)	(16)	198
3-MeC_6H_4	H	(—)	(—)	563
3-MeC_6H_4	Me	(—)	(—)	563
3,4-$(MeO)_2C_6H_3$	H	(—)	(—)	427
3,5-$Me_2C_6H_3$	H	(—)	(—)	563
3,4-$(MeO)_2C_6H_3$	Me	(—)	(—)	427
3,5-$Me_2C_6H_3$	Me	(—)	(—)	563
3-ClC_6H_4	Ph	(0)	(30)	198
3-MeC_6H_4	Ph	(—)	(—)	563
3,5-$Me_2C_6H_3$	Ph	(—)	(—)	563
3,4-$(MeO)_2C_6H_3$	Ph	(—)	(—)	427

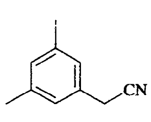
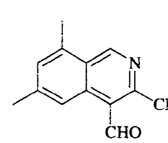
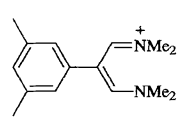
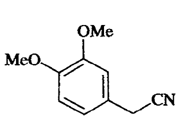
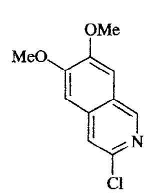
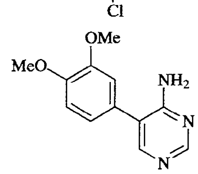
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMF, $POCl_3$, 110-120°, 4 h	 (3)	561
	1. DMF, $POCl_3$ 2. HCl 3. $HClO_4$	 ClO_4^- (59)	529
	DMF, $POCl_3$, 110–120°, 4 h	 (8)	561
	NH_2CHO, $POCl_3$	 (—)	427

TABLE XVII. NITRILES (*Continued*)

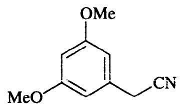
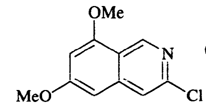
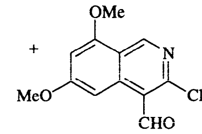
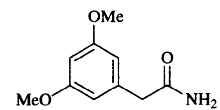
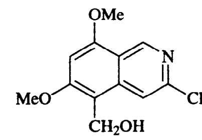
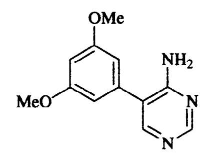
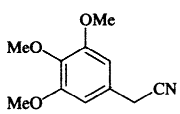
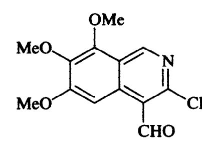
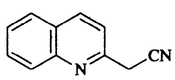
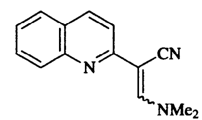
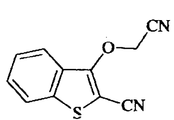
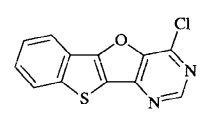
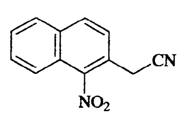
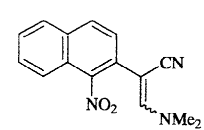
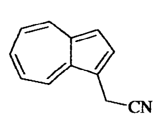
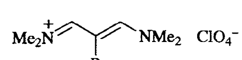
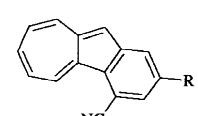
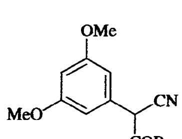
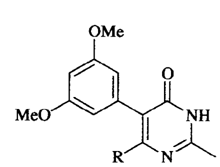
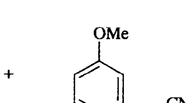
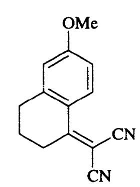
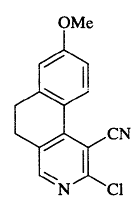
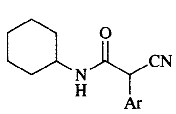
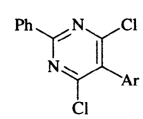
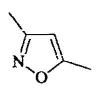
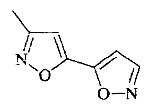
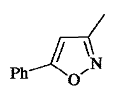
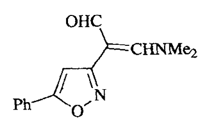
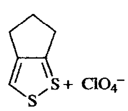
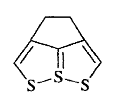
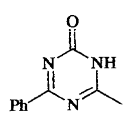
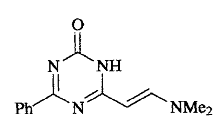
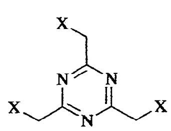
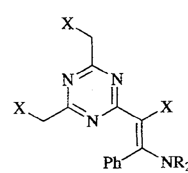
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$, 90-95°	 (62) +  (1) I	561, 456
	1. DMF, $POCl_3$, 10-12° 2. 60-70°	 (4) + I (52) +  (3)	560
	H_2NCHO, $POCl_3$	 (—)	425
C_{11}			
	DMF, $POCl_3$, 110-120°, 4 h	 (8)	561
	DMF, $POCl_3$	 (81)	157
	DMF, $POCl_3$	 (7)	564
C_{12}			
	DMF, $POCl_3$	 (81)	218
		 R: H (41); Ph (79)	214
C_{12}-C_{13}			
	H_2NCOMe, $POCl_3$	 I +  II R: Me, I (58), II (6); Et, I (45), II (9)	198

TABLE XVII. NITRILES (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{14}				
	DMF, $POCl_3$		(12)	196
C_{15}-C_{16}				
	$PhCONMe_2$, $POCl_3$, 100°, 16-18 h		Ar: Ph (80); 2-MeC_6H_4 (69)	557

[a] This entry is from reference 191 only.

