Journal of Organometallic Chemistry, 180 (1979) 301—453

TRANSITION METALS IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1978

Louis S. Hegedus
Department of Chemistry, Colorado State University, Fort Collins, CO 80523 U.S.A.

CONTENTS

Transition metal derivatives in organic synthesis; Annual Survey covering the year 1977 see J. Organometal. Chem., 163 (1978) p. 187-323.

References p. 430

I. General Comments

This annual survey covers the literature for 1978 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 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 affected 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.

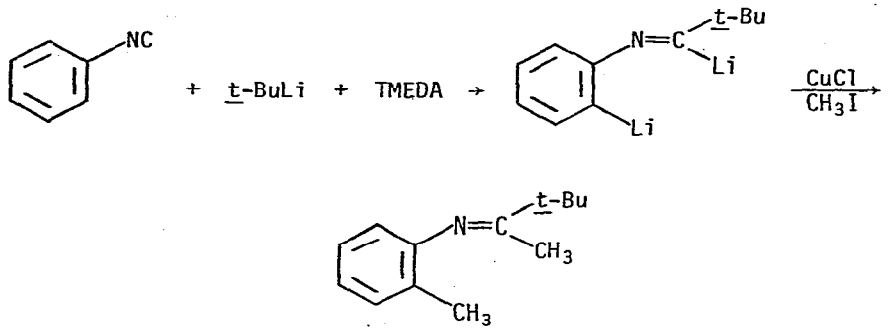
The number of papers reviewed this year has again increased over that of last year, with most of the increase in the areas of carbon-carbon bond forming reactions, asymmetric homogeneous hydrogenation and solid phase supported catalysis. This increase reflects the growing activity in these areas.

II. Carbon-Carbon Bond Forming Reactions

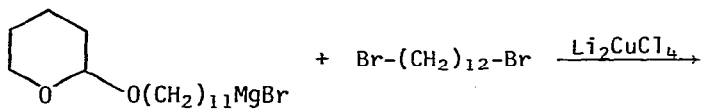
A. Alkylations

1. Organic Halides

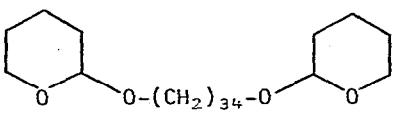
Treatment of (3-methyl-3-methoxy-1-butynyl)copper, readily available from the acetylenic ether $MeOCMe_2C{\equiv}CH$, with a variety of organolithium reagents produces soluble mixed cuprates which efficiently alkylate a variety of organic halides. In addition this reagent also transfers its R group to α,β-unsaturated ketones to produce β-alkylated saturated ketones [1]. Phenyl isocyanide reacts with t-butyllithium and TMEDA to form an o-lithiated t-butyliminolithium compound, which dialkylates in the presence of copper(I) chloride and methyl iodide (eq. 1) [2]. Long chain terminally bifunctionalized (i.e., diols and bromoethers) alkane and alkyne derivatives were prepared by the reaction of the Grignard reagent, a tetrahydropyranyl ether of an eleven carbon ω-hydroxyalkyl bromide, with a long chain (C_{12}-C_{14}) α,ω-dihalide using Li_2CuCl_4 as catalyst (eq. 2) [3]. α-Haloketones reacted with Grignard reagents to form the corresponding α-halomagnesium alkoxides. These reacted with aryl or vinyl Grignard reagents to replace the halogen with aryl or vinyl groups, producing tertiary alcohols [4]. The copper catalyzed coupling reactions between Grignard reagents and functionalized organic halides is the topic of a dissertation [5]. Mixed lithium halide-magnesium halide salts of vinyl copper complexes reacted with β-iodoalkynes to produce eneynes in excellent yield (eq. 3) [6]. Long chain alkyl

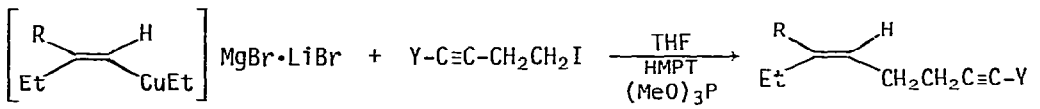


(1)

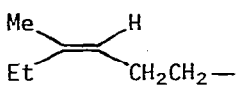


(2)





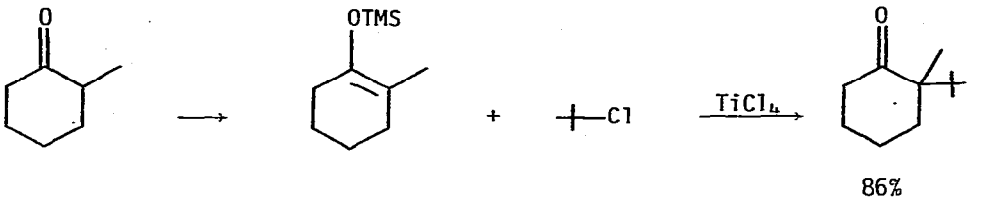
(3)

R = Ph, Me, 

Y = H, TMS

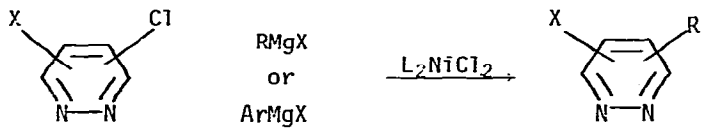
tosylates reacted with long chain Grignard reagents in the presence of Li_2CuCl_4 catalyst to form even longer chain alkyl products. Both members contained a chiral center remote from the site of reaction, whose stereochemistry was maintained [7]. Terminal alkynes bearing remote hydroxyl, methoxyl, and tetrahydropyranyl ether groups reacted with propargylic and allylic halides in the presence of copper(I) chloride and DBU to couple. This procedure was used to synthesize eicosatetraynoic acid, alcohol and aldehyde as well as nonadecatetraynesulfonamide [8].

Ketones were α-t-butylated by conversion to the silylenol ether followed by reaction with t-butyl chloride in the presence of titanium tetrachloride, ferric chloride or zinc chloride (eq. 4)[9]. Alkenyl iodides coupled with alkenyl Grignard reagents in the presence of palladium(0) catalysts to form 1,3-dienes



(4)

in which the stereochemistry of each double bond had been maintained. Alkyl and alkynyl Grignard reagents couple in a similar fashion [10]. Arylcopper complexes reacted with 1-ethoxy-2-iodoacetylene to produce 1-ethoxy-2-arylacetylenes in fair yield [11]. Unsymmetrical internal alkynes were prepared by the nickel(mesalen)$_2$ complex catalyzed reaction of trialkylaluminum complexes with bromoacetylenes [12]. Alkyl and aryl pyridazines were synthesized by the cross coupling reaction of chloropyridazines and Grignard reagents catalyzed by nickel phosphine complexes (eq. 5) [13]. Reaction of the same substrates with terminal



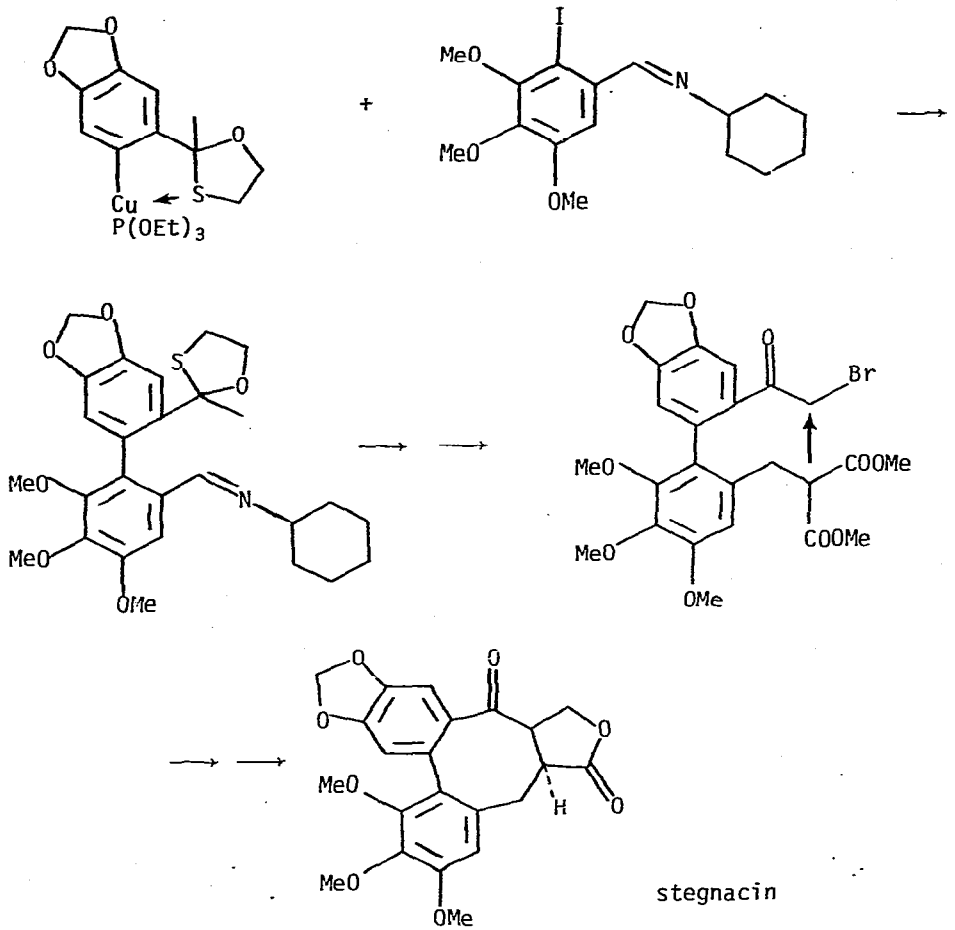
(5)

X = 6-Me, Ph, MeO, —N⟨ ⟩; R = Me, Et; Ar = Ph, α-naphth-, α-thienyl

alkynes in the presence of a $PdCl_2(PPh_3)_2$-CuI catalyst and one equivalent of diethylamine produced alkynylpyridazines [14]. In a similar fashion, polychloropyrimidines were polyalkylated or arylated by Grignard reagents in the presence of a nickel-phosphine complex catalyst [15].

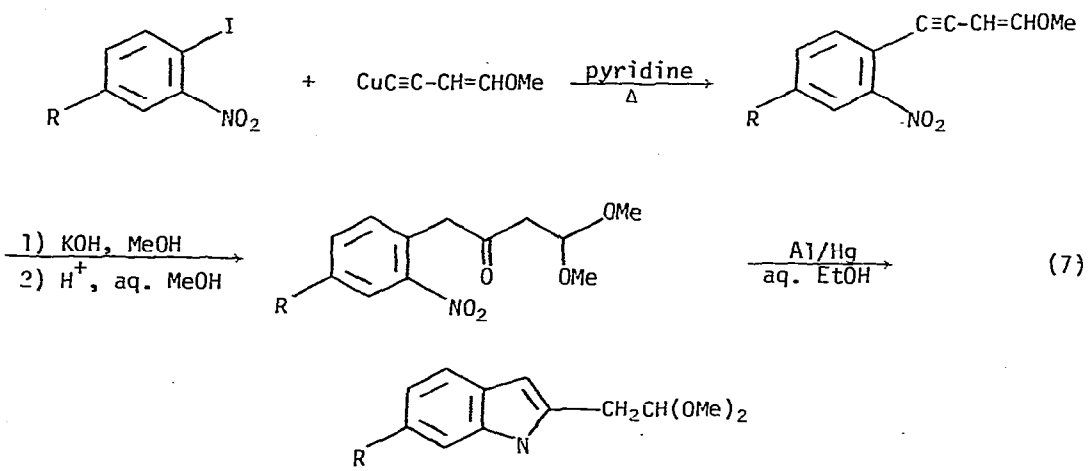
Monosubstituted acetylenes condensed with aryl or pyridyl iodides in the presence of copper(I) iodides, producing disubstituted acetylenes [16]. Alkynylzinc reagents condensed with aryl halides in the presence of $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ catalysts in a similar fashion to produce internal arylalkynes. Substituents including methyl, methoxy, cyano, and nitro were tolerated, and heteroaromatic halides such as 2-bromothiophene reacted well [17]. Polystyrene supported palladium(0)-phosphine complexes catalyzed the reactions of aryl halides with olefins to give styrenes (Heck arylation), with terminal alkynes to produce aryl acetylenes, and with Grignard reagents. The activity of the supported catalyst in these reactions was comparable to that observed for the corresponding homogeneous catalysts [18].

A key step in the synthesis of stegnacin was the reaction of an arylcopper complex with a tetrasubstituted aryl iodide to form the biaryl for further reaction (eq. 6) [19]. An approach to the indole ring system involved the



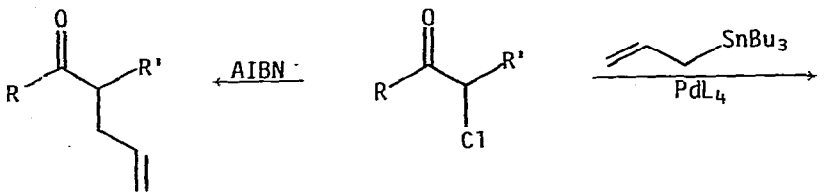
(6)

reaction of an aryl iodide with a copper functionalized acetylide (eq. 7). This copper reagent also cleanly alkylated acid halides, as well as vinyl, allyl and benzyl halides [20].

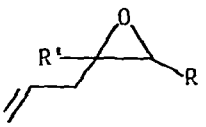


(7)

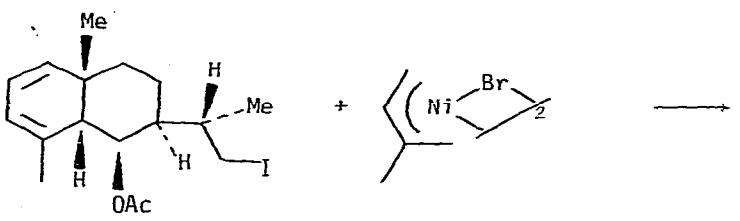
Allyltributyltin reacted with α-chloroketones to produce epoxides in the presence of $Pd(PPh_3)_4$ (eq. 8). In contrast, replacement of halogen by allyl



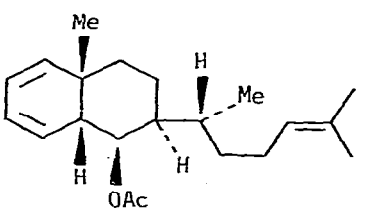
(8)



was observed in the presence of AIBN [21]. The reaction of a π-allylnickel halide with a primary alkyl iodide was used to introduce an isoprenyl group in the synthesis of dictyolene (eq. 9) [22]. The terpene geraniol was synthesized by the reaction of prenyl bromide with oxygen functionalized π-allylnickel halide complexes [23].



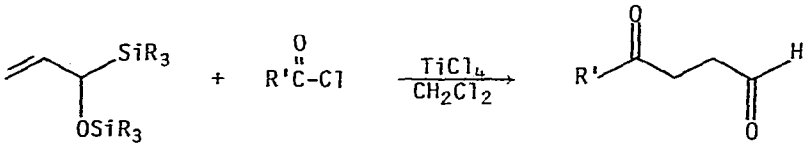
(9)



2. Acid Chlorides

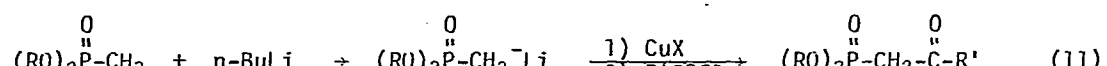
Highly branched ketones were prepared by the reaction of hindered acid chlorides with neopentyl magnesium halides in the presence of copper(I) chloride [24]. Diaryl ketones were obtained by the reaction of substituted aroyl chlorides with bis-(1,5-cyclooctadiene)nickel. Side products included biaryls and diketones [25]. An extremely wide variety of acid chlorides were converted to ketones by reaction with tetraalkyl, aryl or benzyltins in the presence of $PhCH_2Pd(PPh_3)_2Cl$ as a catalyst. The reactions were rapid, proceeded in high yield, and were not air sensitive. Functional groups including cyano,

chloro, bromo, nitro, carbomethoxy, formyl, furanyl and olefin were tolerated [26]. A similar reaction using $Pd(PPh_3)_4$ as a catalyst in benzene required considerably more severe conditions and went in lower yield [27]. Acid halides reacted with substituted allylsilanes in the presence of titanium tetrachloride to produce dicarbonyl compounds (eq. 10) [28].



(10)

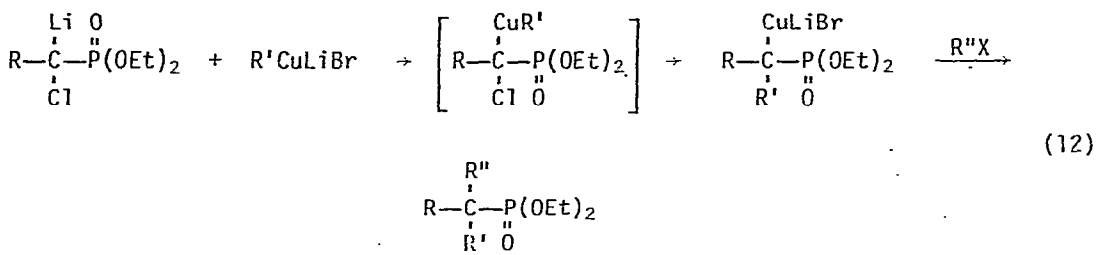
β-Ketophosphonates were synthesized from the methylphosphonates by a sequence involving lithiation, reaction with copper(I) halide, and coupling of this organocuprate with an acid halide (eq. 11)[29]. With ethyl chloro-



(11)

R' = alkyl, aryl, alkenyl, alkynyl, $PhOCH_2$

formate as the acid halide ethyl dialkylphosphonopyruvates were available [30]. Organocuprates alkylated α-phosphonate carbenoids and α-ester carbenoids, forming an unsymmetrical cuprate which itself can be further alkylated or acylated by addition of an alkyl or acid halide (eq. 12) [31,32].

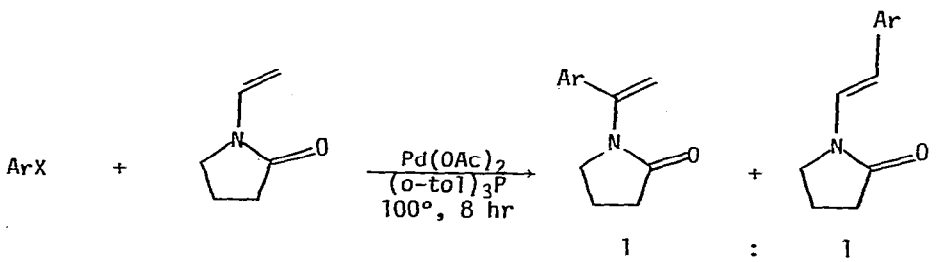


(12)

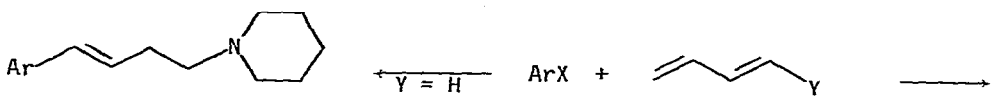
3. Olefins

Palladium(II) complexes continue to be the most efficient reagents for the direct alkylation of olefins and a number of useful procedures based upon "Heck" arylation have been developed recently. Aryl halides bearing a wide variety of functional groups including nitro, amino, acetamide, formyl, bromo, carboxy and pyridinyl react with ethylene in the presence of palladium(II) acetate and tri(o-tolyl)phosphine at 125° in DMF to form the corresponding styrenes in 40-80% yield. Small amounts of stilbene byproduct were observed [33]. A number of heteroaromatic bromides react in a similar fashion, adding to more complex olefins such as 4-vinylpyridine, styrene, and methyl acrylate. The heteroaromatic halides used included 2- and 3-bromothiophene, 5-bromoindole, 3-bromoquinoline and 4-bromoisoquinoline. The yields were 50-80%, with

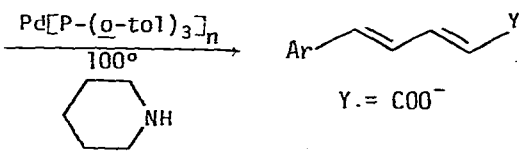
arylation occurring exclusively at the less substituted end of the olefin [34]. Aryl halides also added to N-vinylpyrrolidinone and N-vinylphthalimide (eq. 13) [35]. With 1,3-dienes, this same arylation system gave fair yields of 1-substitution if the diene was conjugated to a carboxylic acid group. Simple alkyldienes produced tertiary allylic amines via π-allylpalladium complex intermediates (eq. 14) [36]. This chemistry was used to an advantage in the introduction of alkyl side chains into pyrimidines. Thus, 5-iodo- or 5-(chloromercurio)pyrimidines reacted with vinyl acetate (eq. 15) [37] to produce 5-vinylpyrimidines, while it or the 5-(chloromercurio)pyrimidine reacted with dihydropyran to introduce the dihydropyran group at the 5-position (eq. 16) [38,39].

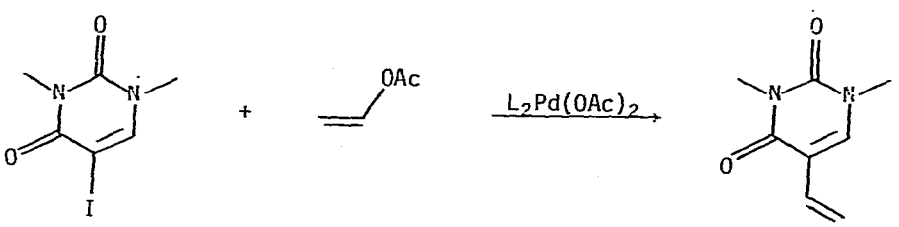


(13)

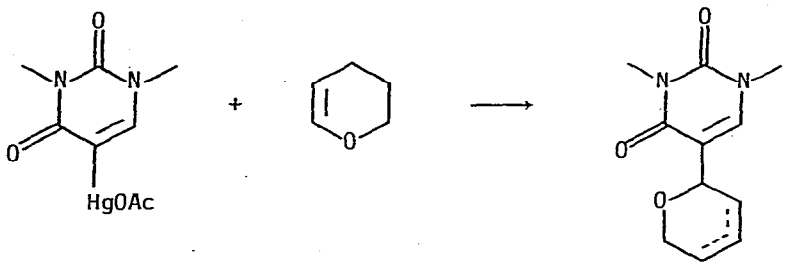


(14)





(15)

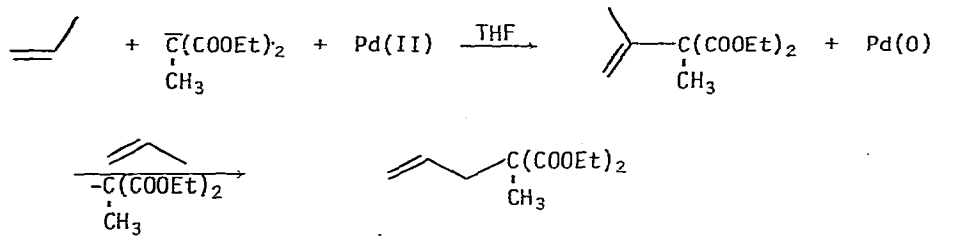


(16)

Styrene reacted with phenylmagnesium bromide in the presence of $PdCl_2$, lithium chloride, tributylamine and acetonitrile to produce stilbene in 1000% yield based on palladium. Copper(II) chloride was used as the oxidant [40]. Benzene and toluene directly arylated 1-octene and 1,3-dienes in the presence of palladium(II) salts [41]. Diphenylketene reacted with aromatic hydrocarbons and carbon monoxide to produce aryl ketones in the presence of $Rh_4(CO)_{12}$ catalyst. Isocyanates reacted similarly to produce benzanilides (eq. 17) [42]. Propene underwent a

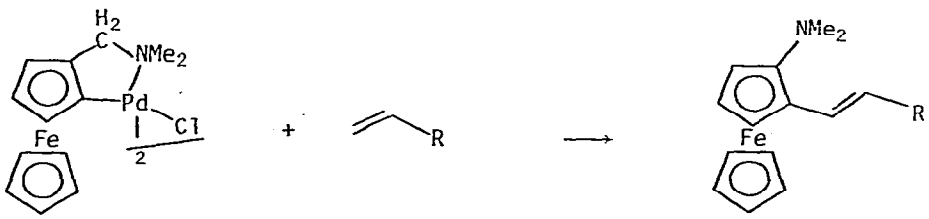
$$Ph_2C{=}C{=}O + PhH + CO \xrightarrow[\substack{200° \\ 30\ kg/cm^2}]{Rh_4(CO)_{12}} Ph_2CHCOPh \qquad 68\% \qquad (17)$$

a direct allylic alkylation by diethylmethylmalonate in the presence of a heterogeneous palladium(0) catalyst species produced by β-hydride elimination from the vinylic alkylation of propene (eq. 18) [43].



(18)

(Dimethylaminomethyl)ferrocene was o-palladated and the resulting complex reacted with a number of olefins to give 1,2-disubstituted ferrocene derivatives (eq. 19) [44]. Olefins were hydroaluminated with $LiAlH_4$, then coupled to allylic halides in the presence of copper(I) chloride. Since the product has the allyl olefin at its terminus, the procedure can be repeated, allowing

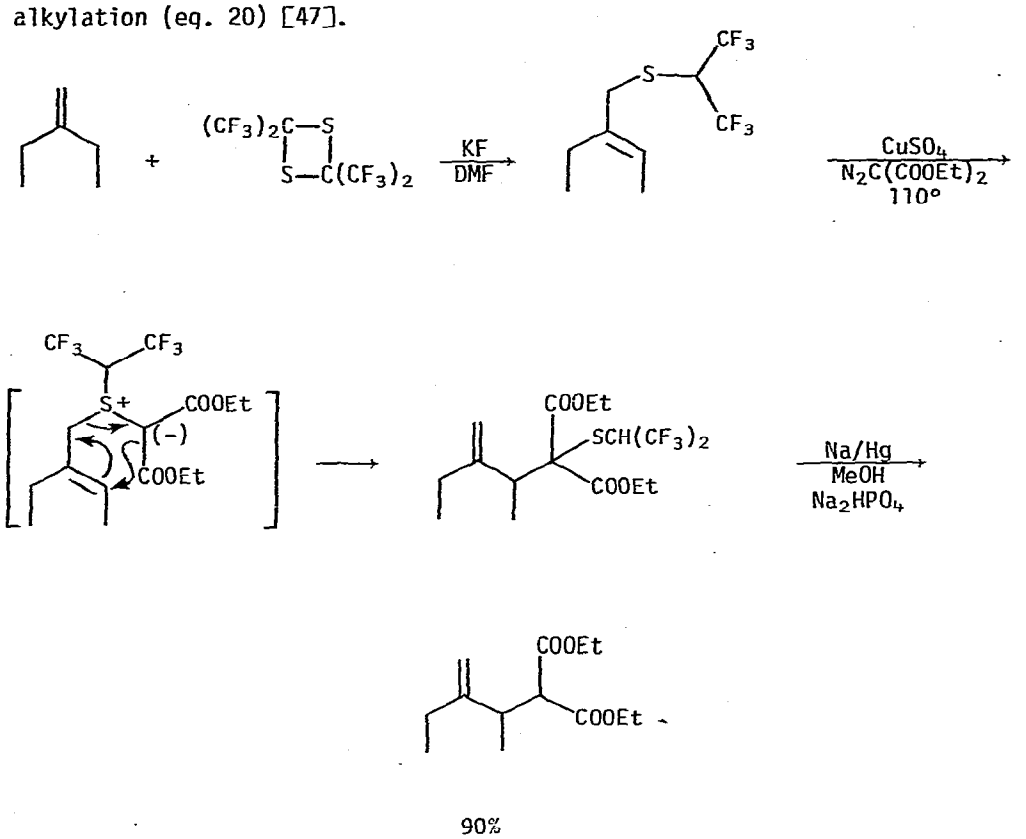


(19)

R = Ph, COOEt, COOMe, CN, COMe, COPh

References p. 430

facile chain extension [45]. Dialkylaluminum halides alkylated 3-butene-1-ol in the presence of titanium tetrachloride [46]. Copper sulfate promoted the addition of diazomalonates to allylsulfides to result in an overall allylic alkylation (eq. 20) [47].

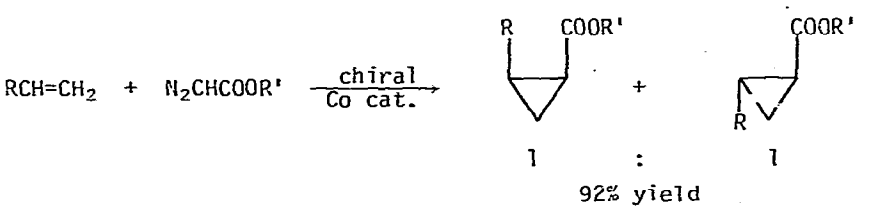


(20)

90%

4. Decomposition of Diazocompounds

The full details of the formation of cyclopropanes from olefins and ethyl diazoacetate in the presence of chiral cobalt catalysts have appeared (eq. 21) [48]. The olefin must be styrene or a butadiene, since simple olefins

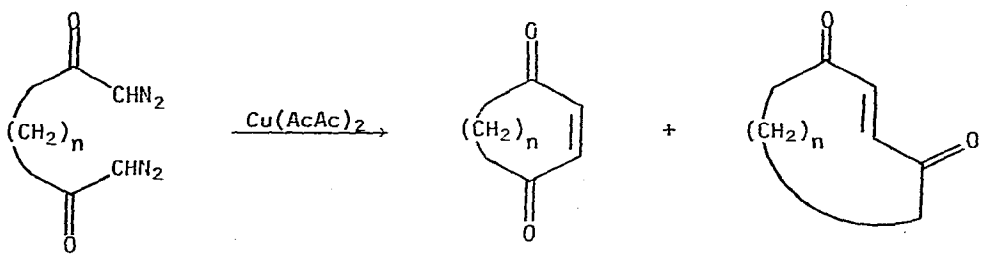


(21)

92% yield

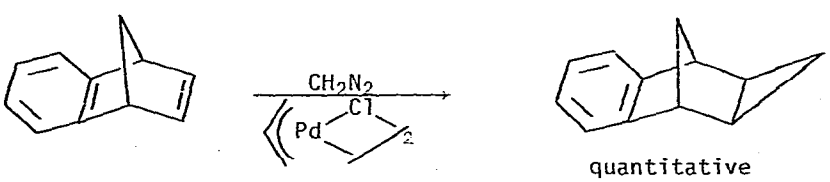
do not react to any extent, nor do electrophilic olefins such as acrylonitrile or ethyl acrylate. With the ethyl ester a 1:1 mixture of cyclopropane isomers was obtained in up to 75% optical yield. With the neopentyl ester, greater than 95% trans product was obtained [49]. The mechanism was claimed to involve coordination of the diazoester to cobalt, formation of the cobalt carbene,

attack of the olefin to form a cobaltacyclobutane, and decomposition to products [50]. The use of this type of reaction for the asymmetric synthesis of chrysanthemummonocarboxylic acid has been reviewed (25 ref.) [51]. The use of palladium complexes to catalyze the reactions of ethyl diazoacetate with olefins led to somewhat different results. The reaction showed a strong dependence upon the halide, and was independent of added ligand. Hence use of chiral ligands led to no asymmetric induction [52]. The reaction of methyl diazoacetate with alkynes to give cyclopropenes was catalyzed by $Rh_2(OAc)_4$. The reaction proceeded in quite good yield with aliphatic alkynes, but failed entirely with phenylacetylene and ethoxyacetylene. With acetylenic alcohols insertion of the carbene into the O-H group was competitive with cyclopropenation [53]. Bis-diazo diketones cyclized to cyclic enediones when treated with copper(II) acetylacetonate (eq. 22) [54]. The cyclopropanation of strained olefins by diazomethane was catalyzed by π-allylpalladium chloride complexes (eq. 23) [55].



(22)

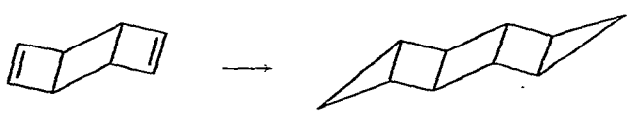
n = 4,7,8,9,10,12,16 n = 7,8,9,10,12,16
ratios from 1:3 to 1:10 cis to trans



and

quantitative

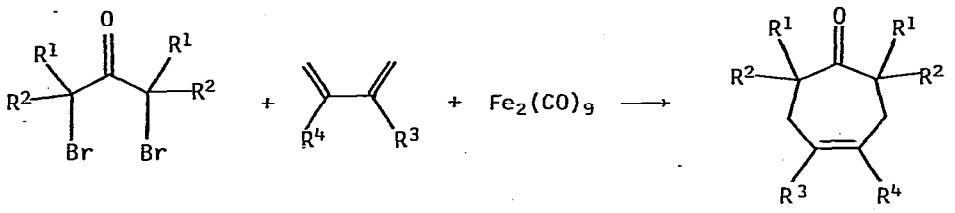
(23)



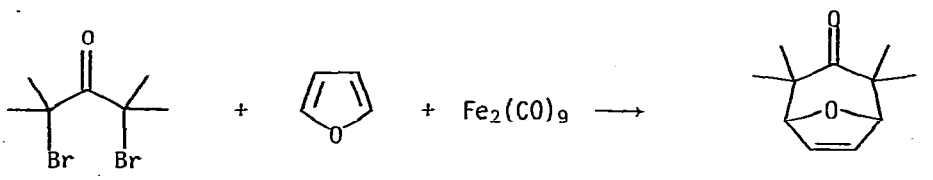
5. Cycloaddition Reactions

The reaction of α,α'-dibromoketones with iron carbonyl produced an oxallyl iron(II) species which underwent a number of reactions of great synthetic utility. The mechanistic aspects of this reaction were studied, and it was concluded that the reagent formed through an enolate intermediate which

converted to the reactive oxallyl cation complex [56]. Reaction of this oxallyl complex with dienes led to cycloheptenones, in a 3+4-cyclocoupling (eq. 24). With furans and pyrroles, bridged bicyclic compounds formed (eq. 25,26) [57]. This chemistry was used in the synthesis of the tropanoides thujaplicin (eq. 27) and nezukone (eq. 28) [58], as well as the tropane alkaloids (eq. 29) [59]. With styrenes a 3+2 → 5 cycloaddition occurred to produce 3-aryl-cyclopentanones (eq. 30) [60]. The olefin had to be able to stabilize positive

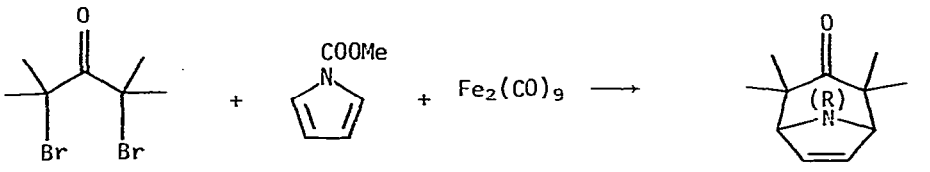


(24)



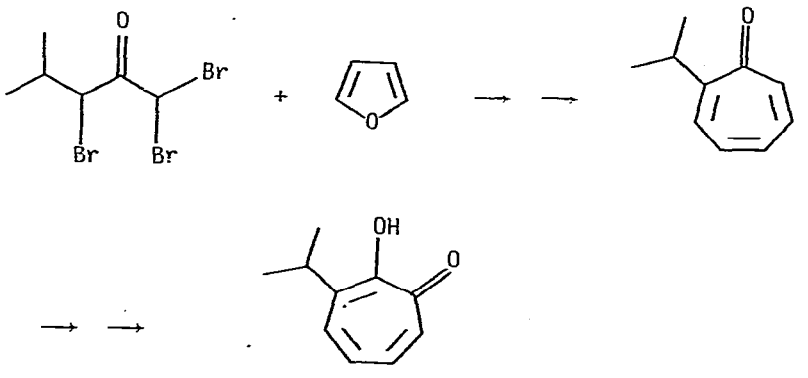
(25)

80%



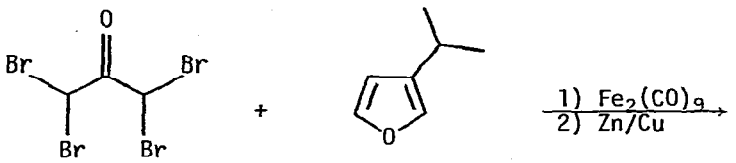
(26)

70%

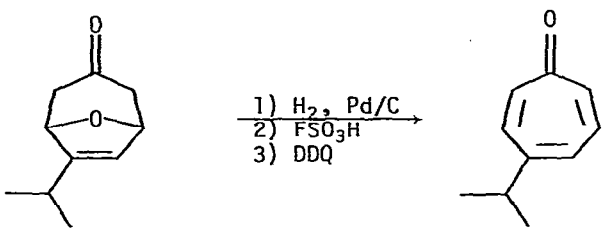


(27)

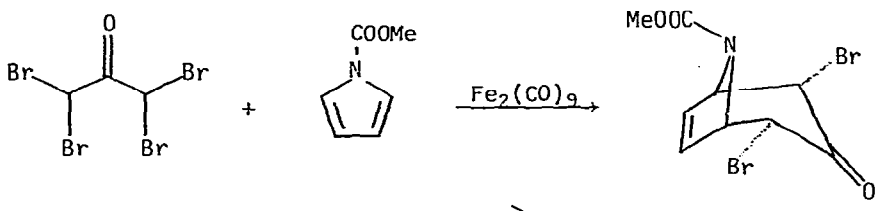
α-thujaplicin



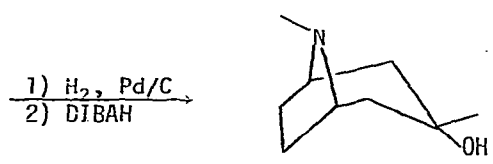
(28)

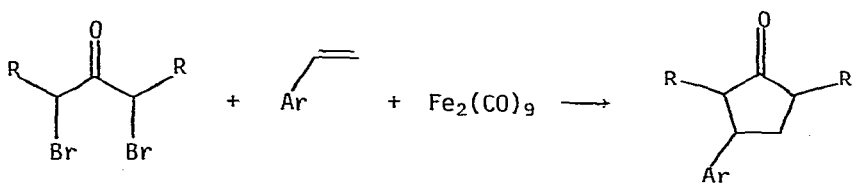


nezukone



(29)



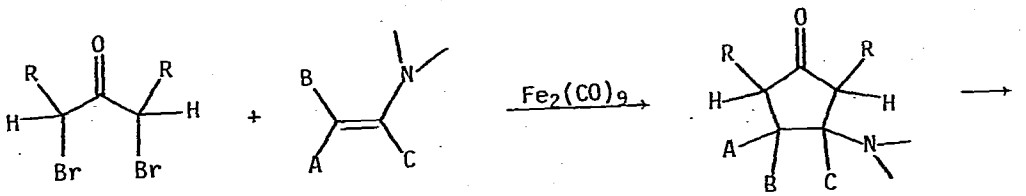


(30)

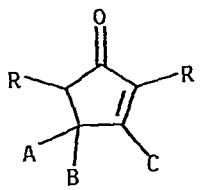
charge for this reaction to be successful. Enamines coupled in a similar fashion to produce cyclopentenones (eq. 31) [61]. This chemistry was used in a one-step synthesis of (±)-α-cuparenone (eq. 32) [62].

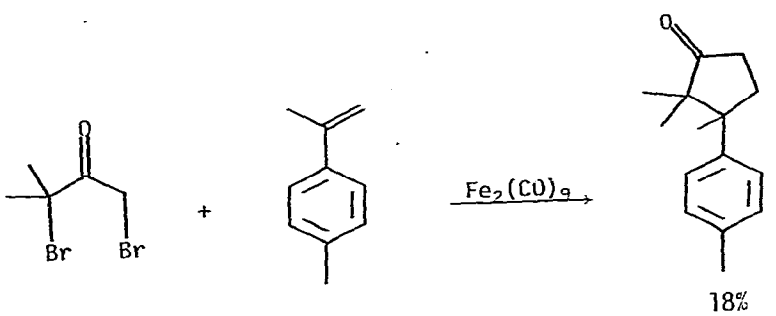
The adduct with furan was used to develop an elegant stereocontrolled approach to C-nucleosides such as pseudouridine (eq. 33) [63] and showdomycin (eq. 34) [64]. Simple olefins reacted with α,α'-dibromoketones and $Fe_2(CO)_9$ to give a number of products (eq. 35)[65].

Copper triflate catalyzed the photocycloaddition of allyl alcohols to norbornene systems to produce tricyclic compounds (eq. 36) [66]. Norbornadiene



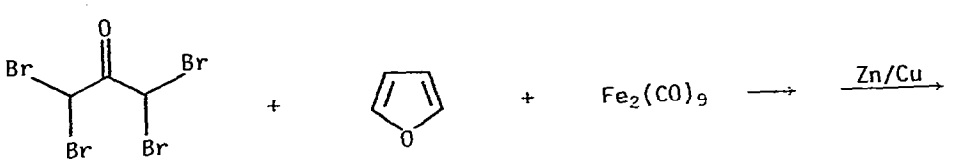
(31)

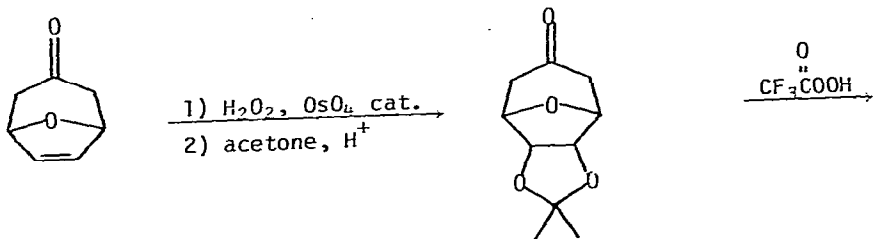




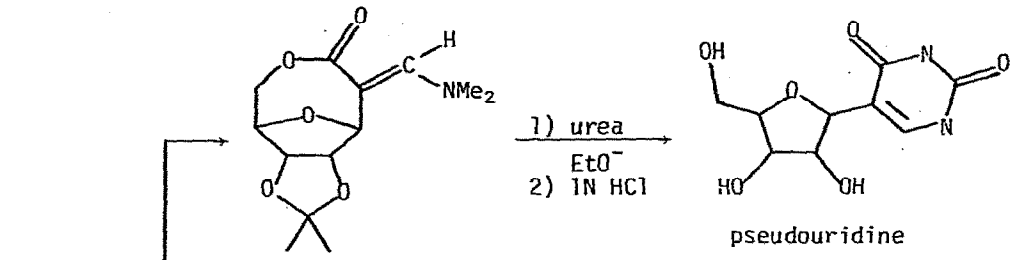
18%

(32)

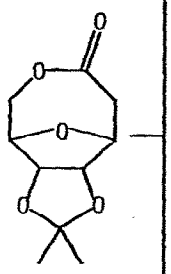


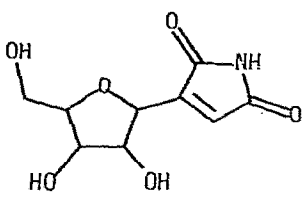


70%

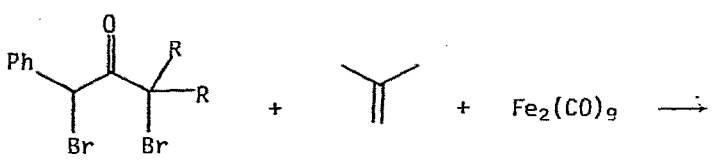


(33)

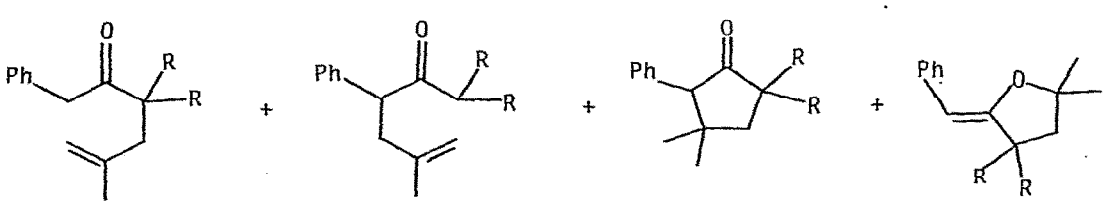




(34)

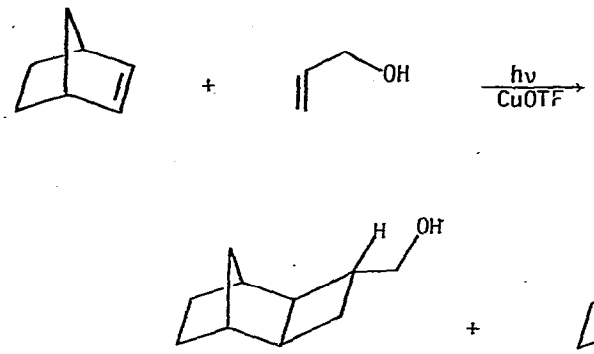


(35)



52 : 5 : 14 : 29

35% overall yield



(36)

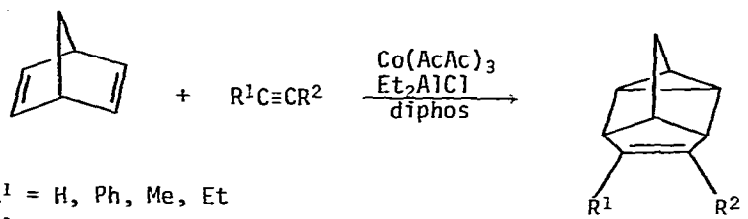
4 : 1

76%

underwent a cycloaddition with alkynes in the presence of a $Co(AcAc)_3/Et_2AlCl$/diphos catalyst (eq. 37) [67]. A thesis entitled "Metal Assisted Cycloadditions. The Formation of Substituted Carbocycles" has appeared [68].

6. Alkynes

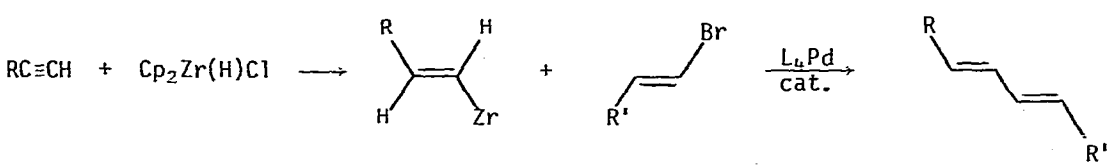
A number of new methods for the alkylation of alkynes involve hydrometallation followed by alkylation of the vinyl metal complex. In this fashion



(37)

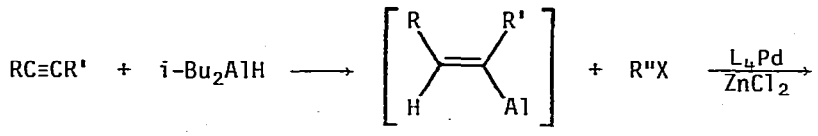
R^1 = H, Ph, Me, Et
R^2 = H, Ph

1,3-dienes were produced by hydrozirconating terminal alkynes followed by treatment of the vinylzirconate with vinylbromides and a palladium(0) catalyst (eq. 38) [69]. Only terminal alkynes reacted in this system. However, internal alkynes were alkylated when treated in diisobutylaluminum hydride, followed by aryl, alkynyl or alkenyl halides and a palladium(0) catalyst as well as zinc chloride cocatalyst (eq. 39) [70]. Vinyl zirconates from hydrozirconation of

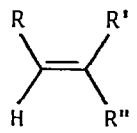


>90% E,E

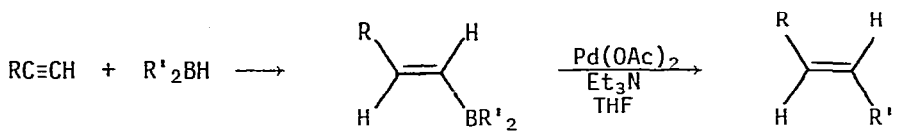
(38)



(39)

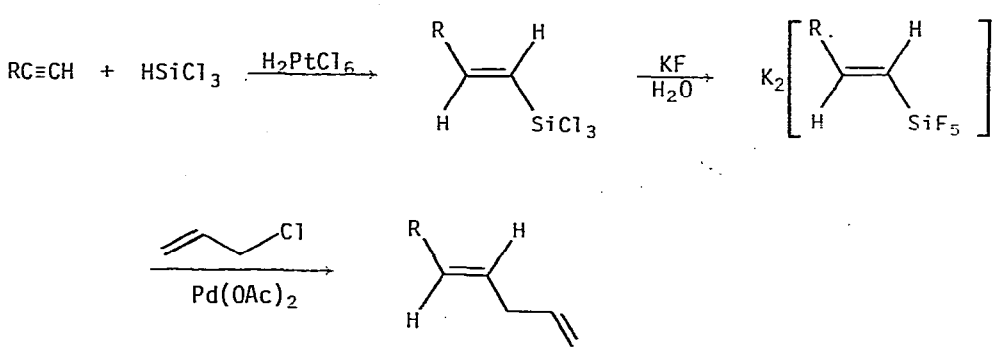


internal alkynes also underwent alkylation by halides in the presence of both Pd(0) and zinc chloride cocatalysts. Hydroboration of terminal alkynes with dialkylboranes followed by treatment with palladium(II) acetate in triethylamine/THF led to alkylation of the alkyne, while the same reaction with internal alkynes resulted in simple reduction to the alkene (eq. 40) [71]. Hydrosilation



(40)

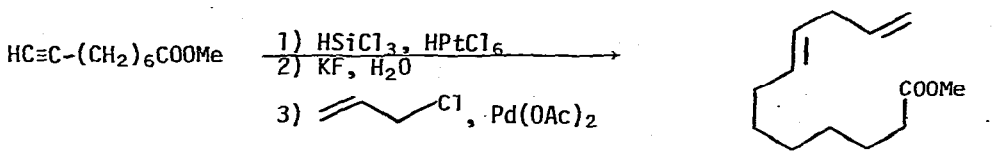
R = Bu, Hex, Ph, Oct; R' = Bu, Et, Ph, $(CH_2)_7COOMe$



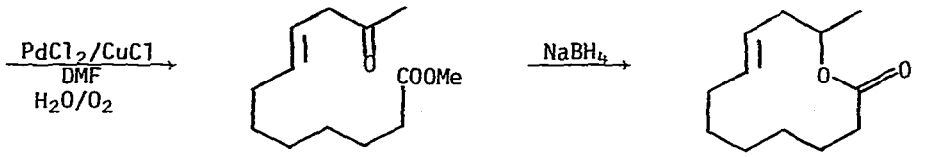
(41)

of terminal alkynes followed by treatment with allyl chloride and palladium(II) acetate resulted in alkylation (eq. 41). This process provided an approach to macrocyclic lactones (eq. 42) [72].

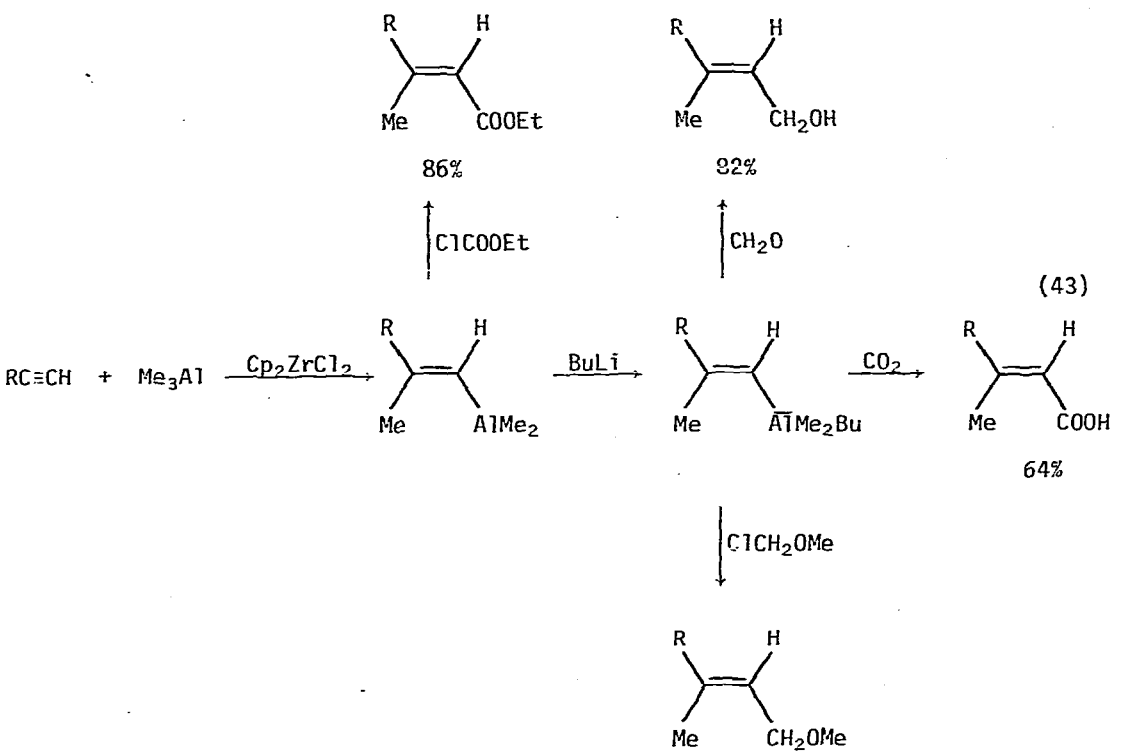
References p. 430



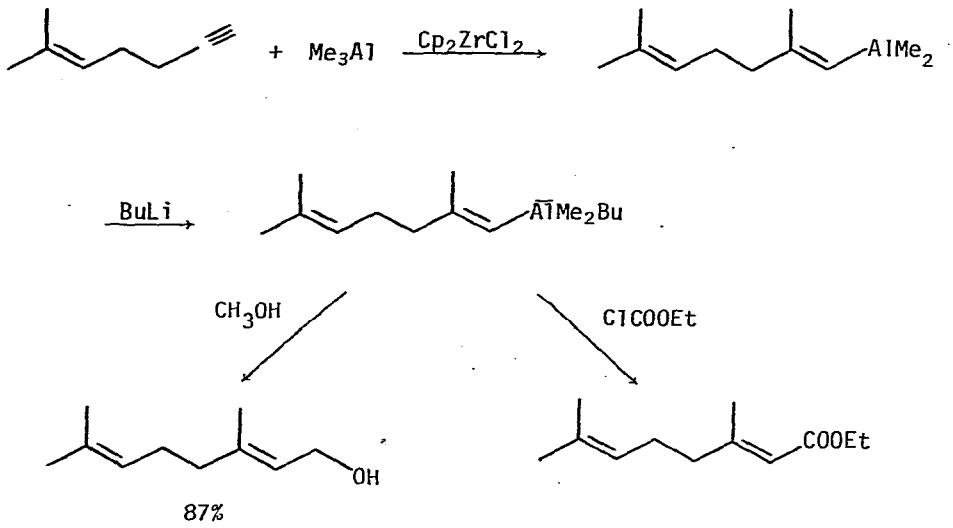
(42)



Alkynes were methylated by reaction with trimethylaluminum in the presence of Cp_2ZrCl_2 as a catalyst. The reaction was an exclusive cis addition [73]. This chemistry was shown to proceed through a vinyl alane rather than a vinyl zirconate, and the reactive aluminum compound had a great deal of useful chemistry of its own (eq. 43). Geraniol and ethyl geranate were prepared by this procedure (eq. 44) [74]. The reagent resulting from the reaction of trimethylaluminum and Cp_2TiCl_2 also methylates alkynes in a cis addition [75].



(43)



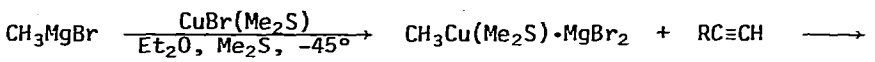
(44)

Methylmagnesium bromide added to trimethylsilyl-1-octyne in the presence of a $Me_3Al/Ni(AcAc)_2$ catalyst produced a mixture of vinyl magnesium halide complexes. These reacted with a variety of electrophiles including aldehydes, iodine, and alkyl halides to allow further functionalization of the alkene (eq. 45). When ethylmagnesium bromide was used, hydrometallation resulted [76]. The reagent $CH_3Cu(Me_2S)\cdot MgBr_2$ added in a syn fashion to terminal alkynes to give the corresponding vinylcuprate which reacted with allyl bromide, acetyl chloride, 2-cyclohexenone and ethylene oxide to undergo reactions typical of such copper species (eq. 46)[77]. Polymeric RCu complexes add to alkynylsulfoxides in a cis fashion to produce the vinyl sulfoxide (eq. 47) [78]. The use of R_2CuLi

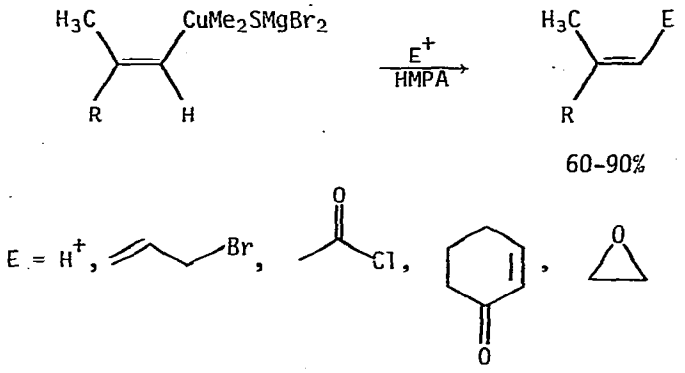
$$C_6H_{13}C{\equiv}CSiMe_3 + CH_3MgBr \xrightarrow[Ni(AcAc)_2]{Me_3Al} \xrightarrow{E^+} \quad (45)$$

9 : 1

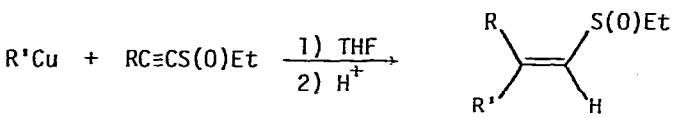
E = RCHO, RX, I_2, H^+



(46)

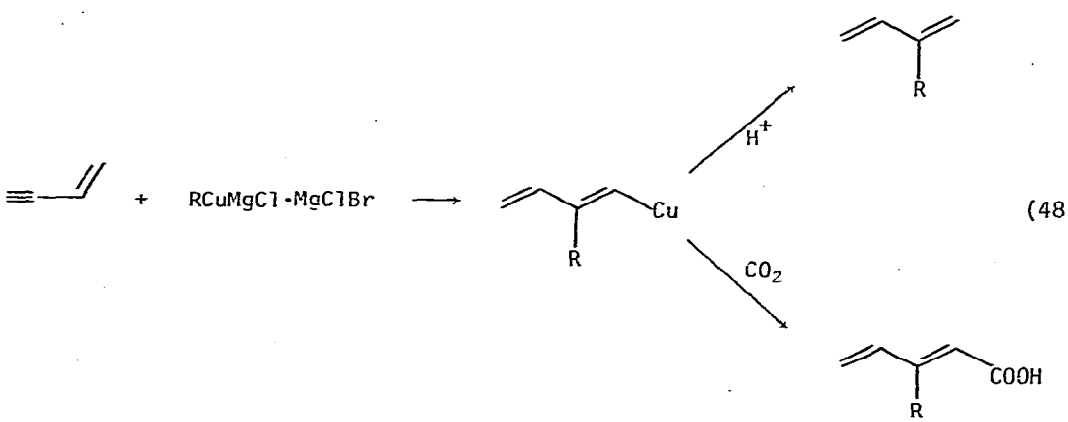


(47)

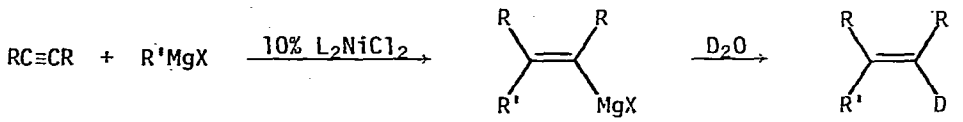


100% cis addition

complexes in place of RCu lead to lower yields of less pure material. The triple bond of conjugated enynes also underwent alkylation with RCuMgCl·MgClBr complexes to give vinyl coppers which react further with electrophiles (eq. 48) [79]. Finally, L_2NiCl_2 catalyzed the addition of Grignard reagents to internal alkynes to produce vinyl Grignard complexes (eq. 49) [80].

