# TRANSITION METAL DERIVATIVES IN ORGANIC SYNTHESIS

## ANNUAL SURVEY COVERING THE YEAR 1977

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CONTENTS

## I. General Comments

This annual survey covers the literature for 1977 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review but is limited to reports of discrete

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*Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 143(1977)309-383 systems that lead to at least moderate yields of organic compounds, or that allow unique organic transformations, even if low yields are obtained. Catalytic reactions that lead cleanly to a major product and do not involve extreme conditions are also included.

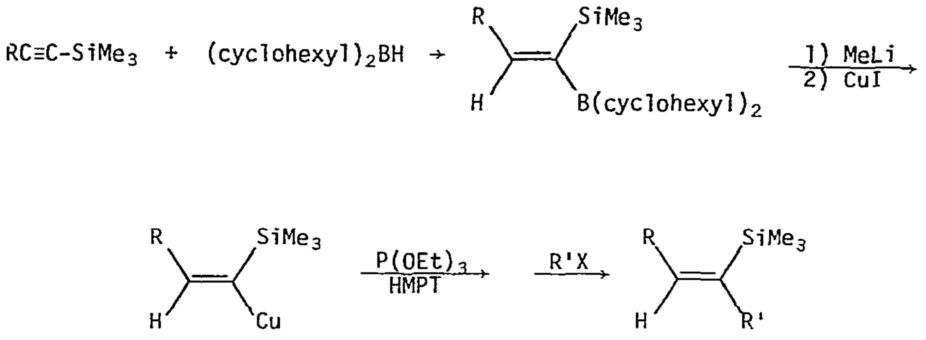
The papers in this survey are grouped primarily by reaction type rather than by organometallic reagent, since the reader is likely to be more interested in the organic transformation effected than the metal causing it. Specifically excluded are papers dealing with transition metal catalyzed hydrosilation, since these are covered by another survey in this series. Also excluded are structural and mechanistic studies of organometallic systems unless they present data useful for synthetic application. Finally, reports from the patent literature have not been surveyed since patents are rarely sufficiently detailed to allow reproduction of the reported results.

The number of papers reviewed this year is roughly twice that of last year, with most of the increase in the areas of carbon-carbon bond forming reactions, asymmetric homogeneous hydrogenation and solid phase supported catalysis. This increase reflects the growing activity in these areas and, to a lesser extent, more efficient coverage of the literature.

## II. Carbon-Carbon Bond Forming Reactions

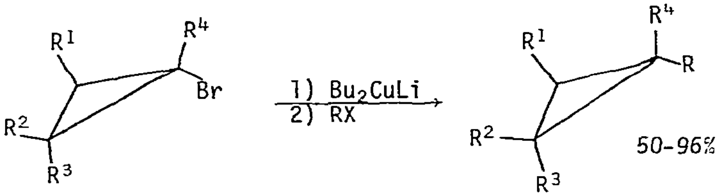
### A. Alkylation

Organocuprates continue to be extensively exploited for the alkylation of a variety of organic substrates, with much activity in the development of new organocuprate reagents, and their application to the synthesis of natural products. The composition of lithium methylcuprates in ether solvents was studied by $^1$H NMR and molecular association data. Evidence for the discrete existence of $LiCu_2Me_3$ and $Li_2Cu_3Me_5$ was obtained [1]. Subsequently, the reactions of $LiCu_2(Me)_3$, $Li_2CuMe_3$ and $Li_2Cu_3Me_5$ with alkyl, cycloalkyl and aryl halides were studied. In general $Li_2CuMe_3$ was most reactive, and THF was the superior solvent [2]. Trimethylsilyl vinyl cuprates formed by exchange with the vinyl borane resulting from trimethylsilylacetylides, reacted with a variety of halides to produce trimethylvinylsilanes (eq. 1) [3]. Cyclopropyl bromides were alkylated with retention of configuration by treatment with $Bu_2CuLi$ followed by RX (eq. 2) [4]. A cyclopropyl cuprate was claimed as an intermediate. Similarly, gem dihalocyclopropanes were dialkylated [5]. This procedure was used to synthesize sirenin and sesquicarene (eq. 3). An asymmetric cross coupling of phenylmagnesium bromide with 4-bromo-1-butene was effected using nickel chloride and a chiral ferrocenyl phosphine. The use of the (R)(S) phosphine gave 34% ee of the (R) product while the use of the (S)(R) phosphine produced 34% ee of the (S) product (eq. 4) [6].



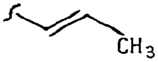
(1)

R = m-$C_6H_{13}$-, -$(CH_2)_4$OTHP, $CH_2$OTHP
R'X = MeI, allyl X, etc.

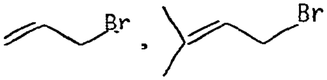


(2)

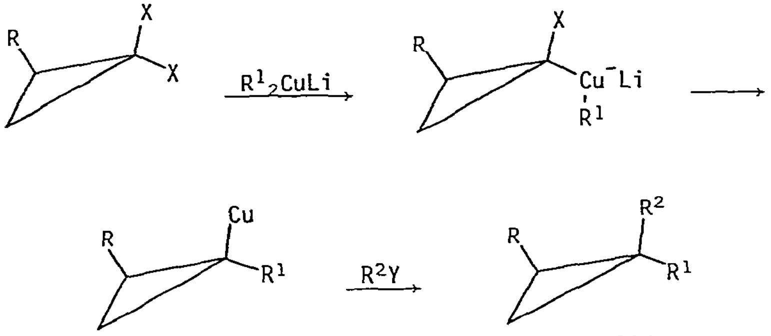
$R^1$ = H, -$(CH_2)_4$-
$R^2$ = Ph, H, cyclohexyl, $PhCH_2OCH_2$
$R^3$ = H, Ph, Me
$R^4$ = H, Me,



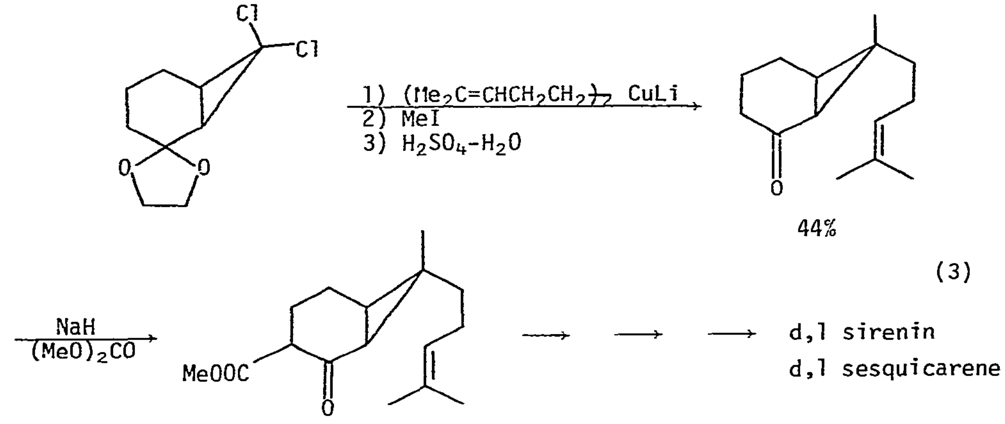
RX =



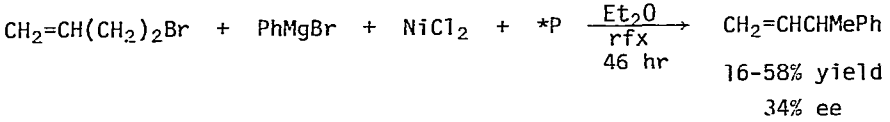
, MeI,
$BrCH_2COOMe$, n-$C_8H_{17}Br$



R = Ph, n-hexyl, $PhCH_2OCH_2$
$R^1$ = n-Bu, s-Bu, t-Bu
$R^2Y$ = MeI, EtI, $CH_3COBr$, EtOH



(3)



$$CH_2{=}CH(CH_2)_2Br \ + \ PhMgBr \ + \ NiCl_2 \ + \ {*P} \ \xrightarrow[\text{rfx}]{Et_2O} \ CH_2{=}CHCHMePh$$

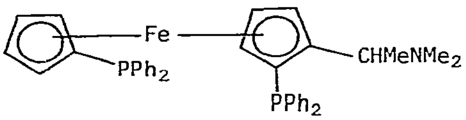
46 hr

16-58% yield

34% ee

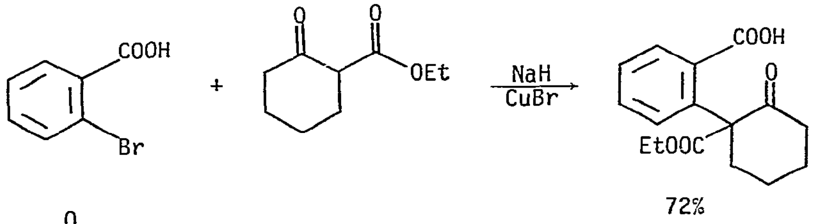
(4)

*P =

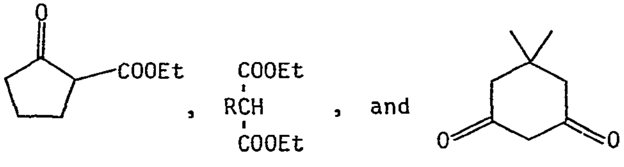


(R)(S) or (S)(R)

The alkylation of o-bromobenzoic acids by stabilized enolates was accomplished in high yield using sodium hydride and cuprous bromide (eq. 5) [7]. Terminal arylacetylenes were synthesized by coupling *in situ* generated copper acetylides with aryl iodides (eq. 6) [8]. Vinyl zirconates, from hydrozirconation of alkynes, were coupled to aryl halides to produce styrenes

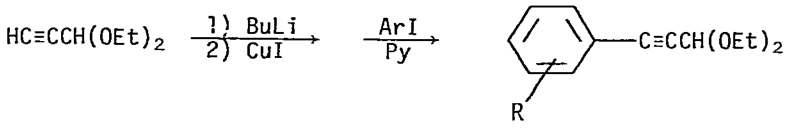


(5)



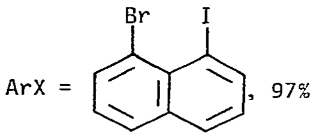
also work.

using a nickel(0) catalyst. Terminal alkynes reacted in high yield while internal alkynes gave only 35% yields (eq. 7) [9]. In a similar fashion

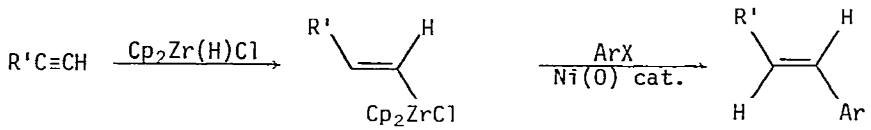


(6)

TMSC≡CCu and ArBr failed.



R = H 71%
R = p-Me 45%
R = m-Me 50%
R = p-OMe 50%



(7)

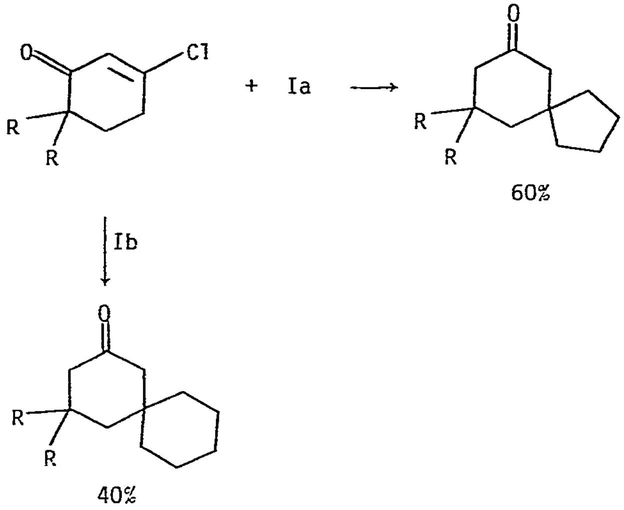
75-99%

R' = n-pentyl, EtO, n-Bu, $THPOCH_2CH_2$-

Tolerates Cl, OMe, CN and COOMe on aryl group.

unsymmetrical biaryls and diarylmethanes were prepared in high yield by the $L_4Ni$ or $L_2PdCl_2$ catalyzed coupling of aryl halides with aryl or benzyl zinc or magnesium halides [10]. Very little homocoupling was observed. Unsymmetrical biaryls containing fluorine were prepared in 80-92% yield by the palladium chloride catalyzed cross coupling of aryl halides with aryl magnesium halides [11]. Allylbenzenes were produced by the palladium(0) catalyzed reaction of allyl-tri-n-butyltin with aryl halides at 100°. The reaction tolerated nitro, chloro, o-methyl and acetyl groups. Chlorobenzene failed to react [12]. Finally, phenylacetic acids were prepared by the nickel(0) or palladium(0) catalyzed coupling of the Reformatsky reagent ($BrZnCH_2COOEt$) with aryl iodides [13].

Vinyl iodides were alkylated with retention of stereochemistry in 50-70% yield by treatment with n-butyl-, n-pentyl-, i-propyl-, t-butyl-, methyl-, phenyl-, benzyl- or allyl-Grignard reagents in the presence of copper(I) salts. Use of vinyllithium led to polymers [14]. Treatment of trialkylboranes with methyllithium followed by cuprous iodide produced copper-tetraalkylborate salts. These reacted with cis and trans β-bromoethyl acrylate to replace the halide with the alkyl (not the methyl) group with complete retention of stereochemistry [15]. The reaction of β-haloenones with a α,ω-bis cuprate led to the production of spiro compounds by combined 1,4-addition and alkylation of a halide (eq. 8) [16]. Diketones were produced by treatment of the bis cuprate with acid halides. Vinyl halides reacted with alkynyl zinc halides in the presence of a palladium catalyst to produce ene-ynes in high yield and high stereospecificity (eq. 9) [17].

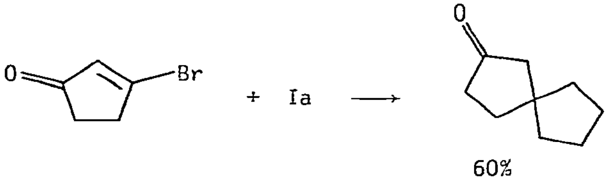


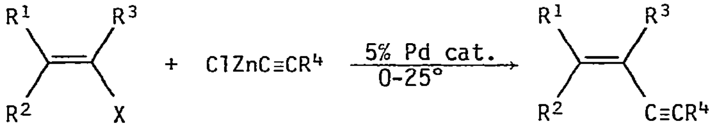
$Li(L)Cu-(CH_2)_n-Cu(L)Li$

Ia n = 4
Ib n = 5

R = H, Me

(8)





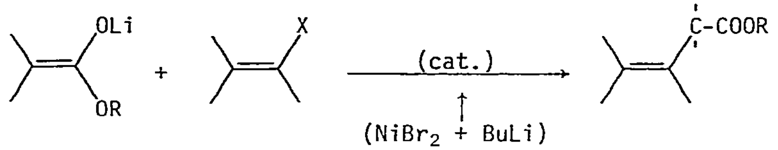
(9)

X = Br, I
$R^1$ = H, n-Bu, COOMe
$R^2$ = n-Bu, H, Et, Me
$R^3$ = H
$R^4$ = H, n-pentyl, n-Bu

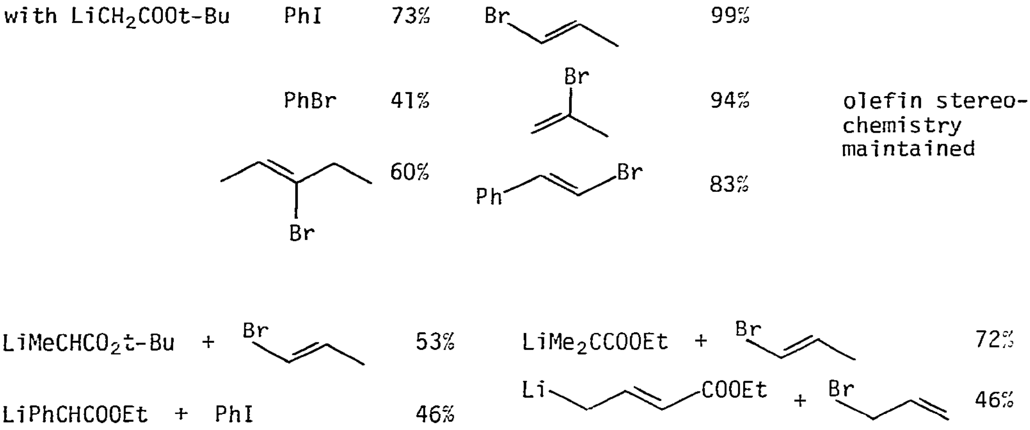
∿80% yield
⩾97% stereospecific

Aryl and alkyl Grignard reagents cleanly coupled with β-bromovinylethyl ether in the presence of $Ni(Ph_2P(CH_2)_3PPh_2)Cl_2$ (eq. 10) [18]. A similar coupling with vic bromotrimethylsiloxyalkenes was also successful [19]. Finally, a nickel(0) catalyst, produced by treating nickel bromide with butyllithium, promoted the reaction between lithium ester enolates and vinyl halides (eq. 11) [20].

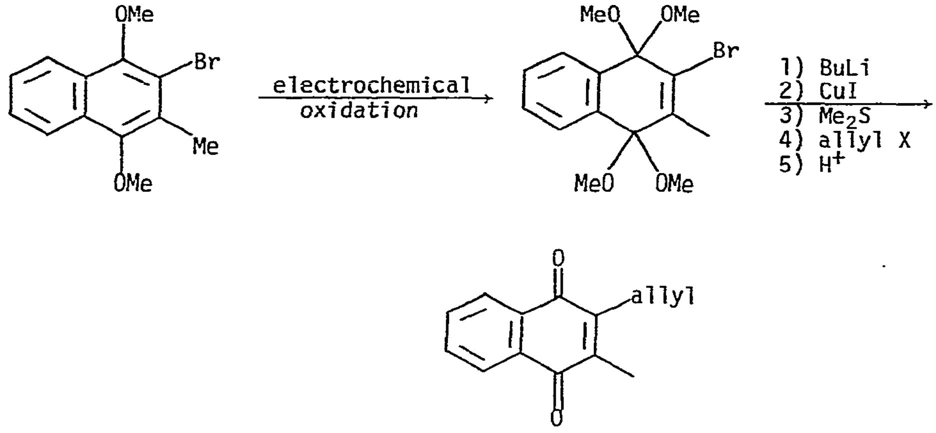
$$\mathrm{RMgBr} + \mathrm{BrCH{=}CHCEt} \xrightarrow{\mathrm{Ni(diphos)Cl_2}} \underset{53\text{-}77\%}{\mathrm{RCH{=}CHOEt}} \qquad (10)$$



(11)

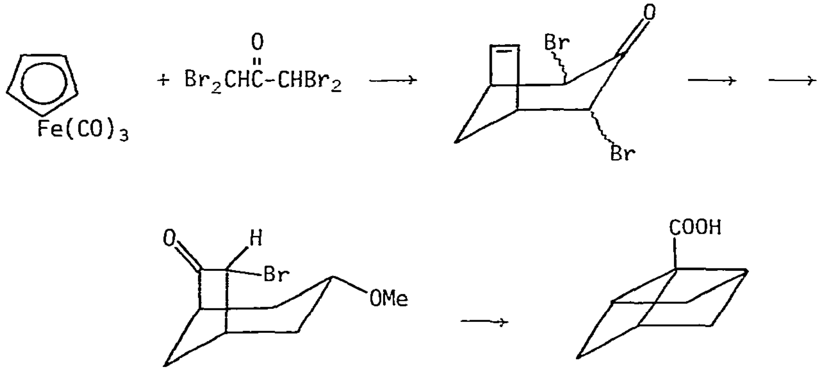


Allylic halides were alkylated by copper methyltrialkylborate complexes, alkylating with n-hexyl, n-octyl, or 5-chloropentyl borates. With 3-chloro-1-phenyprop-1-ene, allylic transposition was observed, while propargyl halides produced allenes [21]. Quaternary allylammonium salts reacted with a variety of Grignard reagents ($C_{2-7}$ alkyl, Ph, $PhCH_2$, $Me(CH_2)_7C{=}CH_2$, MeCH =$CHCH_2$, $CH_2{=}CH$-, HC≡C-, $HC{\equiv}CCH_2$) in the presence of copper(I) salts to give mixtures of allyl isomers with displacement of the trialkylamine group [22]. Allylic halides were alkylated with complete allylic rearrangement using $RCu{\cdot}BF_3$ complexes as alkylating agents [23]. A very neat synthesis of isoprenoid quinones via quinone bis ketal alkylation has recently been developed (eq. 12) [24], and involves alkylation of a vinyl cuprate. α-Bromoacids and esters were cleanly alkylated by methyl, ethyl and isopropyl cuprates [25]. Tricyclo[3.1.1.$0^{3,6}$]heptan-6-yl derivatives were prepared from compounds produced in the reaction of cyclopentadiene iron tricarbonyl with α,α',β, β' tetrabromoacetone (eq. 13) [26]. β-Bromoethers, acetates and alcohols were alkylated by n-heptyl, n-butyl and cyclohexyl Grignards in the presence



(12)

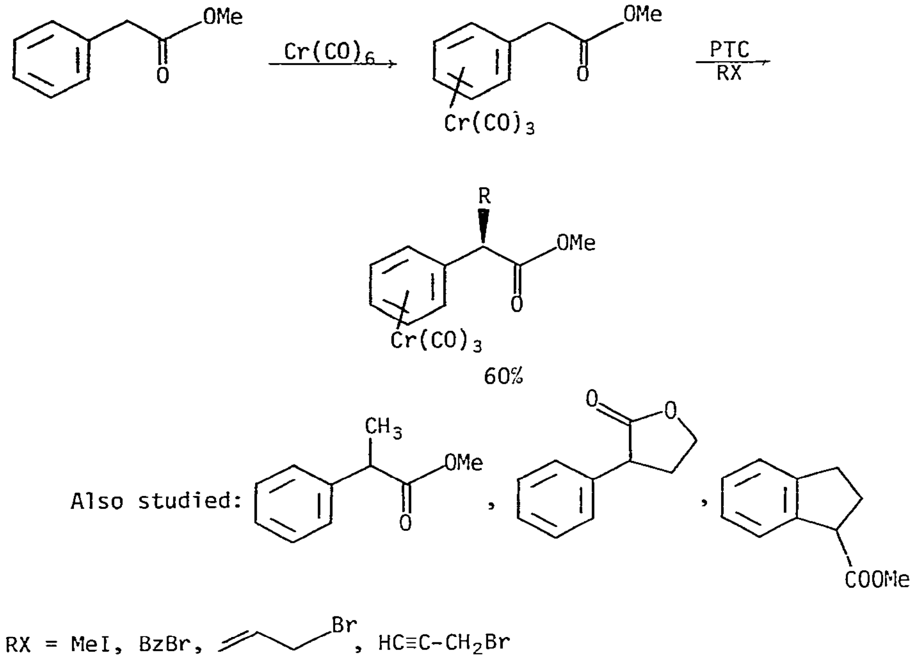
| | |
|---|---|
| prenyl | 92% |
| geranyl | 96% |
| phytyl | 93% |



(13)

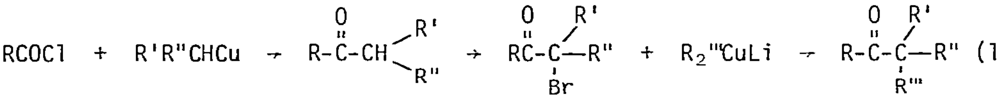
of 5% cuprous iodide. t-Butyl Grignards failed to react with the ethers and acetates but reacted well with the alcohols [27]. The chromium tricarbonyl group was used to both activate and alter stereochemistry in the alkylation of arylacetic esters by phase transfer catalysis and sodium hydride. Alkylation of cyclic ester complexes is stereospecifically exo (with respect to the $Cr(CO)_3$ group) while acyclic analogs undergo alkylation with less stereoselectivity (eq. 14) [28]. Finally, cyclopentadienyl copper alkylates benzylic halides, α-haloketones and pyrylium ion to introduce a cyclopentadienyl group [29].

Several new methods for the conversion of acid halides to ketones have been developed. The rhodium(I) complex $L_2Rh(Cl)CO$ was anchored to a phosphine containing polystyrene resin, treated with n-butyl or phenyllithium to produce the alkylrhodium(I) complex, which then reacted with an acid



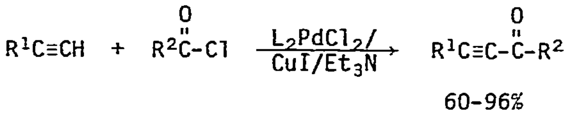
(14)

halide to produce ketone and the starting chlororhodium(I) complex. This supported system was claimed to be more convenient to use than the previously reported identical homogeneous system, although the yields were lower, and both systems were purified by simple filtration [30]. Copper(I) methyltrialkylborates reacted with aroyl chlorides to produce alkyl aryl ketones in 75-92% yield. The alkyl groups used were n-propyl, n-butyl- i-butyl and n-hexyl. Only one of the three alkyl groups transferred [31]. Ditertiary ketones were prepared by a sequence involving the alkylation of acid halides by 2° alkyl cuprates, bromination of the resulting ketone, and alkylation of the α-haloketone with a different alkylcuprate (eq. 15) [32]. Phenyl



$$\mathrm{RCOCl} + \mathrm{R'R''CHCu} \rightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}CH}\!\begin{smallmatrix}\mathrm{R'}\\ \mathrm{R''}\end{smallmatrix} \rightarrow \mathrm{RC{-}\underset{Br}{\overset{R'}{C}}{-}R''} + \mathrm{R_2'''CuLi} \rightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\underset{R'''}{\overset{R'}{C}}{-}R''} \quad (15)$$

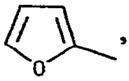
and n-butylacetylene were acylated with a variety of acid halides by treatment with $L_2PdCl_2$ and cuprous iodide catalyst in triethyl amine (eq. 16) [33]. Allyl ketones were prepared in 37-86% yield by treating acid halides with allyl-trimethyltin with $ClRh(PPh_3)_3$ as a catalyst [34]. Alkyl, alkenyl and alkynyl ketones were prepared by the treatment of acid chlorides with organomanganese(II) iodides. Aldehydes underwent competitive alkylation at the aldehyde group and conjugated acid chlorides were polymerized [35]. Symmetrical ketones were produced by the reaction of acid chlorides with



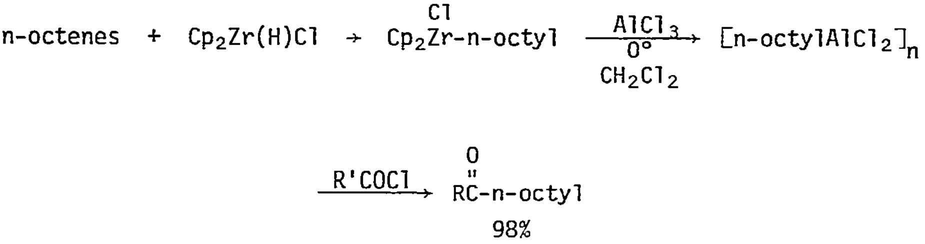
$$R^1C\equiv CH + R^2\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[CuI/Et_3N]{L_2PdCl_2/} R^1C\equiv C-\overset{O}{\overset{\|}{C}}-R^2 \qquad (16)$$

60-96%

$R^1$ = Ph, n-Bu

$R^2$ = Ph, PhCH=CH, t-Bu, i-Pr, , $NMe_2$

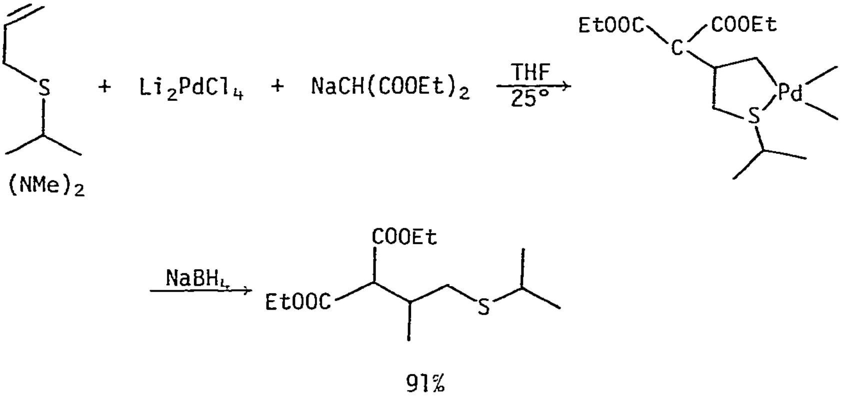
Fe$_2$(CO)$_9$ in refluxing ether. Fe(CO)$_5$, Fe$_3$(CO)$_{12}$, and Co$_2$(CO)$_8$ do not cause this reaction to occur [36]. Transmetalation from zirconium to aluminum was used to acylate olefins with acid chlorides (eq. 17) [37]. Alkyl zirconiums, formed by the hydrozirconation of olefins, are not reactive towards acid chlorides but give a rapid transmetalation to aluminum trichloride which does react with acid chlorides.



$$\text{n-octenes} + Cp_2Zr(H)Cl \rightarrow Cp_2\overset{Cl}{Zr}\text{-n-octyl} \xrightarrow[0°,\ CH_2Cl_2]{AlCl_3} [\text{n-octyl}AlCl_2]_n \qquad (17)$$

$$\xrightarrow{R'COCl} R\overset{O}{\overset{\|}{C}}\text{-n-octyl}$$

98%



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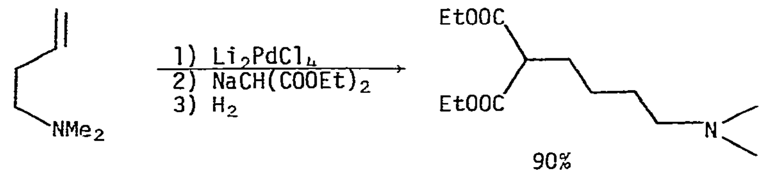
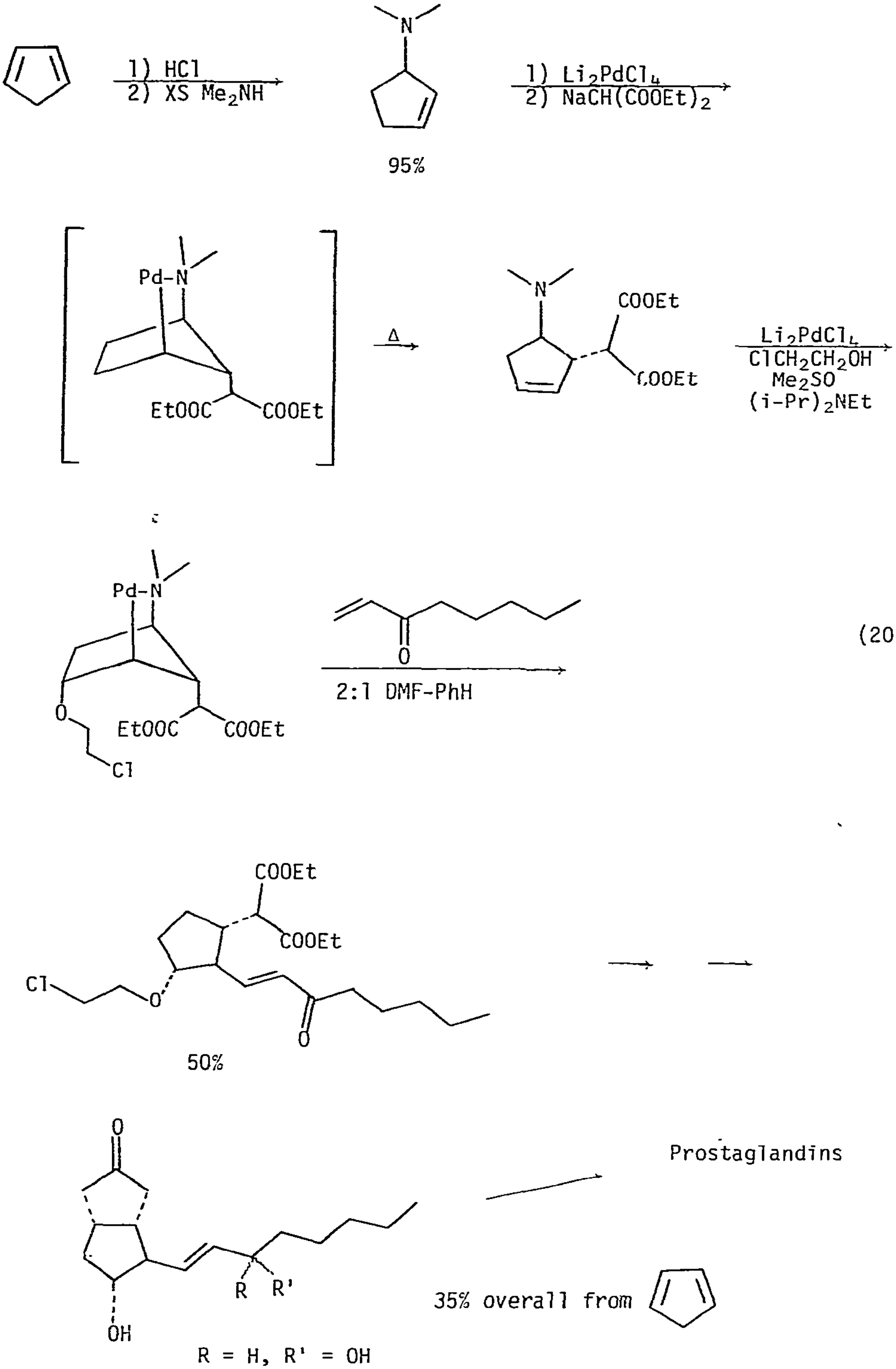
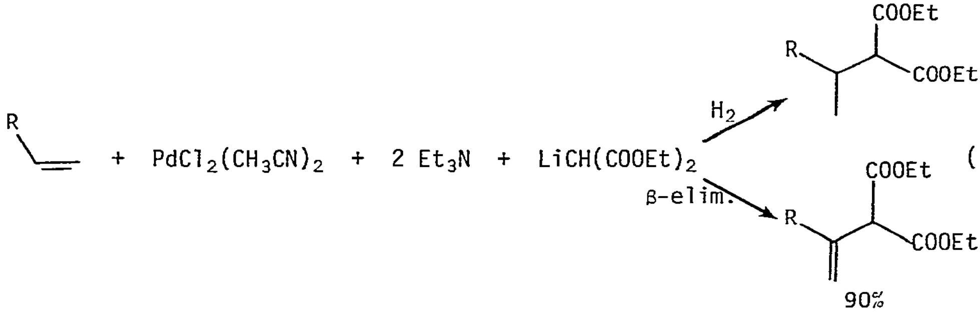


(19)


1) HCl
2) XS Me$_2$NH
N
95%
1) Li$_2$PdCl$_4$
2) NaCH(COOEt)$_2$
Pd–N
EtOOC
COOEt
Δ
N
COOEt
COOEt
Li$_2$PdCl$_4$
ClCH$_2$CH$_2$OH
Me$_2$SO
(i-Pr)$_2$NEt
Pd–N
O
Cl
EtOOC
COOEt
O
2:1 DMF-PhH
COOEt
COOEt
Cl
O
O
50%
O
OH
R
R'
R = H, R' = OH
Prostaglandins
35% overall from

(20)

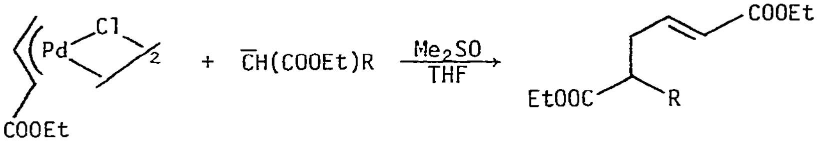
The direct alkylation of olefins with soft carbanions has been reported by several groups. Allyl amines and sulfides reacted with lithium chloropalladate and stabilized carbanions to produce a stable σ-alkylpalladium(II) complex. The organic ligand was freed by reduction with sodium borohydride (eq. 18) [38]. Allyl alcohols and ethers, conjugated esters and simple olefins failed to alkylate. Grignard reagents, organocuprates and ketone enolates led to reduction of palladium rather than alkylation. Homoallylic amines and sulfides were also successfully alkylated by stabilized carbanions (eq. 19) [39]. This chemistry was used in a very elegant synthesis of a prostaglandin precursor (eq. 20) [40]. Under appropriate conditions simple olefins could be alkylated by stabilized carbanions using palladium chloride (eq. 21) [41] or $Fe(CO)_4$ (eq. 22) [42]. The full experimental details of



(21)

$$\|\text{—Fe(CO)}_4 + \bar{C}H(COOMe)_2 \xrightarrow[0°]{THF} \xrightarrow[2)\ ox.]{1)\ TFA} \underset{68\%}{EtCH(COOEt)_2} \qquad (22)$$

the addition of stabilized carbanions to cyclopentadiene iron dicarbonyl olefin cation complexes to produce stable σ-alkyliron complexes have appeared [43]. The paper covers thé addition of enolates, enamines, Grignards, cuprates and ylids, and has extensive tables of data. The alkylation of π-allylpalladium complexes by stabilized carbanions has also been reported (eq. 23) [44]. A series of new π-allylpalladium complexes for use as models of key intermediates in allylic alkylation have been synthesized and their reactions studies [45].



(23)

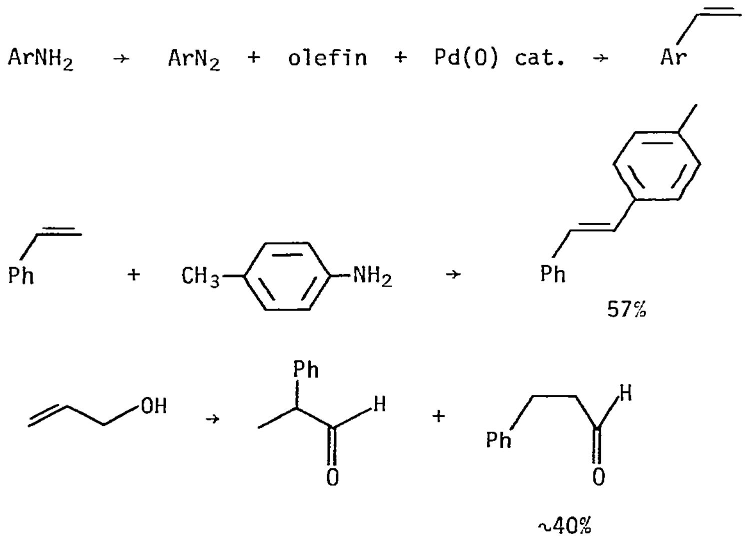
R = CN 70%

R = $SO_2Me$ 52%

R = COOEt quantitative

Palladium catalyzed "Heck" type alkylations and arylations continue to be used synthetically. Iodoferrocene was reacted with a variety of olefins in the presence of palladium acetate to produce alkenylferrocenes. Acetylene reacted with iodoferrocene in the presence of copper(I) iodide and palladium to produce diferrocenylacetylene [46]. The reaction of acrylonitrile, allyl cyanide and methacrylonitrile with bromobenzene and palladium(II) catalysts led predominantly to arylation of the olefin but gave mixtures of both positional and geometric isomers. The reaction also went with methyl vinyl ketone and mesityl oxide, but yields were only moderate and side products resulted [47]. The dimethylacetal of acrolein was phenylated with bromobenzene using palladium(II) acetate as a catalyst in the presence of triethylamine and tri-o-tolylphosphine to give up to 98% arylation as a mixture of the dimethyl acetal of cinnamaldehyde and methyl-2-phenylpropionate [49]. Styrene was converted to trans β-methylstyrene in 90% yield by reaction with methyllithium using Pd(acac)$_2$ as a catalyst. The reaction consisted of a cis addition-cis elimination sequence. Substituents such as p-Cl(90%), m-Cl(80%) and p-Me(60%) were tolerated, but p-OMe substituted styrene led to low (15%) yields. With stabilized carbanions such as sodium diethylmalonate, only a low yield of alkylation (α) was observed [49]. Kinetic studies on the arylation of styrene by benzene in the presence of palladium(II) acetate to form trans stilbene indicated that formation of a σ-complex was the rate limiting step [50]. Vinyl heterocycles were formed by the reaction of ethylene with thiophene, furfural and furan in the presence of palladium salts [51].

Vinylidene chloride reacted with isobutene in the presence of palladium(II)

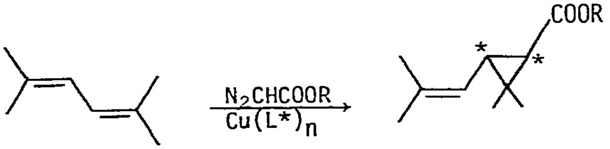


(24)

acetate at 60° to oxidatively couple, producing 1,1-dichloro-4-methylpentadie in ∿70% yield. Nitrite was found to suppress dehydrodimerization of isobutene [52]. Palladium(0) complexes were used to catalyze the arylation of olefins by aromatic diazonium salts. Allyl alcohols led to phenylaldehydes (eq. 24) [53].

Styrene was also directly arylated by anilines to produce stilbenes using palladium(II) acetate. The reaction involved C-N bond cleavage [54].

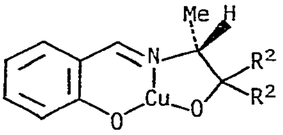
By using a chiral copper complex to catalyze the decomposition of alkyldiazoacetates, trans-ℓ-menthyl chrysanthemate was prepared in 72% yield and 94% ee (eq. 25) [55]. The bulkier the alkyl group of the diazo



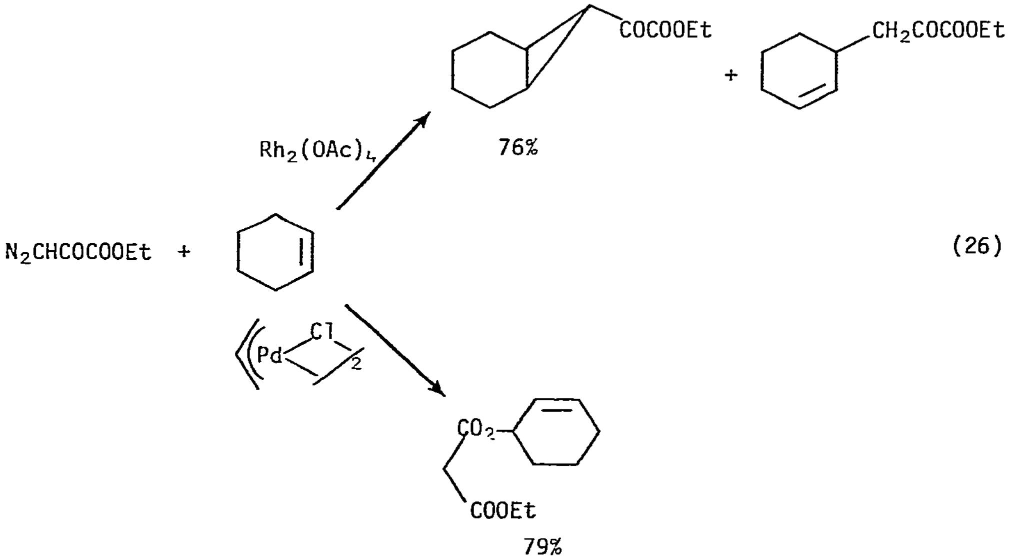
7.4% cis
89.9% trans d    94% ee(25)
2.7% trans ℓ

R = 2,3,4-trimethyl-3-pentyl

catalyst =



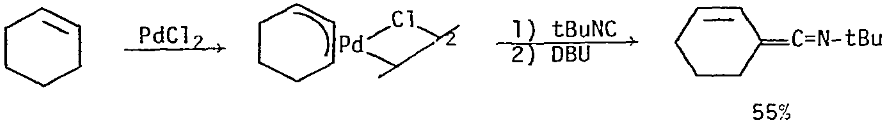
$R^2$ = 5-t-butyl-2-octyloxyphenyl



(26)

compound, the more trans product was formed, and the higher was the ee of the trans isomer. Cyclopropanation reactions of diazoalkanes with substituted olefins in the presence and absence of nickel(0) and palladium(0) complexes of the type $M(Me_3CNC)_2$ or $M(PPh_3)_2(C_2H_4)$ were studied and intermediate complexes were isolated and characterized by x-ray crystallography [56]. The reaction of ethyl diazopyruvate with cyclohexene produced drastically different products when $Rh_2(OAc)_4$ was used as a catalyst rather than π-allylpalladium chloride (eq. 26) [57].

Olefins were alkylated by isonitriles via π-allylpalladium complexes or σ-alkylpalladium complexes. Isonitrile complexes were intermediates (eq. 27) [58]. α,β-Unsaturated chromium carbene complexes underwent 1,4-alkylation by enolate anions (eq. 28) [59]. The role of puckered



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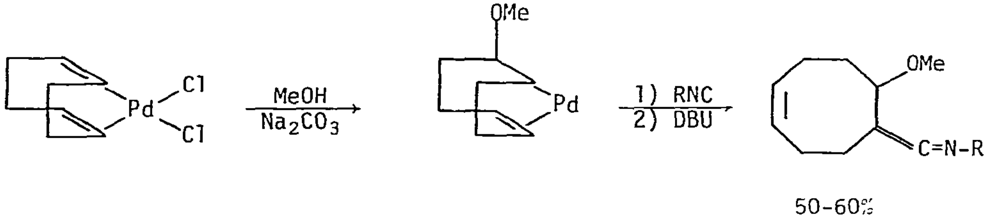
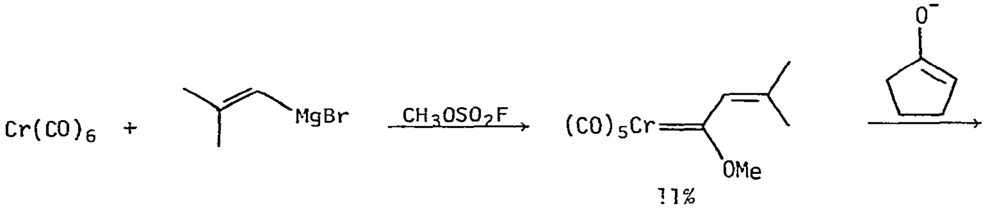
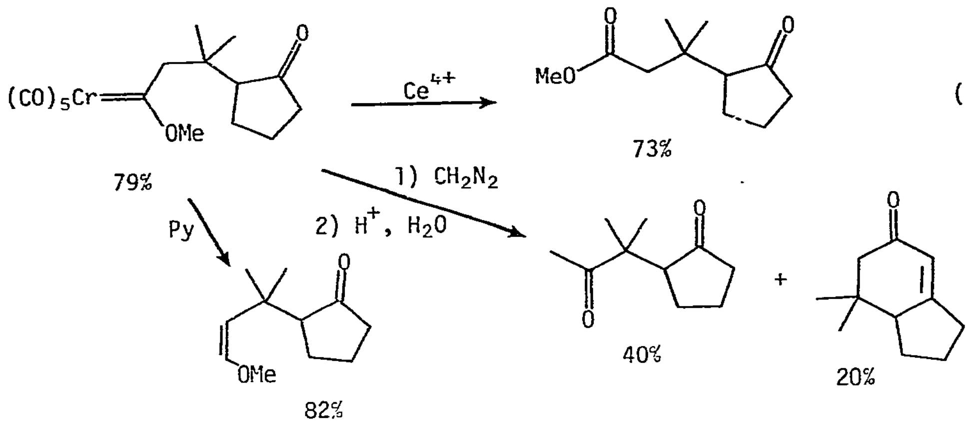




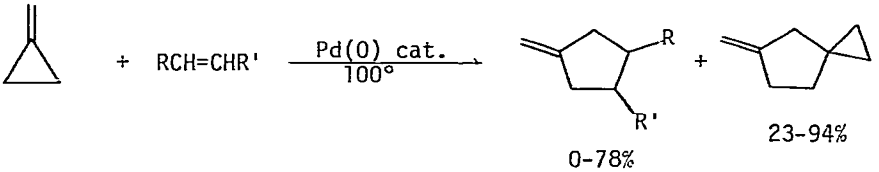
metallocyclobutanes (from metal carbenes and olefins) in the stereochemistry of cyclopropane formation was studied by the in situ generation of $(CO)_5WC(Ph)H$ [60].

The [2σ + 2π] cycloadditions of methylene cyclopropane.to alkenes catalyzed by palladium(0) complexes were found to give mixtures of cycloaddition products and cyclodimerization products. Unstrained olefins and



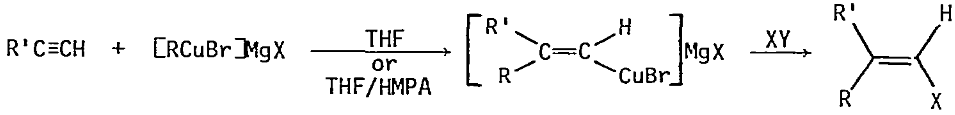
(28)

1- or 2-alkenes were unsuitable (eq. 29) [61]. Olefin insertion in transition metal catalysis has recently been reviewed [62].



(29)

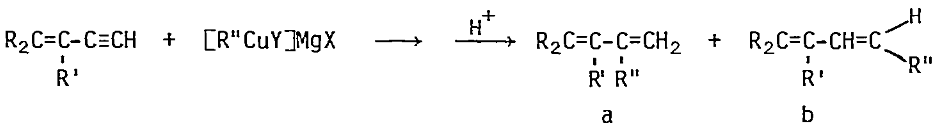
The effect of solvents and lithium salts on the addition of lithium alkylcuprates to 1-alkynes to produce lithium vinyl cuprates has been studied in detail. Lithium dibutylcuprate added to phenylacetylene and 1-octyne at C-2 with greater than 90% regioselectivity. In contrast, with [RCuI]Li the regioselectivity was lost. In THF $R_2CuLi$ simply deprotonated the alkyne without addition. Lithium bromide suppressed this deprotonation [63]. Vinyl bromides were prepared from alkynes in greater than 90% yield and greater than 98% stereospecificity by the treatment of terminal alkynes with [RCuBr]Mg followed by treatment of the thus-formed vinylcuprate with iodine, N-bromosuccinimide or N-chlorosuccinimide (eq. 30) [64]. Essentially the same chemistry was reported by another group [65]. In a general study of the reactivity of [RCuY]MgX with terminal alkynes, it was found that [RCuBr]MgCl was the best reagent for the introduction of 1° alkyl (R) groups into acetylene, propyne and phenylacetylene (forming RR'C=$CH_2$) while [t-BuOCuR]MgX was best for other terminal alkynes. THF was particularly good for introduction of branched chain alkyl groups [66]. It was found that $R_2CuMgX$ complexes transferred only one R group and were more reactive than [RCuBr]MgX [67]. The reaction of eneynes with [RCuY]MgX was also studied. The regiochemistry of addition depended on the nature of R. This chemistry was used in a synthesis of myrcene (eq. 31) [68].



(30)

R = Et, i-Pr, cyclohexyl, t-Bu, *n*-Bu    X = Br, I, Cl    >90%

R' = Ph, Me, Bu, H    XY = NBS, NCS, $I_2$    >98% stereochemistry

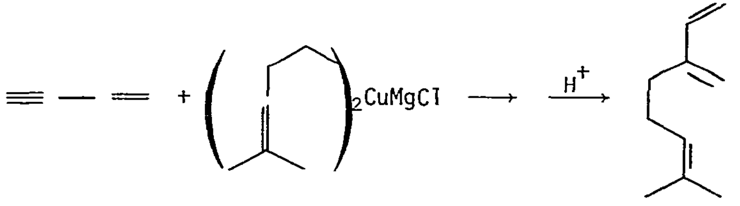


$$R_2C{=}\underset{R'}{C}{-}C{\equiv}CH + [R''CuY]MgX \longrightarrow \xrightarrow{H^+} \underset{a}{R_2C{=}\underset{R'}{C}{-}\underset{R''}{C}{=}CH_2} + \underset{b}{R_2C{=}\underset{R'}{C}{-}CH{=}C\begin{smallmatrix}H\\R''\end{smallmatrix}}$$

R" = 1° alkyl, >95% a

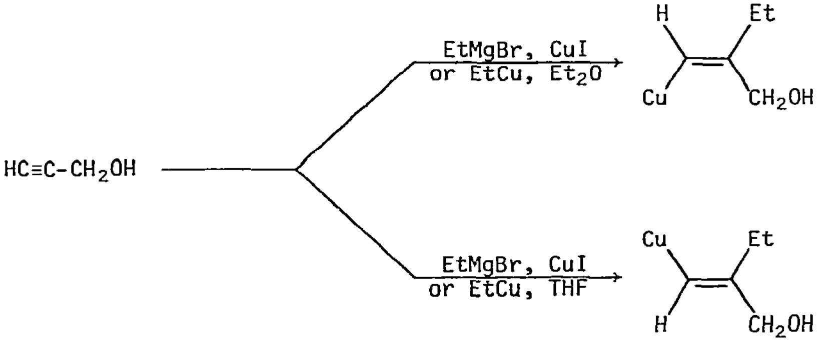
R" = t-Bu, 1:1 a to b

(31)

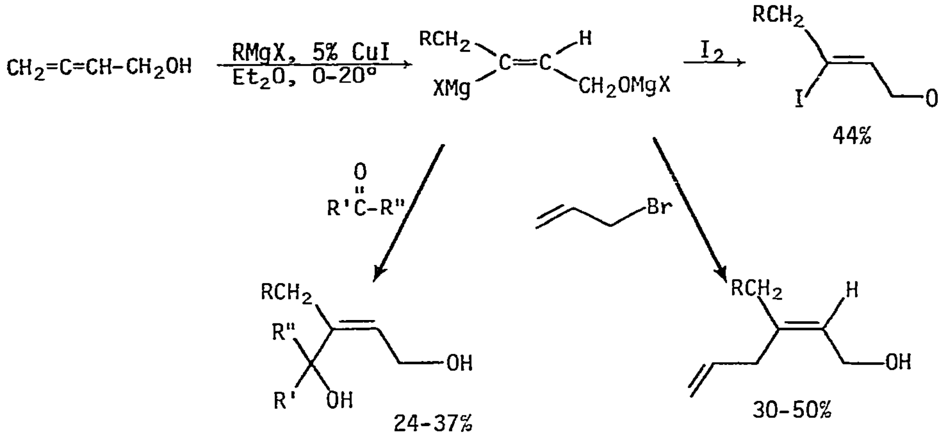


90%
myrcene

The reactions of propargyl alcohol with EtCu and with EtMgBr in the presence of copper(I) salts were compared. In ether both reagents added trans to place the metal on the terminal carbon, while in THF, a cis addition occurred (eq. 32) [69]. Similar studies were carried out on the corresponding allenic alcohol. The intermediate vinyl magnesium halide was further functionalized (eq. 33) [70]. Cumulenic ethers reacted with Grignard reagents in the presence of cuprous bromide catalyst to produce eneynes (eq. 34) [71]. Use of discrete [RCuBr]M complexes led to reductive alkylation. Propargylic ethers, sulfides and amines reacted with organocopper species in an addition reaction whose regioselectivity depended on the nature of the heteroatom (eq. 35) [72]. The chemistry of the vinyl cuprate intermediates was also examined.