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3NO			
C_5			
	1. "Vilsmeier-Haack" 2. H_2NOH	 (—)	200
C_{10}			
	—	 (—)	200
C_3S_2			
C_6			
	Me_2NCHS, $POCl_3$	 (59)	220
C_3N_3			
C_{10}			
	DMF, $4\text{-}MeC_6H_4SO_2Cl$	 (—)	201
C_{24}			
	$PhCONR_2$, $POCl_3$		202

X	R, R	
$4\text{-}ClC_6H_4$	Me	(63)
$4\text{-}ClC_6H_4$	$—(CH_2)_5—$	(21)
Ph	Me	(58)
Ph	$—(CH_2)_2O(CH_2)_2—$	(45)

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

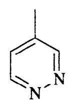
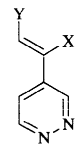
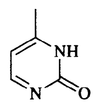
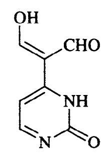
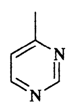
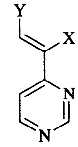
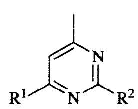
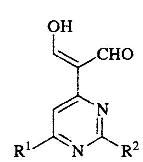
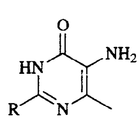
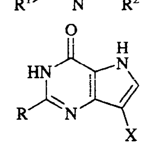
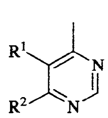
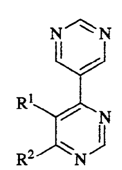
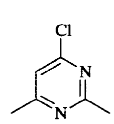
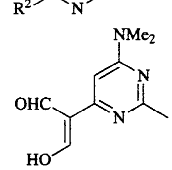
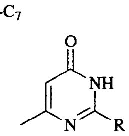
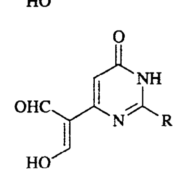
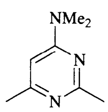
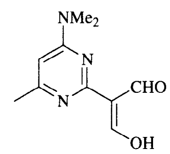
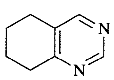
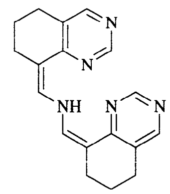
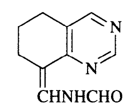
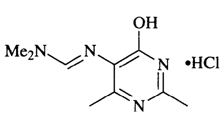
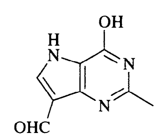
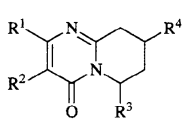
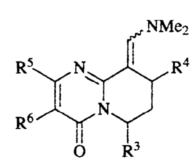
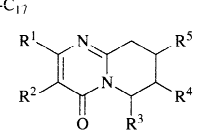
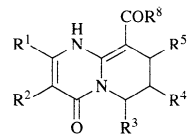
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4N_2			
Pyridazines			
C_5			
	DMF, $POCl_3$	 **I** X = CHO, Y = NMe_2 (91)	199
	1. DMF, $POCl_3$ 2. HO^-	**I** X = CHO, Y = OH (—)	199
Pyrimidines			
C_5			
	DMF, $(COCl)_2$	 (40)	565
	1. DMF, $COCl_2$ 2. HCl	 **I** X = H, Y = NMe_2•2HCl (80)	204, 566
	1. $[ClCH{=}NMe_2]^+ Cl^-$ 2. HO^-	**I** X = H, Y = NMe_2 (56)	567
	DMF, $(COCl)_2$	**I** X = CHO, Y = NMe_2 (—)	568
	1. DMF, $COCl_2$ 2. H_2O	**I** X = CHO, Y = OH (—)	566
	$[ClCH{=}NMe_2]^+ Cl^-$ (excess)	**I** X = CHO, Y = OH (47)	567
C_5-C_{11}			
	1. DMF, $POCl_3$ 2. HO^-	 R^1 R^2 H H (10) Ph H (62) H Ph (48)	569
	1. DMF, $POCl_3$ 2. $NaHCO_3$ (aq)	 **I**, X = CHO R **I** H (70) Me (67)	228 570
	DMF, $POCl_3$	**I**, R = Ph; X = $CH{=}NMe_2^+ Cl^-$ (63)	228
C_6			
	$HCONH_2$, $POCl_3$	 R^1 R^2 H Me (6) Me H (12)	571
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (43)	569
C_6-C_7			
	1. DMF, $POCl_3$ 2. K_2CO_3 (aq)	 R Me (10) Et (28)	569

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (6)	569
	H_2NCHO, $POCl_3$	 (23) +  (0.4)	571
C_9			
	1. DMF, $POCl_3$ 2. H_2O	 (65)	572
C_9-C_{15}			
	DMF, $POCl_3$		573

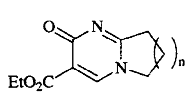
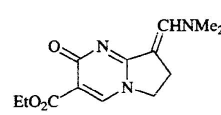
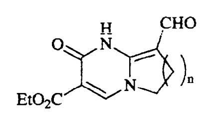
R^1	R^2	R^3	R^4	Temp	R^5	R^6	
H	H	Me	H	95°	H	CHO	(70)
OMe	H	H	H	—	Cl	CHO	(73)
H	$CONH_2$	Me	H	—	H	CN	(98)
Me	H	Me	H	—	Me	CHO	(36)
H	CONHMe	Me	H	15°	H	CONHMe	(72)
H	CONHMe	Me	H	95°	H	CON(CHO)Me	(85)
H	$CONHNH_2$	Me	H	25°	H	$CONHN{=}CHNMe_2$	(70)
H	$CONHNH_2$	Me	H	60°	H	CO_2H	(45)
H	$CONH_2$	Me	Me	—	H	CN	(78)
Ph	H	Me	H	—	Ph	CHO	(89)

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

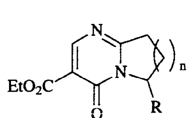
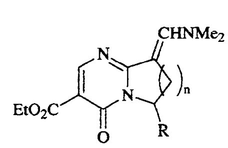
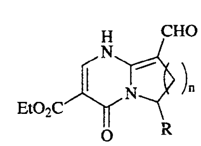
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9-C_{17} 	$R^6R^7NCOR^8$, $POCl_3$, rt-95°		