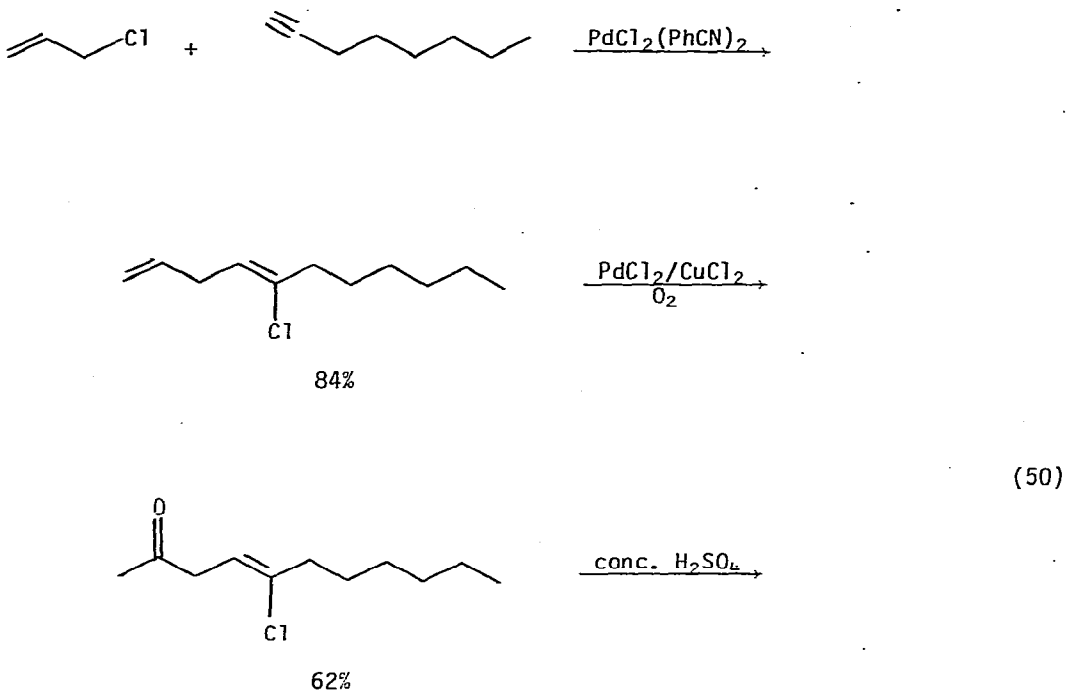


(48)

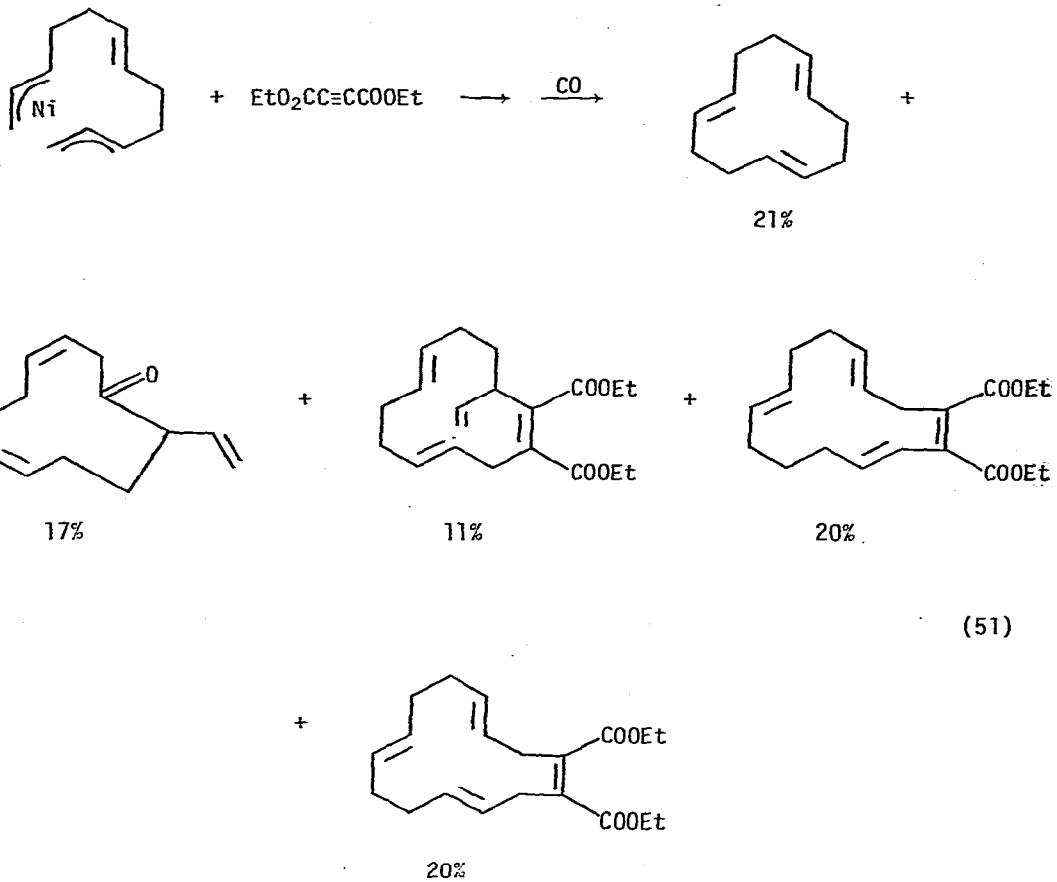


(49)

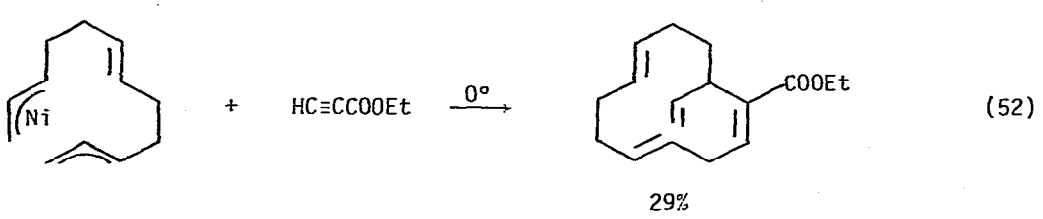
Terminal alkynes reacted directly with allylic halides in the presence of palladium(II) chloride to couple. The resulting diene was oxidized with $PdCl_2/O_2$ and then ring closed to form dihydrojasmone (eq. 50) [81]. The mechanism of the reaction of diphenylacetylene with $CpCo(Me)_2PPh_3$ to produce $PhCH(Me)C(Ph)=CH_2$ has been studied [82]. Dimethylacetylene dicarboxylate reacted with α,ω-dodecatrienylnickel to produce a number of large ring compounds (eq. 51). Ethyl propiolate reacted to give a single product, but in low yield (eq. 52) [83].



(50)



(51)

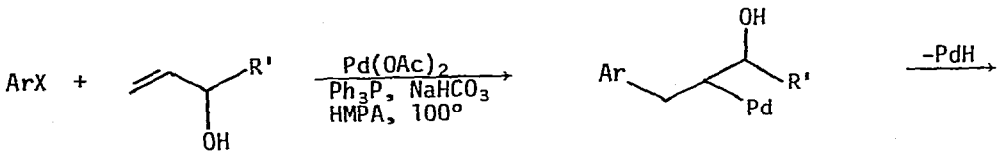


(52)

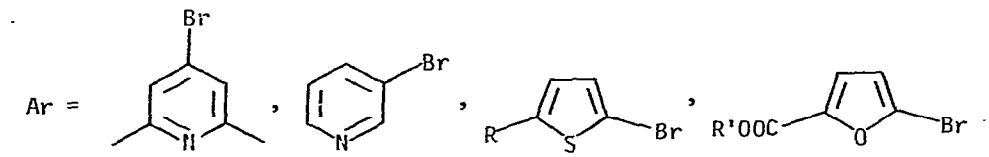
7. Allylic and Propargylic Alcohols, Acetates and Halides

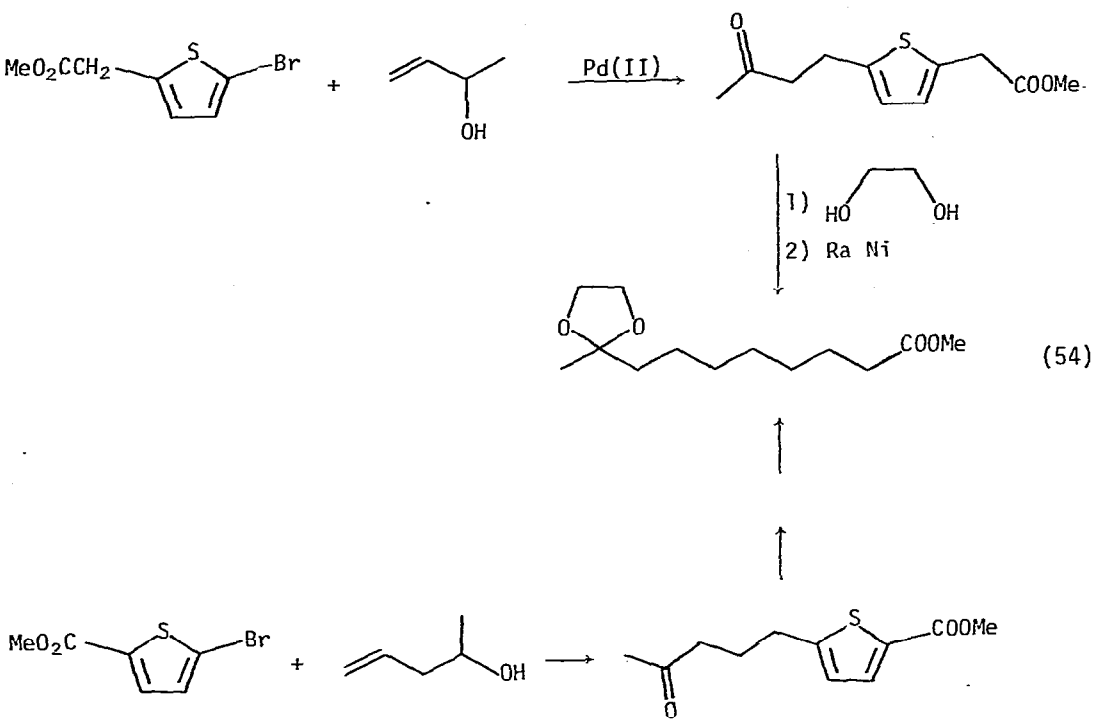
Allyl alcohols were reacted with heteroaromatic halides in the presence of palladium(II) catalysts in polar solvents to replace the halogen with a carbonyl containing side chain. The reaction involves addition of "Ar-Pd" to the olefin followed by elimination of "PdH" towards the alcoholic carbon, producing an enol which rearranges to the ketone (eq. 53). In this fashion, 4-bromo-2,6-lutidine [84], 3-bromopyridine [85], 2-bromothiophenes [86], and 2-bromo-5-carboxyfurans [87] were alkylated. The reaction with the bromothiophenes

was used to prepare the queen bee substance (eq. 54) [86].



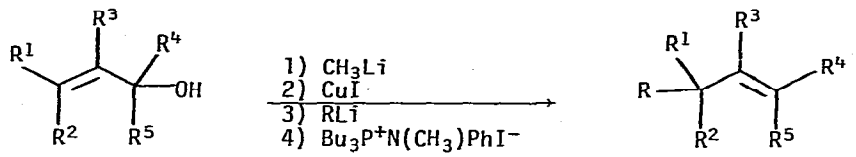
(53)



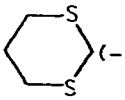


(54)

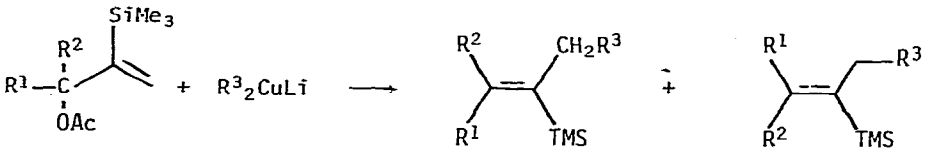
The hydroxyl group of allylic alcohols was directly displaced by $RCuBF_3$ with allylic transposition. Allylic acetates reacted in a similar fashion while allyl ethers were unreactive [88]. A similar reaction was affected as in eq. 55 [89].



(55)

1°, 2°, 3° allylic alcohols react R = nBu,  (-), etc.

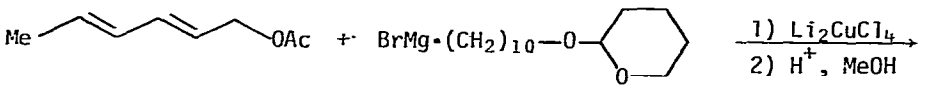
Allyl acetates containing a trimethylsilyl group on the olefin reacted with dialkylcuprates to undergo alkylation with allylic transposition, producing trisubstituted vinyl silanes (eq. 56) [90]. As an early step in the synthesis of cytochalasins, 2,4-hexadienyl acetate was alkylated (without allylic transposition) with a long chain ω-THP Grignard reagent in the presence of Li_2CuCl_4 (eq. 57) [91]. The alkylation of all four double bond isomers of 2,4-heptadienyl acetate by Grignard reagents in the presence of Li_2CuCl_4 was studied. For the EE substrate, the alkylation was stereospecific. For the other isomers, double bond isomerization occurred to some extent [92].



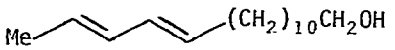
(56)

60-80%

from 1:1 to 92:8 E:Z depending on bulk

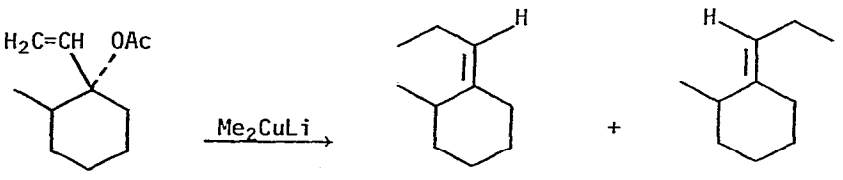


(57)



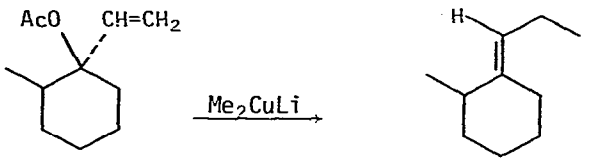
The reaction of trans-2-methyl-1-vinylcyclohexyl acetate with lithium diorganocuprates gave a 1:1 mixture of E and Z isomers of the S_N2' product, while the cis-substrate gave exclusively the E olefinic product (eq. 58) [93]. Allyl

acetates were directly alkylated by terminal alkynes without allylic transposition using a nickel(0) catalyst [94].



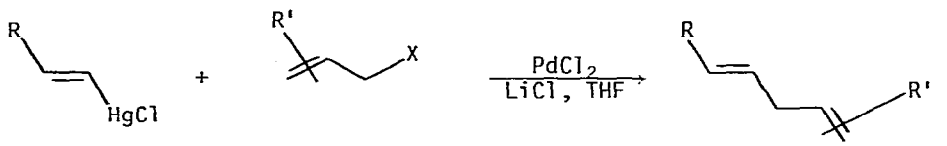
1 : 1 (79%)

but (58)



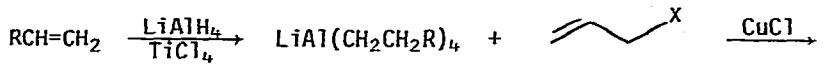
76%

Treatment of 5-(chloromercuri)uracil nucleosides with allyl chloride in the presence of lithium chloropalladate gave 5-allyluridine in good yield. Rhodium(III) and rhodium(I) complexes did not catalyze this reaction [95]. Vinyl mercuric halides reacted with allylic halides in the presence of palladium(II) chloride to produce 1,4-dienes in which the allylic group had undergone an allyl transposition (eq. 59) [96]. Allylic chlorides underwent alkylation without allylic



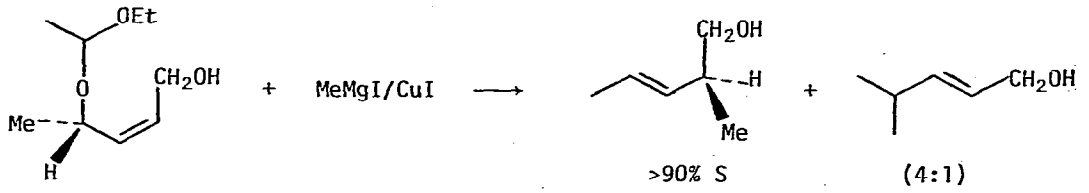
(allylic transposition) (59)

transposition when treated with the complex resulting from an organolithium reagent, copper(I) iodide and dimethyl sulfide [97]. Lithium tetraalkylaluminates, produced in the titanium tetrachloride catalyzed reaction of lithium aluminum hydride with alkenes, alkylated allylic halides in the presence of copper(I) chloride. Some allylic transposition was noted (eq. 60)[98]. Cis and trans allylic ethers containing a chiral center α to the olefin reacted with methylmagnesium iodide/copper(I) iodide. The reaction was shown to be a trans substitution (eq. 61) [99]. An allylic dithiocarbamate reacted with butylmagnesium bromide/copper(I) iodide with almost complete allylic transposition in THF/ether and almost complete retention in ether (eq. 62) [100].

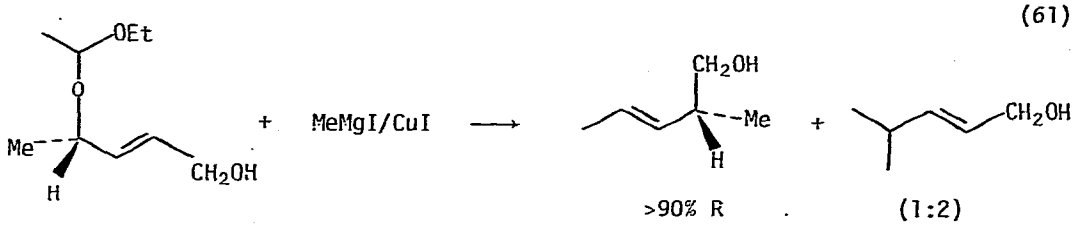


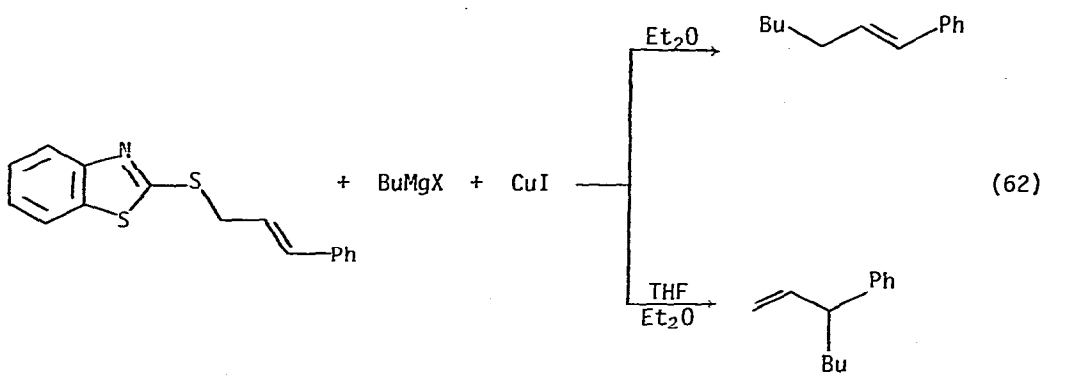
(60)

$RCH_2CH_2CH_2CH=CH_2$



(61)

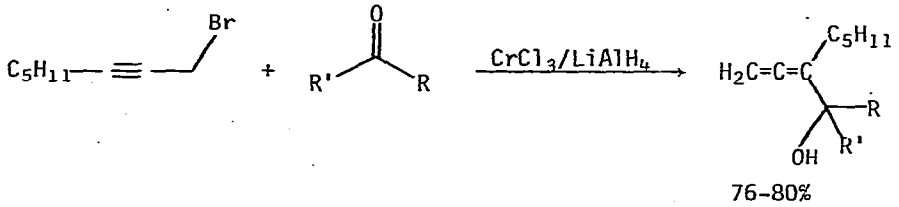




(62)

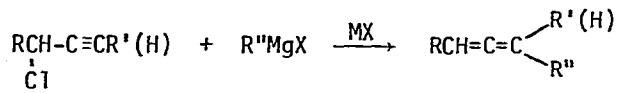
Propargyl halides reacted with ketones when treated with low valent chromium species (generated by the reaction of lithium aluminum hydride with chromium(III) chloride) to produce allenic alcohols (eq. 63) [101]. Grignard reagents reacted with propargyl halides in the presence of $CuBr_2$, $FeCl_3$ or $NiBr_2$ to produce allenes by an S_N2' type process in excellent yield (eq. 64). Chromium, manganese,

rhodium and silver salts did not catalyze this reaction, and t-butyl Grignards did not react [102]. In contrast, lithium dialkylcuprates reacted with propargyl



76-80%

(63)

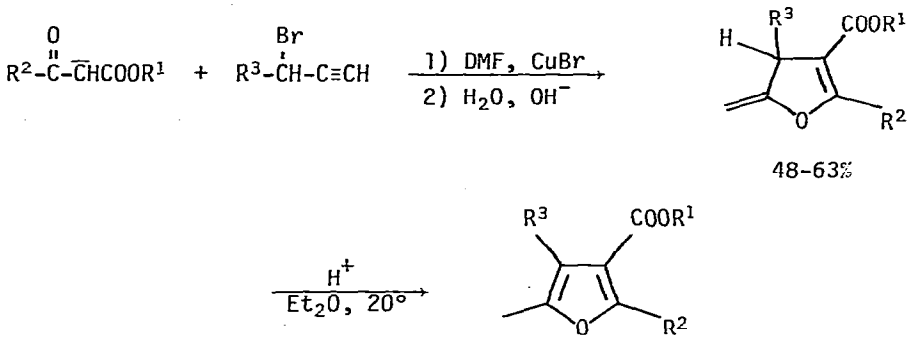


80-90%

(64)

R" = n-Bu, sec-Bu, Et, Me

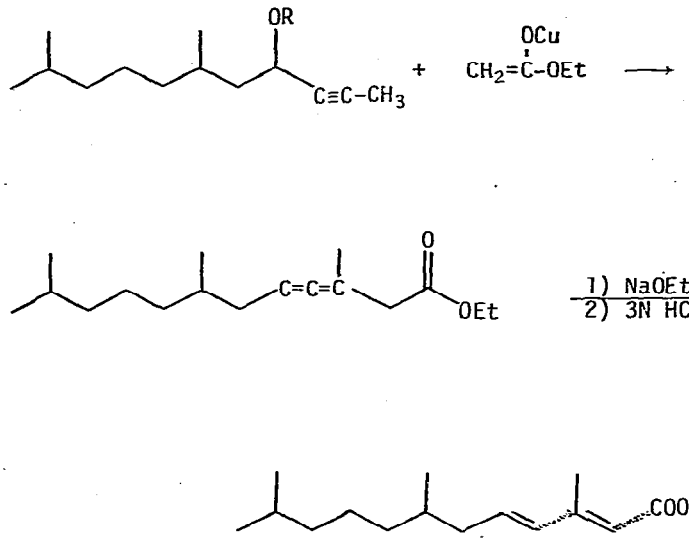
halides to produce allenes as well, but t-butylcuprates reacted cleanly, forming t-butyl allenes in high yield [103]. Propargyl halides reacted with enolates of β-ketoesters to form furans ultimately (eq. 65) [104]. Lithium tetraalkylaluminates formed from the titanium tetrachloride catalyzed addition of lithium



48-63%

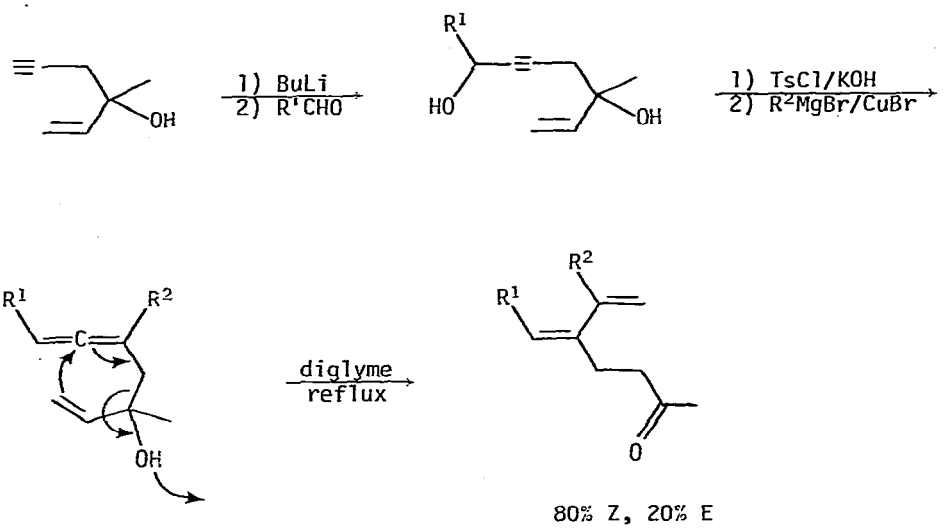
(65)

aluminum hydride to alkenes, reacted with propargyl bromide itself in the presence of copper(I) chloride to produce terminal allenes by an S_N2' reaction [105]. In contrast, propargyl acetates of trimethylsilyl acetylenes underwent alkylation by lithium dialkylcuprates exclusively by an S_N2 path, with no allenic product having been formed. This was attributed to the steric bulk of the trimethylsilyl group, which suppressed attack on the acetylenic position [106]. The copper enolate of ethyl acetate reacted with propargyl halides or tosylates to form allenic products. In contrast the lithium enolate produced strictly acetylenic products. This allene forming reaction was used to synthesize the odor constituent of Bartlett pears (eq. 66) [107]. Propargyl tosylates reacted



(66)

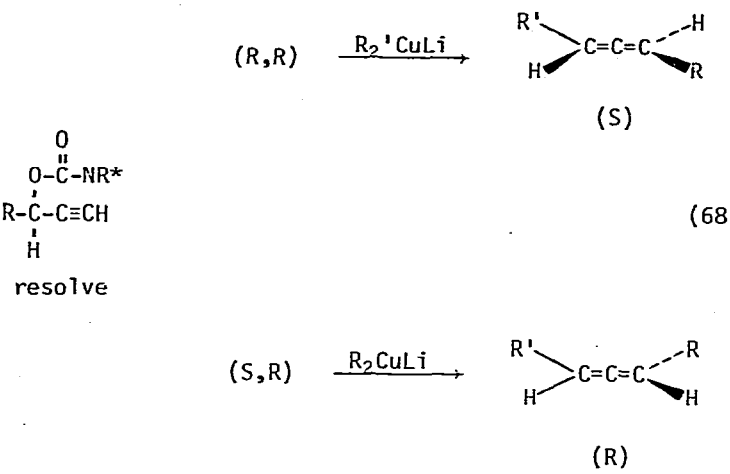
with Grignard reagents in the presence of copper(I) bromide to form allenes, which when subjected to refluxing diglyme underwent a Cope rearrangement (eq. 67)[108]. Simple chiral allenes were prepared by converting racemic propargyl



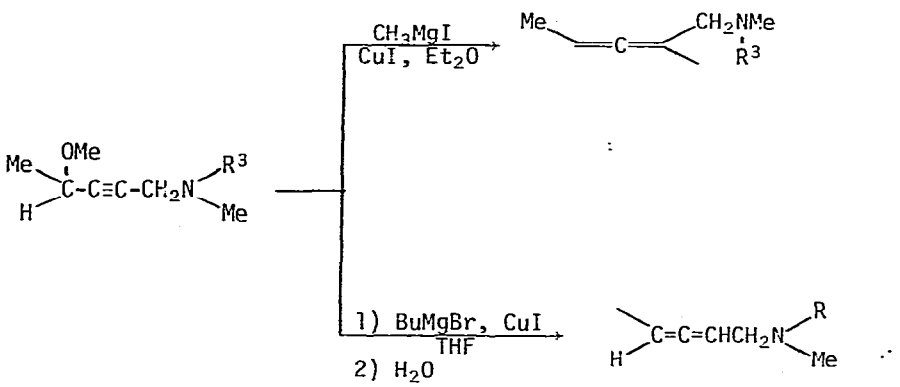
(67)

80% Z, 20% E

alcohols to diastereomeric carbamates with a chiral isocyanate. Resolution of these carbamates followed by reaction with lithium dialkylcuprates led to the chiral allenes in 60-70% yield and 20 to 82% enantiomeric excess (eq. 68) [109]. Propargyl alcohols were made to undergo S_N2' formation of allenes upon reaction with Grignard reagents in the presence of copper(I) iodide by initial treatment of the alcohol with 2-fluoro-N-ethylpyridinium salts [110]. Acetylenic systems

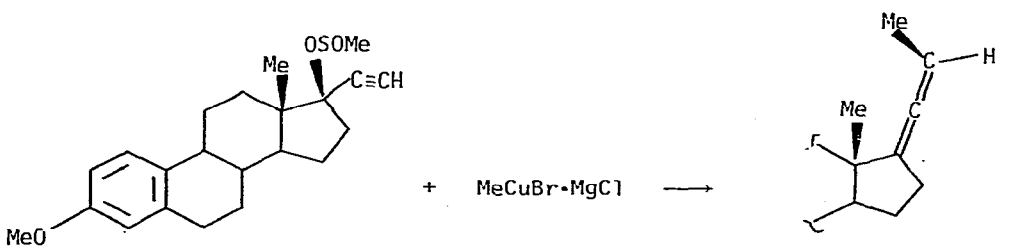


which had an ether group at one propargyl position and a dialkylamino group at the other underwent reaction with methylmagnesium iodide and copper(I) iodide to produce the allene resulting from S_N2' displacement of the ether group. In contrast, use of n-butylmagnesium bromide and copper(I) iodide in THF led to a formal S_N2' displacement by hydride (eq. 69)[111].

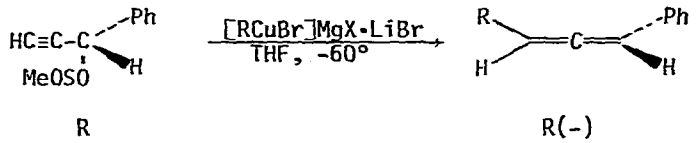


(69)

Propargyl sulfinates reacted with organocopper(I) complexes in a syn 1,3 substitution reaction to produce allenes. The stereochemistry was demonstrated in a steroid system (eq. 70) [112]. In contrast in an open chain compound the same reaction was shown to proceed by an anti 1,3-substitution (eq. 71) [113].



(70)

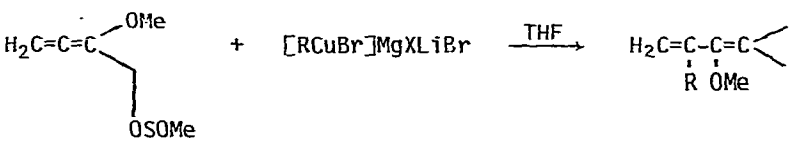


(71)

R R(-)

90% yield,
88% optical yield

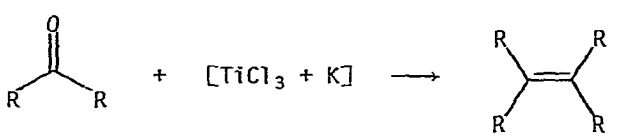
Tetraalkylaluminates reacted with allenic halides in the presence of copper(I) chloride to produce alkynes in a S_N2' reaction [114]. In contrast, allenic sulfinates reacted with [RCuBr]MgXLiBr at the central carbon of the allene system, producing 1,3-dienes (eq. 72) [115]. Allenic carbonyl, phosphine oxide [116], sulfone and sulfoxide [117] compounds reacted with organocuprates via a 1,2-addition to the activated carbon-carbon double bond to produce unstable allylcuprates which reacted further with electrophiles. These intermediate complexes were characterized by NMR and IR spectroscopy [118].



(72)

8. Coupling Reactions

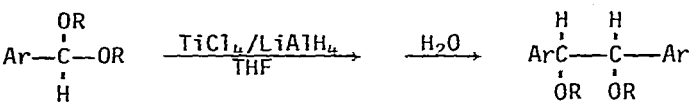
The full details of the reduction dimerization of ketones and aldehydes to olefins by low valent titanium have been published (eq. 73). Treatment of titanium trichloride with either lithium or potassium produced finely divided "Ti" which coupled (dimerized) valeraldehyde, decanal, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, adamantanone, diisopropyl ketone, cholestanone,



(73)

benzaldehyde and retinal to the symmetrical olefin. Benzophenone was further reduced to bibenzyl. Mixed couplings with acetone and other ketones went in moderate yield when a large excess of acetone was used. Intramolecular coupling of diketones to cyclic olefins was also successful with $TiCl_3$/Zn-Cu as the reducing agent and under high dilution. In this fashion 1,2-diphenylcyclobutene, and cyclic olefins from C_6-C_{14} were prepared. Civetone was synthesized in this fashion in 83% [119]. Bis-phenylketones cyclized to diphenylcycloalkenes in fair yield when treated with the reagent resulting from the reaction of titanium trichloride with lithium aluminum hydride. Ring sizes from three to eleven were

synthesized in this manner [120]. Highly hindered olefins were synthesized by the cross coupling of dicyclopropyl ketone with diisopropyl ketone using the reagent prepared by the reduction of titanium trichloride with potassium [121]. Carbonyl compounds including substituted benzaldehydes, acetophenone, benzophenone, cyclohexanone and propionaldehyde were reductively coupled to olefins by tungsten hexafluoride-lithium aluminum hydride or molybdenum carbonyl. The WCl_6-$LiAlH_4$ reagent also "reduced" epoxides to olefins [122]. The reagent resulting from the treatment of titanium trichloride with 0.25 equiv. of lithium aluminum hydride also converted epoxides to the corresponding olefin. The reaction was nonstereospecific. Bromohydrins were similarly converted to the olefins nonstereospecifically. Allylic and benzylic alcohols were dimerized by this same reagent in high yield, while simple alcohols were unreactive. Intramolecular coupling failed [123]. This allylic alcohol coupling was the topic of a dissertation [124]. Finally, $LiAlH_4/TiCl_4$ reacted with aromatic acetals or ketals to produce 1,2-diethers by a reductive coupling (eq. 74) while aliphatic acetals or ketals were reduced to the monoether [125].

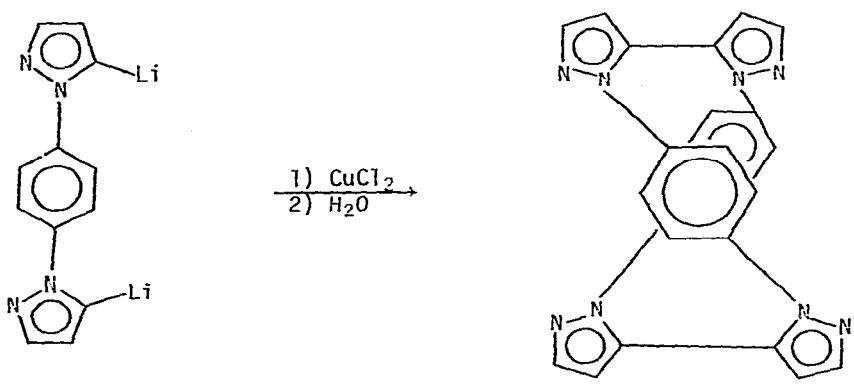


77-97%

(74)

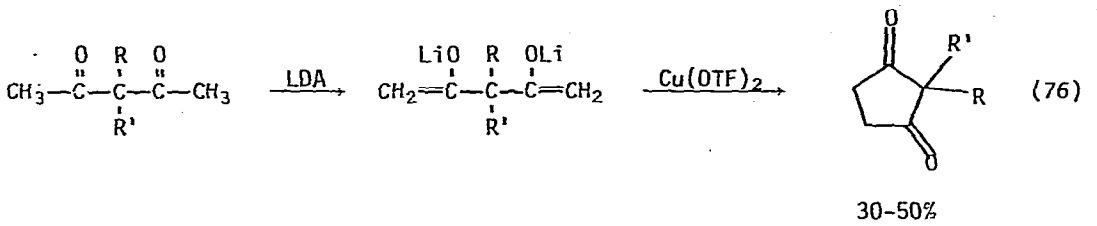
Benzyl bromide was dimerized to bibenzyl and allyl bromide to biallyl by electrochemically generated chromium(II). In the absence of chromium no coupling was observed at the potentials used in the presence of chromium [126]. Aryl halides including chloropyridines were coupled to biaryls by treatment with alkaline sodium formate-palladium on carbon-surfactant [127]. Alkyl halides were reductively coupled by electrochemically generated iron(0) [128]. Benzyl halides and benzyl alcohols were dimerized to bibenzyls, and gem dihalides to olefins by WCl_6-$LiAlH_4$ or tungsten hexacarbonyl [129].

Face-to-face benzenes were prepared by the coupling of lithiated <u>para-bis</u>-imidazolobenzenes with copper(II) chloride (eq. 75) [130]. The 1,5-



(75)

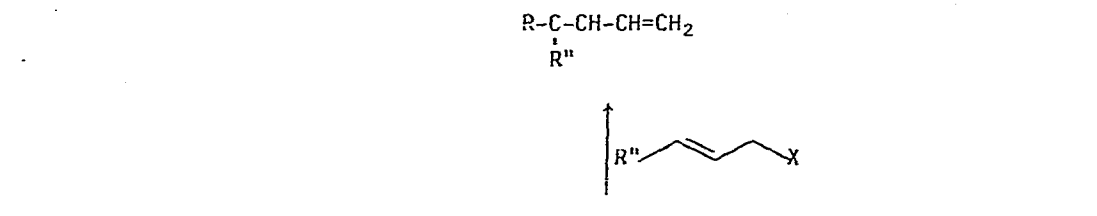
dianions of β-diketones underwent intramolecular coupling to form cyclic diketones when treated with copper(II) triflate (eq. 76) [131]. Copper(II) acetate caused



30-50%

(76)

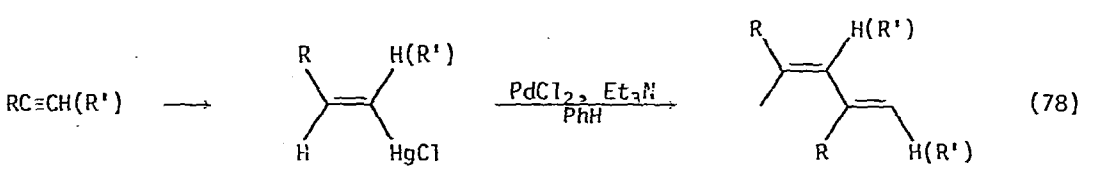
lithium monoalkylaluminum trihydrides to couple, giving a statistical mixture of all possible coupling products (eq. 77). In contrast, the same aluminum



(77)

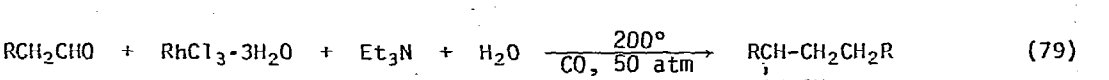
$$R\text{-}R + R'R + R'R'$$

compounds selectively alkylated allylic halides in the presence of copper(II) acetate [132]. Vinylmercuric halides underwent a novel head-to-tail coupling to form 1,3-dienes when treated with palladium(II) chloride and triethylamine in benzene (eq. 78) [133].

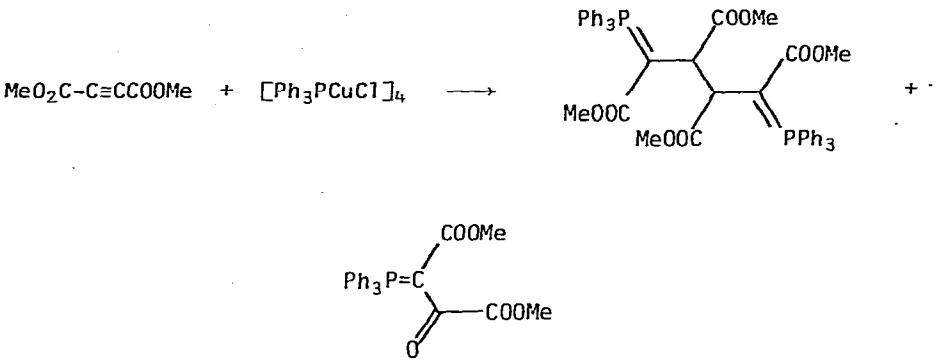


(78)

Aldehydes underwent a reductive coupling to give branched alcohols when reacted with carbon monoxide in water and ethanol in the presence of $RhCl_3 \cdot 3H_2O$ as catalyst (eq. 79) [134]. Dimethyl acetylenedicarboxylate reacted as in eq. 80 with $[Ph_3PCuCl]_4$ [135]. Phenylmagnesium bromide was coupled to biphenyl and benzyl chloride to bibenzyl when treated with CpL_2FeX [136].



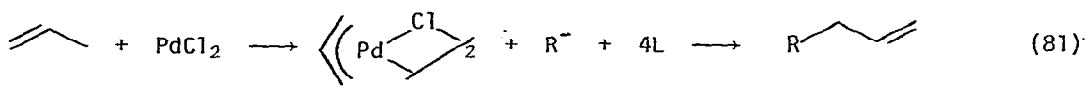
(79)



(80)

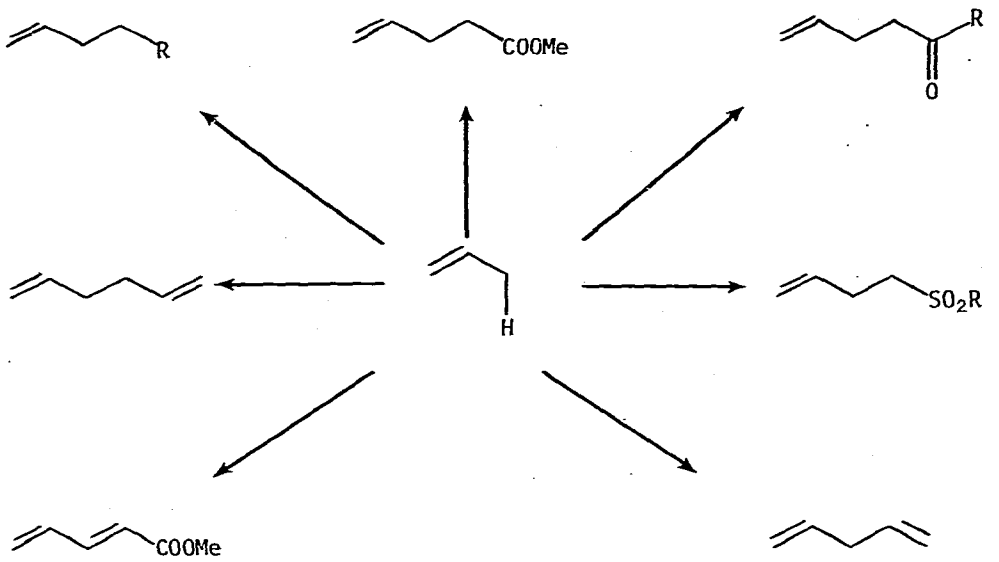
9. π-Allylpalladium Complexes

Allylic alkylation of olefins via π-allylpalladium complex intermediates has been developed into a very useful synthetic procedure (eq. 81). The full details of this work have now been published. Detailed procedures for preparing



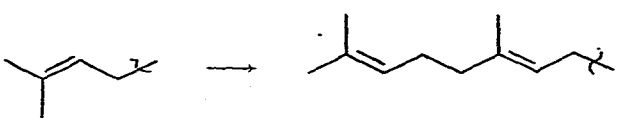
(81)

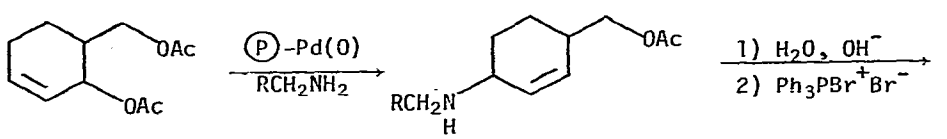
π-allylpalladium chloride complexes from olefins for use in allylic alkylation reactions have been developed, and the scope and limitations of the reaction are presented [137]. In the allylic alkylation of π-allylpalladium complexes by stabilized carbanions, attack at the less substituted position predominated, but the ratio of products was dependent on both carbanion and ligand, but not in a predictable fashion. Attack was shown to occur on the face opposite the palladium in the π-allyl complex [138]. This allylic alkylation was used to produce dienes, and an isoprenylation procedure involving allylic alkylation by a stabilized isoprenyl anion was developed. Using this procedure the conversion of olefins to a number of more highly functionalized systems was possible (eq. 82) [139]. Palladium(0) complexes also catalyzed the allylic alkylation of allyl acetates by stabilized carbanions, and was used in a stereocontrolled approach to steroid side chain elaboration [140]. With stoichiometric π-allylpalladium complex chemistry, estrone methylether was converted to 3-methoxy-19,24-bisnor-20-isocholane-1,3,5(10)-tetraenoate, while under catalytic conditions 3-methoxy-19,24-bisnor-cholane-1,3,5(10)-tetraenoate was produced. This chemistry was used for a partial synthesis of 5α-cholest-24-enone and 5α-cholestanone from testosterone. Palladium(0) complexes were supported on silica gel and polystyrene and used for the catalytic allylic amination of allyl acetates. While homogeneous palladium(0) complexes led to mixed stereochemistry, supported catalysts gave replacement of acetate by amine with clean retention. This chemistry was used to synthetize isoquinuclidines (eq. 83) [141]. Vitamin A was synthesized using π-allylpalladium chemistry (eq. 84) [142].


R
COOMe
R
O
H
SO2R
COOMe

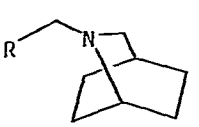
(82)

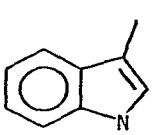
and

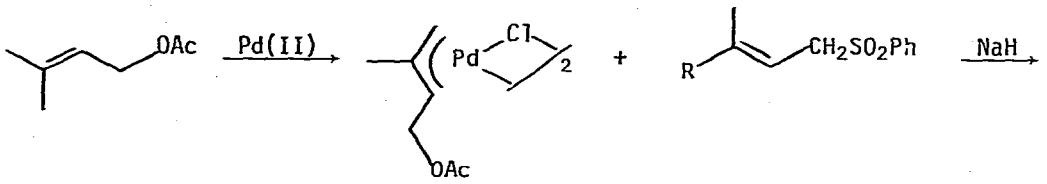



OAc
OAc
P-Pd(0)
RCH2NH2
RCH2N
H
OAc
1) H2O, OH⁻
2) Ph3PBr⁺Br⁻

(83)

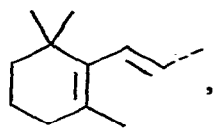
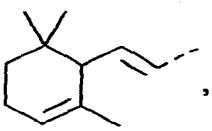
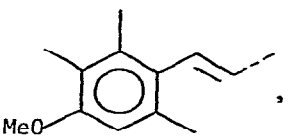

R
N

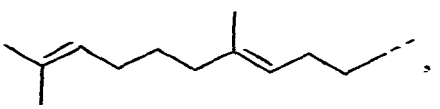
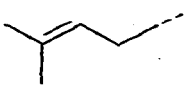
R = 
N

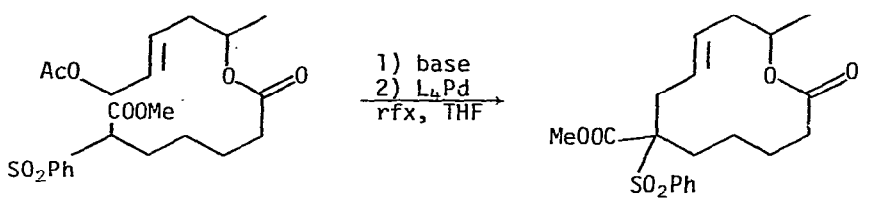


(84)

all trans 67%

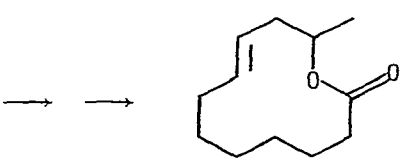
R =  ,  , 

,  , 

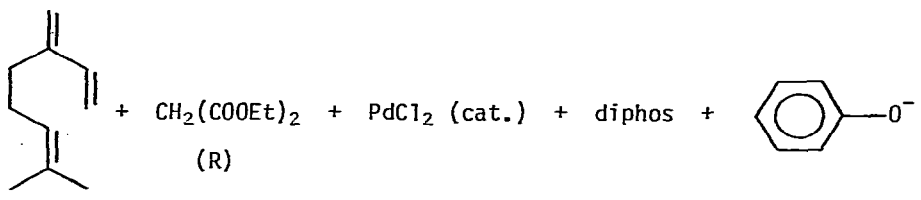


78%

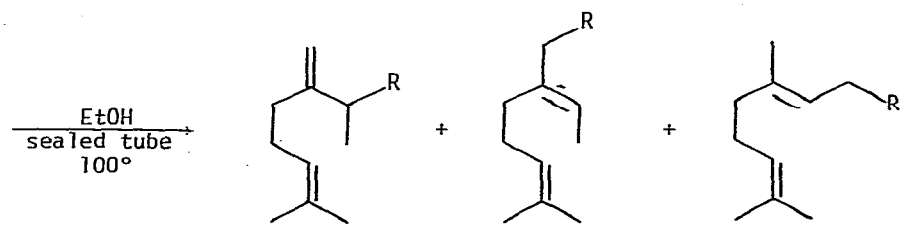
(85)

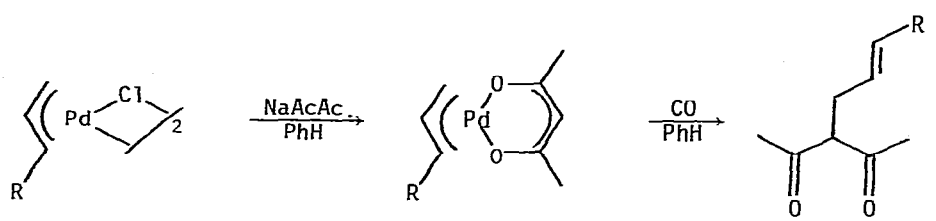


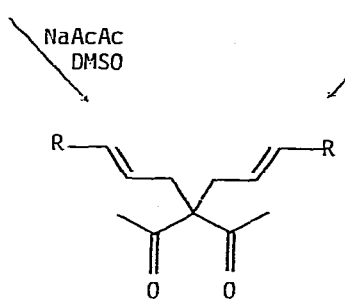
Intramolecular allylic alkylation, catalyzed by palladium(0) complexes, was used to synthesize ±-reciferolide (eq. 85) [143]. Allylphenyl ether and 2-acetylcyclohexanone reacted in the presence of a chiral (DIOP) phosphine-palladium(0) complex to give 100% 2-allyl-2-acetylcyclohexanone with 10% enantiomeric excess [144]. Terpenoid dienes were alkylated by diethylmalonate and a palladium-diphos catalyst in the presence of phenoxide. The ratio of products was dependent on the ligands present (eq. 86) [145]. π-Allylpalladium complexes reacted with sodium acetylacetonate in DMSO to give dialkylation products, while upon treatment with carbon monoxide in benzene, monoalkylation resulted (eq. 87) [146]. Finally, substituted π-allylpalladium complexes were synthesized by the reaction of vinylmercuric chlorides with palladium chloride, lithium chloride and substituted alkenes [147].



(86)



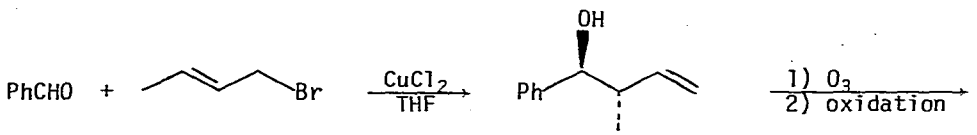


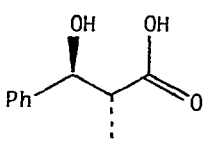


(87)

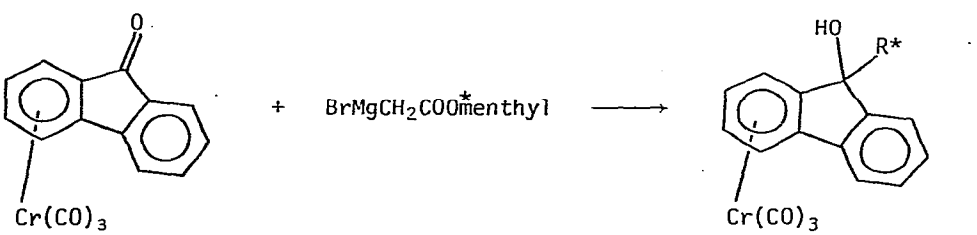
10. Ketones

Benzaldehyde underwent alkylation by crotyl bromide in the presence of chromium(II) chloride to produce only one diastereoisomer (SR, SR) of the homoallylic alcohol. Ozonolysis followed by an oxidative work-up gave the threo-3-hydroxy-2-methylcarboxylic acid (eq. 88) [148]. The π-arene chromium complex of fluorenone reacted with the optically pure magnesium enolate of menthyl acetate to give the corresponding alcohol in 20-50% yield and 40-70% asymmetric induction (eq. 89). With open chain compounds the asymmetric induction was lower [149]. In the allylation of quinones by π-allylnickel halide complexes, the reaction was shown to proceed by formation of the quinol followed by rearrangement to the allylhydroquinone (eq. 90) [150]. Quinols were also the initial products in the allylation of quinones by allyltrimethylsilanes catalyzed by titanium tetrachloride. Tetrahydrofurans were formed from ketones and these reagents (eq. 91) [151]. Phenyl hydrazones underwent catalytic allylation at the carbonyl carbon when treated with allyl acetate and nickel(0) complex catalysts (eq. 92) [152]. The natural products pestalotin and epipestalotin were synthesized using the titanium tetrachloride assisted condensation of aldehydes with β-methylene-β-lactones (eq. 93) [153].



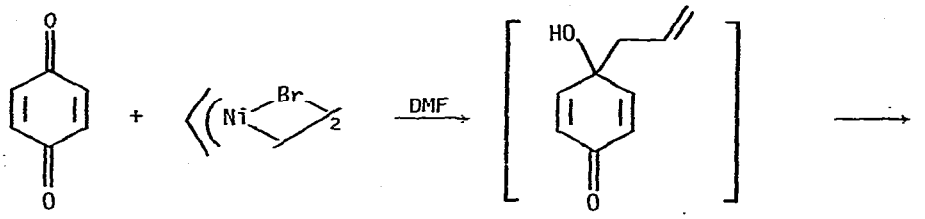


(88)

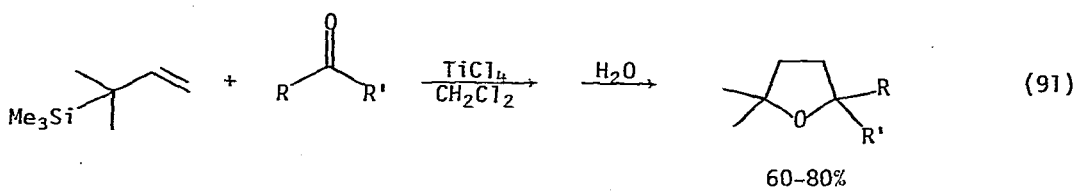


(89)

The complex $Cp_2TiCH_2AlMe_3$ reacted with ketones as if it were a Wittig reagent replacing the C=O with a $C=CH_2$ [154]. Ketones were similarly converted to methylenes by reaction with dibromomethane and zinc-titanium tetrachloride. Open chain ketones and aldehydes, cyclic ketones including camphor, and geranylacetone reacted well in this system [155]. Diaryl thioketones were



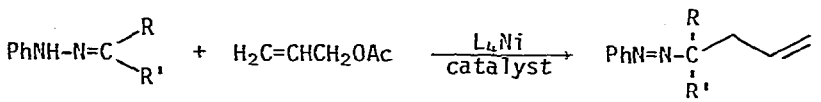
(90)



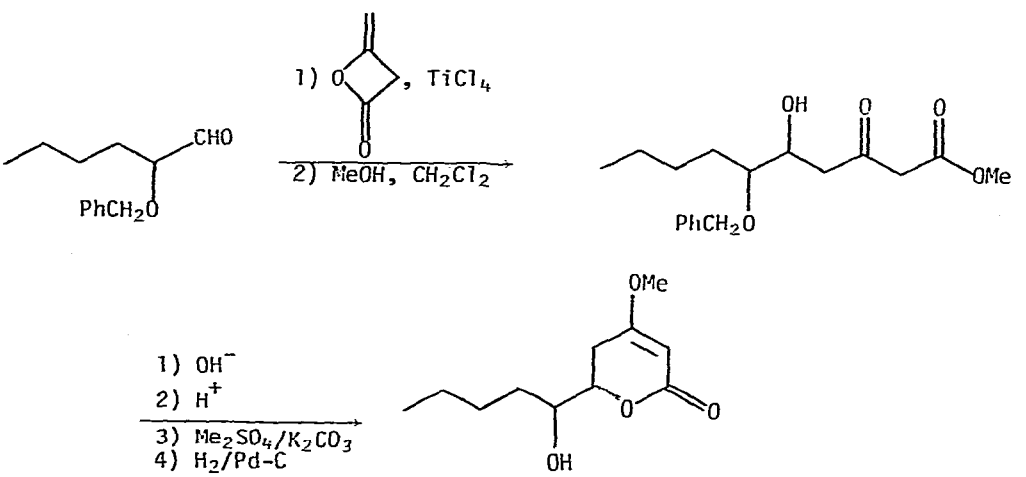
(91)

60-80%

R = H, OMe; R' = Ac, $PhCH_2CH_2$-, n-Pr, sec-Bu

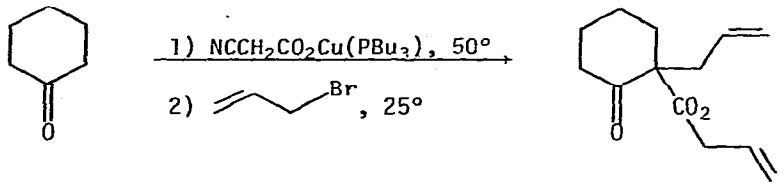


(92)



(93)

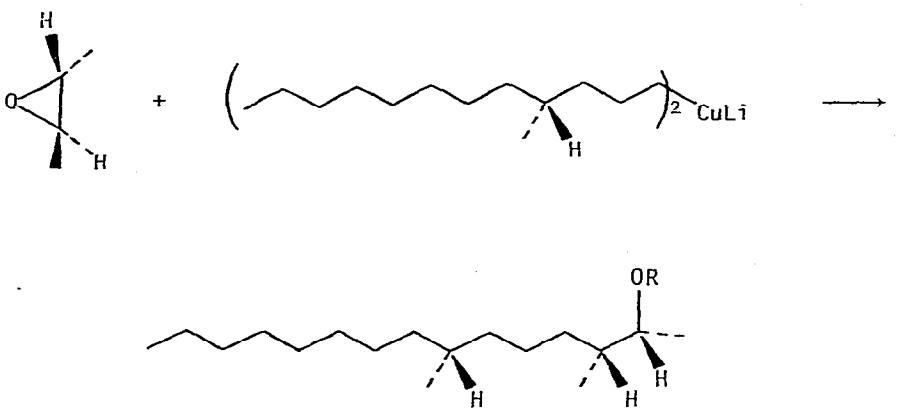
converted into diaryl fulvenes by treatment with cyclopentadienyl complexes of iron, tungsten and molybdenum [156]. Cyclohexanone was α carboxylated and α-allylated by the sequence shown in eq. 94 [157]. Reaction of cyclohexanone or acetophenone with aqueous formaldehyde in the presence of rhodium(III) chloride catalyst at 180° led to α-methylation [158].