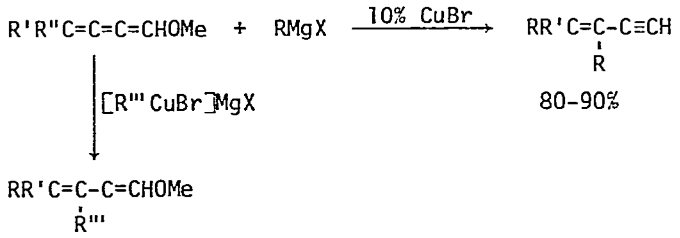


(32)



(33)

R = Me, Bu, i-Pr, Ph

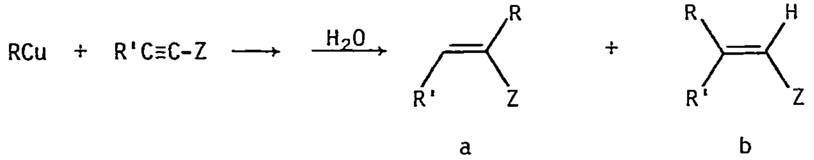


$$R'R''C{=}C{=}C{=}CHOMe + RMgX \xrightarrow{10\%\ CuBr} RR'C{=}\underset{R}{C}{-}C{\equiv}CH \quad 80\text{-}90\%$$

$$R'R''C{=}C{=}C{=}CHOMe \xrightarrow{[R'''CuBr]MgX} RR'C{=}\underset{R'''}{C}{-}C{=}CHOMe$$

(34)

R = alkyl, Ph
R', R" = H, Me



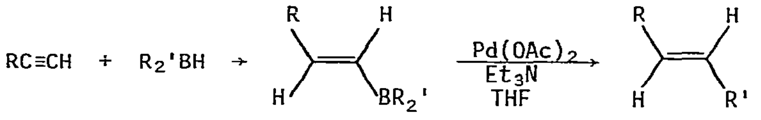
(35)

R = n-heptyl, n-Bu
R' = H, $CH_3$
Z = SR
} 77-95% b
<u>No</u> a

R = Et, n-Bu
R' = H, n-Bu, Me
Z = OEt, $NEt_2$, $NPh_2$
} 54-92% a
<u>No</u> b

Terminal alkynes were converted to <u>trans</u> disubstituted alkenes by hydroboration with dialkylboron hydrides followed by palladium acetate catalyzed decomposition of the vinyl borane (eq. 36) [73]. Styrene and terminal alkynes were coupled to halobutadienes by treatment with palladium chloride, lithium chloride and oxygen in acetic acid (eq. 37) [74].

The alkynols 3-butyn-1-ol, 3-pentyn-1-ol, 4-pentyn-2-ol and 4-pentyn-1-ol were ethylated by diethylaluminum chloride using <u>bis</u> cyclopentadienyl



(36)

58-98%

R = Ph, t-Bu, $Cl(CH_2)_3$-

R' = CHMeCHMe, cyclohexyl, 2-methylcyclohexyl

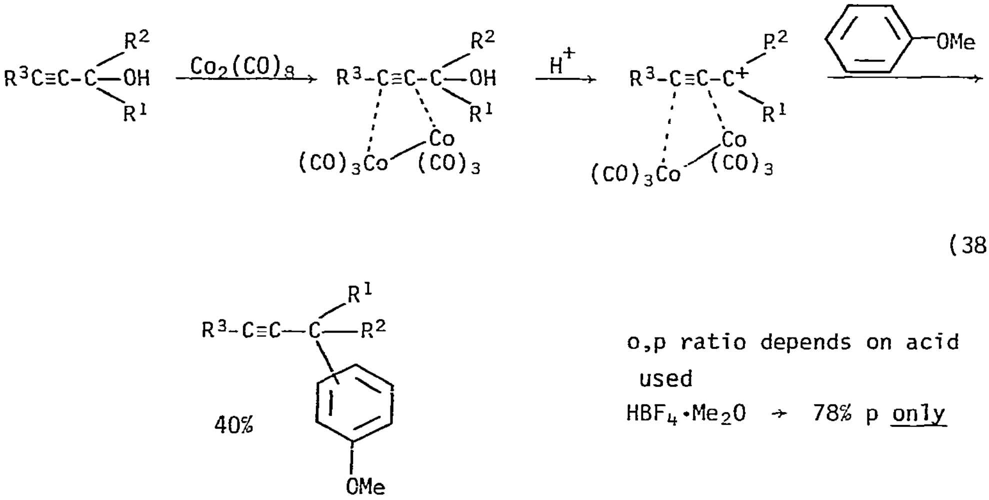
$$PhCH{=}CH_2 + RC{\equiv}CH \xrightarrow[O_2,\ AcOH]{PdCl_2,\ LiCl} PhCH{=}CHCH{=}CCl\text{-}R \qquad (37)$$

R = Ph, n-Pr, n-Am, Et

40-60% on alkyne

50-2400% on Pd

titanium dichloride as a promotor. Terminal alkynes underwent both terminal and internal ethylation while 3-pentyn-1-ol gave exclusively 4-methyl-3-hexen-1-ol [75]. Terminal acetylenes were converted to (E)-2,4-dialkyl-1,3-butadienes and/or trialkylbenzenes by treatment with trialkylaluminums in the presence of bis (N-methylsalicylaldimine)nickel [76]. Finally, propargyl alcohols were alkylated by aromatic hydrocarbons through an unusual sequence involving protection of the triple bond as a cobalt complex (eq. 38) [77].



(38)

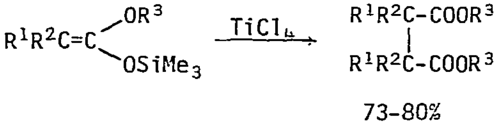
40%

o,p ratio depends on acid used

$HBF_4{\cdot}Me_2O$ → 78% p only

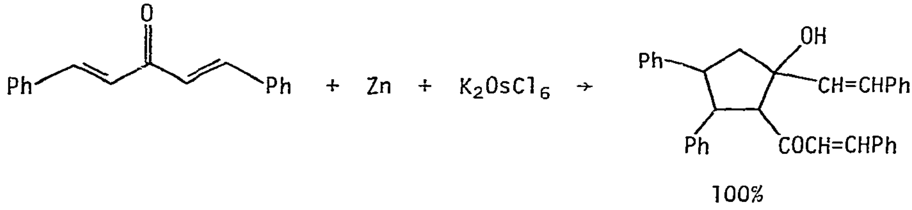
Transition metals continue to be extensively used for coupling reactions. The oxidative coupling of ketone enolates to 1,4-diketones by copper(II) chloride was carefully studied. Ketones with a single type of enolizable hydrogen coupled very well. Methyl ketones coupled in moderate to excellent yield. Substituted methyl ketones coupled in very low yield. Ketones having two different enolizable hydrogens gave mixtures but the least hindered 1,4-diketone predominated. Olefins, cyclopropanes, ferrocenyl and ester functionality was tolerated. Attempted cross couplings gave all possible products but two different methyl ketones were cross coupled in moderate yield by using a large excess of one. Intramolecular couplings of diketones failed except for diacetyl ferrocene [78]. Similar chemistry using copper(II) triflate has also been reported. This reagent also coupled trimethylsilylenol ethers [79]. Ketene silylenol acetals were coupled to succinates by titanium tetrachloride (eq. 39) [80].

Osmium(IV) salts coupled dibenzlidene acetone to produce a cyclopentanol product (eq. 40) [81], while palladium chloride dimerized ethynyl vinyl ketones (eq. 41) [82].



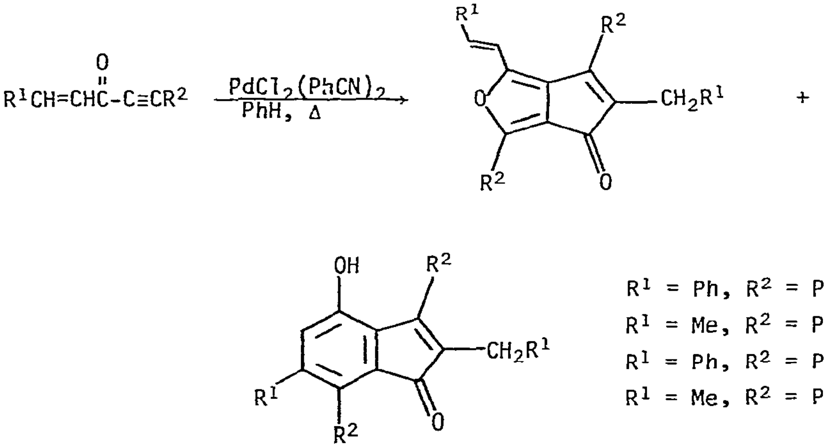
$$R^1R^2C{=}C(OR^3)(OSiMe_3) \xrightarrow{TiCl_4} R^1R^2C(COOR^3){-}C(COOR^3)R^1R^2 \qquad (39)$$

73-80%



(40)

100%

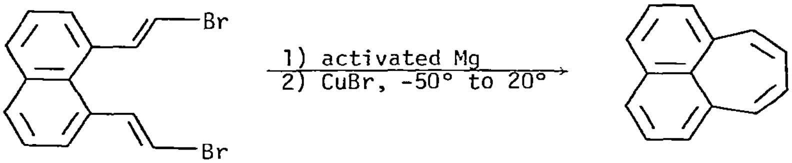


(41)

$R^1$ = Ph, $R^2$ = Ph, mesityl
$R^1$ = Me, $R^2$ = Ph
$R^1$ = Ph, $R^2$ = Ph, Me
$R^1$ = Me, $R^2$ = Ph, Me, Et

Reduced titanium species have proven useful for the reductive coupling of ketones, aldehydes and diols. Large ring ($C_{13}$-$C_{16}$) olefins were prepared in high yield by cyclization of the corresponding α,ω-dialdehydes or ketones with a titanium species resulting from the reduction of titanium trichloride with zinc-copper couple. Small ring cyclic olefins could also be prepared by this route (i.e., 1,2-diphenylcyclobutene, 87%) [83]. Ketones, including dineopentyl ketone, adamantanone and dicyclopropyl ketone were dimerized to symmetrical olefins by $TiCl_2$/py, produced by reduction of $TiCl_4$ with zinc. Unsymmetrical ketones gave mixtures of geometrical isomers [84]. The reagent resulting from the reduction of titanium tetrachloride with lithium aluminum hydride coupled the appropriate diketones to 1,2-diphenylcyclobutene (61%) and 1,2-diphenylcyclohexene (35%). 1,3-Diphenylpropane-1,3-diol coupled to give a mixture of *cis* and *trans* 1,2-diphenylcyclopropanes [85]. Benzhydrols were reductively coupled to the corresponding hydrocarbons by heating to 190° in the presence of $RuCl_2(PPh_3)_3$. The corresponding palladium and platinum complexes promoted only ether formation from benzhydrols [86].

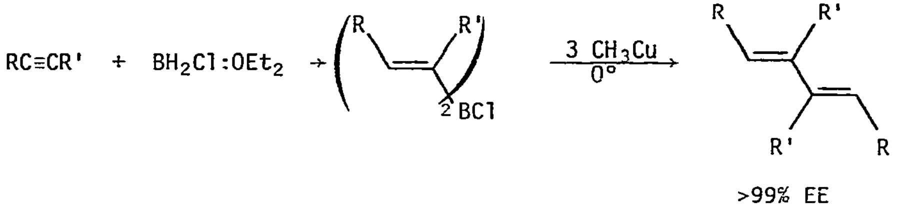
A variety of metals have been used for the reductive coupling of halides. Unsymmetrical allylic halides were coupled to give all possible coupling products by treatment with a reagent formed by reducing chromium(III) chloride with lithium aluminum hydride [87]. Benzylbromides were coupled to bibenzyls and vinyl bromides to dienes by treatment with $VCl_3/LiAlH_4$, while *vic* dihalides were dehalogenated to the corresponding alkenes [88]. Aromatic halides were coupled to biaryls (PhBr, 89%, *p*-MePhBr, 73%, *p*-MeCOPhBr, 58%, *p*-$MeO_2$CPhBr, 83%, *p*-MeCONHPh, 37%, o-tolyBr, 12%, 2-bromothiophene, 41%) by treatment with zinc, $L_2NiCl_2$ and excess phosphine in DMF [87]. Pleiadiene was synthesized by copper(I) catalyzed coupling of the appropriate vinyl Grignard reagent (eq. 42) [90]. Cuprous catalysts were found more effective than cupric catalysts for the Ullmann condensation of haloanthraquinone derivatives with amines in aprotic solvents [91].



(42)

45%
Pleiadiene

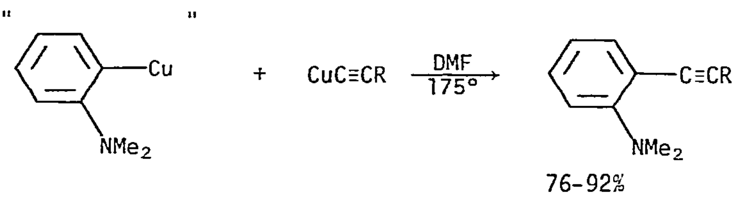
Diaryl, alkynyl, vinyl and benzyl mercurials were catalytically coupled to produce the corresponding hydrocarbon dimer by treatment with $L_3RhCl$ in HMPA at 50-130°. Dialkylmercurials did not couple under these conditions [92]. Similarly, vinylmercuric halides were catalytically coupled to 1,3-dienes by treatment with rhodium catalysts and lithium chloride in HMPA. Aryl mercuric halides coupled to biaryls under these conditions [93]. Symmetrical (E,E)-1,3-dienes were also prepared from alkynes by hydroboration with $BH_2Cl{\cdot}OEt_2$ followed by treatment with methyl copper (eq. 43).



(43)

R = n-Bu, R' = H 93%
R = R' = Et 99%
R = R' = n-Bu 95%
R = R' = Ph 45%
R = cyclohexyl, R' = H 71%
R = $Cl(CH_2)_3$, R' = H 99%

"Ate" complexes were implicated as intermediates [94]. Selective coupling of a variety of aryl copper aggregates to form biaryls was explained in terms of intraaggregate electron transfer processes [95]. In the cross coupling of aryl copper species with alkynyl copper complexes (eq. 44), the reaction was shown to proceed via $Ar_4Cu_6(C\equiv CR)_2$ clusters, which were isolated and characterized. Selective cross coupling occurred because the cluster contains exclusively triangular copper faces occupied by one aryl and one alkynyl ligand [96].

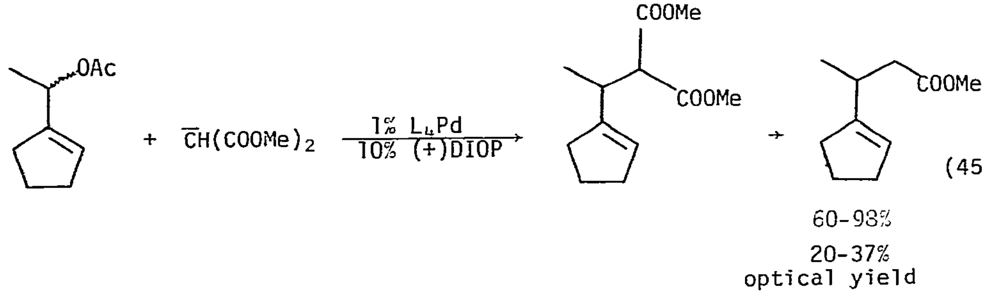


(44)

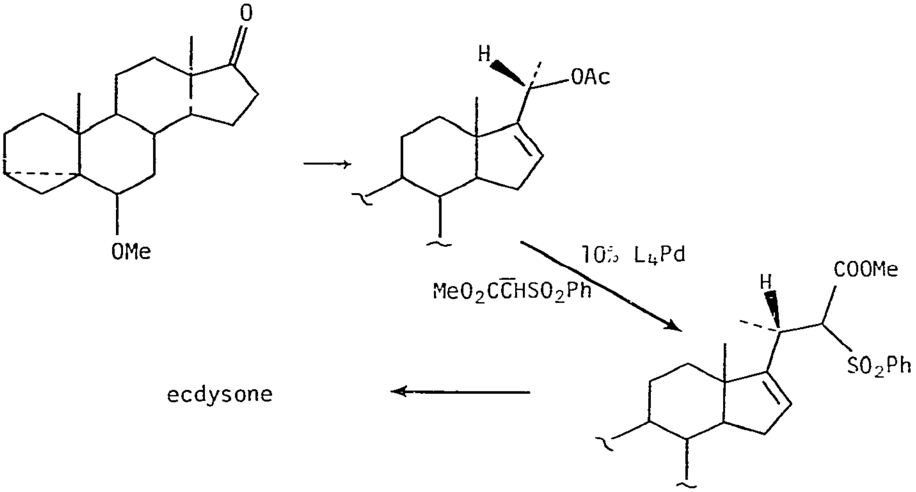
R = Ph, p-tolyl, 2,4-xylyl, 2,4,6-mesityl, 4-MeOPh, 4-$NO_2$-Ph, 4-Cl-Ph.

Alkylbenzenes were oxidatively coupled to biaryls by treatment with palladium salts in heteropolyacids [97]. Furans were coupled to bifurans by treatment with palladium acetate [98]. Palladium catalyzed oxidative dimerization of aromatic compounds has recently been reviewed (88 references) [99], as have coupling reactions via transition metal complexes (500 references) [100]. Dialkyl anilines were coupled to 4,4'-diaminodiphenylmethanes by palladium acetate [101].

Catalytic alkylation of allylic acetates has accounted for several interesting transformations. Treatment of an allylic acetate with the anion of diethylmalonate using 1% $L_4Pd$ catalyst and 10% (+)DIOP led to 60-98% yields of allylic alkylation with 20-37% optical yields (eq. 45) [102]. The same chemistry was used to elaborate the side chain of ecdysone, having palladium(0) catalyzed alkylation of a steroidal allylic acetate by a stabilized carbanion (eq. 46) [103]. A macrolide ester was synthesized by an intramolecular catalytic alkylation of an allylic acetate (eq. 47) [104]. This was also a key step in a new synthesis of humulene (eq. 48) [105].



(45)



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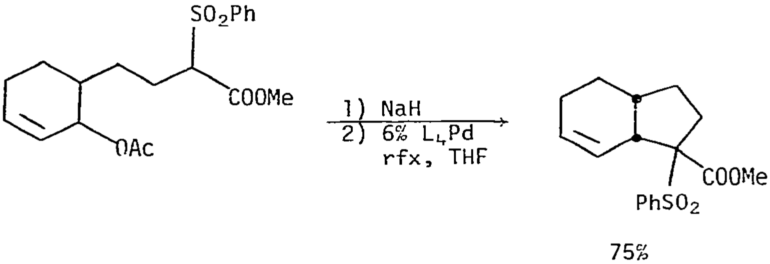
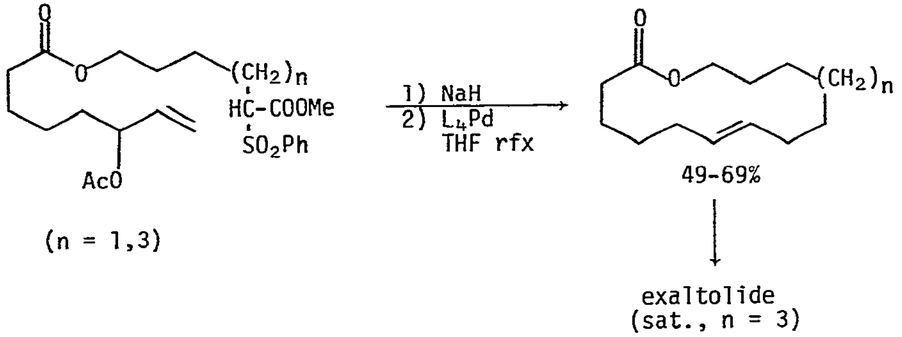


(47)

β-Diketones were synthesized from terpenic alcohols by the manganese(III) acetate assisted reaction with allyl acetate to introduce the acetonyl group, via a radical pathway. No yields were reported [106]. The reaction of allylic acetates with [MeCuX]Li where X is methyl, cyanide or thiophenoxide went by either $Sn^2$ or $Sn^{2'}$ pathways depending on X (eq. 49) [107]. In an attempt to develop the nucleophilic α-alkylation of ketones, lithium dialkylcuprates were reacted with acetoxyepoxides. A maximum yield of 43% of α alkylketone was obtained, with major product being the <u>non alkylated</u>



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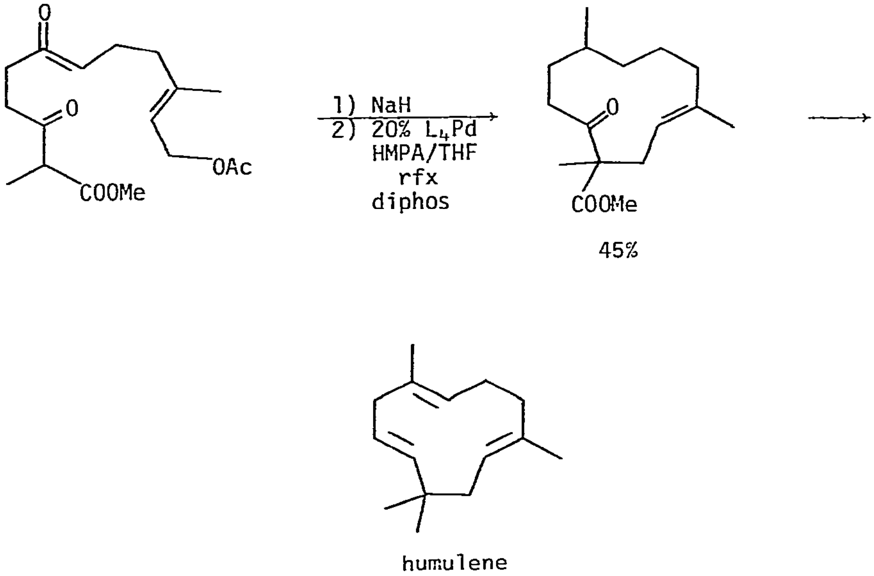
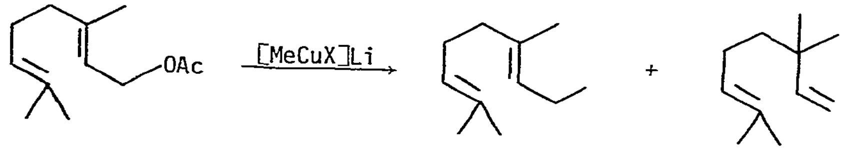


(48)

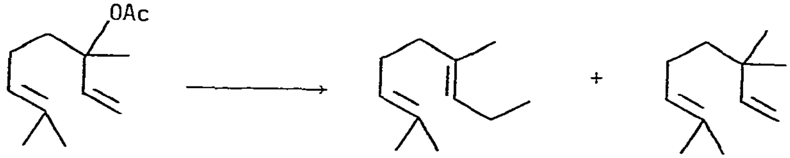
ketone, from a formal elimination of acetic acid [108]. The direct replacement of OH by R in allylic alcohols was achieved by the sequence described in eq. 50 [109]. Similar chemistry was achieved using $(Ph_3P)_2NiCl_2$ catalyzed reactions of Grignard reagents with allylic alcohols, although significant allylic transposition was observed in this case [110]. Allylic 1-perfluoroalkyl alcohols of the type $CH_2{=}CHCHR_F(OH)$ reacted with iodobenzene in the presence of palladium salts regioselectively at the terminal olefinic carbon to give mixtures of $PhCH_2CH_2COR_F$ and $PhCH{=}CHCH(R_F)OH$ [111]. Grignard reagents reacted with monoallyl phosphates in the presence of copper(I) bromide to replace the phosphate regioselectively in 80-90% yield. Small amounts of allylic transposition were noted [112]. Allyl sulfonium salts reacted under similar conditions to replace the $R_2S$ by the Grignard alkyl



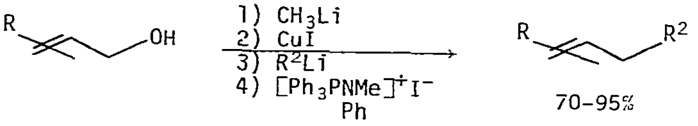
| | | |
|---|---|---|
| X = Me | >95% | 0% |
| X = CN | 0% | >95% |
| X = SPh | 25% | 75% |

but

(49)



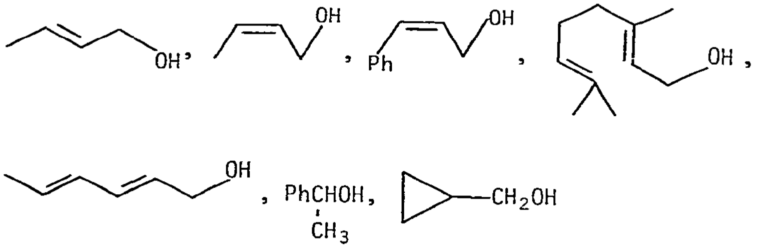
| | | |
|---|---|---|
| X = Me | 60% | 40% |
| X = CN | 54% | 46% |
| X = SPh | 55% | 45% |

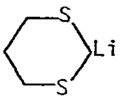


70-95%

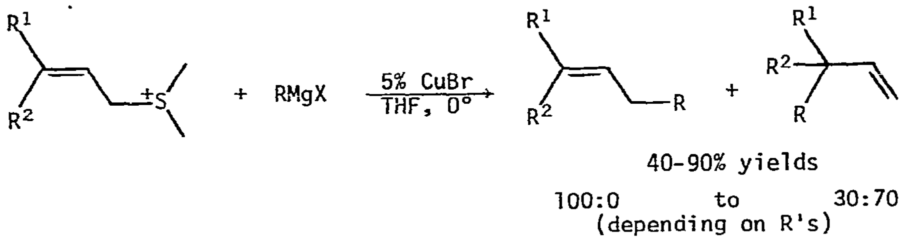
(50)

with

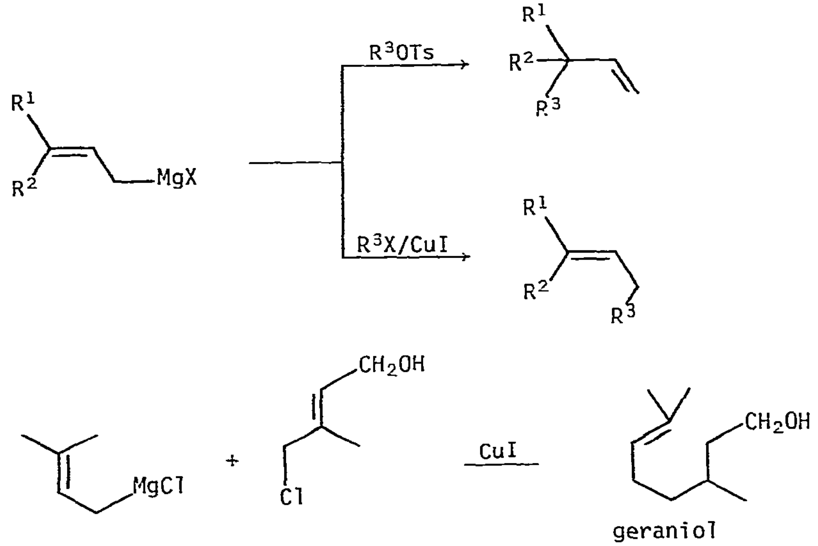


$R^2$ = BuLi, Li , MeLi, sec-BuLi, PhLi, EtLi, BuC≡CLi

group. Depending on the substitution on the double bond, varying amounts of allylic transposition were observed (eq. 51) [113]. Finally, allyl Grignard reagents were selectively alkylated by halides or tosylates and copper(I) iodide (eq. 52) [114]. Geraniol was synthesized in this manner.

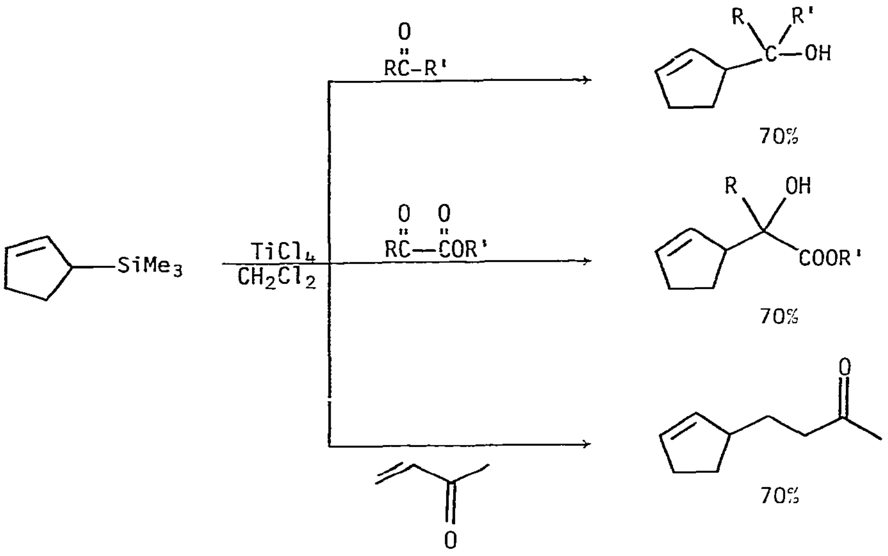


(51)

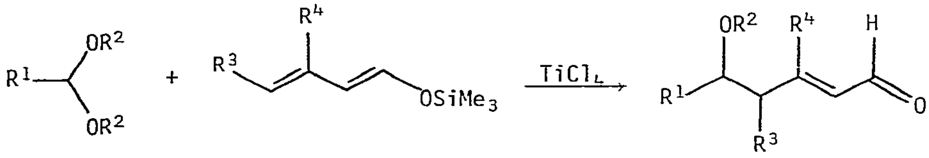


(52)

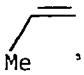
4-t-Butylcyclohexanone reacted with MeLi-LiBr, MeLi-LiI, MeLi-$LiClO_4$, and MeLi-$LiCuMe_2$ in ether to give higher (87-93) amounts of equatorial attack than was obtained with MeLi alone (69% equatorial attack) [115]. Allyltrimethylsilanes reacted with ketones in the presence of titanium tetrachloride to give high yields of alcohols by 1,2-addition to the carbonyl group. Conjugated enones underwent 1,4-addition (eq. 53) [116]. Titanium tetrachloride also effected the reaction between acetals and α,β,γ,δ-unsaturate silylenol ethers (eq. 54) [117]. Simple silylenol ethers themselves condensed with α-ketoesters to give 2-hydroxy-1,4-diketones. Chiral α-ketoesters induced optical activity in the newly-formed tertiary center (eq. 55) [118]. The Reformatskii reaction between α bromoethylacetate and aldehydes and ketones proceeded in higher yields using zinc-copper couple than when the traditional procedure was followed [119]. Chromium(II) salts were used to promote the alkylation of ketones and aldehydes by allylic halides to give homoallylic alcohols. Coupling always occurred at the most substituted allylic terminus. Aldehydes were more reactive than ketones,

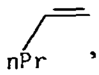


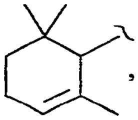
(53)

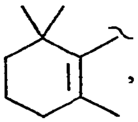


(54)

$R^1$ = Ph, 16%; PhCH=CH-, 88%; 

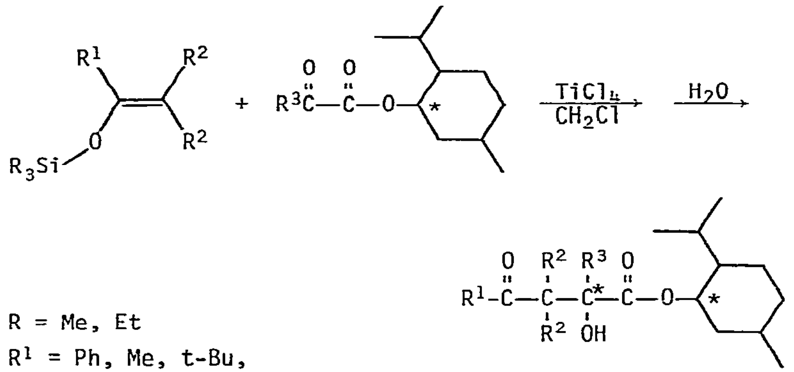
, 86%; 

, 70%; , 69%;

, 68%.

$R^2$ = Me, Et

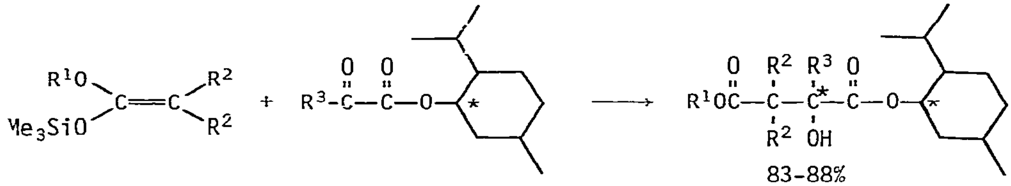
and ester and cyano groups were tolerated [120]. Titanium tetrachloride promoted the photo reaction of alcohols with C=O and C=N containing compounds. While many substrates gave low yields and/or complex mixtures, the synthetically useful ones are recorded in eq. 56 [121]. Alkylmanganese iodide reacted with ketones to give tertiary alcohols in high yield. Acid chlorides reacted with this reagent at low temperatures, aldehydes at moderate tem-



R = Me, Et
R$^1$ = Ph, Me, t-Bu,
R$^2$ = H, Me
R$^3$ = Me, Ph

77-100% yields
18-60% optical yield

(55)



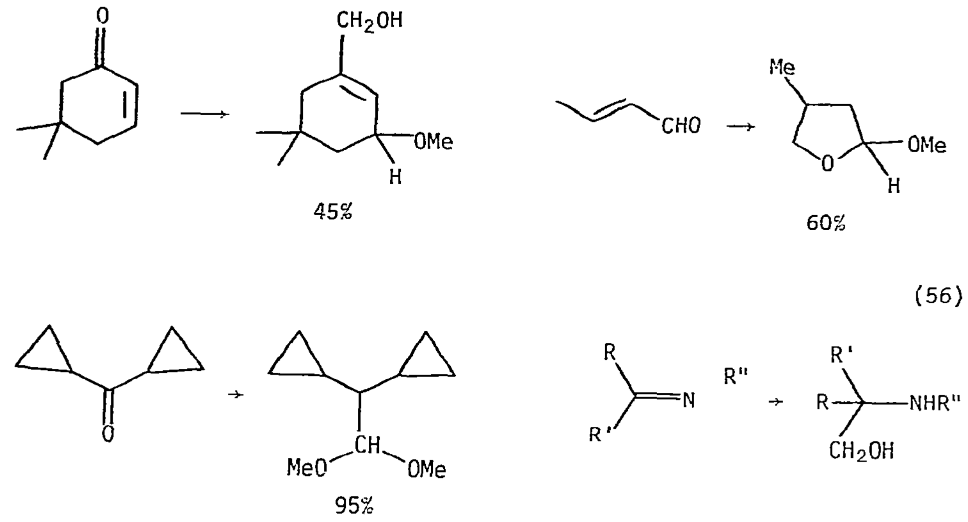
83-88%
35-68% optical yield

R = Me, t-Bu
R$^1$ = Me, Et
R$^2$ = Me, H
R$^3$ = Me, Ph

peratures, ketones at room temperature, and esters were inert. The reagent could discriminate between aldehyde and keto groups in the same molecule [122]. Isoprenoid hydroquinones resulted from the reaction quinones with allyltrimethylsilane in the presence of titanium tetrachloride. The reaction proceeded through the quinol, which was isolated in some cases (eq. 57) [123].

Epoxides were cleanly alkylated with no need for excess reagent by using [RCuCN]Li salts rather than $R_2CuLi$ complexes. The reactions went in high yield with the expected regiochemistry [124]. Enol esters (acetates) reacted with iodobenzene and palladium acetate to produce styrenes and small amounts of styryl acetates [125]. α-Mono or α,α'-dimethyl or phenyl derivatives of p-tolylsulfonylhydrazones were prepared by addition to excess $R_2CuLi$ [126].

Oxidative phenolic couplings to form polycyclic skeletons common to a variety of natural products has long been used, but proceeds normally in low yield. Several new, higher yield processes have been developed and are



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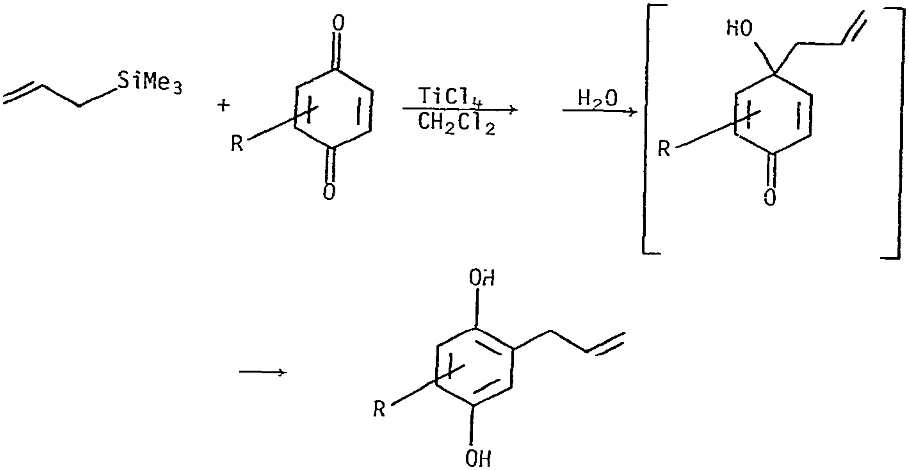

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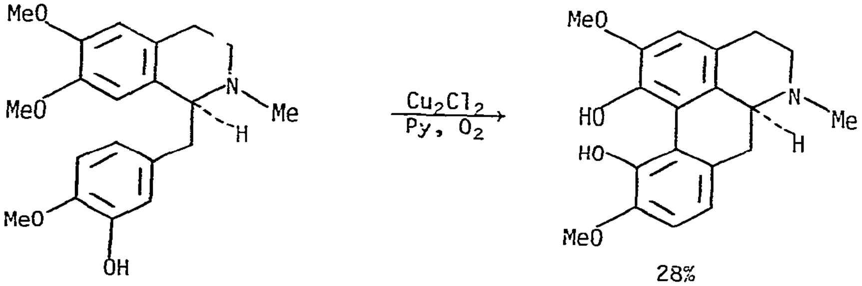
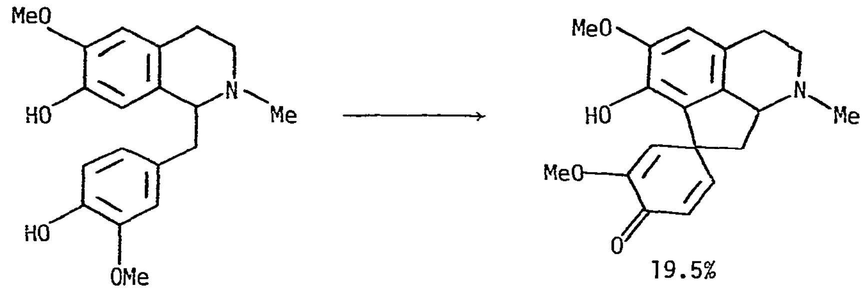
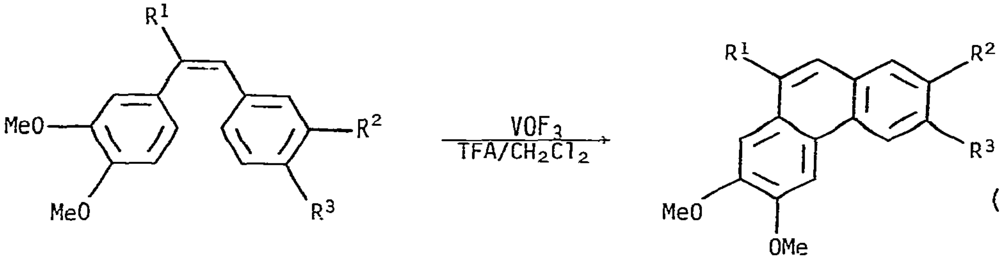


28%

corytuberine

(58)

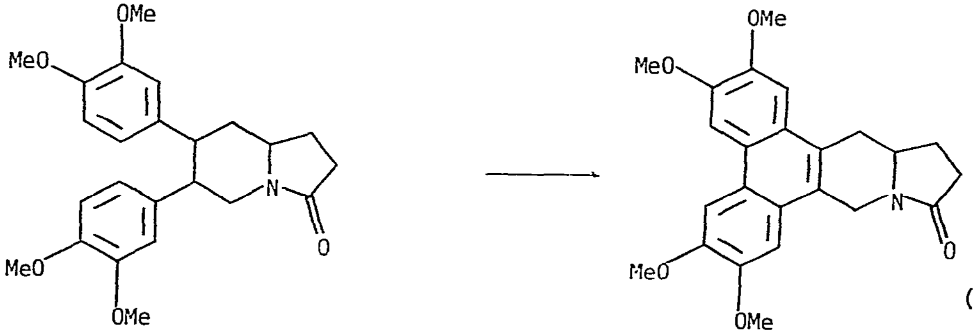




(59)

$R^1$ = COOMe, $R^2$, $R^3$ = OMe 75%
$R^1$ = COOMe, $R^2$, $R^3$ = -$OCH_2$-O- 85%
$R^1$ = CN, $R^2$, $R^3$ = -$OCH_2$-O- 91%

(Worked for benzophenanthridines, methyl-picene-14-carboxylate, also.)

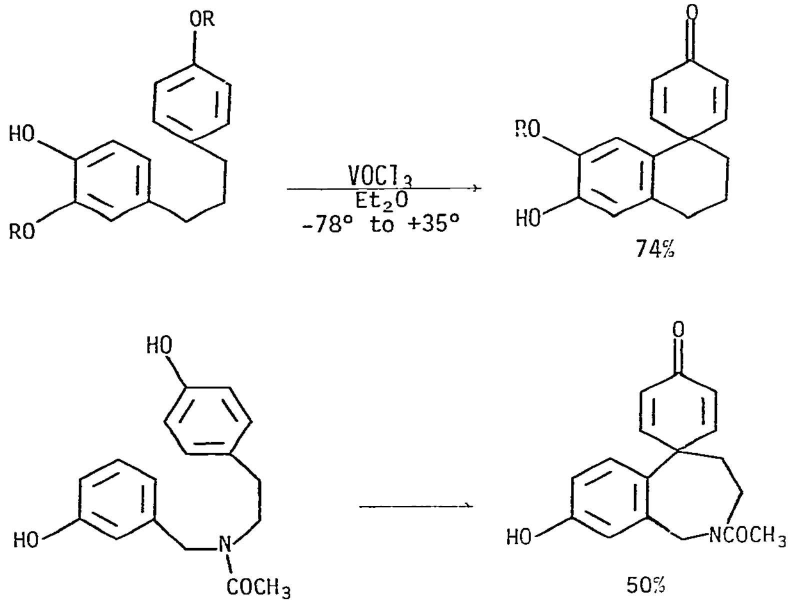


(59)

tylophorine

summarized in eq. 58 [127], eq. 59 [128] and eq. 60 [129]. The specifics of a model oxidative coupling reaction of 2,6-dimethylphenol by copper(II) salts were reported in detail [130].

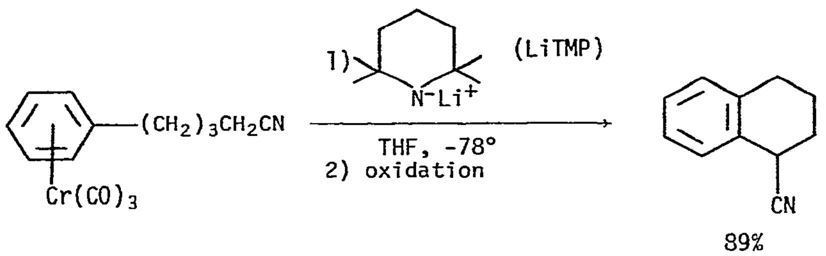
Nucleophilic aromatic substitution on π-arene chromium complexes has accounted for several useful transformations. The toluene complex of chromium carbonyl reacted with a variety of carbanions to give predominately meta substitution with less than 2% para. Similar results were obtained with anisole (94-100% meta). This was particularly true when the carbanion was bulky. Carbanions studied were $LiCH_2CN$, $LiC(CH_3)_2CN$, $LiCH_2COO$-t-Bu and lithiodithiane [131]. An intramolecular version of this reaction was used to form fused, spiro and metacyclophane ring systems (eq. 61) [132]. The reaction of N-methylpyrrole with ethyl diazoacetate in the presence of copper bronze or copper powder resulted in both α and β alkylation of the pyrrole ring. The ratio of isomers (α- always predominated) was dependent on the metal used [133].

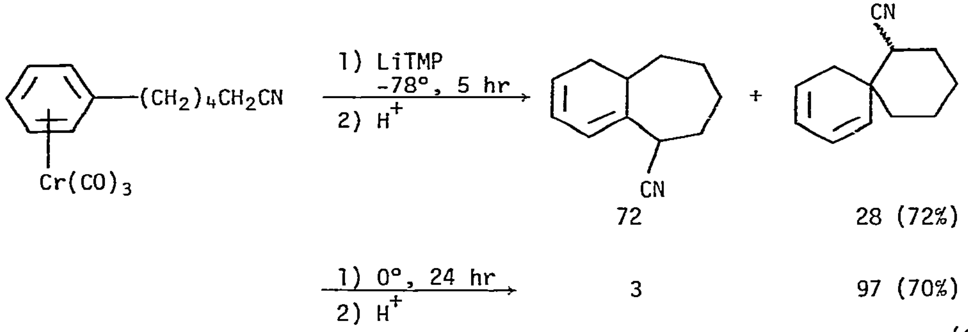


(60)

Grob type fragmentations of five- and six-membered rings were promoted by copper(I) trifluoroacetate. The crude copper complex worked better than purified material (eq. 62) [134]. The nickel promoted reaction between trimethylsilylmethyl magnesium chloride and an unsaturated β lactone produced a compound of use as an isoprenoid synthon (eq. 63) [135].

Cycloaddition of cyclobutenes to cyclobutadienyliron tricarbonyl was used to prepare 1,3,5-cyclooctatrienes (eq. 64) and ultimately cis,trans-1,5-cyclooctadiene [136]. Cyclobutadiene, generated by the oxidation of the iron tricarbonyl complex, reacted with 2,5-di-t-butylbenzoquinones in a Diels Alder reaction. The energy of the strained cyclobutadiene overcame the steric hindrance of the substrate (eq. 65) [137]. Cycloheptatrienyliron tricarbonyl complexes underwent Diels Alder reactions with TCNE to give bridged bicyclic compounds (eq. 66) [138]. The ortho palladation of





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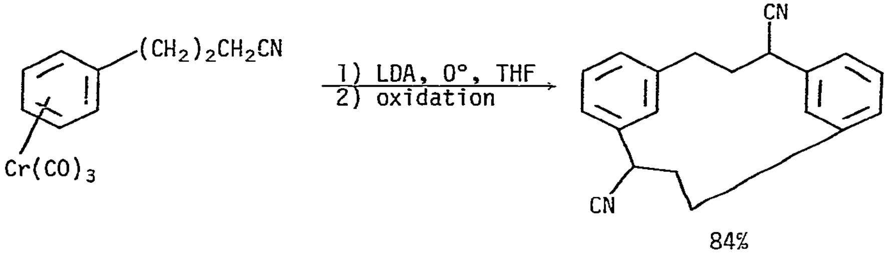
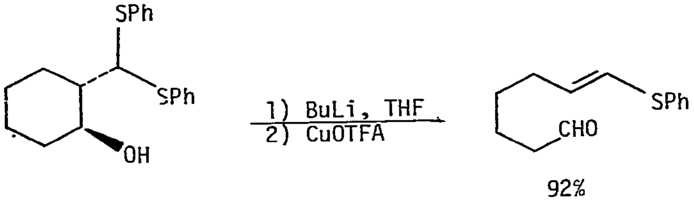
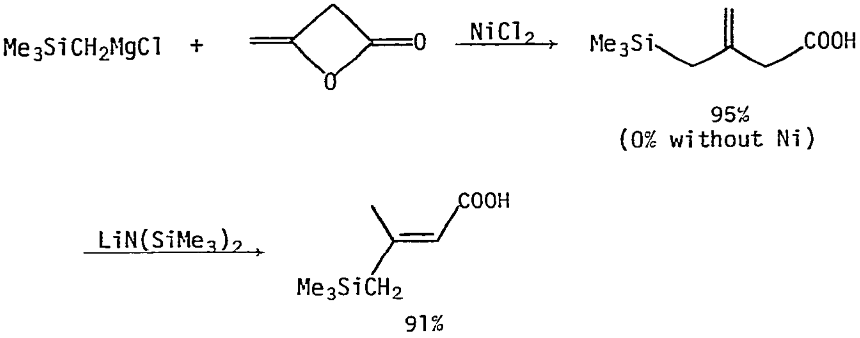




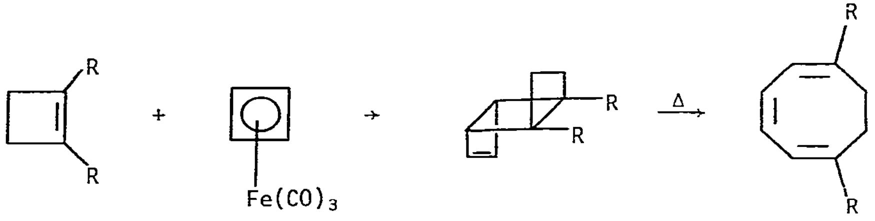
(62)

benzylic tertiary amines was directed exclusively to either the 2 or 6 position of the aromatic ring, depending upon the substituent at C-3. Since these complexes can be functionalized at the palladium carbon bond, this procedure is of some synthetic interest [139].

Applications of π-allyl transition metal complexes in organic synthesis has recently been reviewed (58 references) [140] as has organomercurials as reagents and intermediates in organic synthesis (235 references) [141].

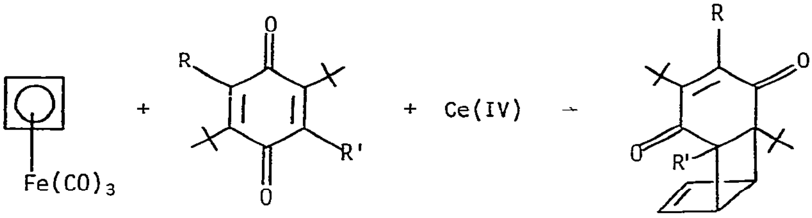


(63)

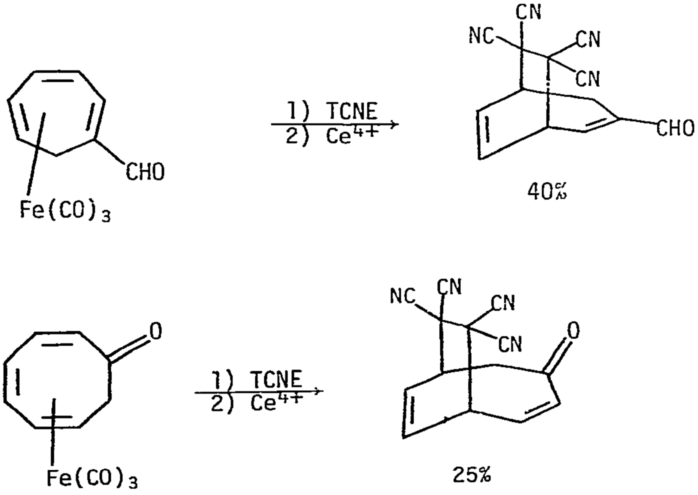


(64)

R = CN, COOMe



(65)

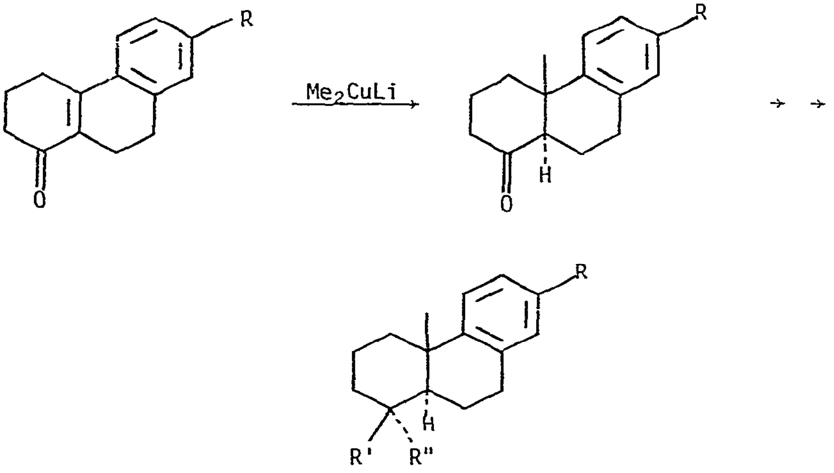


(66)

Theses dealing with in situ generation and use of tris(triphenylphosphine)-nickel [142] and α-carboalkoxyvinyl copper reagents [143] have recently appeared.

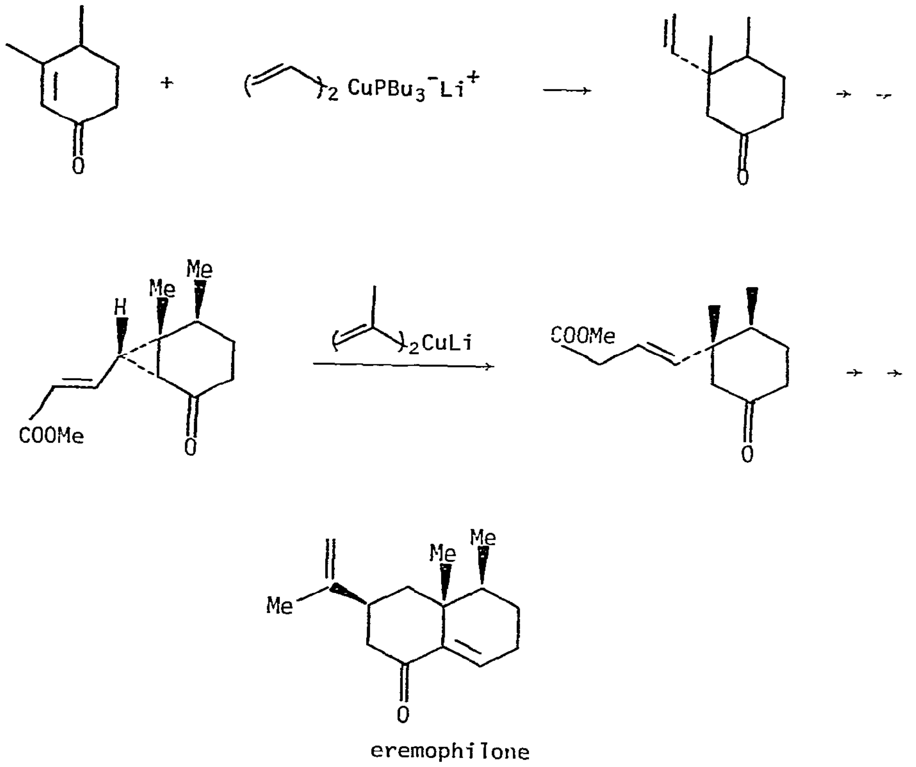
## B. Conjugate Addition

Organocuprates continue to be the reagents of choice for conjugate alkylation of enones. Most current work centers on the development of new reagents and their application to the total synthesis of large molecules. The new organocuprates $LiCu_2(Me)_3$, $Li_2Cu(Me)_3$ and $Li_2Cu_3(Me)_5$ were studied in their reactions with conjugated enones. While each show different, solvent-dependent behavior, $Li_2Cu_3(Me)_5$ in ether gave excellent results with all enones tested, and reacted faster than $R_2CuLi$ [144]. The effect of added lithium iodide or 12-crown-4 on the reactions of $R_2CuLi$ were studied. The crown ether (2 equiv.) completely inhibited the reaction of $Me_2CuLi$ with 4-methylcyclohexenone (conjugate addition), hexanoyl chloride (alkylation) and the enol acetate of ethyl acetoacetate (addition-eliminati Lithium iodide lowered the yields of each of these reactions relative to $Me_2CuLi$, but did not completely stop the reactions. The most efficient conditions for reaction were without any additive at all [145]. A key step in the synthesis of both podocarpic acid and dehydroabietic acid was the conjugate addition of lithium dimethylcuprate to the appropriate tricyclic cyclohexenone (eq. 67) [146]. Lithium methyl-, butyl- and phenyl[(±)-2-(1-dimethylaminoethyl)phenyl]cuprate reagents were prepared and reacted with



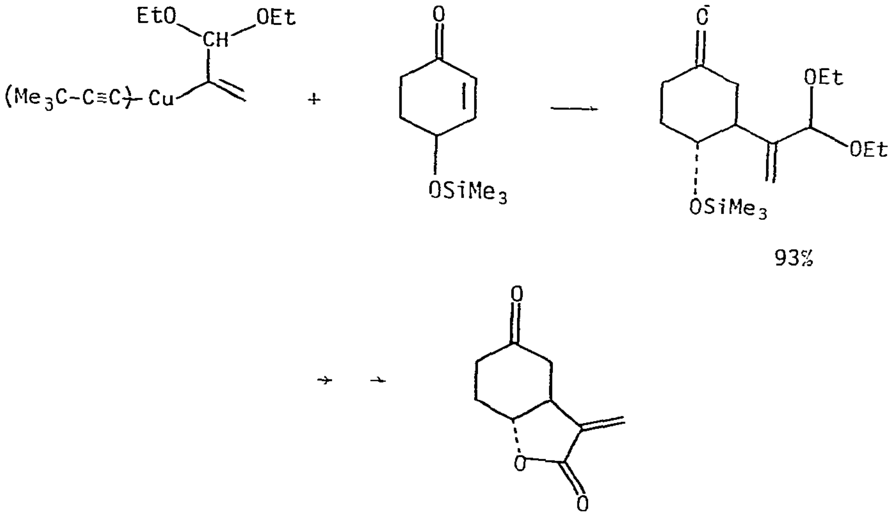
(67)

methylcinnamate, transferring the methyl, butyl or phenyl groups selectively [147]. Divinyl cuprate additions to cyclopropylacrylic esters was used in the s thesis of (±)-eremophilone (eq. 68) [148]. A new organocurpate containing



CuPBu3-Li+
Me
Me
H
COOMe
O
2CuLi
COOMe
Me
Me
Me
O
eremophilone

(68)



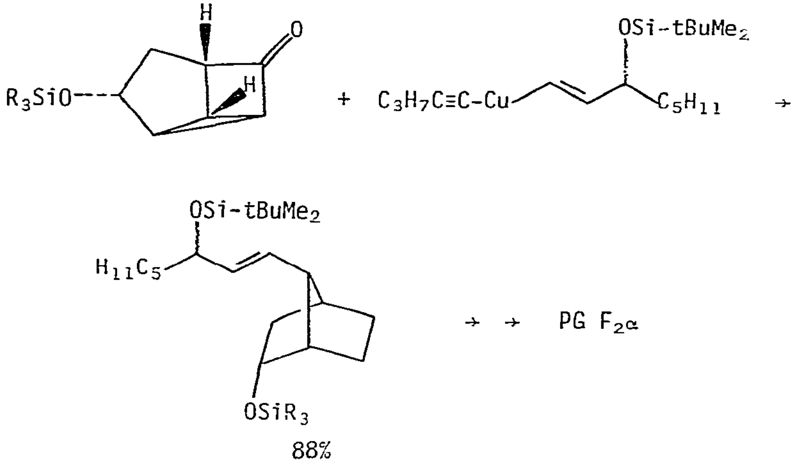
EtO
CH
OEt
(Me3C-C≡C)-Cu
O
OSiMe3
O
OEt
OEt
OSiMe3
93%
O
O
O

(69)

a protected acrolein alkyl group was synthesized and its reactions studied (eq. 69). It reacted well with conjugated enones, but the yield fell as steric hindrance increased. This chemistry offered an approach to $\alpha$-methylene lactones. Vinyl and alkyl halides were unreactive while allylic halides alkylated in high yield [149]. $\omega$-Bromoketones were prepared by the conjugate addition of lithium divinylcuprate to conjugated enones, followed by free radical addition of HBr to the terminal olefin [150].