R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8		Refs.
H	H	Me	H	H	Me	Me	H	(73)[a]	573
H	Me	Me	H	H	—$(CH_2)_5$—		H	(53)	574
H	Me	Me	H	H	Me	Me	H	(81)	573
—$(CH_2)_4$—		H	H	H	Me	Me	H	(63)	575
H	CO_2Et	Me	H	H	Et	Et	Ph	(38)	574
H	CH_2CO_2Et	H	H	H	Me	Me	H	(72)	573
Me	Et	Me	H	H	Me	Me	H	(73)	573
—$(CH_2)_4$—		Me	H	H	Me	Me	H	(74)	575
—$(CH_2)_4$—		H	Me	H	Me	Me	H	(52)	575
H	CH_2CO_2Et	Me	H	H	Me	Me	H	(88)	573
H	CH_2CO_2Et	H	Me	H	Me	Me	H	(85)	573
H	CH_2CO_2Et	H	H	Me	Me	Me	H	(71)	573
H	2,4-$(O_2N)_2C_6H_3$	H	H	H	Me	Me	H	(84)	573
H	$(CH_2)_2CO_2Et$	Me	H	H	Me	Me	H	(79)	573
1-piperidyl	H	Me	H	H	Me	Me	H	(43)	573
H	Ph	Me	H	H	Et	Et	Ph	(35)	574
H	Ph	Me	H	H	Me	Me	H	(86)	573
H	Ph	H	CO_2Et	H	Me	Me	H	(61)	573
Me	Bn	Me	H	H	Me	Me	H	(70)	573

C_{10}-C_{13}

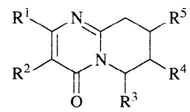
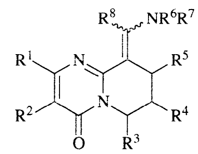
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 I or  II	576

n	I	II
1	(76)	(0)
2	(0)	(56)
3	(0)	(49)
4	(0)	(35)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, $POCl_3$	 I or  II	576

R	n	I	II
H	1	(75)	(0)
Me	1	(88)	(0)
H	2	(45)	(0)
H	3	(42)	(0)
H	4	(0)	(68)

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}-C_{15} 	$R^6R^7NCOR^8$, $POCl_3$		

R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	Yield (%)	Refs.
H	CN	Me	H	H	Me	Ph	H	(82)	574
H	CO_2H	Me	H	H	Me	Me	H	(59)	573
H	CN	Me	H	H	Me	—$(CH_2)_3$—		(44)	574
H	CN	Me	H	H	Me	Me	H	(97)	573
H	CO_2Et	H	H	H	Me	Me	H	(65)	576, 573
H	CO_2Me	Me	H	H	Me	Me	H	(70)	573
H	CO_2Et	Me	H	H	Me	Me	H	(76)	576, 573
H	CO_2Et	Me	H	H	—$(CH_2)_5$—		H	(95)	574
H	CO_2Et	Me	H	H	Me	Ph	H	(88)	574
H	CO_2Et	H	Me	H	Me	Me	H	(72)	573
H	CO_2Et	H	H	Me	Me	Me	H	(68)	573
H	CO_2Et	Me	H	Me	Me	Me	H	(79)	573
H	CH_2CO_2Et	Me	H	H	Me	Ph	H	(51)	574
H	Ph	Me	H	H	Me	Ph	H	(75)	574

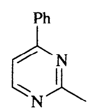
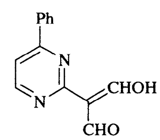
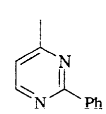
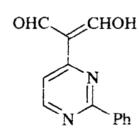
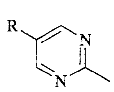
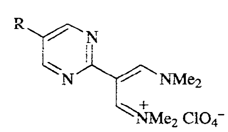
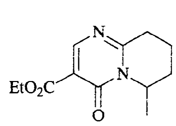
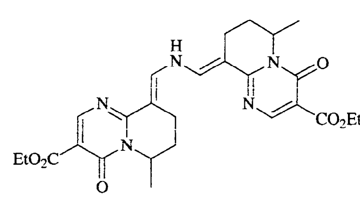
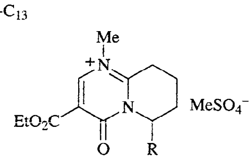
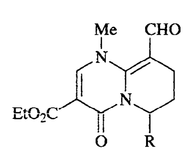
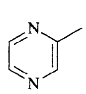
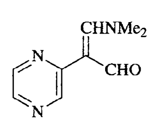
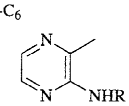
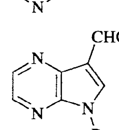
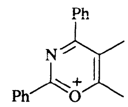
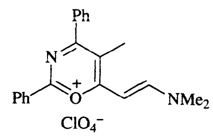
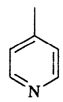
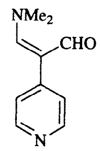
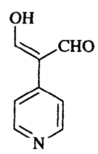
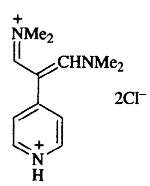
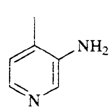
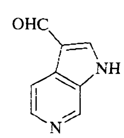
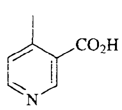
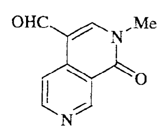
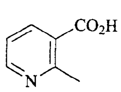
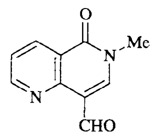
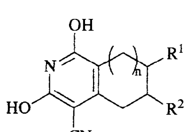
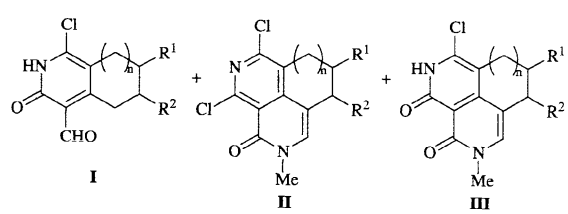
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (8)	569
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (62)	569
C_{11}-C_{15} 	1. DMF, $POCl_3$ 2. $NaClO_4$	 R: 4-BrC_6H_4 (38); 4-*n*-BuC_6H_4 (—); 4-*n*-$BuOC_6H_4$ (37)	203
C_{12} 	H_2NCHO, $POCl_3$	 (15)	574
C_{12}-C_{13} 	DMF, $POCl_3$	 R: H (53); Me (—)	221 576
Pyrazines			
C_5 	DMF, $POCl_3$	 (61)	205
C_5-C_6 	1. DMF, $POCl_3$ 2. H_2O	 R: H (56); Me (20)	229

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4NO			
C_{18}			
 ClO_4^-	DMF, $POCl_3$	 (50)	222
C_5N			
C_6			
	DMF, $POCl_3$	 I (91)	206
	DMF, $COCl_2$	I (51)	206
	1. DMF, $(COCl)_2$ 2. OH^-	 II (68)	577
	1. DMF, $POCl_3$ 2. OH^-	II (80)	206
	DMF, $(COCl)_2$	 (82)	577
	1. DMF, $POCl_3$ 2. KOH (aq)	 (19)	578
C_7			
	DMF, $POCl_3$	 (58)	231
	DMF, $POCl_3$	 (47)	231
C_9-C_{14}			
	DMF, $POCl_3$	 I + II + III	230