(94)

11. Epoxides

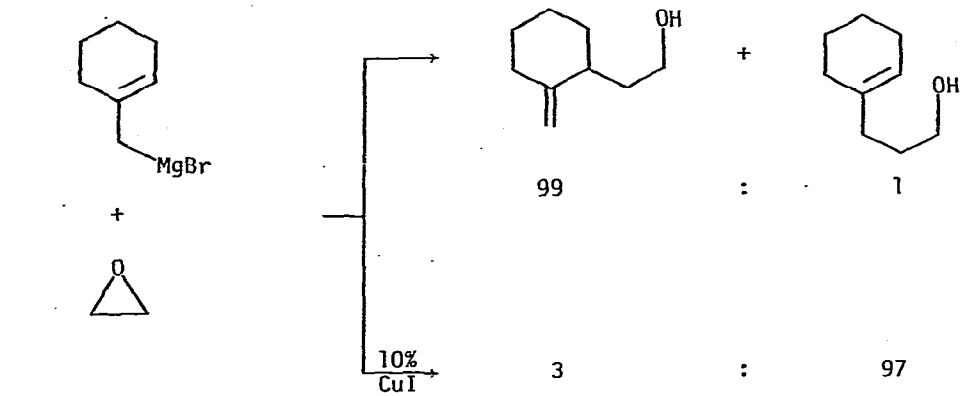
The sex pheremone of the pine saw fly, (2R, 3R, 7R)-3,7-dimethylpentadec-2-yl acetate, was synthesized by the reaction of chiral 2-butene oxide and a chiral lithium dialkylcuprate (eq. 95) [159]. Unsymmetrical allyl Grignard



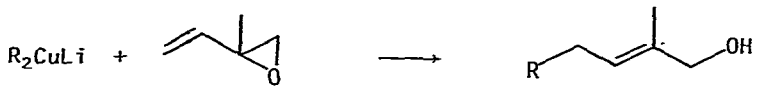
(95)

(2R, 3R, 7R)

reagents reacted with epoxides with clean allylic transposition, while in the presence of 10% copper(I) iodide virtually no allylic transposition was noted (eq. 96) [160]. α,β-Epoxyketones underwent alkylation at the α-position upon treatment with lithium dimethylcuprate followed by methyl iodide. This reaction was quite successful with epoxides of cyclohex-2-en-1-one giving high yields of α-methylated product. n-Butyl iodide failed to react [161]. Butadiene monoxide and isoprene monoxide (allylic epoxides) reacted with vinylic and allylic organocopper reagents in a 1,4 fashion. The regiochemistry and the substitution pattern of the newly formed olefin depended on the nature of the organocopper species (eq. 97). Propargylic epoxides reacted to give allenic alcohols [162].



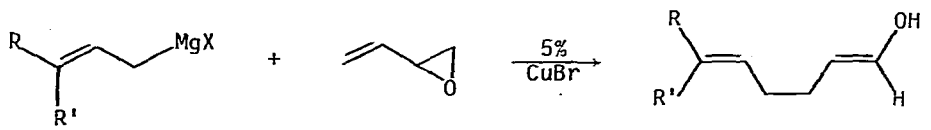
(96)



86-95%
>90% E

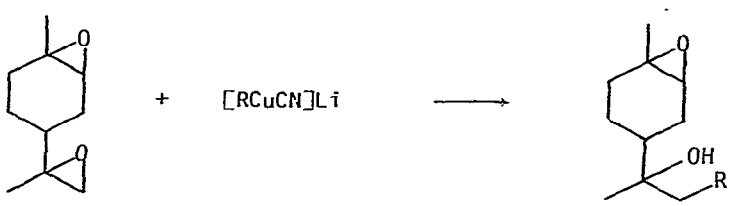
and

(97)



90%
>95% E

This chemistry was used to synthesize the sex pheremone of P. operculella; propylure was also synthesized in this fashion [163]. The diepoxide of limonone reacted with the mixed cuprate [RCuCN]Li exclusively at the acyclic epoxide (eq. 98)[164]. An intermediate in the synthesis of prostanoids was synthesized

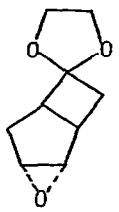


(98)

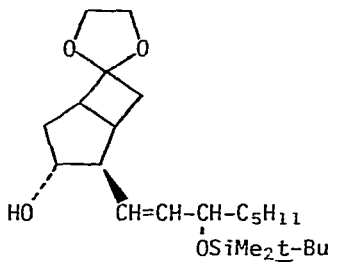
60-84%

R = Me, Bu

by the action of a mixed vinylcuprate on a bicyclic epoxide (eq. 99) [165]. The vinylcuprates resulting from the copper catalyzed addition of Grignards to terminal alkynes was reactive towards epoxides, producing homoallylic alcohols in reasonable yield (eq. 100) [166].



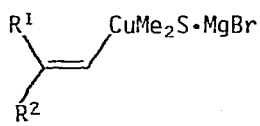
+ $PrC{\equiv}CCuCH{=}CHCH(OSiMe_2\underline{t}\text{-}Bu)C_5H_{11}$ ⟶

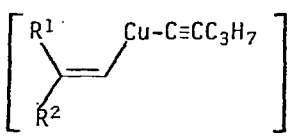


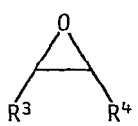
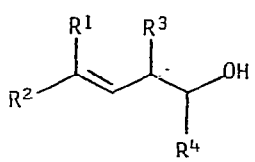
⟶ ⟶ PGE_2 (99)

86%

(80:20 this regioisomer)

$R^1MgBr + R^2C{\equiv}CH \xrightarrow{Me_2SCuBr}$  $\xrightarrow[C_3H_7C{\equiv}C\text{-}Li]{HMPA}$ (100)

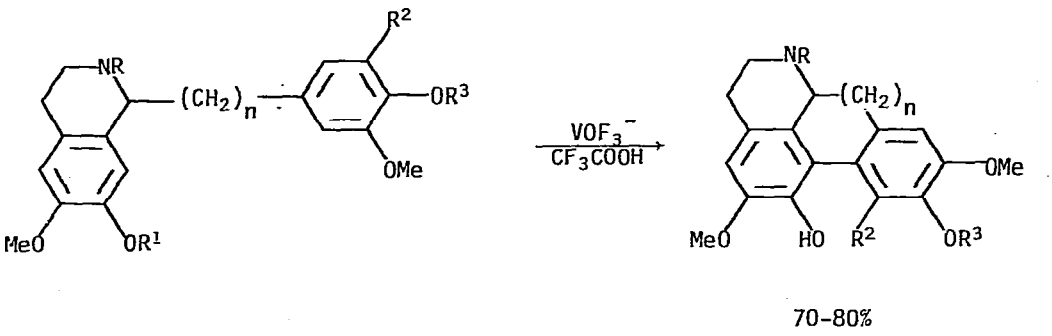


+  ⟶ 

12. Oxidative Coupling Reactions

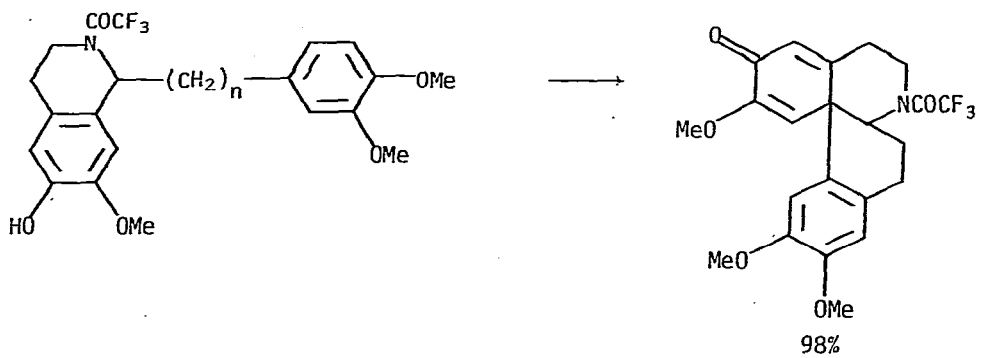
The intramolecular coupling of monophenolic benzyl and phenethyltetrahydroisoquinolines using VOF_3-CF_3COOH-$(CF_3CO)_2O$ as the coupling reagent led to the efficient synthesis of a number of aporphines, homoaporphines, homoproaporphines, and a homoproerythrinadienone (eq. 101). These reactions went in remarkably high yield, since most oxidative couplings of this type go in 10-20%

yields [167]. Mixtures of phenols were coupled to tetrahydrodibenzofuranones using $K_3Fe(CN)_6$ as the oxidizing agent [168]. Phenols underwent oxidative coupling upon treatment with cupric-α-phenethylamine complexes. Thus 2-naphthol



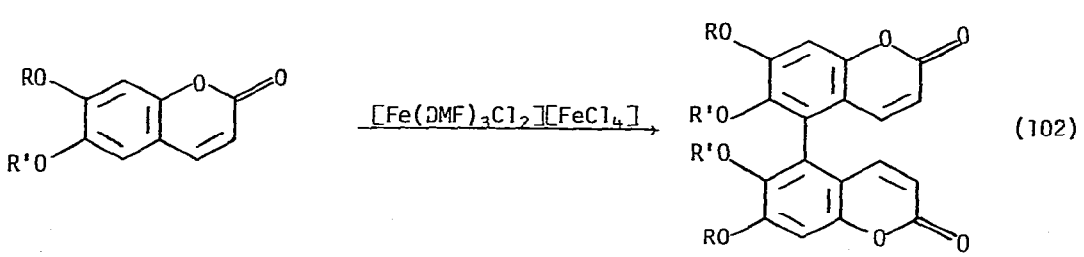
70-80%

and (101)



98%

was coupled to 1,1'-dinaphthol in 62% yield, and griseophenone was converted to dehydrogriseofulvin [169]. The reaction of two equiv. of CuCl with oxygen produced a brown solution capable of catalyzing the oxidative coupling of acetylenes, aromatic amines, and phenols. The catalytically active species was characterized as a pyridine-copper oxide complex which polymerized on standing [170]. The coumarin esculetin was oxidatively coupled to euphorbetin by the complex $[Fe(DMF)_3Cl_2][FeCl_4]$ in 60% yield (eq. 102). This complex was much more efficient than the standard ones used for this type of reaction, $K_3Fe(CN)_6$ and $Mn(AcAc)_3$ [171].

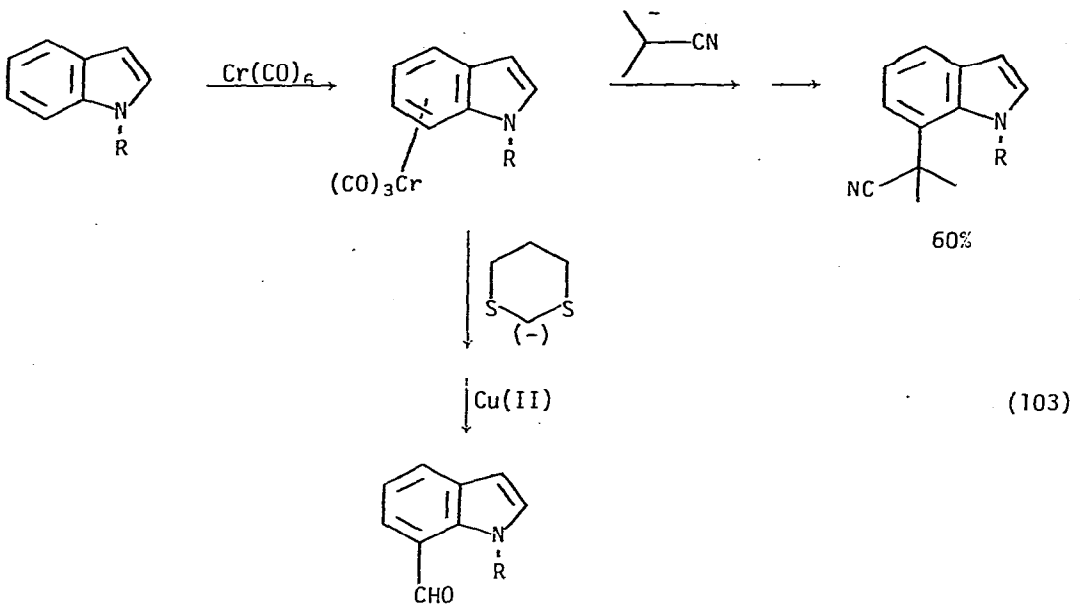


(102)

Styrene was oxidatively dimerized to 1,4-diphenylbutadiene by palladium(II) acetate in acetic acid/sodium acetate solutions. The dimeric complex $Na_2Pd_2(OAc)_6$ was identified as the catalytically active species [172]. Palladium(II) acetate/heteropolyacid complexes (i.e., $H_5PMo_{10}V_2O_{40}$) in DMF catalyzed the oxidative coupling of thiophene and 2-methylfuran to 2,2'- and 2,3'-bithiophene and 5,5'-dimethyl-2,2'-bifuran [173]. Oxygen reacted with 1-arylvinylferrocenes in the presence of silica gel to give dimeric complexes of the type ArCFc=CHCH=CFcAr, $ArCFc(OH)CH_2CH_2C(OH)FcAr$, and tetrahydrofurans [174]. Similarly silver hexafluorophosphate dimerized η^1-allyl and η^1-propargyl complexes of cyclopentadienyl iron dicarbonyl [175].

13. Nucleophilic Aromatic Substitution

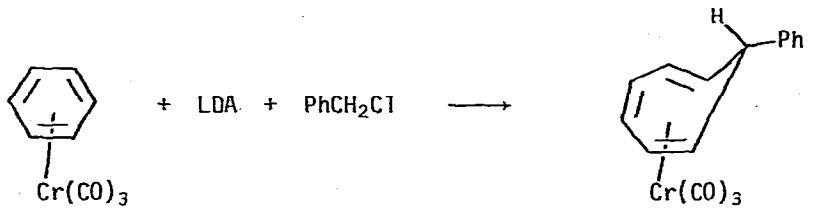
Indole was formylated and alkylated at the 7 position by converting it to the π-arene chromium tricarbonyl complex and affecting a nucleophilic aromatic substitution with lithio dithiane or isopropylnitrile. Carboxylic acid dianions, ester enolates and enamines failed to react (eq. 103) [176]. The application of



(103)

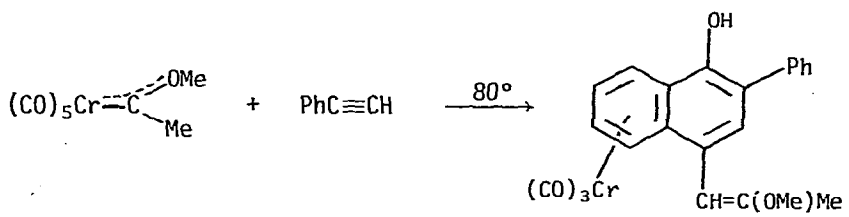
π-arene tricarbonyl chromium complexes to organic synthesis has been reviewed [177]. This chromium assisted nucleophilic aromatic substitution has been enhanced as a synthetic method by the development of a method to free the arene from the chromium and recover the chromium in usable form. The procedure consists of refluxing the arene complex in pyridine. This produced the $Py_3Cr(CO)_3$ complex which reacted with arenes to regenerate the desired complexes [178]. Arene chromium tricarbonyl complexes underwent stereospecific ring expansion to cycloheptatriene complexes upon treatment with LDA and benzyl chloride

(eq. 104) [179]. Chromium carbene complexes reacted with alkynes to produce



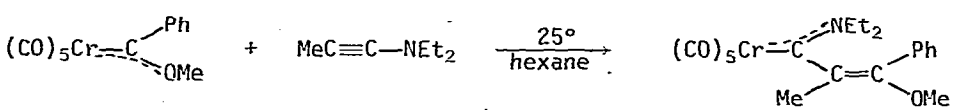
(104)

π-arene complexes of α-naphthol (eq. 105) [180] and indenone (eq. 106) [181]. Although the yields were low, the formation of such complex molecules from simple ones is potentially useful.

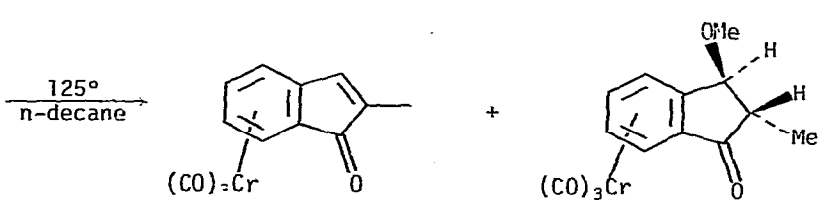


12%

(105)



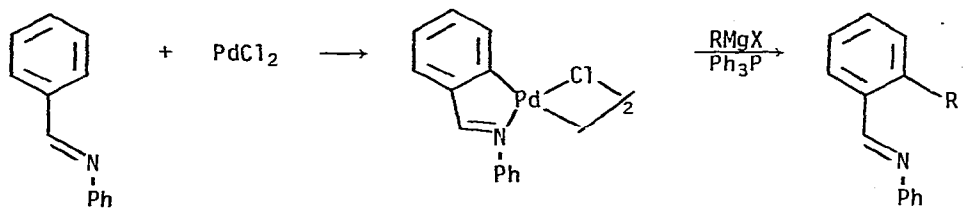
(106)



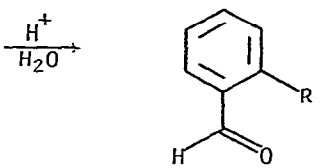
24% 20%

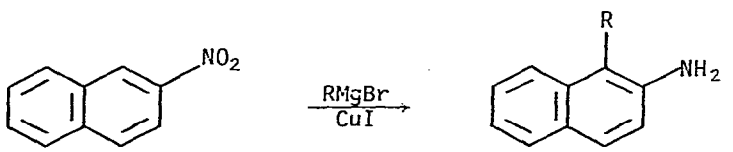
Orthopalladated aromatics underwent replacement of the palladium by an alkyl group of a Grignard or organolithium reagent in the presence of added triphenylphosphine. This alkylation was restricted to unstabilized carbanions, and allowed the o-alkylation of benzaldehydes via their imines or hydrazones (eq. 107) [182]. Certain nitroaromatics reacted with Grignard reagents and copper(I) iodide to undergo ring alkylation and reduction at the same time (eq. 108) [183]. Nitromethane alkylated aromatic hydrocarbons in refluxing acetic

acid in the presence of manganese(III) acetate (eq. 109) [184]. Finally, nickelocene reacted with hexachlorocyclopentadiene to give 1,2,3,4-tetrachloro-5-(4-chloro-2-cyclopentenylidene)-1,3-cyclopentadiene. With trifluoromethyl iodide isomers of trifluoromethylcyclopentadiene were formed [185].



(107)





55-75%

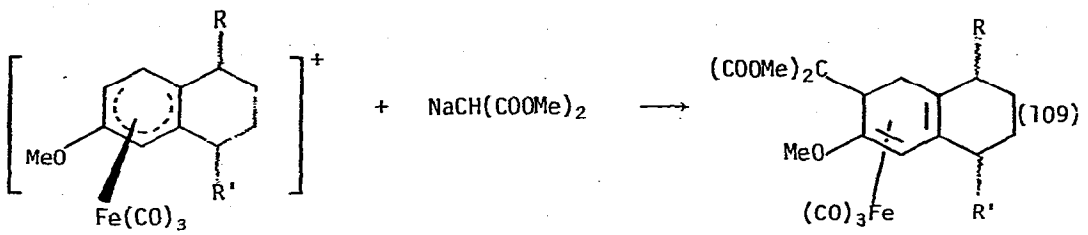
(108)

$$CH_3NO_2 + Mn(OAc)_3 + ArH \xrightarrow[rfx]{HOAc} ArCH_2NO_2$$

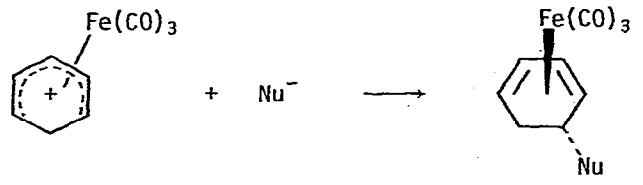
~70%

Ar = Ph, p-tolyl, p-anisyl

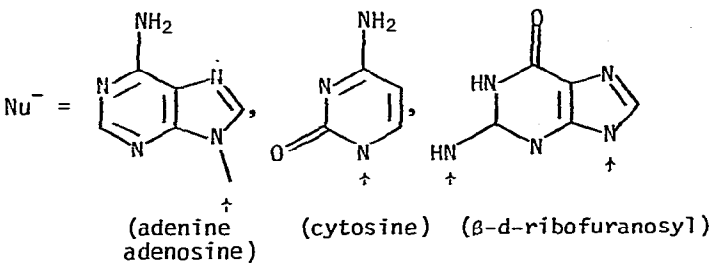
Dienyliron complexes underwent reaction with a number of nucleophiles to permit introduction of the nucleophile onto the dienyl system (eq. 109) [186], (eq. 110) [187], (eq. 111) [188].



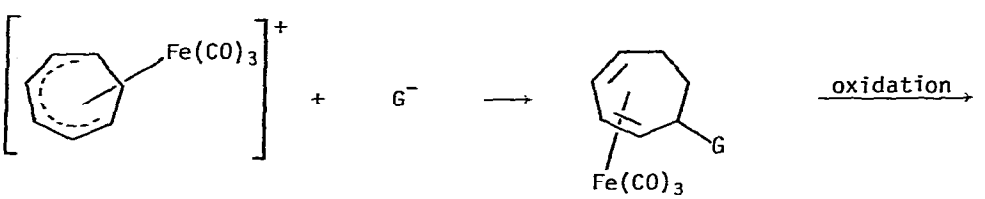
(109)



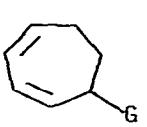
(110)



(adenine adenosine) (cytosine) (β-d-ribofuranosyl)



(111)

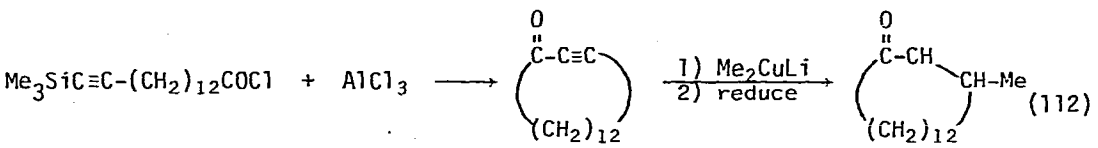


32-72%

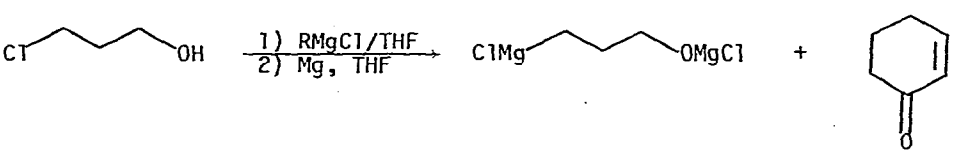
$G^- = OH^-, CH_3O^-, PnO^-, PhS^-, Me_2N^-, t\text{-}BuNH^-, CH_3^-$

B. Conjugate Addition

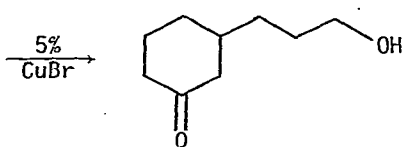
Organocopper complexes continued to be the reagents of choice for conjugate additions, and research continued unabated on several fronts. The naturally-occurring fifteen carbon cyclic ketone, muscone, was synthesized by an aluminum trichloride cyclization of an ω-trimethylsilylacetylenic acid chloride followed by conjugate methylation of the ynone by lithium dimethylcuprate (eq. 112) [189]. The Grignard reagent from 3-chloroethanol underwent a 1,4-addition to cyclohexenone in the presence of 5% copper(I) bromide (eq. 113). This same system also coupled with allylic ethers and aliphatic halides [190]. The lithium cuprate of the anion of acetone dimethylhydrazone added in a conjugate fashion to ethyl cyclohexenecarboxylate to give an intermediate keto ester which was a flexible annelation reagent (eq. 114) [191]. Similarly the cuprate from the terminal anion of the acetal of propionaldehyde added to enones in a 1,4-fashion and permitted subsequent acid catalyzed cyclization to annulate a five-membered ring (eq. 115) [192].



(112)

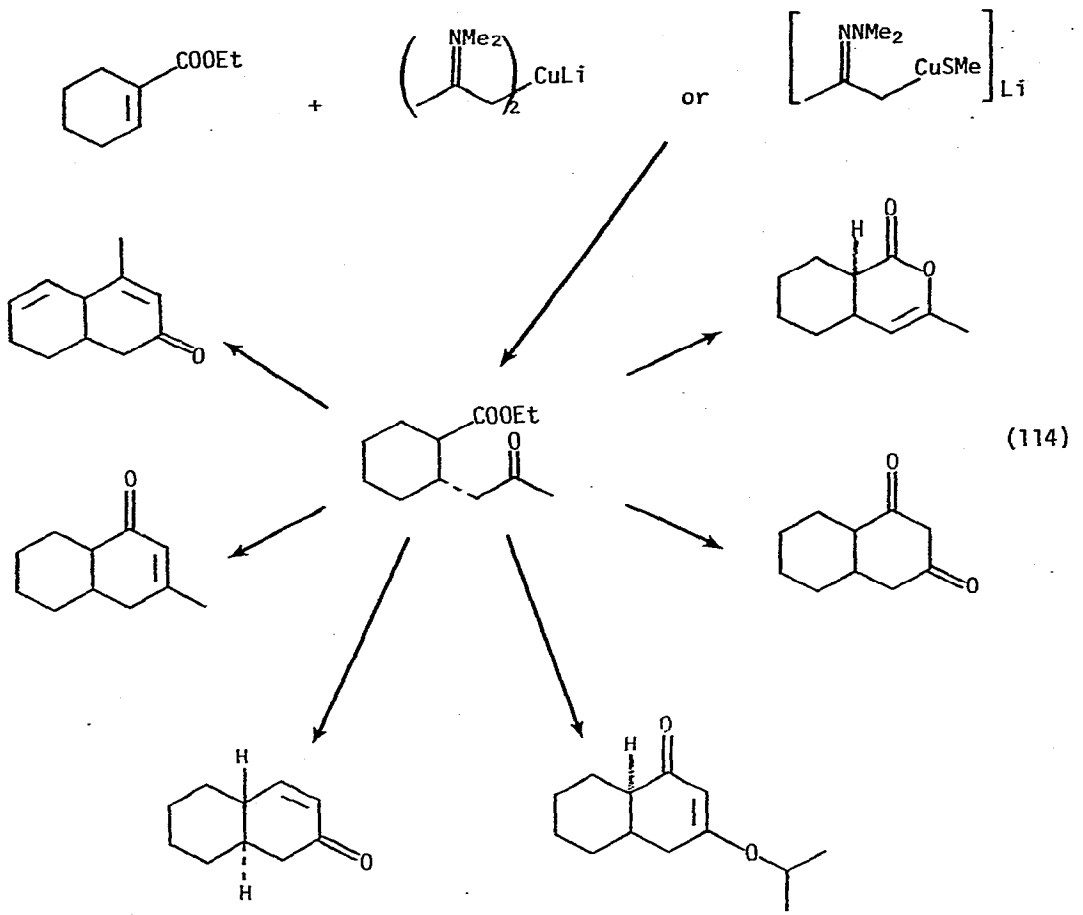


(113)

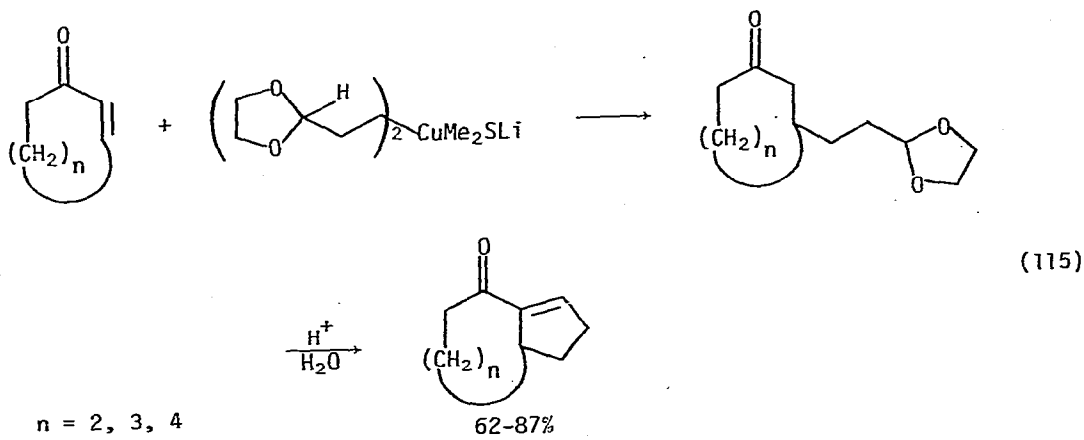


90%

Organocuprates added 1,4 to 2,2-dimethyl-3(2H)-furanone cleanly. This chemistry was used to synthesize bullatenone (eq. 116) [193]. Spirodienones having an exocyclic and an endocyclic double bond in conjugation with the carbonyl group were dialkylated by sequential treatment with lithium dimethylcuprate (eq. 117) [194]. Normally, dialkylcuprates add very poorly to β,β-



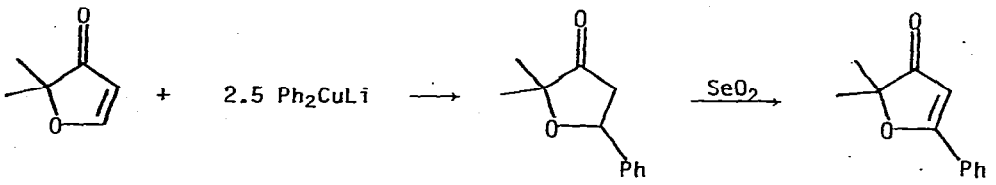
(114)



(115)

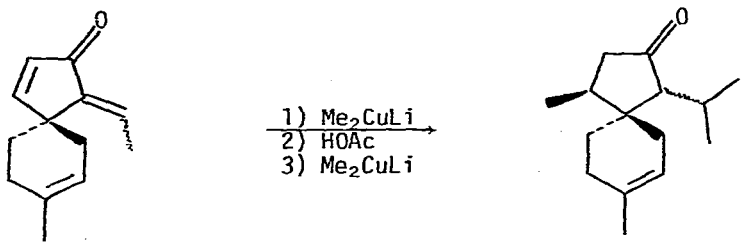
n = 2, 3, 4

62-87%



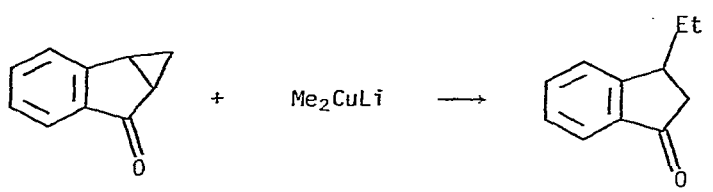
60-70% 94%

bullatenone (116)



acorone (117)

disubstituted enones. However, $RCuBF_3$ reacted cleanly and in high yield with this type of substrate. Furthermore, the amount of 1,2 addition to conjugated aldehydes was much reduced with this reagent. Even α,β-unsaturated carboxylic acids reacted well, as did conjugated esters, ketones and nitriles [195]. Acetylenic nitriles underwent conjugate addition with RCuXM reagents to produce substituted acrylonitriles. The R group was introduced trans to the nitrile [196]. Acetylenic sulfinates added dialkylcuprates to give vinylcuprates [197]. Lithium dimethylcuprate reacted with a cyclopropylketone that was part of an indanone system to open the cyclopropane ring (eq. 118) [198].

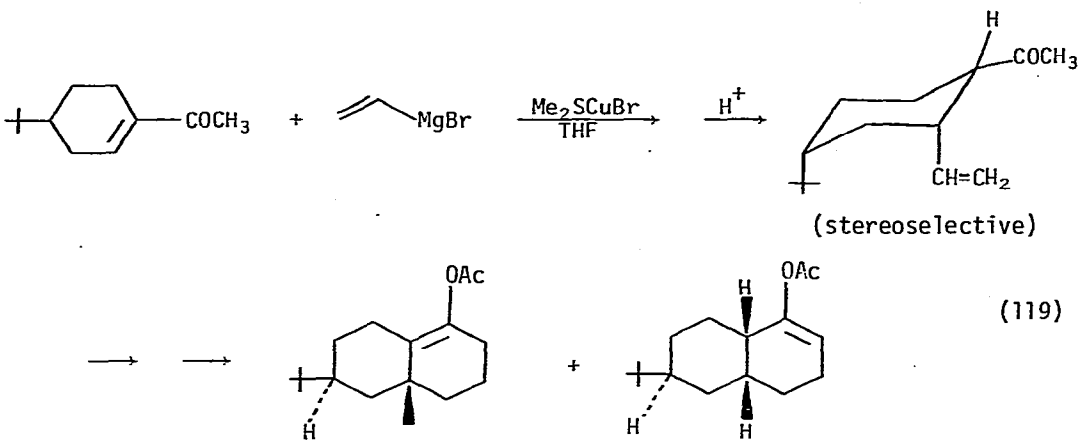


(118)

Several fundamental studies dealing with the nature of the reactive species, selectivity and stereochemistry of organocuprate conjugate additions have been carried out. It was found that a 2:1 mixture of ethylmagnesium bromide-copper(I) iodide consisted of at least three different species, each of which reacted differently with 1-mesityl-3-phenyl-2-propen-1-one [199]. With ω-bromoenones as substrate, the reaction of lithium dimethylcuprate occurred at the conjugated enone (1,4-addition) in diethylether solvent (83-92%) while in HMPA displacement of the bromide was by far the major reaction pathway [200]. Polyalkylcuprates

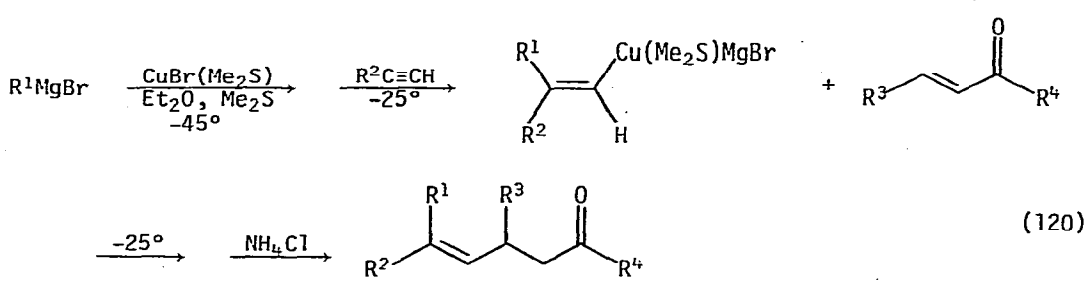
of the type [MeCu•n equiv. BuMgBr] (n=1-4) transferred the butyl group selectively to 3-methylcyclohexenone, in proportions ranging from 16:84 (Me vs Bu) for n=1 to 2:98 for n=4. The same results using sec-butylmagnesium bromide were observed, while the reagents from t-butylmagnesium bromide gave 100% methyl transfer [201]. The most effective reagent for conjugate alkylation was $R_4(Me)Cu_3(MgBr)_2$. This complex transferred R exclusively even when R was a t-butyl group [202]. The effects of solvent and substituents upon the ability of lithium diorganocuprates to add to enones was studied. It was found that good donor solvents such as THF, DME and DMF inhibited conjugate addition. A correlation of the reduction potential of the enone to the type of alkylcuprate that would add was made. It was also suggested that the soluble metal enolates resulting from conjugate addition of lithium dimethylcuprate were lithium, not copper, enolates [203].

The cis-decalone system was synthesized stereospecifically by the addition of vinylmagnesium bromide in the presence of copper(I) catalysts to a conjugated ketone (eq. 119) [204]. The stereochemistry of alkylation of all four isomers



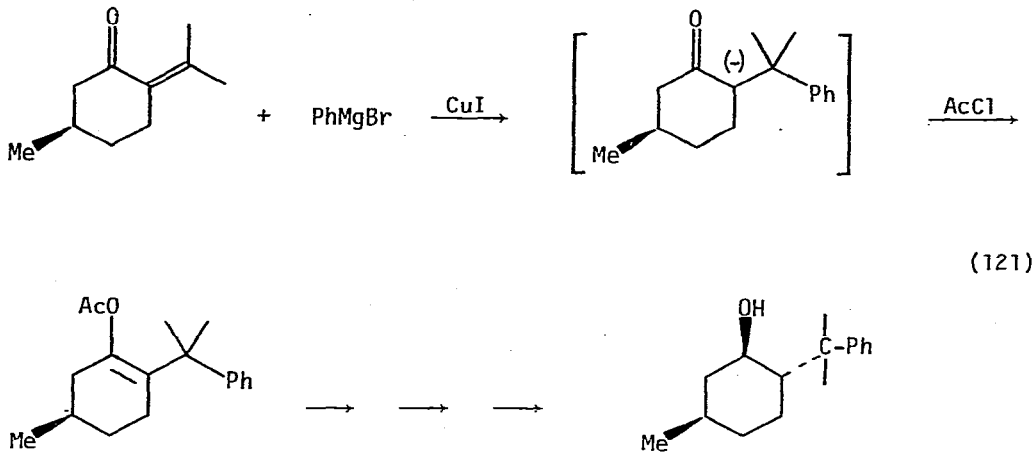
(119)

of 2,4-heptadienyl acetate by Grignards in the presence of Li_2CuCl_4 showed that only the EE isomer reacted stereospecifically [205]. The stereochemistry of addition of Grignard reagents to alkynes in the presence of a copper catalyst was demonstrated to be cis by reacting the resulting vinylcuprate with a conjugated enone (eq. 120)[206].



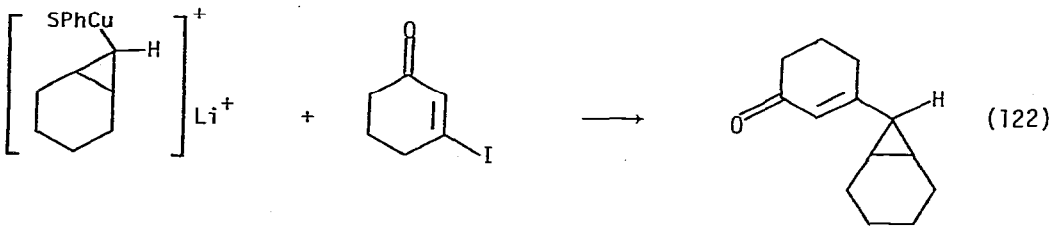
(120)

Methylation of 2-cyclohexenone by MeCu(RY)Li prepared from mono- or bifunctional chiral amines or aminoalcohols resulted in enantiomeric excesses of up to 15%. Chiral alcohols themselves had no effect [207]. A compound used for asymmetric induction in prostaglandin syntheses was prepared using a copper catalyzed conjugate addition of phenylmagnesium bromide to R(+)-pulegone (eq. 121) [208]. The steric effect of added copper and iron halides on the reaction of Grignard reagents with (-)-menthyl crotonate and cinnamate was studied [209].



(121)

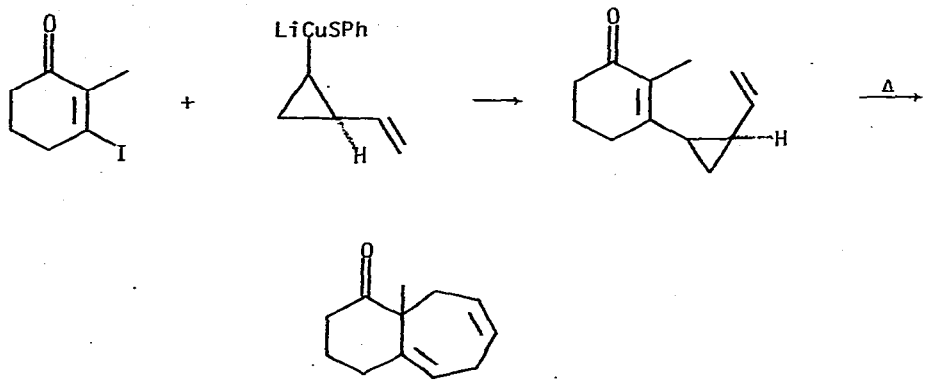
Cyclopropyl copper complexes reacted with β-iodocyclohexenones to produce β-cyclopropylcyclohexenones (eq. 122) [210]. By using vinylcyclopropylcuprates, the product was subjected to a Cope rearrangement to give bicyclic material (eq. 123) [211]. The trimethyltin group was introduced into conjugated enones



(122)

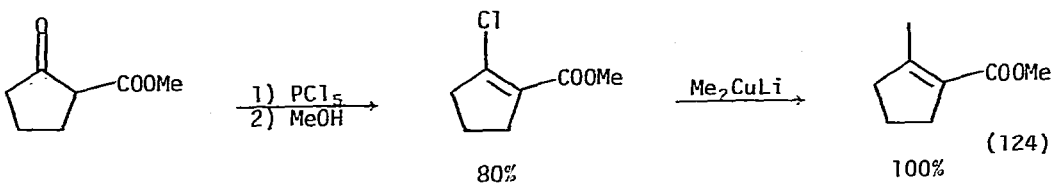
93%

through the reaction of $[PhSCuSnMe_3]^-Li^+$ with β-iodoenones. This reagent was specific for conjugated ketones, in contrast to $Me_3Sn^{(-)}$ itself which reacted with conjugated esters as well [212]. Cyclic β-ketoesters were converted to β-methyl unsaturated esters by treatment with PCl_5 followed by reaction with lithium dimethylcuprate (eq. 124) [213]. Tricyclic material was produced by

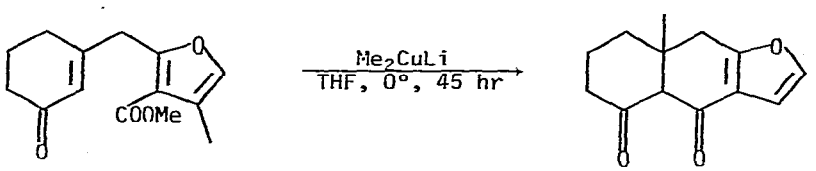


82% (123)

the conjugate alkylation of a β-substituted cyclohexenone followed by intramolecular trapping of the thus-formed enolate (eq. 125) [214].

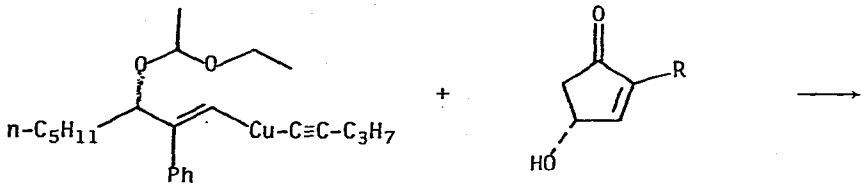


80% 100% (124)

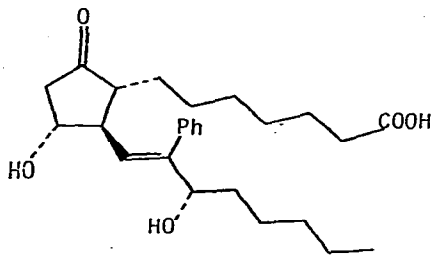


73% (125)

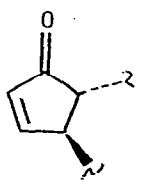
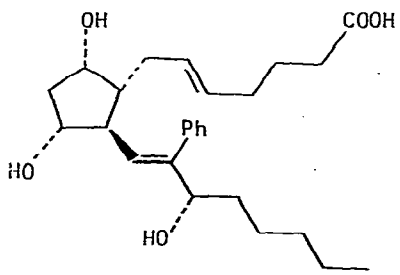
Conjugate additions have been central to several approaches to prostaglandins (eq. 126) [215], (eq. 127) [216], (eq. 128) [217]. "Butterfly compound" was

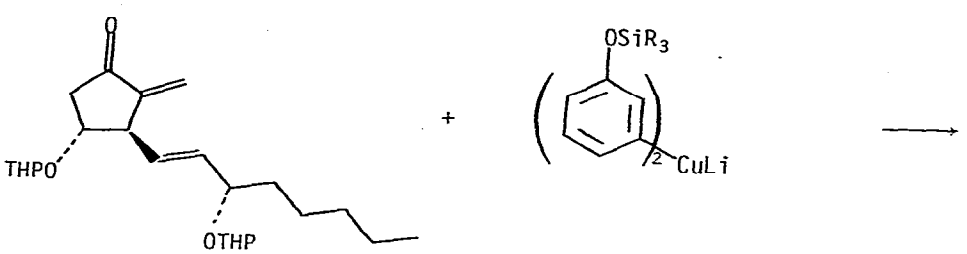


(126)

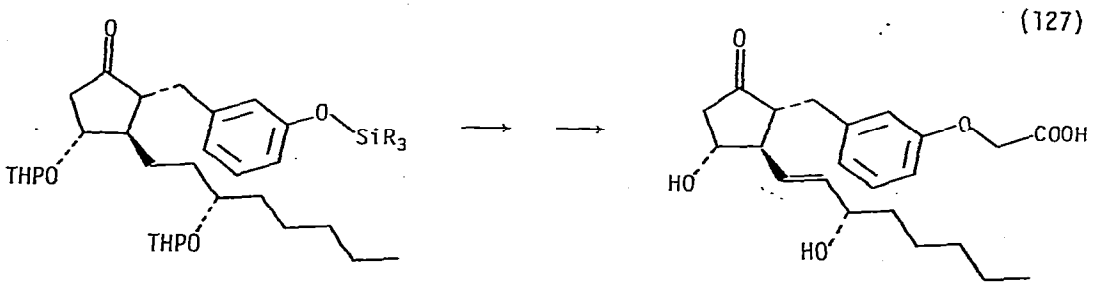


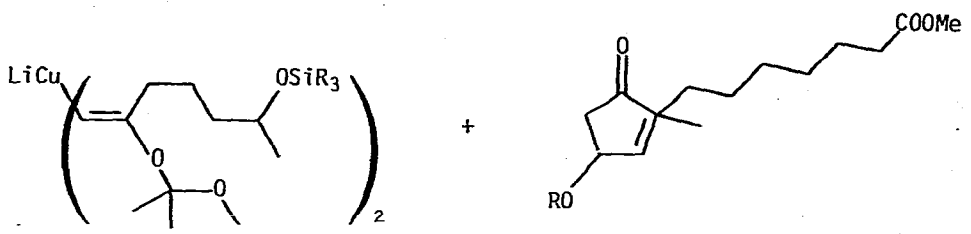
(14-phenyl-PGE^1)

Also used for A^1  and $F_{2\alpha}$ 



(127)



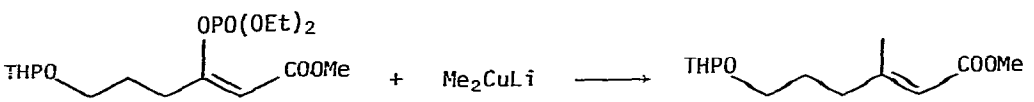


(128)

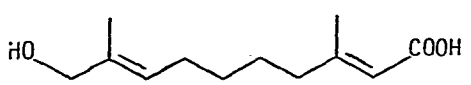
→ → dl-19-hydroxyprostaglandin E_1

dl-13-cis-15-epi-19-hydroxyprostaglandins

synthesized via a conjugate addition-elimination reaction (eq. 129) [218]. The use of organocuprate based α,β-dialkylations of α,β-ethylenic ketones in the synthesis of sesquiterpenes has been reviewed [219]. Conjugate additions have been used in the synthesis of pseudoguaianes (eq. 130) [220] and of confertin (eq. 131) [221].

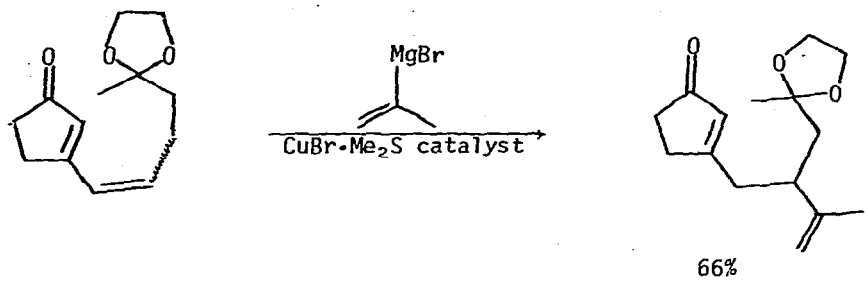


(129)

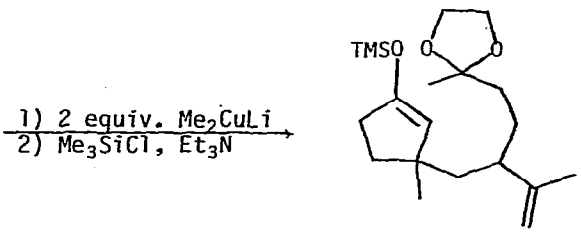
→ → 

"Butterfly" compound

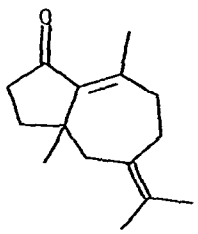
The conjugate addition of arylpalladium complexes to conjugated enones has also been extensively developed recently. The reaction of electron-rich aromatic halides with 1% palladium(II) acetate and tri(o-tolyl)phosphine in the presence of methyl acrylate led to moderate to high yields of vinylic substitution product. In these cases, the olefin is regenerated by elimination of "PdH" and unsaturated esters result [222]. This type of reaction was used to synthesize quinolones by reaction of 2-iodoanilines with acrylate derivatives in the presence of palladium(II) acetate and triethylamine (eq. 132) [223]. Benzene

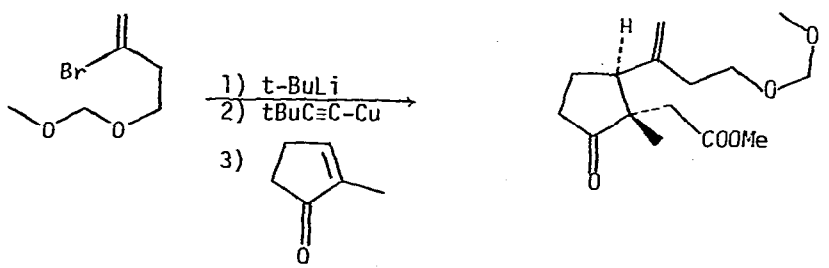

MgBr
CuBr·Me2S catalyst

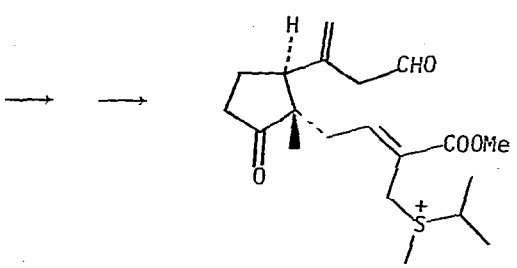
66%


1) 2 equiv. Me2CuLi
2) Me3SiCl, Et3N
TMSO
1.2 equiv
TiCl4
CH2Cl2

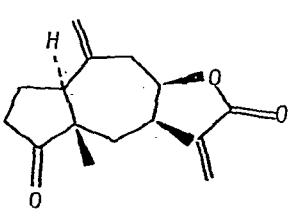
90% (130)

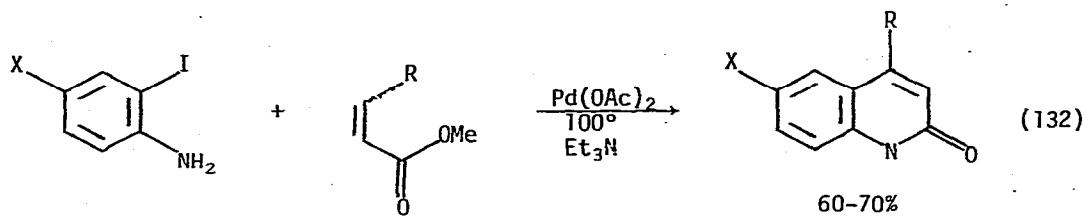



Br
1) t-BuLi
2) tBuC≡C-Cu
3)
4) BrCH2COOMe
COOMe


CHO
COOMe
Ni(COD)2

(131)

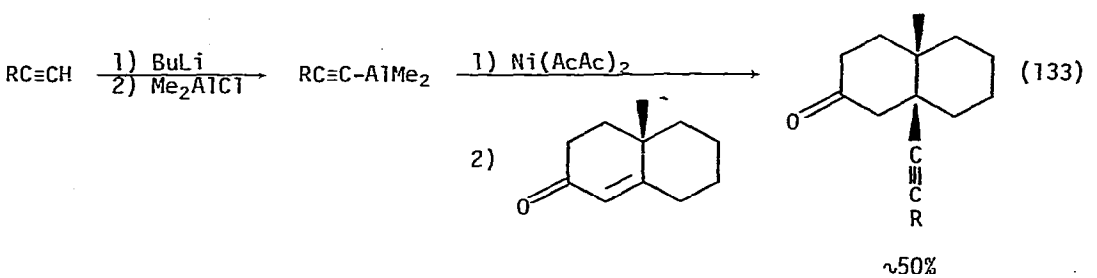




(132)

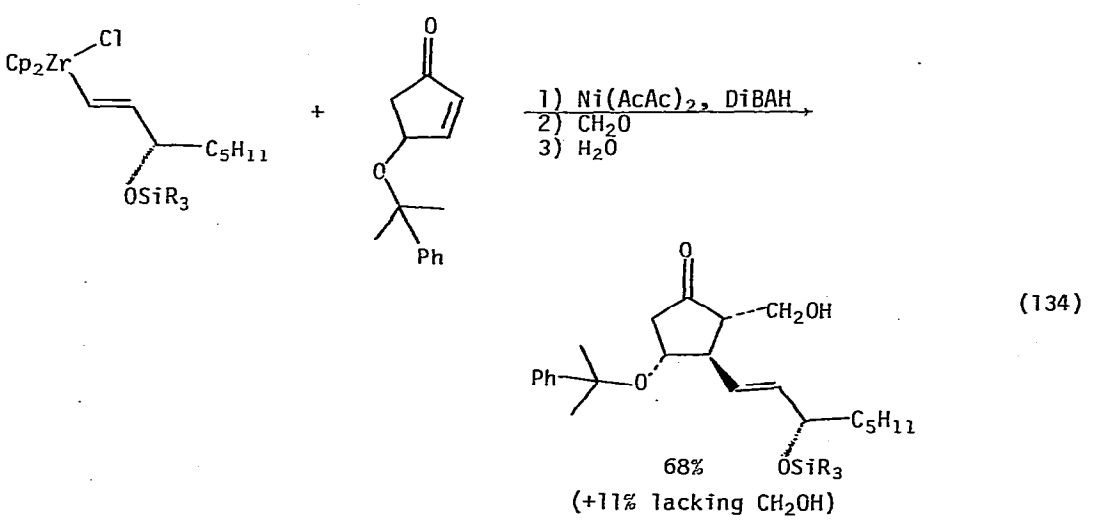
itself added to α-substituted chalcone (when the α-substituent was bulky and strongly electron withdrawing) in the presence of palladium(II) acetate catalyst. In most cases, the saturated product predominated [224]. Alkyl halides alkylated acrylonitrile to produce β-substituted propionitriles when the substrates were electrochemically reduced in the presence of nickel(II) complexes. Ethyl acrylate and ethyl vinyl ketone reacted in a similar fashion, while cinnamaldehyde, methyl vinyl ketone and β-substituted enones reacted in low yield [225].

The conjugate addition of organoaluminum acetylides to conjugated enones was catalyzed by a nickel reagent produced in the reaction of nickel(II) acetylacetonate with diisobutylaluminum hydride (eq. 133) [226]. The same complex catalyzed the 1,4-addition of vinylzirconates to conjugated ketones. This was used to prepare compounds related to the prostaglandins (eq. 134) [227].



~50%

(133)

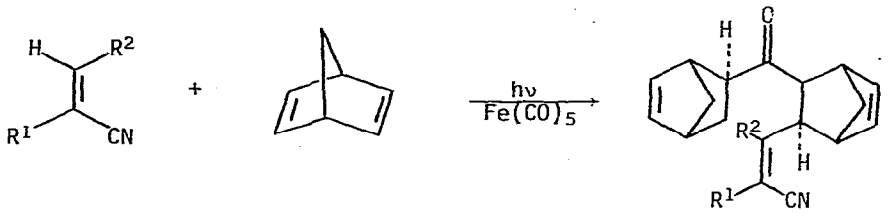


68%

(+11% lacking CH_2OH)

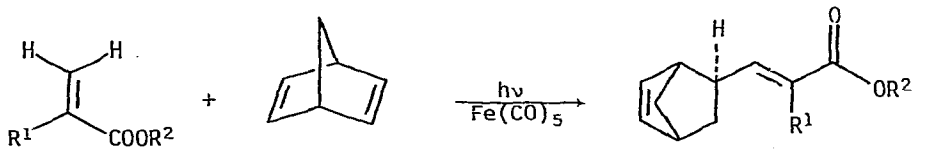
(134)

Iron carbonyl catalyzed the photochemical addition of norbornadiene to a number of α,β-ethylenic systems. The products depended upon the nature of the substrate (eq. 135-137) [228].



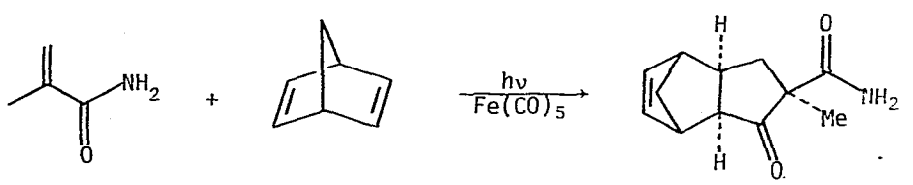
30-90%

(135)



16-27%

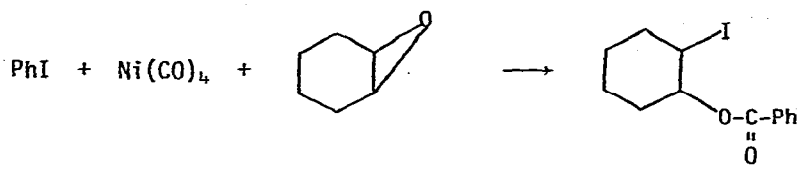
(136)



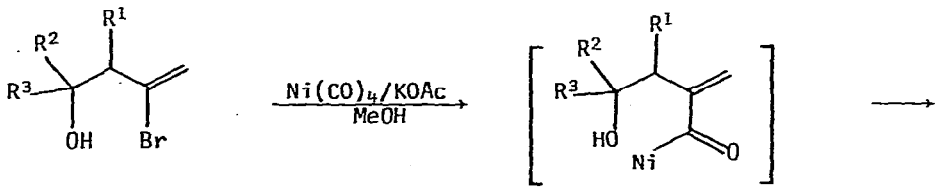
80%

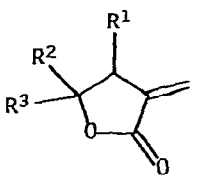
(137)

C. Acylation. The migration reaction of an alkyl group from iron to coordinated carbon monoxide was studied in detail for the $RFe(CO)_4^-$ to $RCOFe(CO)_4^-$ reaction. Ion pairing effects had a major influence on the rate of migratory insertion. It was found that Lewis acids catalyzed the insertion reaction, and that the acyl group was the cation binding site [229]. The stereochemistry of the oxidative addition of benzyl-α-d-chloride to tris-triethylphosphine palladium(0) was shown to be clean inversion, by carbonylation and cleavage of the resulting benzylpalladium(II) complex [230]. Halohydrin esters were produced by the reaction of nickel carbonyl, aryl or vinyl halides, and olefin oxides (eq. 138) [231]. Homoallylic alcohols bearing a 2-bromo group were converted to α-methylene-γ-butyrolactones by treatment with nickel carbonyl and potassium acetate in methanol (eq. 139) [232].



(138)



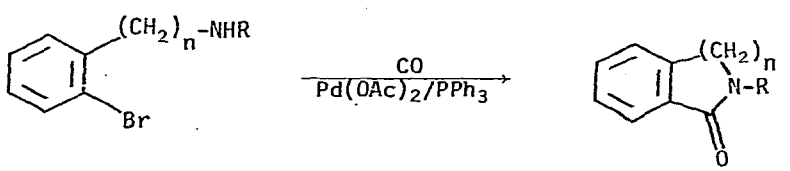


50-75%

(139)

R^1 = H; R^2 = Et; R^3 = H
R^1 = R^2 = $(CH_2)_4$; R^3 = H
R^1 = R^2 = $(CH_2)_5$; R^3 = H
R^1 = R^2 = $(CH_2)_3$; R^3 = H
R^1 = H; R^2 = R^3 = $(CH_2)_5$

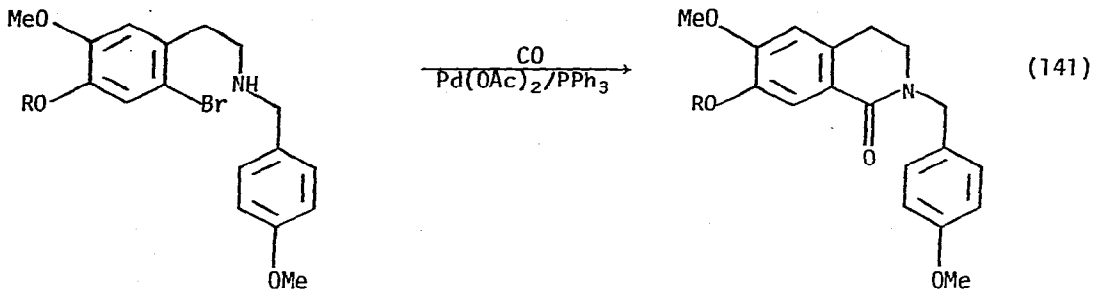
Aryl bromides having ω-amino side chains in the ortho position reacted with a palladium(II) acetate-triphenylphosphine catalyst and carbon monoxide to produce benz fused lactams (eq. 140) [233]. This chemistry was used in the synthesis of sendaverine (eq. 141) [234].