Prostaglandin $F_{2\alpha}$ was synthesized using the alkylation of a cyclopropyl ketone by a mixed cuprate as a key step. The reaction went in high yield (eq. 70) [151]. The reactions of organocuprates with a variety of conjugated cyclic lactones were studied. With hex-2-enopyrano-4-ulosides and hex-3-enopyranosid-2-uloses alkylation occurred completely stereospecifically axial, while hex-1-enopyran-3-uloses produced complex mixtures. Best results were obtained using heterogeneous systems involving cuprous iodide rather than the tri-n-butylphosphine copper complex (eq. 71) [152]. The reaction of organocuprates with 2-furanoacrylic esters with the intent of inducing chirality at the site of alkyation has been reported. Using the menthyl ester of the substrate and a mixed cuprate having a chiral $\alpha$ phenethyl group as the nontransferrable moiety, 7.5% yield of conjugate addition of phenyl, with 10% optical yield was obtained [153]. With the methyl ester of substrate and in the presence of added lithium chloride and the same chiral mixed cuprate, a 65% yield of conjugate addition was obtained but only 2.2% optical yield [154].

Copper catalyzed Grignard reactions also continued to be extensively studied. Mixed cuprates of the type [RCuMe]MgX, where R was allyl,



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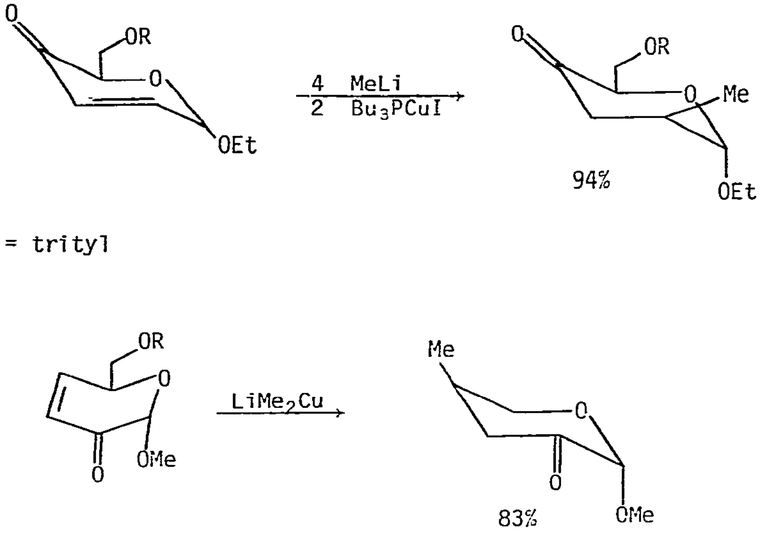
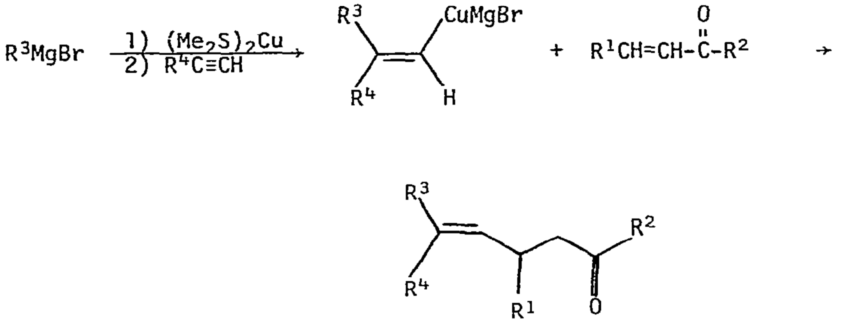


R = trityl

(71)

$CH_2=CH-CH_2CH_2-$, and $CH_2=CH-(CH_2)_3-$ reacted with conjugated enones to primarily transfer the group containing the unsaturation. However, when R was allyl and the substrate was 3-methylcyclohexenone, methylation rather than allylation was the main (75%) product [155]. A variety of tri- and tetrasubstituted enones were examined. A comparison of 1,2 and 1,4 addition of Grignards and organocuprates to 2-furanacrolein has been made. With isopropyl and t-butylmagnesium halides, 1,4 addition was favored by using bromide or iodide salts, while with benzylmagnesium halide the reverse was true. A high concentration of Grignard reagent favored 1,2 addition. Both MeMgI/CuI and $LiMe_2Cu$ led to 1,4 addition [156]. Copper catalyzed conjugate addition of Grignard reagents to ethylacrylate was achieved in fair to good yield by running the reactions at low temperature and using slow addition of acrylate to suppress polymerization. In this fashion the following groups were introduced: Ph (54%), n-pentyl (80%), vinyl (41%), 5-hexenyl (73%), benzyl (69%) and cyclohexyl (68%) [157]. Copper "ate" complexes, prepared from methyl trialkylborates and copper(I) iodide, reacted with ethylpropiolate to transfer the alkyl (not methyl) group, producing E alkylacrylates in 40-60% yield (alkyl = n-propyl, n-butyl, i-butyl, n-hexyl) [158]. Trisubstituted olefins were stereospecifically synthesized by conjugate addition of vinyl cuprates, produced by the copper catalyzed alkylation of alkynes by Grignard reagents, to conjugated enones (eq. 72) [159].

Allenic substrates were also reactive towards organocopper complexes. The copper(I) iodide catalyzed reaction of alkyl- and phenylmagnesium halides with 2,3-butadien-1-ol produced trans $RCH_2CH=CHCH_2OH$ [160]. Conjugated

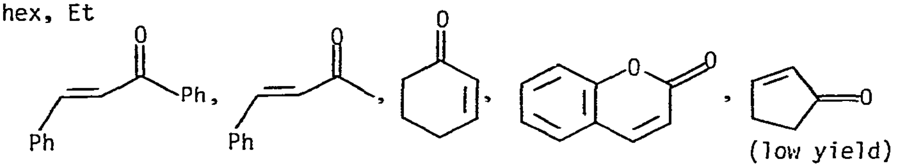


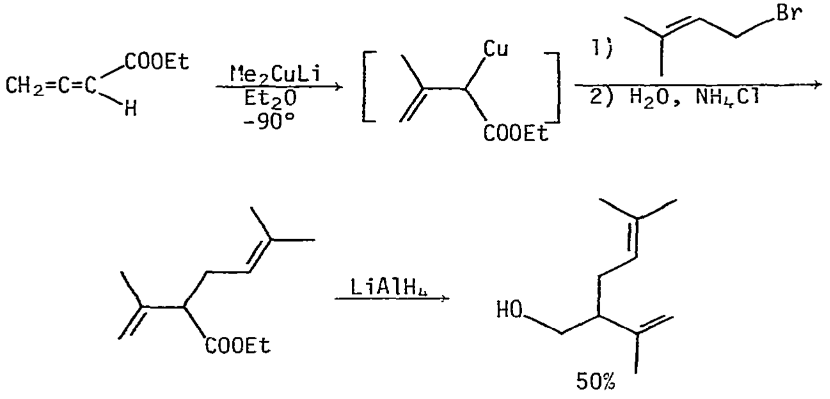
(72)

$R^3$ = Et, n-hex, nBu

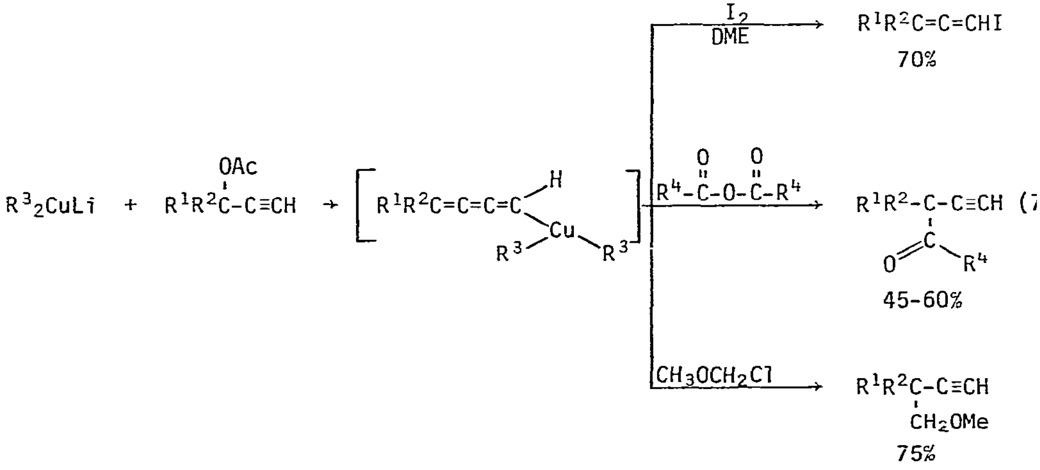
$R^4$ = n-hex, Et

enone =



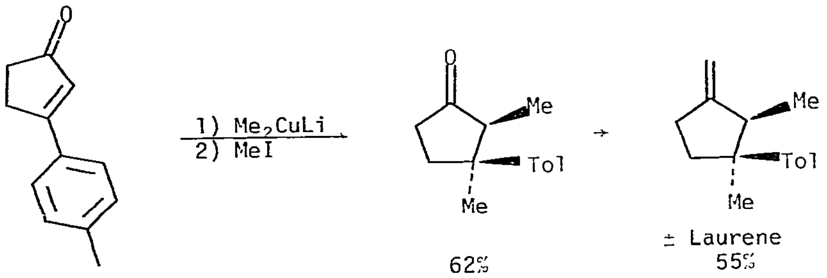


(73)



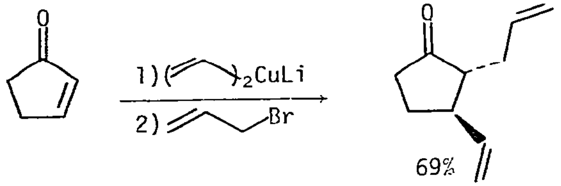
(7

allenic esters underwent 1,4 alkylation to produce a copper enolate, which was reacted with an allylic halide, producing ultimately lavandulol (eq. 73) [161]. Propargylic acetates reacted with organocuprates to produce allenic cuprates, which were further treated with a number of reagents (eq. 74)[162]. Several other cases of further reaction of the copper enolate formed by conjugate addition have been reported. Based on the surprising observation that β-phenyl groups on cyclopentenones led to *cis* α alkylation of the enone (the less stable product) several *cis* 2,3 dialkylated cyclopentanones were prepared. β-Vinyl groups did not have this effect, and *trans* dialkylated species were obtained with vinyl cuprates (eq. 75) [163]. The conjugate addition of lithium dimethylcuprate to cyclohexenone followed by treatment of the enolate with $Me_2N{=}CH\ ^{+}CF_3COO^{-}$ (a new Mannich reagent) led to the production of β-methyl, α-dimethylaminomethyl cyclohexanone in good yield [164]. Treatment of 3-chloro-5,5-dimethylcyclo-hex-2-en-1-one with two equivalents of lithium dimethyl cuprate produced 3,3,5,5-tetramethylcyclohexanone in 76% yield by combined alkylation-conjugate addition [165]. Finally, dimethylcyclohexane dicarboxylates were obtained by the addition of lithium dimethylcuprate to methyl crotonate. This

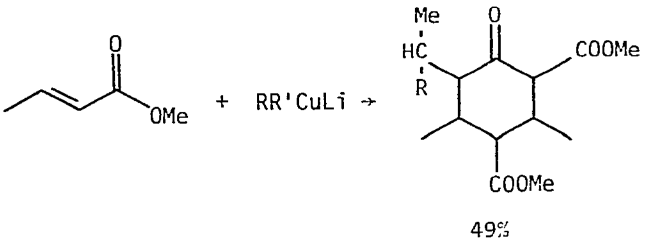


(75)

but



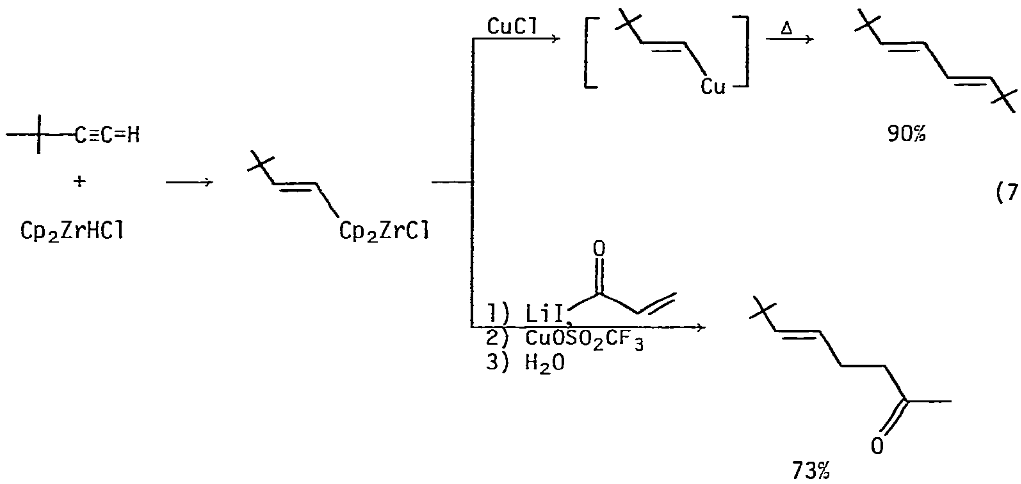
less than 3% *cis*



(76)

product arose from a sequence of 1,4 additions and a final cyclization (eq. 76)[166].

A variety of other metals have been used to effect conjugate additions. Treatment of zinc halide with three equivalents of organolithium reagent produced a complex [$R_3ZnLi$] which 1,4 alkylated cyclohexanone in 94% yield in THF at 0° for thirty minutes [167]. Vinylcopper species were prepared from alkynes by hydrozirconation followed by stereospecific alkenyl transfer to copper. These were then coupled to dienes or added 1,4 to conjugated enones (eq. 77) [168]. Similar chemistry was effected by transfer of the



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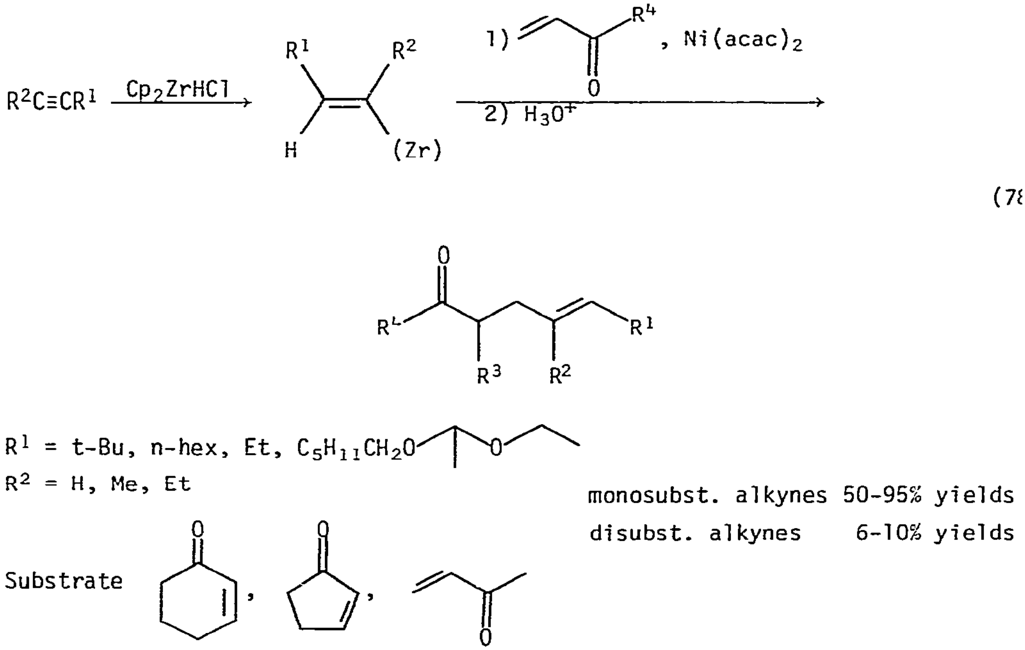
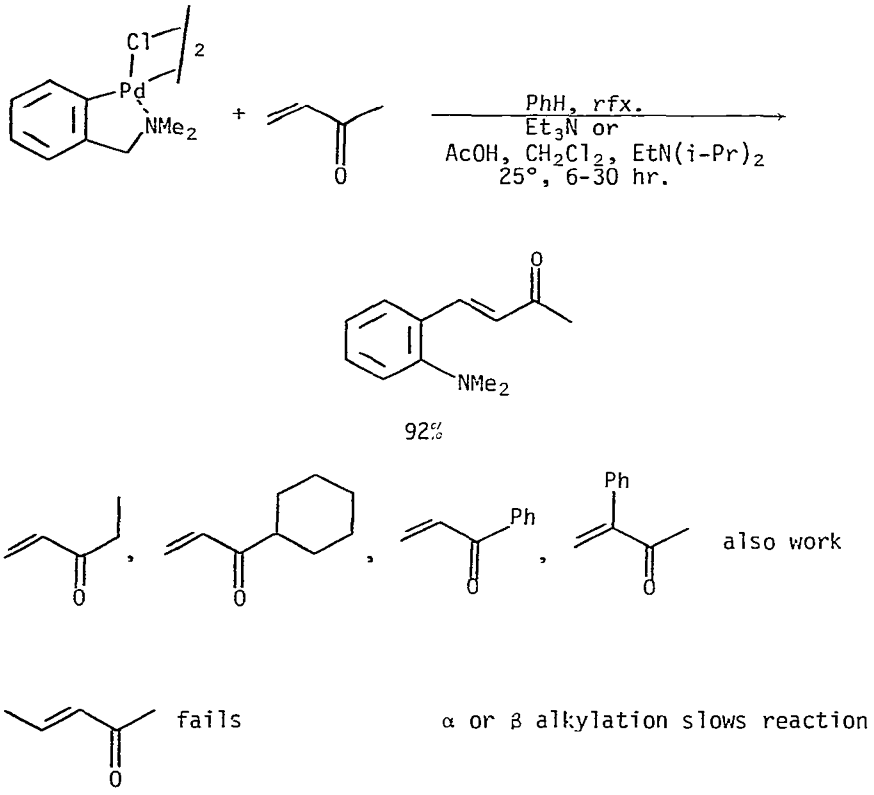


(7

monosubst. alkynes 50-95% yields
disubst. alkynes 6-10% yields

vinyl group to nickel (eq. 78) [169]. The conjugate addition of butylmagnesium bromide to (Z)-(2R,3S)-6-benzylidine-3,4-dimethyl-5,7-dioxo-2-phenylperhydro-1,4-oxazepine catalyzed by nickel chloride, followed by hydrolysis and decarboxylation gave a 92% yield of 3-phenylheptanoic acid 99% enantiomerically pure [170].

Arylpalladium complexes, prepared by the ortho palladation of benzylamines added 1,4 to conjugated enones to replace the palladium by the enone (eq. 79) [171]. The σ-alkylpalladium complexes resulting from methoxylation of allylamine reacted in a similar fashion (eq. 80) [172]. Palladium(0) catalysts promoted β-arylation of conjugated enones by aryl halides (eq. 81) [173]. Both 2-bromo and 3-bromothiophene reacted with allyl alcohols in the presence of palladium acetate catalysts to produce aldehydes or ketones in a formal β-alkylation of allyl alcohol (eq. 82) [174, 175].



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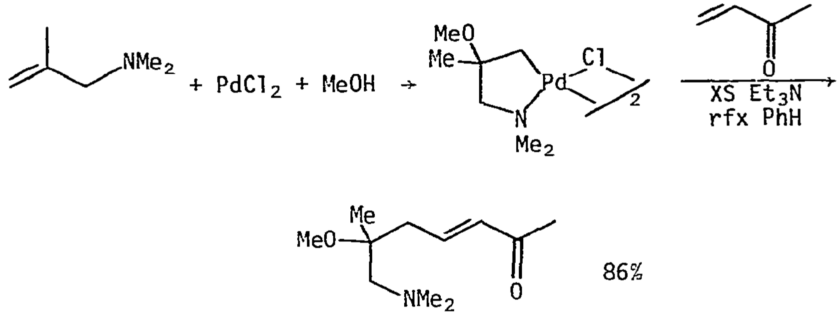

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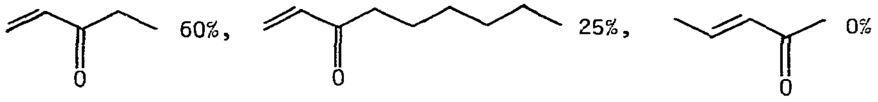

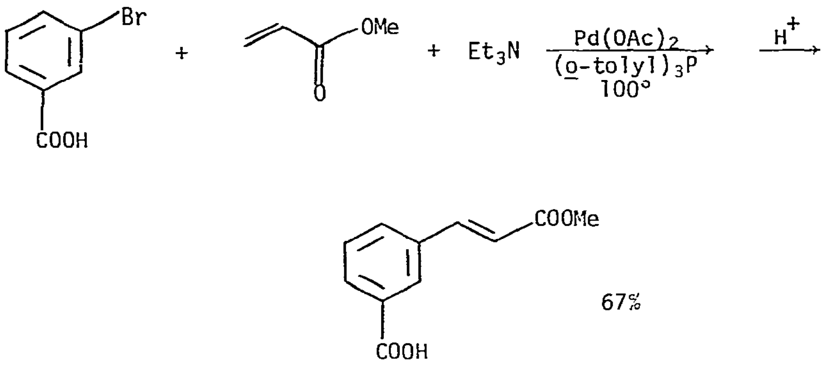

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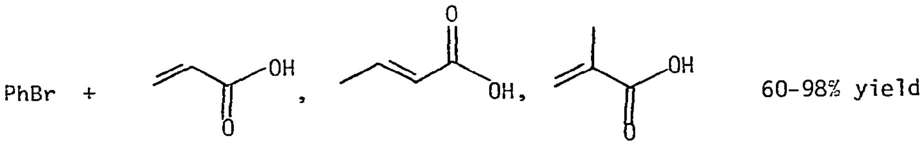
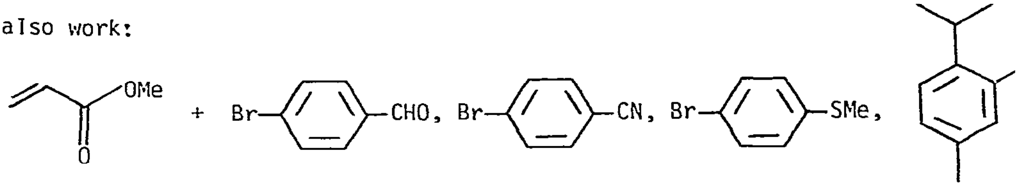
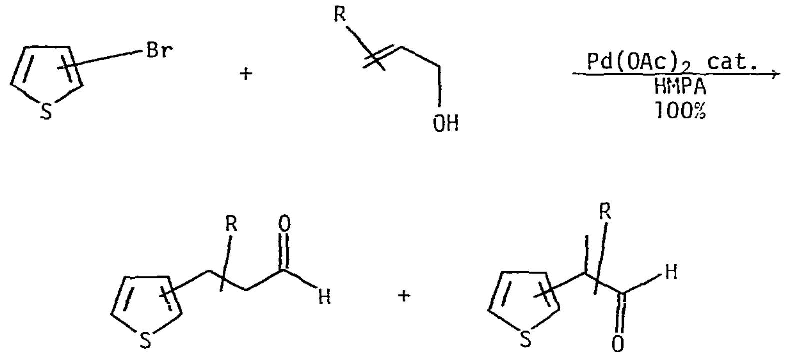


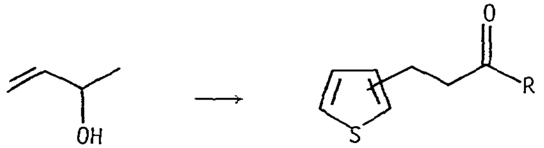
also work:



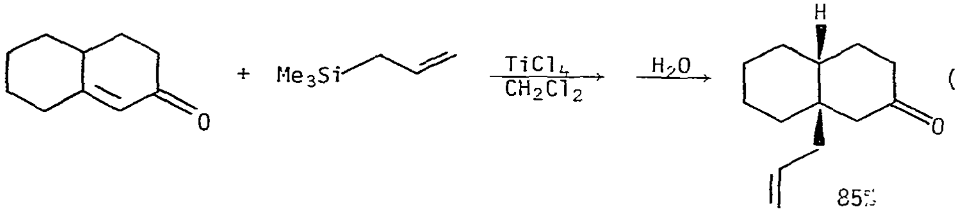
Titanium tetrachloride promoted the conjugate addition of allylsilanes to conjugated enones. The method was used for the direct introduction of an angular allyl group in a fused decalin system (eq. 83) [176]. Alkyl tetracarbonylferrates reacted with conjugated enones to give 1,4-diketones. The reaction also went with acrylonitrile (eq. 84) [177]. Finally, chromium carbene anions added 1,4 to α,β-unsaturated compounds (eq. 85) [178].



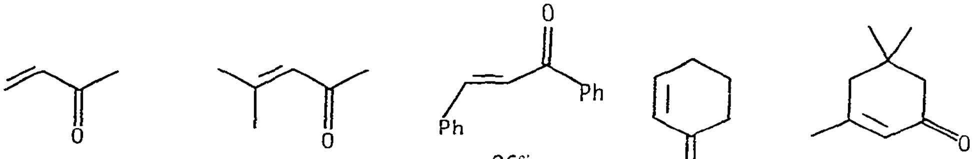
40% yield 5:4 mixture (82)



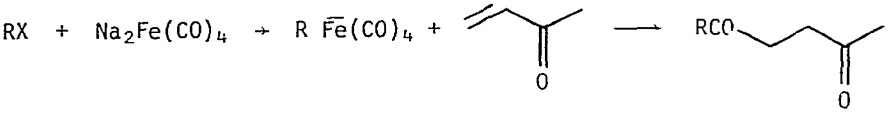
80%



85% (83)

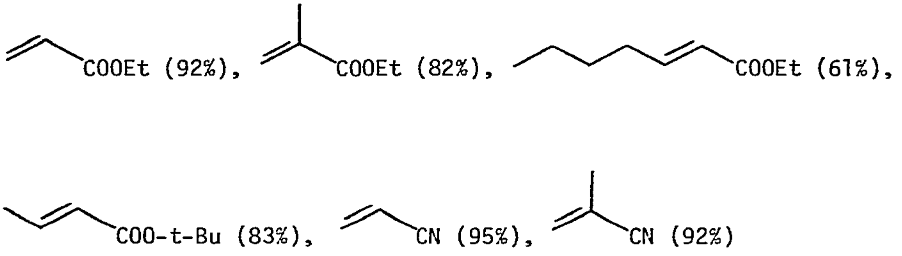


59% 87% 96% 82% 76%



$RX + Na_2Fe(CO)_4 \rightarrow R\bar{F}e(CO)_4 +$ → RCO

R = n-Bu, n-hex, Et



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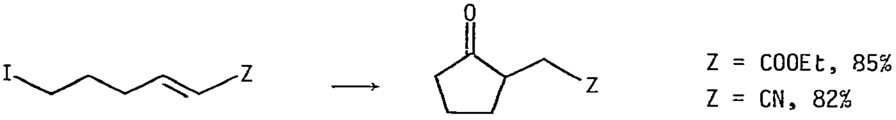
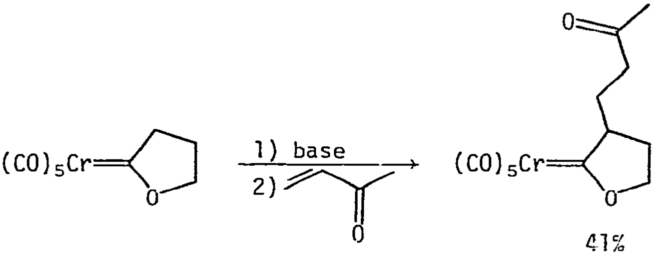
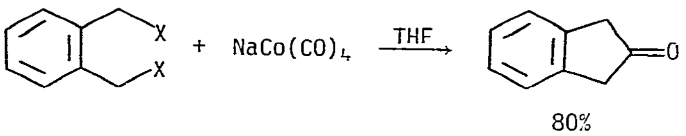




(85)

C. Acylation

Phase transfer catalysis in carbonylations of organic halides has been developed by two groups. Benzyl bromides were carbonylated to the corresponding phenylacetic acids by reacting the halide, carbon monoxide and a catalytic amount of $Co_2(CO)_8$ in a benzene-5N NaOH system, using triethylbenzylammonium chloride as the phase transfer catalyst. With o-methylbenzyl bromide, a double carbon monoxide insertion occurred to give $ArCH(COCOOH)CH_2A$ in addition to the normal products [179]. A similar system using benzyl chloride, carbon monoxide, sodium tetracarbonylcobaltate as catalyst, with a diphenyl ether-aqueous sodium hydroxide solvent system produced phenylacetic acids in 85% yield [180]. Iodobenzene was converted to methylbenzoate by treatment with carbon monoxide in the presence of tetrakis(triphenylphosphine palladium or nickel in methanol-diethylamine solvent [181]. Straight chain $C_1$-$C_5$ alkyl iodides were converted to the corresponding esters by treatment in alcohol with carbon monoxide at 200-250° in the presence of a rhodium-NaX zeolite catalyst [182]. 2-Indanone was produced in 80% yield by treating o-bis(bromomethyl)benzene with sodium tetracarbonyl cobaltate in THF (eq. 86) [183]. Allenes were acylated to produce α,β-unsaturated ketones with acyliron complexes via a π-heterobutadiene iron complex (eq. 87) [184]. Cyclic and polycyclic aliphatic compounds were synthesized by the insertion of olefins and carbon monoxide into nickel-carbon bonds. Strained olefins, ability to chelate, and terminal vinyl groups were required for reaction. Many products were often obtained (eq. 88) [185]. Grignard reagents reacted with aryl halides and carbon monoxide in the presence of dialkylnickel dihalide complexes to produce mixtures of ketones and tertiary alcohols [186]. Reviews dealing with transition metal catalyzed reactions of organic halides with carbon monoxide, olefins and acetylenes (44 references) and with the carbonylation of organic halides (70 references) have appeared [187, 188].



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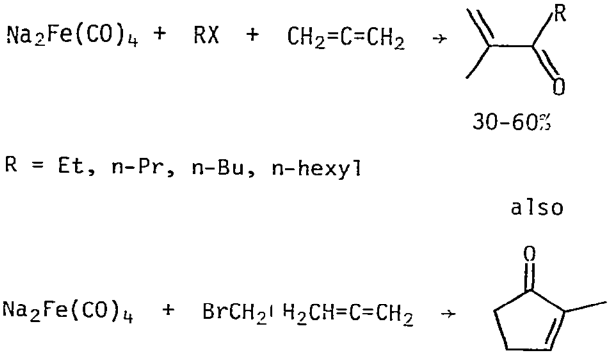
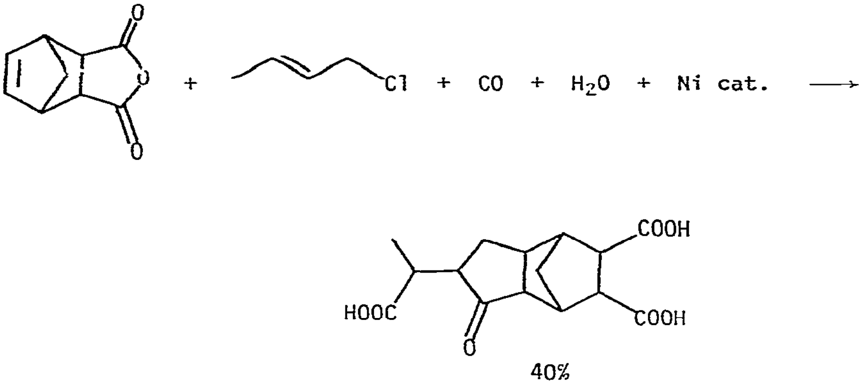


(87)

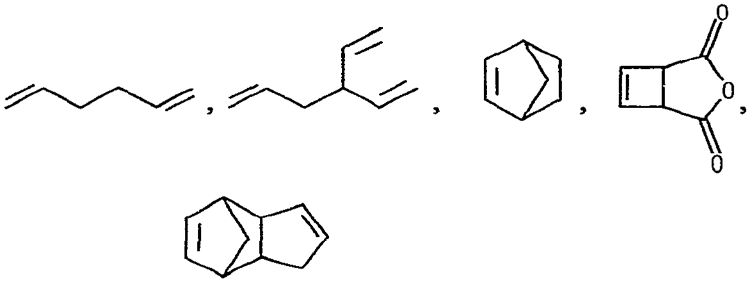
Dialkynylmercury compounds reacted with carbon monoxide and alcohols at room temperature in the presence of palladium(II) catalysts to form dialkylmaleates [189]. Unsymmetrical diarylketones were synthesized by the treatment of aryliodides with arylmercuric halides in the presence of nickel carbonyl (eq. 89)[190].

The hydroformylation of olefins was the subject of extensive research. The stereochemistry of the hydroformylation of olefins with cobalt and rhodium catalysts was examined. Both metals promoted cis addition of the hydride and formyl groups. The mechanism of both the hydroformylation and olefin isomerization was studied [191]. A new catalyst system consisting of a rhodium complex, triphenylphosphite and sodium acetate was developed for the production of normal aldehydes from α-olefins. The sodium acetate both maintained catalyst activity and promoted formation of normal aldehydes [192]. During the course of this reaction traces of oxygen in

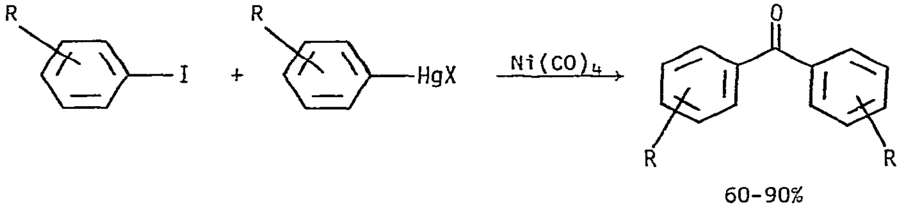


(88)

Very reactive



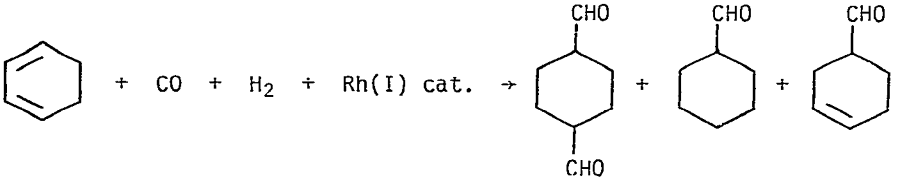
Unreactive



(89)

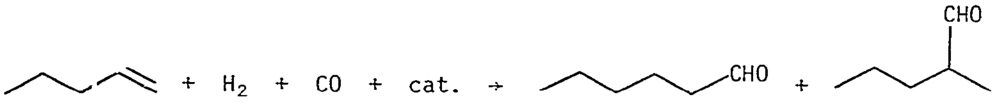
R = H, 4-Me, 4-$NH_2$
R' = H, 4-Me, 4-Cl

the synthesis gas oxidized the phosphite to $(Ph_3O)_3P{=}O$, deactivating the catalyst. Scrubbing of the synthesis gas with triisobutylaluminum in toluene suppressed this oxidation [193]. The hydroformylation of deuterate olefins with cobalt catalysts at high carbon monoxide pressure was studied, and the data obtained were consistent with initial formation of a catalyst-olefin π-complex [194]. The percentage conversions in ethylene hydroformylation over $Rh(CO)Cl[P(C_6H_4R)_3]_2$ correlated with the infrared vibrational frequencies of the phosphorous-rhodium bond [195]. The kinetics of the hydroformylation of ethylene over π-allylrhodium(I) carbonyl bis triphenylphosphine adsorbed on γ alumina were consistent with loss of propionaldehyde from $Rh(III)H_2(acyl)(CO)(PPh_3)_2$ to give $Rh(I)H(CO)(PPh_3)_2$ as a rate limiting step [196]. Cyclic dienes underwent hydroformylation with acetatocarbonylbis(triphenylphosphine)rhodium(I) as a catalyst to give mono- and dialdehydes, depending on ring size. Small rings favored dialdehydes while larger ring compounds underwent reduction rather than a second hydroformylation (eq. 90)[197]. Cobalt carbonyl clusters were used to catalyze the hydroformylation of 1-pentene at 130°, and 500-1200 psi. Under these conditions the clusters were claimed to remain intact, yields were high, and moderate selectivity for terminal hydroformulation was observed (eq. 91) [198]. The catalytic activity of rhodium(I) complexes as hydroformylation



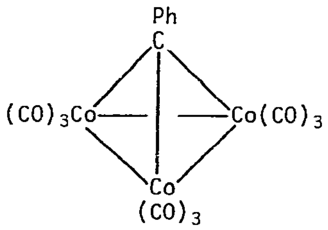
(90)

catalysts depended on the state of coordination. Substitution of one of the phosphines of $RhH(CO)_2(PPh_3)_2$ by one phosphine of a bis or trisphosphine led to bridged complexes of higher activity than the parent complex, while substitution of both phosphines gave complexes of lower activity. Complexation to polymer bound phosphine ligands led to trans square planar complexes in which or at most two polymer bound phosphine groups are coordinated [199]. A



(91)

cat. =

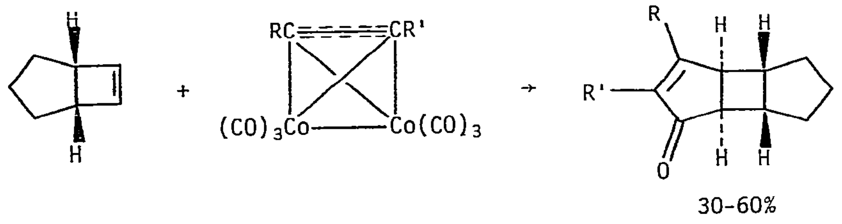


and $(PhC)_2Co_4(CO)_{10}$

catalyst consisting of $(Ph_3P)_2PtCl_2$-$SnCl_2$ hydroformylated α olefins at 60-80° and 800-1500 psig $H_2/CO$ to give 85-90% yields of aldehyde with

85-93% selectivity for straight chain aldehydes [200]. α-Deuteriostyrene was hydroformylated in the presence of a chiral rhodium catalyst to give optically active aldehyde [201]. The product distribution as a function of catalyst in the hydroformylation of ethyl acrylate, methyl methacrylate, methyl crotonate and methyl tiglate at 150° and 100 atmospheres of $H_2/CO$ was studied. Starting with $Rh_2Cl_2(CO)_4$, diphosphines of various chain length ($R_2P(CH_2)_nPR_2$) were added to generate the catalyst. With R equal to phenyl or cyclohexyl and n = 2-4, 80% α acylation was observed, while use of longer diphosphines, triphenylphosphines or $Rh_2Cl_2(CO)_4$ alone gave very low α-selectivity [202]. The use of aliphatic tertiary phosphines and P-substituted phospholanes as cocatalysts in the rhodium carbonyl-tertiary phosphine catalyzed hydroformylation of 1,3 dienes to dialdehydes was investigated [203]. α-Methylstyrene was asymmetrically hydrocarboxylated using a palladium dichloride-(-)DIOP catalyst [204]. Hydrocarboxylation of olefins and related reactions has been reviewed [205].

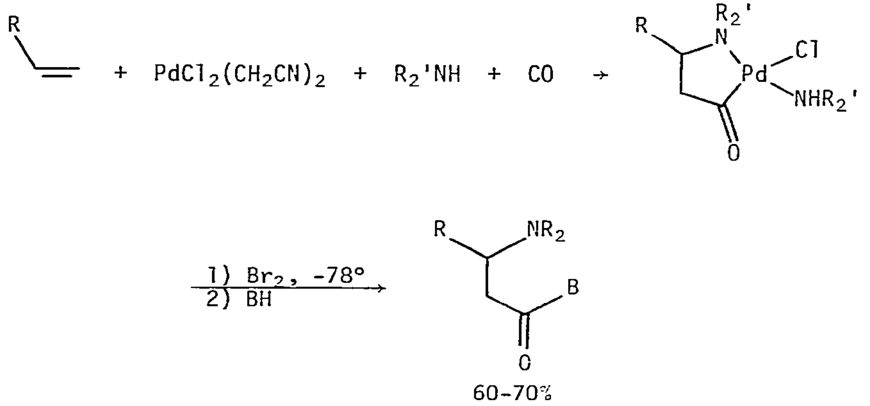
Linear α,β-unsaturated esters were obtained by the $(Ar_3P)_2PdCl_2$-$SnCl_2$ and $(Me_3PPh)_2PdCl_2$-$SnCl_2$ catalyzed carbonylation of 1-alkynes. The reaction proceeded in high yield under mild conditions [206]. 2-Butyne reacted stereospecifically with $(Ph_3P)_2Ni(Ph)Br$ in methanol to give a vinyl complex which upon carbonylation produced 98% cis-α,β-dimethylcinnamate [207]. Treatment of acetylene-hexacarbonyl dicobalt complexes with alkenes or cycloalkenes produced cyclohexenones. With unsymmetrical alkynes, mixtures were obtained (eq. 92) [208]. Carbon monoxide addition to acetylenic substrates for the synthesis of quinones, acrylic and succinic acids has been reviewed (258 references) [209].



(92)

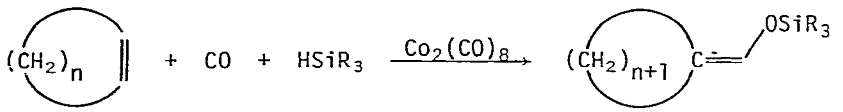
R = H, Me
R' = H, Me, Ph

Several new olefin carbonylations have been developed. Simple terminal monoolefins were aminoacylated, by treatment with diethylamine followed by carbon monoxide in the presence of palladium(II) chloride, to produce β-aminoacid derivatives after oxidative cleavage (eq. 93) [210]. Transition metal catalyzed carbonylation of olefins was reviewed (289 references) [211] Isoprene was acylated to produce 4-methyl-3-pentenoate esters by treatment with carbon monoxide in the presence of a palladium acetate-triphenylphosphine catalyst system. No isoprene dimers were formed [212]. Cyclic olefins were converted to exocyclic trialkylsilenol ethers by treatment with carbon monoxide, trialkylsilane, and dicobalt octacarbonyl (eq. 94) [213].



(93)

BH = $CH_3OH$, $NH_3$, $Et_2NH$

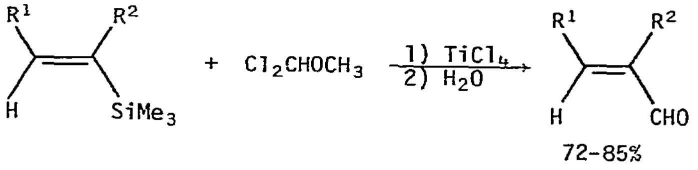


(94)

n = 3 48%
n = 4 71%
n = 5 74%
n = 6 69%

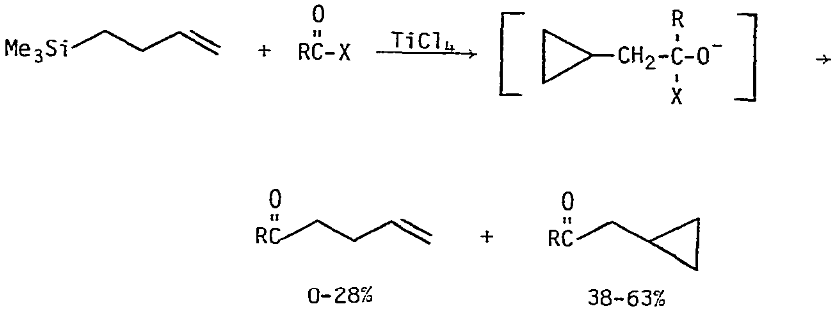
Oxetane, THF and epoxycyclohexane were cleaved by treatment with methyldiethylsilane and carbon monoxide in the presence of dicobalt octacarbonyl to give $Et_2MeSiO(CH_2)_nCHO$ and 2-(methyldiethylsiloxy)cyclohexane carboxaldehyde [214]. Vinyl silanes reacted with dichloromethylmethyl ether in the presence of titanium tetrachloride to produce conjugated aldehydes in good yield (eq. 95) [215]. ω-Unsaturated alkylsilanes were acylated by treatment with titanium tetrachloride and acid halides (eq. 96) [216].

Metal oxides such as $Fe_2O_3$, ZnO, $MoO_3$, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Na_2WO_4$ catalyzed the acylation of isomeric xylenes with benzoyl chloride in 10 hr at 150°. Anisole, halobenzenes and alkylbenzenes acylated in the four position using $Fe_2O_3$ in high yield [217]. The benzoylation of halobenzenes by substituted benzoic acid chlorides catalyzed by $Fe_2(SO_4)_3$ was the subject of a separate report [218]. Pyridine was treated with phenyllithium followed

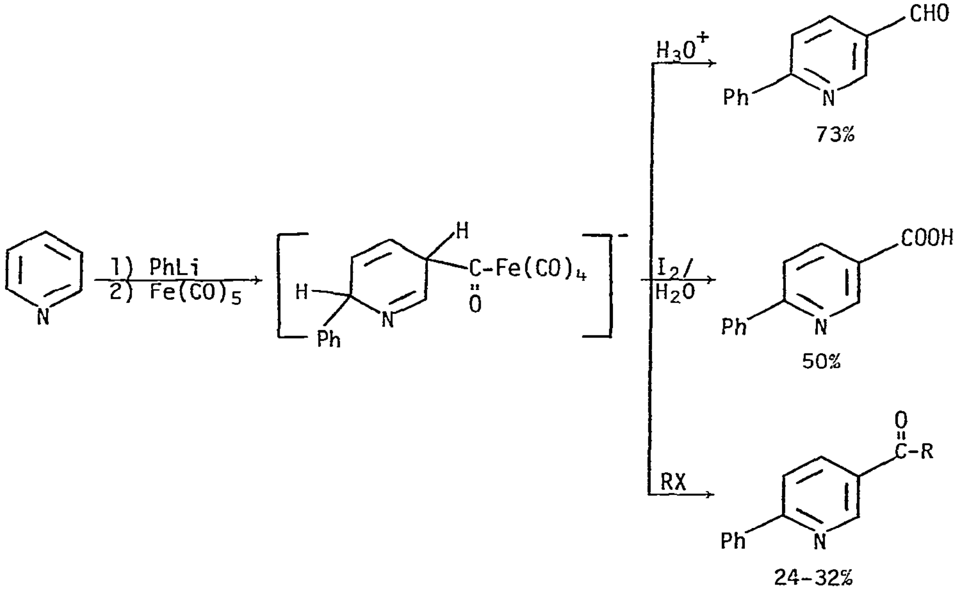

(95

$R^1$ = n-pentyl, n-Bu, Ph, n-propyl

$R^1$ = H, n-propyl


(96)

by iron pentacarbonyl to give direct acylation in the β position, a site not normally accessible to electrophilic substitution (eq. 97) [219]. The Gatterman Koch reaction of toluene was promoted by mixtures of aluminum trichloride and $Cu(PPh_3)Cl$. Triphenylphosphine inhibited this reaction.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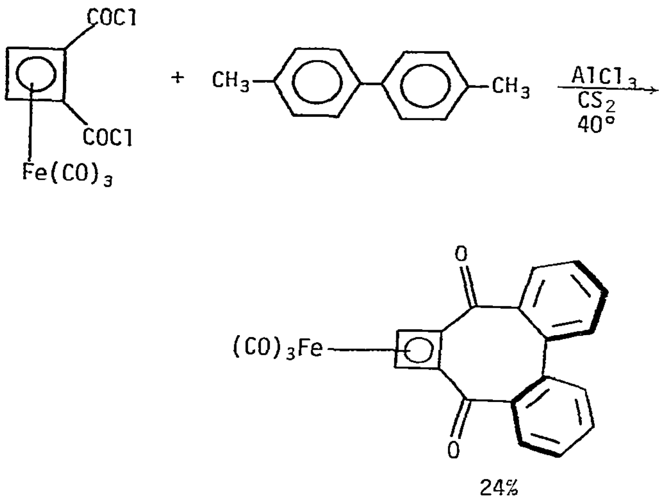

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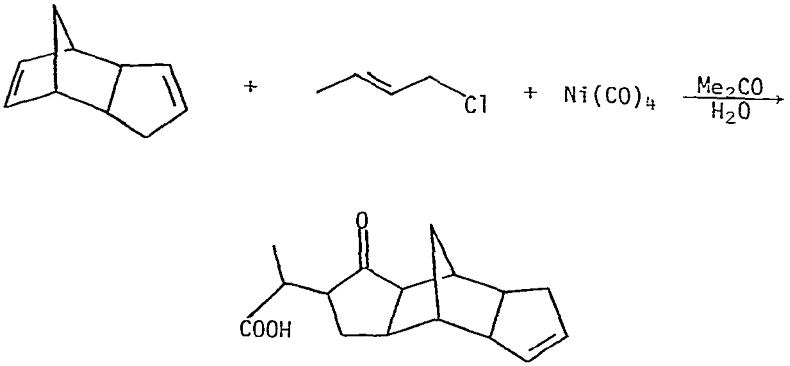

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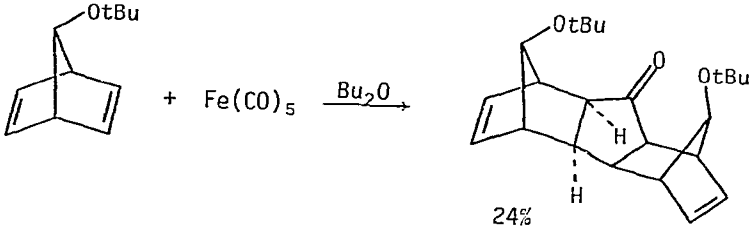
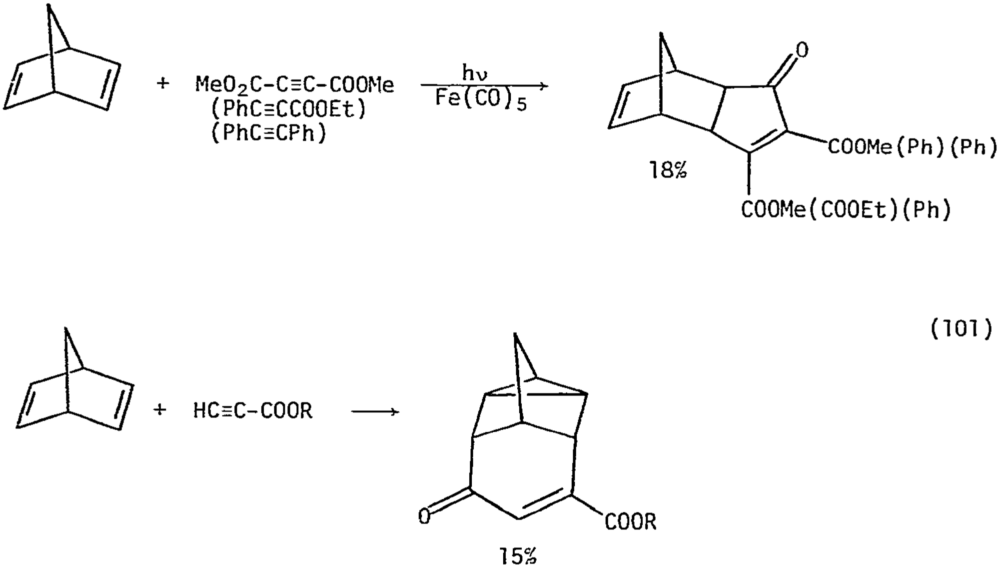


(100)

+ cage dimer + linear trimer ketone
14% 18%

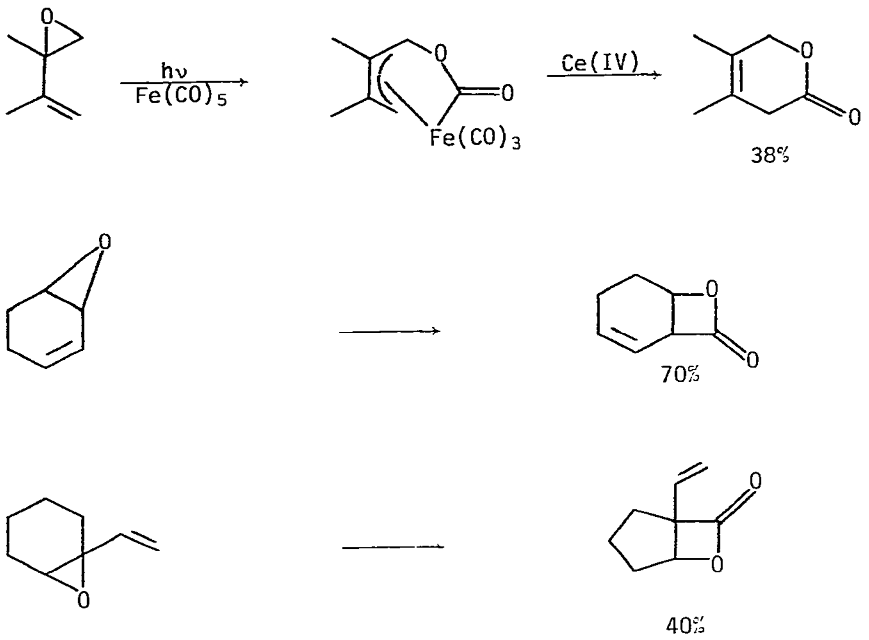
The iron tricarbonyl complex of the acid chloride of cyclobutadiene dicarboxylate acylated 4,4'-dimethylbiphenyl to give a polycyclic complex (eq. 98) [221]. The reaction of endo dicyclopentadiene with nickel carbonyl and crotyl chloride in acetone-water gave a tetracyclic acid (eq. 99) [222]. Iron pentacarbonyl reacted with 7-t-butoxynorbornene to give primarily acylated dimers (eq. 100) [223]. Norbornadiene itself reacted with iron pentacarbonyl and alkynes to give polycyclic ketones (eq. 101) [224]. Lactones were formed by the photolysis of unsaturated epoxides in the presence of iron pentacarbonyl (eq. 102) [225]. Cyclic ketones resulted from similar treatment of unsaturated cyclopropanes (eq. 103) [226]. Finally, an unusual series of carbonylations and rearrangements of iron cyclic olefin complexes was reported (eq. 104) [227].