R^1	R^2	n	I	II	III
H	H	0	(20)	(18)	(10)
H	H	1	(33)	(15)	(8)
H	H	2	(36)	(11)	(6)
Me	H	1	(34)	(13)	(7)
H	Me	1	(36)	(15)	(7)
Et	H	1	(34)	(15)	(6)
t-Bu	H	1	(31)	(12)	(6)

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

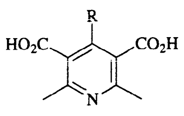
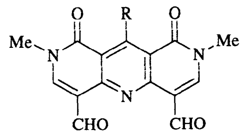
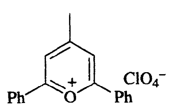
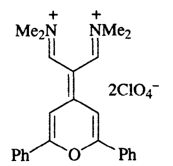
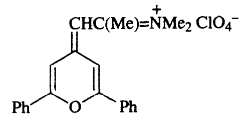
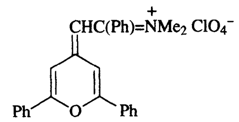
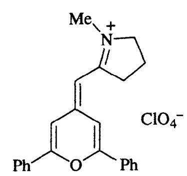
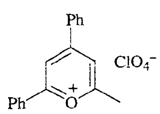
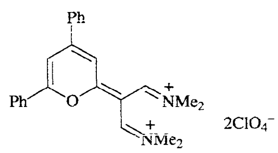
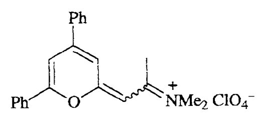
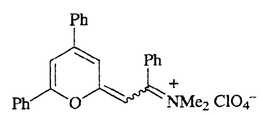
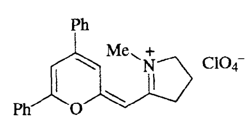
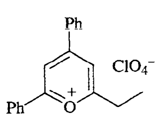
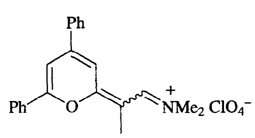
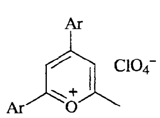
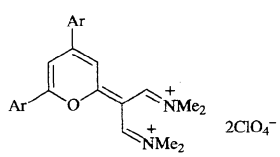
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9-C_{16}			
	DMF, $POCl_3$	 R: H (18); Ph (27); 4-$MeOC_6H_4$ (15)	231
C_5O			
C_{18}			
	DMF, $POCl_3$	 (94)	219
	Me_2NCOMe, $POCl_3$	 (60)	219
	Me_2NCOPh, $POCl_3$	 (84)	219
	1-Me-2-pyrrolidone, $POCl_3$	 (93)	219
	DMF, $POCl_3$	 (83)	219
	Me_2NCOMe, $POCl_3$	 (54)	219
	Me_2NCOPh, $POCl_3$	 (66)	219
	1-Me-2-pyrrolidone, $POCl_3$	 (50)	219
C_{19}-C_{20}			
	DMF, $POCl_3$	 (67)	219
 Ar = 4-$MeOC_6H_4$	DMF, $POCl_3$	 (90)	219

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

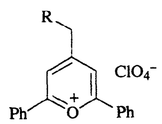
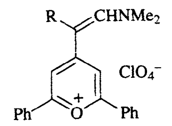
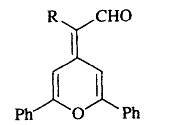
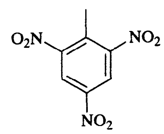
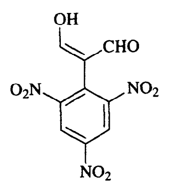
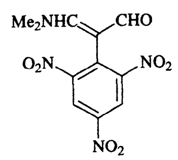
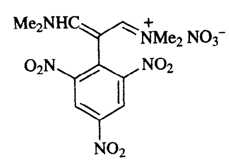
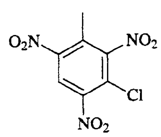
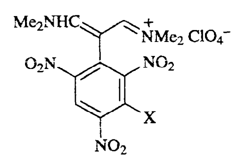
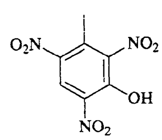
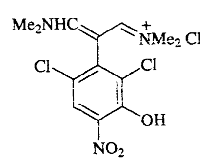
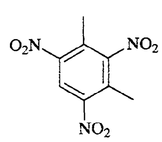
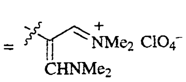
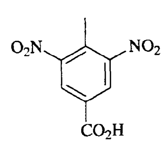
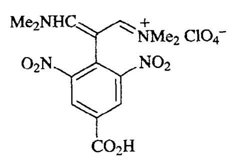
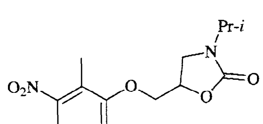
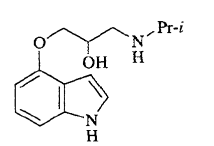
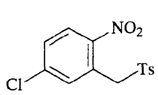
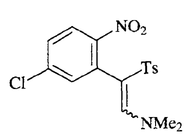
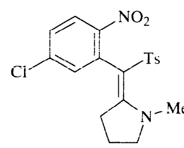
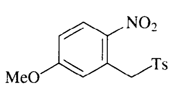
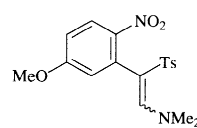
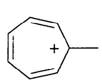
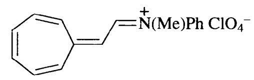
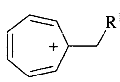
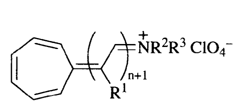
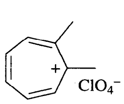
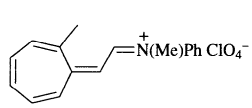
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}-C_{25}			
	DMF, Ac_2O	 R: Me (95); Ph (73); COPh (70)	579
	1. DMF, Ac_2O 2. $HClO_4$, AcOH, H_2O 3. hydrolysis	 R: Me (95); Ph (80); COPh (80)	579
C_6			
C_7			
	1. DMF, $POCl_3$, 80°, 0-5 h 2. HNO_3 3. HO^-	 (42)	207
	1. DMF, $POCl_3$, reflux, 2 h 2. HNO_3 3. HO^-	 (47)	207
	1. DMF, $POCl_3$ 2. HNO_3	 (60)	207
	1. DMF, $POCl_3$ 2. $HClO_4$	 **I**, X = Cl (76)	580
	1. DMF, $POCl_3$ 2. $HClO_4$	**I**, X = OH (33) +  (13)	580
C_8			
	1. DMF, $POCl_3$ 2. $HClO_4$	**I**, X =  (50)	580
	1. DMF, $POCl_3$ 2. $HClO_4$	 (75)	580
C_{14}			
	1. DMF, $SOCl_2$ 2. Pd, H_2	 (63)	581
	DMF, $POCl_3$	 (72-91)	218