40-60%

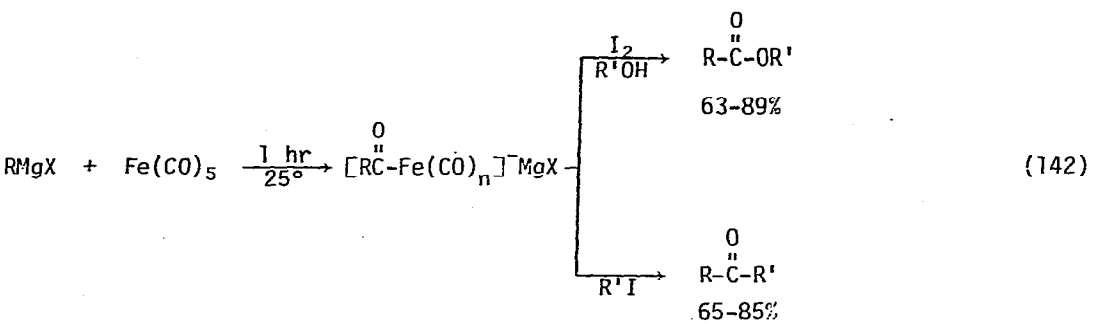
(140)

R = $PhCH_2$, H; n = 1, 2, 3



(141)

Grignard reagents reacted with iron pentacarbonyl, followed by iodine in methanol to produce esters [235]. The reaction of Grignard reagents with iron pentacarbonyl in the presence of alkyl iodides produced ketones instead (eq. 142) [236]. Diarylketones were formed by the reaction of copper or gold aryl



(142)

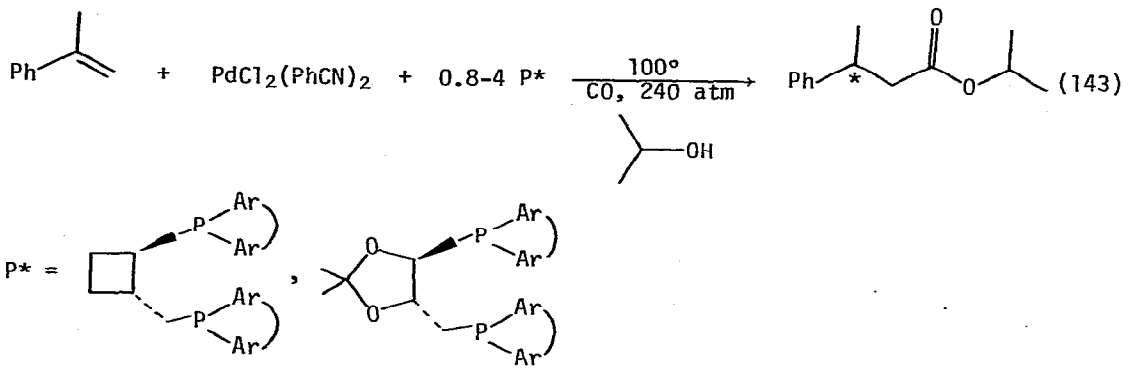
clusters (i.e., $Ar_4Cu_2Li_2$, $Ar_4Au_2Li_2$) with carbon monoxide [237]. The synthesis of carboxylic acids and esters by carbonylation procedures has been reviewed [238].

The hydroformylation of styrene, α-methylstyrene, β-methylstyrene and allyl benzene with dicobalt octacarbonyl as catalyst was studied in detail. The use of pyridine as a cocatalyst both activated the catalyst and influenced selectivity in addition to increasing hydrogenation. The isomeric composition of the product was temperature dependent with α-formylation increasing as the temperature was lowered [239]. A new hydroformylation catalyst was produced by the reaction of dicobalt octacarbonyl with the ethylene glycol ester of 3-(2-pyridyl)proprionic acid. This catalyst was active even at 50° and very low carbon monoxide pressures. With a high hydrogen to carbon monoxide ratio selectivity for linear aldehyde was high. The catalytically active species was thought to be $H_2Co_3(CO)_4(ligand)_n$ [240]. The use of $Rh_4Cl_4(CO)_4(O_2)_2P_2$ as a catalyst for the hydroformylation of 1-heptene at 90° and 1000 psi to give linear and branched aldehydes was examined. In DMA this same complex catalyzed the reduction of terminal alkenes [241]. Hydroformylation of olefins using $RhH(CO)(PPh_3)_3$ as catalyst was enhanced by the addition of small amounts of di- or tri-tertiary phosphines, but was reduced by amounts in excess of equimolar [242]. The hydroformylation of 1-heptene using

cationic rhodium(I) complexes such as $[(COD)RhMPh_3]^+$ was studied. Use of amine, phosphine or arsine ligands enhanced selectivity, while bismuth or antimony ligands lowered selectivity [243]. Basic aqueous alcohol solutions of $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ were active catalysts for the water gas shift reaction ($H_2O + CO \rightarrow H_2 + CO_2$) and the same solutions were used to catalyze the hydroformylation of pentene. The ruthenium based catalyst gave very high proportions of linear aldehydes (97%) while the rhodium based catalyst reduced the aldehydes further to alcohols [244]. The hydroformylation of 1-octene by 1:1 H_2/CO mixtures (100 atm) using $[\eta^5\text{-}C_5H_5M(CO)_2]_2$ (M = Fe, Ru) was studied [245]. The same complexes catalyzed reduction and rearrangement of 1-octene.

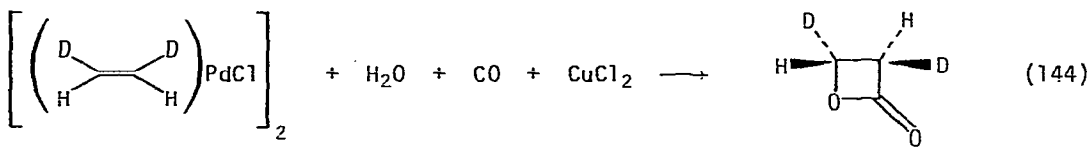
The use of solid phase supported hydroformylation catalysts continued to be an active area of investigation. Cyclopentadienyl groups were chemically attached to macroporous silica gel. Reaction of dicobalt octacarbonyl produced supported mononuclear cyclopentadienyl cobalt dicarbonyl complexes which, while coordinatively unsaturated, were unable to dimerize because they were held apart by the solid support. These solid supported catalysts were good hydroformylation catalysts [246]. The hydroformylation of styrene by $Rh(H)(CO)(PPh_3)_3$ and $RhH(CO)[PPh_2(CH_2)_2PPh_2]PPh_3$ catalysts was compared with polymer anchored analogs. With both homogeneous and solid supported catalysts, the branched/normal ratio decreased as the temperature increased, and increased as the pressure was raised from 100 to 800 psi [247, 248]. The use of $[Rh(H)(CO)[PPh_2(CH_2)_2PPh_2]PPh_3]$ as well as the polymer anchored analog as a catalyst for this hydroformylation of 1-pentene showed similar results [249]. The problem of rhodium catalyst leaching from solid supports under hydroformylation conditions has been studied. Rhodium dissolution decreased as temperature and hydrogen pressure increased, and as carbon monoxide pressure decreased. Solvent effects were particularly noticeable with amine resins [250]. Rhodium carbonyl clusters supported on NaY zeolites were active liquid phase hydroformylation catalysts for olefins, showing high selectivity for aldehyde formation, and branched to normal ratios comparable to that of homogeneous catalysts. Nonconjugated diolefins were converted to dialdehydes by this catalyst system. The catalyst could be recovered by decantation and reused without loss of activity [251]. The clusters $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$ were photochemically attached to poly(vinylpyridine) coated on controlled pore glass particles, and the resulting insoluble material was found to catalyze the hydroformylation of olefins [252].

Several asymmetric hydroformylation reactions have been achieved. Using a catalyst resulting from $PdCl_2(PhCN)_2$ and chiral phosphines, α-methylstyrene was carbonylated in 90-99% yield and 44% optical purity (eq. 143) [253]. Chiral rhodium(I) hydride catalysts hydroformylated cis-2-butene, bicyclo[2.2.2]oct-2-ene, 2,3-dihydrofuran and diethyl maleate in optical yield 3.8-27% [254]. Styrene and butenes were hydroformylated in up to 22% yield using a $[(-)\text{-DIOP}]PtCl_2/SnCl_2$ catalyst system [255]. The selectivity for hydroformylation and the optical

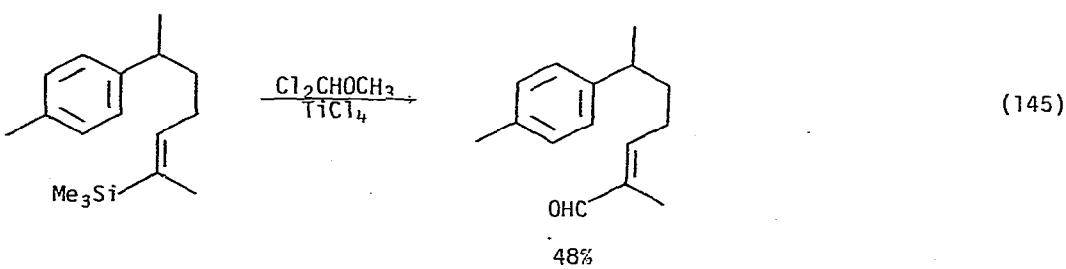


purity of the aldehyde were influenced by both carbon monoxide and hydrogen pressure [256]. Acrylonitrile was hydroformylated using a cobalt carbonyl catalyst in methanol, to produce a 1:10 mixture of α- and β-hydroformylation products. Some α-hydromethoxycarbonylation also occurred, but no β product of this type was detected [257]. The isotope effect in hydroformylation of 1,1,1-d^3-butene was studied. While $Co_2(CO)_8$ catalysts displayed no isotope effect and hydroformylated the 1 and 4 positions equally, $Rh_4(CO)_{12}$ catalysts reacted mostly at the nondeuterated terminus of the substrate [258].

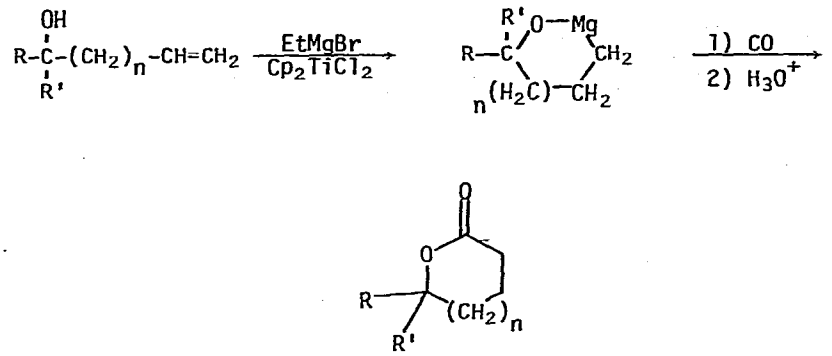
The stereochemistry of hydroxypalladation of ethylene was shown to be trans by using cis-dideuterioethylene and carbonylating the intermediate σ-alkylpalladium complex to produce the β-lactone (eq. 144). The results were cited as evidence for a trans hydroxypalladation in the Wacker process [259]. Lithium tetraalkyl-



aluminates, formed by the reaction of lithium aluminum hydride with olefins in the presence of $TiCl_4$, reacted with carbon monoxide and copper(II) acetate to produce symmetrical ketones in 30-50% yield [260]. Vinyl silanes were formylated by treatment with dichloromethyl methyl ether and titanium(IV) chloride (eq. 145) [261]. ω-Hydroxy olefins were converted to lactones by their reaction with ethyl

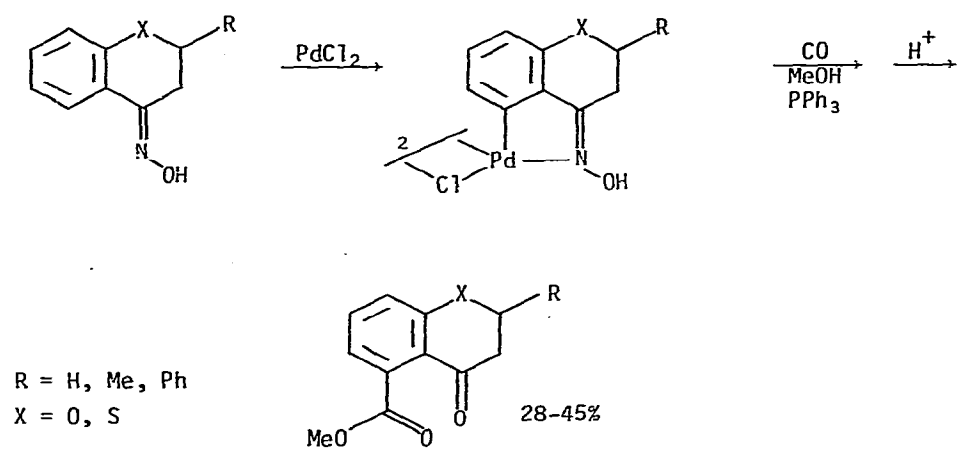


magnesium bromide and Cp_2TiCl_2 followed by carbonylation of the magnesium intermediate (eq. 146) [262]. Methoxycarbonylation of aromatic compounds was



(146)

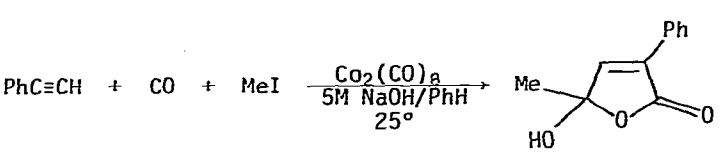
affected by the o-palladation of aryl oximes followed by treatment with carbon monoxide and methanol (eq. 147) [263]. Olefins were carboxylated at room temperature by treatment with carbon monoxide in the presence of strong acid/water/copper(I) carbonyl catalysts [264].



(147)

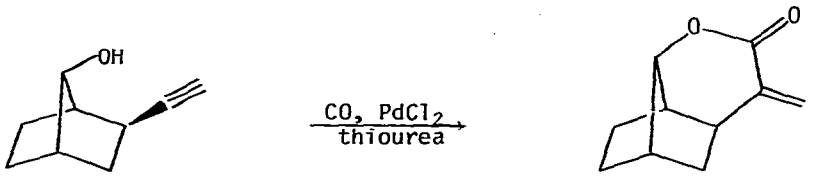
R = H, Me, Ph
X = O, S

Hydroxy-2-butenolides were produced in the reaction of terminal alkynes with methyl iodide and carbon monoxide using dicobalt octacarbonyl as catalysts and carrying out the reaction under phase transfer conditions (eq. 148). In



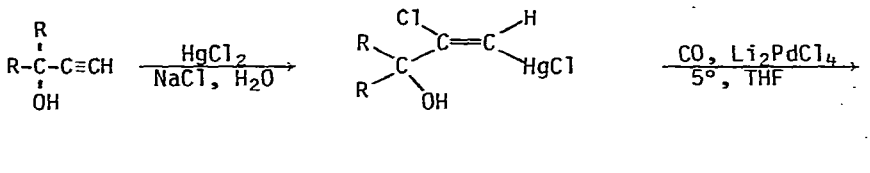
(148)

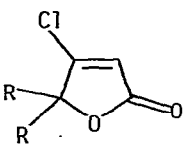
contrast, dienes were acylated by this system [265]. α-Methylene-δ-lactones were produced by the palladium(II) chloride carbonylation of γ-hydroxy acetylenes (eq. 149) [266]. β-Chloro-$\Delta^{\alpha,\beta}$-butenolides were prepared from propargylic alcohols



(149)

by chloromercuration followed by palladium(II) catalyzed carbonylation (eq. 150) [267]. Alkynes were converted to cyclobutenones by the cycloaddition

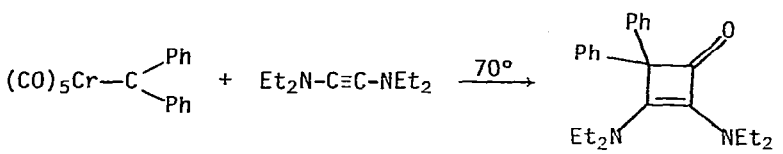




80-95%

(150)

reaction with chromium carbene complexes (eq. 151) [268]. Vinyl mercuric halides reacted with acid halides in the presence of aluminum chloride, titanium(IV) chloride, rhodium(I) complexes or palladium(0) complexes [269].



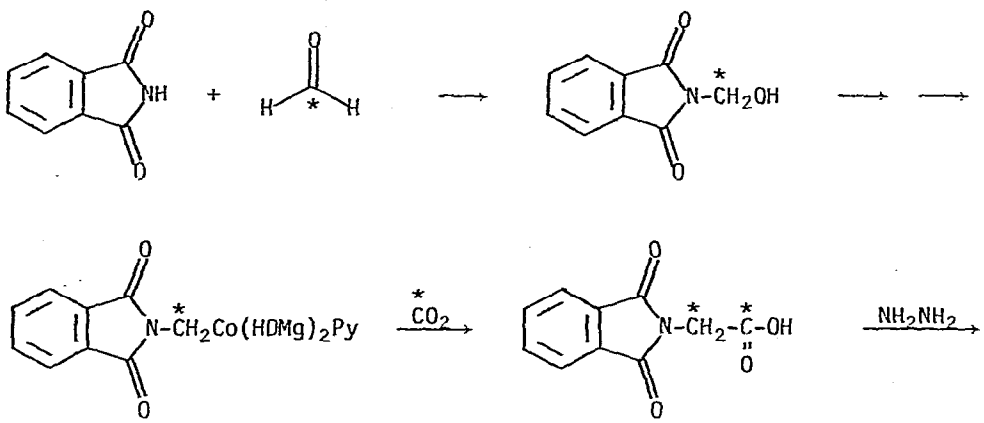
(151)

The vapor phase, alkyl iodide promoted carbonylation of methanol and ethanol was carried out using a rhodium-X zeolite catalyst, and the effect of promoter concentration on selectivity for carbonylation was probed [270]. The same catalyst system was also studied using Fe_2O_3 as a promoter [271]. New catalysts and promoters for the methanol carbonylation reaction was the subject of a dissertation [272]. Alcohols were also carbonylated using palladium carboxylated complexes such as $Pd(CO_2Me)(OAc)(PPh_3)_2$ and $Pd(CO_2Me)_2(PPh_3)_2$. Oxalate esters were also observed in this system [273]. Dimethyl ether was carbonylated to produce ethyl acetate, and methyl acetate was homologated to ethyl acetate using ruthenium catalysts with iodide promoters and proton sources at 200° and CO/H

pressures of 80-250 atm. Methane and ethane were by products [274].

A great deal of effort has been expended in the development of methods to carbonylate aromatic nitro compounds to isocyanates. 2,4-Dinitrotoluene was converted to the bis isocyanate by carbon monoxide (200 atm) at 260° using a $PdCl_2(pyridine)_2/Fe_2O_3/FeVO_4$ catalyst [275]. The use of V_2O_5 and $Fe_2Mo_7O_{24}$ as cocatalysts was also studied [276], as was MoO_3[277, 278]. The activity of palladium(II) chloride for the conversion of nitrobenzene to phenyl isocyanates at 190° and 100 atm carbon monoxide pressure was enhanced by addition of 2% quinoline, but suppressed by the addition of acetonitrile, benzonitrile, triethylamine, 2,2'-bipyridine, or urotropine [279]. Other promoters were MoO_3 and Fe_2O_3[280] and other group V and VI transition metal oxides [281].

Isotopically enriched glycine, labelled at both carbons, was synthesized by the carboxylation of a phthalimidomethylene cobalt complex with labelled carbon dioxide (eq. 152) [282]. Palladium chloride catalyzed the formation of dimethylformamide from carbon dioxide, dimethylamine and hydrogen [283].

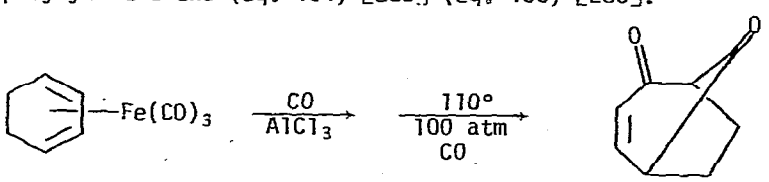


(152)

$H_2N\overset{*}{C}H_2\overset{*}{C}OOH$

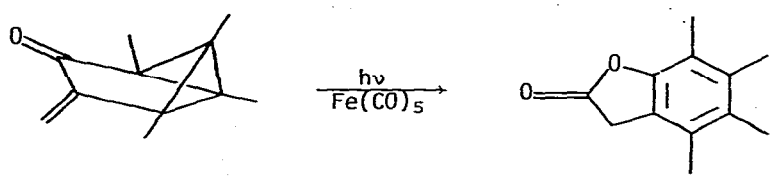
>90% isotopically enriched

Bicyclo[3.2.1]oct-2-ene-4,8-dione was produced by treatment of the 1,3-cyclohexadiene complex of iron carbonyl with carbon monoxide and aluminum halides (eq. 153) [284]. Iron carbonyl induced the carbonylation of a strained, bridged polycyclic diene (eq. 154) [285] (eq. 155) [286].



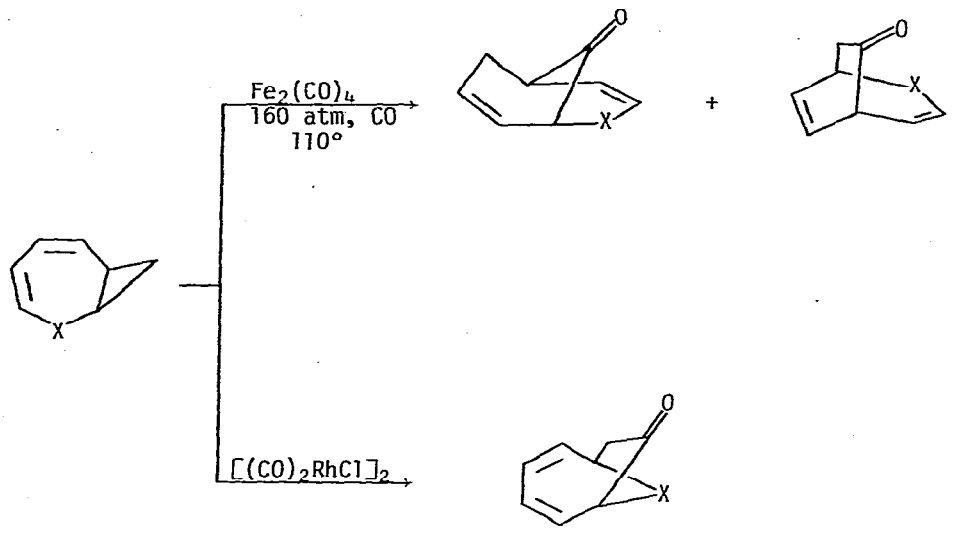
(153)

70%



28%

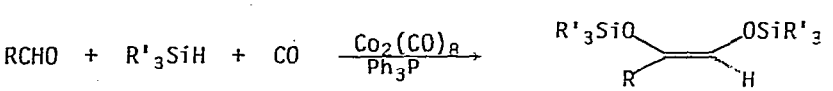
(154)



(155)

X = CH_2, CO, NCOOEt

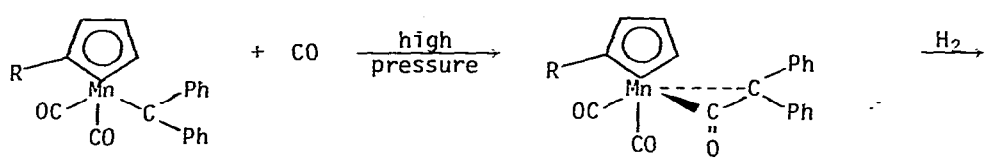
Aldehydes underwent a complex reaction with R_3SiH and carbon monoxide in the presence of dicobalt octacarbonyl (eq. 156) [287]. A manganese coordinated



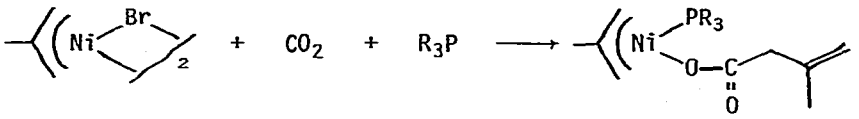
60%

(156)

carbene underwent high pressure carbonylation to produce coordinated ketene (eq. 157) [288]. π-Allylnickel halide complexes underwent carboxylation when reacted with carbon dioxide and trialkyl phosphines (eq. 158) [289].

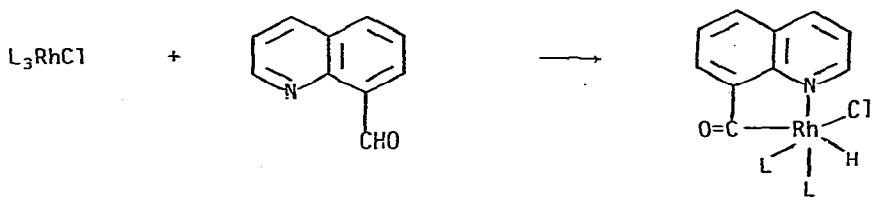


(157)

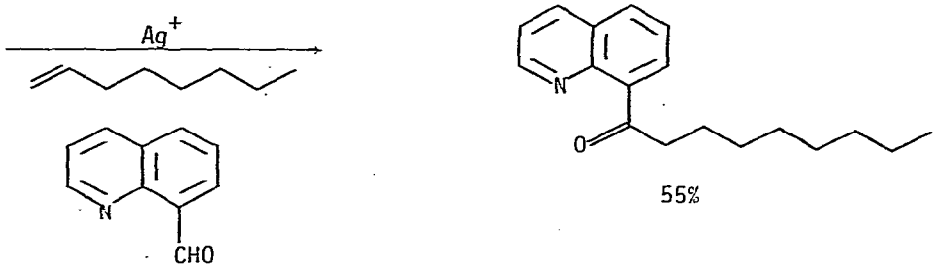


(158)

Olefins were carbonylated by 8-formylquinoline in the presence of Wilkinson complex in a reaction which corresponded to the addition of the aldehyde across the carbon-carbon double bond (eq. 159) [290]. Bis-chelating diphosphine complexes of rhodium(I) were active and relatively mild catalysts for the decarbonylation of aldehydes. Benzaldehyde was converted to benzene in 100% yield at 178° with 10^4 catalyst turnovers [291].

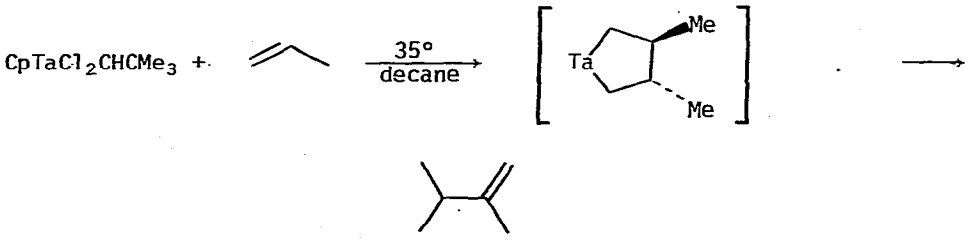


(159)



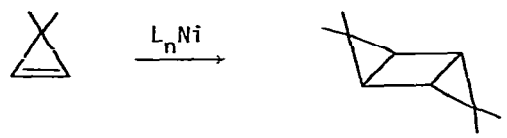
D. Oligomerization. Ethylene was dimerized by the cobalt catalyst $CoX(PPh_3)_3$ in the presence of Lewis acids in bromobenzene solvent. The reaction was thought to involve a hydridocobalt species formed by the oxidative addition of ethylene to a cobalt(I) complex [292]. Rhodium(III) chloride supported on silica gel was 10^4 more active as an ethylene dimerization catalyst than were corresponding homogeneous systems. The presence of hydrogen chloride enhanced the catalyst activity [293]. Ethylene was oligomerized on a nickel(II) oxide dealuminated nordenite catalyst [294]. Nickel(0) phosphine complexes reacted with sulfuric or trifluoroacetic acid to produce a catalyst active for the dimerization of propene. Similar catalytic activity was observed for catalysts produced by the reaction of nickel(II) acetylacetonate with alkyl aluminum complexes [295]. Olefins were selectively dimerized by the tantalum complex $CpTaCl_2CHCMe_3$. The reaction proceeded through metallocyclic intermediates in

which trans β,β-disubstitution was favored. Thus propene was catalytically dimerized at the two position to produce 2,3-dimethylbut-1-ene (eq. 160) [296].

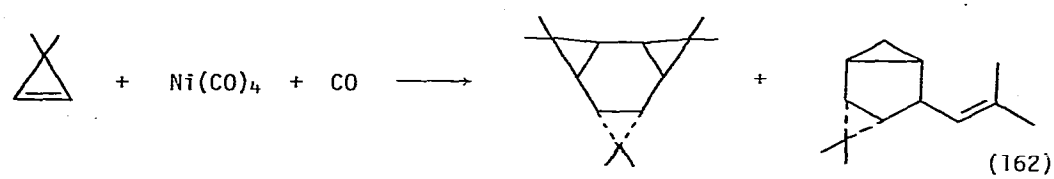


93% (160)

Diphenylketene was dimerized to $Ph_2CHCO_2CH{=}CPh_2$ by bis(cyclooctadiene)nickel after treatment with tetramethyl ethylene diamine or pyridine [297]. 3,3-Dimethyl-cyclo-prop-1-ene was dimerized by treatment with nickel(0) phosphine or bipyridyl complexes (eq. 161) [298]. The same substrate was cyclotrimerized by reaction with nickel carbonyl (eq. 162) [299]. Ethylene and propene co-dimerized to 2-pentene over a silica gel supported rhodium(III) chloride catalyst [300]. The cyclooligomerization and co-oligomerization of strained olefins by transition metal catalysts has been reviewed (122 references) [301].



(161)

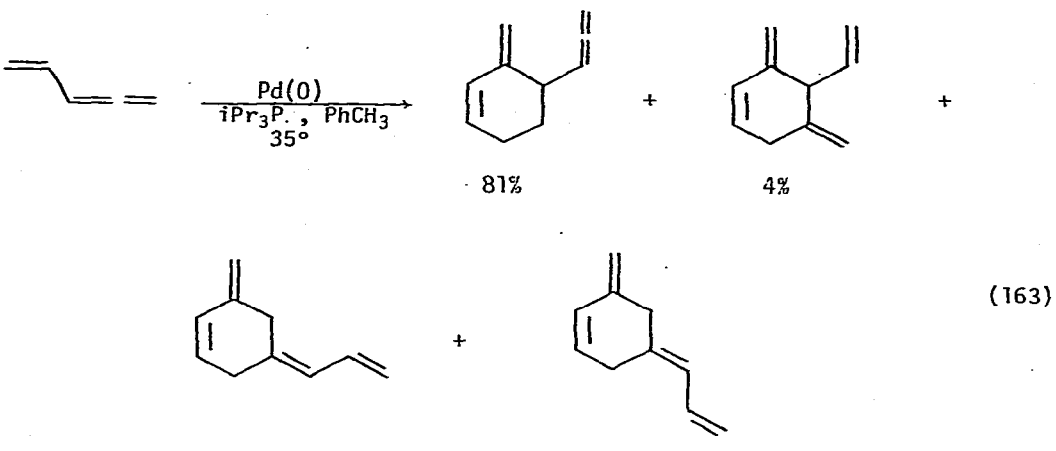


(162)

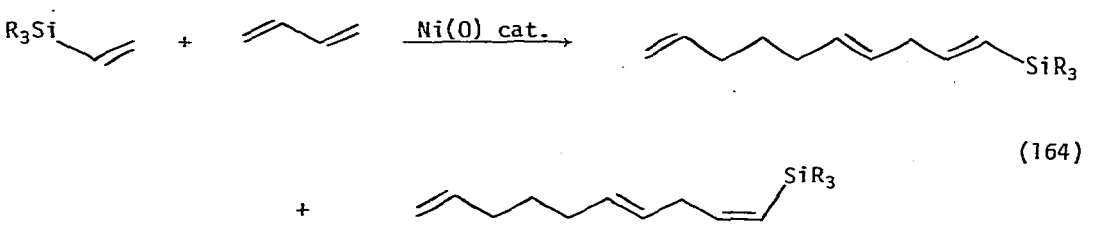
The compound "$Fe(O)(NO)_2$," generated in situ electrochemically from $[Fe(NO)_2Cl]_2$ dimerized butadiene to vinylcyclohexene at room temperature [302]. This same species was also generated by chemical reduction using reagents such as $Cr(C_6H_6)(CO)_3$, $Co(CO)_3NO$, $CoCp(CO)_2$ and $Co_2(CO)_8$, as well as zero valent metals such as Mn, Fe, Co and Ni [303]. Palladium(0) complexes dimerized 1,2,4-pentatriene to a mixture of cyclic products. The reaction was thought to proceed via π-allylpalladium complexes (eq. 163) [304]. Oligomerization of butadiene was catalyzed by palladium acetate anchored to phosphinated polystyrene, and the same product distribution as obtained from the corresponding homogeneous system was observed [305].

Butadiene and styrene were codimerized to 1-phenyl-1,4-hexadiene as the

main product by catalysts consisting of palladium(II) salts, Lewis acids and tertiary phosphines [306]. The linear codimerization of butadiene and methyl methacrylate to methyl-3(E),5(Z)-heptadienoate was favored by an iron-aryl antimony-alkylaluminum catalyst in the presence of other transition metal acetyl acetonates [307]. Butadiene and other 1,3-dienes and vinyl silanes co-oligomerized in the presence of a nickel(II)-Ph_3P-Et_3Al catalyst to produce silicon containing polyenes (eq. 164) [308], which were converted to other useful materials (eq. 165) [309]. Isoprene was trimerized primarily to trans-β-farnescene by a π-allylnickel alkoxide $PPh(NEt_2)_2$ catalyst. This underwent

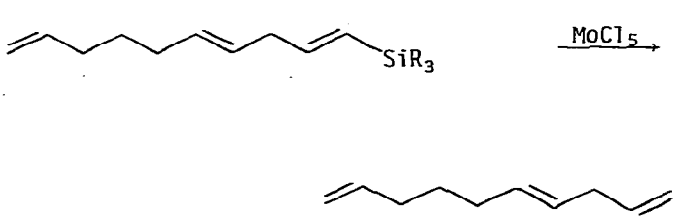


(163)



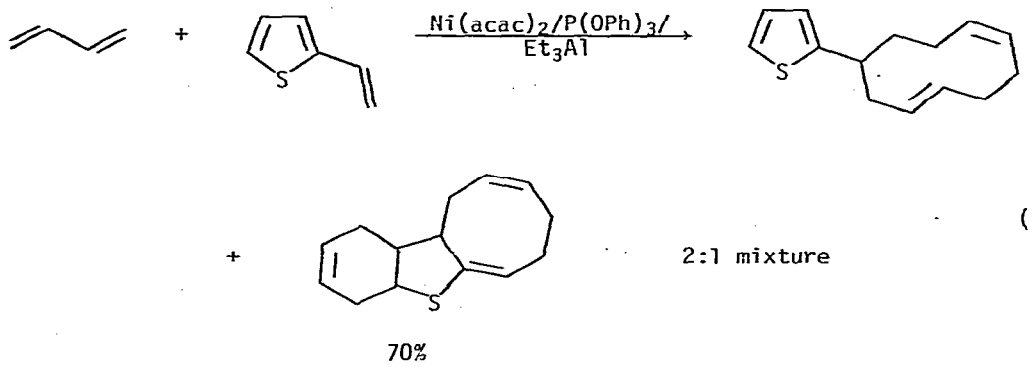
(164)

72% 1:1



(165)

a tail to tail dimerization when treated with palladium(II) nitrate/triphenylphosphine/sodium phenoxide catalyst to produce squalane after reduction [310]. Nickel(0) complexes cooligomerized 2-vinylthiophene and butadiene (eq. 166) [311].

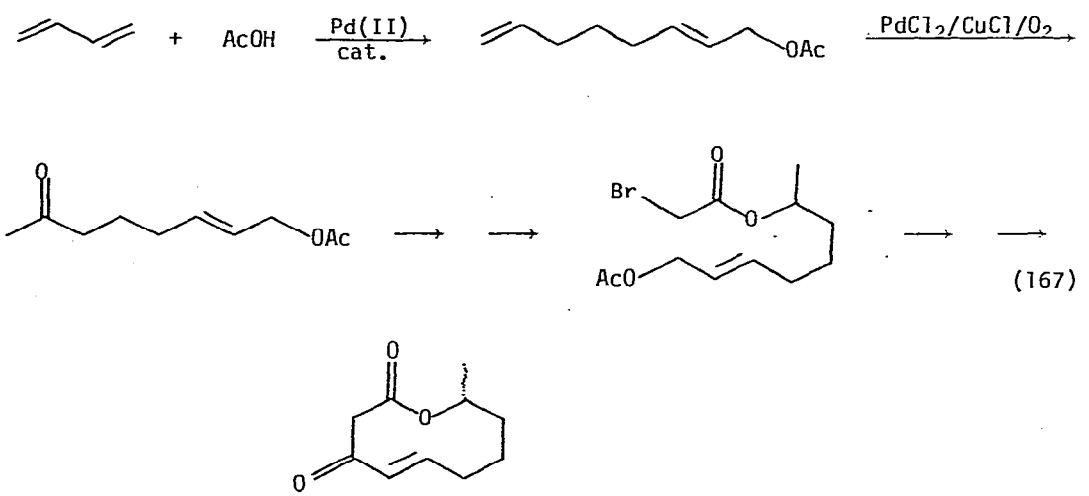


2:1 mixture

70%

(166)

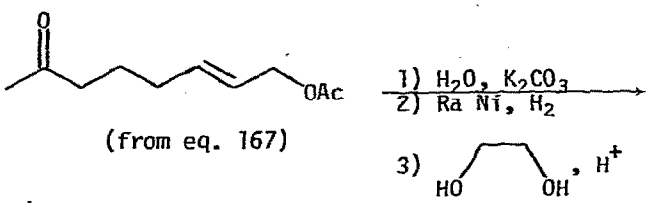
Palladium catalyzed telomerization of butadiene has found extensive application to the synthesis of a number of useful natural products. Diplodialides were synthesized by a sequence of reactions involving the palladium(II) catalyzed production of 1-acetoxy-2,7-heptadiene from butadiene and acetate, and palladium(II) catalyzed oxidation of the terminal double bond to a ketone (eq. 167) [312].



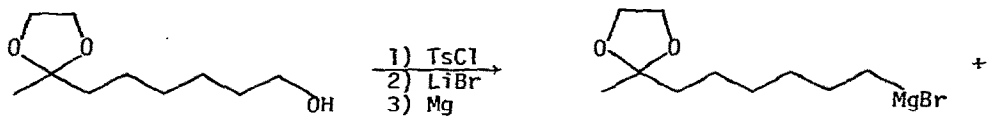
(167)

Other macrocycles were prepared in a similar fashion [313], as was 2,15-hexadecanedione, a precursor to d,l-muscone (eq. 168) [314]. d,l-α-Lipoic acid was synthesized from 3-acetoxy-1,7-octadiene, in turn prepared from butadiene and acetate in the presence of a palladium catalyst (eq. 169) [315].

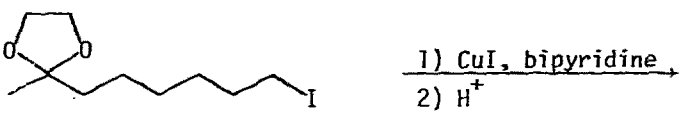
The dimerization-methoxylation of butadiene to mixtures of 1-methoxy-2,7-octadiene and 3-methoxy-1,7-octadiene was catalyzed by a palladium(0) phosphine catalyst supported on phosphinated polystyrene. The rate was faster than with

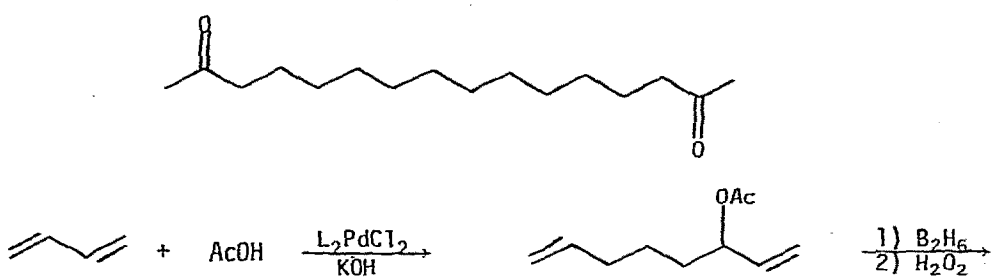


(from eq. 167)

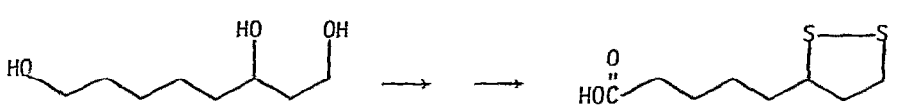


(168)

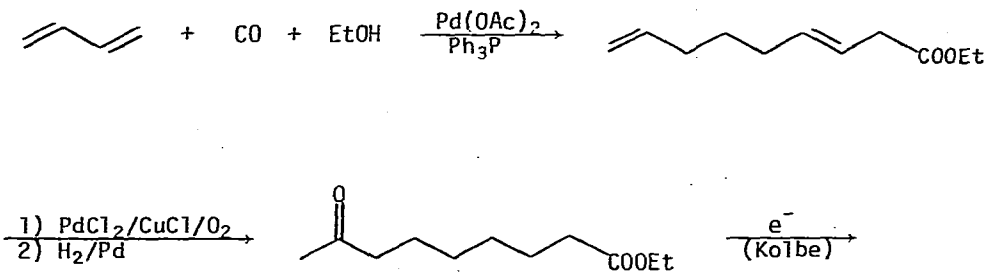




(169)

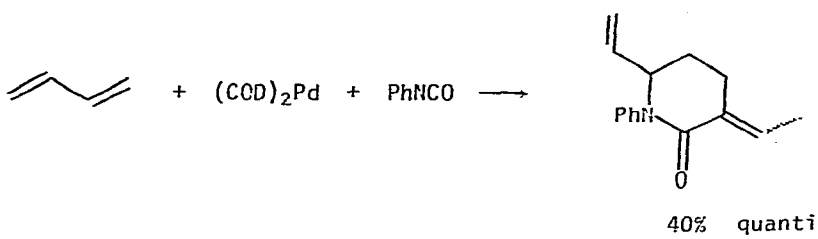


homogeneous catalysts and the solid supported catalyst was easily recycled [316]. 1-Alkoxy-2,7-octadiene was the exclusive product of the reaction of butadiene and alcohols using a palladium(II) chloride/sodium neophylsulfinate catalyst [317]. Butadiene reacted with ethanol and carbon monoxide in the presence of palladium(II) acetate and triphenylphosphine to produce ethyl-3,8-nonadienoate, which was oxidized by palladium(II) chloride/copper(I) chloride/oxygen to give the keto ester. This was dimerized to 2,15-hexadecanedione by a Kolbe electrolysis (eq. 170) [318].



(170)

Butadiene and dialkylamines telomerized to form 1-dialkylamino-2,7-octadiene as the major product in the presence of bis(cyclooctadiene)palladium(0) as catalyst. With isocyanates cyclic amides were formed (eq. 171) [319]. The telomerization of

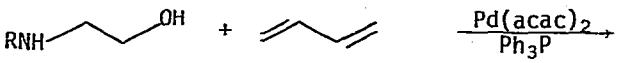


(171)

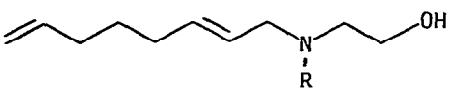
40% quantitative

of butadiene and diethylamine was catalyzed by π-allyl complexes of nickel, palladium and platinum. Triphenylphosphine accelerated the process [320, 321]. The same reaction was catalyzed by silica gel supported palladium-tin complexes [322] and π-allylpalladium phosphine catalysts [323]. Allylamine reacted with butadiene in the presence of a $Pd(acac)_2/Ph_3P/Et_3Al$ catalyst to produce $CH_2=CH(CH_2)_3CH=CHCH_2\overset{H}{N}CH_2CH=CH_2$ in greater than 50% yield [324]. Cycloaliphatic

secondary amines reacted with butadiene in the presence of a $Ni(acac)_2/Ph_3P/AlEt_3/CF_3COOH$ catalyst to produce a mixture of C_4 and C_8 tertiary amines, depending on reaction conditions [325]. β-Hydroxyamines reacted exclusively at nitrogen with butadiene and palladium(II) acetylacetonate catalyst to produce the C-8 alkylated aminoalcohol (eq. 172) [326].

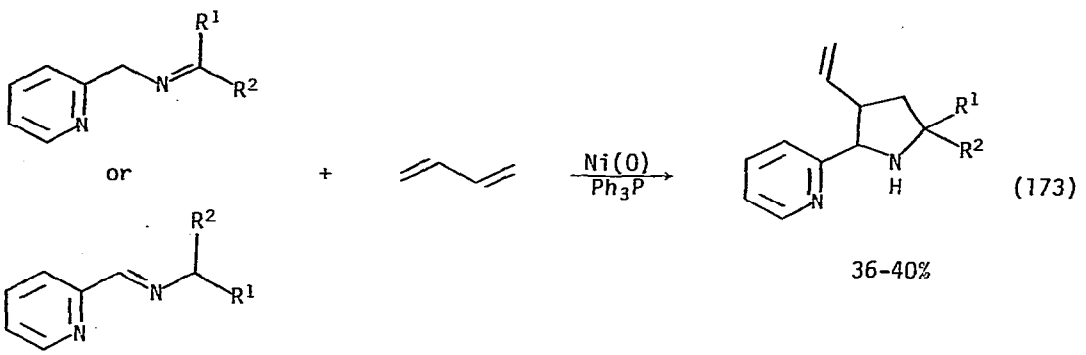


(172)



96-98%

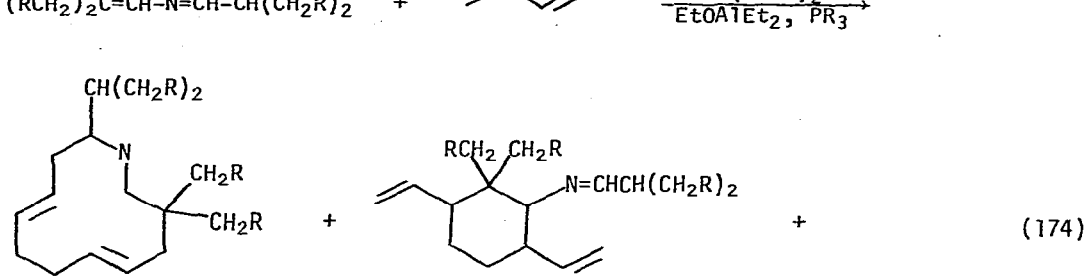
Schiff bases reacted with butadiene in the presence of a nickel(0) catalyst to produce α-*nornicotine* derivatives (eq. 173) [327] by a cycloaddition process.



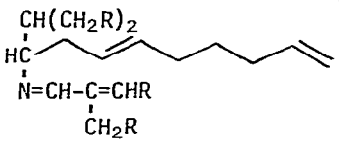
(173)

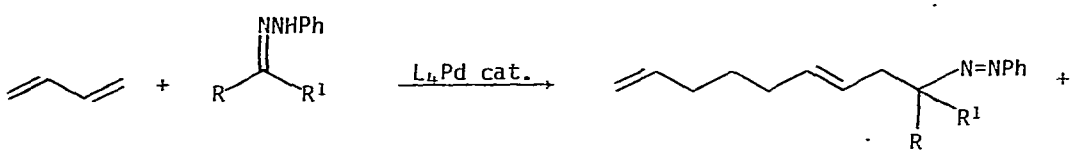
The unsaturated Schiff base $(RCH_2)_2C{=}CH{-}N{=}CHCH(CH_2R)_2$ reacted with butadiene under similar conditions to produce a number of cyclic products (eq. 174) [328]. Hydrazones reacted with butadiene in the presence of a number of palladium catalysts to produce primarily linear telomers (eq. 175) [329]. Nickel(0) catalysts gave similar products, and the effects of catalyst and reactions conditions on product distribution was studied [330].

Stabilized carbanions also reacted with butadiene in the presence of palladium catalysts. Thus, the carbanions of nitroethane (eq. 176) [331] and

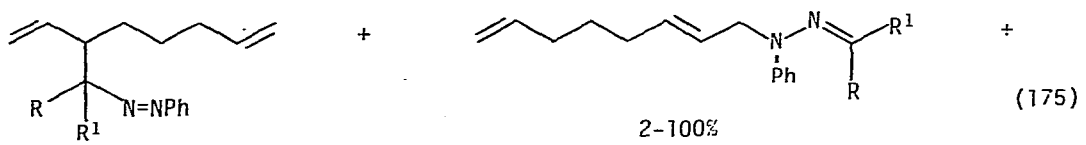


(174)





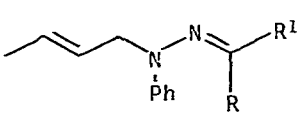
16-72%



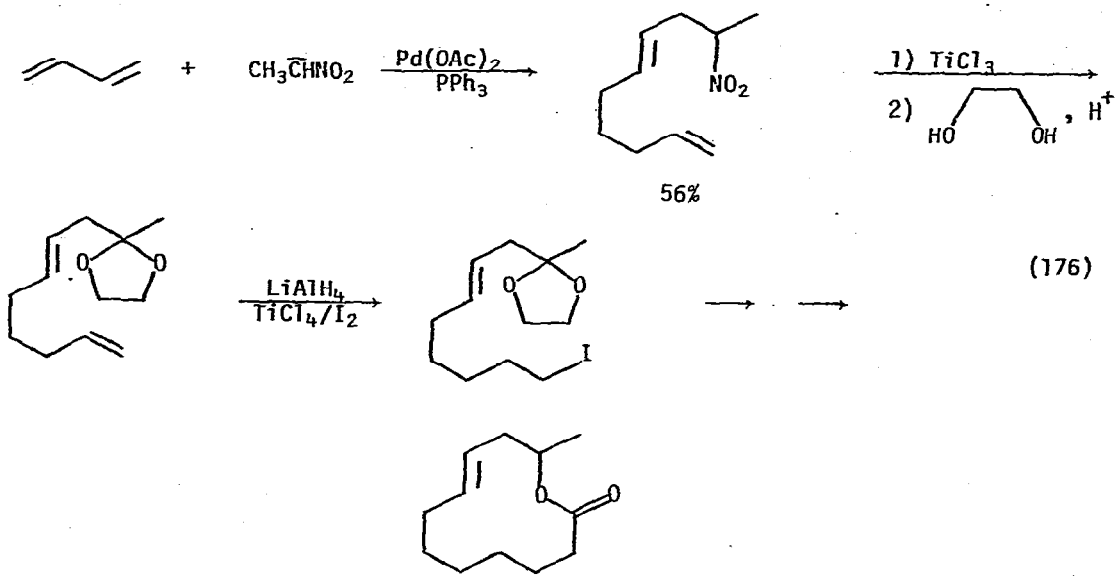
15-84%

2-100%

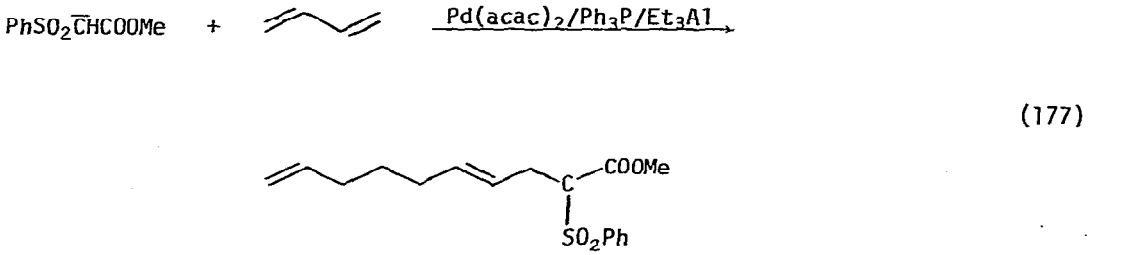
(175)

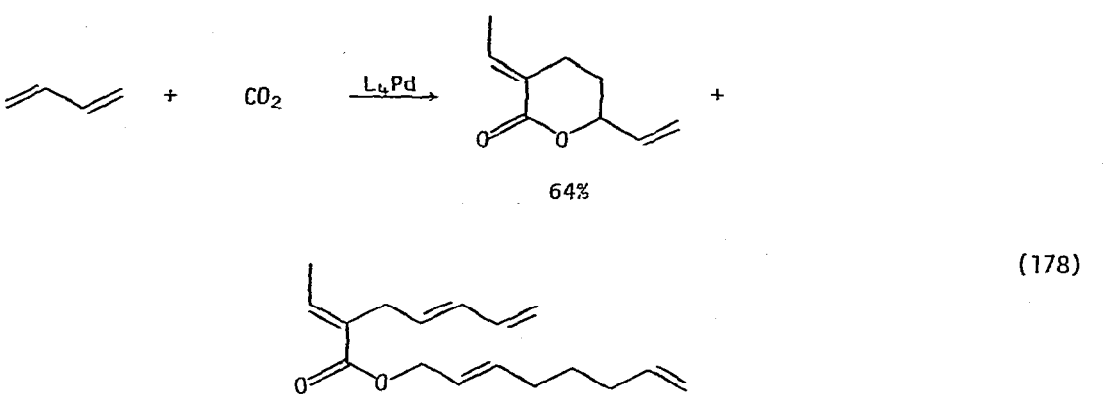


44-83%



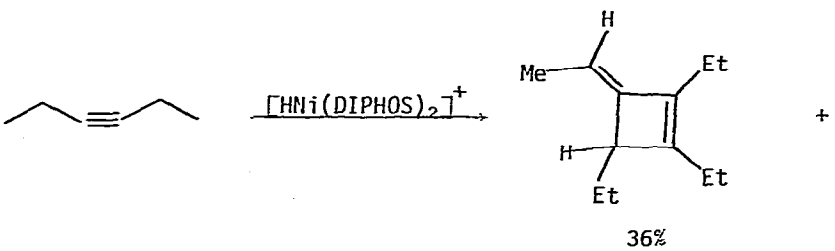
sulfones (eq. 177) [332] telomerized butadiene in the presence of palladium catalysts. Carbon dioxide and butadiene also telomerized under similar conditions (eq. 178) [333, 334].



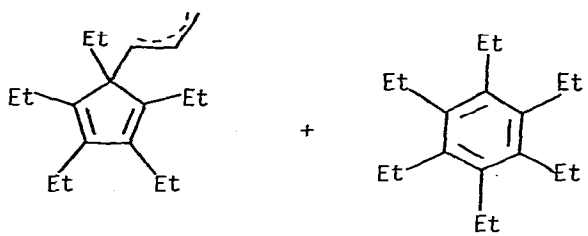


Terminal alkynes dimerized primarily to enynes when treated with Wilkinson's catalyst ($Rh(Cl)(PPh_3)_3$) at 25° (eq. 179) [335]. Alkynes were dimerized to 1,3-dienes when treated with $Cp_2Zr(R)H$ followed by hydrolysis of the resulting zirconacyclopentadiene [336]. Internal alkynes were cyclodimerized and cyclotrimerized when treated with the cationic nickel hydride complex $[HNi(DIPHOS)_2]^+OCOCF_3$ (eq. 180) [337]. Propargyl alcohols of terminal alkynes dimerized to produce 2-penten-4-yne-1,5-diols by rhodium(I) catalysts (eq. 181) [338], whereas nickel(II) catalysts led to production of substituted benzene via cyclotrimerization [339].

$$2\ RC{\equiv}CH + L_3RhCl\ cat. \xrightarrow{25°} RC(=CH_2)-C{\equiv}CR \qquad (179)$$



36%

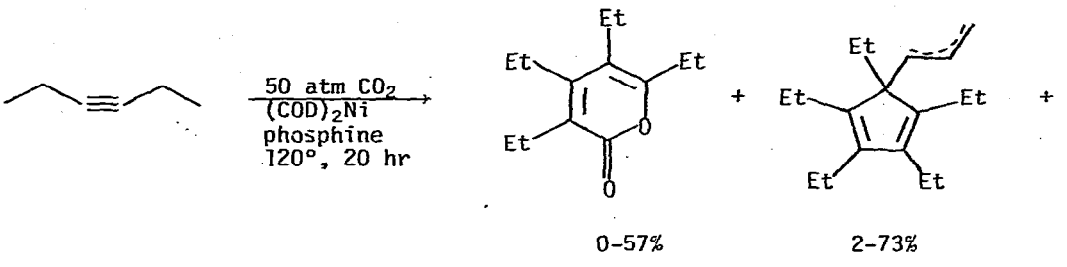


20% 3%

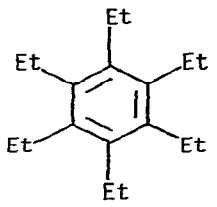
(180)

$$R-C(OH)-C{\equiv}CH \xrightarrow[cat.]{L_3RhCl} R-C(OH)-C=C(H)-C{\equiv}C-C(OH)-R \qquad (181)$$

The synthesis of pyridines by the cocyclooligomerization of alkynes with nitriles using cobalt catalysts has been reviewed (135 references) [340]. The nickel complex Ni(COD)(RC≡CR) was the active species for cyclotrimerization of alkynes [341]. 3-Hexyne reacted with carbon dioxide in the presence of nickel(0) phosphine catalysts to produce a lactone and several cyclotrimers (eq. 182). The

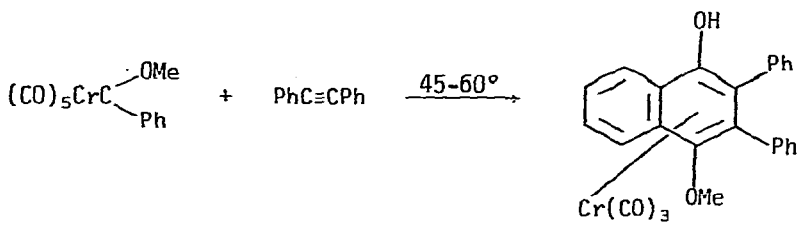


(182)



2-40%

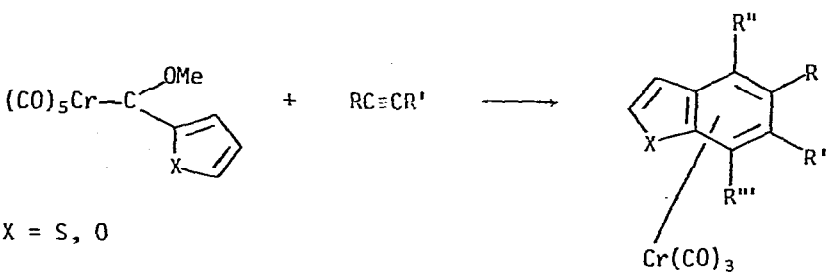
product distribution was strongly dependent upon the phosphine ligand used [342]. Chromium carbene complexes reacted with alkynes to produce the chromium tricarbonyl complexes of unusual arenes (eq. 183) [343].



(183)

40%

and



(183)

X = S, O

19-62%

Cobalt catalyzed acetylene cyclizations have been reviewed (21 references) [344] as have transition metal catalyzed acetylene cooligomerizations for the synthesis of complex molecules (14 references) [345], and organometallic catalysis

in stereospecific polymerization and the nature of active centers (207 references) [346].