The recently developed carbonylation of methanol to acetic acid was studied in detail. No significant difference was noted between the methyl iodide promoted reaction catalyzed by rhodium or iridium complexes, although maximum activity was achieved under different conditions for each of these metals. Iridium was the best catalyst of all the platinum metals examined [228]. Ketone solvents such as acetophenone and benzophenone



(101)

kept both the activity and selectivity of this reaction high, even at elevated temperatures [229]. In a departure from the standard reaction conditions involving methyl iodide as a promotor, pentachlorobenzene thiol was found to also promote the carbonylation of methanol, although less effectively than methyl iodide [230]. The carbonylation of saturated oxygen ated compounds has been reviewed (103 references) [231]. Amines were car-



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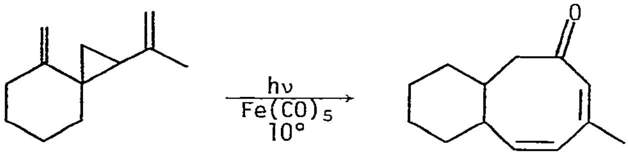
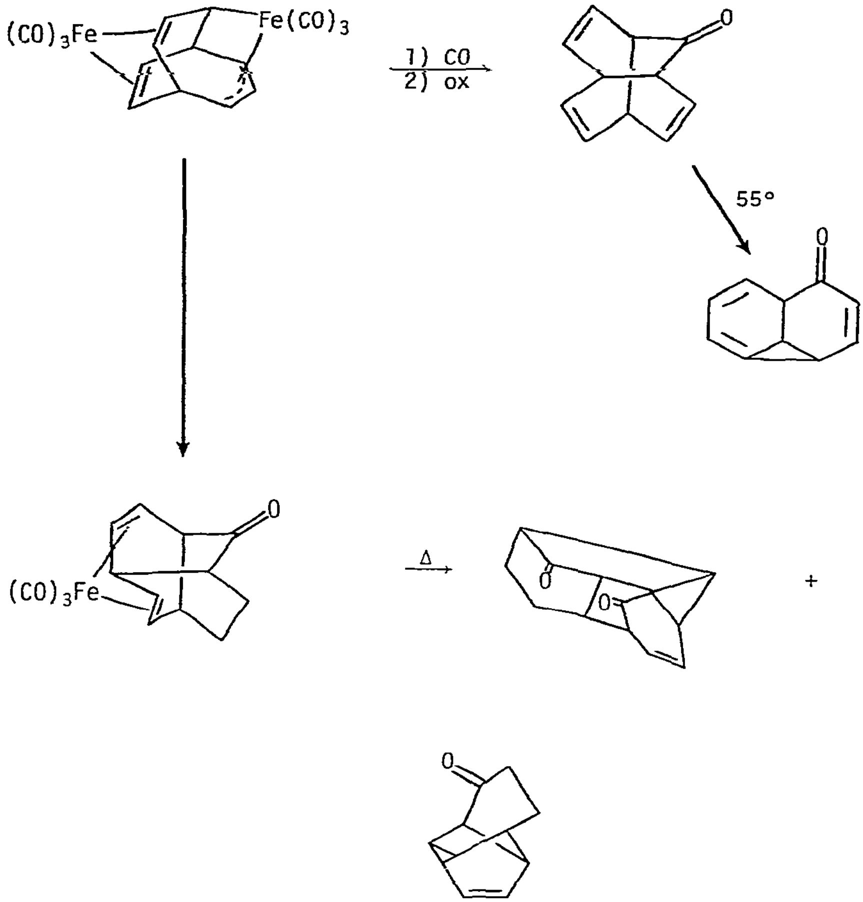


(no yield given)

(103)

bonylated to formamides by treatment with carbon monoxide and iron pentacarbonyl via iron carbamoyl complexes [232]. Acetals were converted to α-diketones by sequential treatment with butyllithium, iron pentacarbonyl and an alkyl iodide (eq. 105) [233]. Transition metal carbonyls as reagents for organic synthesis has been reviewed (81 references) [234], as has synthetic and mechanistic aspects of inorganic insertion reactions [235]. Reviews on carbonylation reactions under mild conditions (53 references) [236], and the chemistry of potassium tetracarbonylhydridoferrate (17 references) [237] have appeared.

Decarbonylation of racemic aldehydes with chiral rhodium complexes was the topic of a thesis [238]. Decarbonylation reactions using transition



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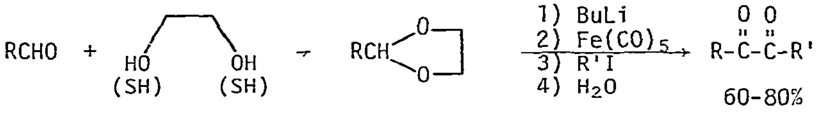


(105)

R = Ph, Et, n-Pr, Me
R' = Me, Et

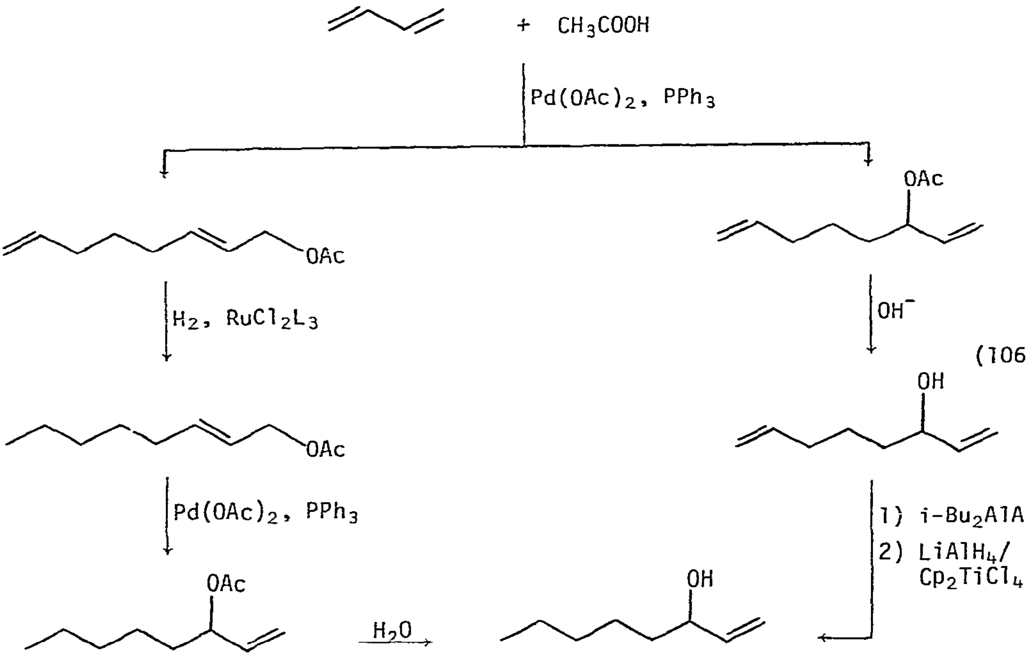
metal compounds has been reviewed (144 references) [239]. The stoichiometri decarbonylation of (S)-(+)-PhCHDCOCl with <u>tris</u>(triphenylphosphine)rhodium(I) gave (S)-(+)-PhCHDCl in 20-27% overall stereospecificity. Rapid halogen scrambling between substrate, product and catalyst was detected by using labelled chloride. The decarbonylation of $C_6D_5CD_2CH_2COCl$ to styrene was also examined. The results favor a mechanism in which a rapid preequilibrium between acyl and alkylrhodium complexes is followed by a concerted cis elimination of rhodium hydride [240]. Substituted cinnamyl cinnamates (styracins) containing hydroxy substituents in the aromatic rings decarboxylated to 1,5-diaryl-1,4-pentadienes upon treatment with platinum and palladium catalysts [241].

## D. Oligomerization

The cationic complex produced by treatment of bis(triphenylphosphine)-pentachlorophenyl(chloro)nickel(II) with silver perchlorate catalyzed the dimerization of ethylene in bromobenzene at 0° and 1 atm. A catalytic amount of added triphenylphosphine enhanced activity [242]. Propylene was dimerized by Ziegler-type catalysts from square planar nickel(II) and palladium(II) complexes, chelating Schiffs base ligands and alkylaluminums in the presence of phosphorus containing ligands [243]. Catalytic systems for the dimerization of propylene based on π-allylnickel halides, alkylaluminum halides and ligands were sensitive to the nature of the ligand. Replacement of phosphine ligands by arsine or stilbene ligands strongly effects the isomerization activity of the complex catalyst, with triphenylarsine and diethylaluminum chloride having the highest isomerization activity and the highest selectivity for 2-methyl-2-pentene [244]. Brominated polystyrene was treated with (tetrakis)triphenylphosphinenickel(0) to form resin bound nickel(II) aryl complexes. Treatment of these resins with boron trifluoride etherate and a catalytic amount of water produced an efficient catalyst for the dimerization of propene. N-hexane was the best solvent although the catalyst was completely insoluble in this solvent [245]. Zerovalent nickel complexes such as $(Ph_3P)_4Ni$, $[(EtO)_3P]_4Ni$, $(Ph_3P)_2Ni(CH_2CH_2)$, and $[(ptoly-O)_3P]_2Ni(CH_2CH_2)$ when treated with sulfuric or trifluoroacetic acid, were effective catalysts for olefin dimerization. The catalytically active species was thought to be a nickel hydride [246]. Polynuclear palladium(II) complexes were implicated as the active catalysts in the oxidative dimerization of styrene to 1,4-diphenylbutadiene. $Pd_3(OAc)_6$ was involved in the rate limiting step [247]. The kinetics of the oxidative dimerization of olefins in the presence of palladium(II) were studied for α-methylstyrene, stryene and 1,1-diphenylethylene [248, 249]. Hydrodehydropolymerization and isomerization polymerization of unsaturated hydrocarbons has been reviewed [250]. Polycyclohexane of molecular weight 2500 was produced by treatment of cyclohexene with a catalyst prepared from chlororhenium pentacarbonyl and ethylaluminum dichloride. The polymer was completely saturated and the rings were retained [251].

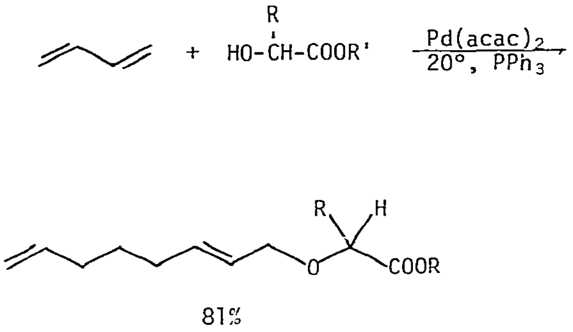
The mechanism of the nickel(0) catalyzed dimerization of 1,3-butadiene was studied by treating cis,cis-1,4-dideuterio-1,3-butadiene with bis-cyclooctadiene nickel, triphenylphosphine in benzene at room temperature. The starting material rapidly isomerized to the trans,trans diene via an allyl isomerization proceeding through σ-complexes [252]. Mixtures of dimethyloctatriene isomers were formed by the tail to tail dimerization of isoprene over phosphine palladium(0) complexes in the presence of $CO_2$. The $CO_2$ assisted in the formation of the catalytically active species [253]. The selective dimerization of butadiene to 4-vinylcyclohexene was effected by catalysts prepared by the metathetical reaction of $NaFe(CO)_3NO$ with metal halides such as $[M(NO)_2X]_2$ where M was Fe and Co, and X was Cl, Br and I [254]. A proper amount of water was found to enhance the catalytic activity of sodium borohydride-amine-bisphosphine nickel dihalide catalyst systems for the dimerization of isoprene. The principle products were linear dienes with n-propylamine, and cyclic ones with pyridine [255]. Butadiene attacked monoolefins such as styrene, propene, methyl methacrylate and $Me_2C$=NMe at the carbon atom of highest absolute value for electron density coefficient in the lowest unoccupied molecular orbital, in the presence of nickel catalysts [256]. Oligomerizations, polymerizations and other diolefi reactions catalyzed by homogeneous nickel complexes have been reviewed (20 references) [257]. A nickel cluster-isonitrile complex $Ni_4(CN\text{-}t\text{-}Bu)_7$, prepared from biscyclooctadiene nickel and t-butylisonitrile was an excellent selective long life catalyst for the dimerization of butadiene to 1,5-cyclooctadiene. The catalyst also cyclotrimerized alkynes, but had a short lifetime. It catalyzed reduction of alkynes to cis alkenes, but did not catalyze reduction of olefins [258].

The combined oligomerization-nucleophilic attack sequence involving



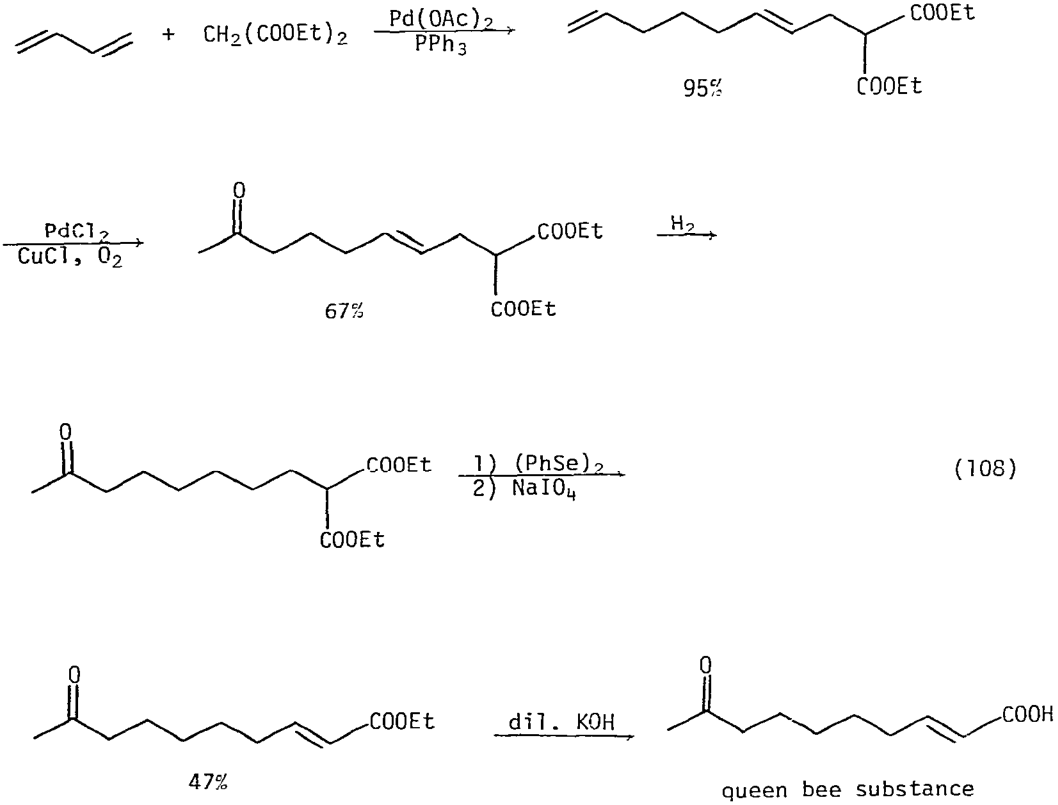
(106)

butadiene has been used to prepare a variety of interesting polyolefinic compounds. Butadiene reacted with acetic acid and palladium acetate in the presence of triphenylphosphine to give ultimately oct-1-en-3-ol (eq. 106) [259]. Butadiene reacted with α-hydroxy acids or esters in the presence of bis(acetylacetonate)palladium(II) and triphenylphosphine to produce unsaturated α-ether esters (eq. 107) [260]. The queen bee sub-



(107)

R = H, Me
R' = n-Bu, Et



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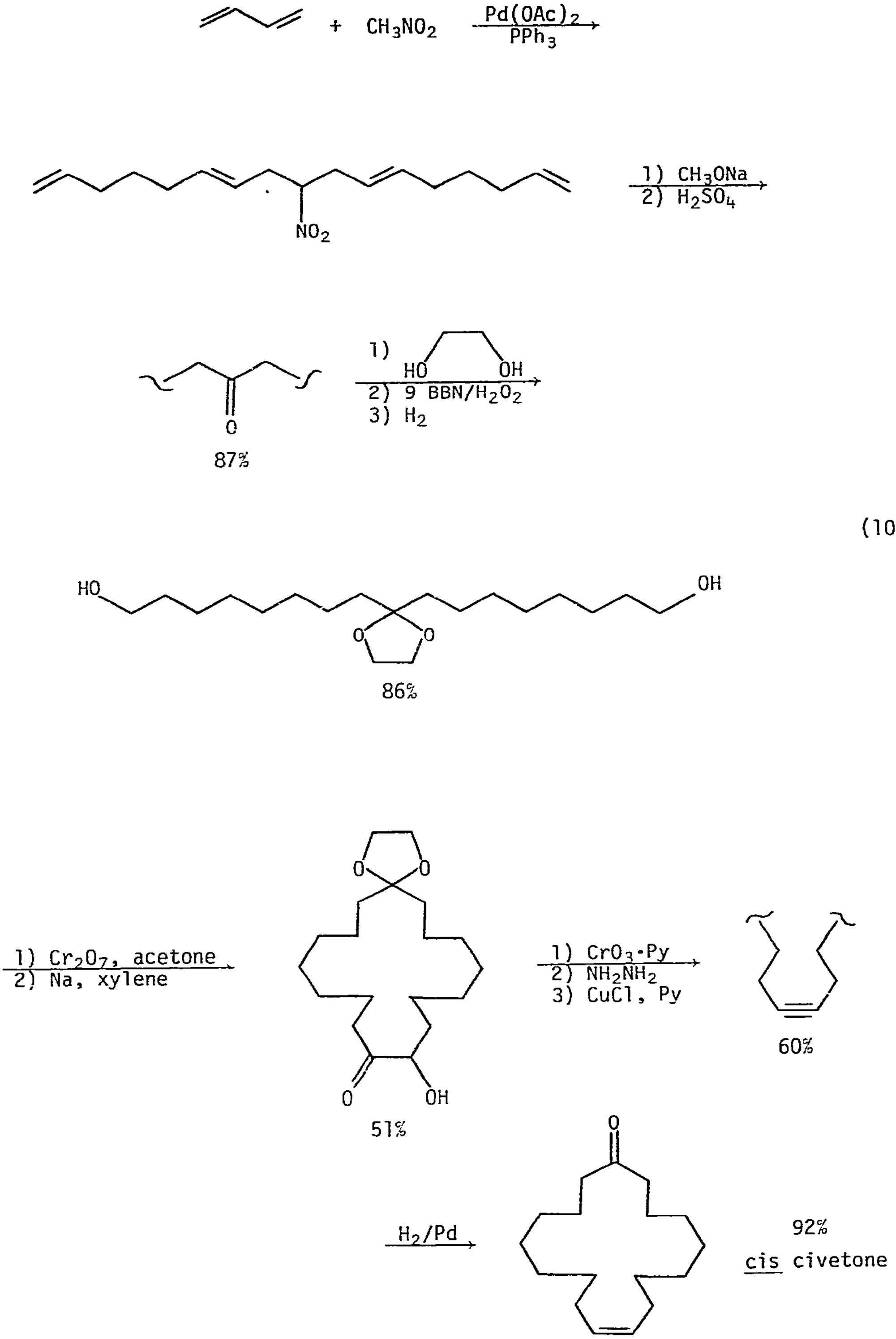
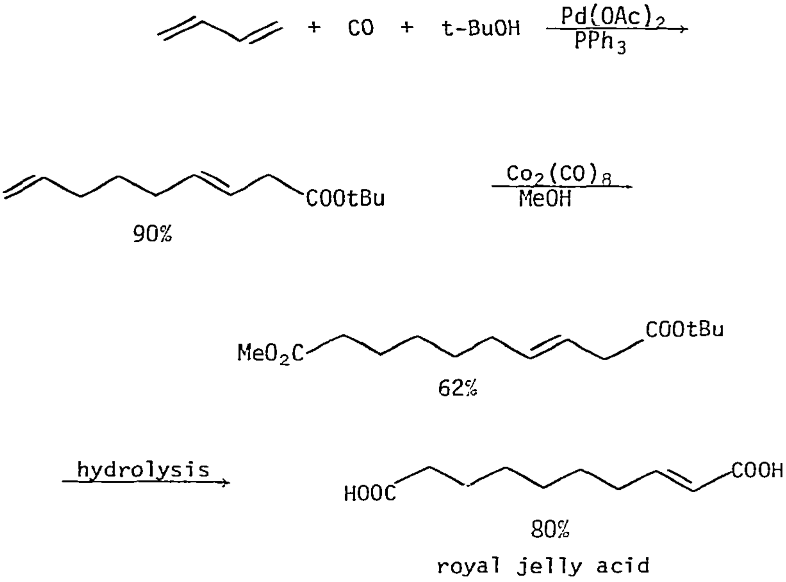

+ $CH_3NO_2$
$Pd(OAc)_2$
$PPh_3$
$NO_2$
1) $CH_3ONa$
2) $H_2SO_4$
O
87%
1) HO OH
2) 9 BBN/$H_2O_2$
3) $H_2$
HO
OH
O O
86%
1) $Cr_2O_7$, acetone
2) Na, xylene
O O
O OH
51%
1) $CrO_3$·Py
2) $NH_2NH_2$
3) CuCl, Py
60%
$H_2$/Pd
O
92%
cis civetone

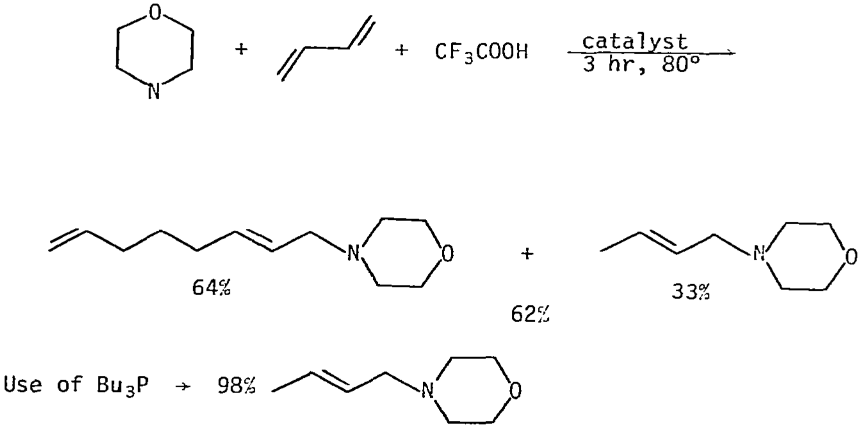
(109)

stance was synthesized by the reaction of butadiene and diethyl malonate in the presence of palladium acetate and triphenylphosphine (eq. 108) [261]. cis Civetone was prepared from nitromethane, butadiene and palladium acetate (eq. 109) [262], while royal jelly acid was prepared from butadiene, carbon monoxide and t-butanol in the presence of palladium acetate and triphenylphosphine (eq. 110) [263].



(110)

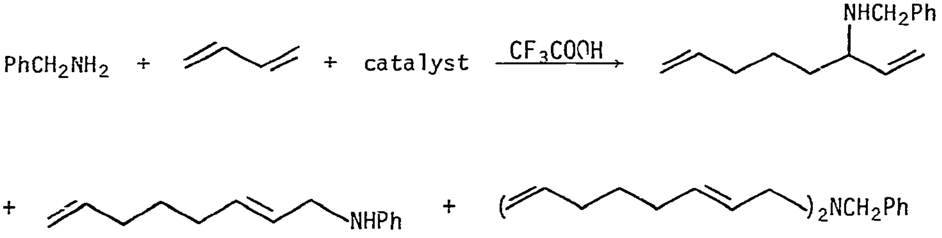
Ni(acac) + COD + AlEt$_3$ + (ArO)$_3$P → catalyst



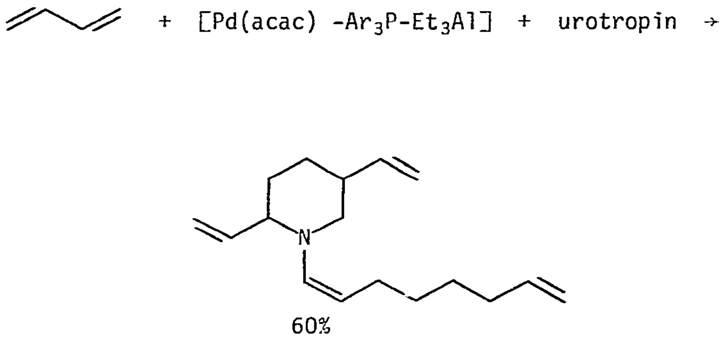
(111)

Reduced nickel species catalyzed the reaction of butadiene with morpholine to give mixtures of morpholines substituted at nitrogen with butene or octadiene groups (eq. 111) [264]. Primary amines reacted with butadiene and reduced palladium species to give octadienyl substituted amines (eq. 112) [265]. A similar catalyst system produced 1,2,3-trisubstituted piperdines from butadiene and urotropine (eq. 113) [266].

$$Pd(acac) + R_3P + Et_3Al \rightarrow \text{catalyst}$$



(112)

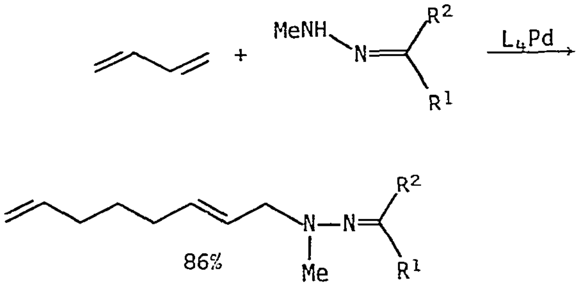


(113)

Hydrazones react at nitrogen with butadiene in the presence of a palladium(0) catalyst, while related nickel catalysts cause reaction at the hydrazone carbon (eq. 114) [267, 268]. The product distribution of the mixed oligomerization of N-benzylidenepropylamine with butadiene in the presence of morpholine was dependent on morpholine concentration [269]. The polymerization and copolymerization of butadiene has been reviewed [270].

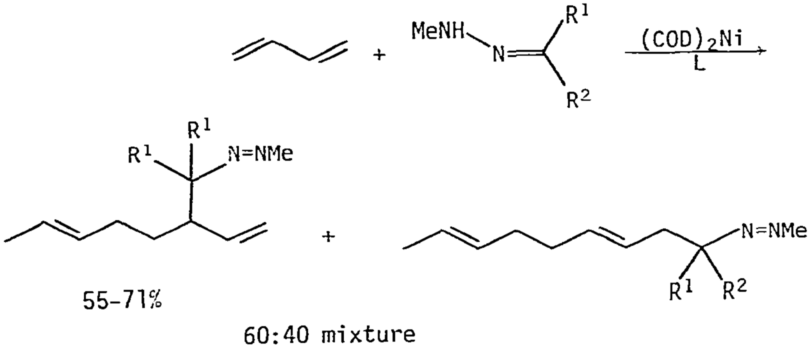
Metal catalyzed cyclotrimerization of alkynes has been developed into a very useful approach to polycyclic materials. The full paper on preparation of benzocyclobutanes, indanes and tetralines via cobalt catalyzed cyclooligomerization of $\alpha,\omega$-diynes with substituted acetylenes has appeared (eq. 115) [271]. An absolutely elegant intramolecular version of this chemistry was used to synthesize the steroid skeleton (eq. 116) [272].

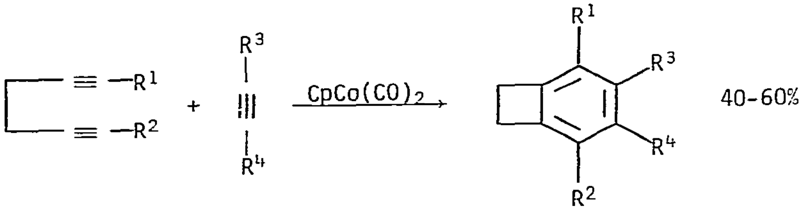
Transition metal catalyzed acetylene cyclizations in organic synthesis has been reviewed [273].



$R^1$ = H, Me
$R^2$ = Me, Et

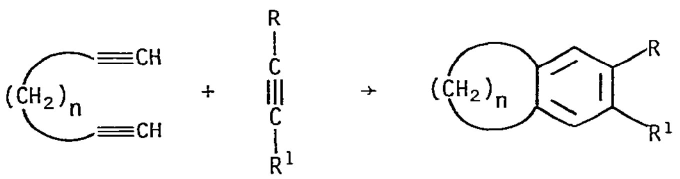
(114)



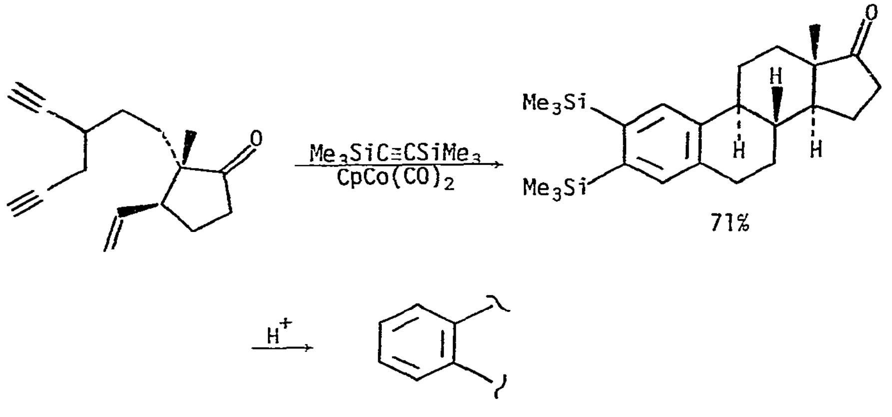


($R^3$ or $R^4$ must be $-SiMe_3$)

(115)



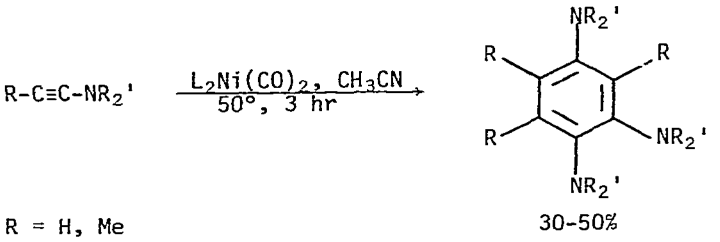
n = 3-5
R's = $SiMe_3$, COOMe, H, Ph, hexyl



(116)

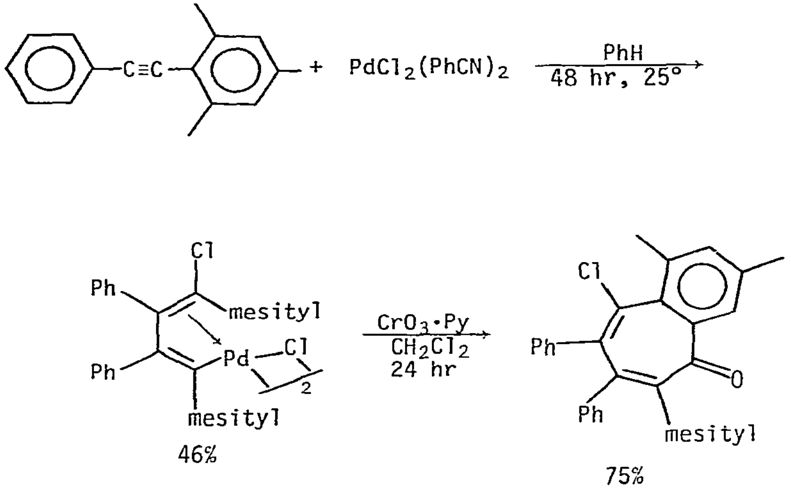
estra-1,3,5(10)-trien-17-one

Ynamines underwent cyclotrimerization using a nickel catalyst to give 1,3,4-triaminobenzenes (eq. 117) [274]. A catalyst prepared by treatment of nickel bromide with mesitylmagnesium bromide catalyzed cyclotrimerization of 3-hexyne to hexaethylbenzene via a tetraethylcyclobutadienyl nickel bromide complex [275]. (S)-3-Methyl-1-pentyne dimerized to (E)-(3S,7S)-3,7-dimethyl-4-methylenenon-5-ene or 1,3,5-tris[(S)-1-methylpropyl]benzene when treated with triisobutylaluminum-titanium tetrachloride, depending on conditions. No racemization was observed [276]. Phenylmesitylacetylene dimerized upon treatment with palladium chloride to give a stable vinyl-palladium complex which, upon oxidation with chromium trioxide-pyridine, gave a cyclic ketone (eq. 118) [277].



(117)

Diynes cyclized with alkynes in the presence of <u>tris</u>(triphenylphosphine) rhodium(I) to form complex polycyclic materials <u>via</u> an intermediate metallacycle (rhodiocyclopentadiene) eq. 119 [278] and eq. 120 [279]. Chromium carbene complexes of the type $(CO)_5Cr{=}CPhR$ reacted with alkynes to give chromium coordinated β-naphthols. The naphthol skeleton was assembled in the coordination sphere of the metal (eq. 121) [280].



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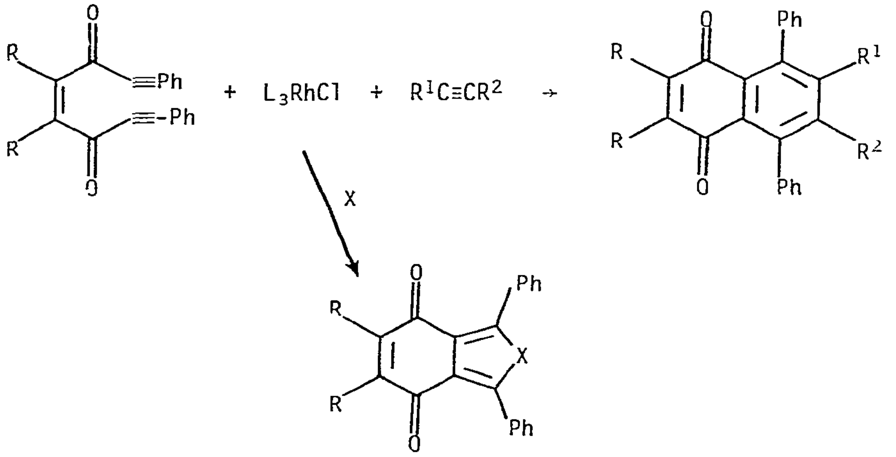
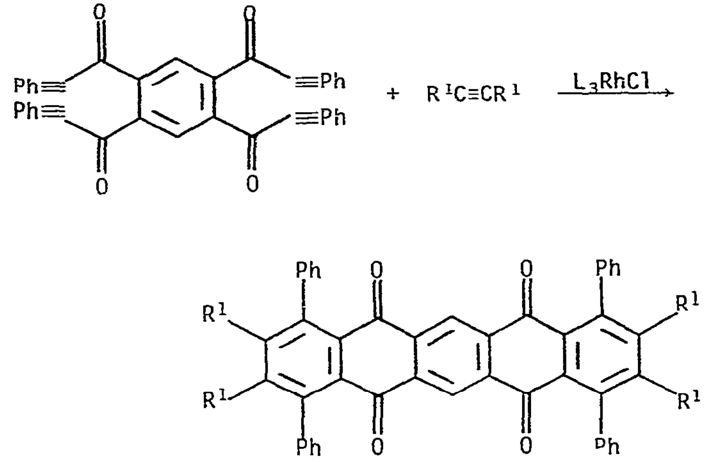


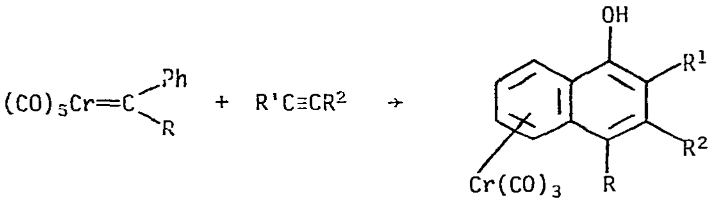
(119)

R = H, Me, Et

The effect of phosphine ligands on the dimerization of 1-alkynes by rhodium(I) complexes was studied in an attempt to alter linear-to-branched product distributions. No simple correlation between steric bulk of the phosphine and the total yields or selectivity of the reaction was discerned [281]. Treatment of terminal alkynes with triisobutylaluminum and nickel, iron or manganese salts led to alkylation-dimerization (eq. 122) [282]. Cyclotrimerization of isoprene with hexafluoro-2-butyne using $\eta^5$-indenyl-rhodium(bisethylene) complex as a catalyst gave $\eta^5$-indenyl- 5-isopropyl-1,2,3,4-tetrakis(trifluoromethyl)-1,3-hexadiene rhodium [283]. Styrene reacted with alkynes in the presence of palladium chloride and lithium chloride to give codimers which are 1-halo-1,3-butadienes [284]. Vinyl-cyclopropane ring opened and oligomerized when treated with phosphine



(120)

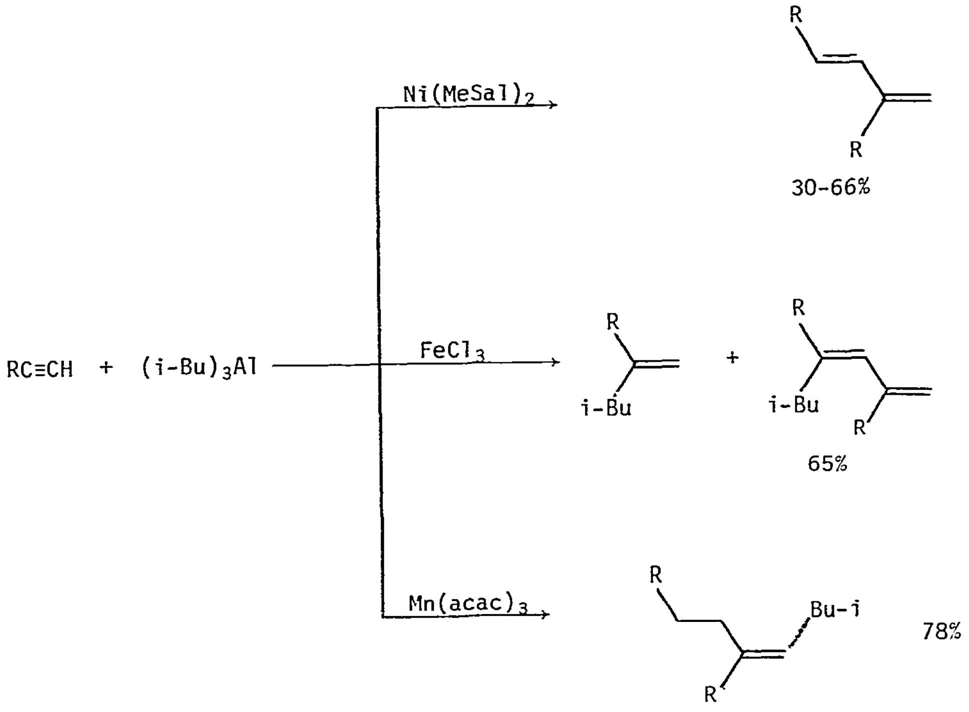


7-68%

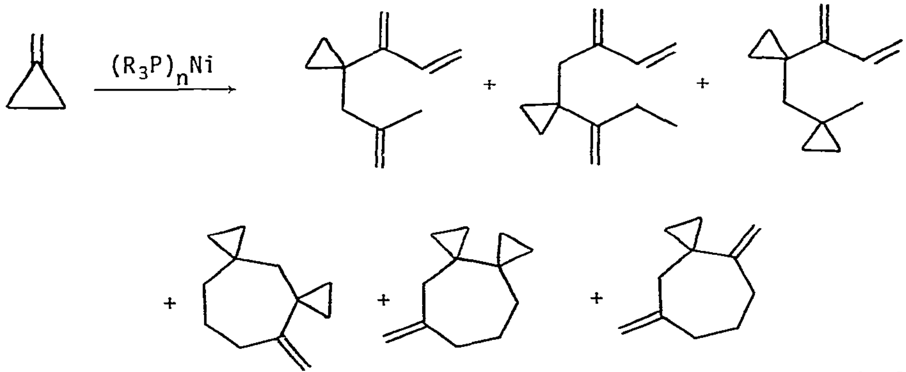
(121)

R = Ph, OMe
$R^1$ = Et, Me, Pr, Bu, Ph
$R^2$ = H, Me, Et, Ph, COOEt

nickel(0) complexes to yield a mixture of products, the composition of which depended on the phosphine present (eq. 123) [285]. 1,2,2-Trimethylcyclopropene was converted to 2,3,6,7-tetramethyloct-4-yne-2,6-diene by treatment with butyllithium and cuprous chloride [286]. *p*-Dibromobenzene was polymerized to poly *p*-phenyl by treatment with magnesium metal and *bis*-phosphine nickel dihalide catalysts in 90% yield. 4,4'-Dibromodiphenyl ether polymerized in 50% yield under the same conditions [287]. *trans*, *trans*-1,5,9,13-Tetradecatetraene reacted with allyl chloride, carbon monoxide and a nickel(0) catalyst to give a compound with three cyclopentanone rings with high selectivity and stereoselectivity (eq. 124) [288]. Nucleophilic catalysis by transition metal complexes including dimerization and oligomerization of ethyl acrylate, acrylonitrile and crotononitrile has been reviewed [289].

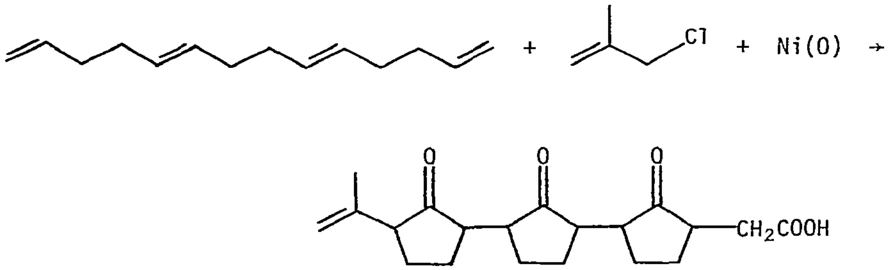


(122)



(123)

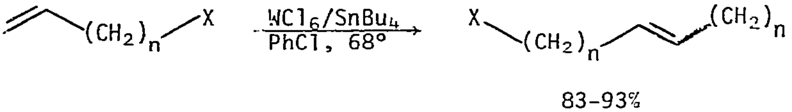
90% yield of mixture



(124)

## E. Rearrangements

The olefin metathesis reaction was the topic of an international symposium in September, 1977. The proceedings of this symposium have now been published [290]. Metathesis catalysts prepared from tungsten hexachloride and metal alkyls such as tetrabutyltin, diethyltin, triethyl aluminum and butyllithium were studied in their reactions with 2-heptene. High yield selectivity was achieved in the tungsten hexachloride-tetrabutylti case by suppressing Friedel Crafts reactions with benzene solvent by adding ether, ethanol or esters [291]. A catalyst prepared from tungsten hexachloride and lithium aluminum hydride (1:4) catalyzed the disproportionation of 1-pentene, 2-pentene and Z-2-octene, as well as the polymerization of Z-cyclooctene and Z-cyclononene [292]. The tungsten hexachloride-tetrabutyltin catalyst was used to disproportionate S-6-methyl-2-octene. The product was (+)-(3S,10S)-3,10-dimethyl-6-dodecene. 1-Pentene did not react [293]. Methyloleate was subjected to metathesis using tungsten tetrachloride and cocatalysts such as tetrabutyltin, tetraethyltin or triethylaluminum [294]. ω-Olefinic esters were metathesized using the tungsten hexachloride-tetrabutyltin catalyst system (eq. 125)[295]. A variety of linear and chiral alkenes were subjected to the metathesis reaction with this same catalyst. The results showed that the metathesis of chiral 2-alkenes occurred with retention of configuration, and that the activity and selectivity of the catalyst depended on the 2-alkene [296]. Metathesis of trans-3-heptene in the presence of (1,5-cyclooctadiene)tungsten tetracarbonyl and isobutylaluminum dichloride produced trans-3-hexene and trans-4-octene [297]. Bimetallic tungsten-tin or tungsten-germanium complexes such as $\pi$-$C_5H_5W(CO)_3$-$MR_3$ (M = Ge, Sn; R = Me, Ph) upon activation by addition of oxygen and isopropylaluminum dichloride gave highly active catalysts for homogeneous metathesis of linear internal olefins [298]. Pyridine pentacarbonyl molybdenum upon activation by treatment with methyl aluminum dichloride promoted metathesis of terminal olefins via metal carbene complexes [299]. Metathesis of cyclic and acyclic olefins by molybdenum catalysts were chain reactions propagated by the union of an olefin with a metal carbene [300].

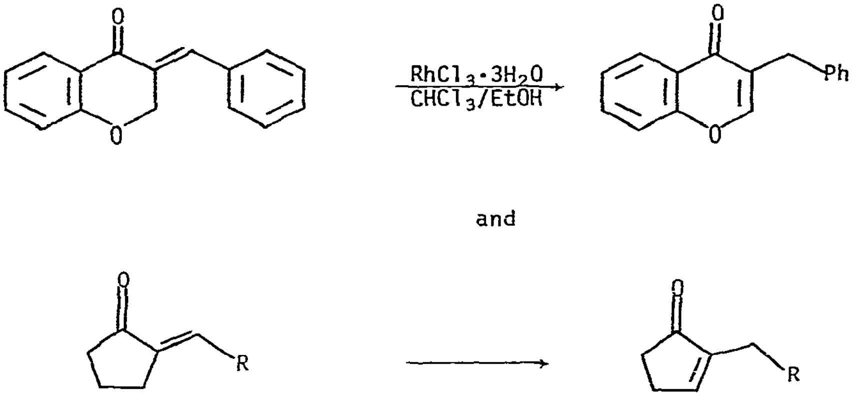


(125)

n = 2, 6, 8 X = COOMe
n = 8 X = $CH_2OAc$

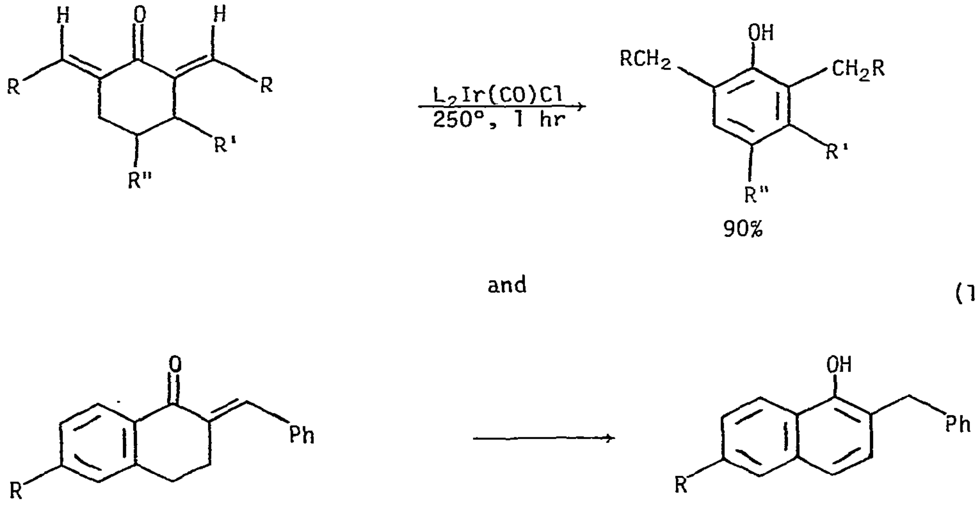
Fulvalene was metathesized with ethylene using (fulvalene)(dicyclopentadiene)(bis titanium)dihydride as a catalyst to produce ethane and butadiene [301]. The conductance of the solution resulting from adding aluminum trichloride to a solution of $W(CO)_3Cl_2(AsPh_3)_2$ in dichloromethane was much greater than expected, and was attributed to the formation of the catalytically active species [302]. Olefin metathesis of cis-2-pentene by zero valent tungsten catalysts both in the homogeneous phase or supported on inorganic oxides were compared. With both systems the primary function of the cocatalyst was to decrease electron density on tungsten. The catalyst on a solid support had a steric effect on the reaction [303]. $\omega$-Unsaturated fatty acids and esters were metathesized to ethylene and long chain internally unsaturated $\alpha,\omega$-diesters using rhenium heptoxide on alumina plus a small amount of tetramethyltin as a heterogeneous catalyst [304]. Alkynes were metathesized by a catalyst prepared by photolysis of molybdenum hexacarbonyl in the presence of chlorophenol. The reaction was thought to occur by a two-step mechanism involving activation of molybdenum hexacarbonyl by the alkyne, and subsequent catalysis by the phenol. Heterogenation of the phenol and the transition metal separately on silica gel supported the two-stage mechanism [305]. The metathesis of cis-2-pentene initiated by $Ph_2CW(CO)_5$ was highly stereoselective, probably because of steric interactions in the four-membered ring transition state [306]. The stereochemistry of the metathesis of cis-2-pentene by zero valent tungsten catalysts showed that four different types of coordination of olefin to the metallocarbene were involved, and all had about the same rate. For internal olefins which are nearly symmetrical, steric factors dominate the initiation. Stereoselectivity of cis and trans olefins was explained on the basis of the steric bulk of the ligands coordinated to tungsten and/or the configuration of the metallocyclobutanes [307]. The olefin metathesis reaction has been reviewed several times [308] (91 references), [309], [310] (60 references). Secondary alkyamines disproportionated to primary and tertiary amines in the presence of triphenylphosphine and a variety of transition metal complexes of Rh, Ru, Ir or Ni [311].

Several new olefin isomerization catalysts have been developed and put to use synthetically. Catalytic isomerization of 1-pentene to cis- and trans-2-pentene by $H_2Ru_4(CO)_{13}$ and $HRu_3(CO)_9C_6H_9$ cluster compounds in toluene involves metal hydride addition-elimination sequences and $\sigma$-alkyl-intermediates, although some suggestion of $\pi$-allyl type intermediates was also observed [312]. Normally difficult or impossible exocyclic to endocyclic double bond rearrangements were promoted by rhodium trichloride trihydrate. However, treatment of ergosterol under these conditions gave a complex mixture (eq. 126)[313]. Cycloalkenones having exocyclic double bonds underwent isomerization and disproportionation to aromatic systems when treated with chlorocarbonylbis(triphenylphosphine)iridium (eq. 172) [314]. The reagent generated from bis-cyclopentadienyltitanium dichloride



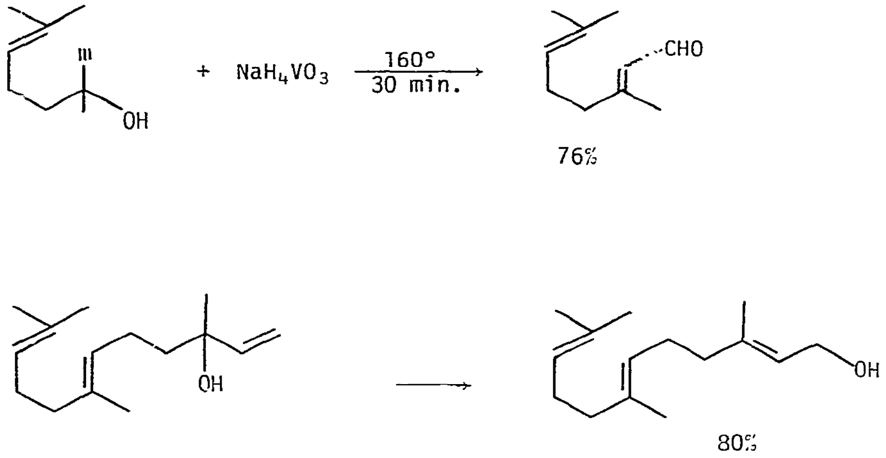
(126)

and lithium aluminum hydride both isomerized and hydrometallated 1-octene giving an isolable titanium complex $Cp_2Ti(AlH_3)(C_6H_{13}CH{=}CH_2)$ [315, 316]. Allylbenzene was rearranged to trans-β-methylstyrene by hydridocobalt carbonyl. Using deuterated substrates, a [1,3]sigmatropic shift was ruled out, while results were consistent with a 1,2-addition-elimination mechanism [317]. α Olefins isomerized when treated with $Co(N_2)(PPh_3)_3$ and $Co(olefin)PPh_3$ [318]. N-allylsulfonamides were rearranged to N-vinylsulfonamides by treatment with iron pentacarbonyl with irradiation. The product was formed in good yield, but was difficult to purify and was used in situ [319]. Allyl alcohols were isomerized to aldehydes in the presence of tris(triphenylphosphine)rhodium carbonyl hydride in



(127)

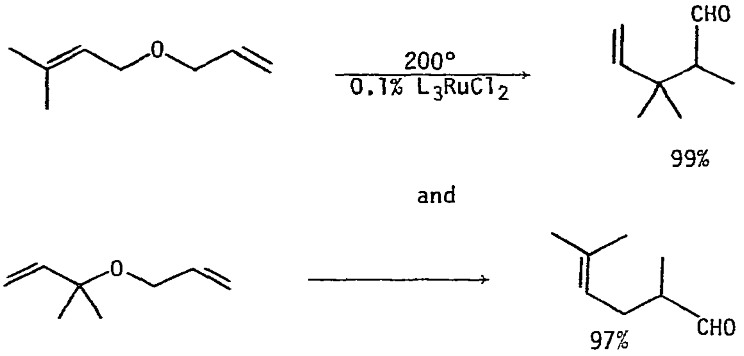
trifluoroacetic acid. With a chiral diphosphine present low optical yields of chiral aldehyde were obtained [320]. Vanadate esters, tungstates, molybdates or rhenates catalyzed the isomerization of α-acetylenic alcohols to carbonyl compounds and α-ethylenic alcohols to allylic alcohols. A large number of cases were studied. The vanadate esters were particularly efficient (eq. 128) [321].