TABLE XVIIIA. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED MONOCYCLIC RING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	N-methylpyrrolidone, $POCl_3$	 (—)	218
C_{15} 	DMF, $POCl_3$	 (—)	218
C_7			
C_8  ClO_4^-	1. Ph(Me)NCHO, $POCl_3$ 2. $NaClO_4$	 (81)	223
C_8-C_{14}  ClO_4^-	1. $R^2R^3N(CH{=}CH)_nCHO$, PCl_5 2. $NaClO_4$		223
C_9  ClO_4^-	MFA, $POCl_3$	 (91)	223

R^1	R^2	R^3	n	
H	Me	Me	0	(96)
H	Me	Ph	0	(74)
H	Me	Ph	1	(—)
Me	Me	Me	0	(93)
Me	—$(CH_2)_5$—		0	(—)
Me	Me	Ph	0	(63)
Ph	Me	Me	0	(62)
Ph	—$(CH_2)_5$—		0	(—)
Ph	Me	Ph	0	(63)

[a] This reaction was carried out at 25°.

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING

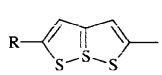
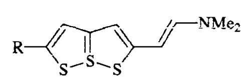
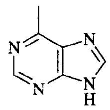
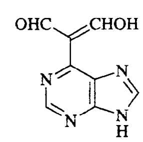
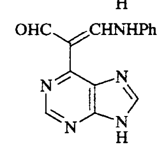
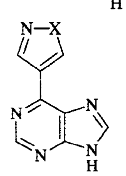
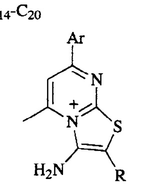
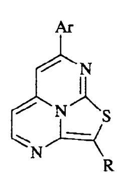
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3S_2/C_3S_2			
C_6-C_7			
	Me_2NCHS, $POCl_3$	 R: H (18); Me (2.5)	208
C_3N_2/C_4N_2			
C_6			
	DMF, $POCl_3$	 (82)	209
	1. DMF, $POCl_3$ 2. $PhNH_2$	 (42)	209
	1. DMF, $POCl_3$ 2. RNH_2	 R, X: OH, O (93); NH_2, NH (86); NHPh, NPh (80); $NHC(S)NH_2$, $N(CS)NH_2$ (94)	209
C_3NS/C_4N_2			
C_{14}-C_{20}			
 ClO_4^- or Br^-	DMF, $POCl_3$	 Ar, R: Ph, Me (47); Ph, CO_2Et (71); Ph, Ph (57); 4-$MeOC_6H_4$, Ph (60)	224

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

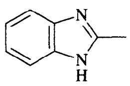
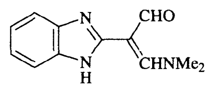
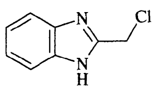
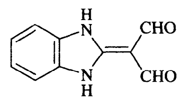
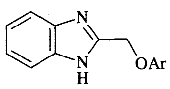
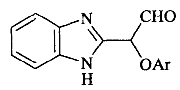
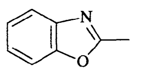
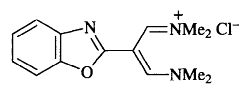
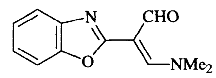
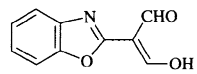
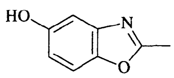
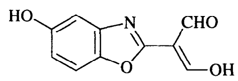
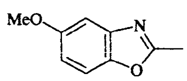
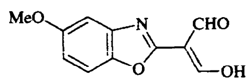
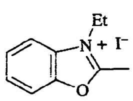
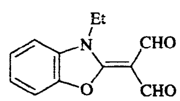
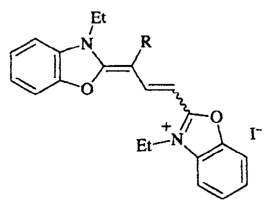
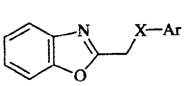
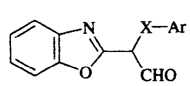
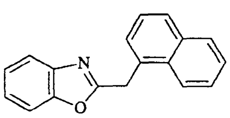
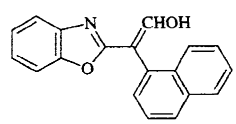
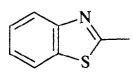
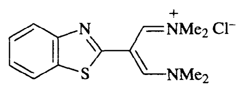
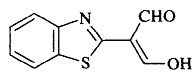
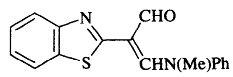
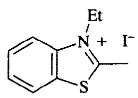
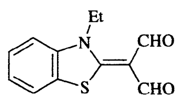
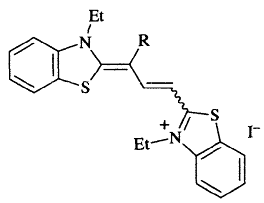
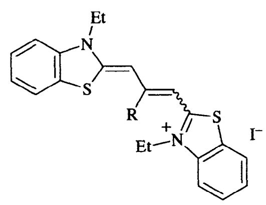
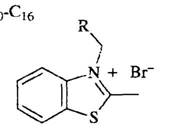
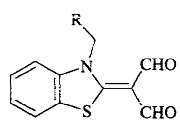
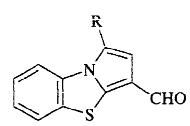
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3N_2/C_6			
C_8			
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (66)	210, 582
	1. DMF, $POCl_3$ 2. K_2CO_3 (aq)	 (—)	210
C_{18}-C_{21}			
	DMF, $POCl_3$	 Ar: 2-naphthyl (70); 3-$PhCONHC_6H_4$ (67)	210
C_3NO/C_6			
C_8			
	$ClCH{=}NMe_2^+\ Cl^-$, DMF, 60°, 6 h	 (82)	211
	DMF, $POCl_3$	 (60) +  (30)	583
	1. DMF, $POCl_3$ 2. KOH (aq)	 (75)	584
C_9			
	1. DMF, $POCl_3$ 2. KOH (aq)	 (80)	584
C_{10}			
	1. $ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h 2. H_2O	 (76)	211
	1. $ClCH{=}NMe_2^+Cl^-$, $CHCl_3$, 60°, 6 h 2. K_2CO_3, H_2O	 R: H (41); CHO (23)	211
C_{15}-C_{21}			
	DMF, $POCl_3$		
		X: CH_2, Ar: Ph (—)	585
		X: $(CH_2)_2$, Ar: Ph (90)	586
		X: O, Ar: 2-naphthyl (—)	587
		X: CH_2, Ar: 2-naphthyl (—)	585
		X: $(CH_2)_2$, Ar: 1-naphthyl (—)	586
		X: $(CH_2)_2$, Ar: 2-naphthyl (—)	586
		X: O, Ar: 3-$PhCONHC_6H_4$ (—)	587
C_{18}			
	DMF, $POCl_3$	 (64)	497