Propionaldehyde was dimerized to $CH_3CH_2CH{=}C(CH_3)CHO$ by a number of nickel(0) catalysts including (bipy)(COD)Ni and $(bipy)(Ph_3P)_2Ni$ [347]. Styrene oxide was dimerized to $PhCH_2CH_2O_2CCH_2Ph$ by rhodium(I) or ruthenium(II) catalysts of the type $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$[348]. Biphenyl and mesitylene coupled to produce mainly p-quaterphenyl in the presence of $AlCl_3/CuCl_2$[349]. Dihaloaromatics were polymerized (by coupling at the halogen sites) by reaction with magnesium and a wide variety of transition metal salts and complexes. In this fashion m-dichlorobenzene, 4,4'-dibromodiphenyl ether, and 4-chlorobenzyl chloride were polymerized [350].

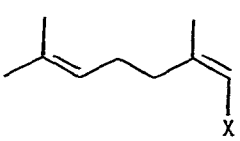
E. Rearrangements. Olefin metathesis continued to be an active area of research this year. Metathesis of 1-octene with $Me_4N^+W(CO)_5Cl/EtAlCl_2$ gave the same type of product as that obtained from 1-heptene and 1-pentene. The initial step of this reaction was thought to be isomerization of the olefin to an internal position, which was followed by homo- and cross metathesis to give the final product [351]. The catalyst systems $WCl_6/EtAlCl_2$ and $MoCl_5/EtAlCl_2$ catalyzed the metathesis and olefin isomerization of 2-pentene in the homogeneous liquid phase [352]. An effective metathesis catalyst was produced by the treatment of tungsten(VI) hexachloride with lithium aluminum hydride [353]. The stereoselectivities of the metathesis of cis and trans 2-alkenes was studied as a function of olefin structure and catalyst. With the catalyst system $W(CO)_6$/phosphine/$EtAlCl_2/O_2$ and olefins $RCH{=}CH{-}CH_3$, high activity was observed. With cis olefins as R went from H to t-Bu, the trans to cis ratio of the product went from 0.73 to 1.00, indicating a loss of stereospecificity. With the less active catalyst system $W(CO)_4Cl_2$ the trans to cis ratio was 4 with the olefin 2-hexene [354].

Several solid supported olefin metathesis systems have been developed. Molybdenum hexacarbonyl was supported on alumina activated at various temperatures. Catalyst on the support activated at 500° was most active for the metathesis of propene to ethene and 2-butene, and had greater than 99% specificity for these primary products [355]. Infrared studies of the active metathesis catalyst $W(CO)_5L$ where L was CO, PPh_3, PBu_3 and $P(OPh)_3$ on activated alumina indicated that the catalyst precursor was interacting with the alumina through aluminum complexation of a carbonyl group [356]. Activated alumina and silica gel was treated with tris(allyl)molybdenum at 0°, and the resulting solid supported complex was heated to ~500° in the presence of hydrogen, producing a highly active supported molybdenum species. This complex catalyzed the metathesis of propene at 0°C, and had a turnover ( /mm/Mo atom) of 0.32 [357]. The catalysts, cobalt(II) oxide/molybdenum(VI) oxide/alumina and tungsten(VI) oxide/silica were active for the metathesis of 3-heptene, but inert to allyl cyanide [358]. A polystyrene supported metathesis catalyst was prepared by treatment of chloromethylated

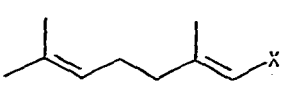
polystyrene with $CpW(CO)_3^-$ to produce a polymer-CH_2-$W(CO)_3Cp$ linkage. This was an active catalyst for the metathesis of 3-heptene, and showed no tendency to leach from the support. In contrast, attachment through coordination to polymer bound phosphine led to catalysts which dissociated from the support and could not be recycled [359]. Coordination of molybdenum or tungsten hexacarbonyl to polystyrene-attached bipyridine followed by treatment with $EtAlCl_2$ produced a catalyst that was an order of magnitude more reactive for the metathesis of 2-pentene and could be recycled a number of times. The same catalyst attached to polymer via phosphine linkages was much less active [360]. A metathesis catalyst for the conversion of 2-pentene to 2-butene and 3-hexene was prepared by the ultraviolet (λ 350 nm) irradiation of a $W(CO)_6/CCl_4$/olefin mixture. High selectivity and stereospecificity was observed [361]. Reviews on the olefin metathesis reaction (125 references) [362] and the application of olefin metathesis to organic synthesis (32 references) [363] have appeared. A study of olefin metathesis catalysts was the subject of a dissertation [364].

Both metal carbene complexes and metallacycles have been implicated in olefin metathesis reactions. An olefin-carbene iron complex has been prepared and characterized [365]. This was deemed significant since this type of complex has been proposed as a key intermediate in olefin metathesis reactions. Phosphine nickelacyclopentanes have been prepared from olefins, and exchange reactions with other olefins as well as rearrangements have been studied [366, 367].

Rhodium trichloride supported on silica was about 100 times more reactive for the isomerization of 1-butene than was the corresponding homogeneous complex [368]. The ethylene released from μ-dichlorotetraethylene dirhodium when used as a butene isomerization catalyst had an inhibiting effect on the isomerization and led to abnormal kinetics [369]. The complex $Ru(H)_2(CO)_2(Ph_3P)_2$ catalyzed olefin isomerizations much more effectively than hydrogenation. Triphenylphosphine inhibited the rearrangement, while oxygen and nitrogen had no effect. At high hydrogen pressures and temperatures in excess of 150° olefin reduction predominated [370]. Polycarboxylate-bound ruthenium(II) complexes displayed higher activity and better selectivity for isomerization of 1-pentene than did homogeneous analogs [371]. Ruthenium(III) acetylacetonate was an efficient cis to trans isomerization catalyst for a number of terpenoids (eq. 184) [372]. The complex



$$\xrightarrow[190\text{–}200^\circ]{0.3\%\ Ru(acac)_3}$$

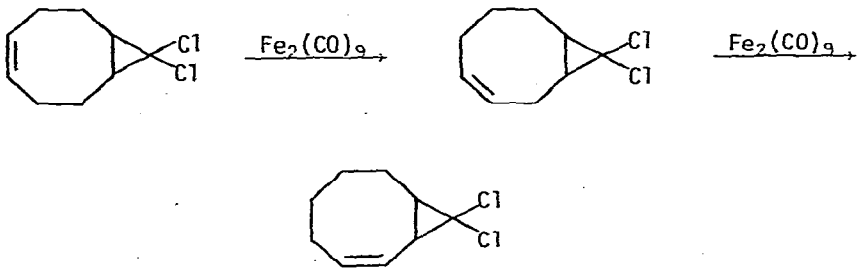


(184)

X = $CH_2CH_2COCH_3$ 57:43
X = $CH{=}CHCOCH_3$ 66:34
X = COOEt 64:36

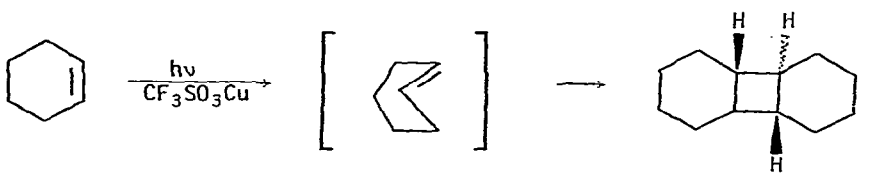
X = CN 73:27
X = CH_2CH_2COOEt 56:44

$(Ph_3P)_3NiCl$ catalyzed the isomerization of olefins by the production of small amounts of a nickel(II) hydride species by reaction with olefin to form a π-allylnickel species [373]. The double bond in 9,9-dichlorobicyclo[6.1.0]non-4-ene was rearranged by treatment with $Fe_2(CO)_9$ (eq. 185) [374]. Cyclohexenes isomerized

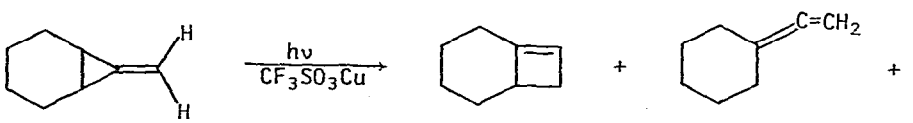


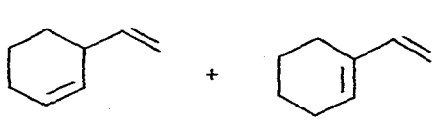
(185)

to their trans isomers, then dimerized when irradiated in the presence of CF_3SO_3Cu catalysts (eq. 186). In contrast, the isomerization of cyclopentene was very slow [375]. The same system catalyzed rearrangements of vinylcyclopropanes (eq. 187) [376]. Vinyl cyclopropanes reacted with zero valent transition



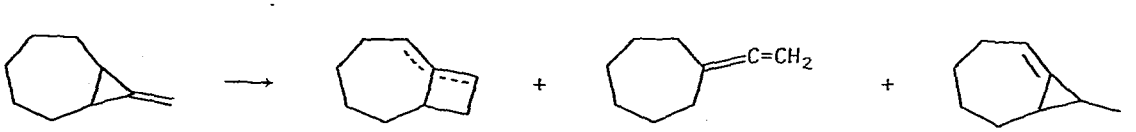
(186)





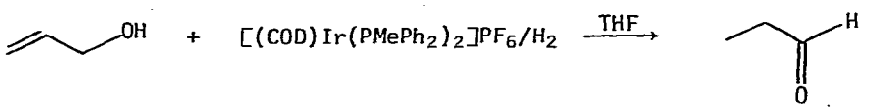
and

(187)

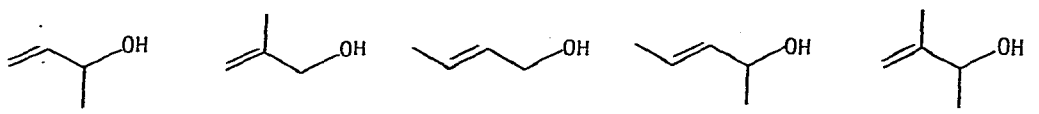


metals in four distinctly different ways. These were heat induced rearrangements to π-diene complexes, photo-induced carbonyl insertions, heat or photo-induced formation of π-allyl complexes and photc-induced acylmetal insertions to produce π-acyl π-allyl complexes [377]. Rhodium(I) complexes catalyzed the isomerization of cycloprop[a]acenaphthylene to phenalene via a π-allyl rhodium(III) complex [378].

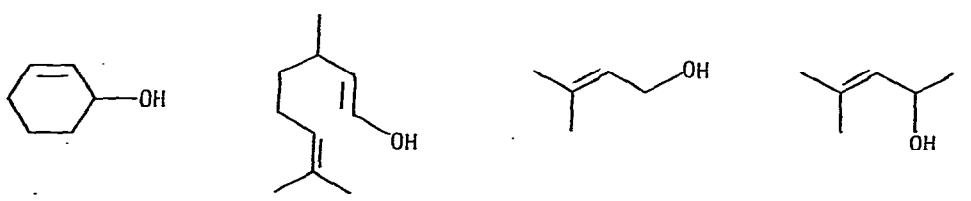
Allyl alcohols rearranged to aldehydes via their enols when treated with a catalyst produced by treatment of $[(COD)Ir(Ph_2PMe)_2]PF_6$ with hydrogen (eq. 188) [379]. This same catalyst rearranged allyl ethers to vinyl ethers [380]. Both



100% (188)

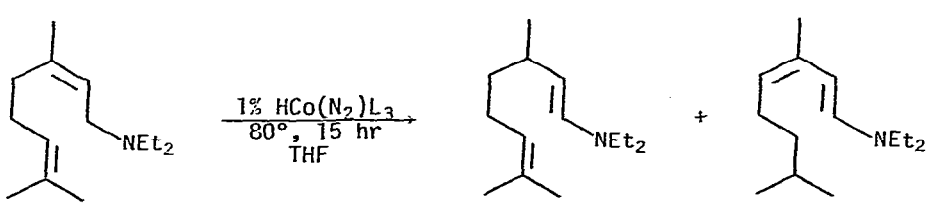


100% 100% 99% 98% 8%



9% 14% 16% 0%

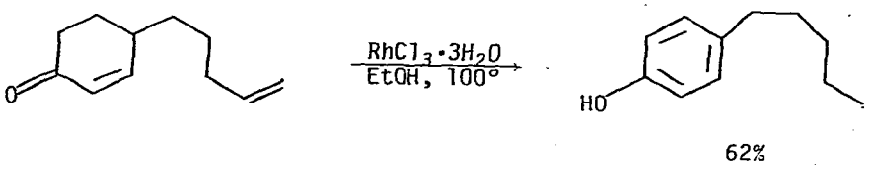
reactions involved π-allyliridium intermediates. Allyl amines were isomerized to enamines by the complex $HCo(N_2)(PPh_3)_3$ (eq. 189). Allyl alcohols and ethers



85% 15% (189)

were inert to this catalyst [381]. Substituted phenols and anilines were pro-

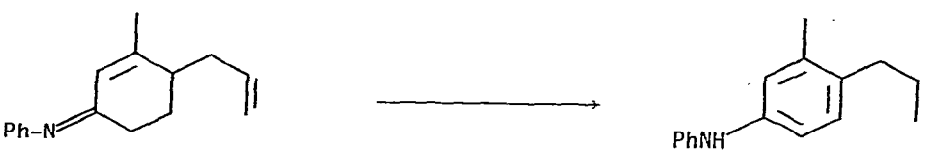
duced from alkenylcyclohexenones or their imines respectively by reaction with rhodium(III) chloride in ethanol containing excess sodium carbonate (eq. 190) [382]. Allyl enol ethers rearranged to C-allylated materials when treated with either $(Ph_3P)_4Pd(0)$ or π-allylpalladium bis phosphine complex catalysts (eq. 191) [383]. The propargyl chloride PhCHClC≡CH rearranged to PhCH=C=CHCl when treated with Bu_4NCuCl_2[384]. Rhodium(I) complexes catalyzed the rearrangement of 3,4-bis(acyloxy)-1,5-hexadiynes to cyclic compounds (eq. 192) [385].



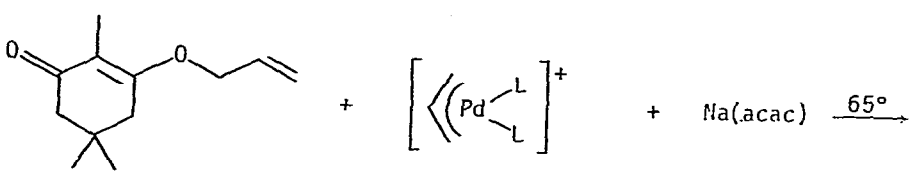
62%

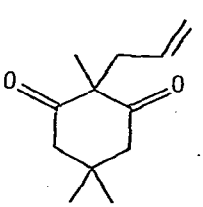
and

(190)



50%

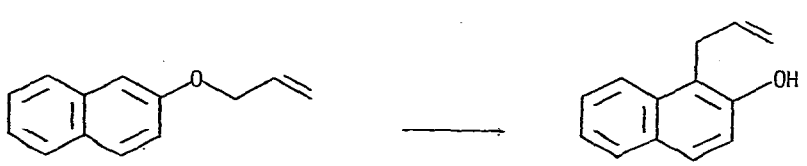




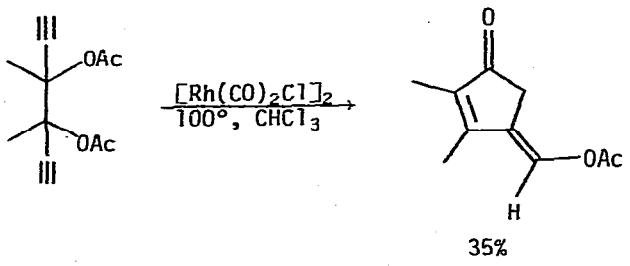
100%

and

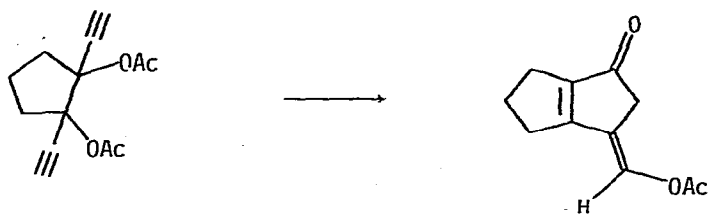
(191)



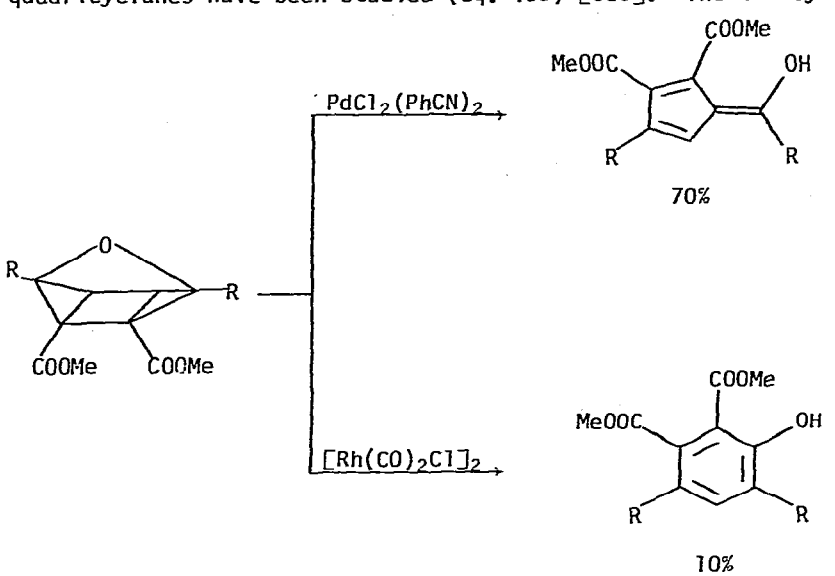
>95%



and (192)

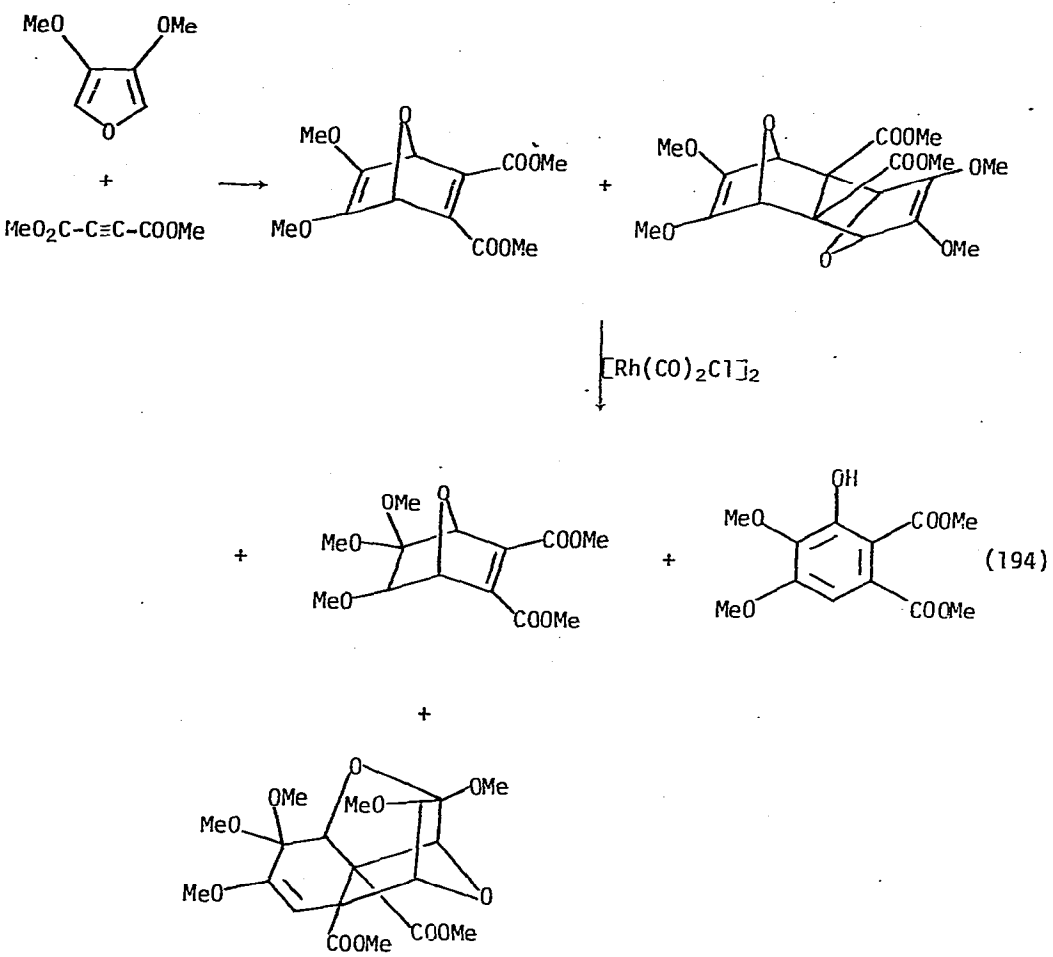


The mechanistic aspects of transition metal catalyzed rearrangements of 3-oxa quadricyclanes have been studied (eq. 193) [386]. The 4+2 cycloadducts of furans

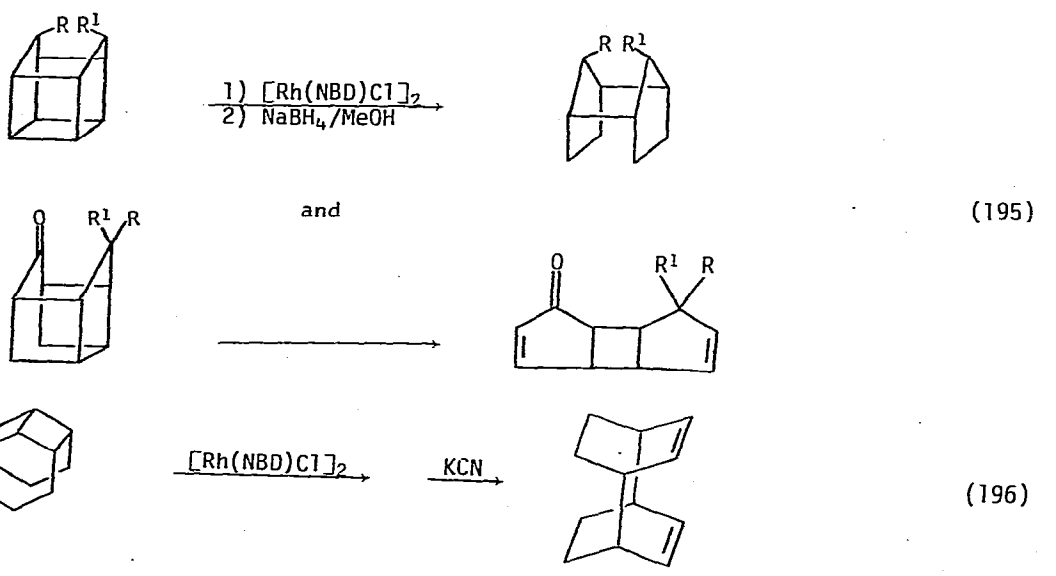


(193)

with dimethylacetylene dicarboxylate rearranged when exposed to $[Rh(CO)_2Cl]_2$ (eq. 194) [387]. Rhodium(I) catalysts also rearranged secopentaprismanes (eq. 195) [388] and other polycyclic compounds (eq. 196) [389]. Anti-tetra-


MeO
OMe
O
+
MeO2C-C≡C-COOMe
MeO
COOMe
MeO
COOMe
+
MeO
COOMe
COOMe
OMe
MeO
O
OMe
[Rh(CO)2Cl]2
+
OMe
MeO
COOMe
MeO
COOMe
+
OH
MeO
COOMe
MeO
COOMe
+
O
OMe
OMe
MeO
MeO
MeO
O
COOMe
COOMe

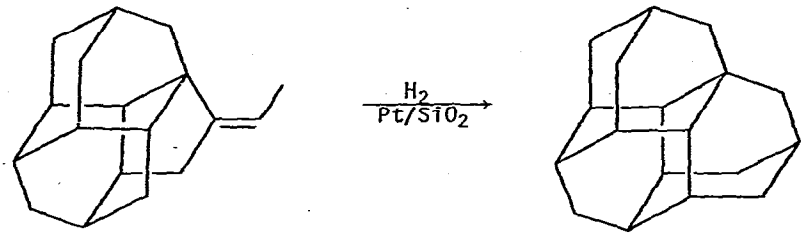
(194)


R R1
1) [Rh(NBD)Cl]2
2) NaBH4/MeOH
R R1
and
O
R1
R
O
R1
R
[Rh(NBD)Cl]2
KCN

(195)

(196)

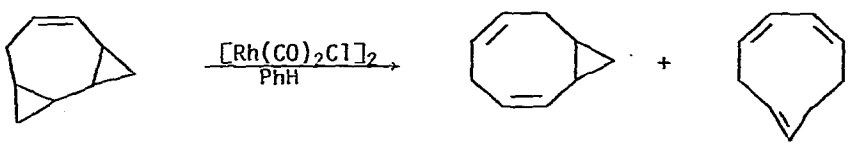
mantane was produced in a gas phase, platinum catalyzed reduction reaction (eq. 197) [390]. A polymer supported bipyridine palladium(II) acetate complex catalyzed the isomerization of quadricyclene to norboradiene and was 30 times



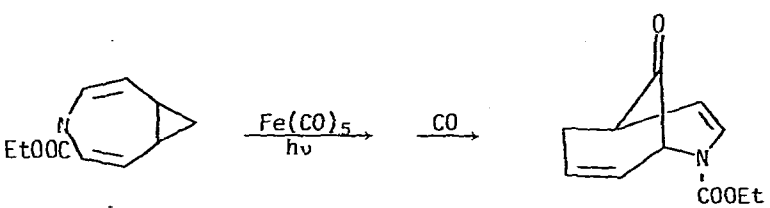
(197)

more active than 10% palladium on carbon [391]. Pinene rearranged to 1,2,3-trimethylbenzene upon treatment with palladium(II) chloride and sodium acetate in acetic acid [392].

Rhodium(I) complexes catalyzed the rearrangement of syn-1,3-bishomocycloheptatriene via a [3,3]-homodienyl sigmatropic shift followed by a 1,5-homodienyl hydrogen migration (eq. 198) [393]. The rearrangement/carbonylation in eq. 199 was catalyzed by $Fe(CO)_5$ [394] while that of eq. 200 was catalyzed by

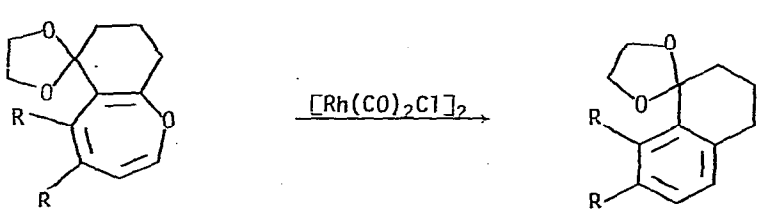


(198)

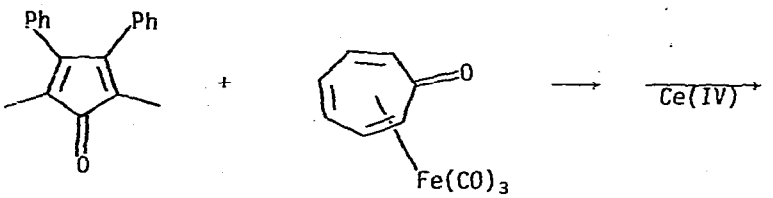


(199)

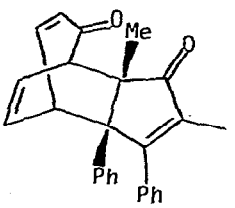
$[Rh(CO)_2Cl]_2$ [395]. Tricarbonyltroponeiron reacted with 2,5-dimethyl-3,4-diphenylcyclopentadienone to ultimately produce polycyclic material (eq. 201) [396]. Diiron eneacarbonyl isomerized 3-phenyl-2-oxa-3-azabicyclo[2.2.2]oct-5-ene to a number of products including a β-lactam (eq. 202) [397].

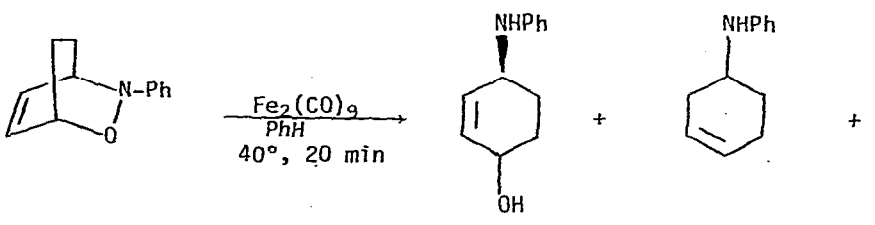


(200)

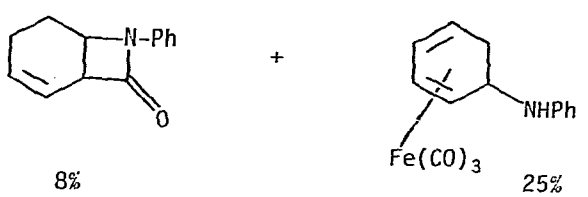


(201)





(202)



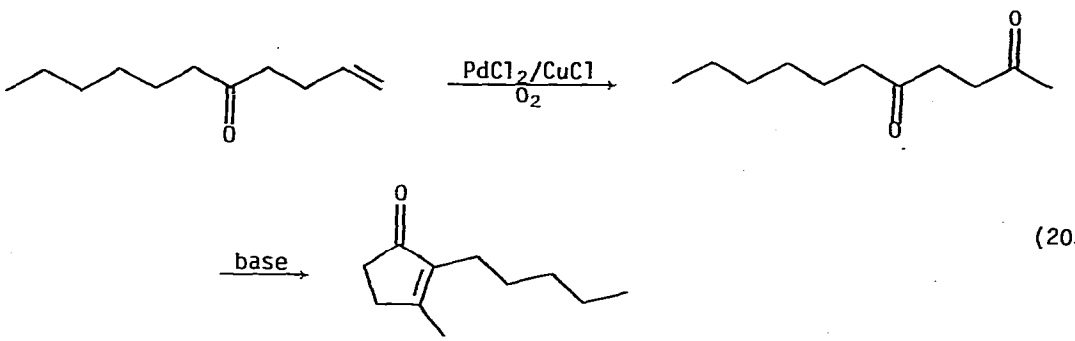
The epimerization of aldoses by molybdate complexes was pH dependent, with a maximum rate at pH 2.5-3.5 [398,399]. Fluxional and nonrigid behavior of transition metal organometallic π-complexes has been reviewed (114 references) [400], as has σ-π rearrangements of organotransition metal compounds (116 references) [401].

III. Oxidation

Cyclohexene was cleanly epoxidized by cumene hydroperoxide at 85° in the presence of $H_2[Mo_2O_4(oxalate)_2(H_2O)_2]\cdot 3H_2O$ *as catalyst [402]. Other molybdenum catalysts such as* $Mo(CO)_6$, $Mo(CO)_5PPh_3$, $Mo(CO)_nPy6\text{-}n$, $Mo(CO)_3(C_6H_6)$ *and* $Mo(CO)_3(PhCH_3)$ *affected similar chemistry [403]. Olefins were epoxidized by* t*-butylhydroperoxide in the presence of* bis*[(+)-3-trifluoroacetylcamphorato]-*

dioxomolybdenum as a catalyst. The corresponding vanadium complex catalyzed the epoxidation of allyl alcohol [404]. The kinetics of the epoxidation of crotonic and citraconic acids by hydrogen peroxide in the presence of a sodium tungstate catalyst was first order in substrate and in catalyst, and zero order in hydrogen peroxide [405]. Aqueous copper(II) chloride and palladium(II) chloride solutions converted 1,3-cyclohexadiene to 2,3-epoxycyclohexene and 2-cyclohexen-1-ol when oxygen was passed through the solutions [406].

1-Undecen-5-one was oxidized to 2,5-undecandione by reaction with palladium(II) chloride catalyst, copper(I) chloride and O_2 (Wacker type oxidation). This material converted to dihydrojasmone upon treatment with base (eq. 203) [407].

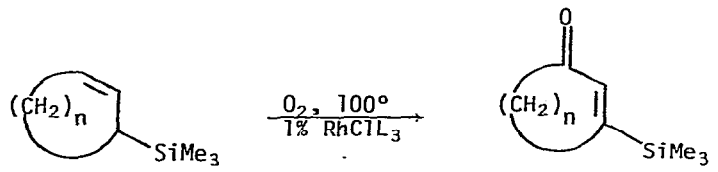


(203)

Palladium(II) salts were supported on Amberlyst A-21 resin and fully characterized by a variety of physical techniques. This material had only a low activity for both the oxidation of ethylene and the ester interchange reaction of vinyl acetate [408]. A much more effective catalyst for the oxidation of ethylene to acetaldehyde was prepared by anchoring palladium(II) salts to organic quinone polymers containing sulfonic acid groups. This catalyst system was particularly useful because cocatalysts such as copper(II) chloride were not required, the quinone polymer support carrying the redox reaction itself [409]. Ethylene was oxidized to ethylene glycol monoacetate by oxygen using a $PdCl_2/NaNO_3/Fe(NO_3)_3 \cdot 9H_2O$ catalyst [410]. The rhodium(I) complex $RhCl(PPh_3)_3$ catalyzed the oxidation of 1-octene to 2-octanone, producing small quantities of 2-octanol as a side product [411]. The cationic rhodium oxygen complex $[Rh(AsPh_3)_4O_2]^+$ oxidized 1-octene to 2-octanone in 85% yield. Internal olefins were unreactive towards this complex. This oxidation occurred via activated oxygen rather than by Wacker type chemistry [412]. The catalyst system consisting of $RhCl_3 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot (HMPA)_4$ catalyzed the oxidation of monosubstituted terminal olefins, to 2-ketones by oxygen. The yields were greater than 98% ketone for 1-hexene, 1-octene, 1-dodecene, 4-methyl-1-pentene, stryene and 1,4-octadiene, and 116 turns of the catalyst were observed. Internal olefins were much less reactive, and 2,2-disubstituted olefins were unreactive. Water inhibited the oxidation. The reaction was thought to proceed by two coupled paths, one involving activation of molecular oxygen, the other involving Wacker type oxidation processes (attack of olefin by Rh-OH) [413].

Linoleic acid was oxidized to a mixture of 9 and 13 positional isomers of linoleate hydroperoxide by hemoglobin, myoglobin, iron(II) and copper(II) ions and oxygen. This regioselectivity resembled that of lipoxygenases [414]. Osmium tetroxide catalyzed the sodium periodate oxidation of maleic, furmaric and cinnamic acids [415]. Manganese triacetate oxidized (-)bornene to a mixture of lactones [416]. Osmium tetroxide catalyzed the potassium chlorate oxidation of 1-methoxy-1-alkynes (RC≡COMe) to α ketoesters (RCOCOOMe) [417].

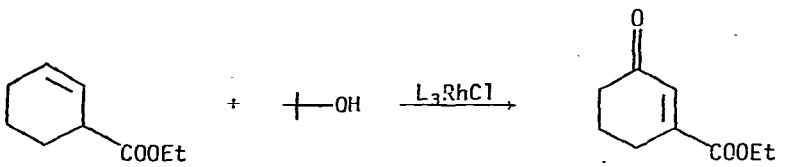
The complex 3,5-dimethylpyrrazole CrO_3 oxidized Δ^5 steroids to Δ^5-7-ketosteroids (an allylic oxidation) in good yield [418]. Cyclic allyl esters and silanes were oxidized to cyclic enones by oxygen or t-butylhydroperoxide in the presence of 1% $RhCl(PPh_3)_3$ as a catalyst (eq. 204) [419]. Cyclic ketones



60-84%

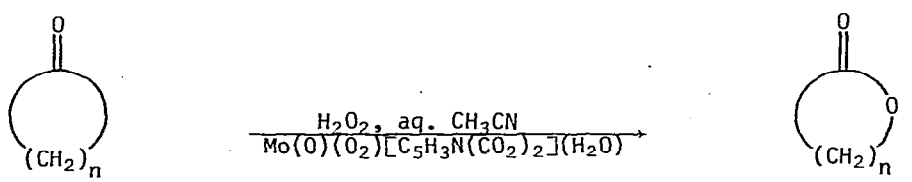
n = 2-5

and (204)

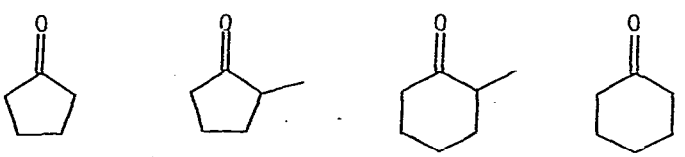


77%

were oxidized to cyclic esters by hydrogen peroxide using $Mo(O)(O_2)$(pyridine-2,6-dicarboxylic acid)(H_2O) as catalyst (eq. 205) [420].



(205)



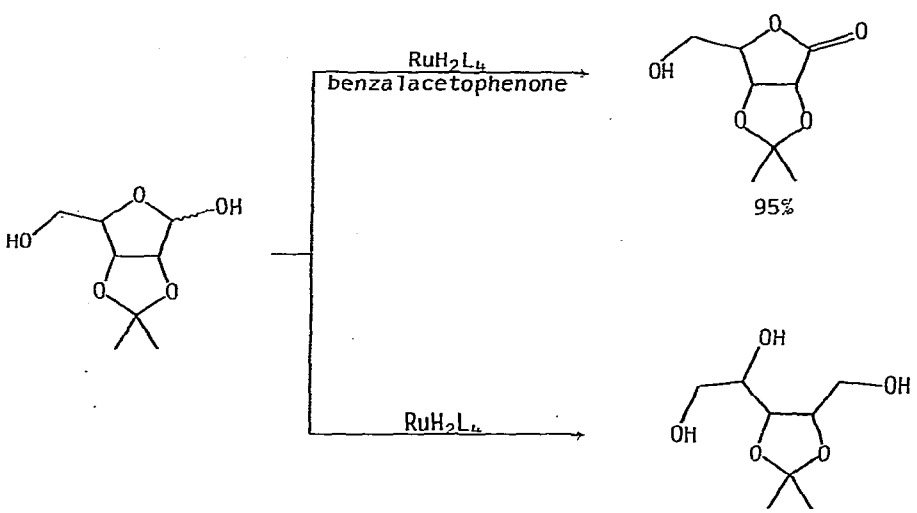
60% 82% 87% 10%

Related molybdenum complexes hydroxylated carbanions. The complex $Mo(O)_5(HMPA)_2$ converted ketone enolates to α-hydroxyketones (eq. 206). Ketones with α methylenes

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overline{C}HR' + MoO_5(HMPA)_2 \rightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{OH}{\underset{|}{C}}H\text{-}R' \qquad (206)$$

or α-methines underwent clean hydroxylation, while α-methyl groups led to variable results. Kinetic enolates could sometimes be specifically hydroxylated. Stabilized enolates did not hydroxylate, while dianions gave mixtures of products [421]. Grignard reagents were similarly hydroxylated by MoO_5/pyridine/HMPA, producing alcohols in good yield [422].

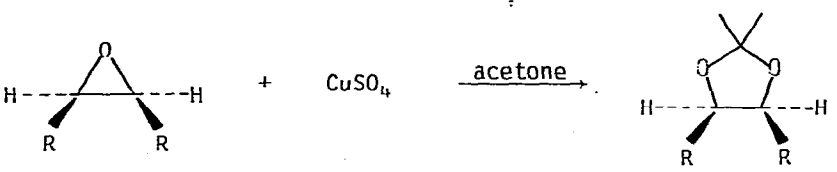
Chromium trioxide was adsorbed on crosslinked polyvinylpyridine in the presence of HCl to produce an insoluble poly[vinyl(pyridinium chlorochromate] which was an efficient and convenient oxidizing agent for the conversion of alcohols to ketones or aldehydes. Less than one molar equivalent of reagent was consumed in the oxidation reaction, the oxidant was easily separated from the product by a simple filtration, and after several reuses and regenerations the reagent was still as reactive as the original material [423]. Benzyl alcohols were oxidized to aromatic aldehydes by $K_2Fe(CO)_4$ while aliphatic alcohols were inert [424]. A hematoporphyrin manganese(IV) complex oxidized benzyl alcohol, benzylamine and benzyl ethers to benzaldehyde in 70-90% yield. The process was catalytic when sodium hypochlorite was used as co-oxidant, and the rate was considerably faster than that observed with sodium hypochlorite alone [425]. Lactols were oxidized to lactones in high yield by $RuH_2(PPh_3)_4$/benzalacetophenone (eq. 207) [426]. In the absence of benzalacetophenone up to 50% diol was obtained. Racemic



(207)

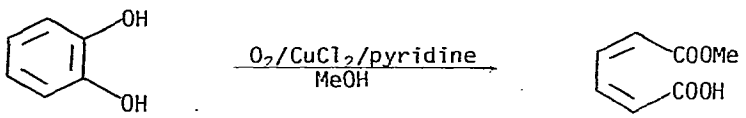
alcohols were asymmetrically dehydrogenated by the chiral catalyst

Ru_2Cl_4[(-)-diop]$_3$ in the presence of unsaturated hydrogen acceptors. The amount of enantioselectivity was dependent on the structure of the alcohol, the acceptor and the reaction temperature [427]. Aromatic aldehydes were oxidized to carboxylic acids in aqueous alkaline solution by nickel peroxide [428]. Epoxides were oxidized directly to acetonides by anhydrous copper(II) sulfate in acetone. With alkyl epoxides the reaction was stereoselective (eq. 208). [429].



(208)

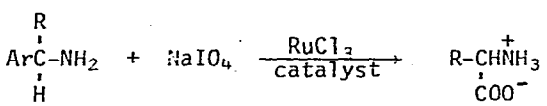
Phenol and o-hydroquinone were both oxidized to the monomethyl ester of muconic acid by $O_2/CuCl_2$/pyridine in methanol. Water inhibited the reaction. Electron rich phenols underwent a similar cleavage, while electron deficient ones did not (eq. 209) [430]. A detailed mechanistic study of this reaction showed that oxygen was not directly activated by this process, but merely carried the copper(I) to copper(II) oxidation chemistry. The initial step was a two electron oxidation to the ortho-benzoquinone, followed by cleavage of the



(209)

82%

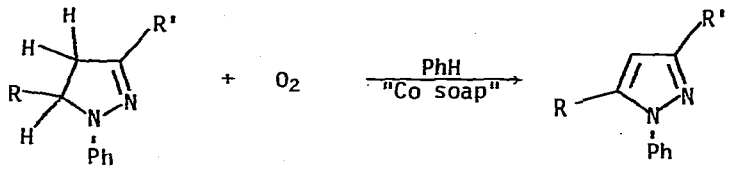
aromatic ring. The catalyst was thought to be a dimeric copper(II) species such as [Py(MeO)CuOH]$_2$ with bridging hydroxyl groups [431]. The same reagent oxidized aromatic ortho diamines to Z,Z-2,4-hexadienedinitrile [432]. Benzyl amines were converted to aminoacids by sodium periodate catalyzed by ruthenium(III) chloride (eq. 210) [433]. Cyclohexanone was oxidatively cleaved to adipic acid



(210)

by hydrogen peroxide and either H_2MoO_4 or H_2WO_4 as a catalyst [434]. In contrast $UO_4 \cdot 4H_2O$ oxidized cyclohexanone to cyclopentane carboxylic acid [435].

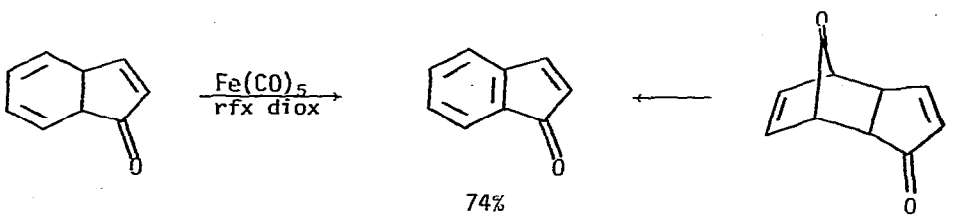
N-Phenylpyrazolines were oxidized to the corresponding pyrazoles by oxygen in the presence of a "cobalt soap" consisting of cobalt(II) sulfate, sodium hydroxide and a C_6-C_{10} fatty acid (eq. 211) [436]. Dihydropyridines were ox-



(211)

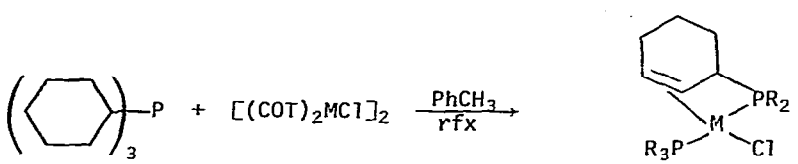
R = Ph-, m-NO_2-Ph, α-furyl, α-thienyl, H
R' = Ph, PhCH=CH-, p-BrPh, p-ClPh, p-MeOPh, Me

dized to pyridines in the presence of a 1:3:3:10 palladium(II) acetylacetonate/tributyl phosphine/triethyl aluminum/trifluoroacetic acid catalyst [437]. Indenone was produced from partially saturated precursors by treatment with iron pentacarbonyl (eq. 212) [438]. Cyclohexene was dehydrogenated to benzene by



(212)

nickel, iron or cobalt intercalated into tantalum disulfide [439]. Dehydrogenation of polycyclic aromatic hydrocarbons has been reviewed (211 references) [440]. A cyclohexyl group of tricyclohexylphosphine was dehydrogenated to a cyclohexene group upon treatment with rhodium(I) or iridium(I) complexes (eq. 213) [441].



(213)

M = Ir, Rh

Tocopherols were oxidized by bis-(salicylidene)ethylenediiminocobalt complexes to give complex mixtures of benzoquinones and aromatic dimers resulting from coupling at several different positions [442]. Oximes were oxidatively cleaved back to their parent ketones in 40-70% yield by pyridinium chlorochromate. Oxime ethers were resistant to this reagent [443]. Olefins were converted to saturated halides by hydrosilation followed by copper(II) halide oxidation of the pentafluorosilicate (eq. 214) [444]. Sodium periodate oxidized sulfimines in the presence

$$RCH{=}CH_2 + HSiCl_3 \longrightarrow RCH_2CH_2SiCl_3 \xrightarrow{KF} K_2[RCH_2CH_2SiF_5] \xrightarrow{CuX_2} RCH_2CH_2X \quad (214)$$

R = n-octyl, Ph–⟨⟩, Ph, $MeO_2C(CH_2)_{10}$-

of ruthenium(IV) oxide under phase transfer conditions (eq. 215) [445]. Amines were oxidized to nitriles and amides by oxygen in the presence of a ruthenium(III) chloride catalyst (eq. 216) [446]. Secondary alcohols were oxidized to ketones by this catalyst.

$$Me_2S{=}N{-}R + NaIO_4 \xrightarrow[H_2O/CH_2Cl_2]{RuO_2} Me_2\overset{O}{\overset{\|}{S}}{=}N{-}R \quad (215)$$

88-95%

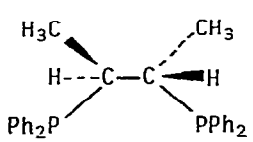
$$RCH_2NH_2 + O_2 \xrightarrow[PhCH_3,\ 100°]{RuCl_3} RCN + R\overset{O}{\overset{\|}{C}}{-}NH_2 \quad (216)$$

70-100%

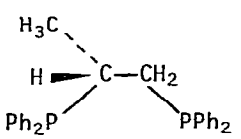
Aliphatic hydroxylations catalyzed by iron was the subject of a dissertation [447]. Reactions of cobalt-oxygen complexes with organic molecules has been reviewed (40 references) [448] as has transition metal complexes as catalysts for the addition of oxygen to reactive organic substrates (524 references) [449]. Transition metal-assisted oxidation of organic compounds was the subject of a dissertation [450].

IV. Reduction

The search for the perfect asymmetric hydrogenation catalysts continued unabated. Several new chiral ligands were synthesized. Particularly interesting in this respect were S,S-chiraphos (I) and R-prophos (II). Studies with



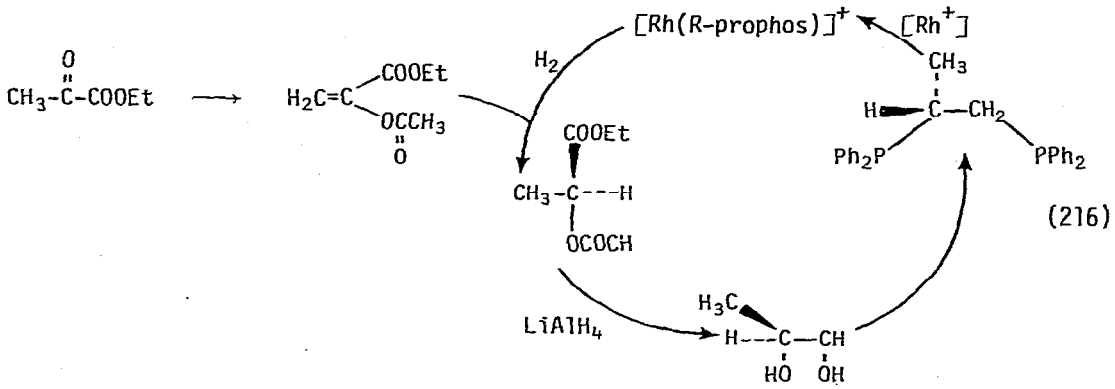
I



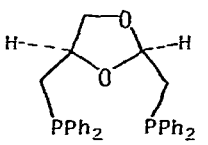
II

these ligands led to the conclusion that discrimination of the prochiral faces of substrates is due to the chiral array of phenyl groups on phosphorous caused by complexation to the metal and being fixed in one conformation with the methyl groups equatorial. Consequently, the phenylphosphine groups are immobile, chiral, and quasi axial and equatorial. Using [Rh(R-prophos)NBD]ClO_4 0.5 CH_2Cl_2 as a catalyst in THF or ethanol, a large number of acrylic acids were reduced

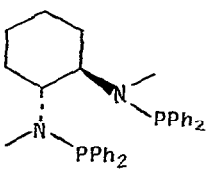
in >90% optical yield to the (S) isomers. What was really unique was R-prophos was used in a cycle to catalytically generate itself (eq. 216) [451]. A



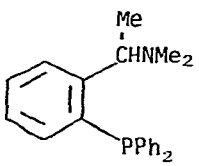
different new chiral ligand, dioxop (III) reacted with cationic rhodium(I) complexes to produce $[Rh(COD)dioxop]^+ClO_4^-$, which in the presence of triethylamine, was an active chiral hydrogenation catalyst for the reduction of α-acetamidoacrylic esters in 78-86% enantiomeric excess (S) [452]. The rhodium catalyst resulting from the reaction of one equivalent of IV with two equivalents of $[(COD)_2RhCl]_2$ produced a catalyst that reduced α-acetamidoacrylic acids under mild conditions



dioxop III

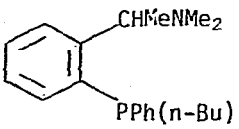


IV



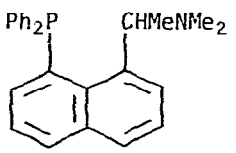
(S)

V



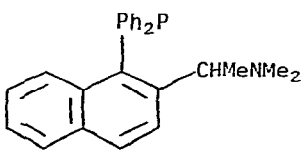
(S,S)

VI



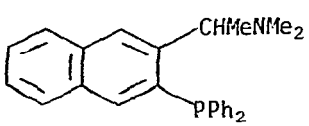
(S)

VII



(R)

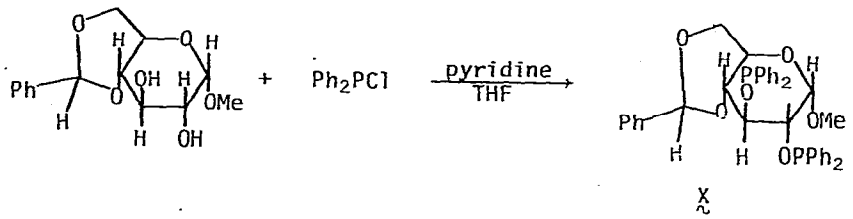
VIII



(R)

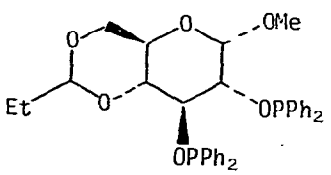
IX

in 97-99% conversion and 73-93% optical yield (S) [453]. The chiral aminophosphines V-IX were used to prepare similar rhodium(I) complexes which catalyzed the reduction of itaconic acid ($H_2C{=}C(COOH)-CH_2COOH$) in up to 40% enantiomeric excess [454]. Optically active methylpropyl (isopropyl) aryl phosphines were prepare and used to make chiral rhodium(I) catalysts for the reduction of α- and β-methylcinnamic acids, α-acetamidoacrylic acids and α-acetamidocinnamic acids. Aryl groups having ortho-methoxy or dimethylamino groups measurably increased the optical yields in the reduction of the α-acetamido acids, but not the cinnamic acids [455]. A number (X-XV) of chiral phosphite ligands were prepared from sugars (eq. 217), and used to produce rhodium(I) catalysts for the reduction of α-acetamidoacrylic and cinnamic acids (up to 80% optical yields) and esters (up to 48% optical yield) [456,457].

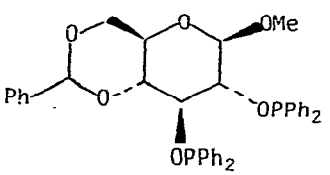


(217)

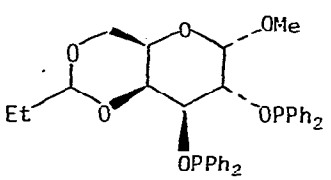
X



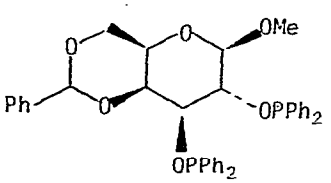
XI



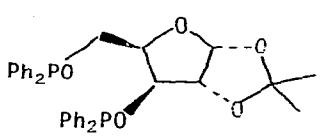
XII



XIII

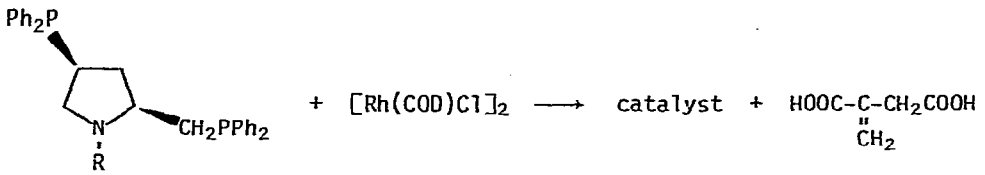


XIV



XV

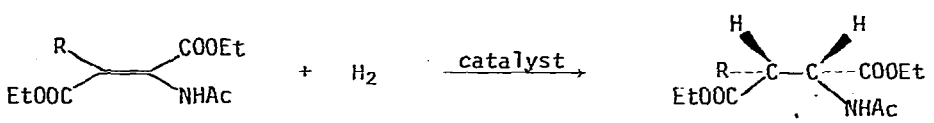
A series of chiral pyrrolidinophosphine ligands has been synthesized and studied in asymmetric hydrogenation. In the reduction of itaconic acid (eq. 218), the optical yield was dependent upon the R group on nitrogen [458,459]. Added triethylamine increased the enantioselectivity to up to 93% enantiomeric excess [460]. The same catalysts were effective in the reduction of α-



(218)

R = t-BuCO 87% optical yield(s)
PhCO 89% " "
HCO 94% " "
t-BuO-C(=O)- 93% " "

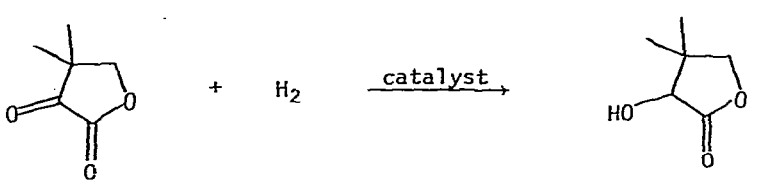
acetamidoacrylic and fumaric esters (eq. 219) [461,462]. The same catalyst system was used to synthesize R-(-)-pantolactone (eq. 220) [463] and (S)- and (R)-salsolidine (45% optical yield) [464]. The mechanism of asymmetric hydro-



(219)

58% optical yield

R = PhCO



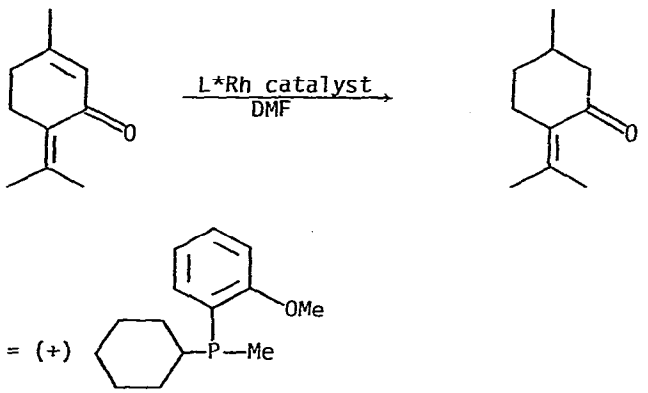
(220)

81% optical yield

R = t-BuOCO

genation by these pyrrolidinophosphine-rhodium(I) catalysts was probed by using nmr and other physical methods to attempt to determine the conformations of the chiral complexes and to relate these to the optical induction observed [465].

Piperitenone was reduced to pulegone in 38% optical purity using a rhodium(I) catalyst containing chiral phosphine ligands (eq. 221) [466]. Ruthenium and

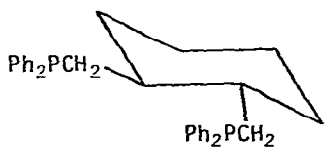


(221)

rhodium hydride complexes containing chiral phosphine or chiral sulfoxide ligands were studied as catalysts for asymmetric hydrogenation of prochiral olefins. Only low (15-25%) optical yields were observed [467]. The mixed hydride complexes of rhodium with triphenylphosphine and d-α-methylbenzylamine were studied as asymmetric hydrogenation catalysts [468]. The mixed platinum-tin DIOP complex [-DIOP]$PtCl_2/SnCl_2$ catalyzed the reduction of α-ethylstyrene in 37% enantiomeric excess. This also was a modest chiral hydroformylation catalyst [469].

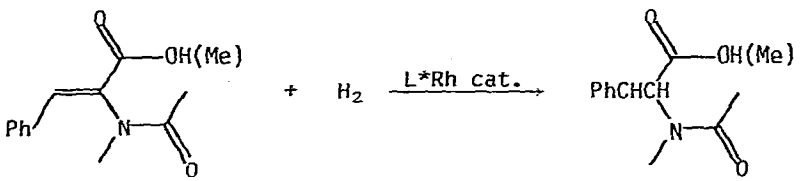
A study of the reduction of the Z and E isomers of α-acetamidocinnamic acid using the chiral rhodium(I) catalyst formed from $[RhCl(C{=}C)_2]_2$ and (+)-DIOP showed that the Z isomer reduced to the S enantiomer in 70% enantiomeric excess in an exclusive (by use of D_2 and nmr) cis reduction, while the E isomer produced the S enantiomer in only 25% enantiomeric excess. These results indicated that the Z isomer reduced faster than the E, and that E to Z isomerization occurred prior to reduction [470]. It was found that the amount of isomerization depended on the solvent, benzene eliminating isomerization and increasing the enantiomeric excess for the E isomer. Rhodium(III) complexes were blamed for the isomerization and the process was thought to proceed through π-allyl complexes [471]. In a different study of the mechanism of asymmetric reduction, it was claimed that the olefin binding step determined the stereochemical course of the reaction and that the addition of hydrogen was of minor importance to optical yield [472]. In studies using HRh[(+)-DIOP]$_2$ as a catalyst, only terminal methylenes were reduced (itaconic, 20% ee; N-acetamidoacrylic, 56% ee; atropic, 37% ee). Maleic acid and other internal or nonactivated olefins were

not reduced. With the bis-DIOP catalyst, enantiomeric excesses were lower than with the mono complex and esters reduced more slowly than the corresponding free acid, suggesting coordination of the free acid was important in this system [473]. The kinetics of enantioselective hydrogenation of α-acetamidocinnamic acid catalyzed by rhodium(I) DIOP catalysts were studied [474]. The reduction of Z(-)-(1R,3R,4S)-menthyl- and bornyl-α-acetamidocinnamates gave 50-78% enantiomeric excess with neutral DIOP rhodium(I) catalysts, while the use of the same type of catalyst having achiral ligands gave only 7-12% enantiomeric excess, indicating that the chiral ester group had little role in the optical induction process [475]. However, using α-acetamidocinnamic esters with bulky ester groups resulted in increased preference for the formation of S enantiomers (from 1% ee for methyl ester to 58% ee for t-butyl ester) when a rhodium(I)-chiral phosphine XVI complex was used. DIOP rhodium(I) complexes did not show

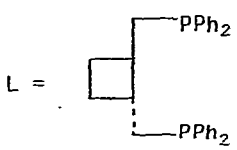


XVI

this effect [476]. A similar catalyst was used to study the reductions in eq. 222 [477].