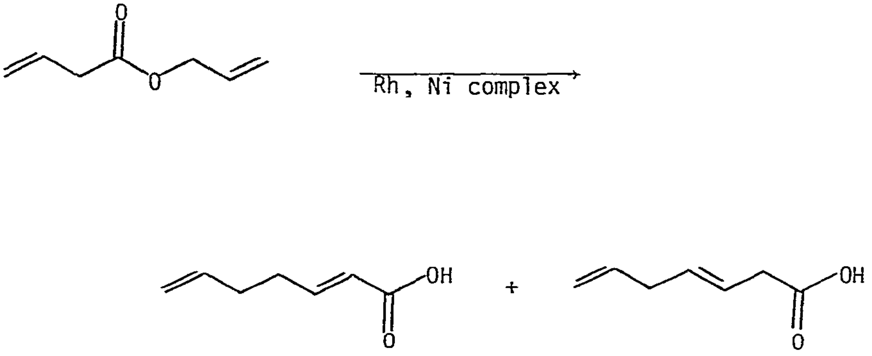
(128)

Unsymmetrical diallylethers rearranged to β,γ-unsaturated aldehydes and ketones via regiospecific rearrangement to allylvinyl ethers followed by Claisen rearrangement with the presence of 0.1% of $(Ph_3P)_3RuCl_2$ for 1-4 hr at 200°. The reaction is retarded by olefin substitution (eq. 129) [322]. Diallylesters rearranged to α,β-ω and β,γ-ω dienoic acids when treated with nickel or rhodium complexes with phosphine ligands (eq. 130) [323]. A variety of 4,4'-disubstituted stilbene oxides rearranged to the corresponding benzylphenylketones in 59-90% by treatment with chlorotris-triarylphosphinerhodium at 159-210°[325]. Epidioxides of α-pellandrene underwent Fe(II) promoted decomposition with little of the expected intramolecular 1,5-hydride abstraction observed in the similar decomposition of levopimaric acid epidioxide epoxide (eq. 131) [325]. Substituted 1,4-arene oxides rearranged to cyclohexadienes or cyclopentadienes depending on the solvent (eq. 132) [326]. 1,2-Arene oxides underwent deoxygenation and ring cleavage when treated with $[Rh(CO)_2Cl]_2$ [327]. dl-Muscone was synthesized by the ferric chloride cleavage of a 1,2(bis)(trimethylsiloxyl)-cyclopropane followed by alkylation of the thus formed enol acetate by lithium dimethylcuprate (eq. 133) [328].

The photoassisted valence isomerization of norboradiene to quadricyclene in the presence of copper(I) salts suggested that the photoactive species is a 1:1 π-complex of diene and copper and that photoreaction originates via the population of an olefin metal charge transfer state of the complex

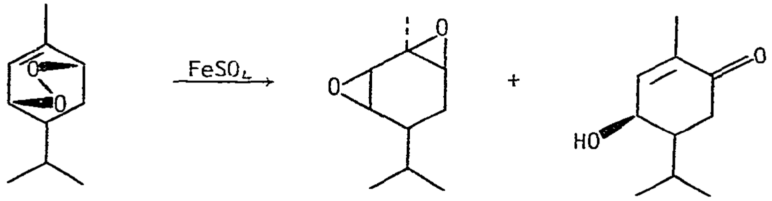


(129)



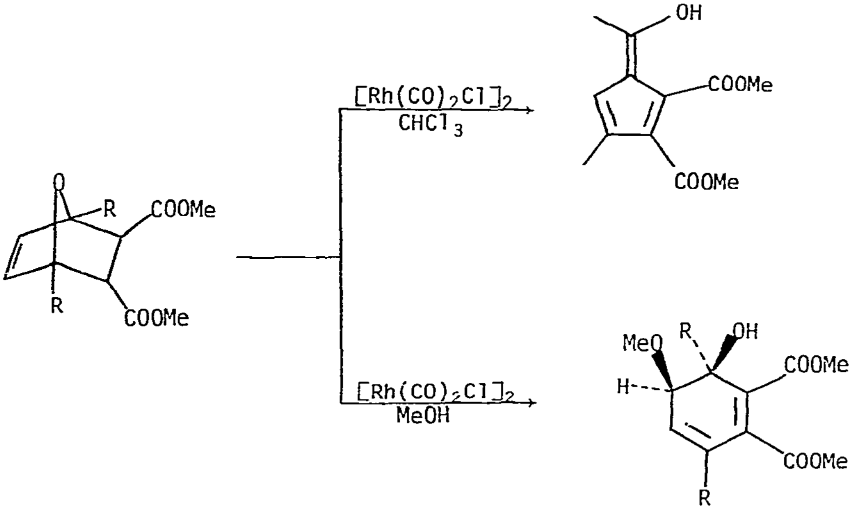
(130)

66-73% mixtures

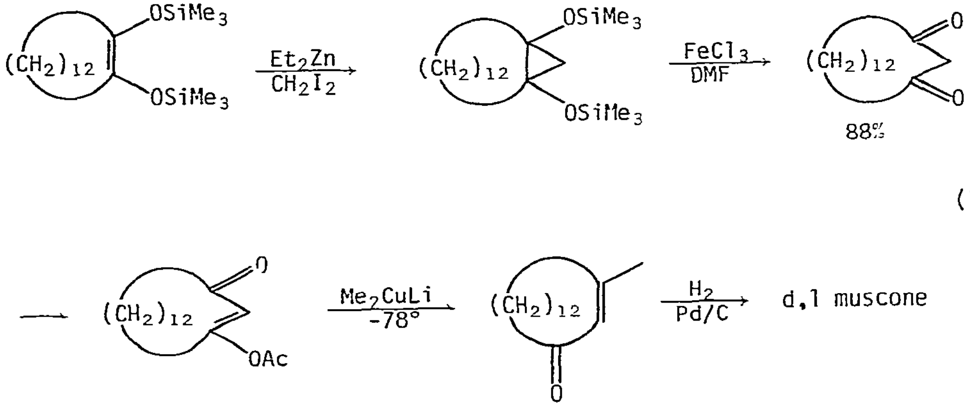


(131)

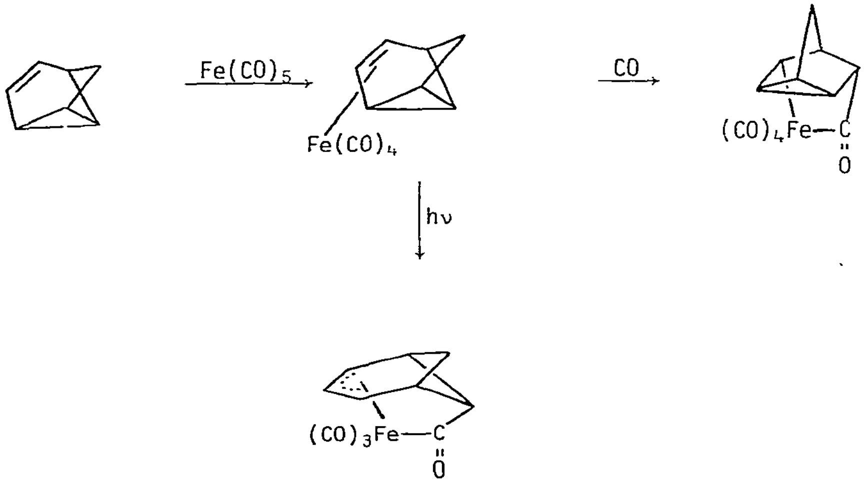
[329]. The quantum yields of this reaction were best with the copper complexes $[PPh_3Cu]BH_4$ and $[MePPh_2Cu]BH_4$ [330]. Strained ring carbon-carbon single bonds underwent rearrangement upon treatment with iron pentacarbonyl to give rearranged hydrocarbons complexed to iron (eq. 134) [331]. Racemic bicyclo[1.1.0]butane derivatives were kinetically resolved in up to 30% enantiomeric excess by treatment with a rhodium(I)(DIOP)complex which


[Rh(CO)$_2$Cl]$_2$
CHCl$_3$
[Rh(CO)$_2$Cl]$_2$
MeOH
R
COOMe
OH
MeO
H

(132)


(CH$_2$)$_{12}$
OSiMe$_3$
Et$_2$Zn
CH$_2$I$_2$
FeCl$_3$
DMF
88%
OAc
Me$_2$CuLi
-78°
H$_2$
Pd/C
d,l muscone

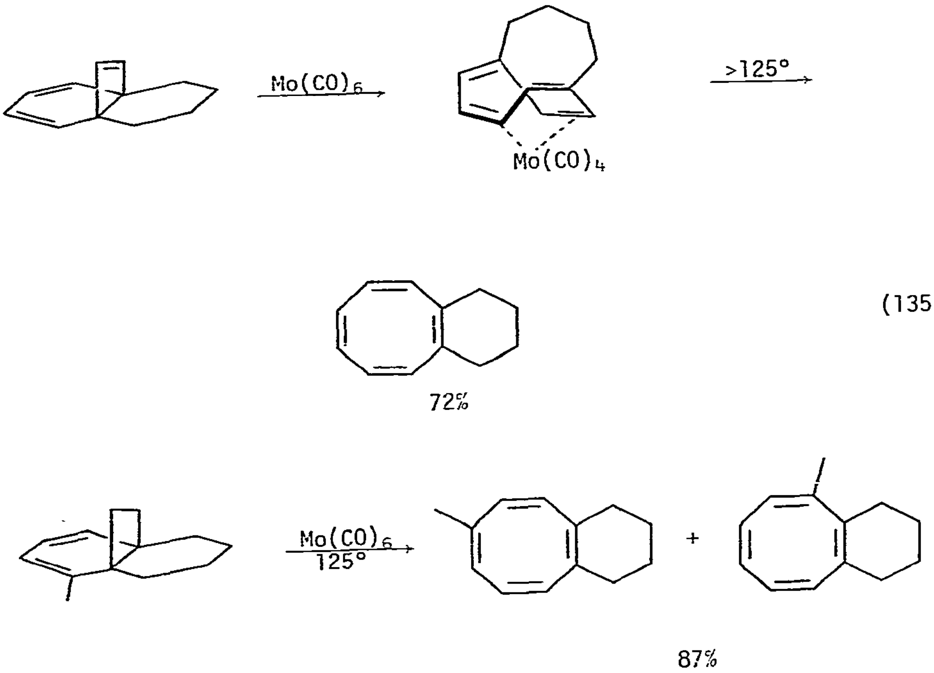
(133)


Fe(CO)$_5$
Fe(CO)$_4$
CO
(CO)$_4$Fe—C
O
hν
(CO)$_3$Fe—C
O

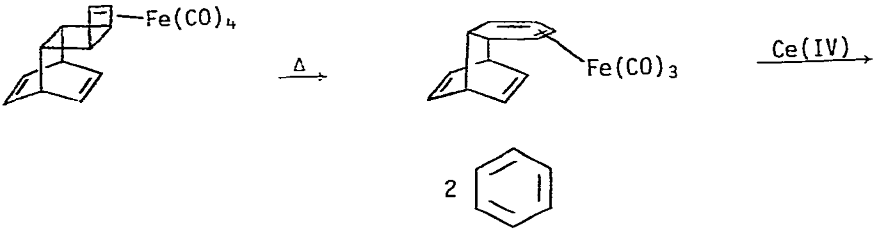
(134)

selectively isomerized one enantiomer to a substituted butadiene, while leaving the other enantiomer intact [332]. Vinylcyclopropanes were epimerized and ring opened to 1,3- and 1,4-dienes by treatment with $[Rh(CO)_2Cl]_2$ [333].

[4.4.2]Propellanes rearranged upon treatment with molybdenum hexacarbonyl at 125° to initially form a complex, which then upon heating released rearranged material (eq. 135) [334]. For the rearrangement to occur, 1,3-cyclohexadiene had to be laterally fused to a strained four-membered ring. Chromium hexacarbonyl and tungsten hexacarbonyl form stable complexes which do not rearrange. Deuterium isotope effects and kinetics of this reaction have been examined [335]. A Diels-Alder dimer of benzene, normally unstable, was stabilized by coordination to iron (eq. 135) [336]. Camphene rearranged to isobornyl acetate without a methyl shift, in the presence of copper(II) chloride [337].



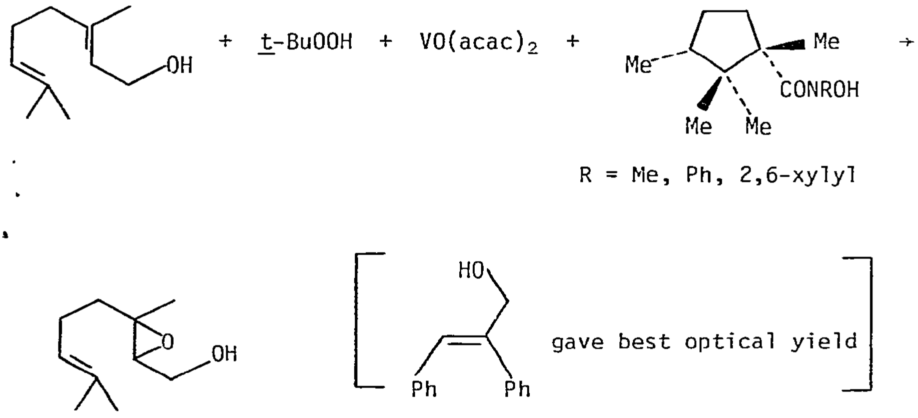
(135)



(136)

## III. Oxidation

Electrophilic epoxidation of propylene by $PhMe_2COOH$ and the epoxidation of cyclohexene by t-butylhydroperoxide were catalyzed by $Mo_2O_5(Me_2NCS_2)_2$ as a heterogeneous catalyst. The reactivity of a variety of olefins towards this system was similar to that with peracetic acid [338]. Vanadium complexes catalyzed the epoxidation of allyl alcohol by organic hydroperoxides such as $Me_3CCOOH$, $PhCHMeOOH$ and $PhCMe_2COOH$. Vanadium was much more active than similar compounds of molybdenum, tungsten or titanium, and the initial oxidation state of the vanadium compound was unimportant [339]. Allylic alcohols were epoxidized by t-butylhydroperoxide in high yield and up to 50% enantiomeric excess using vanadium catalysts with chiral hydroxamic acids as ligands (eq. 137) [340]. Geraniol and nerol were epoxidized in 30-50% yield and 10-30% optical purity by $PhCMe_2OOH$ and the chiral molybdenum complex (acetylacetonato)[(-)-N-alkylephedrine]dioxomolybdenum (eq. 138) [341]. By carrying out molybdenum and vanadium catalyzed



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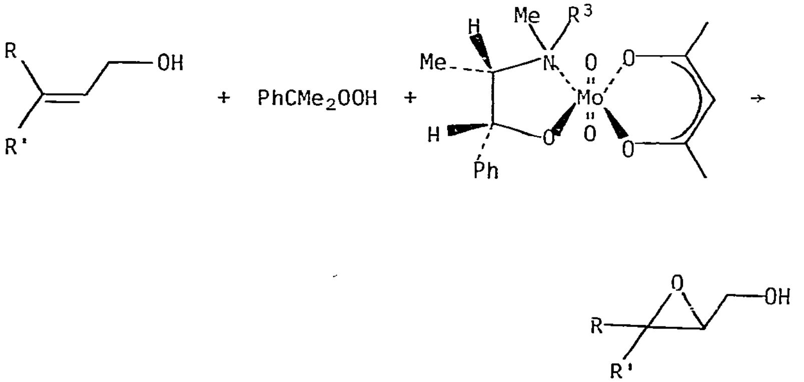
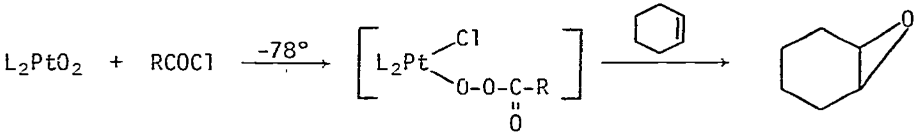


(138)

epoxidation of olefins by hydroperoxides in $H_2{}^{18}O$, it was demonstrated that intact hydroperoxide was present in the active complex [342]. The epoxidation of olefins by hydroperoxides using molybdenum(V) complexes with ligands such as ethylene glycol, lactic acid and amygdalic acid in homogeneous systems, as well as heterogenized catalysts prepared by ion exchange reactions of $Na_2[Mo_2O_4(OX)_2(H_2O)_2]\cdot 3H_2O$ was studied [343]. Oxovanadium(IV) compounds were incorporated on a sulfonic acid ion exchange resin and used as catalyst for the reaction of t-butylhydroperoxide with olefins. This epoxidation was much more selective and went in higher yields than did comparable homogeneous epoxidation reactions. Kinetic studies indicated that the mechanism of the heterogeneous reaction was similar to that of the homogeneous case [344]. The same vanadium compounds were incorporated into several insoluble polymers containing ligand groups such as acetylacetonate, ethylendiamine and pyridine, and were used to catalyze the epoxidation of cyclohexene by t-butylhydroperoxide [345]. The kinetics of the sodium molybdate catalyzed epoxidation of allylalcohol by hydrogen peroxide was zero order with respect to hydrogen peroxide. The epoxidation was considered to be polar in nature [346]. In molydenum catalyzed epoxidatic mixtures containing hydrogen peroxide and hydrochloric acid, $Mo(O_2)(Cl)_2(OH)_2$ and $Mo(O_2)_2(OH)_2$ were present. The monoperoxide complex of molybdenum was thought to be the epoxidizing agent [347]. Acid chlorides reacted with $L_2PtO_2$ to give an intermediate peroxyacid complex which epoxidized norbornene and cyclohexene in moderate yields (eq. 139) [348].



(139)

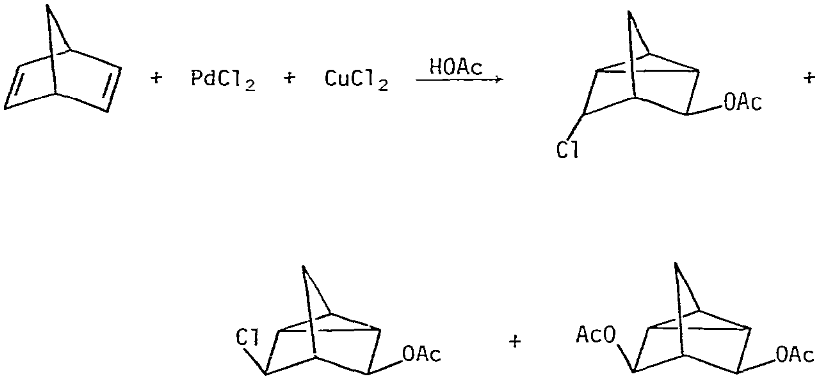
Stereochemical and substituent effects in the hydroxylation of $\Delta^4$-steroic by osmium tetroxide were investigated. It was concluded that the ring A conformation of the reactant was the primary factor determining the stereoselectivity of the reaction and that other substituents merely anchored the ring A conformation (Table 1) [349].

The stereochemistry of the hydroxypalladation step in the Wacker process was shown to be trans by the stereospecific formation of threo-1,2-dideuterio-2-chloroethanol from the Wacker reaction of trans-1,2-dideuterioethane [350]. Studies on the development of new homogeneous catalysts for ethylene oxidation to acetaldehyde have been reviewed (56 references) [351]. A difference in mechanisms was found in the catalytic oxidation of ethylene by palladium(II) in aqueous solution (Wacker conditions) and the same reaction in acetic acid solutions. In acetic acid, an equilibration between 2- and 1-acetoxyethylpalladium(II) prior to decomposi-

Table 1. Hydroxylation of $\Delta^4$-Steroids by $OsO_4$

| Olefin | 4α,5α diol, % | 4β,5β diol, % |
|---|---|---|
| $\Delta^4$ | 24 | 76 |
| 3α-OAc, $\Delta^4$ | 2 | 98 |
| 3β-OAc, $\Delta^4$ | 87 | 13 |
| 19-Nor, $\Delta^4$ | 11 | 89 |
| 3α-OAc, 19-Nor, $\Delta^4$ | | >99 |
| 3β-OAc, 19-Nor, $\Delta^4$ | 77 | 23 |
| 2α-OAc, $\Delta^4$ | 62 | 38 |
| 2β-OAc, $\Delta^4$ | 8 | 92 |

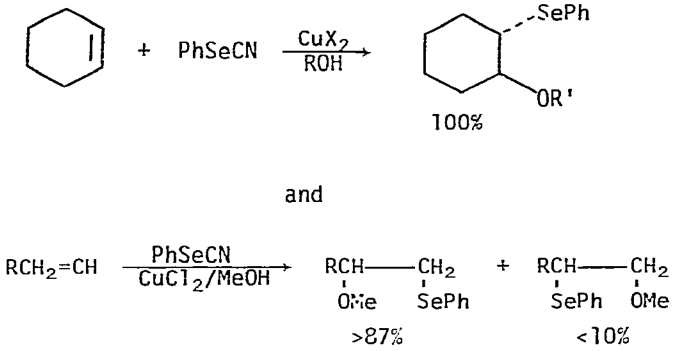
tion to vinyl acetate was proposed, while under Wacker conditions concerted CO formation-hydride shift sequences occur [352]. The oxidation of cyclohexene, cyclooctene, 3,3-dimethyl-1-butene, 1-hexene and cis-2-hexene by oxygen catalyzed by palladium acetate in acetic acid solution was investigated in detail [353]. The oxidation of norbornadiene by palladium chloride-copper(II) chloride in acetic acid gives several products, making the mechanism of the reaction unclear (eq. 140) [354]. Organic synthesis using palladium complexes, including the oxidation reactions of olefins and aromatic compounds has been reviewed (187 references) [355].



(140)

The oxidation of olefins by chromyl chloride to produce epoxides, chlorohydrins and vicinal dichlorides via a cis addition process was examined. The mechanism involved formation of organometallic intermediates containing chromium-carbon bonds [356]. α-Iodoketones were produced by the oxidation of olefins such as 1-hexene, styrene and cyclohexene by a silver chromate-iodine reagent [357]. β-Oxyselenides were produced by the reaction of olefins with aryl or alkyl selenocyanates in the presence of copper or nickel(II) chloride in methanol (eq. 141) [358]. The oxidation of (+)-α-pinene by manganese triacetate produced α-terpineol acetate, cis-pin-3-en-3-ol acetate and myrtenol acetate, as well as other materials [359].

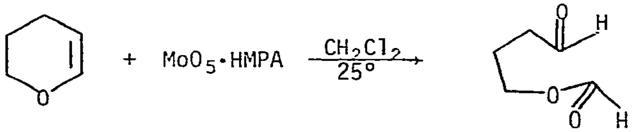
Oxidation of (+)-3-carene by manganese triacetate gave nine products [360]. The application of manganese triacetate as an oxidizing reagent for organic compounds has been reviewed (61 references) [361].



(141)

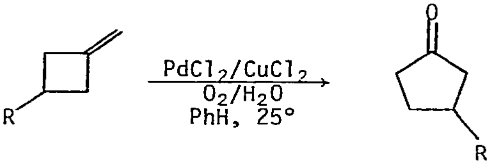
1-Octene was catalytically autoxidized to 2-octanone by treatment with tris(triphenylphosphine)rhodium chloride with oxygen at 1 atm and 25°. Triphenylphosphine was necessary, and this oxidized to triphenylphosphine oxide [362]. The same rhodium complex was used to catalyze the oxidation of cyclohexene to 2-cyclohexen-1-yl hydroperoxide in essentially quantitative yield. Triphenylphosphine and phenols inhibited the reaction [363]. Iron(III porphyrin catalyzed the conversion of cyclohexene to a 1:1 mixture of cyclohexene oxide and cyclohex-1-en-3-ol, by oxygen and molybdenum or vanadium acetylacetonate. There were 5 x $10^3$ moles of product formed per mole of iron porphyrin [364].

Terminal alkenes were oxidized to primary alcohols by hydroalumination by lithium aluminum hydride catalyzed by dicyclopentadienyltitanium dichloride followed by oxidation of the thus-formed alane. Internal olefins gave poor yields, while terminal olefins gave fair to excellent yields. Dienes having both terminal and internal olefins reacted selectively at the terminal position [365]. Dihydropyran was oxidatively ring opened by treatment with $MoO_5$·HMPA (eq. 142) [366]. Vinyl cyclobutanes were oxidized to cyclopentanones by treatment with oxygen and palladium(II) chloride/copper(II) chloride (eq. 143) [367].



(142)

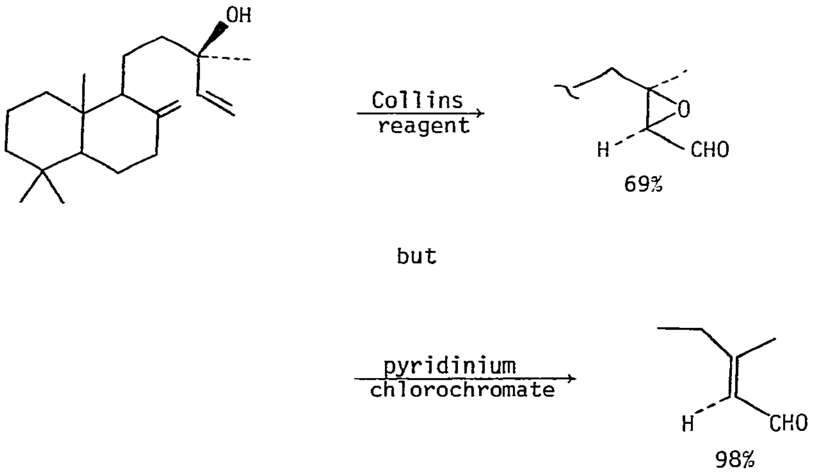
Primary alcohols were oxidized to aldehydes by treatment with copper(I) chloride, oxygen and an amine. The best amine was 9,10-phenanthroline. Benzylic and allylic alcohols reacted faster and gave better yields than aliphatic alcohols. Secondary alcohols gave ketones, but slowly. Benzyl amine was oxidized to benzonitrile in 90% yield under these conditions [368].



R = H 75%
R = CN 82%
R = $CH_2NHCOMe$ 65%

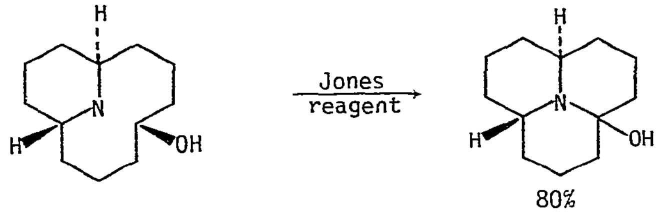
(143)

Secondary alcohols were oxidized to ketones in high yield by treatment with oxygen and a palladium chloride-sodium acetate catalyst. 2-Propanol, 2-octanol, cyclohexanol, cyclobutanol, cyclopentanol and benzyl alcohol all reacted smoothly [369]. Chromyl chloride adsorbed on alumina/silica gel provided a neutral, nonaqueous oxidizing agent for the oxidation of alcohols to aldehydes and ketones. The reaction proceeded in methylene chloride at 25°[370]. The oxidation of unsaturated alcohols by Collins reagent was compared to that using pyridinium chlorochromate. While Collins reagent gave epoxyaldehydes, pyridinium chlorochromate gave α,β-unsaturated aldehydes (eq. 144) [371]. Primary and secondary alcohols were oxidized to aldehydes and ketones by $(Ph_3P)_2M(CO)(O_2CR)$ (M = Ru, Os; R = $CF_3$, $C_2F_5$, $C_6F_5$). The ruthenium catalyst was more reactive than the osmium catalyst [372]. Jones reagent was used for the oxidation in eq. 145. The produced chromium(III) salts were kept in solution to facilitate isolation by addition of trisodium citrate and a small piece of amalgamated mossy zinc [373]. The air oxidation of ethanol was catalyzed by a cobalt-o-diaminoazobenzene complex [374].



(144)

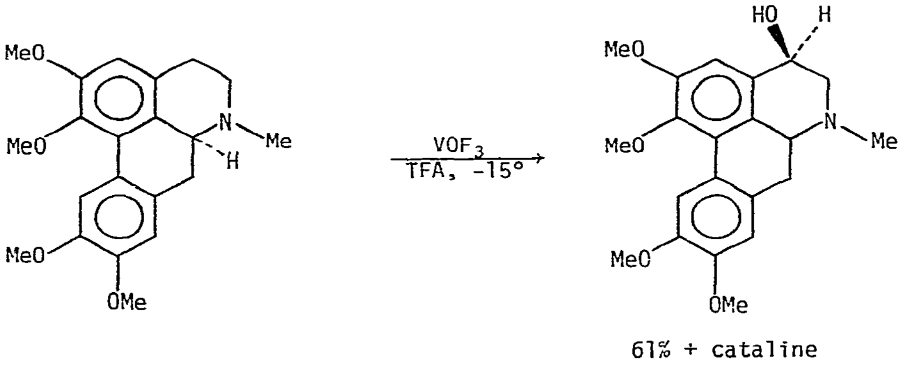
Benzaldehyde was oxidized to perbenzoic acid by $(Ph_3P)_2PdO_2$ in chlorobenzene at 25° via a radical mechanism [375]. Carbon monoxide was oxidized to carbon dioxide, and ketones were oxidatively cleaved to mixtures of carboxylic acids by treatment with oxygen and $Rh_6(CO)_{16}$, $(Ph_3P)_3Pt$ or



(145)

$IrCl(CO)(PPh_3)_2$ at elevated temperatures and pressures [376]. Hydrogen peroxide oxidized 1,3-dicarbonyl compounds in the presence of tungsten(VI) or molybdenum(VI) compounds [377].

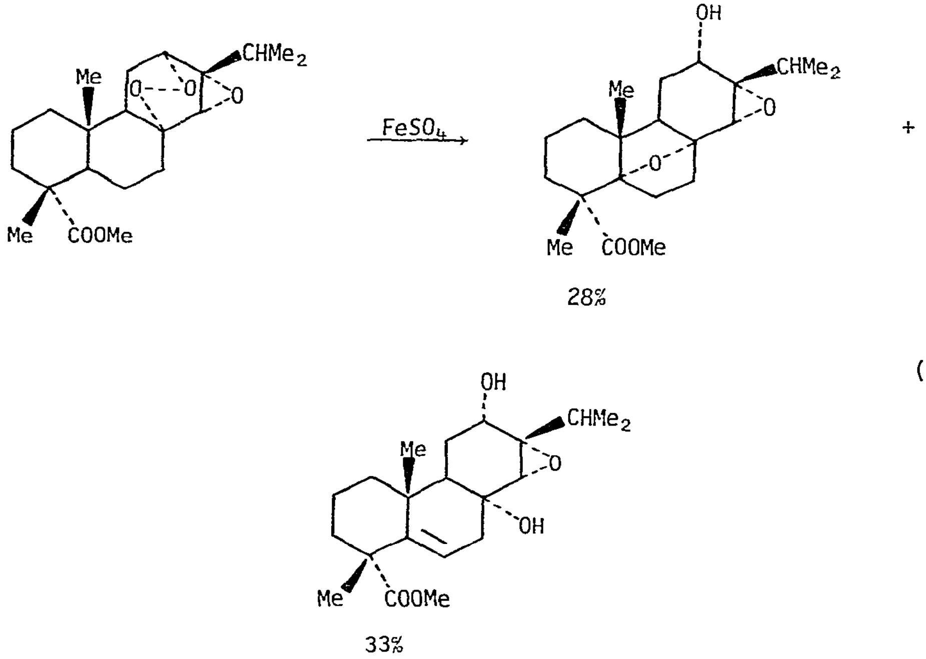
Chromium trioxide oxidized 1,4-cyclohexadiene and tri-_t_-butylcycloprope at the allylic position [378]. The benzylic position of an isoquinoline alkaloid was oxidized by $VOF_3$ to give a 61% yield of +-cataline (eq. 146) [379]. Taurocholanic acid was autoxidized by ferrous ions in aqueous solution to methyl-15α-hydroxy-5β-cholan-24-oate and methyl lithocholate [380]. Iron(II) induced decomposition of a rigid epidioxide led to remote oxidation (eq. 147) [381]. The catalytic oxidation of paraffins such



(146)

as isobutane or propane on ternary $NiO$-$Al_2O_3$-$SiO_2$ catalysts was studied [382, 383]. Naphthalein reacted with oxygen in the presence of iron(II) salts to give products of radical oxidation (eq. 148) [384]. Anthracene was selectively oxidized to anthraquinone by oxygen in the presence of copper(II) bromide in ethylene glycol solution [385].

Substituted β-carbolines were aromatized by treatment with $Rh(PPh_3)_2Cl$, $Rh(PPh_3)_2(CO)Cl$ or $Ir(Ph_3P)_2(CO)Cl$ (eq. 149) [386, 387]. Isoxazoles were prepared from the dihydro compounds by treatment with γ-manganese dioxide (eq. 150) [388]. Palladium on carbon effected an aromatization with decarboxylation via a π-allylpalladium complex (eq. 151) [389]. Both piperidi and cyclohexanone were aromatized by palladium chloride or tetrachloropalladate(II) ion in aqueous base [390]. Spirocyclopentanenaphthaleins



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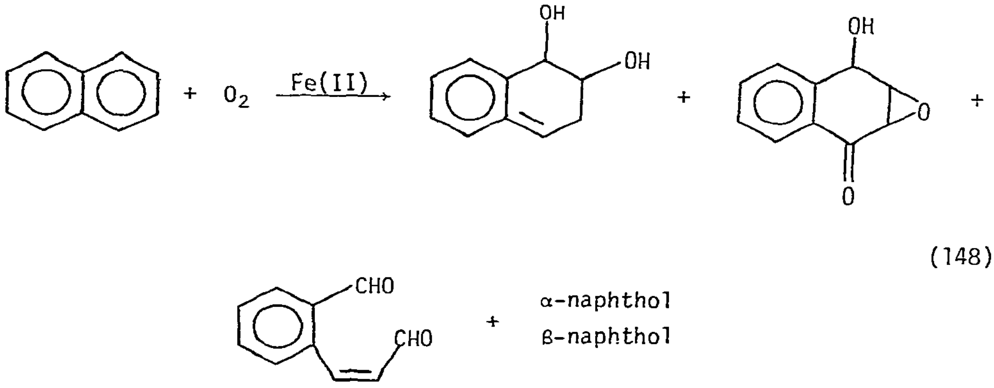
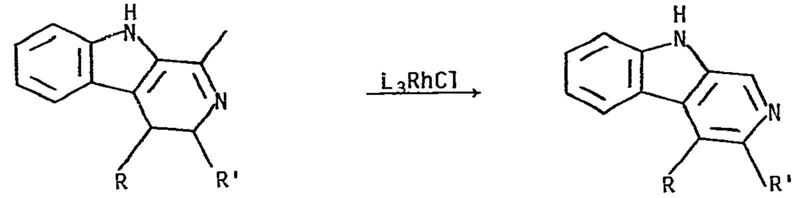


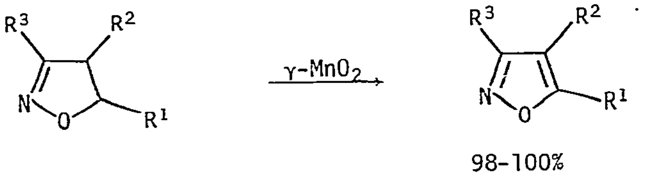
(148)

aromatized with rearrangement over palladium (eq. 152) [391]. Cyclohexanones contained in polycyclic systems were aromatized by treatment with copper(II) bromide/lithium bromide in refluxing acetonitrile. Aromatization occurred with conservation of ring junction stereochemistry and without α halogenation of the nonconjugated carbonyl group (eq. 153) [392]. Ketosteroids were dehydrogenated by treatment with palladium chloride-hydrochloric acid in *t*-butanol. Nine cases were studied (eq. 154) [393]. The chelating diphosphine $Ph_2P(CH_2)_6PPh_2$ was dehydrogenated to $Ph_2PCH_2CH_2CH{=}CHCH_2CH_2PPh_2$ by treatment with rhodium or iridium cyclooctadiene complexes followed by treatment with potassium cyanide [394].



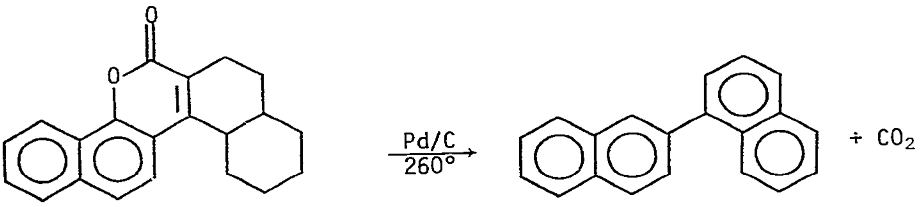
(149)

R = H, Me
R' = $PhCH_2$, Pr



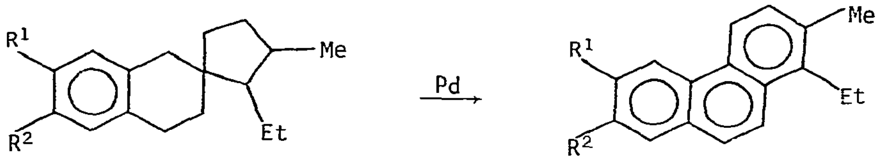
(150)

$R^1$ = Ph, n-octyl, Me, β-naphth, COOMe
$R^2$ = H, $NO_2$
$R^3$ = Me, Ph, 



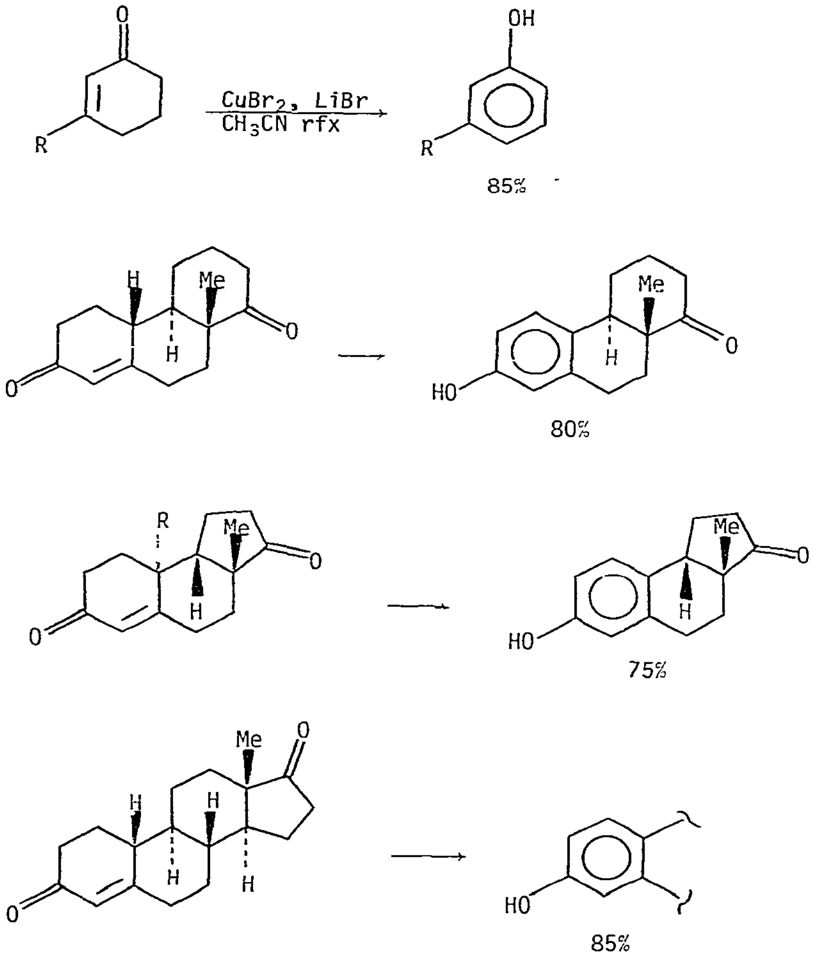
(151)

Cobalt(III) trifluoride was very efficient at cleaving ketone tosylhydrazones, dimethylhydrazones, 2,4-dinitrophenylhydrazones and oximes to the ketone in fair to high yield [395]. N,N-Dialkylanilines were oxidatively coupled to 4,4'-diaminodiphenylmethanes by treatment with palladium(II) acetate. The extra methylene group came from an acetate [396]. Benzyl amine was oxidized to benzonitrile in 35% yield, and β-phenethylamines to benzylcyanides in about 40% yield with copper(I) chloride and oxygen in pyridine [397]. The mechanism of the catalytic oxidation of triphenylphosphine to triphenylphosphine oxide by oxygen and a $Pt(O_2)(PPh_3)_2$ catalyst was reported [398]. Aromatic diazonium salts were converted to the corres-



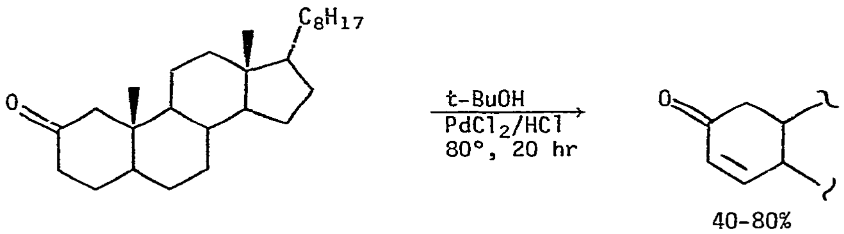
(152)

$$\left.\begin{matrix}R^1 = H, Me\\ R^2 = H, Me\end{matrix}\right\}\ -(CH_2)_4-$$



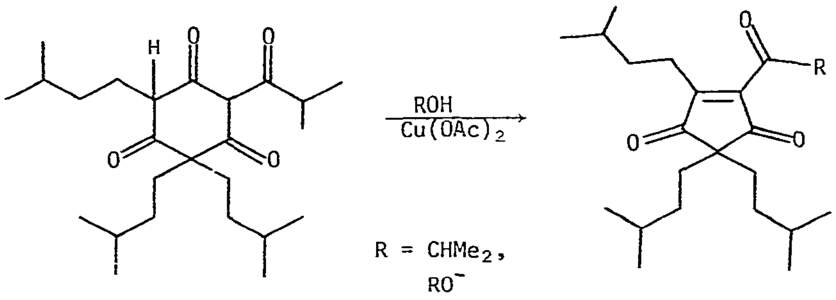
(153)

ponding phenols in high yield by treatment with $Cu_2O$ and $Cu(NO_3)_2$ in water. This procedure was superior in all respects to the acidic water procedure [399]. Aryl Grignards were oxidized to phenols by treatment with



(154)

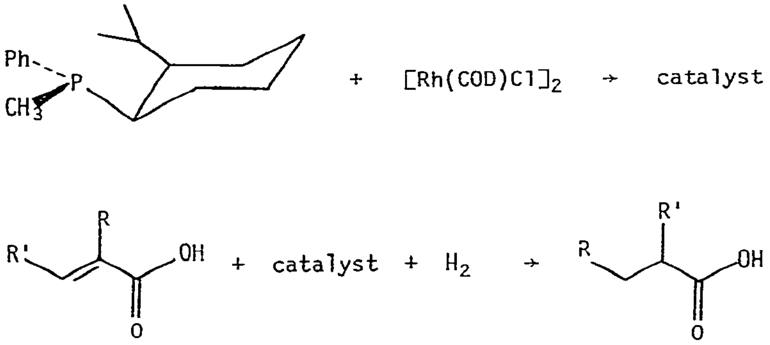
$MoO_5$-Py-HMPA in THF at -78°[400]. Hexahydrocolupulone was oxidized in cyclohexane and small amounts of alcohols in the presence of copper(II) acetate to give cyclopentenediones (eq. 155) [401].



(155)

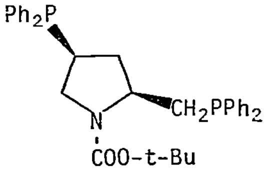
## IV. Reduction

There was a great deal of activity in the area of catalytic reductions, with much emphasis on asymmetric reductions and solid phase supported catalysts The complex from biscyclooctadienerhodium(I) chloride dimer and chiral methylphenylcyclohexylphosphine catalyzed the reduction of conjugated acids in 46-98% yield and 13-67% optical yield (eq. 156) [402]. Chiral diphosphines of pyrrolidine carbamate esters (I-III) were used as ligands on rhodium for the reduction of N-benzyloxycarbonylaniline in 50-60% optical yield [403]. Using a long chain ester group on these ligands gave a hexane soluble catalyst which reduced the ketone group of α ketoesters in 99% yield with 67.3% optical yield [404]. Structural requirements of the chiral diphosphine ligand in rhodium asymmetric hydrogenation catalysts were carefully studied [405, 406]. The response of enantiomeric excess in the reduction of $CH_2C(NHCOMe)COOH$ and $PhCH{=}C(NHCOMe)COOH$ using rhodium(I) complexes of a series of diphosphine ligands was examined. The differences in enantiomeric excess was claimed to be related to the structural rigidity of the ligand (Table 2). Changing the substrate from the acid to a series of esters, and alteration of the aromatic group had little effect on enantiomeric excess [407]. The rhodium complex with the (S,S)bisdiphenylphosphine prepared from

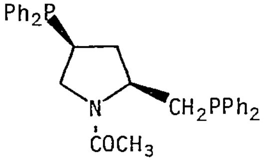


(156)

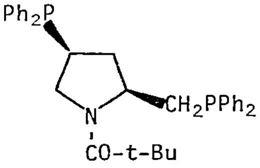
| | yield | ee |
|---|---|---|
| atropic | 46% | 13.5% |
| E-β-methylcinnamic | 98 | 67 |
| α-methylcinnamic | 70 | 61 |
| α-acetocinnamic | 80 | 44 |
| itaconic | 53 | 52 |



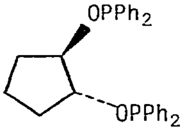
(SS)BPPM
I



(SS)APPM
II



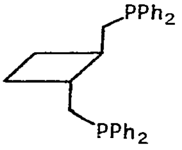
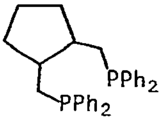
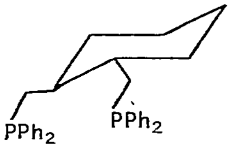
(SS)PPPM
III



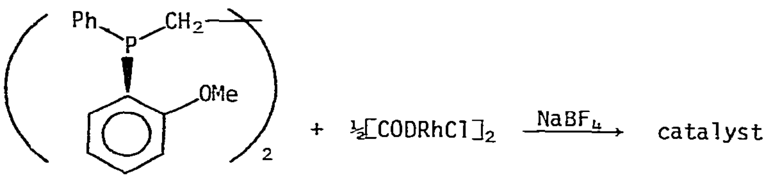
IV

$[(diolefin)RhCl]_2$ + ligand → catalyst

Table 2. Effect of Chiral Diphos on ee in Reduction of RCH=C(NAc)COOH

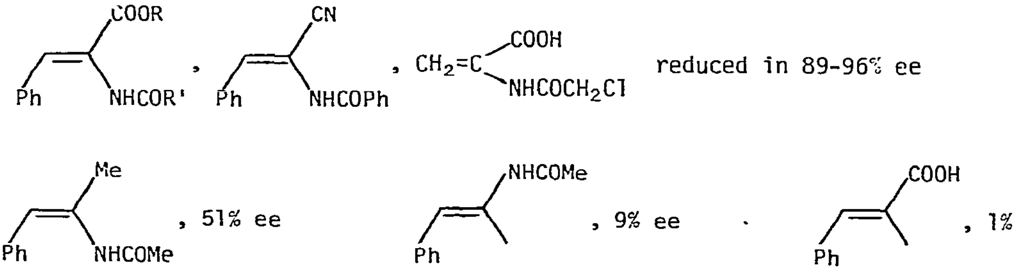
| | DIOP |  |  |  |
|---|---|---|---|---|
| R = H | 73% | 72% | 72% | 40% |
| R = Ph | 82% | 86% | 63% | 35% |

(R,R)-2,3-butanediol catalyzed the reduction of N-acetylamino acids in 92-100% optical yield. L-Dopa was prepared in 83% optical yield with this catalyst [408]. The chiral diphosphonite IV formed a rhodium hydrogenation catalyst that reduced α ethylstyrene to (R)-2-phenylbutane in 60% optical yield. (Diop gave 24% optical yield with this substrate, while N-acetylphenylalanine was reduced in only 43% optical yield.) Unsaturated carboxyli acids were reduced with quite low stereoselectivity, while moderate stereoselectivity was observed with unsaturated esters [409]. The importance of the molecular asymmetry induced by olefins in the enhancement of enantioselective dehydrogenation of racemic alcohols by (+)neomenthyldiphenylphosph complexes or rhodium or ruthenium was investigated [410]. Asymmetric hydrogenation of α acylaminoacrylic acids using chiral biphosphine V based rhodiu catalysts was studied in great detail. "Tridentate" substrates (olefin and two carbonyl groups) gave the best optical yields (89-96% ee) while bidentate substrates were much less stereoselective. α Methylcinnamic acid reduced in only 1% ee (eq. 157) [411]. α-Aminoacrylic acids and esters were reduced over (S)-RhCl[$Ph_2PN(CHPhMe)CH_2CH_2N(CHPhMe)PPh_2$] in 49-84% optical yield [412].

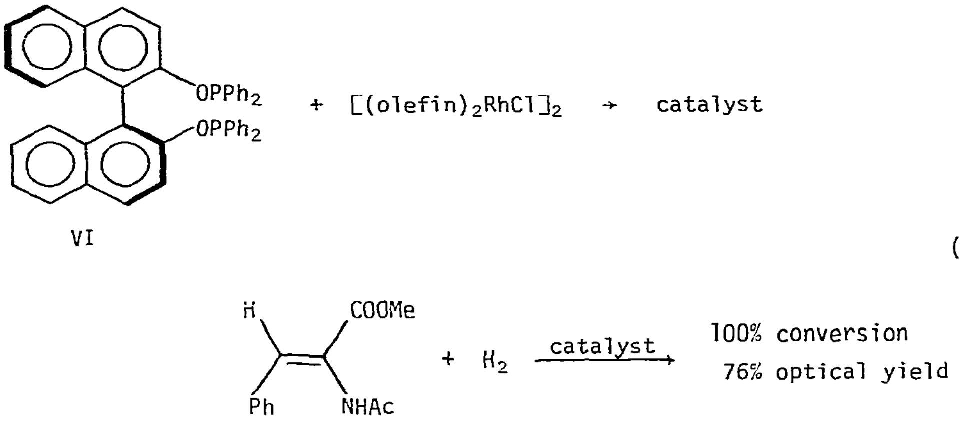


V

(157)

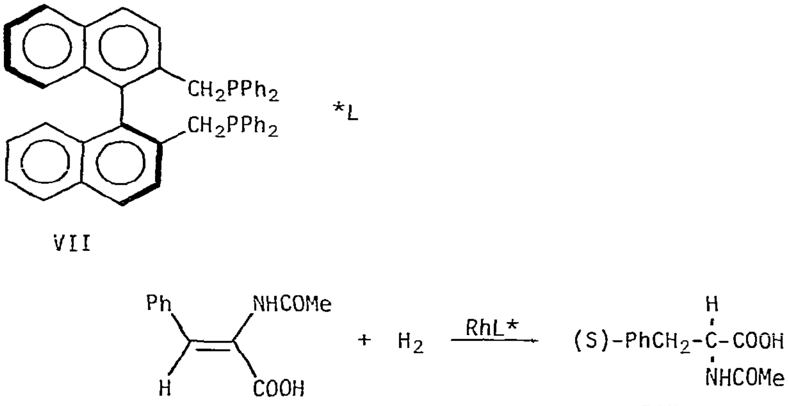


The use of chiral ferrocenylphosphine ligands on transition metals was effective for asymmetric reduction of α-acetamidoacrylic acids, for asymmetri hydrosilation of ketones and for asymmetric Grignard cross coupling reactions [413, 414]. Atropic and α-acetamidoacrylic acids were hydrogenated in low (4-7%) optical yields using the usual rhodium cationic catalysts containing chiral bidentate phosphines of the type $Ph_2PN(R)-CH_2CH_2N(R)PPh_2$ where R was derived from (+)-camphoric acid, (-)-nopinylamine and (-)-pinane-3-carboxylic acid [415]. Prochiral unsaturated esters were reduced in up to 76% optical yield using catalysts derived from bisphosphite VI (eq. 158) [416], while bisphosphine VIII based catalysts were used to reduced the corresponding acids in 54% ee (eq. 159) [417]. The complex $L_2Rh(amine)Cl$



VI

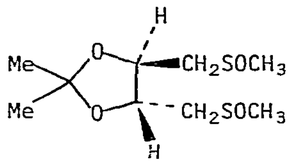
(158)



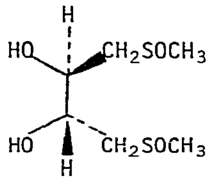
VII

54% ee

Where the amine was d α-phenethylamine catalyzed the reduction of α-acetamamidocinnamic acid in 80% yield and 20% ee [418]. High optical yields (77%) were obtained in the hydrogenation of 2-phenyl-1-butene with an insoluble phosphinite derived from 6-o-triphenylmethylcellulose [419]. A Rh-DIOP catalyst was attached to macroporous silica gel and used to reduce α-acetamidoacrylic acid. The optical yields were comparable to those of the corresponding homogeneous system, but the rate was ten times slower [420]. Ruthenium cluster compounds of the type $H_4Ru_4(CO)_8[(-)DIOP]_2$ and $Ru_6(CO)_{18}[(-)DIOP]_3$ were used as catalyst precursors for the reduction of (Z)-α-methylcinnamic acid. Up to 58% asymmetric induction was observed, with the $Ru_4$ catalyst, while 61% symmetric induction was obtained with $Ru_6$ [421]. Reduction of α-acetamidoacrylic esters using ruthenium catalysts of the type $RuCl_2L_2$ where L was the chiral sulfoxide $EtCHMeCH_2SOMe$ gave very low (<2%) optical yields of reduced product [422]. Using sulfoxides resembling DIOP (VIII and IX) led to 25% ee in the reduction of itaconic ac [423]. Benzil was reduced to benzoin in 79% ee using a chiral cobalt catal containing a ligand formed by the condensation of 2,3-butandione monooxime with 1,3-propanediame [424]. The structure of a cobalt asymmetric hydrogenation catalyst containing a bis-dimethylglyoximato group was determined [425]. Metal complex catalysts with chirality recognizing function have be reviewed (93 references) [426].