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3NS/C_6			
Benzo[*d*]thiazoles			
C_8 	$ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h	 (63)	211
	1. DMF, $POCl_3$ 2. KOH (aq)	 (70)	212
	1. MFA, $POCl_3$ 2. Na_2CO_3 (aq)	 (60)	212
C_{10} 	1. $ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h 2. H_2O	 (62)	211
	1. $ClCH{=}NMe_2^+Cl^-$, $CHCl_3$, 60°, 6 h 2. K_2CO_3, H_2O	 **I**, R = H (23) + **I**, R = CHO (43)	211
	DMF, $POCl_3$	**I**, R = H (87)	29
	H_2NCOMe, $POCl_3$	 **II**, R = Me (52)	29
	H_2NCOEt, $POCl_3$	**II**, R = Et (40)	29
	H_2NCOBu-*t*, $POCl_3$	**II**, R = *t*-Bu (44)	29
	H_2NCOPh, $POCl_3$	**II**, R = Ph (42)	29
C_{10}-C_{16} 	DMF, $POCl_3$	 **I** or  **II**	225

R	I	II
CN	(0)	(52)
CO_2Me	(0)	(61)
Ph	(81)	(0)
4-BrC_6H_4CO	(0)	(78)
PhCO	(0)	(53)

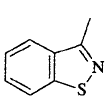
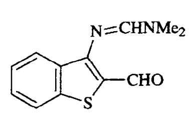
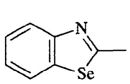
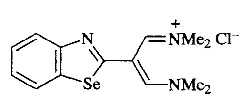
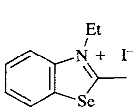
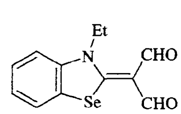
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
Benzo[*d*]isothiazoles			
C_8 	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (85)	212
C_3NSe/C_6			
C_8 	$ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h	 (71)	211
	1. $ClCH{=}NMe_2^+Cl^-$ DMF, 60°, 6 h 2. H_2O	 (70)	211

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

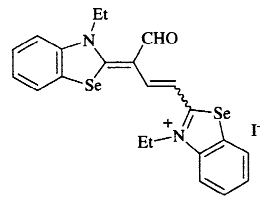
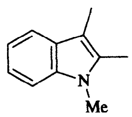
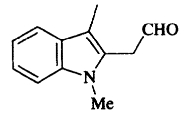
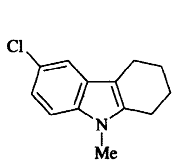
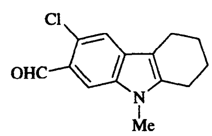
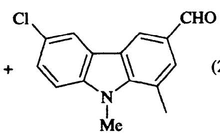
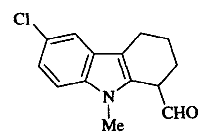
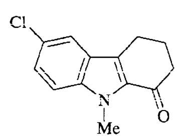
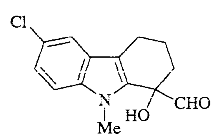
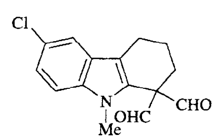
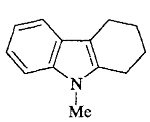
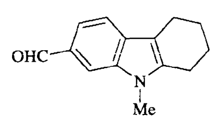
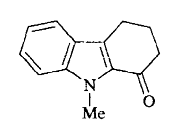
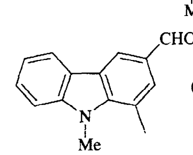
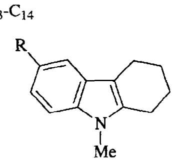
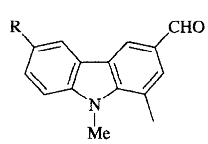
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $ClCH=NMe_2^+Cl^-$, $CHCl_3$, 60° 2. K_2CO_3, H_2O	 (32)	211
C_4N/C_6 C_{11} 	DMF, $POCl_3$	 (80)	213
C_{13} 	DMF, $POCl_3$ (1.3 eq), 100°	 (2) +  (2-8) +  (2-21)	227
	DMF, $POCl_3$ (3 eq)	 (12) +  (10) +  (65)	227
	Et_2NCHO, $POCl_3$	 (—) +  (2) +  (27)	227
C_{13}-C_{14} 	DMF, $POCl_3$	 R Cl (—) H (55) Me (—)	 588 588 588, 227