(222)



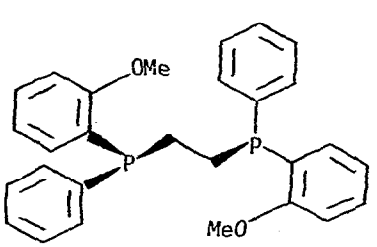
XVII

For ester 73% ee DIOP
43% XVII
20% XVI

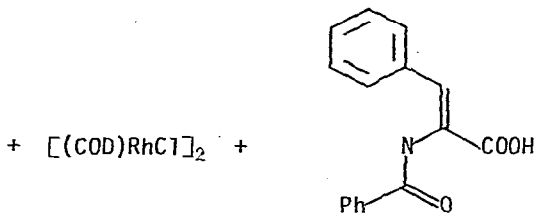
For acid 87% DIOP
68% XVII

Phosphorus 31 nmr studies of rhodium(I) complexes with chiral pyrrolidinophosphine ligands in the presence and absence of substrate indicated that two

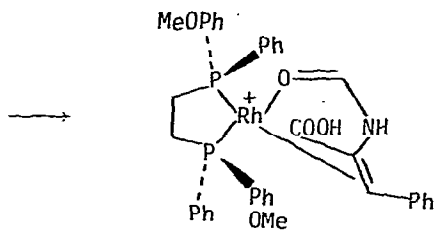
conformations of the complex were present in the absence of substrate, while upon coordination one conformer was preferred and ultimately led to asymmetric induction [478]. Asymmetric reduction reactions using dipamp(XVIII) were studied by nmr spectroscopy and isolation and characterization of intermediates (eq. 223). From the nmr studies, it was claimed that asymmetric induction de-



XVIII

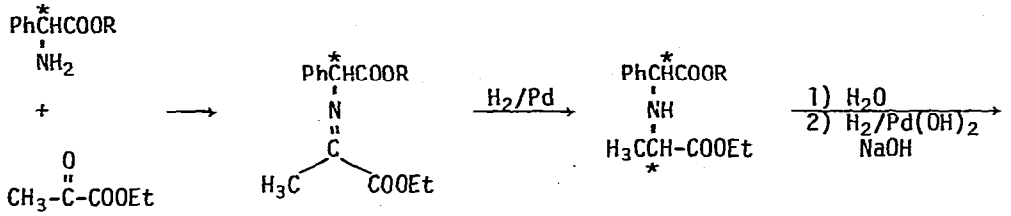


(223)

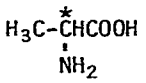


rived from stereoselectivity in the binding process rather than relative rates of hydrogenation of diastereomeric complexes [479]. Hydrogenation of α-ethylstyrene and 2-ethyl-1-hexene with a rhodium(I)-neomenthyldiphenylphosphine catalyst in benzene occurred by the addition of two hydrogen atoms to the alkene in a suprafacial fashion, while in benzene-ethanol the addition was antarafacial [480]. The mechanism of the asymmetric action of chiral heterogeneous hydrogenation catalysts modified by optically active ligands has been studied [481]. In the asymmetric hydrosilation of acetophenone by α-naphthylphenylsilane catalyzed by a rhodium(I)(DIOP) complex, added spin traps resulted in the the detection of esr signals [482]. Heating either (R) or (S) CH_2=CHCH(Me)OH in the presence of rhodium(I) chiral phosphine complexes resulted in intramolecular hydrogen transfer, producing CH_3CH_2CH(Me)OH [483]. Asymmetric transfer hydrogenation of prochiral CH_3CH=C(Me)COOH by α-D-glucofuranose derivatives or p-methoxyphenol in the presence of $RuCl_2(PPh_3)_3$ or ruthenium DIOP complexes led to α-methylbutyric acid in 22.5% enantiomeric excess (maximum) [484].

Chiral aminoacids were prepared by a hydrogenolytic asymmetric transamination involving a catalytic reduction (eq. 224) [485]. Treatment of heterogeneous copper catalysts with (2R,3R)-(+)-tartaric acid produced a Raney copper catalyst capable of asymmetric hydrogenation [486].



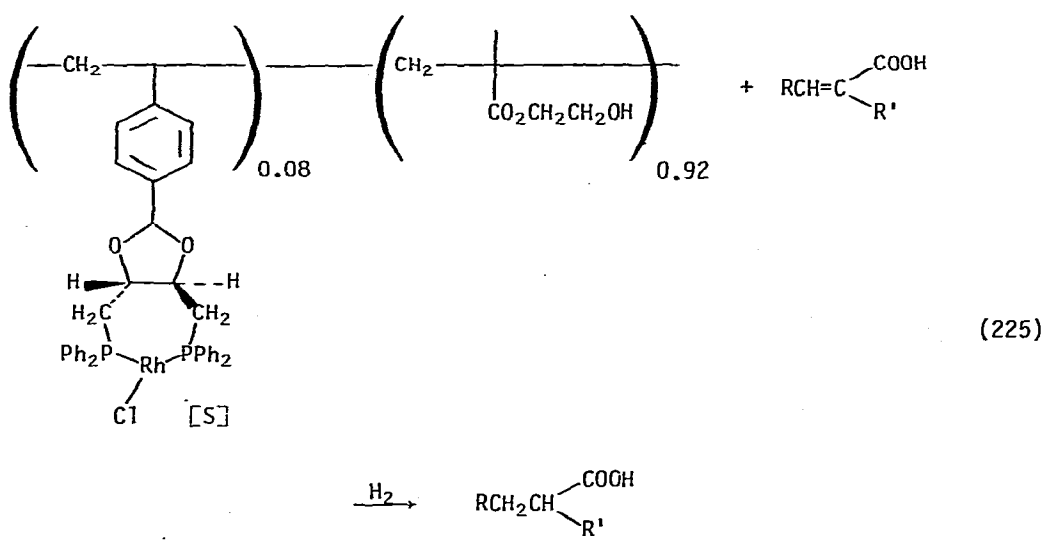
(224)



9-34% optical purity

Asymmetric hydrosilation by means of homogeneous catalysts with chiral ligands has been reviewed (75 references) [487], as has asymmetric hydrogenation reactions over solid catalysts (27 references) [488], and asymmetric hydrogenations (9 references) [489]. The asymmetric reduction of carbenium ions by organosilicon hydrides having chiral ligands was the subject of a dissertation [490].

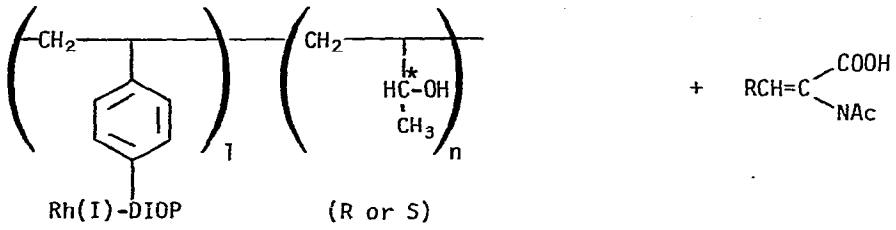
Solid phase supported catalysis has also been a very active field. A hydrophilic copolymer of hydroxyethylmethacrylate and styrene containing the chiral ligand DIOP was prepared, and rhodium complexes supported on this polymer were studied as hydrogenation catalysts (eq. 225). This material gave the same yields



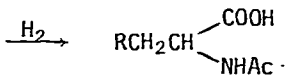
(225)

and optical yields as homogeneous complexes, and was easily removed by filtration and recycled [491]. A similar copolymer of DIOP-containing styrene and methylvinyl ketone in which the pendant keto group had been reduced to either an (R) or (S) secondary alcohol group was prepared and used as a hydrogenation catalyst for α-acetamidoacrylic acids, α-acetamidocinnamic acids and atropic acid in

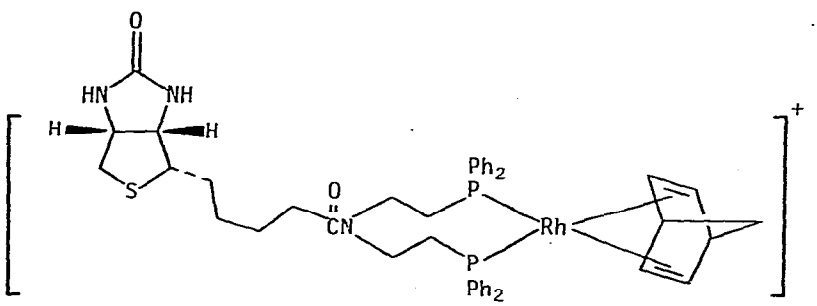
alcohol solvents. The absolute configuration and optical yield obtained with each of these substrates was identical to that observed with homogeneous catalysts. However, in THF solvents the optical yields depended on the absolute configuration of the chiral OH center (eq. 226) [492]. A chelating diphosphine ligand was



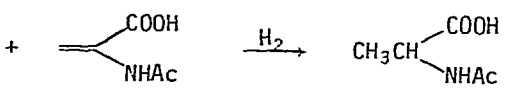
(226)



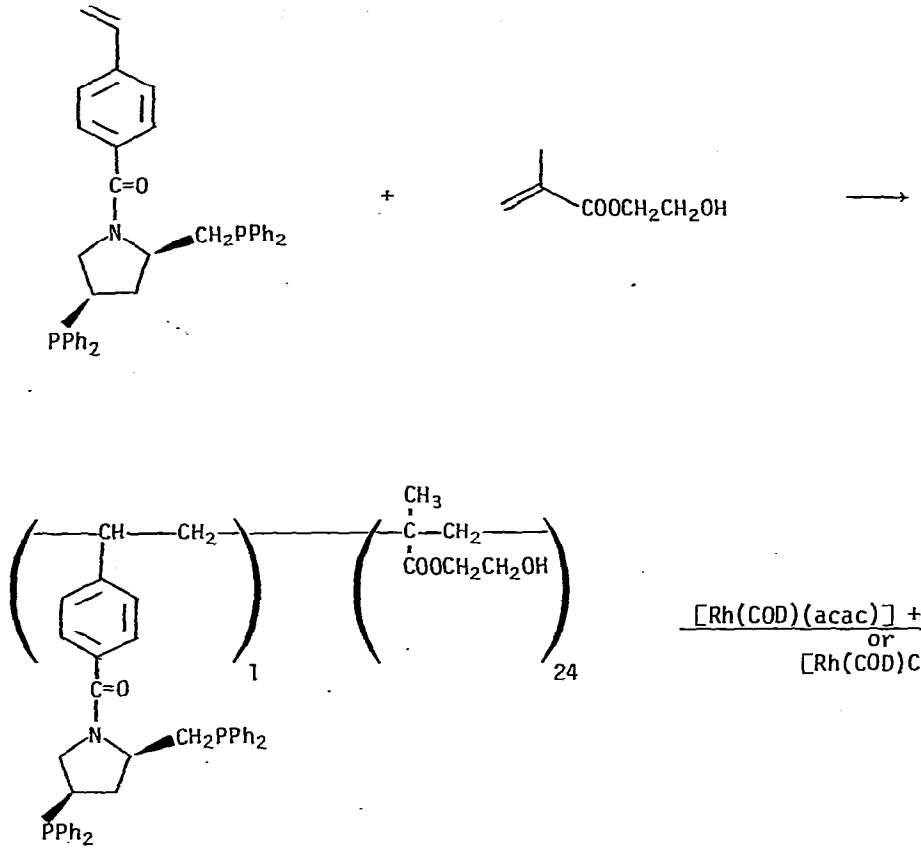
attached to biotin, which was then treated with avidin, a protein which irreversibly binds biotin. The rhodium(I) complex of this solid (protein) supported diphos catalyzed the reduction of α-acetamidoacrylic acids in up to 44% ee (eq. 227). This optical induction was due solely to the chirality of the protein



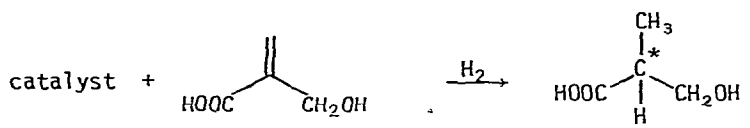
(227)



[493]. Styrene containing a chiral pyrrolidinodiphosphine was copolymerized with hydroxymethylmethacrylate to produce a solid support whose rhodium(I) complexes catalyzed the reduction of itaconic acid in 83% optical yield, and α-acetamidocinnamic acid in 70% optical yield (eq. 228) [494].



(228)



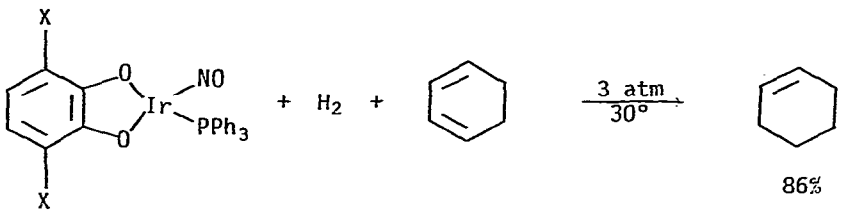
Palladium(II) and rhodium(III) halides supported on copolymers of styrene and maleimide derivatives of (S)-phenylalanine or (R,S)-alanine catalyze the hydrogenation of 1-hexene and α-acetamidocinnamic acids, after activation with hydrogen or sodium borohydride [495]. Polystyrene supported ortho aminobenzoic acid complexed with palladium(II) chloride. This material was an excellent catalyst for the reduction of alkenes to alkanes, 1,3-dienes to monoenes, alkynes to cis alkenes, and benzene to cyclohexane. Conjugated enones were reduced to complex mixtures of products [496]. Palladium(II) chloride supported on phosphinated polystyrene was a good catalyst for the reduction of unsaturated species. The following order of reactivity was observed: conjugated dienes > nonconjugated dienes > terminal olefins > internal olefins. Alkynes were reduced as well [497]. Polymer-supported rhodium catalysts were used to reduce propene [498]. Para-

substituted triphenylphosphine ligands were synthesized and studied as models for polymer bound phosphines as ligands for rhodium based hydrogenation catalysts. With bulky phosphines (p-dodecyl) the maximum rate of reduction was observed for P/Rh of two [499]. α-Pinene, myrtenal and β-ionone were hydrogenated over Pd/C, Pd/Amberlyst 27, Pd/Amberlyst 15, Pd/basic Sephadex QAE 50, and Pd/alginic acid [500]. The selectivity for the reduction of primary and secondary olefins catalyzed by phosphinated polystyrene supported rhodium(I) complexes was dependent on the mode of preparation and the presence of nonpolymeric ligands after preparation [501]. Polystyrene coated silica gel was phosphinated and used to support $[Rh(CO)_2Cl]_2$ to produce a catalyst for hydrogenation, hydroformylation and isomerization of olefins [502]. 1,2-Dicarbadodecaborane (12) was attached to polystyrene and $RhCl(PPh_3)_3$ was introduced by exchange. The resulting rhodium complex, in which the rhodium was bound in a π-fashion, catalyzed the reduction of alkenes [503]. Palladium complexes were supported on ion exchange resins such as vinylpyridine anion exchangers, phosphate type cation exchangers, and ampholites. The resulting complexes catalyzed the hydrogenation and isomerization of allyl-benzene more effectively than Pd black. This supported catalyst also reduced allyl alcohol, cyclopentadiene and nitrobenzene [504]. The cluster compounds $Ir_4(CO)_{11}(PPh_3)$ and $Ir_4(CO)_{10}(PPh_3)_2$ were attached to polymer beads and membranes, and the resulting catalysts were examined by infrared during hydrogenation of ethylene at 1 atm. At 303°K, the infrared spectrum of the working catalyst was distinct from the resting catalyst, while at 373°K the intensity of the carbonyl band decreased and metal aggregation resulted [505]. Attaching $Rh_6(CO)_{16}$ to a polystyrene-divinylbenzene-phosphine membrane produced a catalyst which was studied in a similar fashion. The catalyst reduced olefins, but exposure to oxygen led to formation of rhodium metal which aggregated to give rhodium crystallites 20-25 Å in diameter. This occurred because the phosphines were oxidized to phosphine oxides, allowing rhodium to migrate [506]. EXAFS was used to examine $Rh(Br)(PPh_3)_3$ supported on polystyrene polymers. With 2% divinylbenzene-crosslinked polystyrene the complexes were dimeric, indicating that nonadjacent polymer bound metal sites could react with each other. With 20% crosslinked resin, all the rhodium was monomeric [507]. Rhodium trichloride and poly(vinylpyrrolidone) with methanolic sodium hydroxide produced a colloidal dispersion of rhodium particles 8.8 Å in diameter. This dispersion was an active catalyst for the reduction of internal olefins at 30° and 1 atm of hydrogen pressure [508].

Silica gel was treated with $(EtO)_3SiCH_2CH_2PR_2$ followed by reaction with $Co_2(CO)_8$. The resulting material catalyzed the reduction of polyenes to monoenes under mild conditions [509]. Rhodium on alumina was a catalyst for the reduction of conjugated dienic esters [510]. A very active hydrogenation catalyst was prepared by reacting bis-π-allylpalladium with vitreous materials having surface OH groups, followed by treatment with lithium aluminum hydride [511].

The hydrogenation of 1,2-cyclononadiene over carbon or alumina supported palladium, rhodium and iridium led to trans-cyclononene. The intermediacy of π-allyl complexes was demonstrated [512]. The catalytic hydrogenation of cyclohexene over supported palladium catalysts was studied [513]. A study of methylcyclopropane hydrogenation over supported platinum catalysts was the topic of a dissertation [514].

The water soluble phosphine $^{-}O_3S$-C$_6$H$_4$-PPh_2 (dpm) was synthesized and was used to prepare the rhodium(I) and palladium(II) complexes $RhCldpm_3 \cdot 4H_2O$, $RhCl(COD)dpm \cdot H_2O$, $[Rh(COD)dpm_2]^{+}PF_6^{-}$, $[Rhdpm(COD)]_2$, $RhH(CO)dpm_3 \cdot 4H_2O$, $RhHCldpm_3$, $RuHCldpm_3 \cdot 2H_2O$, $Ptdpm_4 \cdot 4H_2O$, $PtHdpm_3Cl$, $PdCl_2dpm_2 \cdot 3H_2O$ and $Pd(CN)_2dpm_2$, and their activity as reduction and hydroformylation catalysts in two phase systems was investigated [515]. Nitrosylcatecholatoiridium complexes were used as hydrogenation catalysts for 1,3-dienes under mild conditions (eq. 229). Both monoenes and 1,4-dienes reduced, but much more slowly [516].



(229)

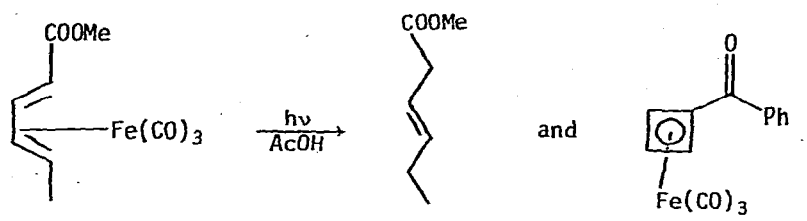
The complex [IrCl(COD)P(cyclohexyl)$_3$] was a highly active and selective catalyst for the reduction of cyclohexene [517]. The catalytic activity of $IrCl(CO)[P(C_6H_{11})_3]_2$, $IrCl(PPh_3)_3$, $IrH(CO)(PPh_3)_3$, and $Ir(H)_3(PPh_3)_3$ in the reduction of seventeen unsaturated substrates including olefins, allyl alcohols and conjugated enones was studied at 95-150°, 10-15 bars pressure and in the absence of solvent [518]. Tritium labelled prostaglandins were prepared by the $RhCl(PPh_3)_3$ catalyzed tritiation of the corresponding alkynes [519]. Kinetic studies of the hydrogenation of cyclohexene catalyzed by $RhCl(PPh_3)_3$ indicated that $Rh(PPh_3)_2H_2Cl$ was the catalytically active species [520]. The influence of bridging groups in homogeneous hydrogenation with p-dimethylamino substituted phenylphosphine rhodium complexes was the topic of a dissertation[521].

The ruthenium catalysts $(p\text{-tol}\ PPh_2)_3RuCl_2$, $(Ph_2AsCH_2CH_2AsPh_2)_2RuCl_2$, $(p\text{-tol}\ PPh_2)_2Ru(CO)_2Cl_2$, $(Ph_3Sb)_3Ru(CO)Cl_2$ and $(Ph_2AsEt)_3Ru(CO)Cl_2$ were studied as hydrogenation catalysts. The tris(p-tolyl)diphenylphosphine complex was most efficient for hydrogenation of terminal olefins. Ethanol increased the rate of reduction, while pyridine or excess ligand decreased the rate [522]. Tricarbonyl chromium complexes of phenanthrene and naphthalene catalyzed the stereospecific and regioselective reduction of 1,3-dienes in a 1,4 fashion to produce Z monoenes. Norbornadienes were reduced less selectively, giving mixtures of norbornene (20%)

and nortricyclane (80%) [523]. Disubstituted allylmanganese phosphine complexes of the type π-$C_3H_5Mn(CO)_2(PR_3)_2$ were effective reduction catalysts for alkenes. Trisubstituted complexes π-$C_3H_5Mn(CO)(PR_3)_3$ were more reactive but underwent competitive loss of the allyl group and subsequent catalyst destruction [524]. Pentamethylcyclopentadienyl rhodium and iridium halide dimers of the type $[CpMX_2]_2$, $[CpM]_2HX_3$ and $[CpMHX]_2$, were active hydrogenation catalysts for the reduction of dienes, alkynes and functionalized olefins in the presence of triethylamine in isopropanol or methylene chloride solvent [525]. Alkynes were reduced to cis alkenes by magnesium hydride-copper(I) iodide or magnesium hydride-copper(I)-tert-butoxide [526]. The hydrogenation of $AcOCMe_2C{\equiv}CCMe_2OAc$ over palladium gave exclusively the cis alkene product [527]. Alkenes and alkynes were reduced quantitatively by equimolar mixtures of lithium aluminum hydride and $TiCl_3$, VCl_3, $CrCl_3$, $FeCl_2$, $FeCl_3$, $CoCl_2$ and $NiCl_2$. However, only $CoCl_2$, $NiCl_2$ and $TiCl_3$ were effective when used in catalytic amounts. Phenyl acetylene was reduced to styrene, and 1-octyne to octane with $LiAlH_4$-$FeCl_2$, and to ethylbenzene and 1-octene by $LiAlH_4$-$NiCl_2$[528].

The complex $RuHCl(\eta^6\text{-}C_6H_6)PPh_3$ catalyzed the reduction of benzene to cyclohexane at 50 atm and 50°C. This complex also catalyzed the transfer hydrogenation from secondary alcohols of olefins to alkanes, dienes to monoenes and cyclooctatetraene to cyclooctadiene [529]. Nickel vapor reacted with toluene and perfluorobromobenzene to produce a bis-perfluorophenylnickel-toluene complex in which the toluene was very labile. This complex catalyzed the reduction of toluene to methylcyclohexane at 25° and 100 atm pressure. However, only ten turns of the catalyst were observed before activity was lost [530]. The full details of the reduction of aromatics using π-allylcobalt-tris-trimethylphosphite as a catalyst has appeared. The reduction proceded at 25° and 1-3 atmospheres pressure, gave predominantly cis reduction and tolerated alkyl, alkoxy, carbethoxy, keto and amino groups. Nitro, cyano and fluoro groups, and steric crowding inhibited the reduction. The catalyst had a short lifetime, acidic protons destroyed the complex, terminal alkenes reduced faster than arenes, and polyenes were isomerized [531]. Alkenes were hydrosilated by H_2SiCl_2 using $RhCl(PPh_3)_2$ as a catalyst [532], and by $HSi(OEt)Cl_2$ with $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ catalysts [533].

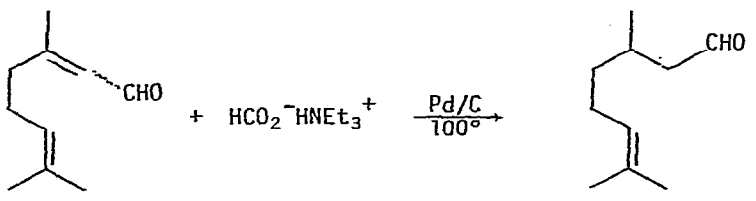
The reduction of conjugated carbonyl compounds including esters, ketones, aldehydes, amides, lactones and nitriles by $NaHFe_2(CO)_8$ was a very efficient process. The complex was easily prepared under mild conditions, and reduced these substrates under mild conditions. The mechanism was shown to involve intact binuclear $NaHFe_2(CO)_8$ rather than monomeric complexes [534]. Irradiation of butadiene iron tricarbonyl complexes in acetic acid led to reduction of one of the alkene groups (eq. 230) [535]. The conjugated olefin of conjugated carbonyl compounds was cleanly reduced by ammonium formate in the presence of Pd/C (eq. 231). Nonconjugated double bonds were inert, while



98%

85%

(230)



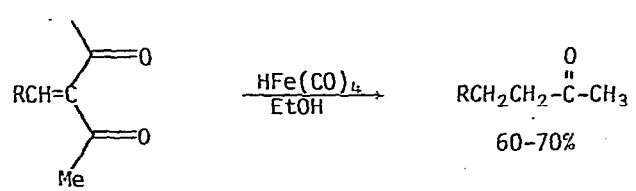
91%

and

69%

(231)

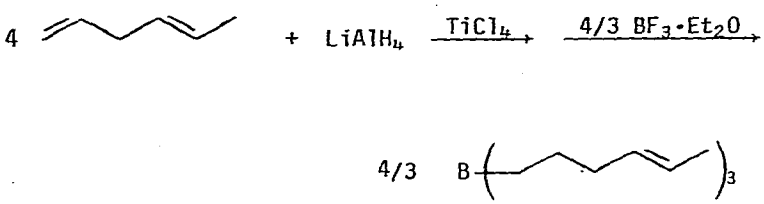
alkynes were reduced to cis alkenes [536]. Knoevenagel condensates of 2,4-pentanedione with aldehydes were reduced and deacylated by hydridotetracarbonyl ferrate (eq. 232) [537]. Similar condensates of keto esters were reduced but not deacylated by this reagent. Long chain conjugated dienic esters were



60-70%

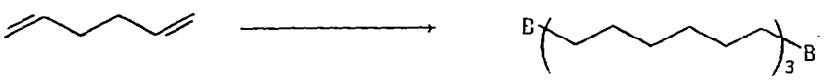
(232)

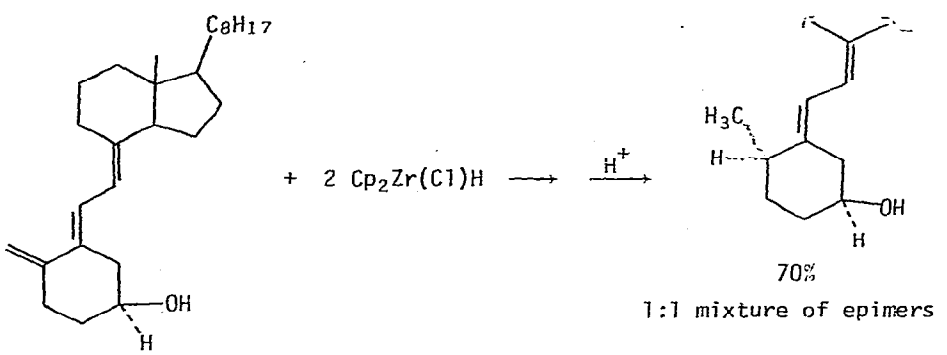
reduced to mixtures of monoenes by treatment with hydrogen and $Co_2(CO)_8$. The double bond was distributed over the entire long alkyl chain [538]. Butadiene was reduced to cis-2-butene by treatment with cobalt(II) chloride, zinc powder and 2,2-bipyridyl in the presence of hydrogen [539]. Dienes were converted to mono- or bis-boranes by reaction with lithium aluminum hydride, titanium(IV) chloride and BF_3 etherate (eq. 233) [540]. The triene in eq. 234 was reduced



(233)

and





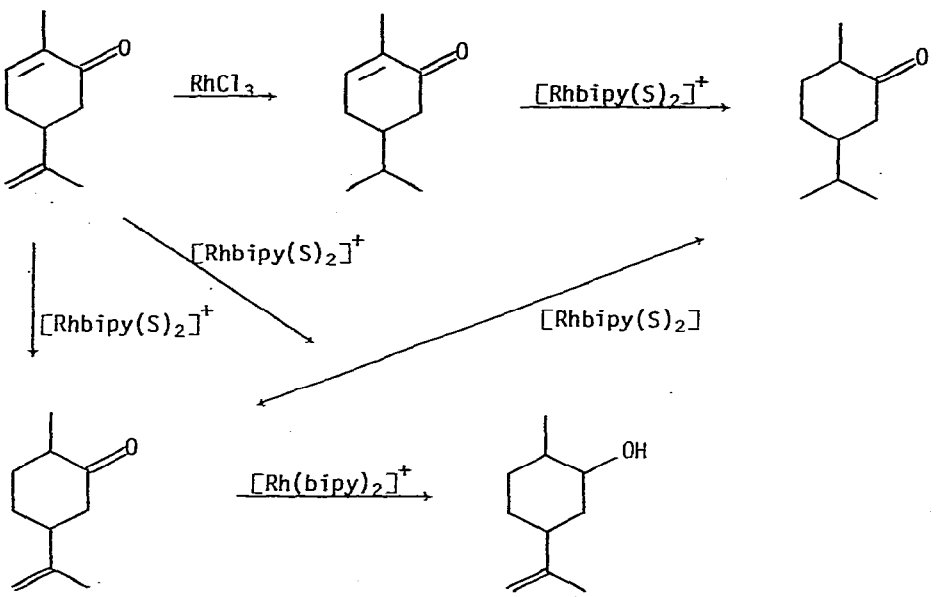
(234)

by $Cp_2Zr(Cl)H$ at the terminal alkene in excellent yield. This process was claimed to be better than that using 9 BBN [541]. Allene was reduced to propene by hydrogen in the presence of a π-allylpalladium chloride complex catalyst [542]. 1,3-Butadiene was hydrogenated to primarily 1-butene over a number of rhenium and sulfur-poisoned rhenium catalysts [543]. Conjugated dienes were reduced over Pt/Al_2O_3 catalysts. Cyclopentadiene was reduced with low selectivity because of the formation of an adsorbed π-allyl intermediate [544].

Vinyl esters, nitriles and acetates underwent hydrosilation to place silicon α to the functional group in the presence of a nickel acetylacetonate catalyst [545]. Isoprene was catalytically hydrosilated in a 1,4 fashion exclusively by

trichloro- or dichloromethylsilane and palladium(II) catalysts, while trialkylsilanes added 30:70 1,4 to 1,2 in the presence of $RhCl(PPh_3)_3$. Myrcene and ocimene reacted in a similar fashion [546]. Chloroplatinic acid catalyzed hydrosilation of isoprene produced both 1,2 and 1,4 adducts depending on the particular silane used [547]. In contrast both $NiCl_2(PPh_3)_2$ and $PdCl_2(PhCN)_2$ catalyzed the hydrosilation of isoprene and 2,3-dimethylbutadiene by $HSiCl_3$, $HSi(OEt)_3$ and $HSiEt_3$ in a 1,4 fashion [548].

Treatment of $[RhCl_2(bipy)_2]^+Cl^-$ with hydrogen produced $[Rh(bipy)_2]^+$, a compound very efficient for catalytic reductions of ketones to alcohols in the presence of olefins, although conjugated ketones underwent reduction of the olefin group first. The chemistry of this and related compounds is presented in eq. 235 [549]. Aldehydes were reduced to alcohols in good yield with high

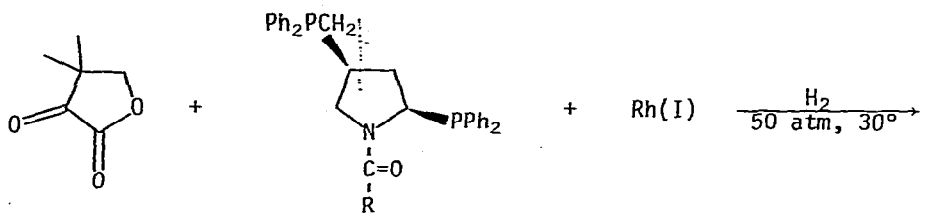


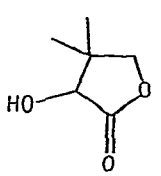
(235)

selectivity and high catalyst turnover under 15 atm of hydrogen at 160°-200° and $RuCl_2(CO)_2(PPh_3)_2$ as catalyst [550]. The kinetics of the reduction of cyclohexanone to cyclohexanol at 100° and 100 atmospheres of hydrogen using $H_4Ru_4(CO)_{12}$ were studied. It was shown that the ruthenium cluster was recovered intact at the end of the reaction [551]. Crotonaldehyde and cinnamaldehyde were reduced to the corresponding allyl alcohols by a catalytic transfer hydrogenation, using $HIrCl_2(Me_2SO)_3$ in aqueous isopropanol as catalyst [552]. Pyrolyzed rhodium carbonyl clusters on TiO_2, ZrO_2 or La_2O_3 catalyzed the reduction of carbon monoxide to methanol and ethanol at 1 atmosphere and 200°C [553]. A wide variety of conjugated ketones, including prostaglandins, were reduced to allyl alcohols by sodium borohydride and $CeCl_3 \cdot nH_2O$ or $SmCl_3 \cdot nH_2O$. The reaction was fast and efficient, tolerated small amounts of water, and almost always resulted in 1,2

addition even in cases where 9 BBN, cyanoborohydride and DIBAH failed [554]. Treatment of CpZr(H)Cl with $BH_3 \cdot Me_2S$ produced $Cp_2Zr(Cl)BH_4$, which was a specific reducing agent for aldehydes and ketones. It was air stable and soluble in nonpolar solvents, in contrast to sodium borohydride. Conjugated ketones gave both 1,2 and 1,4 reduction products [555].

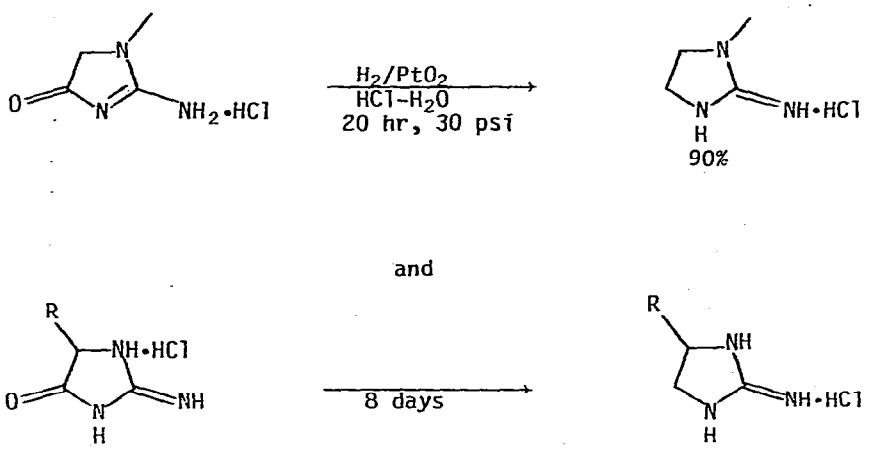
Ketones and aldehydes were reduced to alcohols by mixtures of NaH-t-amyl-alkoxide-$Ni(OAc)_2$ [556]. Acetophenone was reduced to the corresponding alcohol by hydrogen and rhodium(I) cationic complex catalysts coordinated to DIOP. With DIOP alone as ligand, the reduction proceded in 18-40% yield with up to 54% optical yield. With DIOP plus added achiral phosphine the yields increased to 70% but the optical yields dropped. With (S)(-)-$PhCH_2P(Me)Ph$ as ligand rather than DIOP the reaction went in 48-92% yield with 3-37% optical yield. Maximum optical yield was obtained with a phosphine to rhodium ratio of 3 [557]. Pantoyl lactone was produced in 100% yield and 86.7% enantiomeric excess by reduction of the α-ketolactone with hydrogen and a rhodium(I) BPPM catalyst (eq. 236) [558].





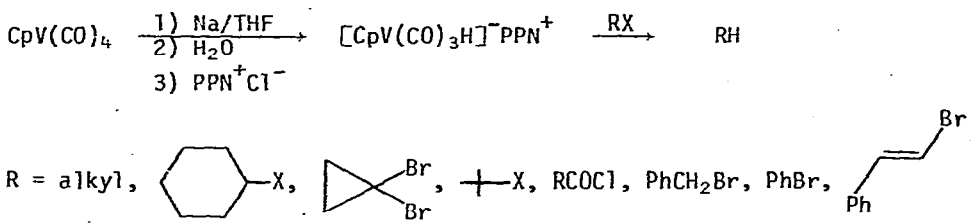
(236)

Unsymmetrical ketones were reduced to chiral alcohols using chiral amino phosphine rhodium(I) complexes as catalyst [559]. Raney nickel catalysts modified with chiral amino acids such as (S)-alanine and (S)-valine, as well as (R,R)-tartaric acid and (S)-lactic acid, catalyzed the asymmetric reduction of the keto group of acetoacetic ester [560]. The reductions of 3,4-, 3,5-2,5-dimethylcyclohexanone by isopropanol using $RuCl_2(PPh_3)_3$ as catalyst proceded more slowly when one of the methyl groups was axial than when all were equatorial. The thermodynamically less stable isomer was the major project in these reductions [561]. Finally, heterocyclic amides were reduced to the corresponding hydrocarbons in HCl solution using PtO_2 as the catalyst (eq. 237) [562].



(237)

A variety of new reagents for the reduction of organic halides has been developed. A number of copper hydrides of general constitution Li_nCuH_{n+1} (n = 1-5) were prepared by treatment of the corresponding methyl complexes with lithium aluminum hydride. The complex Li_4CuH_5 was most reactive for the reduction of primary alkyl halides to the corresponding hydrocarbon. Secondary and aryl halides were unreactive. In contrast, this reagent reduced conjugated enones almost exclusively 1,2, while Li_2CuH_3 reduced the same substrates almost exclusively 1,4 [563]. Bis(triphenylphosphine)copper(I) tetrahydroborate reduced acid chlorides to aldehydes in excellent yield. This material was an air stable crystalline solid soluble in chloroform, acetone and benzene. It tolerated ester, ketone, cyano, epoxy, imino, alkene and alkyne functional groups. One mole of copper per mole of substrate was required and free triphenylphosphine was required [564,565]. Aryl halides were reduced to arenes by sodium formate in the presence of a palladium(0) phosphine catalyst. Nitro, carboxyl, ester, aldehyde, ether and keto groups were tolerated [566]. A similar reduction was affected by sodium methoxide in the presence of $Pd(PPh_3)_4$. With this system aryl bromides were most reactive. Aryl iodides coupled and aryl chlorides were inert [567]. A wide range of organic halides were reduced to hydrocarbons by $[CpV(CO)_3H]^-$ via a radical chain mechanism (eq. 238). Ketones and esters were unreactive, and vic-dihalides underwent elimination [568,569].



(238)

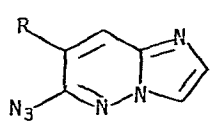
Mixtures of sodium hydride and sodium alkoxides when treated with halide salts of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Mo, Pd and W produced non-characterized material which reduced 1-bromonaphthalene to naphthalene, and also coupled aromatic halides [570]. Organic halides such as 1-chloro- and 1-bromodecane, bromobenzene, cyclohexyl chloride and 3-bromooctane were reduced to the hydrocarbon by lithium aluminum hydride in the presence of $FeCl_2$, $CoCl_2$, $NiCl_2$ or $TiCl_3$[571]. Treatment of bis-1,5-cyclohexadiene-chlororhodium with tertiary phosphines and tertiary amines produced a catalyst that reduced halides to hydrocarbons. Iodides were most reactive. Benzyl halides and α-haloesters were very reactive, while bromobenzene and alkyl bromides were less reactive [572]. Support of $KHFe(CO)_4$ on ammonium ion exchange resins produced a system which reduced α-haloketones and benzyl halides to hydrocarbons, but converted alkyl halides to aldehydes by a carbonylation reaction [573]. Titanium(III) chloride in the presence of HCl converted α,α-dibromoketones into α-chloroketones in excellent yield [574].

Palladium chloride supported on polystyrene attached o-aminobenzoic acid catalyzed the reduction of nitrobenzene to aniline (80°, 1000 psi) and benzonitrile to reduced dimers [575]. Oximes, sulfoxides, haloketones, vinyl dicarboxylic acids and nitroaromatics were reduced by the in situ electrochemical generation of titanium(III) by oxidation of titanium metal [576]. Titanium(III) was used to reduce nitroarginyl peptides to arginyl peptides. This technique was used in the synthesis of arginine vasotocin [577].

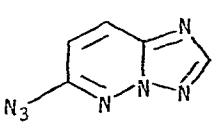
Palladium particles were entrapped in a poly(2-hydroxyethyl)methacrylate, pulverized and used to catalyze the reduction of nitrobenzene to aniline [578]. Azides were reduced to amines by treatment with titanium(III) chloride in ethanol-water (eq. 239) [579]. Aryl-vinylsulfoxides were reduced to the corresponding aryl vinylsulfides by treatment with ethylmagnesium bromide-10% copper(I) chloride and zinc in ether-dichloromethane [581]. Epoxides were catalytically

$$RN_3 \xrightarrow{TiCl_3/EtOH/H_2O} RNH_2 \qquad (239)$$

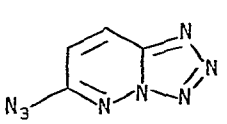
RN_3 =



83%



30%



54%

$ArSO_2N_3$
61-78%

deoxygenated to olefins by $CpMoCl_2$ or $CpWCl_2$ and sodium amalgam [582].

References p. 430

Substituted benzyl alcohols were hydrogenolyzed to substituted toluenes by hydrogen transfer from cyclohexene. The catalyst was aluminum chloride/palladium on carbon. The same system reduced substituted styrenes. Pure alkyl substituted alcohols or olefins were unreactive [583]. The reaction of $RhCl(PPh_3)_3$ and $Rh(H)(PPh_3)_4$ with amines, alcohols, hydroaromatic compounds or dioxane produced a large amount of benzene from hydrogenolysis of the triphenylphosphine groups. The reaction proceded by a rhodium(I) hydrogen transfer reaction [584]. Unsaturated alcohols containing a double or a triple bond were hydrogenolyzed to alkenes by pentacyanocobaltate(II). Terminal alkynes were hydrocyanated and reduced to secondary nitriles or olefins [585]. Aromatic ethers and ketals were converted to the corresponding hydrocarbon by aluminum chloride/palladium on carbon [586]. Enol phosphates, produced from ketones, were reduced to olefins by treatment with activated titanium produced by the reduction of titanium(III) chloride with potassium [587]. Cyclopropane was hydrogenolyzed on supported transition metal catalysts [588,589].

The water gas shift reaction (eq. 240) attracted a great deal of attention this year. When $Rh_6(CO)_{16}$ was heated with carbon monoxide, D_2O and triethylamine,

$$CO + H_2O \underset{\longleftarrow}{\xrightarrow{\text{catalyst}}} CO_2 + H_2 \qquad (240)$$

a catalyst which activated C-H bonds to undergo hydrogen-deuterium exchange reactions resulted. The major product was $Et_3N\text{-}d_4$ [590]. In weakly coordinated solvents such as THF or acetone, platinum(0) complexes of the type PtL_3 catalyzed the water gas shift reaction at 100°. The triisopropylphosphite catalyst was the most reactive complex [591]. The order of reactivity of complex catalysts for the water gas shift reaction in ethylene glycol monoethylether was $H_2FeRu_3(CO)_{13} > Ir_4(CO)_{12} > H_2Ru_4(CO)_{13} \approx H_4Ru_4(CO)_{12} \approx Ru_3(CO)_{12} \approx Fe(CO)_5 > Rh_6(CO)_{16} > Ru_6(CO)_{17} >> H_3Re_3(CO)_{12} >> Re_2(CO)_{10}$ [592]. A variety of metal carbonyls including $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ and $Ru_3(CO)_{12}$ in the presence of sodium or potassium hydroxide were active catalysts in the water gas shift reaction. At 170° 400 moles of hydrogen per mole of catalyst per day could be produced [593]. Aromatic nitro compounds were reduced to amines by a mixture of carbon monoxide and water in basic solutions of iron pentacarbonyl [594]. Reductions of organic compounds by use of carbon monoxide and water rather than hydrogen has been reviewed (14 references) [595].

Several approaches to the reduction of carbon monoxide have been developed. Carbon monoxide reacted with $CpZrCl(H)$ to produce a formyl complex which reacted with HCl to give $CpZrCl_2$ and methanol (eq. 241). With carbon dioxide a zirconium

$$2\ Cp_2Zr(H)Cl + CO \rightarrow (Cp_2ZrCl)_2CH_2O \xrightarrow{HCl/THF} CpZrCl_2 + MeOH \qquad (241)$$

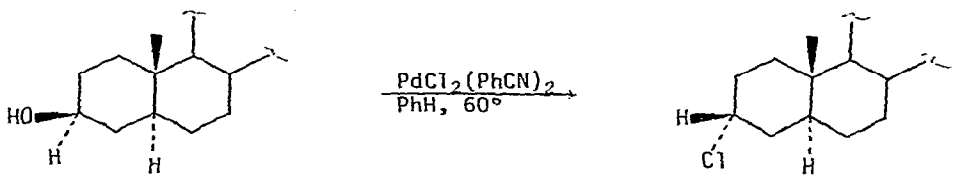
methoxide complex was formed [596]. Reduction of $Cp_2NbH(CO)$ with hydrogen pro-

duced methane in which the carbon was demonstrated to have come from the carbon monoxide [597]. Bis(pentamethylcyclopentadienyl)dihydrozirconium(IV) reacted with carbon monoxide to produce either "Cp_2"$Zr(OCH_3)H$ or ("Cp_2"$ZrH)_2OCH{=}CHO$ depending on conditions. In both of these complexes, carbon monoxide had been reduced [598]. Dicobalt octacarbonyl catalyzed the reaction of hydrogen with carbon monoxide at 240° and 300 atmospheres pressure to produce methanol, ethanol and methyl formate [599]. Finally, the Fischer-Tropsch reaction using ruthenium on alumina as a catalyst has been studied [600].

V. Functional Group Preparation

A. Halides

Aryl bromides were converted to aryl iodides by treatment with potassium iodide and either nickel bromide-zinc or nickel bromide-tri-n-butylphosphine [601]. The same reaction conditions converted vinyl bromides to vinyl iodides with retention of configuration [602]. In both cases chlorides were much less reactive. Steroidal alcohols were converted to the corresponding chlorides by treatment with palladium(II) chloride in benzene at 60° (eq. 241) [603]. Olefins were converted to vis-dichlorides by treatment with $(Bu_4N)_4Mo_8O_{26}$ and acetyl chloride or boron trichloride. The process was a clean cis addition, cis-3-hexene producing meso-3,4-dichlorohexane, and the trans hexene producing the d,l dihalide. Cyclohexene and terminal olefins underwent a similar reaction [604].

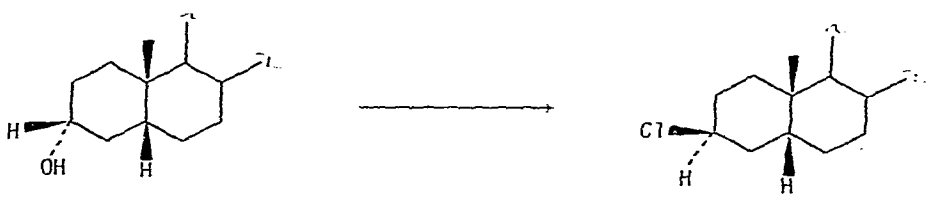


80%

cholestanol
epicholestanol

and

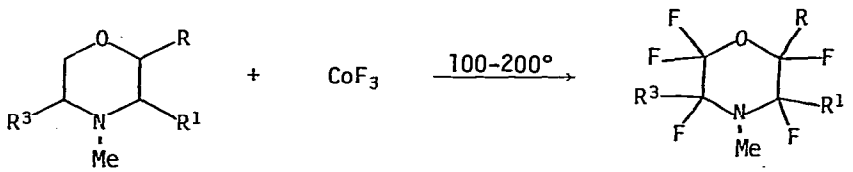
(241)



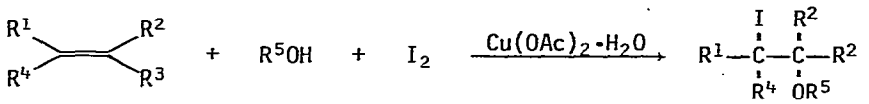
85%

coprostanol
epicoprostanol

Aryl amines were converted to aryl halides by treatment with t-BuSNO or t-$BuSNO_2$ and copper(II) halide in acetonitrile at 0-25°[605]. Substituted toluenes were converted to the corresponding benzyl chlorides by treatment with thionyl chloride in the presence of palladium(0) complexes $Pd(PPh_3)_4$[606]. Morpholines were fluorinated by treatment with cobalt(III) fluoride at 100-200° (eq. 242) [607]. Olefins were converted to vicinal alkoxyiodoalkanes by reaction with iodine and alcohols in the presence of copper(II) acetate (eq. 243) [608].



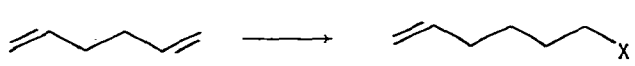
(242)



24-99%

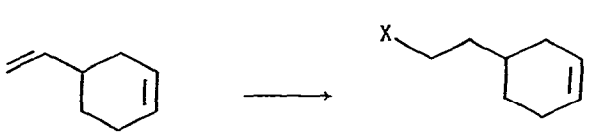
(243)

Terminal alkenes were converted to terminal alkyl halides by the titanium(IV) chloride catalyzed addition of lithium aluminum hydride to the alkene, followed by cleavage of the alane by copper(II) halide. Alkadienes were converted to olefinic halides (eq. 244) [609]. Methylene chloride added to terminal olefins in the presence of $NiCl_2(PPh_3)_2$. Nickel(0) catalysts were unreactive in this



70%

(244)



73%

system (eq. 245) [610]. Carbon tetrachloride added in a similar fashion in the presence of an $RuH_3(SiMe_2Ph)(PPh_3)_3$ catalyst (eq. 246) [611,612]. Conjugated

$$RCH{=}CH_2 + CH_2Cl_2 \xrightarrow[20\ hr,\ 150°]{L_2NiCl} \underset{\underset{Cl}{|}}{RCH}\text{-}CH_2CH_2Cl \qquad (245)$$

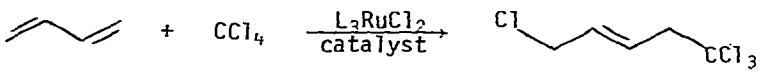
up to 60% yield

$$n\text{-}C_6H_{13}CH{=}CH_2 + CCl_4 \xrightarrow{RuH_3(SiMe_2Ph)(PPh_3)_3} n\text{-}C_6H_{13}\underset{\underset{Cl}{|}}{CH}\text{-}CH_2\text{-}CCl_3 \qquad (246)$$

85%

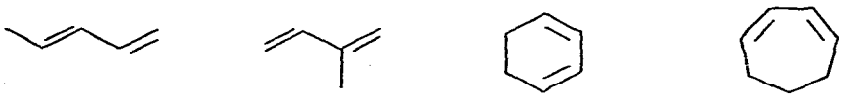
(4,250 catalyst turnovers)

dienes underwent clean 1,4 addition of carbon tetrachloride under $RuCl_2(PPh_3)_3$ catalysis (eq. 247) [613]. Finally, acetylene was converted to trans-1-chloro-1,3-butadiene by reaction with mercury(II) chloride, palladium(II) chloride and iron(III) chloride in aqueous hydrochloric acid [614].



(247)

86%



82% 85% 81% 83%

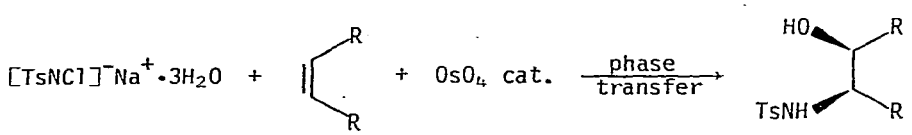
B. Amides, Nitriles

Carbon dioxide reacted with amines and copper(I)-t-butoxide to produce a complex which reacted with methyl iodide to produce carbamates in excellent yield (eq. 248) [615].

$$t\text{-}BuOCu + R_2NH + CO_2 \longrightarrow [R_2NCO_2Cu] \xrightarrow{MeI} R_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}OMe \qquad (248)$$

C. Amines, Alcohols

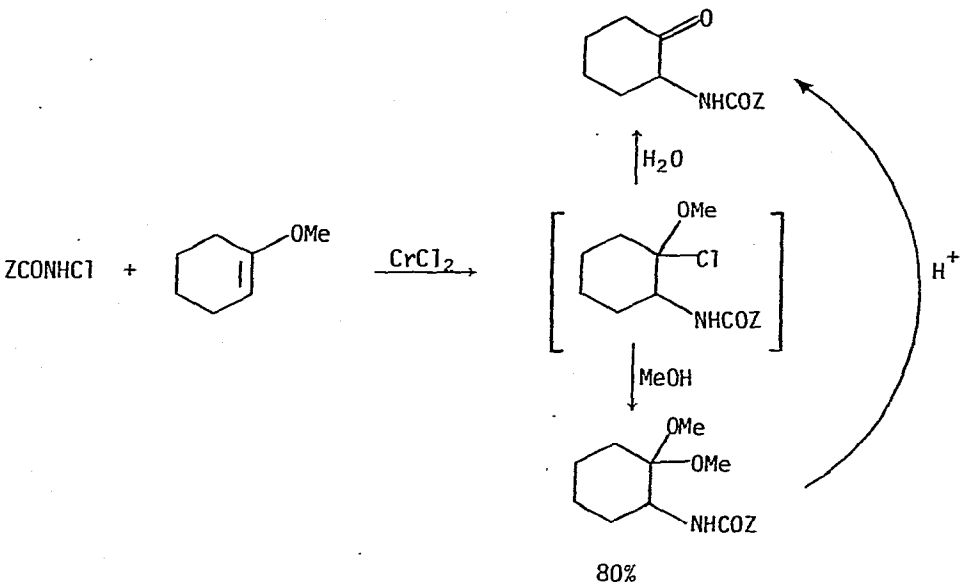
Olefins were oxaminated using chloramine T and osmium tetroxide under phase transfer catalysis conditions (eq. 249). This procedure was preferable to the



(249)

silver nitrate catalyzed method, and worked well with mono- and symmetrically disubstituted olefins [616]. The reagent $O_3Os{=}NR$ was also an efficient complex for the vicinal oxamination of olefins. The stereochemistry of the reaction was cleanly cis, and the nitrogen always attacked the least substituted carbon

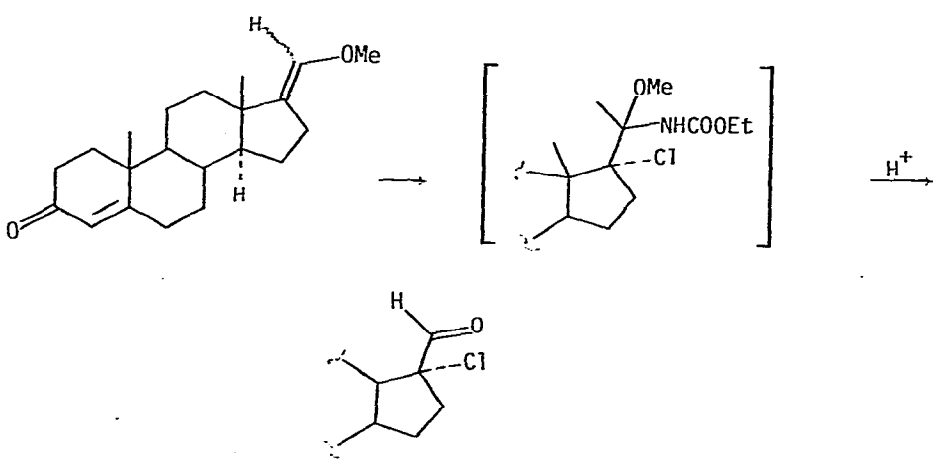
atom. Pyridine was the best solvent. Monosubstituted olefins reacted faster than disubstituted olefins, which, in turn, reacted faster than trisubstituted olefins. The reaction was compatible with cyano, chloro, methoxy, methyl and dimethylamino groups in ring substituted styrenes [617]. N-Chlorocarbamates also oxaminated olefins in the presence of silver nitrate, t-butylhydroperoxide and catalytic amounts of osmium tetroxide. This method produced α-hydroxy-carbamates, which were easily recovered [618]. Chromium(II) chloride promoted



80%

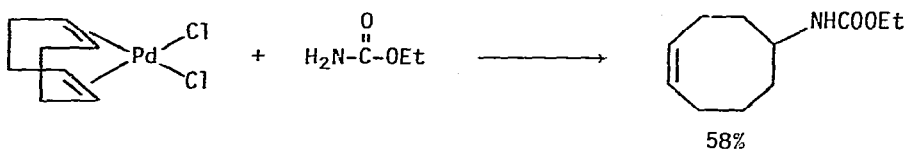
Z = EtO, $Cl(CH_2)_2O$, CH_3, $ClCH_2$, CH_3O

and (250)

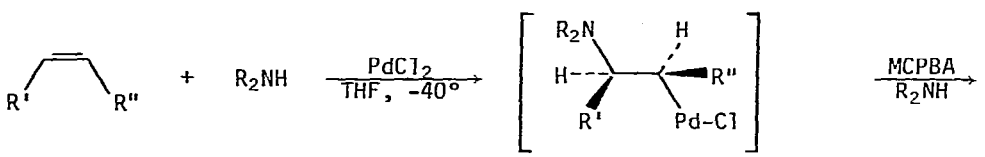


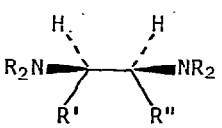
the addition of N-chloroamides to electron rich olefins (eq. 250). This procedure was used to prepare acyloxy and acyl derivatives of α-aminoacetates and 2-amino sugars [619].

Dimethylamine reacted with bis(duroquinone)nickel to produce 2,3-dimethyl-5,6-bis[dimethylamino]hydroquinone [620]. The nitrogen of carbamates attacked an olefin group of cyclooctadiene palladium(II) chloride to produce the 5-substituted cyclooctene (eq. 251) [621]. Olefins were stereospecifically vicinally diaminated by treatment with palladium(II) chloride, dialkylamine and subsequent oxidation with N-bromosuccinimide or meta-chloroperbenzoic acid (eq. 252) [622]. Vinyl halides, olefins and secondary amines reacted in the presence of palladium(II) acetate and tri(o-tolyl)phosphine to produce homologated olefinic amines (eq. 253). The process was thought to proceed by amination of the π-allylpalladium complex produced by insertion of the alkene into the vinyl palladium complex [623].