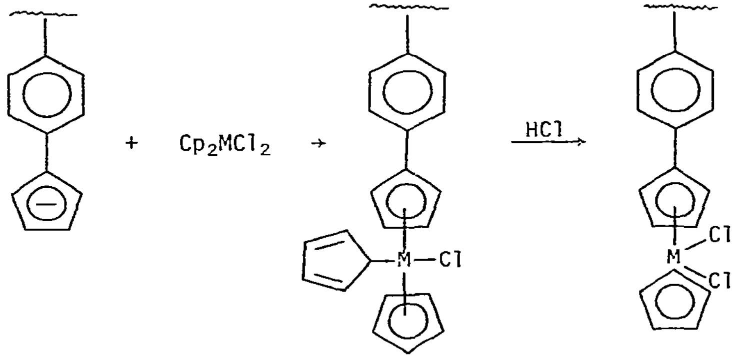


VIII



IX

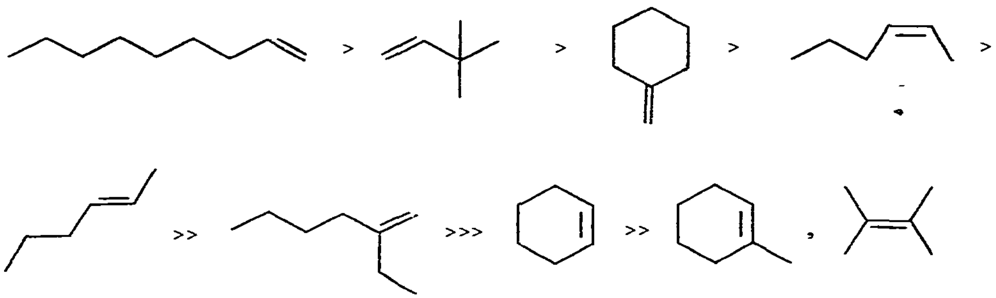
The reduction of ethylene over $(Ph_3P)_3RhCl$ supported on a copolymer of styrene, divinylbenzene and diphenyl-p-styrylphosphine was studied in the gas phase. The catalytic activity of this system changed abruptly at 68°. The change was ascribed to the glass transition in the polymer support [427 Chloromethylated polystyrene was treated with o-aminobenzoic acid, followed by rhodium trichloride. This polymer was then treated with sodium borohydride to give black polymer beads which catalyzed the reduction of cyclohexene and benzene [428]. The first supported metallocarborane catalyst, [3,3-$(Ph_3P)_2$-3-H-4-(polystyrylmethyl)-3,1,2-$RhC_2B_4H_{10}$], was an effective catalyst for the reduction of hindered olefins, as was its homogeneous counterpart [429]. Polystyrene resins differing in their porosity were chloromethylated, phosphinated and treated with $[(olefin)_2RhCl]_2$. The reactivity of these different supported catalysts for the reduction of cycl hexene was examined and was found to be a function of loading and porosity. Aging under hydrogen led to the formation of metallic particles active for benzene hydrogenation [430]. Rhodium trichloride was reacted with polymeri $Ph_2PCH_2PPh_2$ producing a paramagnetic rhodium(II) complex active for the hydr genation of monoolefins and dienes [431]. A method for the introduction of cyclopentadienyl complexes of Ti, Zr, Hf, Nb, Ta, Mo and W into polymer supports consisted of synthesizing polymer-bound cyclopentadiene anion, and treating this polymer with bis-cyclopentadienyl metal dichloride, and hydrog chloride (eq. 160) [432]. The extent of metal-metal interactions among polymer attached metallocene catalysts such as $Cp_2TiCl_2$ was probed by measuring hydrogenation rates relative to polymer loading. The expected maximum in this curve was observed [433]. Rhodium(I) catalysts immobilized on phosphinate styrene/2-20% divinylbenzene copolymers were efficient for



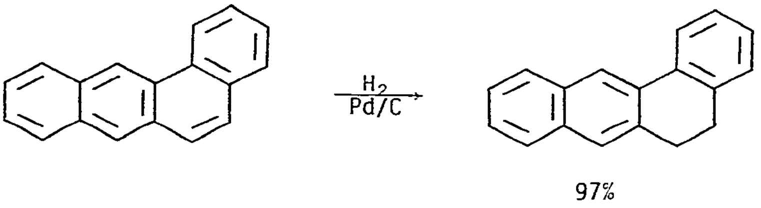
(160)

the hydrogenation of olefins, diolefins and alkynes. The effect of substrate concentration and the role of uncoordinated phosphine was examined [434]. Transition metal complexes supported on phosphine modified silica gel carriers were two to four times more active as hydrogenation catalysts than the corresponding homogeneous systems. The complexes studied were $L_3RhCl$, $L_3RhHCl_2$, $L_3RhH_2Cl$, $L_3RhCl_3$, $L_2CoCl_2$, $L_2NiCl_2$, $L_2PdCl_2$ and $L_2NiBr_2$[435]. Potassium tetrachloropalladate was supported on carbon, $BaSO_4$ or alumina and reduced in the presence of tetraalkylammonium hydroxides to produce a catalyst for the reduction of allyl alcohol to n-propanol, propionaldehyde and propane [436]. Platinum catalysts supported on zeolites were used for the hydrogenation of cyclopropane [437]. Silica coated with an organosilicon ladder polymer was chloromethylated, phosphinated and treated with rhodium(I) complexes. These supported catalysts were much more active towards olefin hydrogenation than were their homogeneous analogs [438]. Colloidal palladium supported on the polyion complex composed of polyacrylic acid and polyethylene imine was the highly selective catalyst for the reduction of linear and cyclic dienes to monoenes at 30° under hydrogen [439]. An unusual approach to heterogenizing homogeneous catalysts was to use a two-phase system consisting of the substrate olefin and product alkane as the organic phase, and the water soluble phosphine $Ph_2P(o\text{-}SO_3Na\text{-}Ph)$ complex of rhodium trichloride in an immiscible aqueous phase. The reactions were governed by the solubility of the olefin in the aqueous phase. Very high conversions were obtained with this system [440].

Treatment of 10 equivalents of iron(III) chloride with 60 equivalents of sodium hydride in THF and t-butanol produced a black powder which reduced alkenes and alkynes (including phenylacetylene) to alkanes quantitatively. Ketones reduced only slowly, and olefins could be reduced in the presence of ketones. Vinylcyclohexene underwent exclusive reduction at the exocyclic olefin in 98% yield [441]. Treatment of nickel(II) acetate with sodium hydride in the same proportions in the presence of t-amylalcohol produced a black catalyst which also reduced alkenes and alkynes to alkanes, and dienes to monoenes [442]. Dicyclopentadiene titanium dichloride catalyzed the hydroalumination of alkenes and alkynes by $HAl(NR_2)_2$, resulting in reduction upon hydrolysis. The order of reactivity was

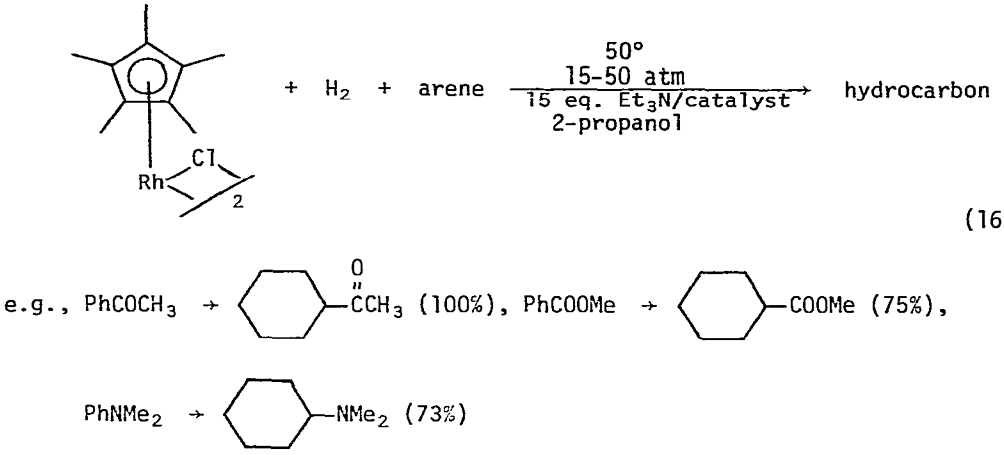


[443]. A similar hydroalumination with lithium aluminum hydride was catalyzed by titanium or zirconium tetrachloride. With nonconjugated dienes, aluminum hydride and lithium aluminum hydride added to the least hindered olefin [444]. Reduction of $CH_2{=}CH(CH_2)_3CH(OH)CH{=}CH_2$ with lithium aluminum hydride catalyzed by dicyclopentadienylpalladium dichloride gave $CH_3(CH_2)_4CH(OH)CH{=}CH_2$ in a highly selective reduction [445]. A comparison of the stereospecificity of the reducing systems palladium on carbon, $RhH_2Cl(PPh_3)_2$ and $B_2H_6$ in the reduction of olefins homologous to α-pinene was made. Palladium on carbon gave >90% trans reduction with all six olefins studied, while the rhodium catalyst gave from 40-95% trans, depending on substituents [446]. The complexes $[Ir(COD)L_2]^+PF_6^-$ and $[Ir(COD)Lpy]^+PF_6$ were very active catalysts for the hydrogenation of olefins, but were irreversibly deactivated by formation of hydrido bridged dimers [447]. 1-Octene was hydrogenated over cobalt and rhodium complexes of chelating triphosphines $PhP(CH_2CH_2PPh_2)_2$ and $PhP[(CH_3)_3PPh_2]_2$. The most active catalyst was the $H_3CoL$ species where L was the shorter chain phosphine [448]. The complexes $Ru(PPh_3)_3Cl_2$ and $Rh(PPh_3)_3Cl$ were compared with ruthenium and rhodium metal in their reduction of geraniol. Each reduced geraniol to citronellol first, then to 3,7-dimethyloctanol. With the homogeneous catalysts this was considered sequential, while with the heterogeneous one it was simultaneous [449]. Palladium on carbon was an efficient catalyst for the high yield regiospecific reduction of the K region of polynuclear aromatics under mild conditions (eq. 161) [450]. The hydrogenation of α-methylstyrene by $HMn(CO)_5$


(161)

proceeded by a free radical path involving hydrogen atom transfer from the metal hydride to the substrate [451]. Styrene was hydrogenated under low pressure using the cluster catalysts $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$, while $Co_4(CO)_{12}$ was inactive. Addition of trimethyl phosphites enhances the rates of reactions for the active catalyst [452]. 1,3-Butadiene was selectively hydrogenated to cis-2-butene over cobalt(I)-bipyridyl complexes [453]. Treatment of nickel chloride hexahydrate or cobalt chloride hexahydrate with sodium borohydride in DMF produced efficient catalysts for the reduction of unsaturated compounds. 1,3-Cyclohexadiene was reduced exclusively to cyclohexene. The catalysts were very air sensitive [454]. Polyenes were selectively reduced to monoenes over $RuCl_2(PPh_3)_3$ catalysts. In this fashion cyclooctadiene was reduced to cyclooctene (89%), cis,trans,trans-1,5,9-cyclododecatriene to trans-cyclododecene (87%) and ethyl 2-acetyl-4,9-decadienoate to ethyl 2-acetyl-4-decenoate (93%) with 100% selectivity [455]. Neat 1,3-cyclohexadiene was reduced to cyclohexenes selectively in a photoinduced homogeneous reaction using $IrCl(CO)(PPh_3)_2$ as a catalyst [456]. A π-arene complex of ruthenium, $\eta^6$-$C_6Me_6Ru$-$\eta^4$-$C_6Me_6$ was an efficient and long-lived homogeneous catalyst for the reduction of arenes. Extensive hydrogen-deuterium exchange was noted with this catalyst system from both $D_2$ + arene and $H_2$ + perdeuteroarene reactions [457]. Arenes were reduced to cyclohexanes under mild conditions using $[Me_5CpRhCl]_2$ as a catalyst. The reaction was highly stereoselective and all cis isomers were the major products (eq. 162) [458].

Conjugated esters were reduced using $IrCl(CO)L_2$ and photoactivation [459], $IrCl(CO)(PPh_3)_2$ without solvent at 80-120° and 10 atm of hydrogen [460, 461], and with $IrCl(CO)L_2$ (L = various phosphines) [462]. A very efficient catalyst for the homogeneous reduction of unsaturated esters under mild conditions was prepared by treatment of $H_2PtCl_6$ and stannous chloride with hydrobromic acid and water in alcohol solvent [463]. The cationic rhodium complex $[Rh_2(diphos)_2]^{2+}$ was an efficient homogeneous catalyst for the reduction of simple alkenes, acrylic and amidoacrylic acids, etc. [464]. Conjugated ketones were reduced by 2-propanol via a transfer hydrogenation process using $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ as catalyst. The olefin reduced first, followed by the carbonyl [465]. Molybdenum hexacarbonyl in refluxing aqueous diglyme reduced a variety of



(162)

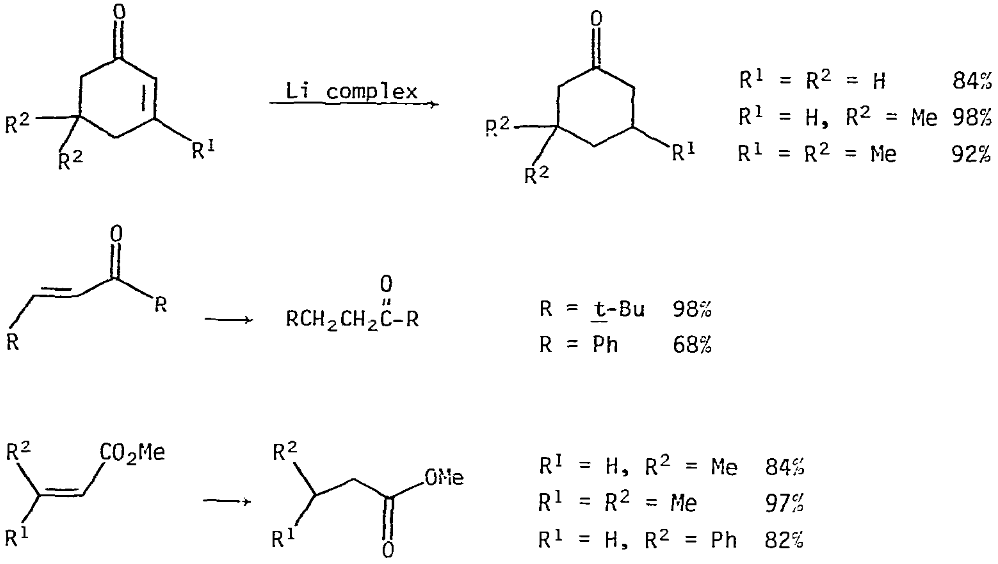
but, $PhCH{=}CH_2 \rightarrow PhEt$ (97%) and $PhC{\equiv}CH$, PhOH, PhX, $PhNO_2$ < 5% reduction

conjugated olefins, including α,β-unsaturated ketones in high yield [466]. Low valent cobalt triisopropylphosphite complexes of the type $H_3CoL_3$, prepared by treating $\eta^3$-allyl cobalt $L_3$ with hydrogen, were selective hydrogenation catalysts for the reduction of α,β-unsaturated ketones and amides to the saturated ketones and amides [467]. Copper hydrides of unspecified composition were very efficient for the conjugate reduction of conjugated carbonyl compounds. The complexes were made by treatment of copper(I) bromide with either $LiAlH(OCH_3)_3$ ("Li complex") or $NaAlH(OCH_2CH_2OCH_3-)_2$ ("Na complex"). The "Li complex" was best for the reduction of cyclohexenones, while the "Na complex" gave highest yields with acyclic unsaturated ketones and esters. Both complexes reduced ynones in poor yield. Aldehydes, ketones and halides were reduced at rates comparable to enone reduction, while nitriles and esters were inert (eq. 163) [468]. Sulfonated triphenylphosphine was used as ligands to make water soluble reduction catalysts of the type $HRu(AcO)L_3$ and $RuCl_2L_2$ for the reduction of unsaturated and oxoacids in aqueous solution. The rates of reaction of olefin and carbonyl groups were dependent upon the pH of the aqueous solution [469].

Treatment of $IrH_3(PPh_3)_3$ with acetic acid produced a homogeneous catalyst system which reduced aldehydes to alcohols at 80-110°, 10 atmospheres of hydrogen. Conjugated aldehydes underwent complete reduction while ketones were not reduced at all [470]. Benzaldehydes, octanal and decanal were reduced to the alcohols using $RuCl_2(PPh_3)_3$ as a catalyst at 10 atmospheres of hydrogen and 50-80° in benzene. Ketones and aryl nitro compounds were not reduced, and benzyl alcohol was not hydrogenalized

$$2LiAlH(OMe)_3 + CuBr \xrightarrow[THF]{0^\circ} \text{"Li complex"}$$

$$NaAlH_2(OCH_2CH_2OCH_3)_2 + CuBr \rightarrow \text{"Na complex"}$$



$R^1 = R^2 = H$ 84%
$R^1 = H, R^2 = Me$ 98%
$R^1 = R^2 = Me$ 92%

(163)

R = t-Bu 98%
R = Ph 68%

$R^1 = H, R^2 = Me$ 84%
$R^1 = R^2 = Me$ 97%
$R^1 = H, R^2 = Ph$ 82%

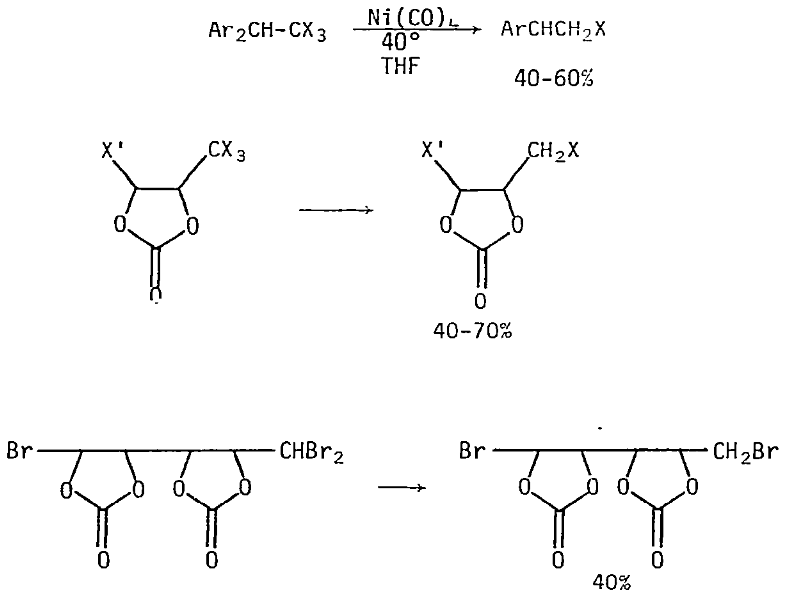
[471]. Cationic bipyridine complexes of rhodium(I) were used as catalysts to reduce ketones to alcohols in the presence of strong base in methanol at 1 atmosphere, 25°C [472, 473]. Treatment of $Rh_2H_2Cl_2(COD)(PPh_3)_2PhCH_3$ (prepared from $CODRh(Cl)PPh_3$ and hydrogen in toluene) with sodium borohydride in methanol produced a catalyst which reduced ketones to alcohols in very high yield in the presence of strong base (NaOH). Acetone, 2-hexanone, acetophenone, benzophenone and adamantanone were reduced [474]. Reduction of nickel halides with sodium borohydride produced a catalyst which reduced conjugated aldehydes all the way to saturated alcohols, although in some cases, the saturated aldehyde was isolable. The corresponding palladium catalyst reduced only the double bond to produce saturated aldehydes [475]. Treatment of ketones with sodium hydride/nickel(II) acetate/t-amyloxide in THF at 40-65°, 10-20 hr reduced ketones to alcohols in high yield. Similar systems reduced olefins to alkanes and alkynes to alkenes [476].

Reduced nickel oxide, modified by the addition of tartaric acid reduced methyl acetoacetate to $CH_3CH(OH)CH_2COOMe$ in 85% optical yield. The presence of aluminum reduced the optical yield. Thus Raney nickel was less effective [477]. Rhodium(I) complexes containing the chiral pyrrolidine diphosphine catalyzed the reduction of α-ketoesters to chiral lactates in

THF at 25° and 20 atmospheres of hydrogen in 36-76% enantiomeric excess [478]. Hydrogenation of unhindered cyclohexanones in isopropanol/HCl with rhodium catalysts selectively gave axial alcohols in high yield. Steroidal 3,17- and 3,20-diones were selectively reduced at C-3 to give 3-axial hydroxy ketones [479]. In contrast, hydrogenation of 5α-cholestan-3-one over palladium catalyst gave the equatorial 3β-ol, while 5α-cholestan-3-one gave axial 3β-ol. Platinum catalysts gave the same results [480]. With simpler cyclohexanones, bulky 4-substituted systems reduced faster than the less bulky substrates [481].

Catalytic transfer hydrogenation from cyclohexene was used to reduce quinones to hydroquinones over palladium on carbon in THF/aq. $H_2P(O)OH$ [482]. Cyclohexanone was reduced to cyclohexanol by transfer hydrogenation using α-phenethyl alcohol as the hydrogen source and $Mo(N_2)(diphos)_2$ or $MoH_4(diphos)_2$ as catalysts [483]. Aminophosphine rhodium(I) complexes catalyzed the reduction of cyclohexanones to cyclohexanols by isopropanol. The reduction was accompanied by isomerization to the more stable epimers [484]. Conjugated aldehydes were reduced to allyl alcohols using rhodium catalysts prepared from $Rh_2Cl_2(CO)_4$ and excess tertiary amine under oxo conditions. With cinnamaldehydes, specificity for carbonyl reduction was high, while with aliphatic unsaturated aldehydes, substantial amounts of olefin reduction was observed. The catalyst remained active when attached to an insoluble polymer [485]. Finally, $PhCH{=}CH{-}CO_2CH_2CH{-}CHPh$ was reductively decarboxylated to $PhCH{=}CH{-}CH_2CH{=}CHPh$ over palladium or platinum in methanol [486].

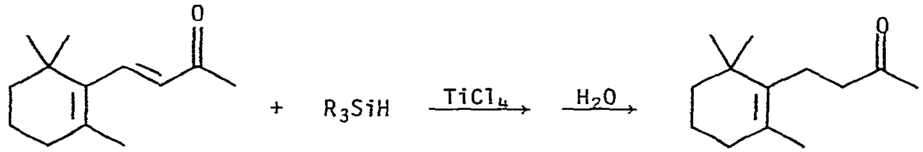
A variety of new systems for reducing organic halides have been developed. In an extensive study of reductions effected by the material resulting from the reduction of the transition metal halides $TiCl_3$, $VCl_3$, $CrCl_3$, $MnCl_2$, $FeCl_2$, $FeCl_3$, $CoCl_3$, $NiCl_2$, CuI and ZnBr with lithium aluminum hydride, it was found that the $LiAlH_4/NiCl_2$ and $LiAlH_4/CoCl_2$ systems reduced primary, secondary, tertiary, cyclic and aryl bromides in good yield [487]. In related work a series of copper hydrides ($LiCuH_2$, $Li_2CuH_3$, $Li_3CuH_4$, $Li_4CuH_5$, $Li_5CuH_6$) prepared by the reaction of lithium alkyl cuprates with lithium aluminum hydride, were found to reduce primary alkyl iodides in excellent yield, chlorides and tosylates in moderate to good yield, and fluorides in very low yield [488]. 1-Bromonaphthalein was reduced by mixtures of sodium hydride, sodium t-amyloxide and metal halide ($Ni(OAc)_2$, $L_2NiCl_2$, $FeCl_3$, $CrCl_2$, $ZrCl_4$, $ZnCl_2$, $MoCl_5$, $WCl_6$, $Mo(OAc)_2$ and $Cp_2TiCl_2$). The reagent from nickel acetate or zinc chloride reduced primary and secondar alkyl, benzyl, aryl and allyl halides to hydrocarbons as well [489]. Aromatic halides were reduced to the hydrocarbon by using palladium chloride catalyzed transfer hydrogenation from secondary cyclic amines as the hydrogen source [490]. Halobenzenes and nitrobenzenes were reduced to benzenes and amines respectively, by triethylammonium formate using palladium on carbon as the catalyst. Nitrile and nitro groups reduced more slowly, olefin and chloro groups were comparable, while bromides were the fastest. Ester, amide and ether groups were tolerated while aldehydes were reduced [491]. Nickel carbonyl reduced tri- and dihalides to monohalides under mild conditions (eq. 164) [492]. Phase transfer conditions were used for the dicobalt octacarbonyl reduction of α-bromoketones to ketones. The ketones studies were all aryl methyl ketones except for 1-adamantylmethyl ketone [493]. Halogen was reductively eliminated from haloalkanes by chromium(II),



(164)

copper(I) and tin(II) [494]. The reagent from treatment of chromium(II) chloride with lithium aluminum hydride reduced α-bromocyclododecanone to cyclododecanone in 96% yield, while 1,1-dibromocyclopropanes were ring opened to the allene [495]. Acid chlorides were reduced to aldehydes by treatment with hydridotetracarbonyl ferrate anion in methylene chloride at 25° in high yield. The acid chlorides studied were benzoyl, furanoyl, hexanoyl, cyclohexanoyl, p-bromobenzoyl and acetyl chloride. Cinnamoyl chloride and p-nitrobenzoyl chloride were reduced in 0-20% yield [496]. Conjugated enones and dienones underwent clean 1,4-reduction to give saturated ketones by treatment with triethylsilane and titanium tetrachloride followed by aqueous isolation (eq. 165) [497]. Hydrosilation of α ketoesters in the presence of chiral rhodium(DIOP) complexes produced lactate esters in up to 80% ee (eq. 166) [498]. Cyclohexenone was reduced by $L_3RhCl$ catalyzed hydrosilation followed by aqueous workup. Monohydrosilanes gave cyclohexanone, trihydrosilanes gave 2-cyclohexen-1-ol, while dihydrosilanes gave mixtures of both products [499]. Cyclohexenone was converted to its silylenol ether in 99% yield by treatment with phenyldimethylsilane and dicobalt octacarbonyl catalyst [500]. Hydrosilation catalyzed by group VIII complexes has been reviewed (85 references) [501].

Substituted hydrazines were synthesized by the hydrogenation of phenylhydrazones over palladium on carbon [502]. Aromatic nitro compounds were reduced by cyclic amines, particularly indolines, using rhodium trichloride



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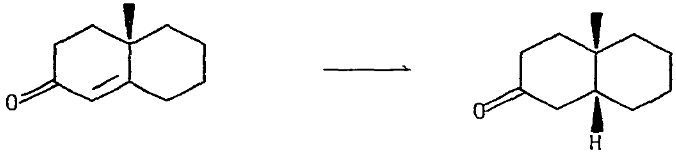
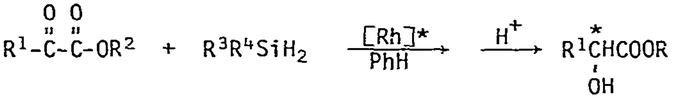


53%



$$R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR^2 + R^3R^4SiH_2 \xrightarrow[PhH]{[Rh]^*} \xrightarrow{H^+} R^1\overset{*}{C}HCOOR \atop \quad\; OH$$

$R^1$ = Me, Ph

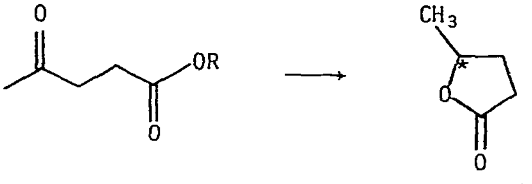
$R^2$ = n-Pr, nBu, i-Bu, Et

80-90% yields

30-80% ee

also

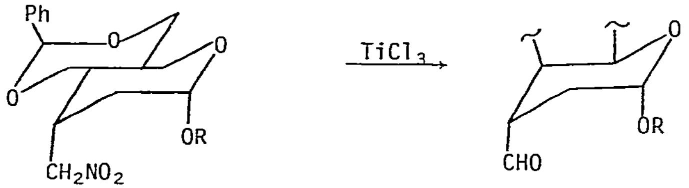
(



95-100%

up to 84% optical yield

or ruthenium trichloride as the transfer hydrogenation catalyst. Palladiur halides were less reactive. Nitrosobenzene was detected as the intermedia [503]. Phase transfer conditions (benzene/aq. sodium hydroxide, benzyltriethylammonium chloride) were used to reduce aromatic nitro compounds to the corresponding anilines in 85-90% yields by $Fe(CO)_5$ or $Fe_3(CO)_{12}$ [504]. The same chemistry using 2-3% [18] crown-6 as the phase transfer catalyst was also carried out [505]. Chromium(II) chloride in methanol reduced nitroaromatics to anilines in 58-97% yield. Aliphatic nitro compounds reduced to the aldehyde in 32-77% yield [506]. Titanium trichloride converted nitro groups to aldehydes in the synthesis of C-formyl branched chain deoxysugars (eq. 167). The nitro sugars were readily available from the condensation of nitromethane with the protected glycosidulose [507]. Chloronitrobenzenes were reduced to the corresponding chloroarylhydroxylamines by hydrazine and palladium on carbon [508].



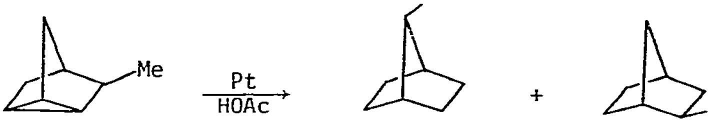
(167)

Molybdenum hexacarbonyl reduced aromatic nitro compounds in carboxylic acid solutions to the corresponding N-carboxylanilines [509]. Arenediazonium tetrafluoroborates decomposed to mixtures of arenes and fluoroarenes in the presence of copper catalysts and [18] crown-6. No decomposition was noted when either copper or [18] crown-6 was not present [510]. Azoarenes were reductively cleaved to anilines upon reaction with cyclohexene (hydrogen source) and 5% palladium on asbestos [511].

Alkyl, aryl and benzyl sulfoxides were reduced to sulfides by treatment with molybdenum hexacarbonyl in acetic acid in 75-95% yield [512]. The same transformation was effected by $K_3W_2Cl_9$ in 88-100% yields. This reagent tolerated halides, sulfones, phosphine oxides, epoxides, ketones, esters, nitriles and nitro compounds [513]. Thioketones were reduced to alkanes by treatment with iron pentacarbonyl and potassium hydroxide, while dicobalt octacarbonyl coupled them to tetrasubstituted olefins [514]. Iron pentacarbonyl deoxygenated epoxides to olefins at 145° in the presence of tetramethylurea. The stereochemistry of the epoxide was lost. The best yields were obtained with $\alpha$ ketoepoxides (95%) while the worst (40%) was obtained with simple alkylepoxides. Ketones, esters, olefins and sulfonyl groups were unreactive [515]. Styrene oxide was reduced to mixtures of $\beta$-phenylethanol and phenylacetaldehyde by hydrogenation in the presence of cationic rhodium complexes [516].

Laminar compounds of graphite with Co, Ru, Fe, Os, Mn, Cr, Ni, Cu, Pt and Pd were treated with potassium to generate a catalyst which converted hydrogen and carbon monoxide to hydrocarbons (mostly methane with cobalt). As the ratio of potassium to metal increased, the catalytic activity of the Co, Fe and Mn complexes also increased [517]. Carbon monoxide was reduced to a mixture of linear alcohols (methanol, ethanol, propanol and butanol) when treated with $(Me_2CHCH_2)_2AlH$ and $Cp_2ZrCl_2$ at room temperature [518]. Using $Ir_4(CO)_{12}$ as a catalyst in molten NaCl•2AlC solvent at 180° a 3:1 mixture of hydrogen and carbon monoxide was converted to alkanes with a catalyst turnover time of about 10-15 minutes [519]. The use of iron pentacarbonyl and alkali to hydroformylate olefins with carbon monoxide and water via the water gas shift reaction was investigated [520]. A catalyst consisting of $[Rh(CO)_2Cl]_2$ in glacial acetic acid with sodium iodide and concentrated hydrochloric acid at 400 mm of carbon monoxi was a water gas shift catalyst giving nine cycles a day. After 45 hr, 8.4 mmol of hydrogen and 8.6 mmol of carbon dioxide were produced, while 7.6 mmol of carbon monoxide was consumed [521].

Hydrogenolysis of 3-methylnortricyclene over platinum in acetic acid gave equal amounts of 7-methylnorbornane and exo-2-methylnorbornane (eq. 168). In contrast vapor phase reactions over supported metal catalysts gav most 2-methyl compounds [522]. Similar reactions of the propellanes tricyclo[4.4.1.$0^{1,6}$]undecane and tricyclo[4.3.1.$0^{1,6}$]decane were studied [523].



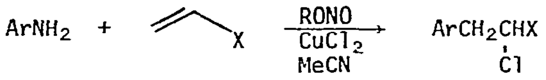
(168)

Benzyl ethers were hydrogenalized to toluene by transfer hydrogenation from indoline using palladium(II) chloride, palladium(II) acetate and rhodium(III) chloride. Benzylamines and β-phenethylacetate were also hydrogenalized under these conditions [524]. Allyl alcohols were hydrogenalized by treatment with propylmagnesium chloride in the presence of a catalytic amount of $L_2NiCl_2$ [525]. The hydrogenalysis of carbon-carbon bonds over supported metal catalysts has been reviewed (18 references) [526], as has catalysis by alloys and bimetallic clusters [527].

## V. Functional Group Preparations

### A. Halides

Bromomagnesium vinyl cuprates, prepared by the regio- and stereospecif addition of bromomagnesium alkyl cuprates to terminal alkynes, were converted to vinyl halides by treatment with N-bromosuccinimide, N-chlorosuccinimi iodine, cyanogen bromide and cyanogen iodide. The stereochemistry of the vinyl cuprate was retained [528]. Aryl amines were converted to aryl halides by treatment with t-butylnitrite and copper(II) halide. High yields and few side products were obtained in this reaction with fifteen representative substrates. The following functional groups were tolerated in the aromatic ring by this reaction: $NO_2$, MeO, COOH, Cl, F, $CF_3$, H and Me [529]. Under similar conditions aryl hydrazines were also converted to aryl halides in 74-90% yield. A range of substitution patterns was tolerated [530]. When this deamination of arylamines by _t_-butylnitrite was carried out in the presence of Michael acceptors such as acrylonitrile, ethyl acrylate and styrene, aryl halide added to the conjugated olefin (eq. 169) [531]. The yields were considerably better using this procedure than they were using the Meerwein reaction ($ArN_2$).

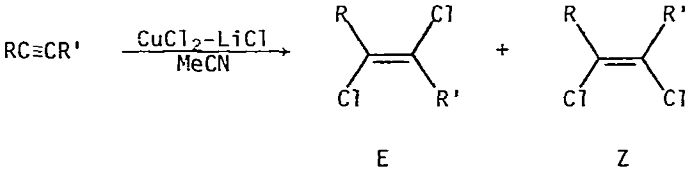


(169)

X = CN, COOEt, Ph

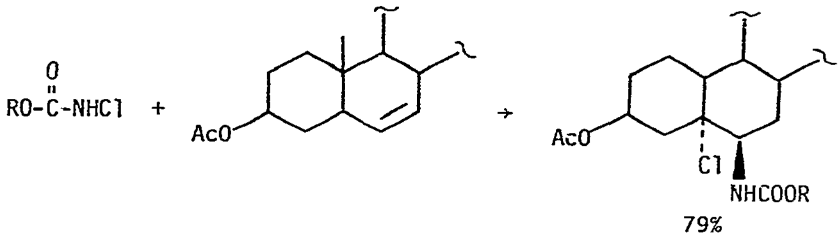
Ar = _p_-$NO_2$Ph (93%), _m_-$NO_2$Ph (74%), _p_-MeOPh (83%), _p_-ClPh (81%), Ph (71%), _p_-MePh (73%), 2,4,6-$Cl_3$Ph (92%), 2,4,6-$(MeO)_3$Ph (0%)

Alkynes were converted to mixtures of E and Z vinyl dihalides in greater than 80% yield by treatment with copper(II) chloride and lithium chloride in acetonitrile (eq. 170) [532]. Chromous chloride promoted the addition of N-haloamides to olefins. N-Chlorocarbonates added to steroidal olefins in fair yield, but cyclopentene gave only 20% yield of addition product. 1-Octyne also reacted in low yield (eq. 171). The addition of N-chlorourethanes to conjugated dienes was also studied. Both 1,2- and 1,4-addition occurred [533]. The reaction mechanism was studied and was shown to go via a radical chain pathway [534]. The complex $(CO)_4FeNMe_3$, prepared from trimethylamine oxide and iron pentacarbonyl, catalyzed the addition of carbon tetrachloride to olefins. Bridged polycyclic olefins underwent rearrangement as well as addition (eq. 172) [535]. Olefins reacted with chromyl chloride in a 2:1 mixture of dichloromethane and acetylchloride to produce predominantly cis chlorohydrin acetates as mixtures of regioisomers in 60-70% yields [536]. Ferric chloride in ether was an efficient reagent to open epoxides to trans chlorohydrins in high yield. It was claimed to be as good or better than HCl or magnesium bromide. However, it was not completely general. Stilbene oxide was rearranged to diphenylacetaldehyde by this reagent [537].



(170)

| | | | | | |
|---|---|---|---|---|---|
| R = Ph, R' = H | 95% | 95:5 E:Z | R = Ph, R' = Et | 94% | 95:5 E:Z |
| R = Ph, R' = Me | 94% | 98:2 E:Z | R = Ph, R' = _t_-Bu | 95% | 21:79 E:Z |



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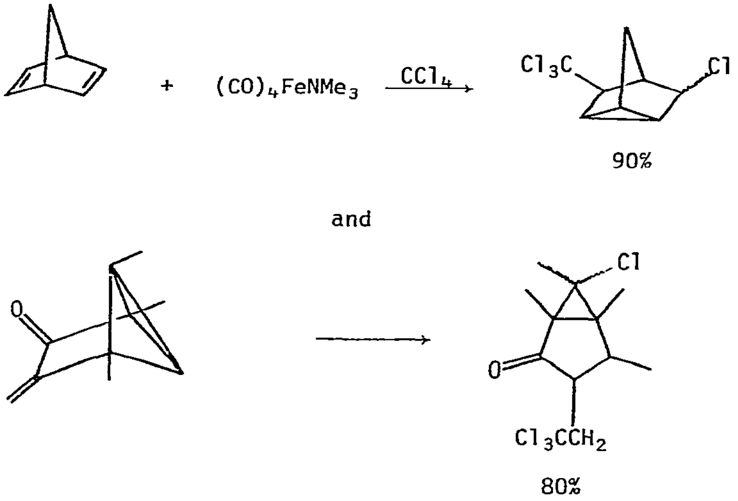
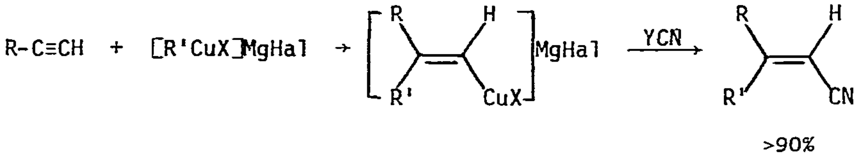


(172)

### B. Amides, Nitriles

Terminal acetylenes underwent a regio- and stereospecific cis addition of alkylcopper halide/magnesium halide complexes to produce terminal vinyl cuprates which were converted to substituted acrylonitriles by treatment with ClCN, $PhSO_2CN$ or TsCN in greater than 90% yield (eq. 173) [538]. Cyclic ketones were cleaved to ω-cyanoesters by treatment with $Na_3Fe(NO)CN_5$ (eq. 174) [539]. An angular nitrile group was introduced into decalin systems by conversion to iron cyclohexadienyl cationic complexes and treatment with sodium cyanide (eq. 175) [540]. The addition of hydrogen cyanide to olefins has been reviewed [541].



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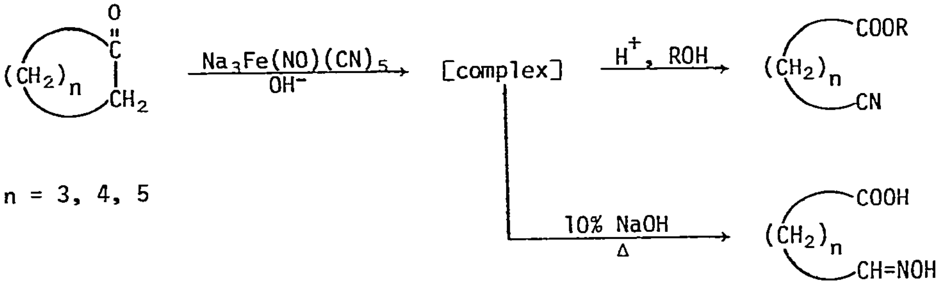

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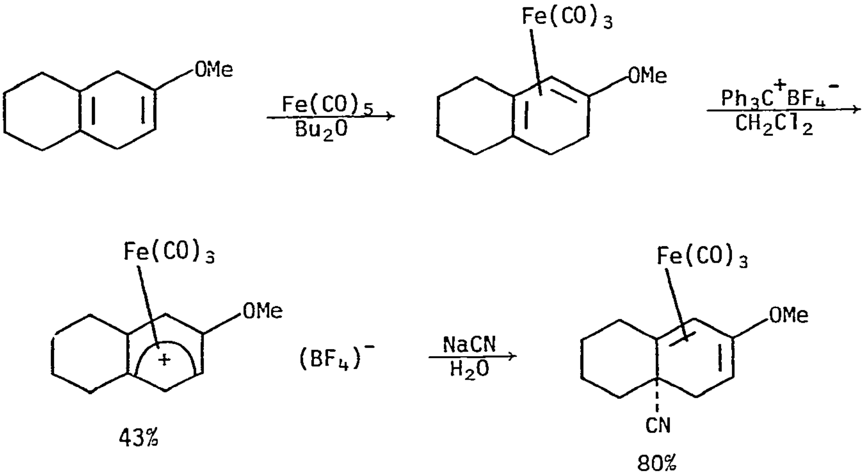
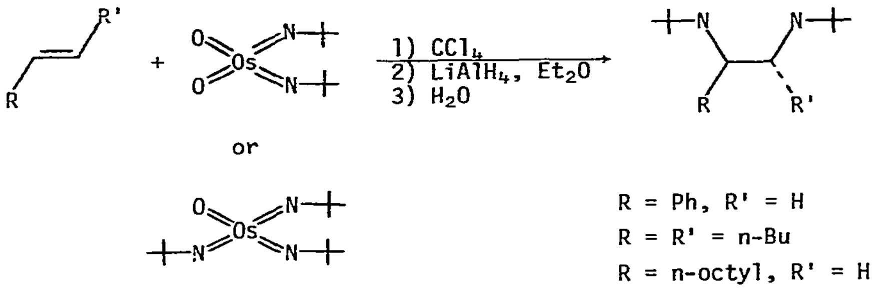


(175)

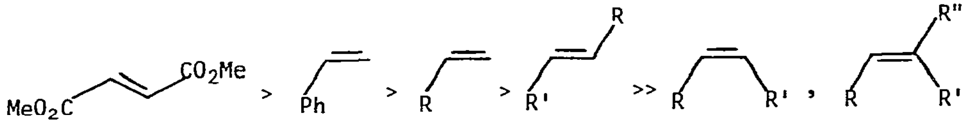
## C. Amines

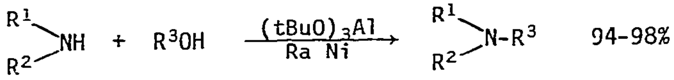
(S)-Glutamic acid was synthesized in 100% yield and 10-46% optical yield from methyl acrylate, sodium Δ-bis[N-salicylideneglycinato]cobaltate(III) and sodium Δ-bis[N-3-methylsalicylideneglyicinato]cobaltate(III) at pH 11.4. Diastereomeric complexes were formed and electrochemically reduced [542]. Styrene, 1-octene and cis-2-octene were converted to the corresponding N-alkylaziridines by treatment with a primary amine and palladium chloride followed by an oxidative cleavage ($Br_2$) of the σ-alkylpalladium complex [543]. Olefins were diaminated by osmium-imine complexes (eq. 176) [544]. Primary and secondary amines were converted to secondary and tertiary amines by alkylation with alcohols in the presence of tri-t-butoxyaluminum and Raney nickel (eq. 177) [545]. α-t-Butyloxy- and α-acetoxyacrylonitriles were converted to imides upon treatment with ferric chloride in acetic anhydride (eq. 178) [546].



(176)

R = Ph, R' = H 89%
R = R' = n-Bu 76%
R = n-octyl, R' = H 63%

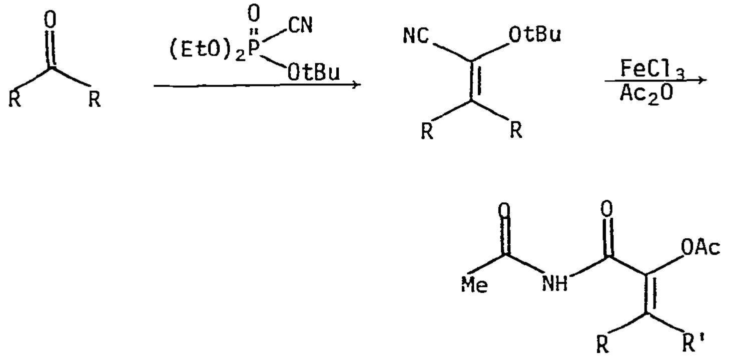




94-98%

(177)

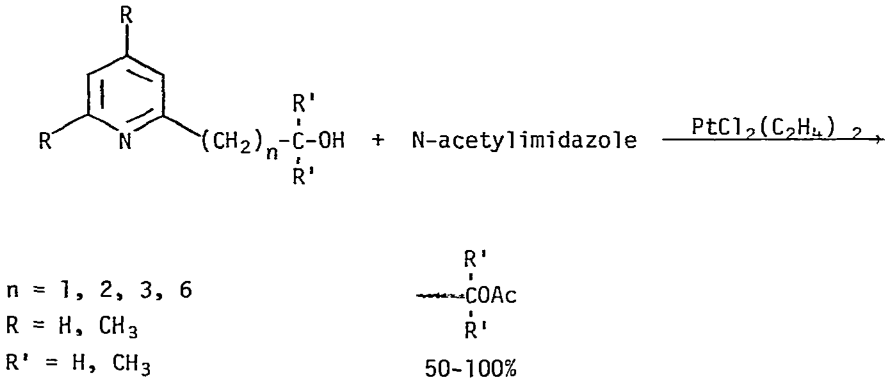
$R^1 = Ph$; $R^2 = H, Me$; $R^3 = n\text{-}Pr.i\text{-}Pr$
$-(CH_2)_5-$



(178)

### D. Ethers, Esters

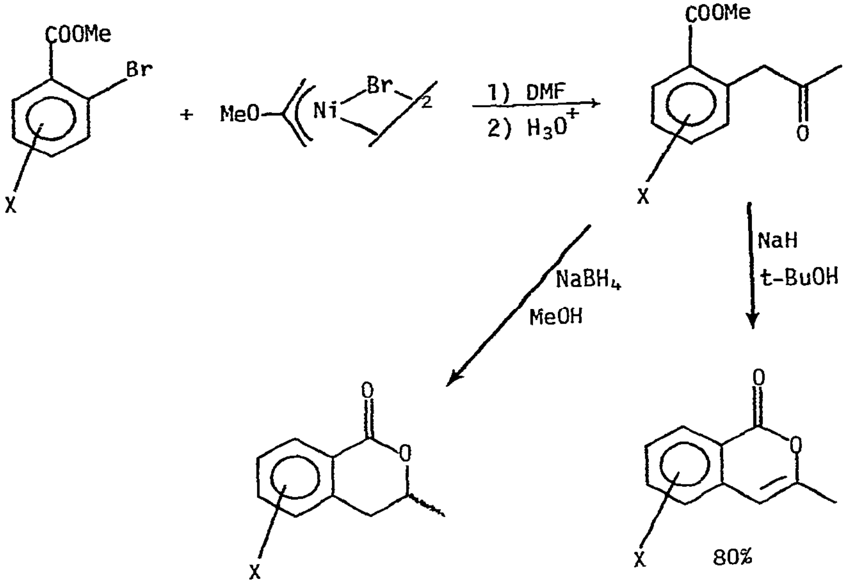
Methanol added 1,4 to methacrylic esters in the presence of nickel(II) acetylacetonate, sodium hydroxide, triphenylphosphine and triethylaluminum in 98% yield. With base but no nickel salts, only 30% yield was obtained [547]. N-Acetylimidazole acetylated alcohols in 50-100% yield in the presence of a platinum(II) olefin complex as catalyst in nonpolar media under mild conditions (eq. 179) [548]. The mechanism of aromatic acetoxylation by potassium peroxydisulfate/acetic acid with 2,2'-bipyridine/palladium(II) acetate complexes as catalyst was studied [549].



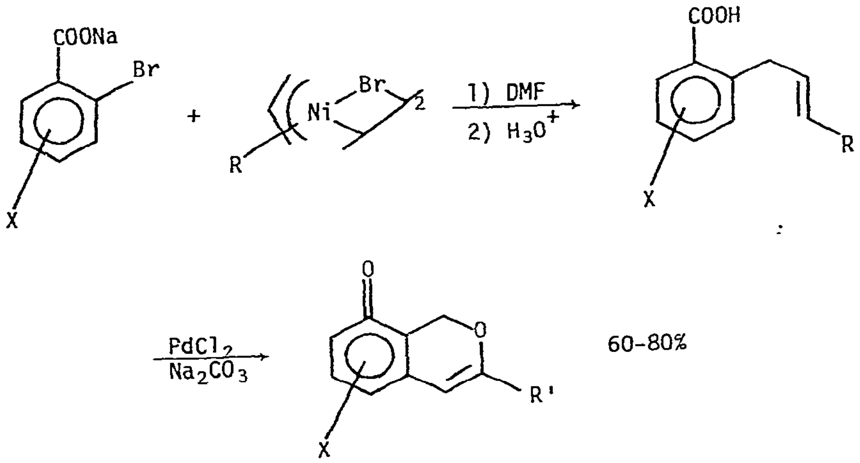
(179)

## E. Heterocycles

Two new approaches to the synthesis of isocoumarins, dihydroisocoumarins and isoquinolones have been developed. Treatment of a variety of substituted 2-bromobenzoic esters with π-(2-methoxyallyl)nickel bromide in DMF produced substituted 2-acetonylbenzoic esters. Treatment of these with sodium hydride in t-butanol produced isocoumarins in excellent yield. Alternatively, reduction by sodium borohydride produced the dihydroisocoumarins (eq. 180). The other approach consisted of the reaction of 2-bromobenzoic acids with π-allylnickel halides to produce 2-allylbenzoic acids. Cyclization to isocoumarins was effected by palladium chloride and sodium carbonate. Isoquinolones were prepared in a similar fashion (eq. 181) [550]. Unsaturated carboxylic acids were cyclized to 2-buten-4-olides upon reaction with lithium chloropalladate (eq. 182) [551]. The mechanism of preparation of α-methylene lactones from acetylenic alcohols and carbon monoxide using $Pd(PPh_3)_4$ as cyclizing agent was found to involve intramolecular acetylene insertion during cyclization [552]. Ring opening of β-methylene-β-lactones by trimethylsilylmethylmagnesium chloride in the presence of a nickel chloride catalyst produced a β-keto-γ-trimethylsilyl carboxylic acid, which upon treatment with an aldehyde, titanium tetrachloride, and acid hydrolysis gave pentenolides in fair yield (eq. 183) [553]. Oxidative cleavage of the copper complex of 3,5-ditertiarybutyl catechol produced a lactone in low yield (eq. 184) [554]. Mixed silylketals of cyclopropanone reacted with aldehydes in the presence of titanium tetrachloride to give γ-lactones in excellent yield (eq. 185) [555]. Vinyl oxiranes reacted with carbon monoxide and rhodium catalysts to give β,γ-unsaturated δ lactones, while iron and cobalt catalysts give α,β-unsaturated δ lactones (eq. 186) [556]. A cyclohexadiene substituted diazoacetylacetonate reacted with copper acetylacetonate in refluxing xylene to give a polycyclic

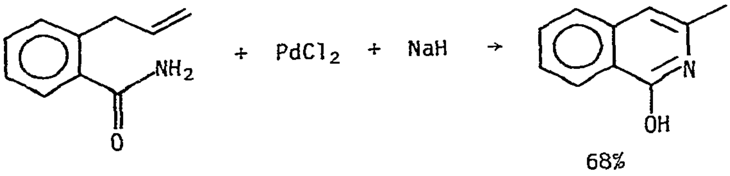

COOMe
Br
X
+
MeO
Ni
Br
2
1) DMF
2) $H_3O^+$
COOMe
O
X
NaBH₄
MeOH
NaH
t-BuOH
O
O
X
O
O
X
80%

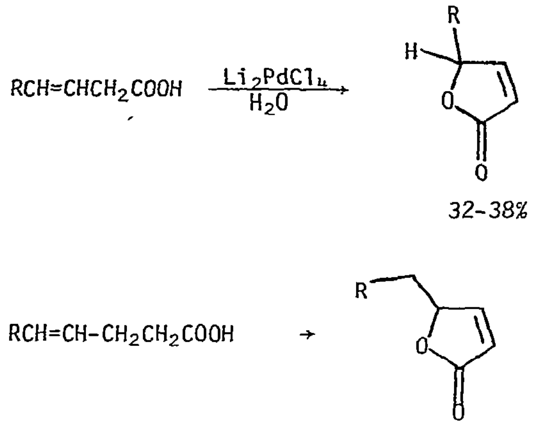
(180)


COONa
Br
X
+
R
Ni
Br
2
1) DMF
2) $H_3O^+$
COOH
R
X
$PdCl_2$
$Na_2CO_3$
O
O
R'
X
60-80%

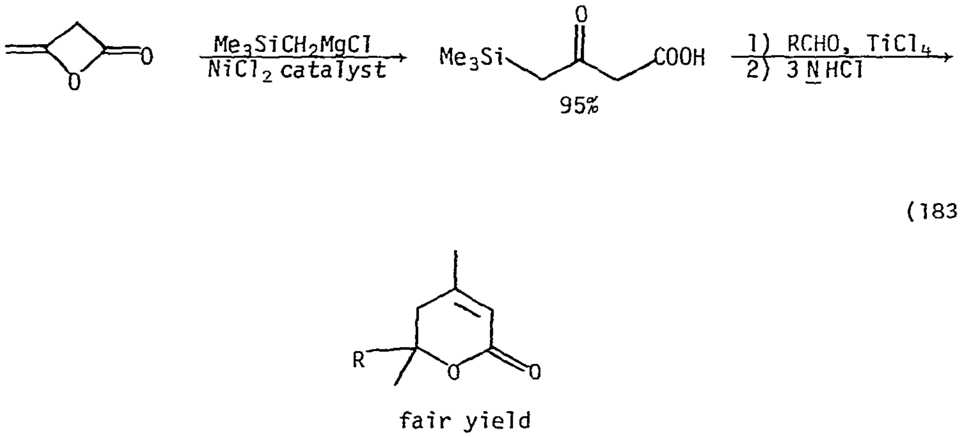
(18

also

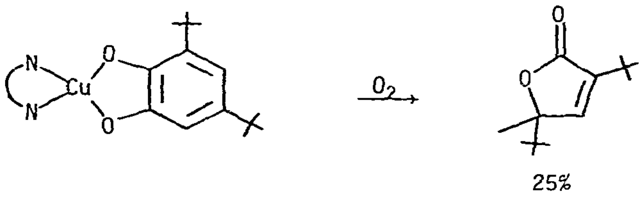

$NH_2$
O
+
$PdCl_2$
+
NaH
→
N
OH
68%



(182)

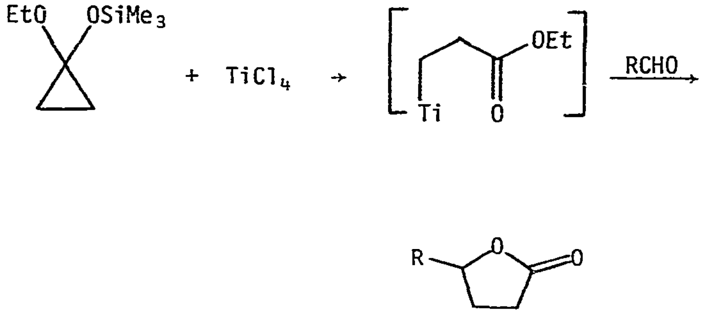


(183)



(184)

lactone in excellent yield (eq. 187) [557]. Certain hydroxyacid salts of rigid conformation lactonized rapidly in the presence of copper(II) and zinc(II) salts [558]. Chiral 4-alkyl-γ-lactones were prepared from alkenyl glutamic acid enantiomers by a sequence which involved organocuprate alkyla-



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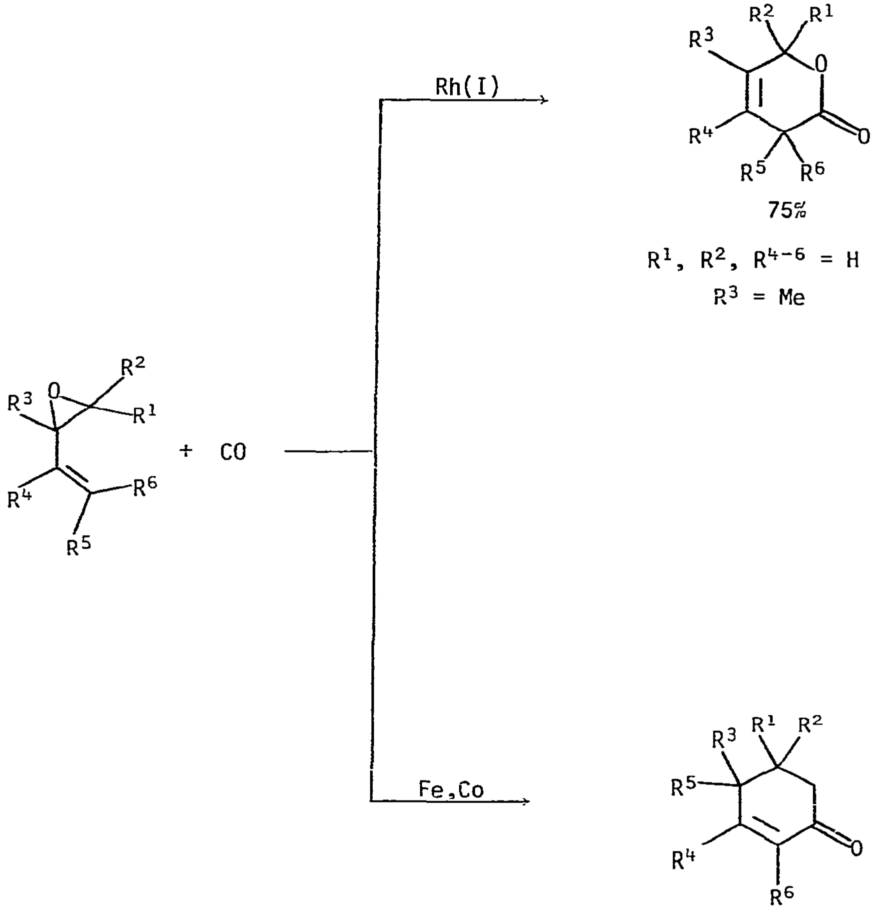


75%

$R^1$, $R^2$, $R^{4-6}$ = H

$R^3$ = Me

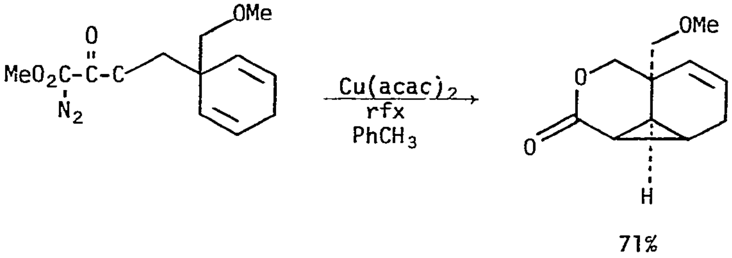
(186)

$R^3$ = alkyl favors lactone

$R^1$, $R^6$ = alkyl → acyclic ketones

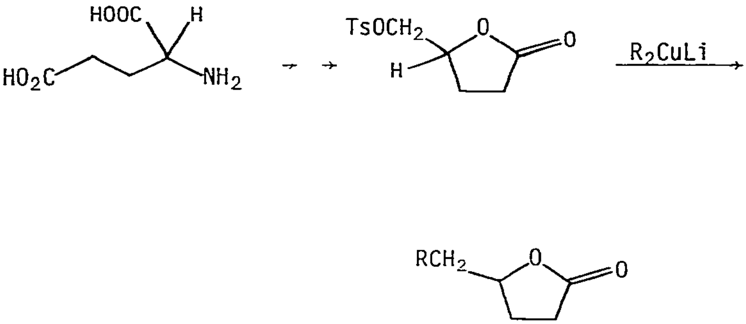
$R^5$ = COOMe → loss of $CO_2$

tion of a tosylate of the lactone without ring opening (eq. 188) [559]. 1-Hexyne reacted with carbon dioxide in the presence of $Ni(COD)_2$ and chelating diphosphines to give 4,6-dibutyl-2-pyrone in low yield [560].