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

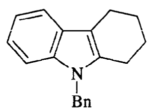
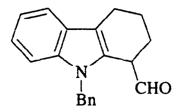
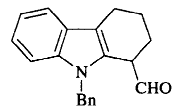
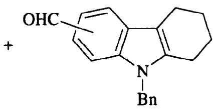
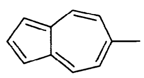
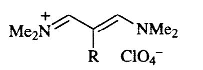
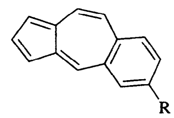
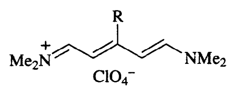
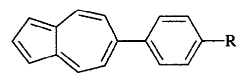
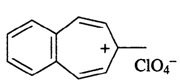
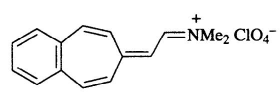
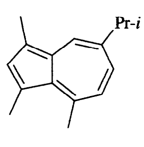
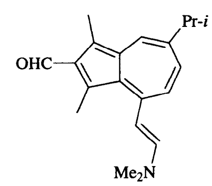
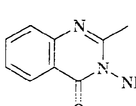
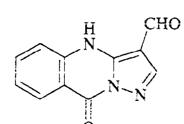
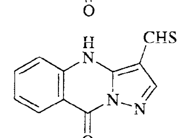
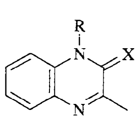
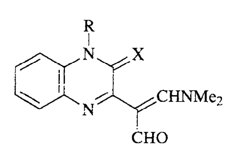
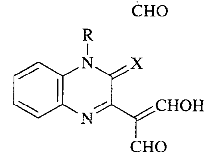
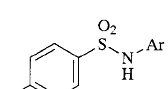
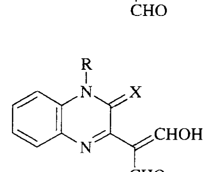
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
	R^1R^2NCHO, $POCl_3$	 R^1 / R^2: —$(CH_2)_4$— (81); Et / Et (57)	589
	Ph(Me)NCHO, $POCl_3$	 (4) +  (79) 5:6:7 (formyl position) = 6:21:57	589
C_5/C_7			
C_{11}			
		 R: H (74); OMe (68); Et (97); Ph (71); Bn (79)	214
		 R: H (60); Ph (57)	214
C_{12}			
	DMF, PCl_5	 (—)	223
C_{16}			
	DMF, $POCl_3$	 (76)	226
C_4N_2/C_6			
C_9			
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (77)	215
	1. DMF, $POCl_3$ 2. NaSH (aq)	 (63)	215
C_9-C_{19}			
	DMF, $POCl_3$	 R / X: H / S (72)	216
		H / O (72)	590
		Me / S (78)	216
		Me / O (75)	216
	1. DMF, $POCl_3$ 2. NaOH (aq)	 R / X: H / S (51)	216
		H / O (46)	590
		Me / S (59)	216
		Me / O (51)	216
R = 	1. DMF, $POCl_3$ 2. NaOH (aq)	 Ar / X: 2-thiazoyl / S (78)	591
		2-thiazoyl / O (70)	592
		2-pyrimidyl / S (72)	591
		2-pyrimidyl / O (71)	592
		2-pyridyl / S (68)	591

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

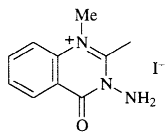
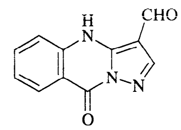
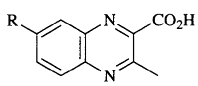
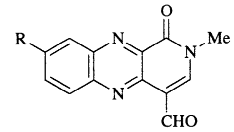
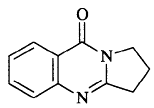
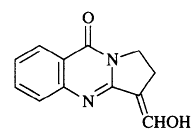
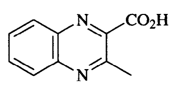
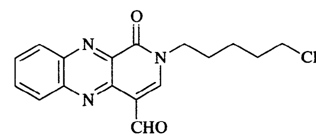
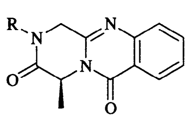
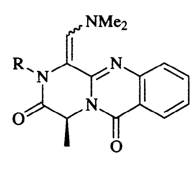
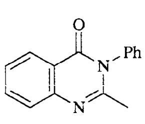
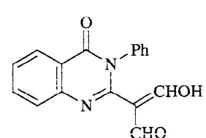
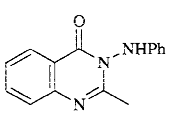
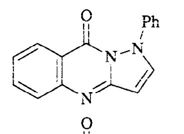
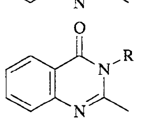
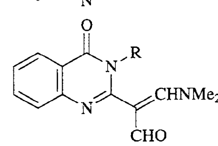
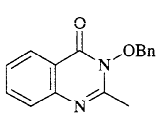
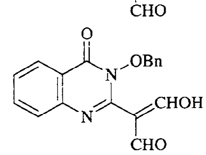
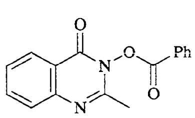
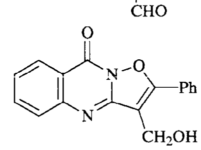
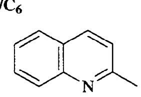
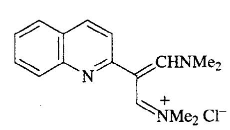
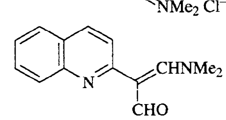
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	DMF, $POCl_3$	 (—)	215
C_{10}-C_{11}			
	DMF, $POCl_3$	 R: H (48); OMe (56)	231
C_{11}			
	—	 (73)	593
	*N*-formylpiperidine, $POCl_3$	 (39)	510
C_{13}-C_{20}			
	$ClCH{=}NMe_2^+\ Cl^-$	 R: Me (96); 4-$MeOCH_2C_6H_4$ (95); Bn (—)	321
			232
C_{15}			
	1. DMF, $POCl_3$ 2. NaOH (aq), heat	 (68)	215
	1. DMF, $POCl_3$ 2. Na_2CO_3 (aq)	 (75)	215
C_{16}			
	DMF, $POCl_3$	 R: OBn (83); N=CHPh (61)	594 595
	1. DMF, $POCl_3$ 2. NaOH	 (75)	594
	DMF, $POCl_3$	 (—)	594
C_5N/C_6			
C_{10} 	$ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h	 (87)	211
	DMF, $POCl_3$	 (—)	498