58% (251)

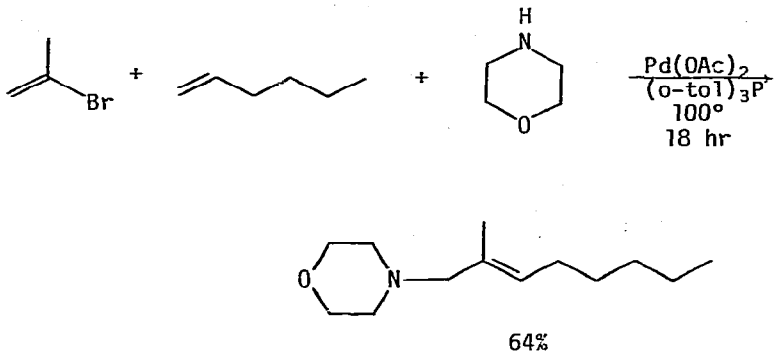




(252)

60-80% for R' = H
35-45% for R',R" = alkyl

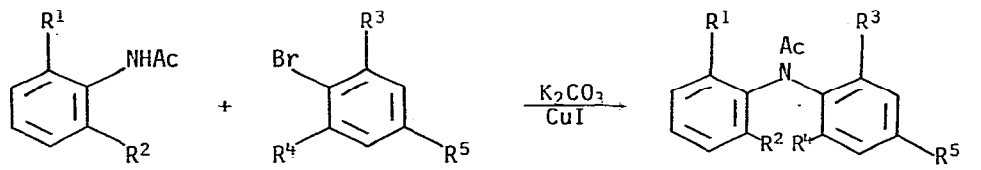
Phthalimide reacted with R_2NiL_2 to produce a nickel-phthalimide complex which reacted with bromobenzene to produce N-phenylphthalimide. This stands in contrast to normal Gabriel synthesis conditions under which aryl halides are unreactive [624]. 2-Methyl-2-hexene was allylically aminated to 2-methyl-3-arylamino-1-hexene by a molybdenum oxaziridine complex [625]. Allyl amines were also prepared by the reaction of dialkylamines with allylic acetates in



(253)

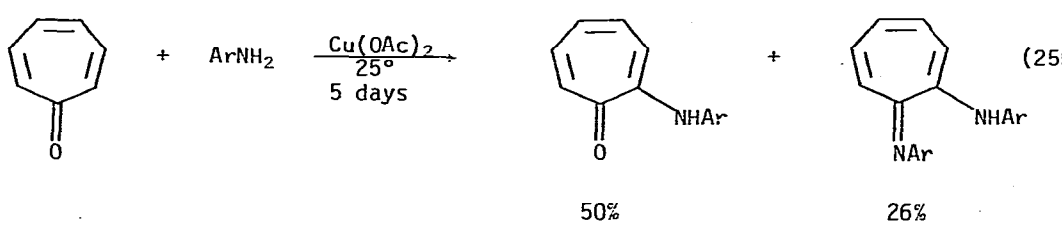
the presence of palladium(0) complexes [626]. Similar reactions were catalyzed by $(Ph_3P)_2PdCl_2$ [627].

1-Substituted anthraquinones reacted with n-butylamine or ammonia in the presence of copper(I) or copper(II) salts to produce 4-aminoanthraquinones in low yield [628]. The Ullmann condensation of 2-aminoethanol with 1-bromoanthraquinone catalyzed by copper(II) salts proceded via radical anion-electron transfer pathway [629]. Acetamides reacted with aryl bromides in the presence of copper(I) iodide to produce diarylacetamides (eq. 254). Aryl chlorides also reacted [630]. Cycloheptatrienone reacted with aniline in the presence



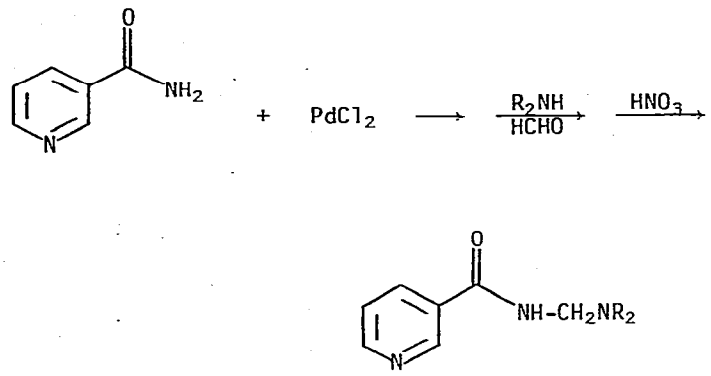
(254)

of copper(II) acetate to produce the α-aminoketone and the imine (eq. 255) [631].



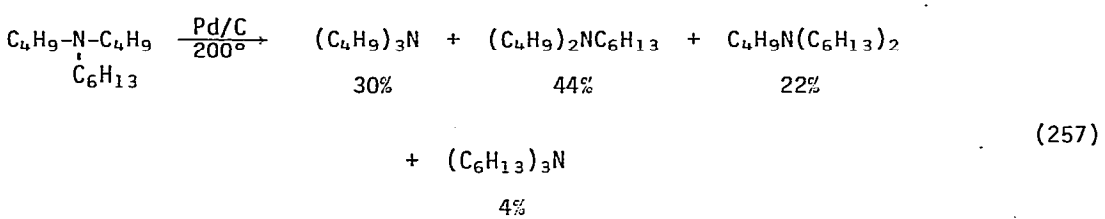
(255)

Nicotinamide was converted to its palladium(II) complex and aminomethylated with amines and formaldehyde to produce N-aminomethylnicotinamides in excellent yield (eq. 256) [632]. Rhodium(III) chloride catalyzed the reductive alkylations



(256)

of amines by aldehydes in moist ethanol under an atmosphere of carbon monoxide. The reaction was likely to have involved the water gas shift reaction to produce hydrogen from water and carbon monoxide [633]. A similar reaction was promoted by $HRh(dmg)_2 \cdot H_2O$ [634]. Amino acids were prepared by the electrochemical reductive amination of keto acids on platinum black and palladium black electrodes [635]. Tertiary amines were scrambled when treated with palladium on carbon at 200° (eq. 257). An improved method for vicinal dihydroxylation of olefins by

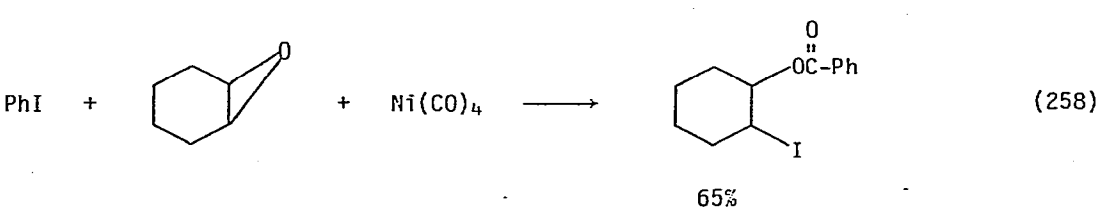


(257)

t-butylhydroperoxide in the presence of an osmium catalyst has appeared [637]. Tri- and tetrasubstituted olefins were sluggish to react and cholesterol was inert.

D. Ethers, Esters

Simple aliphatic primary halides reacted with alkoxides and iron pentacarbonyl to produce esters [638]. Cyclohexene oxide reacted with $Ti(NMe_2)_4$ and carbon dioxide to produce the monocarbamate of 1,2-cyclohexandiol [639]. Epoxides were converted into iodoesters by reaction with aryl and vinyl iodides and nickel carbonyl (eq. 258) [640]. Aldehydes reacted with $RuH_2(PPh_3)_4$ to produce



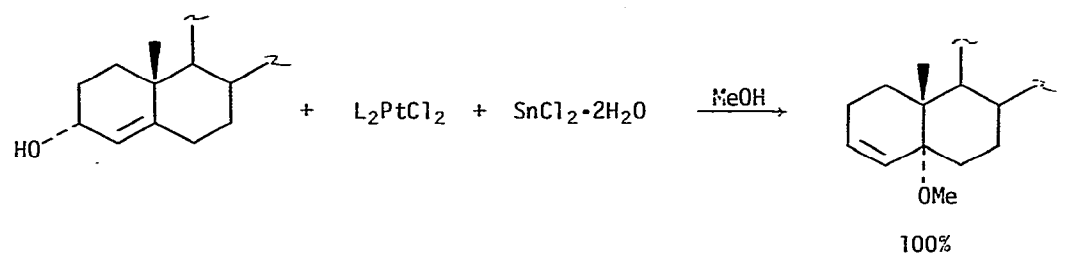
(258)

esters wherein both the acid and alcohol portion arose from the aldehyde by a disproportionation (Cannizaro) reaction [641]. Ethyl diazoacetate reacted with 2-methylcyclohexanone in the presence of copper(I) chloride to produce predominantly the less substituted enol ester (12:1) in 65% yield [642].

Potassium selenocyanide reacted with olefins including styrene, 1-octene, cis-2-octene, cyclohexene, ethyl vinyl ether, vinyl acetate and acrolein to produce vicinal alkoxyselenocyanides (eq. 259). The reaction proceded as if

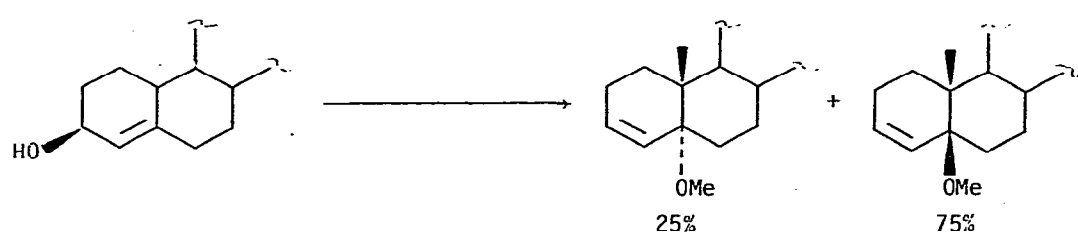
(259)

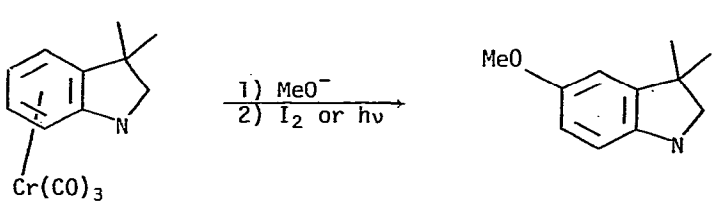
it were an electrophilic addition of $SeCN^+$ [643]. Allylic alcohols were converted to allyl ethers with clean allylic transposition by reaction with tin(II) chloride-$(Ph_3P)_2PtCl_2$ in methanol (eq. 260) [644]. The π-arene chromium complex of 3,3-dimethylindoline was methoxylated in the 5 position by treatment with sodium methoxide followed by removal of chromium (eq. 261) [645].



but

(260)

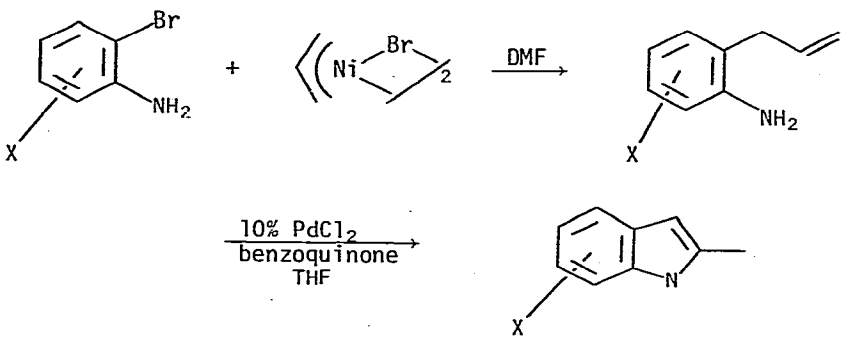




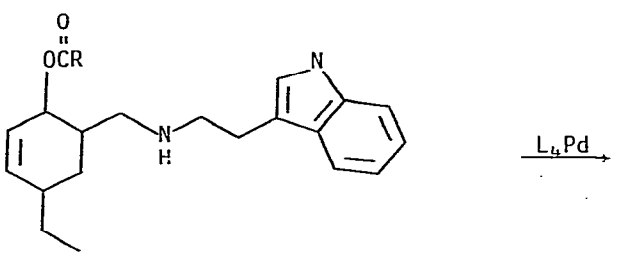
(261)

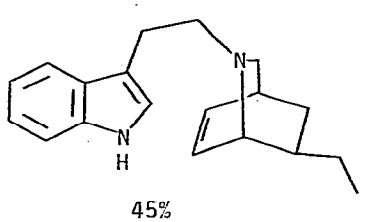
Ethyl chloroformate reacted with alkylmanganese(II) iodide to produce the corresponding alkyl ethyl esters [646]. Alkyl halides reacted with the copper(I) alkoxide complexes $ROCu(PPh_3)_2$ to produce ethers. Acid chlorides and anhydrides produced esters. These complexes were also catalysts for transesterification reactions between esters and alcohol [647]. Reduced copper species catalyzed the conversion of primary alcohols into esters and ketones [648]. Iron(III) chloride was a catalyst for the esterification of carboxylic acids [649].

E. Heterocycles



(262)

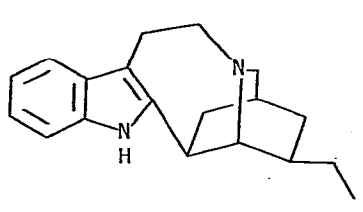




45%

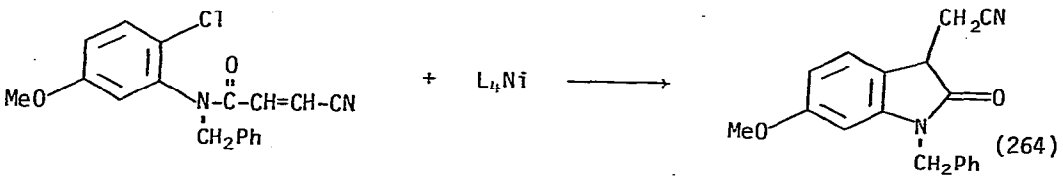
(263)

1) $PdCl_2(CH_3CN)_2$
$AgBF_4$
2) $NaBH_4$



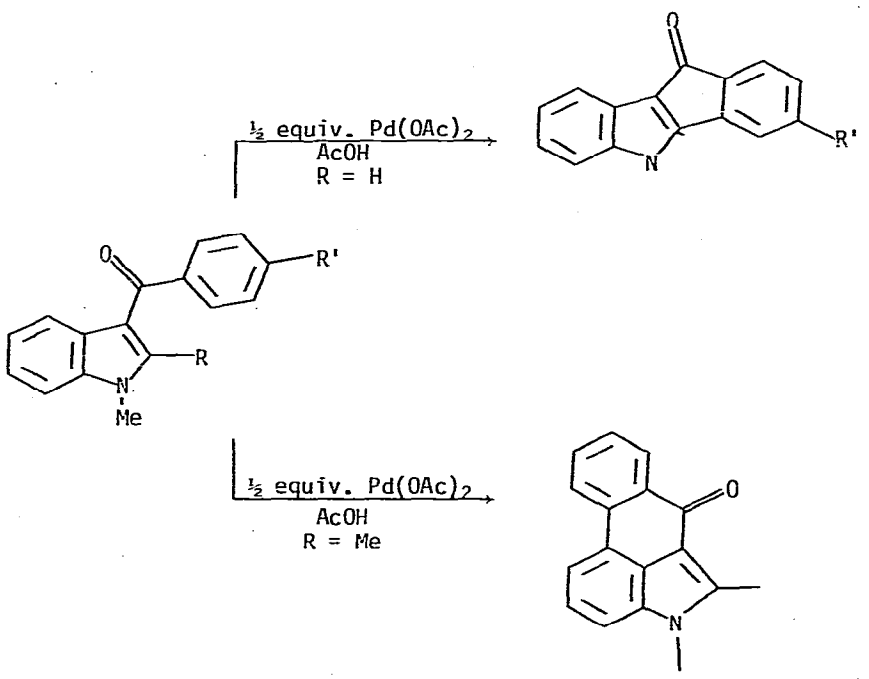
ibogamine
40-45%

Transition metal complexes continue to be used for the synthesis of heterocyclic systems. Palladium(II) chloride was used to catalyze the intramolecular amination reaction of 2-allylanilines, producing indoles in excellent yield. The process tolerated a variety of functional groups in the aromatic ring (eq. 262) [650]. The alkaloid ibogamine was synthesized by a route involving both palladium(0) catalyzed amination of an allylic acetate followed by a palladium(II) catalyzed insertion of a double bond (eq. 263) [651]. Oxindoles were prepared



(264)

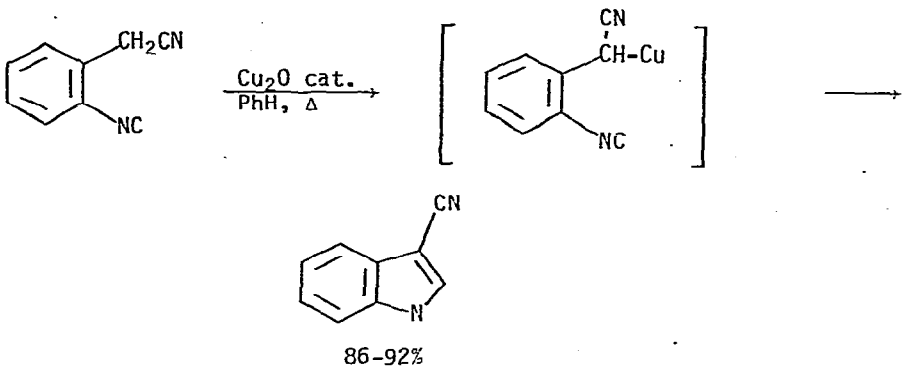
by the nickel(0) assisted cyclization (eq. 264) [652]. Benzoylindoles were cyclized in a palladium(II) acetate assisted reaction (eq. 265) [653]. Copper(I)



(265)

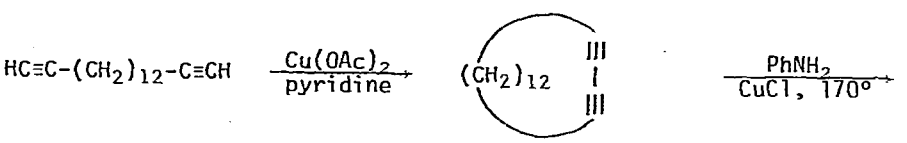
oxide catalyzed the cyclization of o-(α-cyanoalkyl)phenyl isocyanides to indoles (eq. 266) [654]. Cyclic 1,3-diynes reacted with aniline and copper(I) chloride

to produce N-phenyl pyrroles (eq. 267) [655]. Olefinic N-chloroamides cyclized to lactams when treated with chromium(II) chloride (eq. 268) [656].

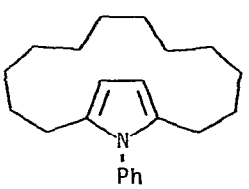


86-92%

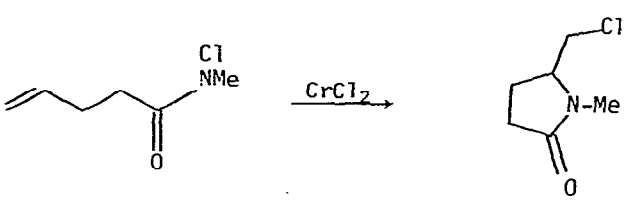
(266)



(267)

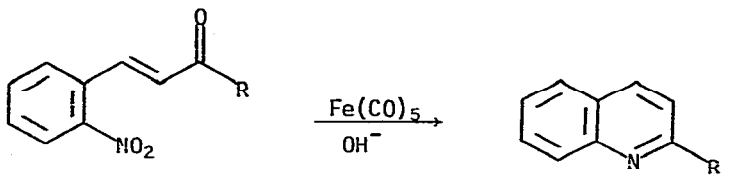


50%



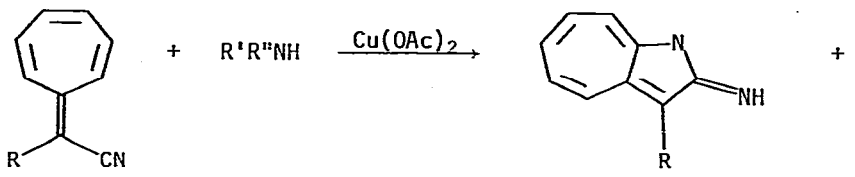
(268)

Quinolines were produced by the cyclization of o-nitrobenzalketones with iron pentacarbonyl and base (eq. 269) [657]. Isoquinolines resulted from the reaction of 8,8-disubstituted heptafulvenes with amines in the presence of copper(II) acetate (eq. 270) [658]. Bis imines of α-diketones reacted with diiron enneacarbonyl ($Fe_2(CO)_9$) to produce 2(3H)-imidazolones (eq. 271) [659].



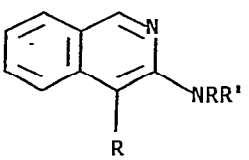
(269)

R = H, 100%
R = Me, 55%
R = Ph, 17%



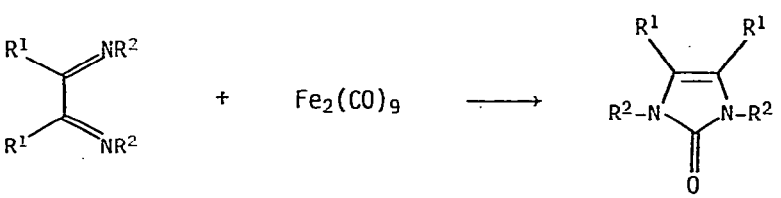
10-30%

(270)



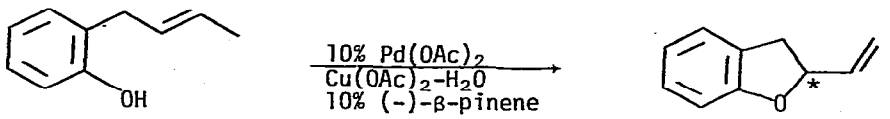
19-52%

R = CN, OMe
R' = H, Me, Et, $PhCH_2$
R" = H



(271)

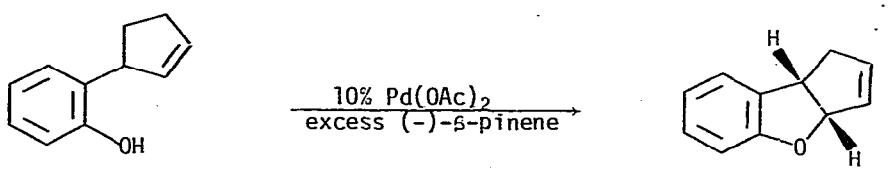
Palladium(II) acetate catalyzed the cyclization of 2-allylphenols to 2-substituted dihydrobenzofurans. When the reaction was carried out in the presence of 10% (-)-β-pinene, the dihydrobenzofuran was obtained in 62% yield and 12% optical yield. Excess (-)-β-pinene stopped the reaction, while excess (+)-α-pinene allowed the reaction to ensue, but resulted in no optical induction (eq. 272) [660]. The cyclization of 2-cyclohexenylphenol to the benzofuran



62%
12% optical yield

(272)

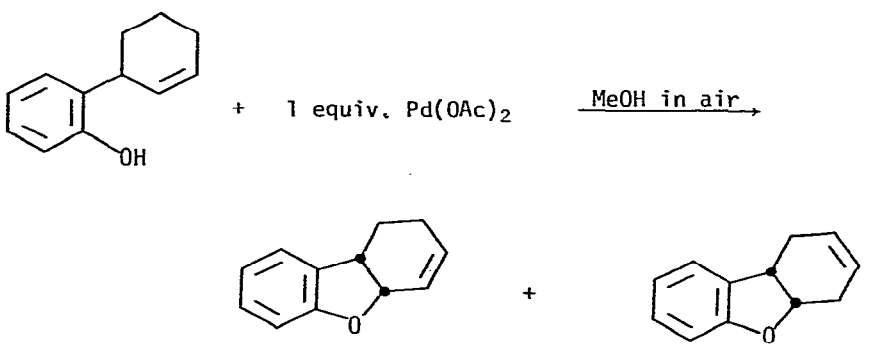
but



16%

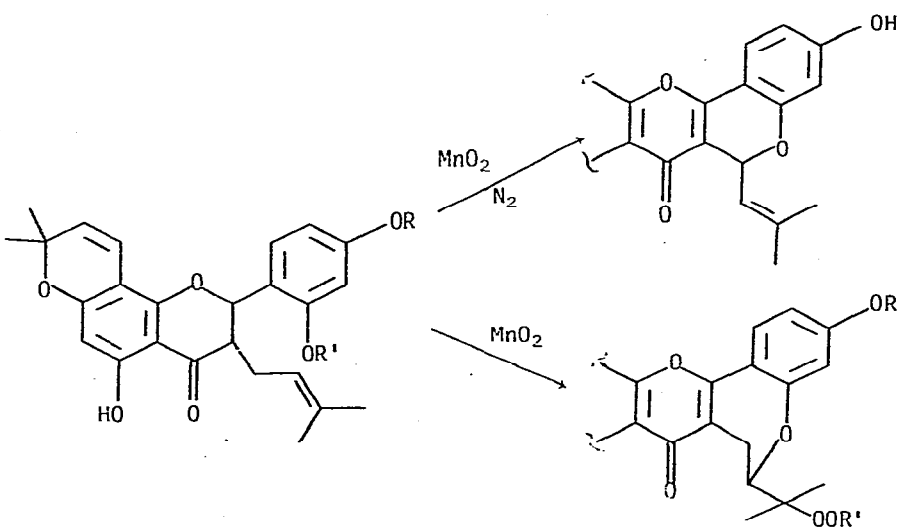
(272)

could be influenced by the amount of addition of excess olefin (eq. 273). This cyclization process was catalytic in the presence of oxygen without the use of



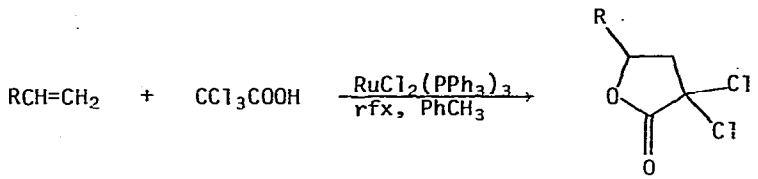
(273)

a cooxidant [661]. Manganese dioxide oxidatively cyclized morusin to the hydroperoxide, but the pyran was formed under nitrogen (eq. 274) [662]. Terminal



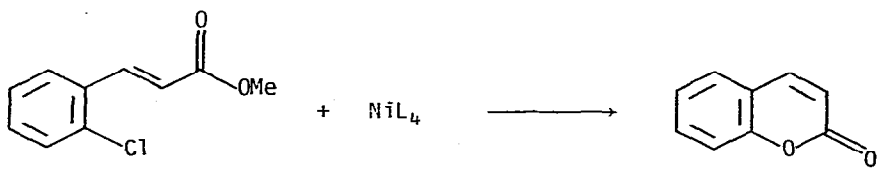
(274)

olefins reacted with trichloroacetic acid in the presence of $RuCl_2(PPh_3)_3$ to give α,α-dichlorolactones (eq. 275) [663]. Coumarin and dihydrocoumarin were produced from the reaction of 2-chlorophenyl acrylate with nickel(0) complexes (eq. 276) [664].



(275)

R = n-alkyl

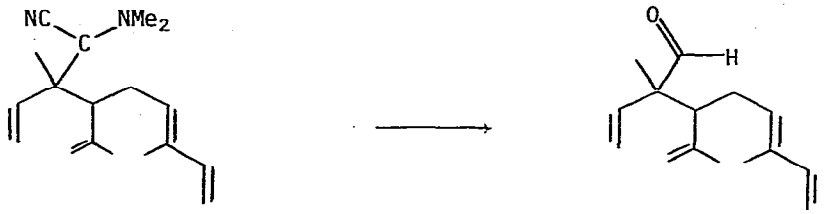


(276)

H. Miscellaneous

Vicinal dihalides were converted to olefins by treatment with $[CpCr(NO)_2]_2$ in a debromination reaction. Other halides including allylic, alkyl, t-butyl, vinyl and aryl halides were inert to this complex. For instance, 3,5,6-tribromocholestane was converted to 3-bromocholest-5-ene in 75% yield by this complex [665]. Terminal allyl acetates and phenyl ethers were converted to 1,3-dienes in 60-80% yield by treatment with palladium(II) acetate and triphenyl phosphine [666]. Dry iron(III) chloride adsorbed on silica gel was mixed with solutions of allylic, tertiary or sterically strained secondary alcohols in a volatile solvent, which was then removed under reduced pressure. Elution of the product from silica gel gave the dehydration product. This reagent converted epoxides to 1,2-diols [667].

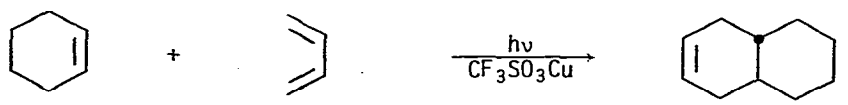
Allyl esters were cleaved to the carboxylate salts by treatment with lithium dimethylcuprate. This procedure was used for selective removal of allyl ester protecting groups [668]. Copper(II) acetate was used to protect the nitrogen of single free aminoalcohol groupings in aminosugars [669]. Copper(II) sulfate was used to catalyze the hydrolysis of aminonitriles to ketones at pH 5.5, so that acid sensitive groups were unaffected (eq. 277) [670]. Tosylhydrazones of ketones and aldehydes were converted to the free carbonyl compound by treatment with copper(II) sulfate in refluxing THF/methanol [671]. Phenylhydrazones, hydrazones, oximes and semicarbazones behaved in a similar fashion [672]. Alkyl iron complexes were converted to olefins by treatment with trityl cation followed by sodium iodide and acetone [673].



82%

(277)

Copper(I) trifluoromethylsulfonate catalyzed the photochemical rearrangement of allylalcohol to propene and acrolein [674]. The photoreduction of butadiene with cyclohexene to give octalin products was also catalyzed by the same complex (eq. 278). Cyclopentene, cycloheptene, cyclooctene and norbornene did not react

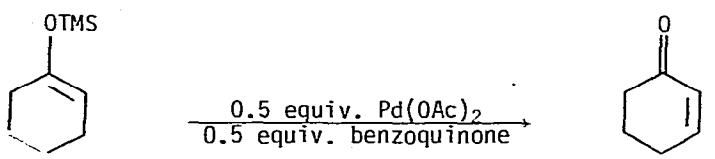


50%

(278)

in this fashion [675]. Catalysis of olefin photoreactions by transition metal salts has been reviewed [676], as has the use of trinuclear metal carbonyl clusters such as $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ as catalysts [677].

Trimethylsilyl enol ethers were converted to conjugated ketones by treatment with 0.5 equivalents of palladium(II) acetate and 0.5 equiv. of benzoquinone (eq. 279) [678]. The complexes resulting from the reaction of $IrCl(CO)(PPh_3)_2$



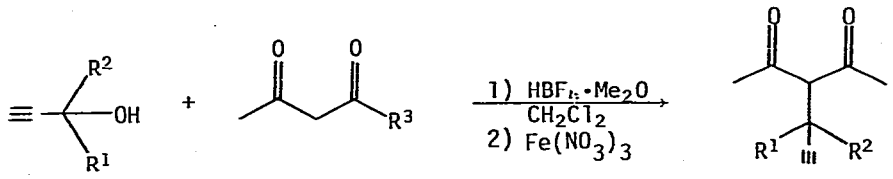
91%

(279)

with $(Me_2SiH)_2O$ induced the disproportionation of $(Me_2SiH)_2O$ to Me_2SiH and polysiloxanes [679]. Allyl chlorides were converted to allylsilanes in good yield by reaction of $R_3Si\text{-}SiR_3$ in the presence of a palladium(0) catalyst at 150-170°[680].

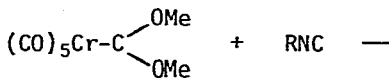
Propargyl alcohols complexed to $Co_2(CO)_8$ and the resulting complex formed stable propargyl cationic species which reacted with a variety of nucleophiles. The cobalt was then removed by treatment with iron(III) nitrate (eq. 280) [681]. Similarly, π-arene chromium tricarbonyl complexes involving benzyl alcohols formed stable benzyl cationic species [682]. Ketenimines were formed by the reaction of isonitriles with chromium carbene complexes (eq. 281) [683]. This same type of complex reacted with alkynes to produce bicyclic compounds (eq. 282) [684].

References p. 430

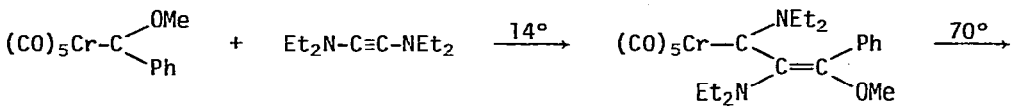


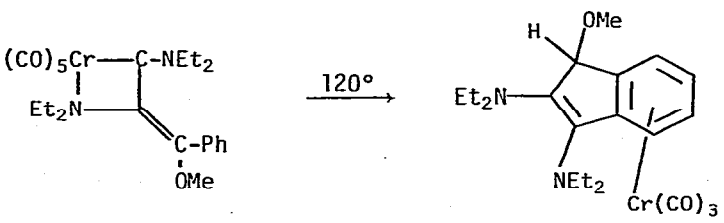
65-90%

(280)



(281)

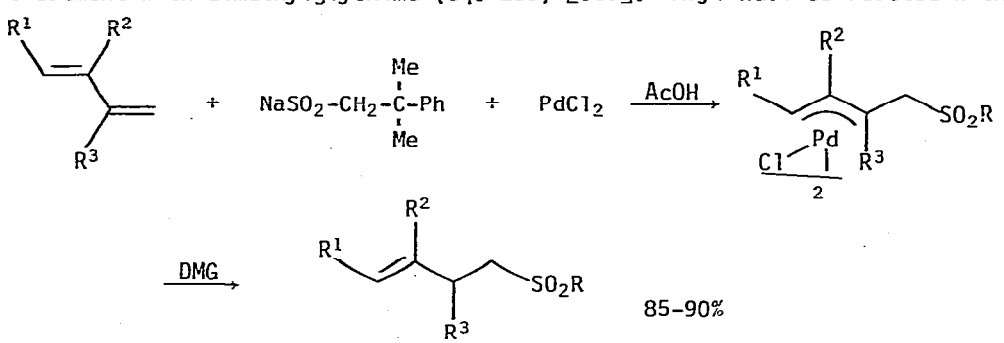




75%

(282)

Triarylsulfonium and selenonium salts were prepared by the copper(II) catalyzed reactions of diaryl sulfides and selenides with diaryliodonium salts [685]. Reaction of 1,3-dienes with palladium(II) chloride and $NaSO_2CH_2CMe_2Ph$ produced a sulfonylated π-allyl complex from which the palladium was removed by treatment with dimethylglyoxime (eq. 283) [686]. Aryl halides reacted with

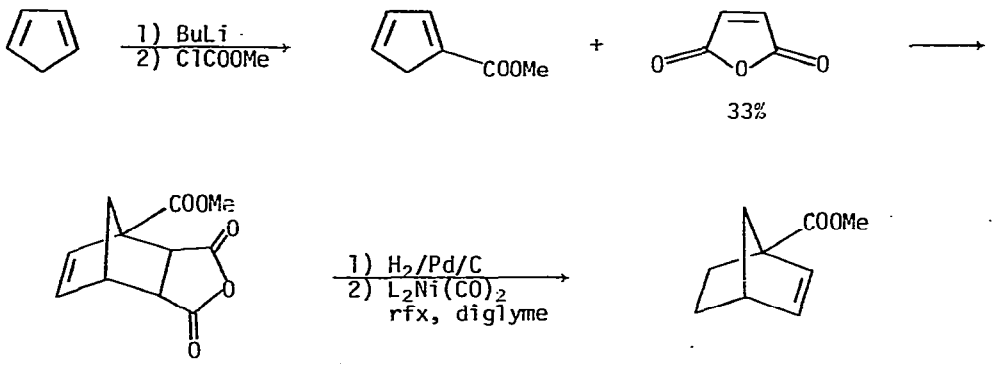


85-90%

(283)

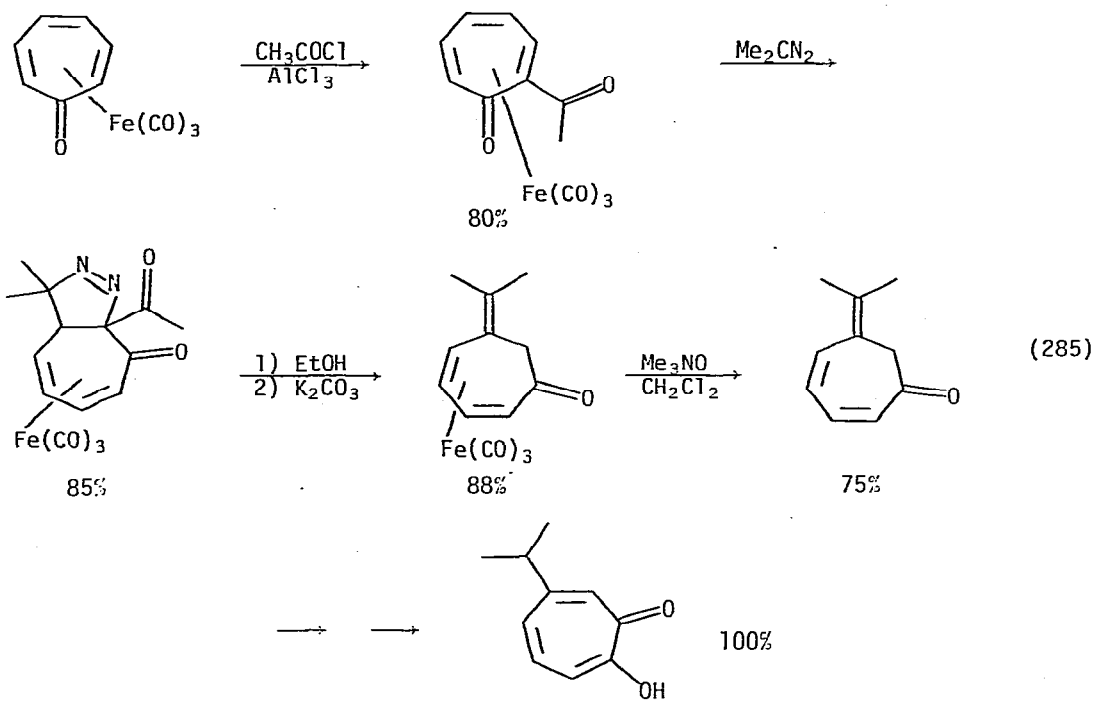
thiolate ions in the presence of palladium(0) complexes in DMSO to produce aryl sulfides [687]. Nitrobenzenes were coupled to azobenzenes in 40-50%

yield by treatment with dicobalt octacarbonyl in refluxing benzene [688]. The nickel(0) complex $Ni(CO)_2(PPh_3)_2$ affected a bis-decarbonylation of a maleic anhydride Diels-Alder adduct (eq. 284) [689]. Nitriles were converted to their



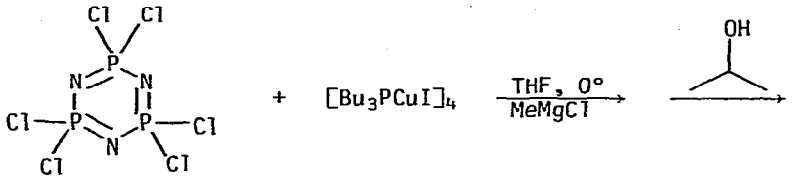
(284)

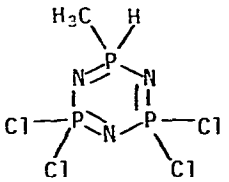
corresponding aldehydes by reaction with a cobalamine(I) complex and activated zinc in aqueous acetic acid [690]. α-Thujaplicin was prepared from the iron tricarbonyl complex of cycloheptatrienone (eq. 285) [691]. Hydridocyclophosphazenes



(285)

were prepared via organocopper reagents (eq. 286) [692]. Dimethyldiazomalonate reacted with thiophene to form thiophenium bis-methoxycarbonyl methylides [693].





(286)

VI. Reviews

The following reviews and theses have appeared:

"Organometallic Chemistry. Part I. The Transition Elements" [694]

"Organometallic in Synthesis" (223 references) [695]

"The Use of Organometallics in Organic Syntheses" [696]

"Organometallic Reagents in Organic Synthesis" [697]

"Viewing Approach and Recent Development of Organic Synthesis Using Metal Complex Catalysts. I" (15 references) [698]

"Viewing Approach and Recent Development of Organic Synthesis Using Metal Complex Catalysts. III" (16 references) [699]

"Iron Carbonyls in Organic Synthesis" (15 references) [700]

"Studies Directed Toward the Total Synthesis of (±)-Vernolepin. Novel Rhodium Catalysis in Organic Synthesis" [701]

"Part One: Tris(triphenylphosphine)nickel(0). In Situ Generation and Utilization. Part Two: The Total Synthesis of Steganacin and Isosteganacin" [702]

"Metal Carbonyls" (95 references) [703]

"Reactivity of Monoolefinic Ligands in Iron-Carbonyl Complexes" (36 references) [704]

"Reactions of Coordinated Olefins and Acetylenes" (23 references) [705]

"Reactivity of Monoolefin Ligands in Transition Metal Complexes" (131 references) [706]

"Chemistry of Diene and Enone Iron Tricarbonyl Complexes (31 references) [707]

"Bisphosphine Nickel and Platinum Complexes: Reactivity and Catalytic Properties Towards Acetylenes" (63 references) [708]

""Organocobalt Complexes, Part XII. Uses of Cobalt-Carbonyl Acetylene Complexes in Organic Synthesis" (28 references) [709]

"Organometallic Reaction Mechanisms: Catalytic Cyclotrimerization of Alkynes, Reduction of Carbon Monoxide and Reductive Elimination from an Alkylhydride Complex" [710]

"Catalytic Applications of Palladium in Organic Synthesis" [711]
"Organic Synthetic Reactions Using Palladium Compounds" (146 references) [712]
"New Applications of Palladium in Organic Synthesis" [713]
"Recent Aspects in the Study of Model Intermediates Related to Organic Synthesis Using Palladium and Platinum Complexes" (92 references) [714]
"Homogeneous Catalysis by Arene Group-VIB Tricarbonyls" (128 references) [715]
"Examples of the Use of Chromium Tricarbonyl-Arene Complexes in Organic Synthesis" (68 references) [716]
"Arene-Metal Complexes in Organic Synthesis" (49 references) [717]
"Synthetic and Mechanistic Studies in Organolithium and Organocopper Chemistry" [718]
"Part 1: New Uses of Organocopper Reagents in Organic Synthesis. Part 2: Studies Toward the Total Synthesis of Obtusilactone; A Synthesis of Deoxy-obtusilactone" [719]
"Grignard-Type Reactions with Zerovalent Nickel Complexes" [720]
"Stoichiometric vs Catalytic Use of Cu(I) Salts in the Synthetic Use of Main Group Organometallics" [721]
"Asymmetric Syntheses Using Heterogeneous Catalysts" (20 references) [722]
"Asymmetric Synthesis" (333 references) [723]
"Syntheses of Chiral Phosphine Ligands for Catalytic Asymmetric Reactions" (76 references) [724]
"Organometallic Syntheses with Diazoalkanes" (131 references) [725]
"Titanocene"-Catalyzed Reactions of Olefins" (26 references) [726]
"Low Valent Titanium in Organic Synthesis" [727]
"Organomercury Compounds in Organic Synthesis" (162 references) [728]
"Transmetalation: Organic Synthesis via Transfer of Organic Groups from One Metal to Another" (35 references) [729]
"Homogeneous Catalysis by Transition-Metal Complexes" (181 references) [730]
"Homogeneous Catalysis" (135 references) [731]
"Organotransition Metal Compounds as Intermediates in Homogeneous Catalytic Reactions" [732]
"Homogeneous Catalytic Reactions of Transition Metal Complexes Involving Olefins, Carbon Monoxide and Hydrogen" (8 references) [733]
"Industrial Applications of Homogeneous Catalysis. A Review" (128 references) [734]
"(Pentamethylcyclopentadienyl)rhodium and -iridium Complexes: Appraoches to New Types of Homogeneous Catalysts" (34 references) [735]
"Heterogeneous Catalysis" (41 references) [736]
"Polymeric Catalysts" (154 references) [737]
"Organometallic Polymers as Catalysts" (10 references) [738]
"Reactions of Electrophiles with σ-Bonded Organotransition Metal Complexes" (92 references) [739]
"Coupling of Alkyl Groups Using Transition Metal Catalysts" (49 references) [740]

References p. 430

"Oxidative Combination of Aromatic Systems in the Presence of Transition Metal Compounds" (124 references) [741]

"Organometallic Synthetic Route for Special Surfactants with Heteroatoms" (26 references) [742]

"Acetonylating Reagents" (25 references) [743]

"The Versatility of 3 Phosphine Ligands in Coordination and Organometallic Chemistry" (138 references) [744]

"Mechanism of Beta-Hydride Elimination of Some Platinum(II) Monoalkyls" [745]

"Metal-alkyl, -aryl and -allyl Bond Formation and Cleavage" (53 references) [746]

"The Thermochemistry of Organometallic Compounds" (34 references) [747]

"Organic Chemistry of Metal Vapors. π-Complexes to Solvated Metals to Metal Clusters" (54 references) [748]

"Oxidative Addition and Reductive Elimination" (23 references) [749]

"Theoretical Aspects of the Coordination of Molecules to Transition Metal Centers" (21 references) [750]

REFERENCES

1. E. J. Corey, David Floyd and B. H. Lipschutz, J. Org. Chem., 43, 3418 (1978).
2. H. M. Walborski and P. Ronman, J. Org. Chem., 43, 731 (1978).
3. G. Schill and C. Merkel, Chem. Ber., 111, 1446 (1978).
4. J. F. Normant, T. Mulamba, F. Scott, A. Alexakis and C. Cahiez, Tetrahedron Lett., 3711 (1978).
5. G. A. Mora Lopez, Diss. Abst. Int. B, 38, 3199 (1978).
6. H. Westmijze, H. Kleijn and P. Vermeer, Tetrahedron Lett., 3125 (1978).
7. K. Mori, T. Suguro and S. Masuda, Tetrahedron Lett., 3447 (1978).
8. K. Eiter, F. Lieb, H. Disselnkotter and H. Oedigen, Liebigs Ann. Chem., 658 (1978).
9. M. T. Rietz and W. F. Maier, Angew. Chem. Int. Ed., 17, 48 (1978).
10. H. P. Dang and G. Linstrumelle, Tetrahedron Lett., 191 (1978).
11. W. Verboom, H. Westmijze, H. J. Bos and P. Vermeer, Tetrahedron Lett., 1441 (1978).
12. G. Giacomelli and L. Lardicci, Tetrahedron Lett., 2831 (1978).
13. A. Ohsawa, Y. Abe and H. Igeta, Chem. Pharm. Bull., 26, 2550 (1978).
14. Y. Abe, A. Ohsawa, H. Arai and H. Igeta, Heterocycles, 9, 1397 (1978).
15. H. Yamanaka, K. Edo, F. Shoji, K. Konno, T. Sakamoto and M. Mizugaki, Chem. Pharm. Bull., 26, 2160 (1978).
16. M. S. Shvartsberg, A. A. Moroz and A. N. Kozhevnikove, Izv. Akad. Nauk SSSR Ser Khim., 875 (1978).
17. A. O. King, E. I. Negishi, F. J. Villani, Jr., and A. Silveira, Jr., J. Org. Chem., 43, 358 (1978).

18. M. Terasawa, K. Kaneda, T. Imanaka and S. Teranishi, J. Organometal. Chem., 162, 403 (1978).
19. F. E. Ziegler, K. W. Fowler and N. Sinha, Tetrahedron Lett., 2767 (1978).
20. G. A. Kraus and K. Frazier, Tetrahedron Lett., 3195 (1978).
21. M. Kasugi, H. Arai, A. Yoshimo and T. Migita, Chem. Lett., 795 (1978).
22. J. A. Marshall and P. G. M. Wuts, J. Am. Chem. Soc., 100, 1627 (1978).
23. K. Sato and S. Morii, Chem. Abstr., 89, 197734j (1978).
24. C. Lion, J. E. Debois and Y. Bonzougon, J. Chem. Res., 46 (1978).
25. G. P. Chiusoli, M. Costa, G. Pecchini and G. Cometti, Transition Met. Chem., 2, 270 (1977).
26. D. Milstein and J. D. Stille, J. Am. Chem. Soc., 100, 3636 (1978).
27. M. Kosugi, Y. Shimizu and T. Migita, Chem. Lett., 1423 (1977).
28. A. Hosomi, H. Hashimoto and H. Sakurai, J. Org. Chem., 43, 2552 (1978).
29. F. Mathey and Ph. Savignac, Tetrahedron, 34, 649 (1978).
30. P. Coutrout and Ph. Savignac, Synthesis, 36 (1978).
31. J. Villieras, A. Reliquet and J. F. Normant, J. Organometal. Chem., 144, 17; 263 (1978).
32. J. Villieras, A. Reliquet and J. F. Normant, Synthesis, 27 (1978).
33. J. E. Plevyak and R. F. Heck, J. Org. Chem., 43, 2454 (1978).
34. W. C. Frank, Y. C. Kim and R. F. Heck, J. Org. Chem., 43, 2947 (1978).
35. C. B. Ziegler and R. F. Heck, J. Org. Chem., 43, 2949 (1978).
36. B. A. Patel, J. E. Dickerson and R. F. Heck, J. Org. Chem., 43, 5018 (1978).
37. I. Arai and G. D. Daves, Jr., J. Het. Chem., 15, 351 (1978).
38. I. Arai and G. D. Daves, Jr., J. Am. Chem. Soc., 100, 287 (1978).
39. I. Arai and G. D. Daves, Jr., J. Org. Chem., 43, 4110 (1978).
40. N-T-L Thi and H. Riviere, JCS Chem. Comm., 918 (1978).
41. Y. Fujiwara, R. Asano and S. Teranishi, Israel J. Chem., 15, 262 (1977).
42. P. Hong, H. Yamazi, K. Sonogashira and N. Hagihara, Chem. Lett., 535 (1978).
43. L. S. Hegedus, T. Hayashi and W. H. Darlington, J. Am. Chem. Soc., 100, 7747 (1978).
44. T. Izumi, K. Endo, O. Saito, I. Shimizu, M. Maemura and A. Kasahara, Bull. Chem. Soc. Japan, 51, 663 (1978).
45. F. Sato, H. Kodama and M. Sato, J. Organometal. Chem., 157, C30 (1978).
46. A. V. Youngblood, S. A. Nichols, R. A. Coleman and D. W. Thompson, J. Organometal. Chem., 146, 221 (1978).
47. B. B. Snider and L. Fuzesi, Tetrahedron Lett., 877 (1978).
48. A. Nakamura, Pure Appl. Chem., 50, 37 (1978).
49. A. Nakamura, A. Konishi, Y. Tatsuno and S. Otsuka, J. Am. Chem. Soc., 100, 3443 (1978).
50. A. Nakamura, A. Konishi, R. Rsujitani, M-a Kudo and S. Otsuka, J. Am. Chem. Soc., 100, 3449 (1978).
51. T. Aratani, Chem. Abstr., 89, 24541r (1978).

52. A. Nakamura, T. Koyama and S. Otsuka, Bull. Chem. Soc. Japan, 51, 593 (1978).
53. N. Petincot, A. J. Anciaux, A. F. Noels, A. J. Hubert and Ph. Teyssie, Tetrahedron Lett., 1239 (1978).
54. S. Kulkowit and M. A. McKervey, JCS Chem. Comm., 1069 (1978).
55. I. G. Dinulescu, L. N. Enescu, A. Ghenculescu and M. Avram, J. Chem. Res., 456 (1978).
56. R. Noyori, Y. Hayakawa, H. Takaya, S. Murai, R. Kobayashi and N. Sonada, J. Am. Chem. Soc., 100, 1759 (1978).
57. H. Takaya, S. Makino, Y. Hayakawa and R. Noyori, J. Am. Chem. Soc., 100, 1765 (1978).
58. H. Takaya, Y. Hayakawa, S. Makino and R. Noyori, J. Am. Chem. Soc., 100, 1778 (1978).
59. Y. Hayakawa, Y. Baba, S. Makino and R. Noyori, J. Am. Chem. Soc., 100, 1786 (1978).
60. Y. Hayakawa, K. Yokoyama and R. Noyori, J. Am. Chem. Soc., 100, 1791 (1978).
61. Y. Hayakawa, K. Yokoyama and R. Noyori, J. Am. Chem. Soc., 100, 1799 (1978).
62. Y. Hayakawa, F. Shimizu and R. Noyori, Tetrahedron Lett., 993 (1978).
63. R. Noyori, T. Sato and Y. Hayakawa, J. Am. Chem. Soc., 100, 2561 (1978).
64. T. Sato, R. Ito, Y. Hayakawa and R. Noyori, Tetrahedron Lett., 1829 (1978).
65. R. Noyori, F. Shimizu and Y. Hayakawa, Tetrahedron Lett., 2091 (1978).
66. R. G. Salomon and A. Sina, Tetrahedron Lett., 1367 (1978).
67. J. E. Lyons, H. K. Myers and A. Schneider, JCS Chem. Comm., 636 (1978).
68. P. J. Lennon, Diss. Abstr. Int. B, 38, 5942 (1978).
69. N. Okukado, D. E. Van Horn, W. L. Klima and E-i. Negishi, Tetrahedron Lett., 1027 (1978).
70. E-i Negishi, N. Okukado, A. O. King, D. E. Van Horn and B. I. Spiegel, J. Am. Chem. Soc., 100, 2254 (1978).
71. H. Yatagai, Y. Yamamoto and K. Maruyasa, JCS Chem. Comm., 702 (1978).
72. J-i. Yoshida, K. Tamao, M. Takahashi and M. Kumada, Tetrahedron Lett., 2160 (1978).
73. D. E. Van Horn and E-i. Negishi, J. Am. Chem. Soc., 100, 2252 (1978).
74. N. Okukado and E-i. Negishi, Tetrahedron Lett., 2357 (1978).
75. D. E. Van Horn, L. F. Valente, M. J. Idacavage and E-i. Negishi, J. Organometal. Chem., 156, C20 (1978).
76. B. B. Snider, M. Karras and R. S. E. Conn, J. Am. Chem. Soc., 100, 4624 (1978).
77. A. Marfat, P. R. McGuirk and P. Helquist, Tetrahedron Lett., 1363 (1978).
78. W. E. Truce and M. J. Lusch, J. Org. Chem., 43, 2252 (1978).
79. F. Scott, G. Cahiez, J. F. Normant and J. Villieras, J. Organometal. Chem., 144, 13 (1978).
80. J. G. Duboudin and B. Jousseaume, J. Organometal. Chem., 162, 209 (1978).
81. J. Tsuji, Synth. Comm., 8, 103 (1978).

82. E. R. Evitt and R. G. Bergman, J. Am. Chem. Soc., 100, 3237 (1978).
83. R. Baker, P. C. Bevan, R. C. Cookson, A. H. Copeland and A. D. Gribble, JCS Perkin I, 480 (1978).
84. Y. Tamaru, Y. Yamada, T. Arimoto and Z-i. Yoshida, Chem. Lett., 975 (1978).
85. Y. Tamaru, Y. Yamada and Z-i. Yoshida, J. Org. Chem., 43, 3396 (1978).
86. Y. Tamaru, Y. Yamada and Z-i. Yoshida, Tet. Lett., 919 (1978).
87. Y. Tamaru, Y. Yamada and Z-i. Yoshida, Chem. Lett., 529 (1978).
88. Y. Yamamoto and K. Maruyama, J. Organometal. Chem., 156, C9 (1978).
89. Y. Tanigawa, H. Ohta, A. Sonada and S-i. Murahashi, J. Am. Chem. Soc., 100, 4612 (1978).
90. R. Amouroux and T. H. Chan, Tetrahedron Lett., 4456 (1978).
91. S. J. Bailey, E. J. Thomas, W. B. Truner and J. A. J. Jarvis, JCS Chem. Comm., 474 (1978).
92. D. Samain, C. Descoins and Y. Langlois, Nov. J. Chem., 2, 250 (1978).
93. P. Crabbe, J-M. Dollat, J. Gallina, J-L. Luchi, E. Valardi, M. L. Maddox and L. Tokes, JCS Perkin I, 730 (1978).
94. M. Calellani, G. P. Chiusoli, G. Salerno and F. Dallatomasama, J. Organomet. Chem., 146, C19 (1978).
95. J. L. Ruth and D. E. Bergstrom, J. Org. Chem., 43, 2870 (1978).
96. R. C. Larock, J. C. Bernhardt and R. J. Driggs, J. Organomet. Chem., 156, 45 (1978).
97. G. L. van Mourik and H. J. Pabon, Tetrahedorn Lett., 2705 (1978).
98. F. Sato, H. Kodama and M. Sato, J. Organomet. Chem., 157, C30 (1978).
99. A. Claesson and L.-I. Olsson, JCS Chem. Comm., 621 (1978).
100. P. Barsauti, V. Calo, L. Lopez, G. Marchese, F. Naso and G. Pesce, JCS Chem. Comm., 1085 (1978).
101. P. Place, F. Delbecq and J. Gore, Tetrahedron Lett., 3801 (1978).
102. D. J. Pasto, S-K. Chow, A. Waterhouse, R. H. Shults and G. F. Hennion, J. Org. Chem., 43, 1385 (1978).
103. D. J. Pasto, S-K. Chow, E. Fritzen, R. H. Shults, A. Waterhouse and G. F. Hennion, J. Org. Chem., 43, 1389 (1978).
104. R. Couffignal, Synthesis, 581 (1978).
105. F. Sato, K. Oguro and M. Sato, Chem. Lett., 805 (1978).
106. R. S. Brinkmeyer and T. L. MacDonald, JCS Chem. Comm., 876 (1978).
107. R. A. Amos and J. A. Katzenellenbogen, J. Org. Chem., 43, 555 (1978).
108. A. Doutheau, G. Balme, M. Malacria and J. Gore, Tetrahedron Lett., 1802 (1978).
109. W. H. Pirkle and C. W. Boeder, J. Org. Chem., 43, 1950 (1978).
110. T. Mukaiyama and K. Kawata, Chem. Lett., 785 (1978).
111. A. Claesson and C. Sahlberg, Tetrahedron Lett., 1319 (1978).
112. P. Vermeer, H. Westmijze, H. Kleijn and L. A. van Dijck, Rec. Trav. Chim., 97, 56 (1978).

113. G. Tadema, R. H. Everhardus and P. Vermeer, Tetrahedron Lett., 3935 (1978).
114. F. Sato, H. Kodama and M. Sato, Chem. Lett., 789 (1978).
115. H. Kleijn, H. Westmijze and P. Vermeer, Tetrahedron Lett., 1133 (1978).
116. J. Berlan and K. Koosha, J. Organomet. Chem., 153, 99 (1978).
117. J. Berlan and K. Koosha, J. Organomet. Chem., 153, 107 (1978).
118. J. Berlan, J. P. Battioni and K. Koosha, J. Organomet. Chem., 152, 359 (1978).
119. J. E. McMurray, M. P. Fleming, K. L. Kees and L. R. Krepski, J. Am. Chem. Soc., 43, 3255 (1978).
120. A. L. Baumstark, C. J. McCloskey and K. E. Witt, J. Org. Chem., 43, 3609 (1978).
121. S. Nishida and F. Kataoka, J. Org. Chem., 43, 1612 (1978).
122. Y. Fujiwara, R. Ishikawa, F. Akiyama and S. Teranishi, J. Org. Chem., 43, 2477 (1978).
123. J. E. McMurray, M. G. Silvestri, M. P. Fleming, T. Hoz and M. W. Grayston, J. Org. Chem., 43, 3249 (1978).
124. M. G. Silvestri, Diss. Abstr. Int. B, 38, 698 (1977).
125. H. Ishikawa and Y. Muraiyama, Bull. Chem. Soc. Japan, 51, 2059 (1978).
126. J. Wellmann and E. Steckhan, Synthesis, 901 (1978).
127. P. Bamfield and P. Quan, Synthesis, 537 (1978).
128. J. L. Hall, Diss. Abst. Int. B, 38, 2665 (1977).
129. Y. Funiwara, R. Ishikawa and S. Teranishi, Bull. Chem. Soc. Japan, 51, 589 (1978).
130. T. Kauffmann and H. Lexy, Angew. Chem. Int. Ed., 17, 755 (1978).
131. Y. Kobayashi, T. Taguchi and T. Morikawa, Tetrahedron Lett., 3555 (1978).
132. K. Isagawa, M. Ohige, K. Tatsumi and Y. Otsuji, Chem. Lett., 1155 (1978).
133. R. C. Larock and B. Riefling, J. Org. Chem., 43, 1468 (1978).
134. Y. Watanabe, K. Takatsuki and Y. Takegami, Tetrahedron Lett., 3369 (1978).
135. R. Ketari and A. Foucand, Tetrahedron Lett., 2563 (1978).
136. H. Felkin and B. Meunier, J. Organometal. Chem., 146, 169 (1978).
137. B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton and T. J. Dietsch, J. Am. Chem. Soc., 100, 3407 (1978).
138. B. M. Trost, L. Weber, P. E. Strege, T. J. Fullerton and T. J. Dietsch, J. Am. Chem. Soc., 100, 3416 (1978).
139. B. M. Trost, L. Weber, P. Strege, T. J. Fullerton and T. J. Dietsch, J. Am. Chem. Soc., 100, 3426 (1978).
140. B. M. Trost and T. R. Verhoeven, J. Am. Chem. Soc., 100, 3435 (1978).
141. B. M. Trost and E. Keinan, J. Am. Chem. Soc., 100, 7779 (1978).
142. P. S. Manchand, H. S. Wong and J. F. Blount, J. Org. Chem., 43, 4769 (1978).
143. B. M. Trost and T. R. Verhoeven, Tetrahedron Lett., 2275 (1978).
144. J. C. Fiaud, A. Hibon de Gournay, M. Larcheveque and H. B. Kagan, J. Organomet. Chem., 154, 175 (1978).
145. R. Baker and R. J. Popplestone, Tetrahedron Lett., 3575 (1978).
146. W. R. Jackson and J. U. Strauss, Aust. J. Chem., 31, 1073 (1978).