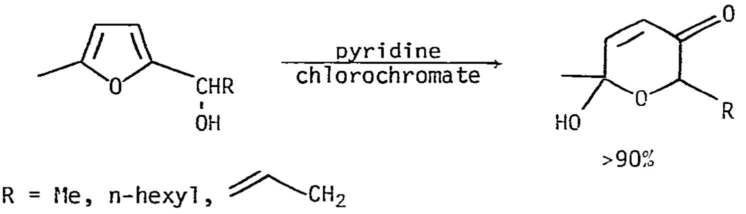


(187)

Oxidation of 2-hydroxyalkylfurans with pyridinium chlorochromate gave hydroxypyranones in high yield (eq. 189) [561]. Carbon monoxide reacted with some chloro-π-allylpalladium chloride complexes to produce butenolides (eq. 190) [562].



(188)



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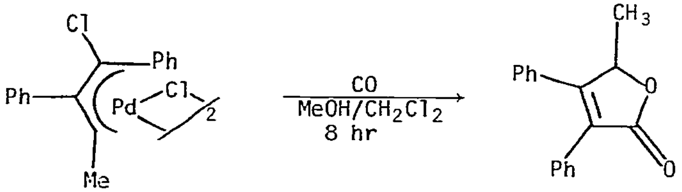
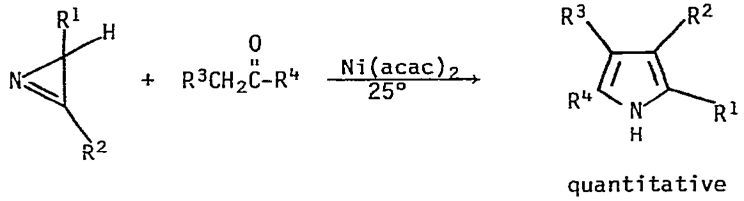


(190)

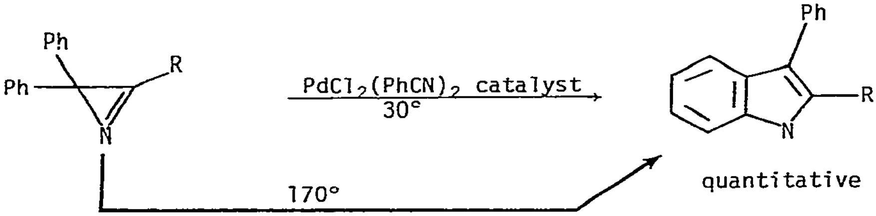
Azirenes reacted with ketones in the presence of nickel(II) acetylacetonate to produce pyrroles in quantitative yield (eq. 191) [563]. Diphenylazirenes reacted with palladium(II) chloride catalyst at 30° or without catalyst at 170° to produce indoles quantitatively (eq. 191) [564].

Carbazole was prepared from phenothoazine by desulfurization with $(COD)_2Ni$ and 2,2'-bipyridyl in 60% yield (eq. 193) [565]. N-Allyl-2-bromoacetamides reacted with a catalytic amount of palladium acetate, triphenylphosphine and TMEDA in DMF at 125° to produce N-acetylindoles. A similar procedure with N-allyl-benzylamines gave isoquinolines in low yield (eq. 194) [566]. Annelated pyridines were prepared by the cobalt catalyzed cooligomerization of $\alpha,\omega$-diynes and nitriles (eq. 195) [567]. Pyridones were prepared in a



(191)

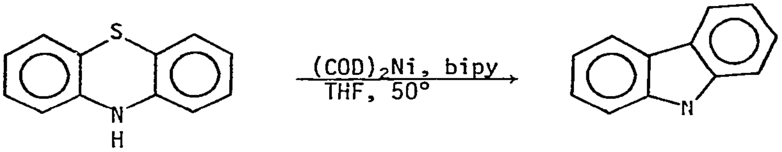
$R^1$ = H, Me, Ph
$R^2$ = Ph
$R^3$ = COMe, COPh, CN, COOEt
$R^4$ = Me, Ph



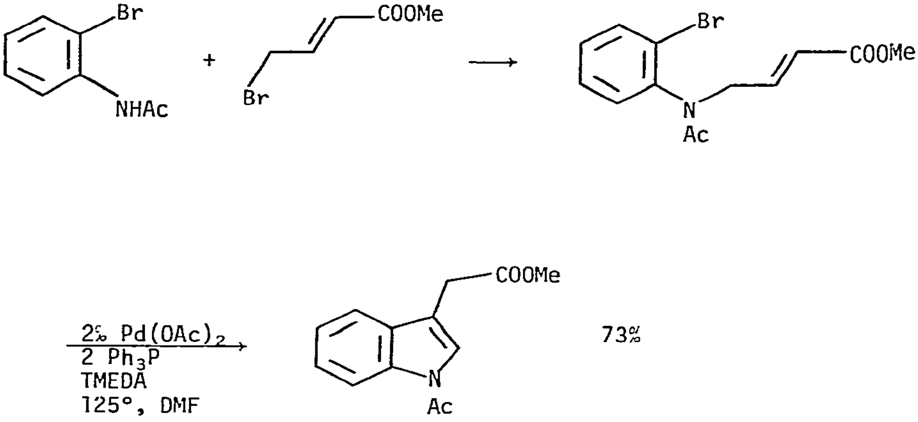
(192)

R = H, Me, Ph

similar fashion from alkynes and isocyanates (eq. 196) [568]. The same products resulted from treatment of the intermediate cobaltacyclopentadiene with isocyanates (eq. 197) [569]. Isoquinoline N-oxides were produced by treatment of 2-bromobenzaldehyde- or -acetophenone oximes with stabilized carbanions in the presence of copper(I) bromide (eq. 198) [570]. Imines condensed with silyl acetals in the presence of titanium tetrachloride to produce $\beta$-lactams in 40-90% yields (eq. 199) [571]. In an elegant approach to $\beta$-lactams, cyclopentadienyl iron olefin cationic complexes were aminated, then oxidatively cyclized (eq. 200) [572]. Copper(II)

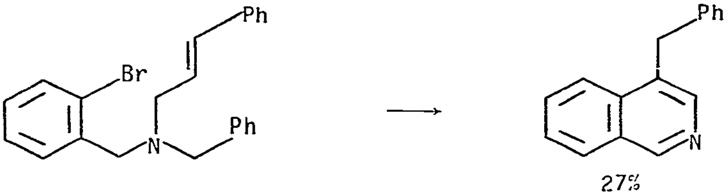


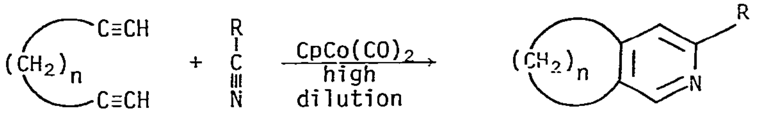
(193)



73%

also (194)



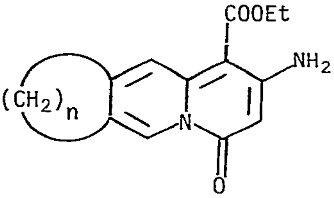


(195)

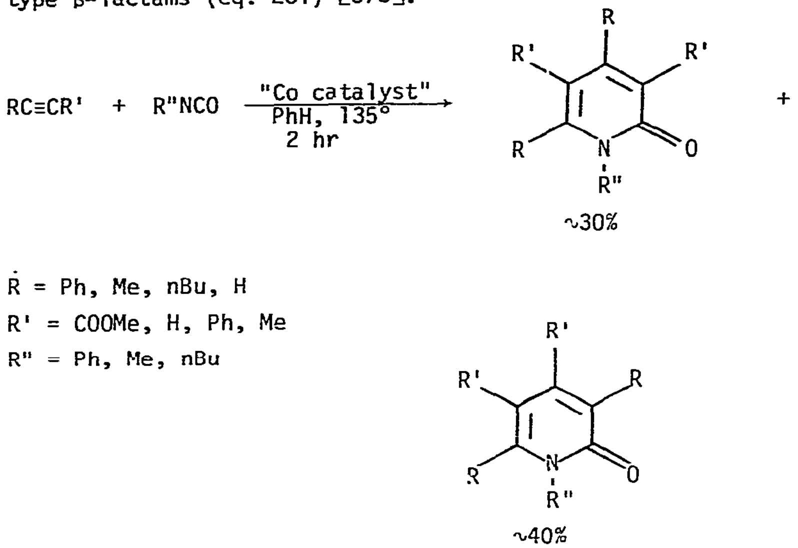
n = 3, 4, 5 n = 3, 4

R = n-Bu, Ph, Me, $CH_2OMe$, COOEt, $CH_2COOEt$, $CH_2CH_2CN$, $C_6F_5$, t-Bu

with R = $CH_2COOEt$ and excess RCN →



acetylacetonate rearranged penicillin type β-lactams to cephalosporin type β-lactams (eq. 201) [573].

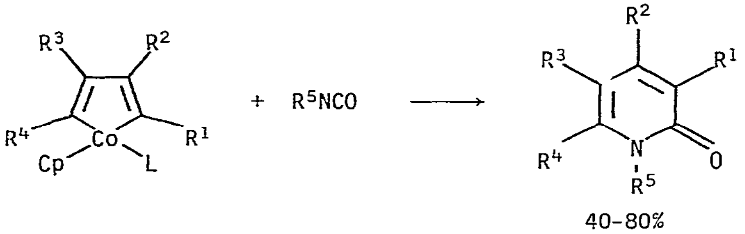


(196)

R = Ph, Me, nBu, H

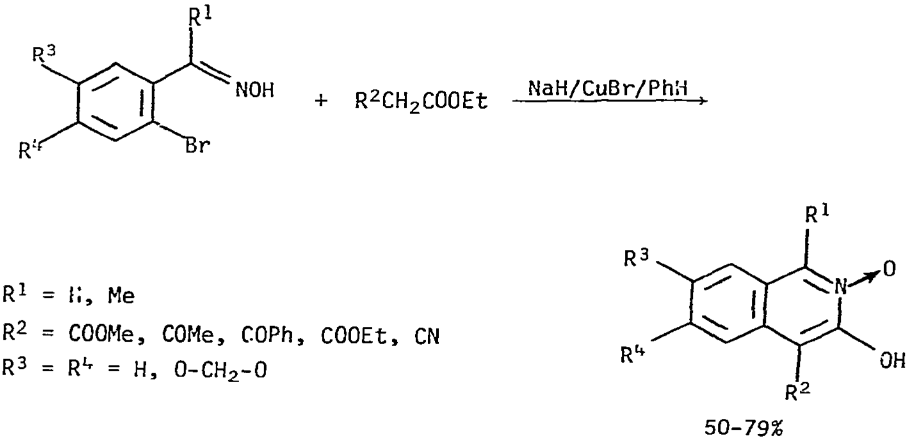
R' = COOMe, H, Ph, Me

R" = Ph, Me, nBu



(197)

(from alkyne) same R's as in eq. 196.

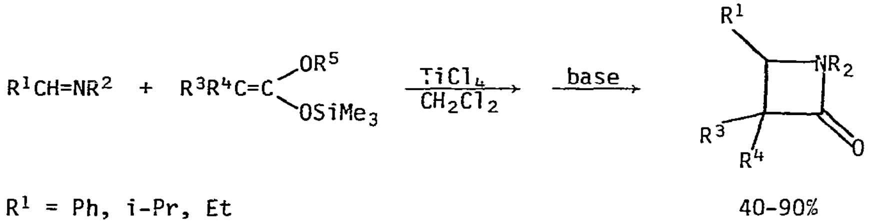


(198)

$R^1$ = H, Me

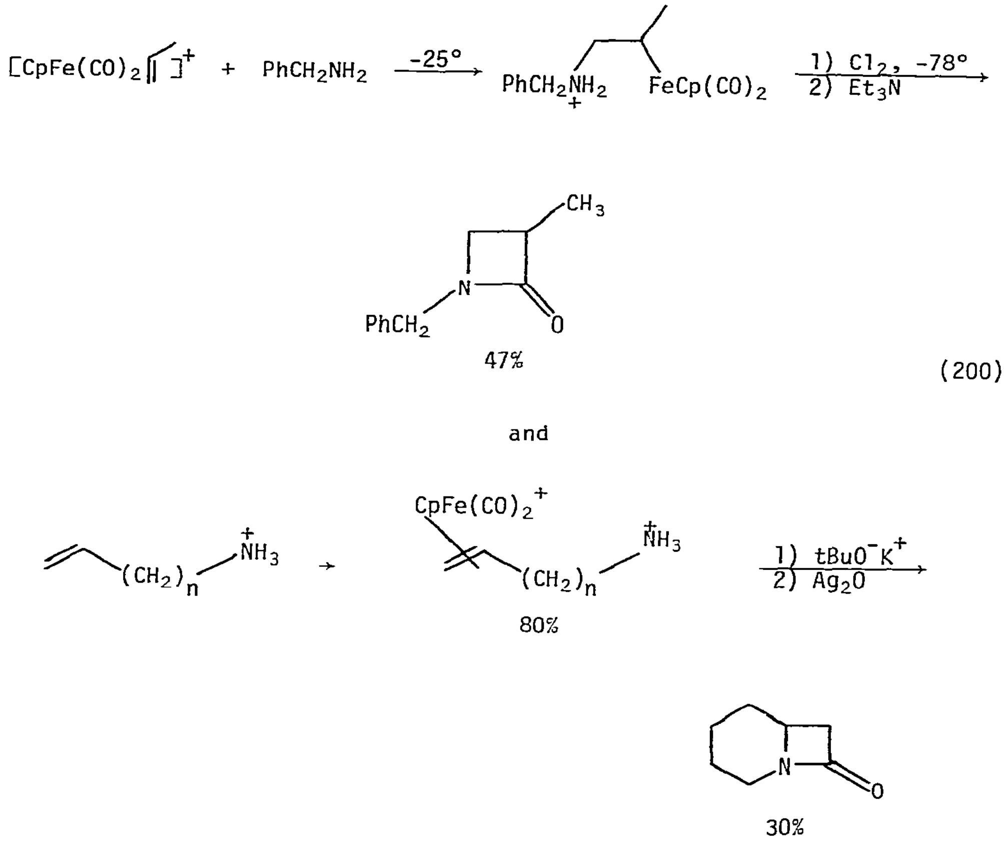
$R^2$ = COOMe, COMe, COPh, COOEt, CN

$R^3$ = $R^4$ = H, O-$CH_2$-O



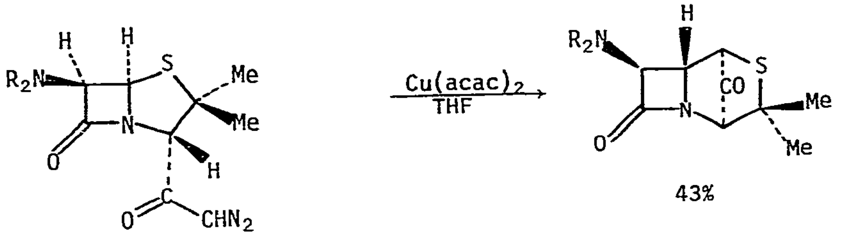
(199)

$R^1$ = Ph, i-Pr, Et
$R^2$ = Ph, $PhCH_2$, Me
$R^3$ = $R^4$ = Me, $(CH_2)_5$
$R^5$ = Me



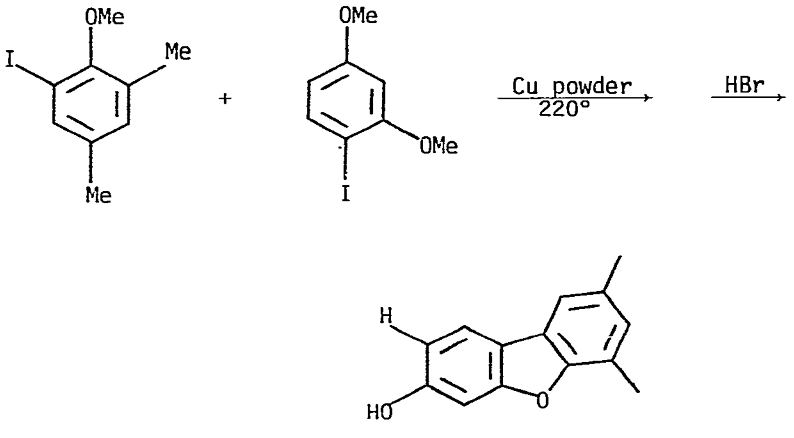
(200)

Chlorodibenzofurans were formed by the cyclization of diphenylethers with palladium acetate [574]. Dibenzofurans were also formed by the condensation of iodoarenes with 2,4-dimethoxyiodobenzene by copper powder at 220° (eq. 202) [575]. Diazodimethylmalonate condensed with enol ethers of cyclohexanone in the presence of $(MeO)_3PCuI$ to produce after several other steps β-methylfurans (eq. 203) [576]. The iron catalyzed decomposition of unsaturated cyclic peroxides from butadiene produced furans in high yield

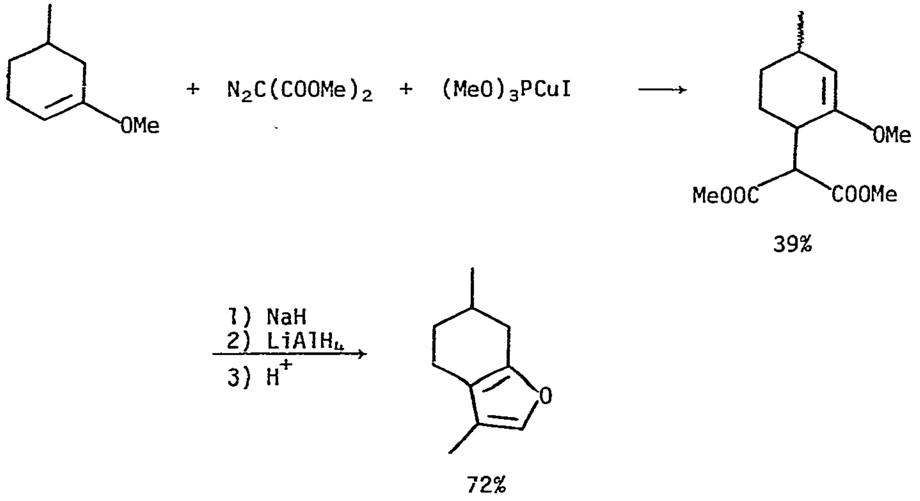


(201)

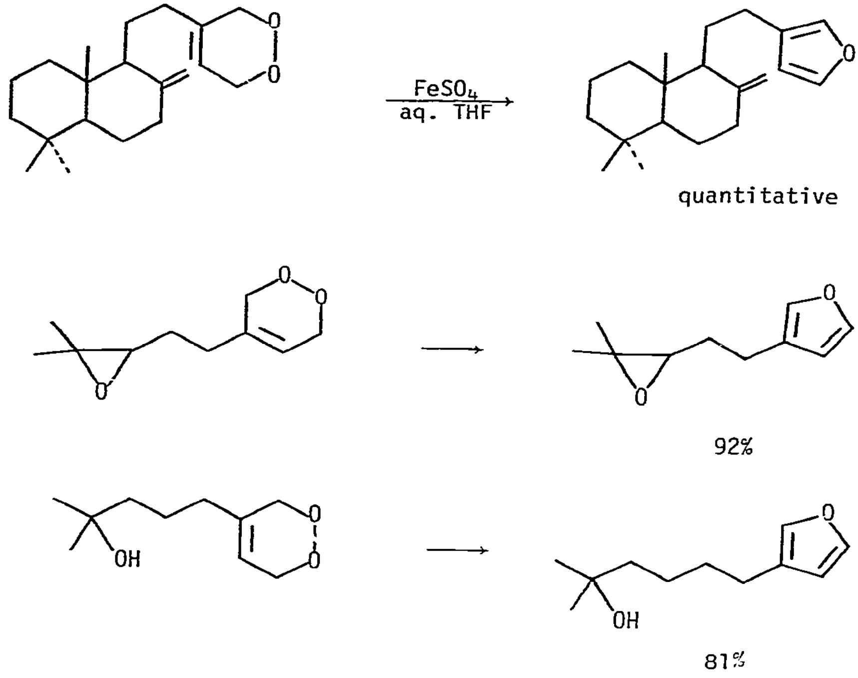
(eq. 204) [577]. Diiron enacarbonyl effected the condensation of amides with α,α'-dibromoketones to produce 3(2H)-furanones. This was used as a route to muscarines (eq. 205) [578]. Palladium chloride catalyzed the cyclization of 1,4-diols to furans, and 1,5-pentanediol to tetrahydropyran in high yield [579]. A bridged bicyclic triether was produced from acetylacetone via a platinum complex (eq. 206) [580].



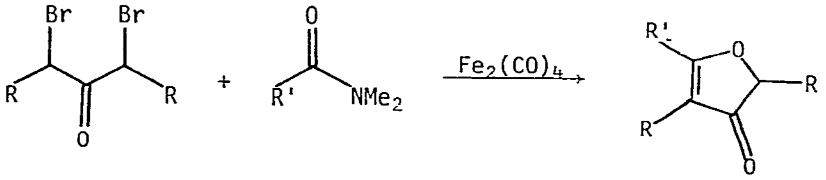
(202)



(203)

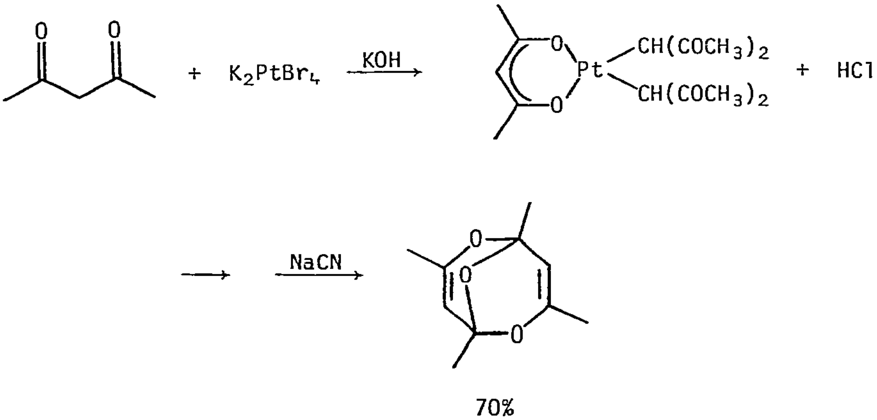


(204)



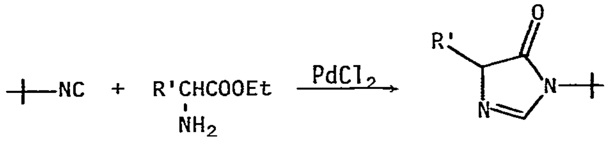
(205)

R = Me, Et, i-Pr, t-Bu
R' = H, Me, Ph



(206)

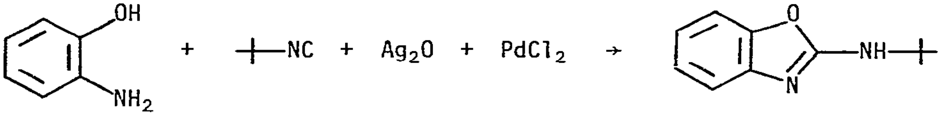
Imidazolones and iminoxazolidines were prepared by the palladium chloride assisted reaction of isonitriles with α-aminoesters and 2-hydroxyaniline respectively (eq. 207) [581]. π-Allylpalladium chloride reacted with 1,3 dipolar species $Ph\overset{+}{C}{=}N{=}\overset{-}{N}{-}Ph$ to give both the dimer and the allyl adduct of the dipolar species. The allyl adduct was thought to occur via



(20

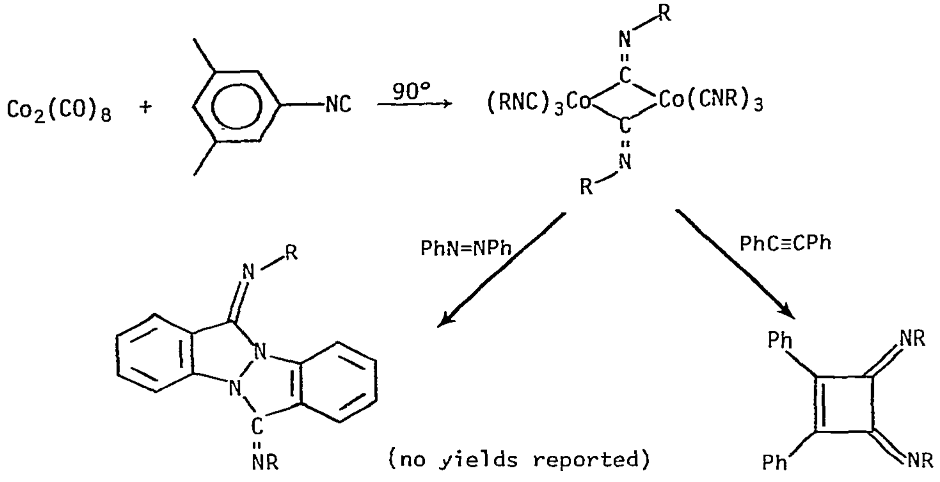
R' = Me (42%); $PhCH_2$ (80%); i-Pr (82%); sec Bu (70%)

also



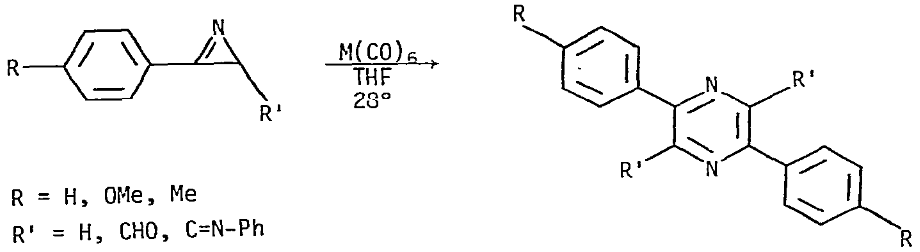
84%

generation of allyl chloride followed by cycloaddition, rather than by cycloaddition to the palladium complex itself [582]. A variety of heterocycles were available from the intermediate produced from the reaction of isonitriles with dicobalt octacarbonyl (eq. 208) [583]. Phenylazirenes dimerized upon treatment with chromium, molybdenum and tungsten carbonyls. Other heterocycles were available by slight variation of this scheme (eq. 209) [584]. Azobenzenes reacted with isonitriles in the presence of dicobalt octacarbonyl to produce 6H,12H-indazolo[2,1,a]-6,13-diiminoindazol (eq. 210). Yields were not reported [585]. Oxazoles were synthesized by the tungsten hexachloride decomposition of α-diazoketones in the presence of nitriles (eq. 211) [586]. Isoxazolidines were formed in the reaction of oximes with butadiene and palladium nitrate-triphenyl phosphine (eq. 212) [587]. Reactions of organometallic compounds in the heterocyclic field has been reviewed (7 references) [588].



(no yields reported)

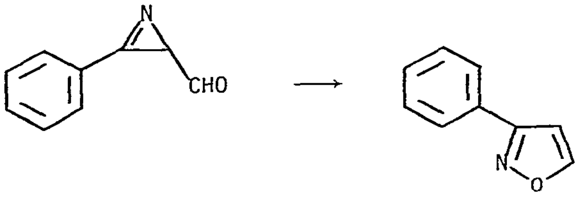
(208)



60%

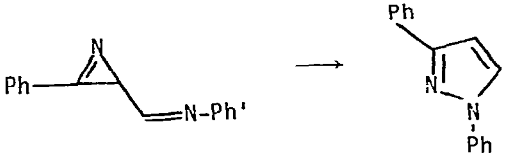
R = H, OMe, Me
R' = H, CHO, C=N-Ph

also

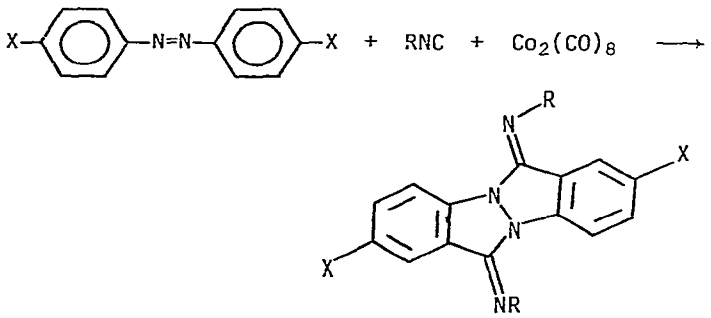


80%

(209)



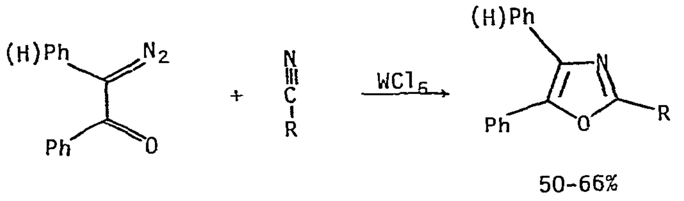
67-86%



(210)

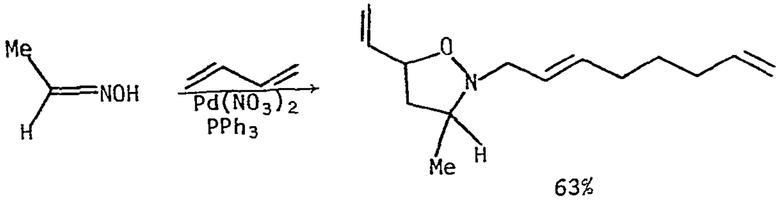
## H. Miscellaneous

Allylphenyl and benzylphenyl ethers underwent carbon-oxygen bond cleavage upon treatment with zero valent nickel complexes such as $(COD)_2Ni$ and $Ni(PEt_3)_4$[589]. Similarly, para substituted (H, Br, Me, OMe, Cl, $SiMe_3$, $CMe{=}CH_2$, $CH_2CH_2OAc$, COOMe, $CHOAcCH_3$) benzylallyl ethers were cleaved



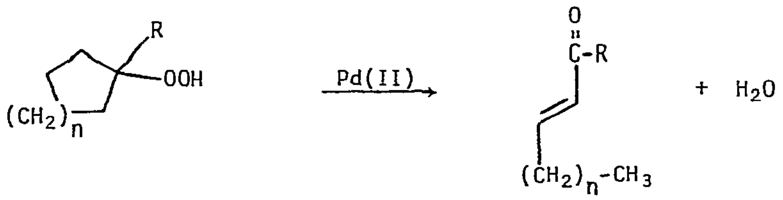
(211)

R = Ph, Me, Et, vinyl



(212)

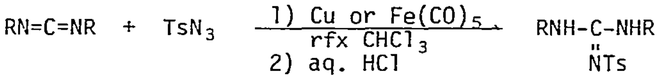
to the corresponding para substituted benzaldehyde in 64-83% yield using homogeneous $RuCl_2(PPh_3)_3$ as a catalyst [590]. Epoxides were cleaved to a mixture of glycol mono- and diformates by $RuCl_2(PPh_3)_3$ catalyst, carbon dioxide and hydrogen at 100° and 40 atmospheres [591]. Imidazole esters hydrolyzed $10^3$ to $10^5$ faster when catalyzed by hydroxo species of nickel(II) and cobalt(II), compared to the hydroxide ion mediated hydrolysis [592]. Cyclic hydroperoxides were ring opened to conjugated ketones by palladium(II) catalysts (eq. 213) [593].



(213)

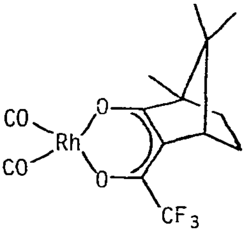
R = H n = 1, 75%; n = 2, 50%; n = 3, 35%; n = 4, 20%
R = Me n = 2, 80%

Dimethyl diazomalonate reacted with sulfoximines in the presence of copper salts to replace oxygen by the malonate group in 40-60% yield. Using chiral sulfoximines the reaction went with retention [594]. Thioesters were converted to t-butylesters by treatment with metal salts ($Hg(TFA)_2$, AgTFA, CuTFA, $AgBF_4$). This conversion was used in a partial synthesis of cytochalasins A and B [595]. Carbodiimides were converted to N-tosyliminoureas by treatment with tosylazide in the presence of copper or iron pentacarbonyl (eq. 214) [596]. Aryl iodides were converted to aryl selenocyanates by treatment with KSeCN in HMPT at 100° using copper(I) iodide as a catalyst [597]. Alkyl selenocyanates and thiocyanates were prepared from olefins by hydroboration followed by aqueous ferric selenocyanate or thiocyanate [598]. Allyl alcohol reacted with 2-bromothiophene in the presence of palladium acetate, sodium iodide and sodium carbonate to give the aldehyde 2-thienyl-$CH_2CH_2CHO$ in 77% yield. Other allylic alcohols also reacted in a similar fashion [599].



$$RN{=}C{=}NR \;+\; TsN_3 \;\xrightarrow[\text{rfx } CHCl_3 \quad 2)\text{ aq. } HCl]{1)\text{ Cu or } Fe(CO)_5}\; RNH{-}\underset{\underset{\displaystyle NTs}{\|}}{C}{-}NHR \qquad (214)$$

R = o-ClPh (72%), o-MePh (86%), Ph (57%), cyclohexyl (66%)

Treatment of glucose with anhydrous iron(III) chloride in dry acetone produced 1,2,5,6-di-o-isopropylidene-o(-D-glucofuranose) in 82% yield. This was claimed to be a good procedure for making sugar acetonides [600]. Finally, a squalene solution of chiral  was used as a liquid phase for the separation of the two enantiomers of 3-methylcyclopentene. Quantitative resolution in 3 hr at 27° was reported [601].

## VI. Reviews

The following reviews and theses have appeared:

"Preparations of Highly Reactive Metal Powders and Their Use in Organic and Organometallic Synthesis" [602]

"Titanium Tetrachloride in Organic Synthesis" (59 references) [603]

"Recent Advances in the Organometallic Chemistry of Titanium" (21 references) [604]

"Low Valent Titanium in Organic Synthesis" (thesis) [605]

"Organic Synthesis via Metal Carbonyls" (book) [606]

"Organopalladium Intermediates in Organic Synthesis" (219 references) [607]

"Selective Organic Transformations via π-Allylpalladium Compounds" (thesis) [608]

"Organic Synthesis with Palladium Compounds" (157 references) [609]

"Recent Progress in Organic Synthesis using Iron Carbonyl Complexes" (126 references) [610]

"Organic Synthesis with Iron Carbonyl" (197 references) [611]

"Organic Synthesis with Tetracarbonylferrate" (43 references) [612]

"Reactions of Olefins with Palladium and Rhodium Complexes" (7 references) [613]

"Organic Synthesis Using Transition Metal Compounds" (19 references) [614]

"Metal-Carbene Complexes in Organic Synthesis" (>150 references) [615]

"α Anions of Metal-Carbene Complexes in Organic Synthesis" (61 references) [616]

"Arene-Metal Complexes in Organic Synthesis" (55 references) [617]

"Organic Syntheses via Allylic Complexes of Metal Carbonyls" (300 referenc
[618]

"Transition Metal Hydrides in Organic Synthesis" (thesis) [619]

"Cyclometallation Reactions" (157 references) [620]

"Ortho-Metallation Reactions" (133 references) [621]

"Heterogeneous Catalysis: Some Recent Developments" (38 references) [622]

"Catalysis by Polynuclear Complexes: A Bridge Between Homogeneous and Heterogeneous Catalysis" (20 references) [623]

"How Asymmetry Might Be Induced in the Chiral Transition Metal Complex Catalyzed Reaction" (63 references) [624]

"Development and Applications of Homogeneous Catalysis and Organometallic Chemistry" (34 references) [625]

"Free Radicals in Organometallic Chemistry" (195 references) [626]

"Transition Metal Complexes of Olefinic Compounds" (285 references) [627]

"Organonitrile Complexes of Transition Metals" (156 references) [628]

"Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis" (298 references) [629]

"Catalysis of Symmetry Restricted Reactions by Transition Metal Compounds" (93 references) [630]

"Coordination in Applied Heterogeneous Catalysis" (90 references) [631]

"Activation of Alkanes by Transition Metal Compounds" (102 references) [632]

"The Homogeneous Catalytic Activation of Carbon-Hydrogen Bonds" [633]

"Mechanism of Oxidative Addition of Organic Halides to Group 8 Transition Metal Complexes" (49 references) [634]

"Cyclobutadienylmetal Complexes" (355 references) [635]

## REFERENCES

1. E. C. Ashby and J. J. Watkins, *J. Am. Chem. Soc.*, **99**, 5312 (1977).
2. E. C. Ashby and J. J. Lin, *J. Org. Chem.*, **42**, 2805 (1977).
3. K. Uchida, K. Utimoto and H. Nozaki, *Tetrahedron*, 2987 (1977).
4. H. Yamamoto, K. Kitatani, T. Hayama and H. Nozaki, *J. Am. Chem. Soc.*, **99**, 5816 (1977).
5. K. Kitatani, T. Hiyama and H. Nozaki, *Bull. Chem. Soc. Japan*, **50**, 1600 (1977).
6. M. Zembayashi, K. Tamao, T. Hayashi, T. Mise and M. Kumada, *Tetrahedron Lett.*, 1799 (1977).
7. A. McKillop and D. P. Rao, *Synthesis*, 759 (1977).
8. J. S. Kiely, P. Boudjouk and L. L. Nelson, *J. Org. Chem.*, **42**, 2626 (1977).
9. E.-i. Negishi and D. E. Van Horn, *J. Am. Chem. Soc.*, **99**, 3168 (1977).
10. E.-i. Negishi, A. O. King and N. Okukado, *J. Org. Chem.*, **42**, 1823 (1977).
11. A. Sekiya and N. Ishikawa, *J. Organomet. Chem.*, **125**, 281 (1977).
12. M. Kosugi, K. Sasazawa, Y. Shimizu and T. Migita, *Chem. Lett.*, 301 (1977).
13. J. F. Fauvarque and A. Jutland, *J. Organomet. Chem.*, **132**, C-17 (1977).
14. A. Commercon, J. F. Normant and J. Villieras, *J. Organomet. Chem.*, **128**, 1 (1977).
15. N. Miyaura, N. Sasaki, M. Itoh and A. Suzuki, *Tetrahedron Lett.*, 3369 (1977).
16. P. A. Wender and S. L. Eck, *ibid.*, 1245 (1977).
17. A. O. King, N. Okukado and E.-i. Negishi, *JCS Chem. Comm.*, 683 (1977).
18. K. Tamao, M. Zembayashi and M. Kumada, *Chem. Lett.*, 1237 (1976).
19. *Ibid.*, 1239 (1976).
20. A. A. Millard and M. W. Rathke, *J. Am. Chem. Soc.*, **99**, 4833 (1977).
21. N. Miyaura, M. Itoh and A. Suzuki, *Bull. Chem. Soc. Japan*, **50**, 2199 (1977).
22. M. B. Commercon, J. F. Normant and J. Villieras, *C. R. Hebd. Seances Acad. Sci. Ser. C*, **285**, 211 (1977).
23. K. Marwyama and Y. Yamamoto, *J. Am. Chem. Soc.*, **99**, 8068 (1977).
24. P. W. Raynolds, M. J. Manning and J. S. Swenton, *JCS Chem. Comm.*, 499 (1977).

25. C. Lion, *C. R. Hebd. Seances Acad. Sci. Ser. C*, **284**, 893 (1977).
26. S. A. Monti and J. M. Harless, *J. Am. Chem. Soc.*, **99**, 2690 (1977).
27. J. R. Normant, J. Villieras and F. Scott. *Tetrahedron Lett.*, 3263 (1977).
28. H. des Abbayes and M. A. Boudeville, *J. Org. Chem.*, **42**, 4104 (1977).
29. J. E. Mansson, M. Nilsson and O. Wennerstrom, *Acta Chem. Scand., Ser. B*, **B31**, 47 (1977).
30. C. U. Pittman and R. M. Haines, *J. Org. Chem.*, **42**, 1195 (1977).
31. N. Miyaura, N. Sasaki, M. Itoh and A. Suzuki, *Tetrahedron Lett.*, 173 (1977)
32. J-E. Dubois, P. Fournier and C. Lion, *Bull. Soc. Chim. Fr.*, 1871 (1976).
33. Y. Tohda, K. Sonoagashira and N. Hagihara, *Synthesis*, 777 (1977).
34. M. Kosugi, Y. Shimiza, T. Migata, *J. Organomet. Chem.*, **129**, C36 (1977).
35. G. Cahiez, P. Bernard and J. F. Normant, *Synthesis*, 130 (1977).
36. T. C. Flood and A. Sarhangi, *Tetrahedron Lett.*, 3861 (1977).
37. D. B. Carr and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 640 (1977).
38. R. A. Holton and R. A. Kjonaas, *J. Am. Chem. Soc.*, **99**, 4177 (1977).
39. R. A. Holton and R. A. Kjonaas, *J. Organomet. Chem.*, **142**, C15 (1977).
40. R. A. Holton, *J. Am. Chem. Soc.*, **99**, 8083 (1977).
41. T. Hayashi and L. S. Hegedus, *J. Am. Chem. Soc.*, **99**, 7093 (1977).
42. B. W. Roberts and J. Wong, *JCS Chem. Comm.*, 20 (1977).
43. P. Lennon, A. M. Rosan and M. Rosenblum, *J. Am. Chem. Soc.*, **99**, 8426 (1977).
44. W. R. Jackson and J. U. Strauss, *Aust. J. Chem.*, **30**, 553 (1977).
45. S. Numata and H. Kurosawa, *J. Organomet. Chem.*, **131**, 301 (1977).
46. A. Kasahara, T. Izumi and M. Maemura, *Bull. Chem. Soc. Japan*, **50**, 1021 (1977).
47. D. Salari and A-A Entezami, *C. R. Hebd. Seances Acad. Sci. Ser. C*, **285**, 81 (1977).
48. T. C. Zebovitz and R. F. Heck, *J. Org. Chem.*, **42**, 3907 (1977).
49. S.-i. Murahashi, M. Yamamura and N. Mita, *ibid.*, **42**, 2870 (1977).
50. A. K. Yatsimirskii, A. D. Ryabov and I. V. Berezin, *Dokl. Akad. Nauk SSSR*, **236**, 942 (1977).
51. I. Kozhevnikov, *React. Kinet. Catal. Lett.*, **5**, 439 (1976).
52. D. Holland, D. J. Milner and H. W. B. Reed, *J. Organomet. Chem.*, **136**, 111 (1977).
53. K. Kikukawa and T. Matsuda, *Chem. Lett.*, 159 (1977).
54. F. Akiyama, S. Teranishi, Y. Fujiwara and H. Taniguchi, *J. Organomet. Chem.*, **140**, C7 (1977).
55. T. Aratani, Y. Yoneyoshi and T. Nagase, *Tetrahedron Lett.*, 2599 (1977).
56. A. Nakamura, Y. Yoshida, M. Cowie and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2108 (1977).
57. S. Bien and Y. Segal, *J. Org. Chem.*, **42**, 1685 (1977).
58. Y. Ito, T. Hirao, N. Ohta and T. Saegusa, *Tetrahedron Lett.*, 1009 (1977).

59. C. P. Casey and W. R. Brunswold, *Inorg. Chem.*, **16**, 391 (1977).
60. C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc.*, **99**, 6097 (1977).
61. P. Binger and U. Schuchordt, *Angew. Chem. Int. Ed.*, **16**, 249 (1977).
62. G. Henrici-Olive and S. Olive, *Top. Curr. Chem.*, **67**, 107 (1976).
63. H. Westmijze, H. Kleijn and P. Vermeer, *Tetrahedron Lett.*, 2023 (1977).
64. H. Westmijze, J. Meijer and P. Vermeer, *Rec. Trav. Chim.*, **95**, 268 (1976).
65. A. B. Laz, P. Talley and J. A. Dunford, *Rec. Trav. Chim.*, **95**, 3545 (1977).
66. H. Westmijze, J. Meijer, H. J. T. Bos and P. Vermeer, *ibid.*, **95**, 299 (1977).
67. *Ibid.*, **95**, 304 (1976).
68. H. Westmijze, H. Kleijn, J. Mejier and P. Vermeer, *Tetrahedron Lett.*, 869 (1967).
69. J. Duboudin, B. Jousseaume, A. Alexis, G. Cahiez, J. Villieras and J. F. Normant, *C. R. Hebd. Seances Acad. Sci. Ser. C*, **285**, 29 (1977).
70. J. Douboudin, B. Jousseaume and A. Bonakdar, *ibid.*, **284**, 351 (1977).
71. H. Kleijn, J. Meijer, H. Westmijze and P. Vermeer, *Rec. Trav. Chim. Pays-Bas.*, **96**, 251 (1977).
72. A. Alexis, G. Cahiez, J. F. Normant and J. Villieras, *Bull. Soc. Chim. Fr.*, 693 (1977).
73. H. Yatagai, Y. Yamamoto, K. Mauryama, A. Sonada and S-i. Murahashi, *JCS Chem. Comm.*, 852 (1977).
74. K. Kaneda, T. Uchiyama, H. Kobayashi, Y. Fujiwara, T. Imanaka and S. Teranishi, *Tetrahedron Lett.*, 2005 (1977).
75. L. C. Smedley, H. E. Tweedy, R. A. Coleman and D. W. Thompson, *J. Org. Chem.*, **42**, 4147 (1977).
76. A. M. Caporusso, G. Giacomelli and L. Lardicci, *J. Org. Chem.*, **42**, 914 (1977).
77. R. F. Lockwood and K. M. Nicholas, *Tetrahedron Lett.*, 4163 (1977).
78. Y. Ito, T. Konoike, T. Harada and T. Saegusa, *J. Am. Chem. Soc.*, **99**, 1487 (1977).
79. Y. Kobayashi, T. Taguchi and E. Tokimo, *Tetrahedron Lett.*, 3741 (1977).
80. S-i. Inaba and J. Ojima, *Tetrahedron Lett.*, 2009 (1977).
81. A. Z. Rubezł , *Tetrahedron Lett.*, 2189 (1977).
82. W. Muenzenmaier and H. Straub, *Justus Liebigs Ann. Chem.*, 313 (1977).
83. J. E. McMurray and K. L. Kees, *J. Org. Chem.*, **42**, 2655 (1977).
84. D. Lenoir, *Synthesis*, 553 (1977).
85. A. L. Baumstark, C. J. McCloskey, T. J. Tolson and G. T. Syriopoulous, *Tetrahedron Lett.*, 3003 (1977).
86. I. Pir-Bar, O. Buchman and J. Blum, *Tetrahedron Lett.*, 1443 (1977).
87. Y. Okude, T. Hiyama and H. Nozaki, *Tetrahedron Lett.*, 3829 (1977).
88. T-L. Ho and G. Olah, *Synthesis*, 170 (1977).
89. M. Zembayashi, K. Tamao, J-i Yoshida and M. Kumada, *Tetrahedron Lett.*, 4089 (1977).

90. R. H. Mitchell, B. N. Ghose and M. C. Williams, *Can. J. Chem.*, **55**, 210 (1977).

91. S. Arai, Y. Yamagishi, S-G Totake and M. Hida, *Bull. Chem. Soc. Japan*, **50**, 547 (1977).

92. K. Tagaki, N. Hayama, T. Okamoto, Y. Sakakibara and S. Oka, *Bull. Chem. Soc. Japan*, **50**, 2741 (1977).

93. R. C. Larock and J. C. Bernhardt, *J. Org. Chem.*, **42**, 1680 (1977).

94. Y. Yamamoto, H. Yatagai, K. Maruyama, A. Sonoda and S-i. Murahashi, *J. Am. Chem. Soc.*, **99**, 5652 (1977).

95. G. van Koten, J.T.B.H. Jastrzebski and J. G. Noltes, *J. Org. Chem.*, **42**, 2047 (1977).

96. G. van Koten, R.W.M. ten Hoedt and J. G. Noltes, *ibid.*, **42**, 2705 (1977).

97. G. U. Menenga, A. I. Rudenkov, K. I. Matveev and I. V. Kozhevnikov, *React. Kinet. Catal. Lett.*, **5**, 401 (1976).

98. I. V. Kozhevnikov, *ibid.*, **5**, 415 (1976).

99. H. W. Krause, R. Selke and H. Pracejus, *Z. Chem.*, **16**, 465 (1977).

100. R. Noyori, *Org. Chem.*, **33**, Vol. 1, 83 (1977).

101. T. Sakakibara, J. Kotobuki and Y. Dogomori, *Chem. Lett.*, 25 (1977).

102. B. M. Trost and P. E. Strege, *J. Am. Chem. Soc.*, **99**, 1649 (1977).

103. B. M. Trost and Y. Matsumura, *J. Org. Chem.*, **42**, 2036 (1977).

104. B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc.*, **99**, 3867 (1977).

105. Y. Kitagawa, A. Itoh, S. Hashimoto, H. Yamamoto and H. Nozaki, *ibid.*, **99**, 3864 (1977).

106. M. Chatzopoulos and J. P. Montheard, *C. R. Hebd. Seances. Acad. Sci. Ser. C*, **284**, 133 (1977).

107. J. Levisalles, M. Rudler-Chaurrin and H. Rudler, *J. Organomet. Chem.*, **136**, 103 (1977).

108. R. Amos and J. A. Katzenellenbogen, *J. Org. Chem.*, **42**, 2537 (1977).

109. Y. Tanigawa, H. Kanamura, A. Sonada and S-i. Murahashi, *J. Am. Chem. Soc.*, **99**, 2361 (1977).

110. C. Chuit, H. Felken, C. Frazerman, G. Roussi and G. Swierczewski, *J. Organomet. Chem.*, **127**, 371 (1977).

111. K. von Werner, *J. Organomet. Chem.*, **136**, 385 (1977).

112. J. F. Normant, M. Commercon and J. Villieras, *J. Chem. Res. (S)*, 183 (1977).

113. Y. Gendreawe, J. F. Normant and J. Villieras, *J. Organomet. Chem.*, **142**, 1 (1977).

114. F. Derguini-Boumechal, R. Lorne and G. Linstrumelle, *Tetrahedron Lett.*, 1181 (1977).

115. E. C. Ashby, J. J. Lin, J. J. Watkins, *Tetrahedron Lett.*, 1709 (1977).

116. I. Ojima, M. Kumagai and Y. Miyazawa, *Tetrahedron Lett.*, 1385 (1977).

117. A. Ishida and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **50**, 1161 (1977).
118. I. Ojima, K. Yoshida and S-i. Inaba, *Chem. Lett.*, 429 (1977).
119. A. Manzocchi and E. Santaniello, *Synthesis*, 698 (1977).
120. Y. Okude, S. Hirano, T. Hiyama and H. Nozaki, *J. Am. Chem. Soc.*, **99**, 3179 (1977).
121. T. Sato, S. Yoshiie, T. Imamura, K. Hasegawa, M. Miyahara, S. Yamamura and O. Ito, *Bull. Chem. Soc. Japan*, **50**, 2714 (1977).
122. G. Cahiez and J. F. Normant, *Tetrahedron Lett.*, 3383 (1977).
123. A. Hosomi and H. Sakurai, *ibid.*, 4041 (1977).
124. R. O. Acker, *Tetrahedron Lett.*, 3407 (1977).
125. A. Kasahara, I. Izumi and N. Fukuda, *Bull. Chem. Soc. Japan*, **50**, 551 (1977).
126. S. Cacchi, M. Felici and G. Rosini, *J. Chem. Soc., Perkin Trans 1*, 1260 (1977).
127. T. Kametani, M. Ihara, M. Takemura, Y. Satoh, H. Terasawa, Y. Ohta, K. Fukumoto and K. Takahashi, *J. Am. Chem. Soc.*, **99**, 3805 (1977).
128. A. J. Liepa and R. E. Summons, *JCS Chem. Comm.*, 826 (1977).
129. M. A. Schwartz, B. F. Rose, R. A. Holton, S. W. Scott and B. Vishnuvjjala. *J. Am. Chem. Soc.*, **99**, 257 (1977).
130. S. Tsuruya, Y. Kishikawa, R. Tanaka and T. Kuse, *J. Catal.*, **49**, 254 (1977).
131. M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, **99**, 1675 (1977).
132. M. F. Semmelhack, Y. Thebtaranoth and L. Keller, *J. Am. Chem. Soc.*, **99**, 959 (1977).
133. B. E. Maryanoff, *J. Het. Chem.*, **14**, 1 (1977).
134. M. F. Semmelhack and J. C. Tomesch, *J. Org. Chem.*, **42**, 2657 (1977).
135. K. Itoh, T. Yogo and Y. Ishi, *Chem. Lett.*, 103 (1977).
136. H. D. Martin, M. Hekman, G. Rist, H. Sauter and D. Bellus, *Angew. Chem.*, **89**, 420 (1977).
137. E. G. Georgescu and M. D. Gheorghiu, *Rev. Roum. Chim.*, **22**, 907 (1977).
138. Z. Goldschmidt and Y. Bakal, *Tetrahedron Lett.*, 955 (1977).
139. R. A. Holton and R. G. Davis, *J. Am. Chem. Soc.*, **99**, 4175 (1977).
140. L. S. Hegedus, *J. Organomet. Chem. Libr.*, **1**, 329 (1976).
141. R. C. Larock, *ibid.*, **1**, 257 (1976).
142. L. S. Liebeskind, *Diss. Abstr. Int. B*, **38**, 693 (1977).
143. D. M. Floyd, *ibid.*, **37**, 5082 (1977).
144. E. C. Ashby, J. J. Lin and J. J. Watkins, *J. Org. Chem.*, **42**, 1099 (1977).
145. C. Quannes, G. Dressaire and Y. Langolois, *Tetrahedron Lett.*, 815 (1977).
146. J. W. Huffman and P. G. Harris, *J. Org. Chem.*, **42**, 2357 (1977).
147. M. Nilsson, M. T. Rahman and C. Ullenius, *Acta Chem. Scand. Ser. B*, **31**, 514 (1977).