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

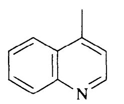
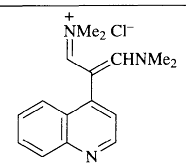
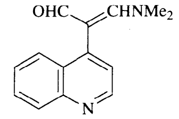
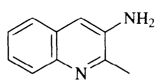
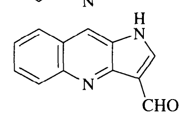
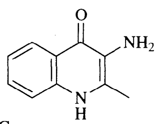
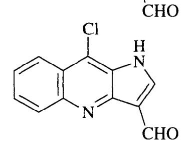
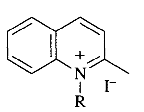
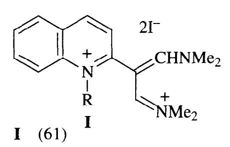
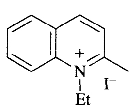
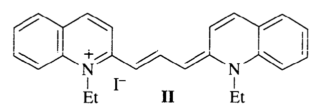
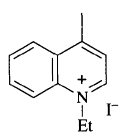
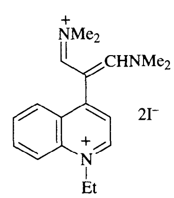
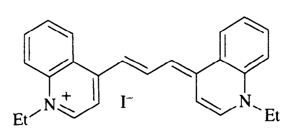
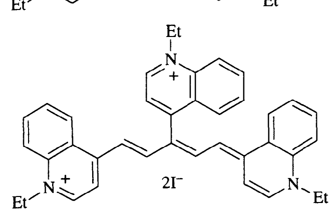
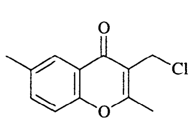
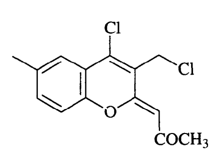
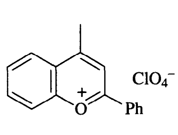
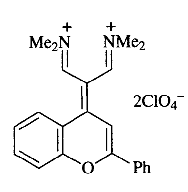
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	$ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h	 (93)	211
	DMF, $POCl_3$	 (—)	498
	1. DMF, $POCl_3$ 2. KOH (aq)	 (35)	578
	DMF, $POCl_3$	 (97)	596
C_{11}-C_{12}			
 R = Me	DMF, $POCl_3$	 **I** (47)	597
R = Et	$ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h	**I** (61)	211
	DMF, $POCl_3$	 **II** (92)	29
	1. $ClCH{=}NMe_2^+Cl^-$, $CHCl_3$, 60°, 6 h 2. K_2CO_3, H_2O	**II** (32)	211
C_{12}			
	$ClCH{=}NMe_2^+Cl^-$, DMF, 60°, 6 h	 (92)	211
	DMF, $POCl_3$	 (45)	29
	1. $ClCH{=}NMe_2^+Cl^-$, $CHCl_3$, 60°, 6 h 2. K_2CO_3, H_2O	 (41)	211
C_5O/C_6			
C_{12}			
	DMA, $POCl_3$	 (—)	217
C_{16}			
	DMF, $POCl_3$	 (73)	219

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

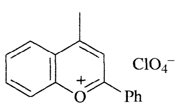
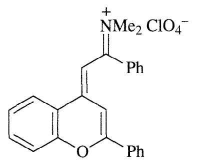
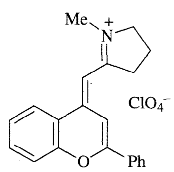
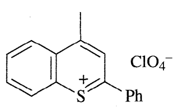
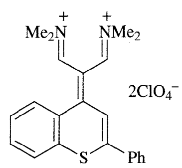
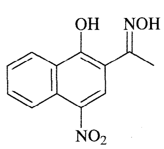
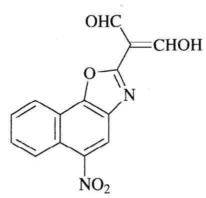
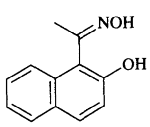
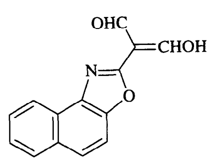
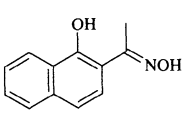
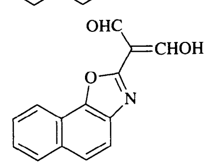
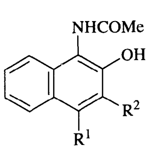
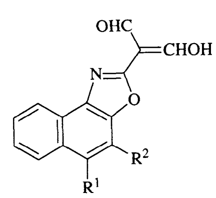
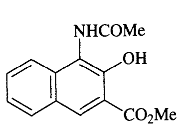
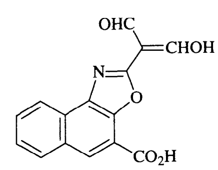
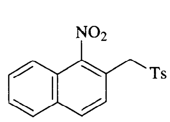
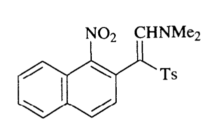
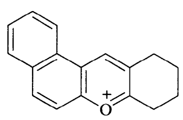
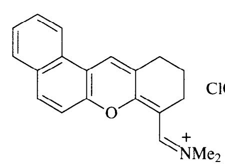
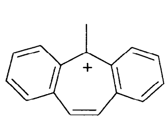
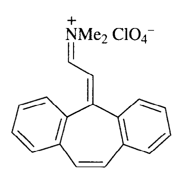
Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
	Me_2NCOPh, $POCl_3$	 (51)	219
	1-Me-2-pyrrolidone, $POCl_3$	 (95)	219
C_5S/C_6			
C_{16}			
	DMF, $POCl_3$	 (78)	219
C_6/C_6			
C_{12}			
	DMF, $POCl_3$	 (90)	598
	DMF, $POCl_3$	 (50)	584
	DMF, $POCl_3$	 (85)	584
C_{12}-C_{19}			
	DMF, $POCl_3$	 R^1 / R^2: H / H (85) NO_2 / H (85) CN / H (—) H / CONHPh (95)	584, 599 599 599 599
C_{14}			
	DMF, $POCl_3$	 (92)	599
C_{18}			
	DMF, $POCl_3$	 (62)	218

TABLE XVIIIB. METHYL AND METHYLENE GROUPS ACTIVATED BY A FULLY CONJUGATED POLYCYCLIC RING (*Continued*)

Substrate	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_5O/C_6/C_6$			
C_{17}			
 ClO_4^-	DMF, $POCl_3$	 ClO_4^- (70)	219
$C_6/C_6/C_7$			
C_{16}			
 ClO_4^-	DMF, PCl_5	 (96)	223

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