148. F. A. Ziegler, G. R. Reid, W. L. Studt and P. A. Wender, *J. Org. Chem.*, **42**, 1991 (1977).

149. R. K. Boeckman, Jr., and M. Ramaiah, *J. Org. Chem.*, **42**, 1581 (1977)

150. H. O. House, C-Y Chu, W. V. Phillips, T. S. B. Sayer and C. C. Yau, *ibid.*, **42**, 1709 (1977).

151. M. J. Dimsdale, R. E. Newton, D. K. Rainey and C. F. Webb, *JCS Chem. Comm.*, 716 (1977).

152. M. Y. Yunker, D. E. Plaumann and B. Fraser-Reid, *Can. J. Chem.*, **55**, 4002 (1977).

153. B. Gustafsson and C. Ullenius, *Tetrahedron Lett.*, 3171 (1977).

154. B. Gustafsson, M. Nilsson and C. Ullenius, *Acta Chem. Scand. B.*, **31**, 667 (1977).

155. F. Leyendecker, J. Drouin, J. J. Debesse and J. M. Conia, *Tetrahedron Lett.*, 1591 (1977).

156. B. Gustafsson, *Acta Chem. Scand. Ser. B*, **B31**, 382 (1977).

157. S-H Liu, *J. Org. Chem.*, **42**, 3209 (1977).

158. K. Yamada, N. Miyaura, M. Itoh and A. Suzuki, *Bull. Chem. Soc. Japan*, **50**, 3431 (1977).

159. A. Marfat, P. R. McGuirk, P. Kramer and P. Helquist, *J. Am. Chem. Soc.*, **99**, 253 (1977).

160. J. Duboudin, B. Jousseaume and A. Bonakdar, *C. R. Hebd. Seances Acad. Sci. Ser. C*, **284**, 351 (1977).

161. M. Bertrans, G. Gils and J. Viala, *Tetrahedron Lett.*, 1785 (1977).

162. J. M. Dollat, J-L Louche and P. Crabbe, *JCS Chem. Comm.*, 761 (1977).

163. G. H. Posner and C. M. Lentz, *Tetrahedron Lett.*, 3215 (1977).

164. N. L. Holz and Y. F. Wang, *J. Am. Chem. Soc.*, **99**, 944 (1977).

165. J. L. Coke, H. J. Williams and S. Natarajan, *J. Org. Chem.*, **42**, 2380 (1977).

166. T. Olsson, M. T. Rahman and C. Ullenius, *Tetrahedron Lett.*, 75 (1977).

167. M. Isobe, S. Kondo, N. Nagasawa and T. Goto, *Chem. Lett.*, 679 (1977).

168. M. Yoshifuji, M. J. Loots and J. Schwartz, *Tetrahedron Lett.*, 1303 (1977).

169. M. Loots and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 8045 (1977).

170. T. Mukaiyama, T. Takeda and M. Osaki, *Chem. Lett.*, 1165 (1977).

171. R. A. Holton, *Tetrahedron Lett.*, 355 (1977).

172. R. A. Holton and R. A. Kjonaas, *J. Organomet. Chem.*, **133**, C5 (1977).

173. B. A. Patel, C. B. Ziegler, N. A. Cortese, J. E. Plevyak, T. C. Zebovitz, M. Terpko and R. F. Heck, *J. Org. Chem.*, **42**, 3903 (1977).

174. Y. Tamaru, Y. Yamada and Z-i Yoshida, *Tetrahedron Lett.*, 3365 (1977).

175. Z-i Yoshida, Y. Yameda and Y. Tamaru, *Chem. Lett.*, 423 (1977).

176. A. Hosomi and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 1673 (1977).

177. M. P. Cooke, Jr., and R. M. Parlman, *J. Am. Chem. Soc.*, **99**, 5222 (1977)

178. C. P. Casey, W. R. Brunsvold and D. M. Scheck, *Inorg. Chem.*, **16**, 3059 (1977)

179. H. Alper and H. des Abbayes, *J. Organomet. Chem.*, **134**, C11 (1977).

180. L. Cassar and M. Foa, *ibid.*, **134**, C15 (1977).

181. M. Hidai, Y, Uchida and I. Ogata, *Organotransition - Met. Chem.*, Proc. Japan-American Seminar, 1st 1974 (published 1975) 265.

182. B. K. Nefedov, N. S. Sergeeva and L. L. Krasnova, *Izv. Akad. Nauk SSSR Ser. Khim.*, 614 (1977).

183. P. S. Bratterman, B. S. Walker and T. H. Robertson, *JCS Chem. Comm.*, 651 (1977).

184. A. Guinot, P. Cadiot and J. L. Rouslan, *J. Organomet. Chem.*, **128**, C35 (1977).

185. G. P. Chiusoli, G. Sacchelli, B. Guidici, G. Cometti and V. Bellotti, *Gazz. Chim. Ital.*, **107**, 241 (1977).

186. T. Yamamoto, T. Kohara and A. Yamamoto, *Chem. Lett.*, 1217 (1976).

187. R. F. Heck, *Adv. Catal.*, **26**, 323 (1977).

188. T. Weil, L. Cassar and M. Foa, *Org. Synth. Met. Carbonyls*, **2**, 517 (1977).

189. A. Kasahara, T. Izumi and A. Suzuki, *Bull. Chem. Soc. Japan*, **50**, 1639 (1977).

190. I. Rhee, M. Ryang, T. Watanabe, H. Omura, S. Murai and N. Sonada, *Synthesis*, 776 (1977).

191. A. Stefani, G. Consiglio, C. Botteghi and P. Pino, *J. Am. Chem. Soc.*, **99**, 1058 (1977).

192. Y. Matsui, H. Taniguchi, K. Terada, T. Anezaki and M. Iruchyuma, *Bull. Japan Pet. Inst.*, **19**, 62 (1977).

193. *Ibid.*, **19**, 68 (1977).

194. M. Bianchi, F. Piacenti, P. Frediani and U. Matteoli, *J. Organomet. Chem.*, **135**, 387 (1977).

195. N. Rosas, J. Gomez-Lara, A. Cabrera and C. Alvarez, *Rev. Latinoamer. Quim.*, **8**, 121 (1977).

196. P. Tjan and J. J. F. Scholten, *Proc. Int. Congr. Catal. 6th*, **1**, 488 (1976).

197. A. Spencer, *J. Organomet. Chem.*, **124**, 85 (1977).

198. R. C. Ryan, C. U. Pittman, Jr., and J. P. O'Connor, *J. Am. Chem. Soc.*, **99**, 1986 (1977).

199. A. R. Sanger and L. R. Schallig, *J. Mol. Catal.*, **3**, 101 (1977).

200. I. Schwager and J. F. Knifton, *J. Catal.*, **45**, 256 (1976).

201. D. Tatone, *Helv. Chim. Acta*, **60**, 518 (1977).

202. M. Tanaka, T. Hayashi and I. Ogata, *Bull. Chem. Soc. Japan*, **50**, 2351 (1977).

203. B. Fell and H. Bahrmann, *J. Mol. Catal.*, **2**, 211 (1977).

204. G. Consiglio, *J. Organomet. Chem.*, **132**, C26 (1977).

205. P. Pino, F. Piacenti and M. Bianchi, Org. Synth. Met. Carbonyls, 2, 233 (1977).

206. J. F. Knifton, J. Mol. Catal., 2, 293 (1977).

207. S. J. Tremont and R. G. Bergman, J. Organomet. Chem., 140, C12 (1977).

208. P. Bladon, I. U. Khand and P. L. Pauson, J. Chem. Res., Part S, 8 (1977).

209. P. Pino and G. Graca, Org. Synth. Met. Carbonyls, 2, 419 (1977).

210. L. S. Hegedus, O. P. Anderson, K. Zetterberg, G. Allen, K. Siirala-Hansen D. J. Olsen and A. B. Packard, Inorg. Chem., 16, 1887 (1977).

211. J. K. Stille and D. E. James, Chem. Double Bonded Funct. Groups, 2, 1099 (1977).

212. J. Tsuji and H. Yasuda, Bull. Chem. Soc. Japan, 50, 553 (1977).

213. Y. Seki, A. Hidaka, S. Murai and N. Sonada, Angew. Chem. Int. Ed., 16, 174 (1977).

214. Y. Seki, S. Murai, I. Yamamoto and N. Sonada, Angew. Chem., 89, 818 (1977).

215. K. Yamamoto, O. Nunokawa and J. Tsuji, Synthesis, 721 (1977).

216. H. Sakurai, T. Imai and A. Hosomi, Tetrahedron Lett., 4045 (1977).

217. J. O. Morley, J. Chem. Soc., Perkin Trans 2, 601 (1977).

218. J. O. Morley, Synthesis, 54 (1977).

219. C-S. Giam and K. Ueno, J. Am. Chem. Soc., 99, 3166 (1977).

220. L. Toniolo, G. Strukul and M. Graziani, Chim Ind. (Milan), 58, 732 (1976).

221. F. A. Kaplan and B. W. Roberts, J. Am. Chem. Soc., 99, 518 (1977).

222. G. P. Chiusoli, G. Cometti, G. Sacchelli, V. Beldotti, G. D. Andreetti, G. Bocelli and P. Sgarabotto, J. Chem. Soc., Perkin Trans. 2, 389 (1977).

223. A. P. Marchand and B. R. Hayes, Tetrahedron Lett., 1027 (1977).

224. K. Hayakawa and H. Schmid, Helv. Chim. Acta, 60, 2160 (1977).

225. G. D. Annis and S. V. Ley, JCS Chem. Comm., 581 (1977).

226. S. Sarel and M. Langseheim, JCS Chem. Comm., 827 (1977).

227. R. Aumann, Chem. Ber., 110, 1432 (1977).

228. D. Brodzki, B. Denise and G. Pannetier, J. Mol. Catal., 2, 149 (1977).

229. T. Matsumoto, K. Mori, T. Mizoroki and A. Ozaki, Bull. Chem. Soc. Japan, 50, 2337 (1977).

230. K. M. Webber, B. C. Gates and W. Dreuth, J. Catal., 47, 269 (1977).

231. F. Piacenti and M. Bianchi, Org. Synth. Met. Carbonyls, 2, 1 (1977).

232. D. B. Dombek and R. J. Angelici, J. Catal., 48, 433 (1977).

233. M. Yamashita and R. Suemitsu, JCS Chem. Comm., 691 (1977).

234. H. Alper, J. Organomet. Chem. Libr., 1, 305 (1976).

235. F. Calderazzo, Angew. Chem. Int. Ed., 16, 299 (1977).

236. M. Hidai, Yukaguku, 25, 815 (1976).

237. Y. Watanabe and Y. Takegami, Yuki Gosei Kagaku Kyokaishi, 35, 585 (1977).

238. M. L. Banks, *Diss. Abstr. Int. B*, **37**, 3410 (1977).
239. J. Tsuji, *Org. Synth. Met. Carbonyls*, **2**, 595 (1977).
240. K. S. Y. Lau, Y. Becker, F. Huang, N. Baenziger and J. K. Stille, *J. Am. Chem. Soc.*, **99**, 5664 (1977).
241. T. Tokoroyama and M. Nakamura, *Chem. Lett.*, 659 (1977).
242. T. Kocke, K. Kawakami, K. Maruya, T. Mizorki and Z. Ozaki, *Chem. Lett.*, 551 (1977).
243. G. Henrici-Olive and S. Olive, *Transition Met. Chem.*, **1**, 109 (1976).
244. M. Taniewski and H. Tomczyk, *React. Kinetic Catal. Lett.*, **7**, 27 (1977).
245. N. Kawata, T. Mizoroki and A. Ozaki, *J. Mol. Catal.*, **1**, 275 (1976).
246. A. N. Nesmeyanov, F. K. Schmidt, L. V. Mironova, L. S. Isaeva, L. N. Lorens and A. G. Prodakov, *Dokl. Akad. Nauk SSSR*, **233**, 153 (1977).
247. A. K. Yatsimirskii, A. D. Ryabov and I. V. Berezin, *ibid.*, **232**, 1130 (1977).
248. *Ibid.*, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1764 (1977).
249. *Ibid.*, 1759 (1977).
250. B. A. Krentsel, *Russ. Chem. Rev.*, **45**, 738 (1976).
251. M. F. Farona and C. Tsonis, *JCS Chem. Comm.*, 363 (1977).
252. C. R. Graham and L. M. Stephenson, *J. Am. Chem. Soc.*, **99**, 7098 (1977).
253. A. Musco, *J. Mol. Catal.*, **1**, 443 (1976).
254. I. Tkatchenko, *J. Organomet. Chem.*, **124**, C39 (1977).
255. I. Mochida, K. Kitagawa, H. Fujitsu and K. Takeshita, *Chem. Lett.*, 417 (1977).
256. P. Heimback, A. Rolff and H. Schenkluhn, *Angew. Chem.*, **89**, 260 (1977).
257. J. Furukawa and J. Kiji, *Organotransition - Met. Chem. Proc. Japan Amer. Seminar 1st*, 1974, 119.
258. M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 743 (1977).
259. J. Tsuji and T. Mandai, *Chem. Lett.*, 975 (1977).
260. R. Kluter, M. Bernd and H. Singer, *J. Organomet. Chem.*, **137**, 309 (1977).
261. J. Tsuji, K. Masoaka and T. Takahashi, *Tetrahedron Lett.*, 2267 (1977).
262. J. Tsuji and T. Mandai, *ibid.*, 3285 (1977).
263. J. Tsuji and Y. Yasuda, *J. Organomet. Chem.*, **131**, 133 (1977).
264. U. M. Dzhemilev, A. I. Yakupova and G. A. Tolstikov, *Bull. Akad. Nauk SSSR*, **25**, 1691 (1976).
265. U. M. Kzhemilev, R. N. Fakhreldinov and G. A. Tolstikov, *ibid.*, **26**, 1251 (1977).
266. U. M. Dzhemilev, T. A. Selimov, G. A. Tolstikov and E. G. Galkin, *ibid.*, **26**, 1255 (1977).
267. R. Baker, M. S. Nobbs and P. M. Winton, *J. Organomet. Chem.*, **137**, C43 (1977).
268. H. U. Blaser and D. Reinehr, *Helv. Chim. Acta*, **60**, 208 (1977).

269. P. Heimback, B. Hugelin, E. F. Nabbefeld, D. Reinehr, A. Roloff and E. Troxler, Angew. Chem., 89, 261 (1977).
270. D. H. Richards, Chem. Soc. Rev., 6, 235 (1977).
271. R. L. Hillard, III., and K. P. C. Vollhardt, J. Am. Chem. Soc., 99, 4058 (1977).
272. R. L. Funk and K. P. C. Vollhardt, J. Am. Chem. Soc., 99, 5483 (1977).
273. K. P. C. Vollhardt, Accts. Chem. Res., 10, 1 (1977).
274. J. Ficini, J. d'Angelo and S. Falow, Tetrahedron Lett., 1645 (1977).
275. P. Mauret, G. Guerch and S. Martin, C. R. Hebd. Seances Sci. Ser. C, 284, 747 (1977).
276. G. Giacomelli, A. M. Caporusso and L. Lardicci, J. Chem. Soc. Perkin Trans. 1, 1333 (1977).
277. I. G. Dinulescu, S. Staicu, E. Avram, F. Chiraleu and M. Avram, J. Organomet. Chem., 136, C15 (1977).
278. J. Hambrecht and E. Mueller, Liebigs Ann. Chem., 387 (1977).
279. J. Hambrecht and E. Mueller, Z. Naturforsch B., 32B, 68 (1977).
280. K. H. Doetz and R. Dietz, Chem. Ber., 110, 1555 (1977).
281. S. Yoshikawa, J. Kiji and J. Furukawa, Makromol. Chem., 178, 1077 (1977)
282. A. M. Caparusso, L. Lardicci and G. Giacomelli, Tetrahedron Lett., 4351 (1977).
283. P. Caddy, M. Green, E. O'Brien, L. E. Smart and P. Woodward, Angew. Chem., 89, 671 (1977).
284. K. Kaneda, T. Uchiyama, H. Kobayashi, Y. Fujiwara, T. Imanaka and S. Teramshi, Tetrahedron Lett., 2008 (1977).
285. P. Bruger, A. Brinkmann and J. McMeeking; Liebigs Ann. Chem., 1035 (1977).
286. V. I. Sorokin, V. N. Drozd, N. P. Akomova and I. I. Grandberg, J. Org. Chem. USSR, 13, 673 (1977).
287. T. Yamamoto and A. Yamamoto, Chem. Lett., 353 (1977).
288. G. P. Chiusoli, G. Cometti, G. Sacchelli, V. Bellotti, G. P. Andretti, G. Bocelli and P. Sgarabotto, Trans. Met. Chem., 1, 147 (1976).
289. D. A. White, Synth. React. Inorg. Met. - Org. Chem., 7, 433 (1977).
290. Rec. Trav. Chim., 96, m-5-141 (1977).
291. K. Ichikawa, O. Watanabe, T. Takagi and K. Fukuzumi, J. Catal., 44, 416 (1976).
292. R. Rossi and R. Giorgi, Chim. Ind. (Milan), 58, 517 (1976).
293. R. Rossi, ibid., 58, 517 (1976)
294. K. Ichikawa and K. Fukuzumi, Yukagaku, 25, 779 (1976).
295. R. Backer and M. J. Crummin, Tetrahedron Lett., 441 (1977).
296. R. Rossi, Gazz. Chim. Ital., 106, 1103 (1976).
297. S. Warwel and A. Aivasidis, Chem.-Ztg., 101, 361 (1977).
298. S. Warwel and W. Laary, Z. Naturforsch B, 32B, 1145 (1977).

299. V. W. Motz and M. F. Farona, Inorg. Chem., 16, 2545 (1977).
300. T. J. Katz and J. McGinnis, J. Am. Chem. Soc., 99, 1903 (1977).
301. G. Pez, JCS Chem. Comm., 560 (1977).
302. E. K. Tarcsi, F. Ratkovics and L. Bencze, J. Mol. Catal., 1, 435 (1976).
303. J. M. Basset, Y. BenTaarit, J. L. Bilhow, J. Bousquet, R. Mutin and A. Theolier, Proc. Int. Congr. Catal. 6th, 1, 570 (1977).
304. E. Verknijlen, K. Kapteijn, M. C. Mol, and C. Boelhouwer, JCS Chem. Comm., 198 (1977).
305. A. Mortreux, J. C. Delgrange, M. Blanchard and B. Lubochinsky, J. Mol. Catal., 2, 73 (1977).
306. T. J. Katz and W. H. Hersh, Tetrahedron Lett., 585 (1977).
307. J. L. Bilhow, M. J. Basset, R. Mutin and W. F. Graydon, J. Am. Chem. Soc., 99, 4083 (1977).
308. N. Calderon, Chem. Double-Bonded Funct. Groups, 2, 913 (1977).
309. J. J. Rooney and A. Stewart, Catalysis (London), 1, 277 (1977).
310. R. Grubbs, J. Organomet. Chem. Libr., 1, 423 (1976).
311. G.A. Chukhadzhyan, V. P. Kukolev, R. H. Mehkyan, M. M. Chobayan and N. A. Gevorkyan, Arm. Khim. Zh., 30, 301 (1977).
312. G. A. Vaglio, D. Osella and M. Valle, Transition Met. Chem., 2, 94 (1974).
313. J. Andrieux, D. H. R. Barton and H. Patin, J. Chem. Soc., Perkin Trans. 1, 359 (1977).
314. Z. Aizenshtat, M. Hausmann, Y. Pickholtz, D. Tal and J. Blum, J. Org. Chem.,42, 2380 (1977).
315. K. Isagawa, K. Tatsumi, H. Kasugi and Y. Otsuji, Chem. Lett., 1017 (1977).
316. K. Isagawa, K. Tatsumi and Y. Otsuji, Chem. Lett., 1145 (1976).
317. W. E. McCormack and M. Orchin, J. Organomet. Chem., 129, 127 (1977).
318. F. K. Schmidt, L. O. Nindakova, S. M. Krasnopol'skaya, T. V. Dmitrieva, and G. Ratovskii, React. Kinet. Catal. Lett., 7, 247 (1977).
319. A. Hubert, A. Feron, G. Goebbels, R. Warm and P. Teyssie, J. Chem. Soc., Perkin Trans. II, 111 (1977).
320. C. Botteghi and G. Giacomelli, Gazz. Chim. Ital., 106, 1131 (1976).
321. P. Chabardis, E. Kuntz and J. Varagnat, Tetrahedron, 33, 1775 (1977).
322. J. M. Reuter and R. G. Salomon, J. Org. Chem., 42, 3360 (1977).
323. G. P. Chiusoli, G. Salerno and C. Dallatomasina, JCS Chem. Comm., 793 (1977).
324. D. Milstein, O. Buchman and J. Blum, J. Org. Chem., 42, 2299 (1977).
325. J. H. Turner and W. Herz, ibid., 42, 1895 (1977).
326. Ibid., 42, 339 (1977).
327. R.W. Ashworth and G. A. Berchtold, Tetrahedron Lett., 343 (1977).
328. Y. Ito and T. Saegusa, J. Org. Chem., 42, 2326 (1977).

329. D. P. Schwendiman and C. Kutal, *J. Am. Chem. Soc.*, **99**, 5677 (1977).

330. P. A. Grutsch and C. Kutal, *ibid.*, **99**, 6460 (1977).

331. R. Aumann, H. Woermann and C. Krueger, *Chem. Ber.*, **110**, 1442 (1977).

332. P. G. Gassman, T. Sugawara and L. G. Tillotson, *J. Org. Chem.*, **42**, 3785 (1977).

333. R. G. Salomon, M. F. Salomon and J. L. C. Kachinski, *J. Am. Chem. Soc.*, **99**, 1043 (1977).

334. L. A. Paquette, J. M. Photes and R. P. Micheli, *ibid.*, **99**, 7899 (1977).

335. *Ibid.*, 7911 (1977).

336. W. Grimme and E. Schneider, *Angew Chem. Int. Ed.*, **16**, 717 (1977).

337. A. Hermann and B. Waegell, *Nouv. J. Chim.*, **1**, 275 (1977).

338. T. Ikawa, M. Wakakura, T. Yamase and S. Ozaki, *Sekiyu Gaddai Shi*, **18**, 492 (1975).

339. B. N. Bobylev, L. V. Melnik, M. I. Farborov, L. L. Bobyleva and I. V. Subłotina, *Zh. Prikl. Khim.*, **50**, 615 (1977).

340. R. E. Michaelson, R. E. Palermo and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 1990 (1977).

341. S-i. Yamada, T. Mashiko and S. Terashima, *ibid.*, **99**, 1988 (1977).

342. A. O. Chong and K. B. Sharpless, *J. Org. Chem.*, **42**, 1587 (1977).

343. J. Sobzak and J. J. Ziolkowski, *J. Mol. Catal.*, **3**, 165 (1977).

344. G. L. Linden and M. F. Farona, *Inorg. Chem.*, **16**, 3170 (1977).

345. G. L. Linden and M. F. Farona, *J. Mol. Catal.*, **48**, 284 (1977).

346. M. A.Beg and I. Ahmad, *Indian J. Chem., Sec. B.*, **15B**, 656 (1977).

347. U. M. Belousov, K. B. Yatsimirskii, A. P. Filippov and S. B. Gruneko, *Kinet. Catal.*, **18**, 554 (1977).

348. M. J. Y. Chen and J. K. Kochi, *J. Chem. Soc., Chem. Comm.*, 204 (1977).

349. J. R. Bull and J. Floor, *J. Chem. Soc., Perkin Trans. I*, 724 (1977).

350. J. E. Backvall, B. Akermark and S. O. Ljunggren, *JCS Chem. Comm.*, 264 (1977).

351. K. I. Matveev, *Kinet. Katal.*, **18**, 862 (1977).

352. M. Isemura, Y. Kitaura, S. Shimoda and Y. Saito, *J. Mol. Catal.*, **2**, 351 (1977).

353. R. G. Brown, R. V. Chandhari and J. M. Davidson, *J. Chem. Soc., Dalton Trans.*, 183 (1977).

354. A. Heumann and B. Waegell, *Nouv. J. Chem.*, **1**, 277 (1977).

355. J. Tsuji, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 10 (1977).

356. K. B. Sharpless, A. Y. Teranishi and J. E. Backvall, *J. Am. Chem. Soc.*, **99**, 3120 (1977).

357. G. Cardillo and M. Shimizu, *J. Org. Chem.*, **42**, 4268 (1977).

358. M. Okano, *JCS Chem. Comm.*, 166 (1977).

359. R. Witkiewicz and Z. Chabridzinski, *Rocz. Chem.*, **51**, 475 (1977).

360. *Ibid.*, **51**, 825 (1977).

361. R. Witkiewicz, *Wiad. Chem.*, **30**, 659 (1976).

362. P. J. C. Walker, *J. Chem. Soc., Dalton Trans.*, 883 (1977).

363. B. H. Van Vugt and W. Drenth., *Recl. Trav. Chim. Pays-Bas*, **96**, 225 (1977).

364. M. Baccouche, J. Ernst, J. H. Fuhrhop, R. Schlozer and H. Arzoumanian, *JCS Chem. Comm.*, 821 (1977).

365. K. Isagawa, K. Tatsumi and Y. Otsuji, *Chem. Lett.*, 1117 (1977).

366. A. A. Frimer, *JCS Chem. Comm.*, 205 (1977).

367. P. Boontanoda and R. Grigg, *ibid.*, 583 (1977).

368. C. Jallabert and H. Riveriere, *Tetrahedron Lett.*, 1215 (1977).

369. T. F. Blackburn and J. Schwartz, *JCS Chem. Comm.*, 157 (1977).

370. J. San Filippo, Jr., and C-I Chern, *J. Org. Chem.*, **42**, 2182 (1977).

371. P. Suderaraman and W. Herz, *J. Org. Chem.*, **42**, 813 (1977).

372. A. Dobson and S. D. Robinson, *Inorg. Chem.*, **16**, 137 (1977).

373. R. H. Mueller and R. M. DiPardo, *J. Org. Chem.*, **42**, 3210 (1977).

374. C. E. Bibby, R. Grigg and R. Price, *J. Chem. Soc., Dalton Trans.*, 872 (1977).

375. H. Sakamoto, T. Funabiki and T. Tarama, *J. Catal.*, **48**, 427 (1977).

376. G. D. Mercer, W. B. Beaulieu and D. Max Roundhill, *J. Am. Chem. Soc.*, **99**, 6551 (1977).

377. I. I. Moiseev, V. A. Bochkareva, A. E. Gekhman, V. Yu Kokanov and Yu. A. Buslaev, *Dokl. Akad. Nauk SSSR*, **233**, 375 (1977).

378. P. Mueller and Truone Thi Khoi, *Tetrahedron Lett.*, 1939 (1977).

379. J. Hartenstein and G. Saltzinger, *Angew Chem. Int. Ed.*, **16**, 730 (1977).

380. M. Kimura and T. Sawaya, *Chem. Pharm. Bull.*, **25**, 1073 (1977).

381. W. Herz, R. Ligon, J. A.Turner and J. F. Blount, *J. Org. Chem.*, **42**, 1885 (1977).

382. G. Mates, F. Juileet and S. J. Teichner, *Bull. Soc. Chim. Fr.*, 1633 (1976).

383. *Ibid.*, 1637 (1976).

384. J. R. L. Smith, B. A. J. Shaw, D. M. Foulkes, A. M. Jeffrey and D. M. Jerina, *J. Chem. Soc., Perkin Trans. II*, 1583 (1977).

385. B. Brosard, R. Janin, L. Krumenacker and J. Varagnat, *Tetrahedron Lett.*, 2273 (1977).

386. A. V. Ablov, M. O. Broitman, K. I. Kuchkova and A. A. Semenov, *Kinet. Katal.*, **17**, 1331 (1976).

387. M. O. Broitman and A. V. Ablov, *Kinet. Katal.*, **18**, 642 (1977).

388. A. Barco, S. Benetti, G. Pallini and P. G. Baraldi, *Synthesis*, 837 (1977).

389. K. Chebaane and M. Guyot, *Tetrahedron*, **33**, 757 (1977).

390. R. G. Gillard and J. R. Lyon, *Transition Met. Chem.*, **2**, 19 (1977).

391. D. N. Chatterjee and S. R. Chakravorty, *J. Indian Chem. Soc.*, **53**, 610 (1976).

392. D. Bondon, Y. Pietrsanta and B. Pucci, *Tetrahedron Lett.*, 821 (1977).

393. E. Mincione, G.Ortaggi and A. Sirna, *Synthesis*, 773 (1977).

394. P. W. Clark, *J. Organomet. Chem.*, **137**, 235 (1977).

395. G. A. Olah, J. Welch and M. Henninger, *Synthesis*, 308 (1977).

396. T. Sakakibara, J. Kotobuki and Y. Dogomori, *Chem. Lett.*, 25 (1977).

397. T. Kametani, K. Takahashi, T. Ohsawa and M. I. Hara, *Synthesis*, 245 (1977).

398. A. Sen and J. Halpern, *J. Am. Chem. Soc.*, **99**, 8337 (1977).

399. T. Cohen, A. G. Dietz, Jr., and J. R. Miser, *J. Org. Chem.*, **42**, 2053 (1977).

400. N. J. Lewis, S. Y. Gabhe and M. R. DeLaMater, *ibid.*, **42**, 1479 (1977).

401. E. Siaens, D. DeKeukelure and M. Verzele, *Tetrahedron*, **33**, 423 (1977).

402. C. Fisher and H. S.Mosher, *Tetrahedron Lett.*, 2487 (1977).

403. K. Achiwa, *Chem. Lett.*, 777 (1977).

404. K. Achiwa, *Tetrahedron Lett.*, 3735 (1977).

405. R. Glaser and J. Blumenfield, *ibid.*, 2525 (1977).

406. R. Glaser and S. Geresh, *ibid.*, 2527 (1975).

407. R. Glaser, M. Twark, S. Geresh and J. Blumenfield, *Tetrahedron Lett.*, 4635 (1977).

408. M. D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6262 (1977).

409. T. Hayashi, M. Tanaka and I. Ogata, *Tetrahedron Lett.*, 295 (1977).

410. K. Ohkubo, K. Hirata, T. Ohgushi and K. Yoshinaga, *J. Coord. Chem.*, **6**, 185 (1977).

411. B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Backmann and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977).

412. M. Fiorini, G. M. Giongo, F. Marcati and W. Marconi, *J. Mol. Catal.*, **1**, 451 (1976).

413. M. Kumada, T. Hayashi, K. Tamao, K. Yamamoto, T. Mise, Mitajska and S. Mitachi, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku*, **28**, 299 (1976).

414. W. Cullen, E-S Yeh, *J. Organomet. Chem.*, **139**, C13 (1977).

415. W. Beck and H. Menzel, *ibid.*, **133**, 307 (1977).

416. R. H. Grubbs and R. A. DeVries, *Tetrahedron Lett.*, 1879 (1977).

417. K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyaki, T. Hayashi and M. Kumada *ibid.*, 1389 (1977).

418. L. M. Samoilenko, V. K. Latov, and U. M. Belikov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1318 (1977).

419. Y. Kawabata, M. Tanaka and I. Ogata, *Chem. Lett.*, 1213 (1976).

420. I. Kolb, M. Cerny and J. Hetflejs, *React. Kinet. Catal. Lett.*, **7**, 199 (1977).

421. C. Botteghi, S. Gladiali, M. Mianichi, U. Matteoli, P. Frediani, G. Vergamini and E. Benedetti, *J. Organomet. Chem.*, **140**, 221 (1977).

422. B. R. James, R. S. McMillan and K. J. Reimer, J. Mol. Catal., **1**, 439 (1976).

423. B. R. James and R. S. McMillan, Can. J. Chem., **55**, 3927 (1977).

424. R. W. Waldron and J. H. Weber, Inorg. Chem., **16**, 1220 (1977).

425. Y. Ohashi and Y. Sasada, Bull. Chem. Soc. Japan, **50**, 2863 (1977).

426. Y. Ohgo, Yuki Gosei Kagaku Kyokai Shi, **34**, 874 (1976).

427. T. Uematsu, F. Saito, M. Miura and H. Hashimoto, Chem. Lett., 113 (1977).

428. N. L. Holly, Tetrahedron Lett., 3703 (1977).

429. B. A. Sosinsky, W. C. Kalb, R. A. Gray, V. A. Uski and M. F. Hawthorne, J. Am. Chem. Soc., **99**, 6768 (1977).

430. A. Gruyot, C. A. Graillat and M. Bartholin, J. Mol. Catal., **3**, 39 (1977).

431. T. Imanaka, K. Kaneda, S. Teranishi, M. Terasawa, Proc. Int. Congr. Catal. 6th, **1**, 509 (1976).

432. J. G. S. Lee and C. H. Brubaker, Jr., J. Organomet. Chem., **135**, 115 (1977).

433. R. Grubbs, C. P. Lau, R. Cukier and C. Brubaker, Jr., J. Am. Chem. Soc., **99**, 4517 (1977).

434. G. Strukul, P. D'Olimpio, M. Bonivento, F. Pinna and M. Graziani, J. Mol. Catal., **2**, 179 (1977).

435. K. Kochlvefl and W. Liebelt, JCS Chem. Comm., 510 (1977).

436. G. Descotes and J. Sabadie, Bull. Soc. Chim. Fr., 2011 (1976).

437. C. Naccachi, N. Kaufherr, M. Dufaux, J. Bandiera and B. Imelik, ACS Symp. Ser., **40**, 538 (1977).

438. J. Conan, M. Bartholin and A. Gruyot, J. Mol. Catal., **1**, 375 (1976).

439. Y. Nakamura and H. Hirai, Chem. Lett., 1197 (1976).

440. Y. Dror and J. Manassen, J. Mol. Catal., **2**, 219 (1977).

441. J. Brunet and P. Caubere, Tetrahedron Lett., 3947 (1977).

442. J. F. Brunet, P. Gallois and P. Caubere, ibid., 3955 (1977).

443. E. C. Ashby and S. A. Noding, ibid., 4579 (1977).

444. F. Sato, S. Sato, H. Kodama and M. Sato, J. Organomet. Chem., **142**, 71 (1977).

445. J. Tsuji and T. Mandai, Chem. Lett., 975 (1977).

446. M. Barthelemy, A. Gianfermi and Y. Bessiere, Bull. Soc. Chim. Fr., 1821 (1976).

447. R. H. Crabtree, H. Felkin and G. E. Morris, J. Organomet. Chem., **141**, 205 (1977).

448. D. L. Dubois and D. W. Meek, Inorg. Chim. Acta, **19**, L29 (1976).

449. Y. Takagi, S. Teratani, S. Takahashi and K. Tanaka. J. Mol. Catal., **2**, 321 (1977).

450. P. Fu and R. G. Harvey, Tetrahedron Lett., 415 (1977).

451. R. L. Sweeny and J. Halpern, J. Am. Chem. Soc., **99**, 8335 (1977).

452. D. Labrone and P. Poilbanc, *J. Mol. Catal.*, **2**, 329 (1977).

453. N. Yamamoto, H. Kanai and K. Tarama, *Chem. Lett.*, 1377 (1977).

454. W. Strohmeier and H. Steigerwald, *Z. Naturforsch, B*, **32B**, 113 (1977).

455. J. Tsuji and H. Suzuki, *Chem. Lett.*, 1083 (1977).

456. W. Strohmeier and H. Steigerwald, *J. Organomet. Chem.*, **125**, C37 (1977).

457. J. W. Johnson and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 7395 (1977).

458. M. Russell, C. White and P. M. Maitlis, *JCS Chem. Commun.*, 427 (1977).

459. W. Strohmeier and L. Weigelt, *J. Organomet. Chem.*, **129**, C47 (1977).

460. W. Strohmeier and M. Lukacs, *ibid.*, **129**, 331 (1977).

461. W. Strohmeier and L. Weigelt, *ibid.*, **133**, C43 (1977).

462. W. Strohmeier and M. Lukacs, *ibid.*, **133**, C47 (1977).

463. W. Strohmeier and L. Weigelt, *Z. Naturforsch B*, **32B**, 597 (1977).

464. J. Halpern, D. P. Riley, A. S. C. Chan and J. J. Pluth, *J. Am. Chem. Soc.*, **99**, 8055 (1977).

465. V. Z. Sharf, L. Kh. Freidlin, I. S. Shekoyan and V. N. Krutii, *Izv. Akad. Nauk SSSR Ser Khim.*, 834 (1977).

466. A. N. Nesmeyanov, G. B. Shul'pin, V. V. Krivykh and M. I. Rybinskaya, *Dokl. Chem.*, **232**, 76 (1977).

467. M. C. Rakowski and E. Muetterties, *J. Am. Chem. Soc.*, **99**, 739 (1977).

468. M. F. Semmelhack, R. D. Stauffer and A. Yamashita, *J. Org. Chem.*, **42**, 3180 (1977).

469. F. Joo, Z. Toth and M. T. Beck, *Inorg. Chim. Acta*, **25**, L61 (1977).

470. W. Strohmeier and H. Steigerwald, *J. Organomet. Chem.*, **129**, C43 (1977).

471. J. Tsuji and H. Suzuki, *Chem. Lett.*, 1085 (1977).

472. G. Mestroni, G. Zassinovich and A. Camus, *J. Organomet. Chem.*, **140**, 63 (1977).

473. G. Zassinovich, A. Camus and G. Mestroni, *Inorg. Nucl. Chem. Lett.*, **12**, 865 (1976).

474. M. Gargano, P. Giannoccaro and M. Rossi, *J. Organomet. Chem.*, **129**, 239 (1977).

475. T. W. Russell, D. M. Duncan and S. C. Hansen, *J. Org. Chem.*, **42**, 551 (1977).

476. J. J. Brunet, L. Mordenti, B. Loubinoux and P. Daubere, *Tetrahedron Lett.*, 1069 (1977).

477. T. Harada, S. Onaka, A. Tai and Y. Izumi, *Chem. Lett.*, 113 (1977).

478. I. Ojima, T. Kogure and K. Achiwa, *JCS Chem. Comm.*, 428 (1977).

479. S. Nishimura, M. Ishige and M. Shiota, *Chem. Lett.*, 963 (1977).

480. *Ibid.*, 535 (1977).

481. T. Chihara and K. Tanaka, *ibid.*, 843 (1977).

482. I. D. Entwistle, R. A. Johnstone and R. P. Telford, *J. Chem. Res (S)*, 117 (1977).

483. T. Tatsumi, K. Kiyawa and H. Tominaga, *Chem. Lett.*, 191 (1977).

484. P. Svoboda and J. Helflejs, *Coll. Czech. Chem. Comm.*, **42**, 2177 (1977).

485. T. Mizorki, K. Seki, S-i Meguro and A. Ozaki, *Bull. Chem. Soc. Japan*, **50**, 2148 (1977).

486. T. Tokoryama and M. Nakamura, *Chem. Lett.*, 659 (1977).

487. E. C. Ashby and J. J. Lin, *Tetrahedron Lett.*, 4481 (1977).

488. E. C. Ashby, A. B. Goel and J. J. Lin, *ibid.*, 3695 (1977).

489. B. Loubinoux, R. Vanaresse and P. Caubere, *ibid.*, 3951 (1977).

490. H. Imai, T. Nishiguchi, M. Tanaka and K. Fukuzumi, *J. Org. Chem.*, **42**, 2309 (1977).

491. N. A. Cortese and R. F. Heck, *J. Org. Chem.*, **42**, 3491 (1977).

492. T. Kunieda, T. Tamura and T. Takizawa, *Chem. Pharm. Bull.*, **25**, 1749 (1977).

493. H. Alper, K. D. Logbo and H. des Abbayes, *Tetrahedron Lett.*, 2861 (1977).

494. I. Mochida, H. Noguchi, H. Fujitsu, T. Sayama and K. Takeshita, *Can. J. Chem.*, **55**, 2420 (1977).

495. Y. Okude, T. Hayama and H. Nozaki, *Tetrahedron Lett.*, 3829 (1977).

496. T. E. Cole and R. Petit, *ibid.*, 781 (1977).

497. E. Yoshii, T. Koizumi, I. Higashi and Y. Hiroi, *Chem. Pharm. Bull.*, **25**, 1468 (1977).

498. I. Ojima, T. Kogure and M. Kumagai, *J. Org. Chem.*, **42**, 1671 (1977).

499. Z. Scharf, L. Kh. Freidlin, I. S. Shekoyan and V. Krutii, *Bull. Akad. Nauk. SSSR Ser Khim.*, **26**, 995 (1977).

500. H. Sakurai, K. Miyoshi and Y. Nakadaira, *Tetrahedron Lett.*, 2671 (1977).

501. J. F. Harrod and A. J. Chalk, *Org. Synth. Met. Carbonyls*, **2**, 673 (1977).

502. A. A. Siddiqui, N. H. Khan, N. Ali and A. Kidwai, *Synth. Comm.*, **7**, 71 (1977).

503. H. Imai, T. Nishiguchi and K. Fukuzumi, *J. Org. Chem.*, **42**, 431 (1977).

504. H. des Abbayes and H. Alper, *J. Am. Chem. Soc.*, **99**, 98 (1977).

505. H. Alper, D. des Roches and H. des Abbayes, *Angew. Chem. Int. Ed.*, **16**, 41 (1977).

506. Y. Akita, M. Inaba, H. Uchida and A. Ohta, *Synthesis*, 792 (1977).

507. J. J. Niewwenhuis and J. H. Jordaan, *Tetrahedron Lett.*, 369 (1977).

508. C. S. Rondeslvedt and T. A. Johnson, *Synthesis*, 850 (1977).

509. T-L Ho, *J. Org. Chem.*, **42**, 3755 (1977).

510. G. D. Hartmann and S. E. Biffar, *ibid.*, **42**, 1468 (1977).

511. T-L Ho and G. A. Olah, *Synthesis*, 169 (1977).

512. T-L Ho, *Synth. Comm.*, **7**, 321 (1977).

513. R. G. Nuzzo, H. J. Simon and J. San Filippo, Jr., *J. Org. Chem.*, **42**, 568 (1977).

514. H. Alper and H. N. Pak, *ibid.*, **42**, 3522 (1977).

515. H. Alper and D. des Roches, *Tetrahedron Lett.*, 4155 (1977).

516. I. Mochida, S. Shirahama, H. Fujitsu and K. Takeshita, *Chem. Lett.*, 421 (1977).

517. V. I. Mashinskii, V. A. Postnikov, Yu N. Novikov, A. L. Lapidus, M. E. Volper and Ta. T. Eidus, *Bull. Akad. Nauk SSSR*, **25**, 1894 (1976).

518. L. I. Shoer and J. Schwartz, *J. Am. Chem. Soc.*, **99**, 5831 (1977).

519. G. C. Pemitras and E. L. Muetterties, *ibid.*, **99**, 2796 (1977).

520. H. C. Kang, C. Mauldin, T. Cole, W. Slegeir, K. Cann and R. Pettit, *ibid.*, **99**, 8323 (1977).

521. C-H. Cheng, D. E. Hendriksen and R. Eisenberg, *ibid.*, **99**, 2791 (1977).

522. N. M. Akhtar, J. J. Rooney, N. G. Samman, H. M. Hugel, R. W. Jackson, D. M. Nicolson and D. Rash, *Aust. J. Chem.*, **30**, 1509 (1977).

523. K. R. Gooding, R. W. Jackson, C. F. Pincombe and D. Rash, *ibid.*, **30**, 1517 (1977).

524. T. Nishiguchi, H. Imai and K. Fukuzumi, *Chem. Lett.*, 1113 (1977).

525. H. Felkin, E. Jampel-Costa and G. Swierczewski, *J. Organomet. Chem.*, **134**, 265 (1977).

526. R. W. Jackson, *Proc. R. Aust. Chem. Inst.*, **43**, 198 (1976).

527. J. H. Sinfelt, *Acc. Chem. Res.*, **10**, 15 (1977).

528. H. Westmijze, J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **96**, 168 (1977).

529. M. P. Doyle, B. Siegfried and J. F. Dellaria, Jr., *J. Org. Chem.*, **42**, 2426 (1977).

530. M. P. Doyle, B. Siegfried and W. Fobare, *Tetrahedron Lett.*, 2655 (1977).

531. M. P. Doyle, B. Siegfried, R. C. Elliot and J. F. Dellaria, Jr., *J. Org. Chem.*, **42**, 2431 (1977).

532. S. Uemura, H. Okazaki, A. Onoe and M. Okano, *J. Chem. Soc., Perkin Trans. I*, 676 (1977).

533. H. Driguez, J. M. Paton and J. Lessard, *Can. J. Chem.*, **55**, 700 (1977).

534. H. Driguez and J. Lessard, *Can. J. Chem.*, **55**, 720 (1977).

535. J. Elzinga and H. Hogeveen, *JCS Chem. Comm.*, 705 (1977).

536. J. E. Backvall, M. W. Young and K. B. Sharpless, *Tetrahedron Lett.*, 3523 (1977).

537. J. Kagan, B. E. Firth, N. Y. Shih and C. G. Boyajian, *J. Org. Chem.*, **42**, 343 (1977).

538. H. Westmijze and P. Vermeer, *Synthesis*, 784 (1977).

539. A. Ishigaki, M. Oue, Y. Matsushita, I. Masuda and T. Shono, *Bull. Chem. Soc. Japan*, **50**, 726 (1977).

540. A. J. Pearson, *JCS Chem. Comm.*, 339 (1977).

541. E. S. Brown, *Org. Synth. Met. Carbonyls*, **2**, 655 (1977).

542. Yu. N. Belokon, T. F. Savel'eva, M. B. Saporouskaya and W. M. Belikov, *Bull. Akad. Nauk SSSR Khim. Sci. Ser.*, **26**, 387 (1977).

543. J. E. Backvall, *JCS Chem. Comm.*, 413 (1977).

544. A. O. Chong, K. Oshima and K. B. Sharpless, J. Am. Chem. Soc., 99, 3420 (1977).

545. M. Botta, F. DeAngelis and R. Nicolleti, Synthesis, 722 (1977).

546. P. M. Diamond, S. E. Dinizo, R. W. Freerksen, R. C. Haltwangen and D. S. Watt, JCS Chem. Comm., 298 (1977).

547. U. M. Dzhemilev, R. N. Fakhreldinov and G. A. Tolstikov, Bull. Akad. Nauk SSSR Chem., 26, 327 (1977).

548. J. C. Chattard, E. Mulliez and D. Mansing, J. Am. Chem. Soc., 99, 3531 (1977).

549. L. Eberson and L. Jonsson, Justus Liebigs Ann. Chem., 233 (1977).

550. D. E. Korte, L. S. Hegedus and R. K. Wirth, J. Org. Chem., 42, 1329 (1977).

551. A. Kasahara, T. Izumi, K. Sato, M. Maemura and T. Hayasaka, Bull. Chem. Soc. Japan, 50, 1899 (1977).

552. T. F. Murray, V. Varma and J. R. Norton, J. Am. Chem. Soc., 99, 8085 (1977).

553. K. Itoh, M. Fukui and Y. Kurachi, JCS Chem. Comm., 500 (1977).

554. D. G. Brown, L. Beckman and C. H. Ashby, Tetrahedron Lett., 1363 (1977).

555. E. Nakamura and I. Kuwajima, J. Am. Chem. Soc., 99, 7360 (1977).

556. R. Aumann and H. Ping, Angew Chem. Int. Ed., 16, 50 (1977).

557. F. Zutterman, P. DeClercq and M. Vanderwalle, Tetrahedron Lett., 3191 (1977).

558. X. Creary and S. P. Fields, J. Org. Chem., 42, 1470 (1977).

559. U. Ravid and M. Silverstein, Tetrahedron Lett., 423 (1977).

560. Y. Inoue, Y. Itoh and H. Hashimoto, Chem. Lett., 855 (1977).

561. G. Paincatelli, A. Scettri and M. D'Auria, Tetrahedron Lett., 2199 (1977).

562. I. G. Pinuleseu, S. Staicu, F. Chiraleu and M. Auram, J. Organomet. Chem., 140, 91 (1977).

563. P. Faria dos Santos Filho and U. Schuchardt, Angew. Chem. Int. Ed., 16, 647 (1977).

564. K. Isomura, K. Uto and H. Taniguchi, JCS Chem. Comm., 664 (1977).

565. J. J. Eisch and K. R. Im, J. Organomet. Chem., 139, C51 (1977).

566. M. Mori, K. Chiba and Y. Ban, Tetrahedron Lett., 1037 (1977).

567. A. Naiman and K. P. C. Vollhardt, Angew. Chem. Int. Ed., 16, 708 (1977).

568. P. Hong and H. Yamazaki, Tetrahedron Lett., 1333 (1977).

569. P. Hong and H. Yamazaki, Synthesis, 50 (1977).

570. A. McKillop and D. P. Rao, ibid., 760 (1977).

571. I. Ojima, S-i Inaba and K. Yoshida, Tetrahedron Lett., 3643 (1977).

572. P. K. Wong, M. Madhavarao, D. F. Marten and M. Rosenblum, J. Am. Chem. Soc., 99, 2823 (1977).

573. I. Ernest, *Tetrahedron*, **33**, 547 (1977).

574. A. Norstrom, K. Andersson and C. Rappe, *Chemosphere*, **5**, 419 (1976).

575. M. A. El Sohly, D. J. Slatkin, J. E. Knapp, N. J. Doorenbos, M. W. Quimby, P. L. Schiff, Jr., E. M. Gopalakrishna and W. H. Watson, *Tetrahedron*, **33**, 1711 (1977).

576. E. Wenkert, M. E. Alonso, B. L. Buckwalter and K. J. Chow, *J. Am. Chem. Soc.*, **99**, 4778 (1977).

577. J. A. Turner and W. Herz, *J. Org. Chem.*, **42**, 1900 (1977).

578. Y. Hayakawa, H. Takaya, S. Makino, N. Hayakawa and R. Noyori, *Bull. Chem. Soc. Japan*, **50**, 1990 (1977).

579. T. E. Nalesnik and N. L. Holy, *J. Org. Chem.*, **42**, 372 (1977).

580. A. de Renzi, A. Panunzi, L. Paolillo and A. Vitagliano, *J. Organomet. Chem.*, **124**, 221 (1977).

581. Y. Ito, T. Hirao and T. Saegusa, *J. Organomet. Chem.*, **131**, 121 (1977).

582. M. C. Ashraf, T-G. Burrowes and W. R. Jackson, *Aust. J. Chem.*, **29**, 2643 (1976).

583. Y. Yamamoto and H. Yamazaki, *J. Organomet. Chem.*. **137**,C31 (1977).

584. H. Alper, J. E. Prickett and S. Wollowitz, *J. Am. Chem. Soc.*, **99**, 4330 (1977).

585. Y. Yamamoto and H. Yamazaki, *J. Org. Chem.*, **42**, 4137 (1977).

586. K. Kitatani, T. Hiyama and H. Nozaki, *Bull. Chem. Soc. Japan*, **50**, 1647 (1977).

587. R. Baker and M. S. Nobbs, *Tetrahedron Lett.*, 3759 (1977).

588. A. Marxer, *Lect. Heterocycl. Chem.*, **3**, 131 (1976).

589. J. J. Aisch and K. R. Im, *J. Organomet. Chem.*, **139**, C45 (1977).

590. R. G. Salomon and J. M. Reuter, *J. Am. Chem. Soc.*, **99**, 4372 (1977).

591. H. Koinuma, H. Kato and H. Hirai, *Chem. Lett.*, 517 (1977).

592. M. A. Wells and T. C. Bruice, *J. Am. Chem. Soc.*, **99**, 5341 (1977).

593. K. Formank, J. P. Anne, M. J. Jouffret and J. Metzger, *Nov. J. Chem.*, **1**, 12 (1977).

594. N. Furukawa, F. Takahashi, T. Yoshimura and S. Oae, *Tetrahedron Lett.*, 3633 (1977).

595. S. Masamune, Y. Hayase, W. Schilling, W. K. Chan and G. S. Bates, *J. Am. Chem. Soc.*, **99**, 6756 (1977).

596. I. Yamamoto, H. Tokanow, H-a Uemura and H. Gotoh, *J. Chem. Soc., Perkin Trans. I*, 1241 (1977).

597. H. Suzuki and M. Shinoda, *Synthesis*, 640 (1977).

598. A. Arase and Y. Masuda, *Chem. Lett.*, 1115 (1976).

599. Z. Yoshida, Y. Yamada and Y. Tamaru, *Chem. Lett.*, 423 (1977).

600. P. P. Singh, M. M. Gharia, F. Dasgupta and H. C. Srivastava, *Tetrahedron Lett.*, 439 (1977).

601. V. Schurig, *Angew. Chem. Int. Ed.*, **16**, 110 (1977).

602. R. D. Rieke, *Accts. Chem. Res.*, **10**, 301 (1977).
603. T. Mukayama, *Synthesis*, 817 (1977).
604. R. J. H. Clark, S. Moorhouse and J. A. Stockwell, *J. Organomet. Chem. Libr.*, **3**, 223 (1977).
605. M. P. Fleming, *Diss. Abst. Int. B*, **38**, 686 (1977).
606. *Organic Synthesis via Metal Carbonyls*, I. Wender and P. Pino, eds., Wiley, New York (1977).
607. B. M. Trost, *Tetrahedron*, **33**, 2615 (1977).
608. P. E. Strege, *Diss. Abst. Int. B*, **37**, 5096 (1977).
609. J. Tsuji, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 94 (1977).
610. H. Takaya and R. Noyori, *ibid.*, **35**, 615 (1977).
611. H. Alper, *Org. Synth Met. Carbonyls*, **2**, 545 (1977).
612. Y. Watanabe and Y. Takegami, *Kagaku (Kyoto)*, **31**, 678 (1976).
614. R. Oda, *ibid.*, **32**, 163 (1977).
614. J. Tsuji, *ibid.*, **32**, 159 (1977).
615. C. P. Casey, *Org. Chim.*, **33** (Vol. 1), 189 (1976).
616. C. P. Casey, *J. Organomet. Chem. Libr.*, **1**, 397 (1976).
617. M. F. Semmelhack, *ibid.*, **1**, 361 (1976).
618. G. P. Chinsoli and L. Cassar, *Org. Synth. Met. Carbonyls*, **2**, 297 (1977).
619. D. W. Hart, *Diss. Abst. Int. B*, **37**, 1259 (1976).
620. M. I. Bruce, *Angew. Chem. Int. Ed.*, **16**, 73 (1977).
621. H. P. Abicht and K. Issleit, *Z. Chem.*, **17**, 1 (1977).
622. J. H. Sinfelt, *Science*, **195**, 641 (1977).
623. J. R. Norton, *Prepr. Div. Pet. Chem. Am. Chem. Soc.*, **21**, 343 (1976).
624. I. Ogata, *Sekiyu Gakkai Shi*, **20**, 392 (1977).