147. R. C. Larock and M. A. Mitchell, J. Am. Chem. Soc., 100, 180 (1978).
148. C. T. Buse and C. H. Heathcock, Tetrahedron Lett., 1685 (1978).
149. C. Mioskowski, A. Solladie-Davallo and G. Solladie, J. Organomet. Chem., 149, C63 (1978).
150. L. S. Hegedus and B. R. Evans, J. Am. Chem. Soc., 100, 3461 (1978).
151. A. Hosomi and H. Sakuri, Tetrahedron Lett., 2589 (1978).
152. U. Bersellini, G. P. Chiusoli and G. Salerno, Angew. Chem. Int. Ed., 17, 352 (1978).
153. I. Izawa and Y. Mukaiyama, Chem. Lett., 409 (1978).
154. F. N. Tebbe, G. W. Parshall and G. S. Reddy, J. Am. Chem. Soc., 100, 3611 (1978).
155. K. Takai, Y. Hotta, K. Oshima and H. Nozaki, Tetrahedron Lett., 2417 (1978).
156. H. Alper and H. N. Park, J. Am. Chem. Soc., 100, 508 (1978).
157. T. Tsuda, Y. Chujo and T. Saegusa, J. Am. Chem. Soc., 100, 630 (1978).
158. Y. Watanabe, Y. Shimizu, K. Takatsuki and Y. Takegami, Chem. Lett., 215 (1978).
159. K. Mori, S. Tamada and M. Matsui, Tetrahedron Lett., 901 (1978).
160. G. Linstrumelle, R. Lorne and H. P. Dang, Tetrahedron Lett., 4069 (1978).
161. R. P. Szajewski, J. Org. Chem., 43, 1819 (1978).
162. G. Cahiez, A. Alexakis and J. F. Normant, Synthesis, 528 (1978).
163. A. Alexakis, G. Cahiez and J. F. Normant, Tetrahedron Lett., 2027 (1978).
164. R-D. Acker, Tetrahedron Lett., 2399 (1978).
165. R. F. Newton, C. C. Howard, C. P. Reynolds, A. H. Wadsworth, N. M. Crossland, and S. M. Roberts, JCS Chem. Comm., 662 (1978).
166. P. R. McGuirk, A. Marfat and P. Helquist, Tetrahedron Lett., 2465 (1978).
167. S. M. Kupchan, O. P. Dhingra and C-K. Kim, J. Org. Chem., 43, 4076 (1978).
168. C. W. Bird and Y. P. S. Chauhan, Tetrahedron Lett., 2133 (1978).
169. B. Feringa and H. Wynberg, Tetrahedron Lett., 4447 (1977).
170. I. Bodek and G. Davies, Inorg. Chem., 17, 1814 (1978).
171. D. K. Sharma and T. R. Seshadri, Ind. J. Chem., 15B, 939 (1979).
172. A. K. Yatsimirski, A. D. Ryabov and I. V. Berezin, J. Mol. Catal., 4, 151 (1978).
173. V. E. Tarabando and I. V. Kozhevnikov, React. Kinet. Catal. Lett., 8, 77 (1978).
174. M. Hisatomi, S. Koshikawa, K. Chimura, H. Hashimoto and K. Yamakawa, J. Organomet. Chem., 145, 225 (1978).
175. P. S. Waterman and W. P. Giering, J. Organomet. Chem., 155, C47 (1978).
176. A. P. Kozikowski and K. Isobe, JCS Chem. Comm., 1076 (1978).
177. M. Yoshifuji, Chem. Abstr., 89, 24403x (1978).
178. G. Cargianio, P. Del Buttero, S. Maiorana and G. Riccardi, JCS Chem. Comm., 989 (1978).
179. G. Simonneaux, G. Faouen, R. Dabard and M. Louer, Nouv. J. Chim., 2, 203 (1978).

180. R. Dietz, K. H. Doetz and D. Neugebauer, Nouv. J. Chim., 2, 59 (1978).
181. K. H. Doetz and I. Pruskil, Chem. Ber., 111, 2059 (1978).
182. S-i. Murahashi, Y. Yanba, M. Yamamura and N. Yoshimura, J. Org. Chem., 43, 4099 (1978).
183. G. Bartoli, A. Medici, G. Rosini and D. Tavernari, Synthesis, 436 (1978).
184. M. E. Kurz and T-Y R. Chen, J. Org. Chem., 43, 239 (1978).
185. C. Moberg, Acta Chem. Scand., B32, 149; 293 (1978).
186. A. J. Pearson, J. Chem. Soc. Perkin I, 495 (1978).
187. F. Franke and I. D. Jenkins, Aust. J. Chem., 31, 595 (1978).
188. B. Y. Shu, E. R. Biehl and P. C. Reeves, Synth. Comm., 8, 523 (1978).
189. K. Utmoto, M. Tanaka, M. Kitai and H. Nozaki, Tetrahedron Lett., 2301 (1978).
190. G. Cahiez, A. Alexakis and J. F. Normant, Tetrahedron Lett., 3013 (1978).
191. E. J. Corey and D. L. Boger, Tetrahedron Lett., 4597 (1978).
192. A. Marfat and P. Helquist, Tetrahedron Lett., 4217 (1978).
193. A. B. Smith, III., and P. J. Jerris, Synth. Comm., 8, 421 (1978).
194. S. F. Martin and T. S. Chow, J. Org. Chem., 43, 1027 (1978).
195. Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 100, 3240 (1978).
196. H. Westmijze, H. Kleijn and P. Vermeer, Synthesis, 454 (1978).
197. V. Fiandanese, G. Marchese and F. Naso, Tetrahedron Lett., 5130 (1978).
198. H. O. House, W. C. McDaniel, R. F. Sieloff and D. Vanderveer, J. Org. Chem., 43, 4316 (1978).
199. F. Four, P. LeTri and H. Riviere, J. Organomet. Chem., 133, 385 (1977).
200. H. O. House and T. U. Lee, J. Org. Chem., 43, 4369 (1978).
201. J. Drouin, F. Leyendecker and J. M. Conia, Nouv. J. Chim., 2, 267 (1978).
202. F. Leyendecker, J. Drouin and J. M. Conia, Nouv. J. Chim., 2, 271 (1978).
203. H. O. House and J. M. Wilkins, J. Org. Chem., 43, 2443 (1978).
204. H. O. House and W. V. Phillips, J. Org. Chem., 43, 3851 (1978).
205. D. Samain, D. Descoins and Y. Langlois, Nouv. J. Chim., 2, 249 (1978).
206. P. R. McGuirk, D. Marfat and P. Helquist, Tetrahedron Lett., 2973 (1978).
207. F. Ghozland, J. L. Lucke and P. Crabbe, Bull. Soc. Chim. Belg., 87, 369 (1978).
208. E. J. Corey, H. E. Ensley and C. A. Parnell, J. Org. Chem., 43, 1610 (1978).
209. S. Sawada and Y. Inouye, Chem. Abstr., 88, 152788t (1978).
210. E. Piers, I. Nagakura and J. E. Shaw, J. Org. Chem., 43, 3431 (1978).
211. E. Piers, I. Nagakura and H. E. Morton, J. Org. Chem., 43, 3630 (1978).
212. E. Piers and H. E. Morton, JCS Chem. Comm., 1033 (1978).
213. K. E. Harding and C-y. Tseng, J. Org. Chem., 43, 3974 (1978).
214. M. Tada and Y. Takahashi, Chem. Lett., 275 (1978).
215. R. T. Buckler and D. L. Garling, Tetrahedron Lett., 2257 (1978).
216. D. R. Morton and J. L. Thompson, J. Org. Chem., 43, 2102 (1978).
217. C. Luthy, P. Konstantin and K. G. Untch, J. Am. Chem. Soc., 100, 6211 (1978).
218. F. W. Sun and L. Weiler, JCS Chem. Comm., 985 (1978).

219. G. H. Posner, C. E. Whitten, J. J. Sterling, D. J. Brunelle, C. M. Lentz, A. W. Runquist and A. Alexakis, Ann. N.Y. Acad. Sci., 295, 249 (1977).
220. A. Alexakis, M. J. Chapdelaine, G. H. Posner and A. W. Runquist, Tetrahedron Lett., 4205 (1978).
221. M. F. Semmelhack, A. Yamashita, J. C. Tomesch and K. Hirotsu, J. Am. Chem. Soc., 100, 5565 (1978).
222. C. B. Ziegler, Jr., and R. F. Heck, J. Org. Chem., 43, 2941 (1978).
223. N. A. Cortese, C. B. Ziegler, Jr., B. J. Hrnjez and R. F. Heck, J. Org. Chem., 43, 2952 (1978).
224. K. Yamamura, J. Org. Chem., 43, 724 (1978).
225. K. P. Healy and D. Pletcher, J. Organomet. Chem., 161, 109 (1978).
226. R. T. Hansen, D. B. Carr and J. Schwartz, J. Am. Chem. Soc., 100, 2244 (1978).
227. M. J. Loots and J. Schwartz, Tetrahedron Lett., 4381 (1978).
228. H. Schmid, P. Naab and K. Hayakawa, Helv. Chim. Acta, 61, 1427 (1978).
229. J. P. Collman, R. G. Finke, J. N. Cawse and J. I. Brauman, J. Am. Chem. Soc., 100, 4766 (1978).
230. Y. Becker and J. K. Stille, J. Am. Chem. Soc., 100, 838 (1978).
231. I. Rhee, M. Ryang, H. Hasegawa, S. Murai and N. Sonada, Chem. Lett., 15 (1978).
232. I. Matsuda, Chem. Lett., 773 (1978).
233. M. Mori, K. Chiba and Y. Ban, J. Org. Chem., 43, 1684 (1978).
234. M. Mori, K. Chiba and Y. Ban, Heterocycles, 6, 1841 (1977).
235. M. Yamashita and R. Suemitsu, Tetrahedron Lett., 1477 (1978).
236. M. Yamashita and R. Suemitsu, Tetrahedron Lett., 761 (1978).
237. G. Van Koten, J. T. B. H. Jastrzebski and J. G. Noltes, J. Organometal. Chem., 148, 317 (1978).
238. M. El-Chahawi and U. Prange, Chem. Ztg., 102, 1 (1978).
239. C. Botteghi, M. Brance, M. Marchetti and A. Saba, J. Organometal. Chem., 161, 197 (1978).
240. A. Matsuda, S. Shin, J-i. Nakayama, K-i. Bando and K. Murata, Bull. Chem. Soc. Japan, 51, 3016 (1978).
241. W. R. Cullen, B. R. James and G. Strukul, Can. J. Chem., 56, 1965 (1978).
242. A. R. Sanger, J. Mol. Catal., 3, 221 (1978).
243. R. Uson, L. Oro, C. Claver, M. A. Garralda and J. M. Moreto, J. Mol. Catal., 4, 231 (1978).
244. R. M. Laine, J. Am. Chem. Soc., 100, 6451 (1978).
245. C. Cesarotti, A. Fusi, R. Ugo and G. M. Zanderighi, J. Mol. Catal., 4, 205 (1978).
246. F. R. W. P. Wild, G. Gubitosa and H. H. Brinzinger, J. Organometal. Chem., 148, 73 (1978).
247. C. U. Pittman, Jr., and C. C. Lin, J. Org. Chem., 43, 4928 (1978).
248. C. U. Pittman, Jr., A. Hirai, C. Jones, R. M. Hanes and Q. Ng, Ann. N.Y. Acad. Sci., 295, 15 (1977).

249. C. U. Pittman, Jr., and A. Hirao, J. Org. Chem., 43, 640 (1978).
250. W. H. Lang, A. T. Jurewicz, W. O. Haag, D. D. Whitehurst and L. D. Rollmann, Organomet. Polym., 145 (1978).
251. E. Mantovani, N. Palladino and A. Zanobi, J. Mol. Catal., 3, 285 (1978).
252. A. Gupta, A. Rembaum and H. B. Gray, Organomet. Polym., 155 (1978).
253. T. Hayashi, M. Tanaka and I. Ogata, Tetrahedron Lett., 3925 (1978).
254. C. Botteghi, M. Branca, M. Micera, F. Piacenti and G. Menchi, Chim. Ind. (Milan), 60, 16 (1978).
255. Y. Kawabata, T. M. Suzuki and I. Ogata, Chem. Lett., 361 (1978).
256. G. Consiglio, W. Arber and P. Pino, Chim. Ind. (Milan), 60, 396 (1978).
257. V. V. Kashina, M. G. Katsnel'son and G. N. Mishenkova, Zh. Org. Khim., 14, 877 (1978).
258. G. Consiglio, D. A. von Bezard, F. Morandini and P. Pino, Helv. Chim. Acta, 61, 1703 (1978).
259. J. K. Stille and R. Divakaruni, J. Am. Chem. Soc., 100, 1303 (1978).
260. F. Sato, Y. Mori and M. Sato, Chem. Lett., 1337 (1978).
261. K. Yamamoto, J. Yoshitake, N. T. Qui and J. Tsuji, Chem. Lett., 859 (1978).
262. J. J. Eisch and J. E. Galle, J. Organometal. Chem., 160, C8 (1978).
263. T. Izumi, T. Katow, N. Kasabara and K. Hanaya, Bull. Chem. Soc. Japan, 51, 3407 (1978).
264. N. Yoneda, T. Fukuhara, Y. Takahashi and A. Suzuki, Bull. Chem. Soc. Japan, 51, 2347 (1978).
265. H. Alper, J. K. Currie and H. des Abbayes, JCS Chem. Comm., 311 (1978).
266. T. F. Murray, V. Varma, J. R. Horton, J. Org. Chem., 43, 353 (1978).
267. R. C. Larock, B. Riefling and C. A. Fellow, J. Org. Chem., 43, 131 (1978).
268. K. H. Doetz and R. Dietz, J. Organometal. Chem., 157, C55 (1978).
269. R. C. Larock, and J. C. Bernhardt, J. Org. Chem., 43, 710 (1978).
270. B. Christensen and M. S. Scurrell, JCS Faraday Trans. 1, 74, 2313 (1978).
271. B. K. Nefedov, R. V. Dzhaparidze and O. G. Mamaev, Izv. Akad. Nauk SSSR, Ser Khim, 1657 (1978).
272. K. M. Webber, Diss. Abstr. Int. B, 39, 1408 (1978).
273. F. Rivetti and U. Romano, J. Organometal. Chem., 154, 323 (1978).
274. G. Braca, B. Sbrana, G. Valentini, G. Andrich and G. Gregorio, J. Am. Chem. Soc., 100, 6238 (1978).
275. H. Tietz, K. Unverferth and K. Schwetlick, Z. Chem., 17, 368 (1977).
276. H. Tietz, K. Unverferth, and K. Schwetlick, Z. Chem., 18, 98 (1978).
277. H. Tietz, K. Unverferth, D. Sagasser and K. Schwetlick, Z. Chem., 18, 141 (1978).
278. H. Tietz, K. Unverferth and K. Schwetlick, Z. Chem., 18, 217 (1978).
279. B. K. Nefedov, V. I. Manov-Yuvenskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2597 (1977).

280. B. K. Nefedov, V. I. Manov-Yuvenskii and Kh. O. Khoshdurdyev. Izv. Akad. Nauk SSSR, Ser. Khim, 113 (1978).
281. B. K. Nefedov, V. I. Manov-Yuvenskii, A. L. Chimishkyan and V. M. Englin, Kinet. Katal., 19, 1065 (1978).
282. G. L. Blackmer and C-W Tsai, J. Organometal. Chem., 155, C17 (1978).
283. K. Kudo, H. Phala, N. Sugeta and Y. Takezaki, Chem. Lett., 1495 (1977).
284. B. F. G. Johnson, K. D. Karlin and J. Lewis, J. Organometal. Chem., 145, C23 (1978).
285. J. Elzinga and H. Hogeveen, J. Org. Chem., 43, 745 (1978).
286. R. Aumann and J. Knecht, Chem. Ber., 111, 3927 (1978).
287. Y. Seki, S. Murai and N. Sonada, Angew. Chem.IE, 17, 119 (1978).
288. W. A. Herrmann and J. Plank, Angew. Chem. IE, 17, 524 (1978).
289. P. W. Jolly, S. Stobbe, G. Wilke, R. Goddard, C. Krueger, J. C. Sekutowski, and Y. H. Tsay, Angew. Chem., 90, 144 (1978).
290. J. W. Suggs, J. Am. Chem. Soc., 100, 640 (1978).
291. D. H. Doughty and L. H. Pignolet, J. Am. Chem. Soc., 100, 7083 (1978).
292. K. Kawakami, T. Mizoroki and A. Ozaki, Bull. Chem. Soc. Japan, 51, 21 (1978).
293. N. Takahashi, I. Okura and T. Keii, J. Mol. Catal., 3, 277 (1978).
294. A. L. Lapidus, V. V. Mal'tsev, M. I. Loktev, I. V. Mishin and A. A. Slinkin, Chem. Abstr., 88, 136051s (1978).
295. L. V. Mironova, F. K. Shmidt, V. S. Tkach and V. I. Dmitriev, Chem. Abstr., 89, 42272h (1978).
296. S. J. McLain and R. R. Schrock, J. Am. Chem. Soc., 100, 1315 (1978).
297. H. Hobert and J. Korff, J. Organometal. Chem., 152, C39 (1978).
298. P. Binger, M. J. Doyle, J. Organometal. Chem., 162, 195 (1978).
299. P. Binger and A. Brinkmann, Chem. Ber., 111, 2689 (1978).
300. N. Takahashi, I. Okura and T. Keii, J. Mol. Catal., 3, 271 (1978).
301. U. Schuchardt and P. F. Dos Santos Filho, Chem. Abstr., 89, 75269r (1978).
302. E. LeRoy, F. Petit, J. Hennion and J. Nicole, Tetrahedron Lett., 2403 (1978).
303. D. Huchette, B. Thery and F. Petit, J. Mol. Catal., 4, 433 (1978).
304. H. Siegel, H. Hopf, A. Germer and P. Binger, Chem. Ber., 111, 3112 (1978).
305. C. U. Pittman, Jr., and S. E. Jacobson, J. Mol. Catal., 3, 293 (1978).
306. T. Ito and Y. Takami, Bull. Chem. Soc. Japan, 51, 1220 (1978).
307. U. M. Dzhemilev, R. I. Khusnutdinov and G. A. Tolstikov, Zh. Org. Khim., 14, 243 (1978).
308. F. G. Yusupova, G. V. Nurtdinova, G. Gailiunas, G. A. Tolstikov, S. R. Rafikov and V. P. Yur'ev, Dokl. Akad. Nauk SSSR, 239, 1385 (1978).
309. F. G. Yusupova, G. A. Gailiunas, I. I. Furley, A. A. Panasenko, V. D. Sheludyakov, G. A. Tolstikov and V. P. Yur'ev, J. Organometal. Chem., 155, 15 (1978).
310. S. Akutagawa, T. Taketomi, H. Kumobayashi, K. Takayama, T. Someya and S. Otsuka, Bull. Chem. Soc. Japan, 51, 1158 (1978).

311. U. M. Dzhemilev, L. Yu. Gubaidullin and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1469 (1978).
312. J. Tsuji and T. Mandai, Tetrahedron Lett., 1817 (1978).
313. T. Takahashi, K. Kasuga and J. Tsuji, Tetrahedron Lett., 4917 (1978).
314. J. Tsuji, M. Kaito and T. Takahashi, Bull. Chem. Soc. Japan, 51, 547 (1978).
315. J. Tsuji, H. Yasuda and T. Mandai, J. Org. Chem., 43, 3606 (1978).
316. C. U. Pittman, Jr., and Q. Ng, J. Organometal Chem., 153, 85 (1978).
317. Y. Tamaru, M. Kogotani, R. Suzuki and Z-i. Yoshida, Chem. Lett., 1329 (1978).
318. J. Tsuji, M. Kaito, Y. Yamada and T. Mandai, Bull. Chem. Soc. Japan, 51, 1915 (1978).
319. M. Green, G. Scholes and F. G. A. Stone, JCS Dalton, 309 (1978).
320. A. M. Lazutkin and A. I. Lazutkina, React. Kinet. Catal. Lett., 8, 263 (1978).
321. A. M. Lazutkin, V. M. Mastikhin and A. I. Lazutkina, Kinet. Katal., 19, 1061 (1978).
322. A. I. Lazutkina, A. M. Lazutkin and Yu. I. Yermakov, React. Kinet. Catal. Lett., 8, 353 (1978).
323. Yu. I. Ermakov, A. M. Lazutkin, A. I. Lazutkina and V. I. Prozorova, Kinet. Katal., 19, 911 (1978).
324. F. A. Selimov, A. Z. Yakupova and G. A. Tolstijov, Izv. Akad. Nauk SSSR, Ser. Khim., 1412 (1978).
325. U. M. Dzhemilev, A. Z. Yakupova and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1068 (1978).
326. J. D. Umpleby, Helv. Chim. Acta, 61, 2243 (1978).
327. H. Peter and D. Reinehr, Helv. Chim. Acta, 61, 1115 (1978).
328. D. Reinehr, Helv. Chim. Acta, 61, 1122 (1978).
329. R. Baker, M. S. Nobbs and D. T. Robinson, JCS Perkin I, 543 (1978).
330. H. U. Blaser and D. Reinehr, Helv. Chim. Acta, 61, 1118 (1978).
331. J. Tsuji, T. Yamakawa and T. Mandai, Tetrahedron Lett., 565 (1978).
332. R. V. Kunakova, G. A. Tolstikov, U. M. Dzhemilev, F. V. Sharipova and D. L. Sazikova, Izv. Akad. Nauk SSSR, Ser. Khim., 931 (1978).
333. A. Musco, C. Perego and V. Tartiari, Inorg. Chim. Acta, 28, L147 (1978).
334. Y. Inoue, Y. Sasaki and H. Hashimoto, Bull. Chem. Soc. Japan, 51, 2375 (1978).
335. L. Carlton and G. Read, JCS Perkin I, 1631 (1978).
336. M. Yoshifuji, K. I. Gell and J. Schwartz, J. Organometal. Chem., 153, C15 (1978).
337. Y. Inoue, Y. Itoh and H. Hashimoto, Chem. Lett., 911 (1978).
338. H. J. Schmitt and H. Singer, J. Organometal. Chem., 153, 165 (1978).
339. A. Furlani, M-Vittoria Russo and P. Bicev, Gazz. Chim. Ital., 107, 517 (1977).
340. H. Bonnemann, Angew. Chem. IE, 17, 505 (1978).
341. E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day and A. B. Anderson, J. Am. Chem. Soc., 100, 2090 (1978).
342. I. Inoue, Y. Itoh and H. Hashimoto, Chem. Lett., 633 (1978).
343. K. H. Dotz and R. Dietz, Chem. Ber., 111, 2517 (1978).

344. K. P. C. Vollhardt, Nachr. Chem., Tech. Lab., 25, 584 (1977).
345. K. P. C. Vollhardt, Strem. Chem., 6, 1 (1978).
346. B. A. Dolgoplask, Russ. Chem. Rev., 1073 (1978).
347. D. Walther and E. Dinjus, Z. Anorg. Allg. Chem., 440, 22 (1978).
348. J. Blum, B. Zinger, D. Milstein and O. Buchman, J. Org. Chem., 43, 2961 (1978).
349. L-S. Wen, R. C. Zawalski and P. Kovacic, J. Org. Chem., 43, 2435 (1978).
350. T. Yamamoto, Y. Hayashi and A. Yamamoto, Bull. Chem. Soc. Japan, 51, 2091 (1978).
351. P. J. Heenop and J. A. K. DuPlessis, Chem. Abstr., 89, 179301m (1978).
352. J. Beger, R. Sass and G. Zimmermann, J. Prakt. Chem., 320, 283 (1978).
353. S. A. Matlin and P. G. Sammes, JCS Perkin I, 624 (1978).
354. M. Leconte, J. L. Bilhow, W. Reimann and J. M. Bisset, JCS Chem. Comm., 341 (1978).
355. A. Brenner, R. L. Burwell, Jr., J. Catal., 52, 364 (1978).
356. J. L. Bilhou, A. Theolier, A. K. Smith and J. M. Basset, J. Mol. Catal., 3, 245 (1978).
357. Y. I. W. Asawa, S. Ogasaware and M. Soma, Chem. Lett., 1039 (1978).
358. C. Sanchez, R. Keiffer and A. Kiennemann, J. Prakt. Chem., 320, 177 (1978).
359. S. Warwell and P. Buschmeyer, Angew. Chem. IE, 17, 131 (1978).
360. S. Tamagaki, R. J. Card and D. C. Neckers, J. Am. Chem. Soc., 100, 6635 (1978).
361. P. Krausz, F. Garnier and J. E. Dubois, J. Organometal. Chem., 146, 125 (1978).
362. T. J. Katz, Adv. Organometal. Chem., 16, 283 (1977).
363. W. B. Hughes, Ann. N.Y. Acad. Sci., 295, 271 (1977).
364. T. H. Johnson, Diss. Abstr. Int. B, 38, 5941 (1978).
365. W. Priester and M. Rosenblum, JCS Chem. Comm., 26 (1978).
366. R. H. Grubbs and A. Miyashita, J. Am. Chem. Soc., 100, 7416 (1978).
367. R. H. Grubbs and A. Miyashita, J. Organometal. Chem., 161, 371 (1978).
368. N. Takahashi, I. Okura and T. Keii, J. Mol. Catal., 4, 65 (1978).
369. I. Okura, N. Takahashi and T. Keii, J. Mol. Catal., 4, 237 (1978).
370. F. Porta, S. Cenin, S. Giodana and M. Pizzotti, J. Organometal. Chem., 150, 261 (1978).
371. G. Braca, F. Ciardelli, G. Sbrana and G. Valentini, Chim. Ind. (Milan), 59, 766 (1977).
372. Y. Fujita, Chem. Lett., 533 (1978).
373. M. J. D'Aniello, Jr., and E. K. Barefield, J. Am. Chem. Soc., 100, 1474 (1978).
374. J. C. Barborak, L. W. Dasher, A. T. McPhail, J. B. Nichols and K. A. Onan, Inorg. Chem., 17, 2936 (1978).
375. J. Th. Evers and A. Mackor, Tetrahedron Lett., 2321 (1978).
376. R. G. Salomon, A. Sinha and M. F. Salomon, J. Am. Chem. Soc., 100, 520 (1978).
377. S. Sarel, Acc. Chem. Res., 11, 204 (1978).
378. L. A. Paquette and R. Gree, J. Organometal. Chem., 146, 319 (1978).

379. D. Baudry, M. Ephritikhine and H. Felkin, Nouv. J. Chim., 2, 355 (1978).
380. D. Baudry, M. Ephritikhine and H. Felkin, JCS Chem. Comm., 694 (1978).
381. H. Kumobayashi, S. Akutagawa and S. Otsuka, J. Am. Chem. Soc., 100, 3949 (1978).
382. P. A. Grieco and N. Marinovic, Tetrahedron Lett., 2545 (1978).
383. G. Balavoine, G. Bram and F. Guibe, Nouv. J. Chim., 2, 207 (1978).
384. O. J. Muscio, Jr., Y. M. Jun and J. B. Philip, Jr., Tetrahedron Lett., 2379 (1978).
385. S. Purro, A. Pryde, J. Zsinkay and H. Schmid, Helv. Chim. Acta, 61, 266 (1978).
386. H. Hogeveen and B. J. Nusse, J. Am. Chem. Soc., 100, 3110 (1978).
387. P. X. Iten and C. H. Eugster, Helv. Chim. Acta, 61, 1133 (1978).
388. P. E. Eaton and D. R. Patterson, J. Am. Chem. Soc., 100, 2573 (1978).
389. P. E. Eaton and U. R. Chakrabortz, J. Am. Chem. Soc., 100, 3634 (1978).
390. W. Burns, M. A. McKervey, T. R. B. Mitchell and J. J. Rooney, J. Am. Chem. Soc., 100, 906 (1978).
391. R. J. Card and D. C. Neckers, J. Org. Chem., 43, 2958 (1978).
392. R. M. Giddings and D. Whittaker, Tetrahedron Lett., 4077 (1978).
393. L. A. Paquette and M. R. Detty, Tetrahedron Lett., 713 (1978).
394. R. Aumann and J. Knecht, Chem. Ber., 111, 3429 (1978).
395. W. Tochtermann and H. Timm, Tetrahedron Lett., 2145 (1978).
396. M. Bonadeo, R. Gandolfi and C. DeMicheli, Gazz. Chim. Ital., 107, 577 (1977).
397. Y. Becker, A. Eisenstadt and Y. Shvo, Tetrahedron, 34, 799 (1978).
398. V. Bilik, L. Petrus and J. Zemek. Chem. Abstr., 89, 163864m (1978).
399. V. Bilik, E. Jurcova and V. Sutoris, Chem. Abstr., 89, 163876s (1978).
400. J. W. Faller, Adv. Organometal. Chem., 16, 211 (1977).
401. M. Tsutsui and A. Courtney, Adv. Organometal. Chem., 16, 241 (1977).
402. J. Sobczak and J. J. Ziolkowski, Inorg. Chim. Acta, 19, 15 (1976).
403. V. N. Sapunov, I. Yu. Litvintsev, G. I. Magomedov and I. Margitfal'vi, Chem. Abstr., 88, 61797d (1978).
404. C. Doebler and E. Hoeft, Z. Chem., 18, 218 (1978).
405. I. Ahmad and M. Aijaz Beg, Indian J. Chem., Sect. A, 16, 475 (1978).
406. S. Paraskewaw and D. Konstandinidis, Chem.-Ztg., 102, 236 (1978).
407. T. Takahashi, H. Nagashima and J. Tsuji, Tetrahedron Lett., 799 (1978).
408. N. P. Allen, F. O. Bamero, R. P. Burns and C. A. McAuliffe, Inorg. Chim. Acta, 28, 231 (1978).
409. H. Arai and M. Yashiro, J. Mol. Catal., 3, 427 (1978).
410. E. G. Levedeva, A. V. Devekki, Yu. I. Malov, D. V. Mushenko and V. S. Volkova, Zh. Org. Khim., 14, 1589 (1978).
411. G. Read, J. Mol. Catal., 4, 83 (1978).
412. F. Igersheim and H. Mimoun, J. Chem. Soc., Chem. Commun., 559 (1978).
413. H. Mimoun, M. Mercedes Perez Marchirant and I. Seree de Roch, J. Am. Chem. Soc., 100, 5437 (1978).

414. H. W. S. Chan, V. K. Newby and G. Levett, J. Chem. Soc., Chem. Commun., 82 (1978).
415. G. P. Panigrahi and P. K. Misro, Indian J. Chem., Sect. A, 16A, 201 (1978).
416. K. Witkiewicz and Z. Chabudzinski, Rocz. Chem., 51, 2155 (1977).
417. L. Bassignani, A. Brandt, V. Caciagli and L. Re, J. Org. Chem., 43, 4245 (1978).
418. W. G. Salmond, M. A. Barta and J. L. Havene, J. Org. Chem., 43, 2057 (1978).
419. J. M. Reuter, A. Sinha and R. G. Salomon, J. Org. Chem., 43, 2438 (1978).
420. S. E. Jacobson, R. Tang and F. Mares, J. Chem. Soc., Chem. Commun., 888 (1978).
421. E. Vedejs, D. A. Engler and J. E. Telschow, J. Org. Chem., 43, 188 (1978).
422. N. J. Lewis and S. Y. Gabhe, Aust. J. Chem., 31, 2091 (1978).
423. J. M. J. Frechet, J. Warnock and M. J. Farrall, J. Org. Chem., 43, 2618 (1978).
424. Y. Tsuda and S. Nakajima, Chem. Lett., 1397 (1978).
425. I. Tabushi and N. Koga, Tetrahedron Lett., 5017 (1978).
426. G. Descotes, J. Sabadie and D. Sinow, Tetrahedron Lett., 3351 (1978).
427. K. Ohkubo, I. Terada and K. Yoshinaga, Bull. Chem. Soc. Japan, 51, 2807 (1978).
428. K. Nakagawa, S. Mineo and S. Kawamura, Chem. Pharm. Bull., 26, 299 (1978).
429. R. Hanzlik and M. Leinwetter, J. Org. Chem., 43, 438 (1978).
430. J. Tsuji and H. Takayanagi, Tetrahedron, 34, 641 (1978).
431. M. M. Rojic and T. R. Demmin, J. Am. Chem. Soc., 100, 5472 (1978).
432. J. Tsuji and H. Takayanagi, Org. Synth., 57, 33 (1977).
433. D. C. Ayres, J. Chem. Soc., Perkin Trans. 1, 585 (1978).
434. A. Adachi, R. Imai and M. Ogawa, Chem. Lett., 611 (1978).
435. G. A. Olah and J. Welch, J. Org. Chem., 43, 2830 (1978).
436. J. N. Shah and C. K. Shah, J. Org. Chem., 43, 1266 (1978).
437. U. M. Dzhemilev, A. Z. Yajupova, S. K. Minsker and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., 678 (1978).
438. T.-Y. Lin, C. H. Lai and S. W. Tam, Tetrahedron Lett., 5011 (1978).
439. Y. Saito, N. Yamazoe and T. Seiyama, Chem. Lett., 839 (1978).
440. P. P. Fu and R. G. Harvey, Chem. Rev., 78, 317 (1978).
441. S. Hietkamp, D. J. Stufkens and K. Vrieze, J. Organometal. Chem., 152, 347 (1978).
442. N. Minami and S. Kijima, Chem. Abstr., 89, 75337m (1978).
443. J. R. Maloney, R. E Lyle, J. E. Saavedra and G. G. Lyle, Synthesis, 212 (1978).
444. J. Yoshida, K. Tamao, A. Kurita and M. Kumada, Tetrahedron Lett., 1809 (1978).
445. H. S. Veale, J. Levin and D. Sivern, Tetrahedron Lett., 503 (1978).
446. R. Tang, S. E. Diamond, N. Neary and F. Mares, JCS Chem. Comm., 562 (1978).
447. G. A. McClusky, Diss. Abstr. Int. B., 38, 5383 (1978).
448. A. Nishinaga, Biochem. Med. Aspects. Act. Oxygen, (Pap. Symp.), 13 (1978).
449. J. E. Lyons, Aspects Homogeneous Catal., 3, 1 (1977).
450. T. F. Blackburn, Diss. Abstr. Int. B., 37, 3192 (1978).

451. M. D. Fryzuk and B. Bosnich, J. Am. Chem. Soc., 100, 5491 (1978).
452. G. Descotes, D. LaFont and D. Sinou, J. Organometal. Chem., 150, C14 (1978).
453. K. Hanaki, K. Kashiwabara and J. Fujita, Chem. Lett., 489 (1978).
454. K. Yamamoto, A. Tomita and J. Tsuji, Chem. Lett., 3 (1978).
455. L. Horner and B. Schlotthauer, Phosphorus Sulfur, 4, 155 (1978).
456. W. R. Cullen and Y. Sugi, Tetrahedron Lett., 1635 (1978).
457. R. Jackson and D. J. Thompson, J. Organometal. Chem., 159, C29 (1978).
458. K. Achiwa, Tetrahedron Lett., 1475 (1978).
459. K. Achiwa, Chem. Lett., 561 (1978).
460. I. Ojima, T. Kogure and K. Achiwa, Chem. Lett., 567 (1978).
461. K. Achiwa, Tetrahedron Lett., 2583 (1978).
462. K. Achiwa and T. Soga, Tetrahedron Lett., 1119 (1978).
463. K. Achiwa, T. Kogure and I. Ojima, Chem. Lett., 297 (1978).
464. K. Achiwa, Heterocycles, 8, 247 (1977).
465. K. Achiwa, Y. Ohga and Y. Iitaka, Tetrahedron Lett., 4683 (1978).
466. J. Solodar, J. Org. Chem., 43, 1787 (1978).
467. B. R. James, R. S. McMillan, R. H. Morris and D. K. W. Wang, Adv. Chem. Ser., 167 (1978).
468. L. M. Koroleva, E. V. Borisov, V. K. Latov and V. M. Belikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1765 (1978).
469. G. Consiglio and P. Pino, Israel J. Chem., 15, 221 (1977).
470. C. Detellier, G. Gelbard and H. B. Kagan, J. Am. Chem. Soc., 100, 7556 (1978).
471. K. E. Koenig and W. S. Knowles, J. Am. Chem. Soc., 100, 7561 (1978).
472. J. M. Brown and P. A. Chaloner, JCS Chem. Commun., 321 (1978).
473. B. R. James and D. Mahajan, Israel J. Chem., 15, 214 (1977).
474. J. Vilim and J. Hetflejs, Collect. Czech. Chem. Commun., 43, 122 (1978).
475. R. Glaser, S. Geresh, J. Blumenfeld, B. Vainas and M. Twach, Israel J. Chem., 15, 17 (1977).
476. R. Glaser, S. Geresh, J. Blumenfeld and M. Twack, Tetrahedron, 34, 2405 (1978).
477. R. Glaser, S. Geresh, M. Twack and N. L. Benocton, Tetrahedron, 34, 3617 (1978).
478. I. Ojima and T. Kogure, Chem. Lett., 1145 (1978).
479. J. M. Brown and P. A. Chaloner, Tetrahedron Lett., 1877 (1978).
480. G. Paiaro and L. Pandolfo, Gazz. Chim. Ital., 107, 467 (1977).
481. E. I. Klabunovskii and A. A. Vedenyapin, Chem. Abstr., 88, 61803c (1978).
482. J. F. Peyronel and H. B. Kagan, Nouv. J. Chim., 2, 211 (1978).
483. K. Ohkubo, T. Ohgushi, T. Kusaga and K. Yoshinaga, Inorg. Nucl. Chem. Lett., 13, 631 (1977).
484. K. Ohkubo, K. Sugahara, I. Terada and K. Yoshinaga, Inorg. Nucl. Chem. Lett., 14, 297 (1978).
485. K. Hara and Y. Kataoka, Tetrahedron Lett., 2103 (1978).
486. A. A. Vedenyapin, E. I. Klabunovskii, E. V. Leonova, G. Kh. Areshidze and N. E. Barannikova, Izv. Akad. Nauk SSSR, Ser. Khim., 206 (1978).

487. I. Ojima, K. Yamamoto, M. Kumada, Aspects Homogeneous Catal., 3, 185 (1977).
488. Y. Orito, Chem. Abstr., 88, 73719t (1978).
489. Anon., Chem. Abstr., 88, 152942p (1978).
490. G. W. Erickson, Diss. Abstr. Int. B., 39, 748 (1978).
491. N. Takashi, I. Imai, C. A. Bertelo and J. K. Stille, J. Am. Chem. Soc., 100, 264 (1978).
492. T. Masuda and J. K. Stille, J. Am. Chem. Soc., 100, 268 (1978).
493. M. E. Wilson and G. M. Whitesides, J. Am. Chem. Soc., 100, 306 (1978).
494. K. Achiwa, Chem. Lett., 905 (1978).
495. V. K. Latov, V. M. Belikov, T. A. Belyaeva, A. I. Vinogradova and S. I. Soinov, Izv. Akad. Nauk SSSR, Ser. Khim., 2481 (1977).
496. N. L. Holy, J. Org. Chem., 43, 4686 (1978).
497. M. Terasawa, K. Kaneda, T. Imanaki and S. Teranishi, J. Catal., 51, 406 (1978).
498. F. Pinna, C. Candilera, G. Strukul, M. Bonivento and M. Graziani, J. Organometal. Chem., 159, 91 (1978).
499. J. Manassen and Y. Dror, J. Mol. Catal., 3, 227 (1978).
500. C. Allandrieu, G. Descotes, J. P. Praly and J. Sabadie, Bull. Soc. Chim. Fr., 519 (1977).
501. R. H. Grubbs and E. M. Sweet, J. Mol. Catal., 3, 259 (1978).
502. H. Arai, J. Catal., 51, 135 (1978).
503. E. S. Chandrasekaran, D. A. Thompson and R. W. Rudolph, Inorg. Chem., 17, 760 (1978).
504. V. Z. Sharf, V. D. Kopylova, L. P. Karapetyan, E. L. Frumkina, L. Kh. Freidlin, K.M. Saldadze and V. N. Krutii, Izv. Akad. Nauk SSSR, Ser. Khim., 2746 (1977).
505. J. J. Rafalko, J. Lieto, B. C. Gates and G. L. Schrader, Jr., JCS Chem. Commun., 540 (1978).
506. M. S. Jarrell, B. C. Gates and E. D. Nickolson, J. Am. Chem. Soc., 100, 5727 (1978).
507. J. Reed, P. Eisenberger, B-K. Teo, and B.M. Kincaid, J. Am. Chem. Soc., 100, 2375 (1978).
508. H. Hirai, Y. Nakao and N. Toshima, Chem. Lett., 545 (1978).
509. V. L. Kuznetsov, B. N. Kuznetsov and Yu. I. Ermakov, Kinet. Katal., 19, 346 (1978).
510. E. Ucciani and P. Ranguis, C. R. Hebd. Seances Acad. Sci., Ser. C., 286, 629 (1978).
511. G. Carturan and V. Gottardi, J. Mol. Catal., 4, 349 (1978).
512. S. Siegel and G. Perot, JCS Chem. Commun., 114 (1978).
513. E. E. Gonzo and M. Boudart, J. Catal., 52, 462 (1978).
514. P. H. Otero-Schipper, Diss. Abstr. Int. B., 38, 5492 (1978).
515. A. F. Borowski, D. J. Cole-Hamilton, G. Wilkinson, Nouv. J. Chim., 2, 137 (1978).
516. B. Giovannitti, M. Ghedini, G. Dolcetti and G. Dent, J. Organometal. Chem., 157, 457 (1978).

517. W. DeAquino, R. Bonnaire and C. Potvin, J. Organometal. Chem., 154, 159 (1978).
518. W. Strohmeier, H. Steigerwald, M. Lukaid, J. Organometal. Chem., 144, 135 (1978).
519. R. S. P. Hsi, J. Labelled Compd. Radiopharm., 14, 515 (1978).
520. C. Rousseau, M. Evrard and F. Petit, J. Mol. Catal., 3, 309 (1978).
521. C. R. Bennett, Diss. Abstr. Int. B., 38, 5358 (1978).
522. S. Vancheesan, S. Sethi, J. Rajaram and J. C. Kuriacose, Indian J. Chem., Sect. A., 16A, 399 (1978).
523. Y. Eden, D. Fraenkel, M. Cais and E. A. Halevi, Israel J. Chem., 15, 223 (1977).
524. L. S. Stuhl and E. L. Muetterties, Inorg. Chem., 17, 2148 (1978).
525. D. S. Gill, C. White and P. M. Maitlis, JCS Dalton, 617 (1978).
526. E. C. Ashby, J.J. Lin and A. B. Goel, J. Org. Chem., 43, 757 (1978).
527. D. R. Paulson, L. S. Gilliam, V. O. Terry, S. M. Farr, E. J. Parker, F. Y. N. Tang, R. Ullman and G. Ribar, J. Org. Chem., 43, 1783 (1978).
528. E. C. Ashby and J. J. Lin, J. Org. Chem., 43, 2567 (1978).
529. M. A. Bennett, T-N. Huang, A. K. Smith and T. W.Turney, JCS Chem. Comm., 582 (1978).
530. K. Klabunde, B. B. Anderson, M. Bader and L. J. Radonovich, J. Am. Chem. Soc., 100, 1313 (1978).
531. L. S. Stuhl, M. Rakowski DuBois, F. J. Hirsekorn, J. R. Bleeke, A. E. Stevens, and E. L. Muetterties, J. Am. Chem. Soc., 100, 2405 (1978).
532. H. Watanabe, M. Aoki, N. Sakurai, K-i. Watanabe and Y. Nagai, J. Organometal. Chem., 160, C1 (1978).
533. G. K. I. Magomedov, K. A. Andrianov, O. V. Shkolnik, B. A. Izmailov and V. N. Kalinin, J. Organometal. Chem., 149, 29 (1978).
534. J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto and J. I. Brauman, J. Am. Chem. Soc., 100, 1119 (1978).
535. M. Fraudi-Neumann, D. Martina and F. Brion, Angew. Chem. IE, 17, 690 (1978).
536. N. A. Cortese and R. F. Heck, J. Org. Chem., 43, 3985 (1978).
537. M. Yamashita, Y. Watanabe, T-a. Mitsudo and Y. Takegami, Bull. Chem. Soc. Japan., 51, 835 (1978).
538. E. Ucciani, A. Pelloquin and G. Cecchi, J. Mol. Catal., 3, 363 (1978).
539. N. Yamamoto, H. Kanai and K. Tarama, Chem. Lett., 1377 (1977).
540. F. Sato, S. Haga and M. Sato, Chem. Lett., 999 (1978).
541. A. W. Messing, F. P. Ross, A. W. Norman and W. H. Okamura, Tetrahedron Lett., 3635 (1978).
542. G. Carturan and G. Strukul, J. Organometal. Chem., 157, 475 (1978).
543. J. Grant, R. B. Moyes and P. B. Wells, J. Catal., 51, 355 (1978).
544. P. Kripylo, P. Muench, T. Borchert and D. Klose, Chem. Abstr., 89, 23458g (1978).
545. V. V. Kaverin, I. M. Salimgareeva, V. P. Yur'ev, J. Gen. Chem., 48, 103 (1978).

546. I. Ojima and M. Kumagai, J. Organometal. Chem., 157, 359 (1978).
547. R. A. Benkeser, F. M. Merritt, II., and R. T. Roche, J. Organometal. Chem., 156, 235 (1978).
548. V. Vaisarova, J. Schraml and J. Hetflejs, Collect. Czech. Chem. Commun., 43, 265 (1978).
549. G. Mestroni, R. Spogharich, A. Camus, F. Martinelli and G. Zassinovick, J. Organometal. Chem., 157, 345 (1978).
550. W. Strohmeier and L. Weigelt, J. Organometal. Chem., 145, 189 (1978).
551. P. Frediani, U. Matteoli, M. Bianchi, F. Piacenti and G. Menchi, J. Organometal. Chem., 150, 273 (1978).
552. B. R. James and R. H. Morris, JCS Chem. Commun., 929 (1978).
553. M. Ichikawa, JCS Chem. Commun., 566 (1978).
554. J. L. Luche, J. Am. Chem. Soc., 100, 2227 (1978).
555. T. N. Sorrell, Tetrahedron Lett., 4985 (1978).
556. J. J. Brunet, L. Mordenti and P. Caubere, J. Org. Chem., 43, 4804 (1978).
557. S. Toros, B.Heil and L. Marko, J. Organometal. Chem., 159, 401 (1978).
558. O. Ojima, T. Kogure, T. Terasaki and K. Achiwa, J. Org. Chem., 43, 3444 (1978).
559. M. Fiorini, F. Marcati, G. M. Giongo, J. Mol. Catal., 3, 385 (1978).
560. H. Ozaki, Bull. Chem. Soc. Japan, 51, 257 (1978).
561. V. Z. Sharf, L. Kh. Freidlin, I. S. Shekoyan and V. N. Krutii, Izv. Akad. Nauk SSSR, Ser. Khim., 1064 (1978).
562. M. M. Wegner and H. Rapoport, J. Org. Chem., 43, 3841 (1978).
563. E. C. Ashby, J-J. Lin and A. B. Goel, J. Org. Chem., 43, 183 (1978).
564. G. W. J. Fleet, C. J. Fuller and P. J. C. Harding, Tetrahedron Lett., 1437 (1978).
565. T. N. Sorrell and R. J. Spillane, Tetrahedron Lett., 2473 (1978).
566. P. Helquist, Tetrahedron Lett., 1913 (1978).
567. H. Zask and P. Helquist, J. Org. Chem., 43, 1621 (1978).
568. R. H. Kinney, W. D. Jones and R. G. Bergman, J. Am. Chem. Soc., 100, 635 (1978).
569. R. J. Kinney, W. D. Jones and R. G. Bergman, J. Am. Chem. Soc., 100, 7902 (1978).
570. J. J. Brunet, R. Vanderesie and P. Caubere, J. Organometal. Chem., 157, 125 (1978).
571. E. C. Ashby and J. J. Lin, J. Org. Chem., 43, 1263 (1978).
572. P. Kvintovics, B. Heil, J. Palagyi and L. Marko, J. Organometal. Chem., 148, 311 (1978).
573. G. Cannelli, F. Manescalchi, A. Umani-Ronchi and M. Panunzion, J. Org. Chem., 43, 1598 (1978).
574. D. Bright-Angrand, B. Muckensturm, J. Chem. Res. (S), 274 (1977).
575. N. L. Holy, JCS Chem. Commun., 1074 (1978).
576. O. Christofis, J. J. Habeeb, R. S. Steevensz and D. G. Tuck, Can. J. Chem., 56, 2269 (1978).

577. R. M. Freidinger, R. Hirschmann and D. F. Veber, J. Org. Chem., 43, 4800 (1978).
578. S. B. Tong, K. F. O'Driscoll and G. L. Rempel, Can. J. Chem. Eng., 56, 340 (1978).
579. B. Stanovik, M. Tisler, S. Polanc and M. Graener, Synthesis, 65 (1978).
580. G. H. Posner and P.-W. Tang, J. Org. Chem., 43, 4131 (1978).
581. J. Drabowicz and M. Mikolycyzk, Synthesis, 138 (1978).
582. M. Berry, S. G. Davies and M. L. H. Green, JCS Chem. Commun., 99 (1978).
583. G. Olah and G. K. Surya Prakash, Synthesis, 397 (1978).
584. T. Nishiguchi, K. Tanaka and K. Fukuzumi, J. Org. Chem., 43, 2968 (1978).
585. T. Funabiki, Y. Yamazaki and K. Tarama, JCS Chem. Commun., 63 (1978).
586. G. A. Olah, G. Surya Prakash and S. C. Narang, Synthesis, 825 (1978).
587. S. C. Welch and M. E. Walters, J. Org. Chem., 43, 2715 (1978).
588. P. Balaz, I. Sotak and R. Domansky, Chem. Abstr., 89, 197001t (1978).
589. T. Hattori, R. L. Burwell, Jr., JCS Chem. Commun., 127 (1978).
590. R. M. Laine, D. W. Thomas, L. W. Cary and S. E. Buttrill, J. Am. Chem. Soc., 100, 6527 (1978).
591. T. Yoshida, Y. Ueda and S. Otsuka, J. Am. Chem. Soc., 100, 3941 (1978).
592. R. G. Rinker, P. C. Ford, C. Ungermann, R. M. Laine, V. Landis and S. A. Moya, J. Am. Chem. Soc., 100, 4595 (1978).
593. R. B. King, C. C. Frazier, R. M. Hanes, and A. D. King, Jr., J. Am. Chem. Soc., 100, 2929 (1978).
594. K. Cann, T. Cole, W. Slegeir and R. Pettit, J. Am. Chem. Soc., 100, 3969 (1978).
595. R. Pettit, C. Mauldin, T. Cole and H. Kang, Ann. N.Y. Acad. Sci., 295, 151 (1977).
596. G. Fachinetti, C. Floriani, A. Roselli and S. Pucci, JCS Chem. Commun., 269 (1978).
597. J. A. Labinger, K. S. Wong and W. R. Scheidt, J. Am. Chem. Soc., 100, 3254 (1978).
598. J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw. J. Am. Chem. Soc., 100, 2716 (1978).
599. J. W. Rathke and H. M. Feder, J. Am. Chem. Soc., 100, 3623 (1978).
600. R. C. Everson, E. T. Woodburn, A. R. M. Kirk, J. Catal., 53, 186 (1978).
601. K. Tagaki, N. Hayana and T. Okamoto, Chem. Lett., 191 (1978).
602. K. Tagaki, N. Hayama and S. Inokawa, Chem. Lett., 1435 (1978).
603. E. Mincione, G. Ortaggi and A. Sirna, Tetrahedron Lett., 4575 (1978).
604. W. A. Nugent, Tetrahedron Lett., 3427 (1978).
605. Y. H. Kim, K. Shinhama and S. Oae, Tetrahedron Lett., 4519 (1978).
606. H. Matsumoto, T. Nakano, M. Kato and Y. Nagai, Chem. Lett., 223 (1978).
607. R. W. Rendell and B. Wright, Tetrahedron, 34, 197 (1978).
608. C. Gerogoulis and J. M. Valery, Synthesis, 402 (1978).
609. F. Sato, Y. Mori and M. Sato, Chem. Lett., 833 (1978).

610. Y. Inoue, S. Ohno and H. Hashimoto, Chem. Lett., 367 (1978).
611. H. Matsumoto, T. Nakano, Y. Nagai and H. Kono. Bull. Chem. Soc. Japan, 51, 2445 (1978).
612. H. Matsumoto, T. Nakano, K. Takasu and Y. Nagai, J. Org. Chem., 43, 1734 (1978).
613. H. Matsumoto, T. Nakano, T. Nakaido and Y. Nagai, Chem. Lett., 115 (1978).
614. V. S. Shestakova, S. M. Brailovskii, O. N. Temkin and G. I. Tarasava, Kinet. Katal., 19, 157 (1978).
615. T. Tsuda, H. Washito, K. Watanabe, M. Miwa and T. Saegusa, JCS Chem. Commun., 815 (1978).
616. E. Herranz and K. B. Sharpless, J. Org. Chem., 43, 2544 (1978).
617. D. W. Patrick, L. K. Truesdale, S. A. Biller and R. B. Sharpless, J. Org. Chem., 43, 2678 (1978).
618. E. Herranz, S. A. Biller and K. B. Sharpless, J. Am. Chem. Soc., 100, 3596 (1978).
619. H. Drignez, J-P. Vermes and J. Lessard, Can. J. Chem., 56, 119 (1978).
620. A. N. Nesmeyanov, L. S. Isaeva and T. A. Peganova, Dokl. Akad. Nauk SSSR, 240, 352 (1978).
621. S. Ozaki and A. Tamaki, Bull. Chem. Soc. Japan, 51, 3391 (1978).
622. J-E. Backvall, Tetrahedron Lett., 163 (1978).
623. B. A. Patel and R. F. Heck, J. Org. Chem., 43, 3898 (1978).
624. T. Kohara, T. Yamamoto and A. Yamamoto, J. Organometal. Chem., 154, C37 (1978).
625. L. S. Liebeskind, K. B. Sharpless, R. D. Wilson and J. Ibers, J. Am. Chem. Soc., 100, 7062 (1978).
626. Anon. Res. Discl., 169, 35 (1978).
627. G. A. Chukhadzhyan, N. A. Gevorkyan and A. Zh. Gevorkyan, Chem. Abstr., 89, 108394h (1978).
628. K. Toshida, M. Matsuoka, T. Ueyama, Y. Yamashita and T. Kitao, Chem. Lett., 765 (1978).
629. S. Arai, M. Hida and T. Yamagishi, Bull. Chem. Soc. Japan, 51, 277 (1978).
630. H. S. Freeman, J. R. Butler and L. D. Freedman, J. Org. Chem., 43, 4975 (1978).
631. K. Kikuchi, Y. Maki and K. Sato, Bull. Chem. Soc. Japan, 51, 2338 (1978).
632. S. P. Paraskewas, Synthesis, 47 (1978).
633. Y. Watanabe, M. Yamamoto, T-u Mitsudo and Y. Takegami, Tetrahedron Lett., 1289 (1978).
634. M. V. Klyuev, M. V. Gapeeva and M. L. Khidekel, Izv. Akad. Nauk SSSR, Ser. Khim., 2140 (1978).
635. E. A. Jeffrey, O. Johansen and A. Meisters, Aust. J. Chem., 31, 79 (1978).
636. S. Murahashi, T. Hirano and T. Yano, J. Am. Chem. Soc., 100, 348 (1978).
637. K. Akashi, R. E. Palermo and K. B. Sharpless, J. Org. Chem., 43, 2063 (1978).
638. M. Yamashita, K. Mizushima, Y. Watanabe, T. Mitsudo and Y. Takegami, Chem. Lett., 1355 (1978).

639. Y. Yoshida and S. Inoue, Bull. Chem. Soc. Japan, 51, 559 (1978).
640. I. Rhee, M. Ryang, H. Hasegawa, S. Murai and N. Sonada, Chem. Lett., 15 (1978).
641. H. Hormo, T. Ito and A. Yamamoto, Chem. Lett., 17 (1978).
642. J. A. Landgrebe and H. Iranmanesch, J. Org. Chem., 43, 1244 (1978).
643. A. Toshimitsu, Y. Kozawa, S. Uemura and M. Okano, JCS Perkin 1, 1273 (1978).
644. Y. Ichinohe, H. Sakamake and N. Kameda, Chem. Lett., 835 (1978).
645. T. Oishi, M. Fujui and Y. Endo, Heterocycles, 7, 947 (1977).
646. G. Cahiez, J. F. Normant, Bull. Soc. Chim. Fr., 570 (1977).
647. M. Kubota and A. Yamamoto, Bull. Chem. Soc. Japan, 51, 2909 (1978).
648. K. Takeshita, S. Makamura and K. Kawamoto, Bull. Chem. Soc. Japan, 51, 2622 (1978).
649. G. R. Mallavarapu and K. Narasimhan, Indian J. Chem., Sect. B., 16B, 725 (1978).
650. L. S. Hegedus, G. F. Allen, J. J. Bozell and E. L. Waterman, J. Am. Chem. Soc., 100, 5800 (1978).
651. B. M. Trost, S. A. Godleski and J. P. Genet, J. Am. Chem. Soc., 100, 3930 (1978).
652. M. Mori and Y. Ban, Heterocycles, 9, 391 (1978).
653. T. Itahara and T. Sakakibara, Synthesis, 607 (1978).
654. Y. Ito, Y. Inubushi, T. Sugaya, K. Kobayashi and T. Saegusa, Bull. Chem. Soc. Japan, 51, 1186 (1978).
655. A. Stutz and H. Reinshagen, Tetrahedron Lett., 2821 (1978).
656. J. Lessard and R. Cote, J. Org. Chem., 43, 3750 (1978).
657. Y. Watanabe, K. Takatsuki, S. C. Shim, T-a Mitsudo and Y. Takegami, Bull. Chem. Soc. Japan, 51, 3397 (1978).
658. K. Kikuchi, Y. Maki, E. Nomata and K. Tada, Chem. Lett., 677 (1978).
659. H. W. Fruhauf, A. Landers, R. Goddard and C. Kruger, Angew. Chem. IE, 17, 64 (1978).
660. T. Hosokawa, S. Miyagi, S-i. Murahashi and A. Sonoda, JCS Chem. Commun., 687 (1978).
661. T. Hosokawa, S. Miyagi, S-i. Murahashi and A. Sonada, J. Org. Chem., 43, 2752 (1978).
662. T. Nomura, T. Fukai and M. Katayanagi, Heterocycles, 6, 1847 (1977).
663. H. Matsumoto, T. Nakano, K. Ohkawa and Y. Nagai, Chem. Lett., 363 (1978).
664. D. R. Fahey, J. E. Mahan, J. Mol. Catal., 3, 447 (1978).
665. B. W. S. Kolthammer, P. Legzdins and D. T. Martin, Tetrahedron Lett., 323 (1978).
666. J. Tsuji, T. Yamakawa, M. Kaito and T. Mandai, Tetrahedron Lett., 2075 (1978).
667. E. Keinan and Y. Mazur, J. Org. Chem., 43, 1020 (1978).
668. T-L. Ho, Synth. Comm., 8, 15 (1978).

669. S. Hanessian and G. Patel, Tetrahedron Lett., 1035 (1978).
670. G. Buchii, P. H. Liang and H. Wuest, Tetrahedron Lett., 2763 (1978).
671. O. Attanasi and S. Gasperion, Gazz. Chim. Ital., 108, 137 (1978).
672. O. Attanasi, S. Gasperoni and C. Carletti, Chim. Ind. (Milan), 60, 654 (1978).
673. D. E. Laycock and M. C. Baird, Tetrahedron Lett., 3307 (1978).
674. J. Th. M. Evers and A. Mackor, Tetrahedron Lett., 821 (1978).
675. J. Th. M. Evers and A. Mackor, Tetrahedron Lett., 2317 (1978).
676. R. G. Salomon, Adv. Chem. Ser., 168, 174 (1978).
677. R. S. Paonessa, P. J. Giordano and M. S. Wrighton, Adv. Chem. Ser., 168, 189 (1978).
678. Y. Ito, T. Hirao, T. Saegusa, J. Org. Chem., 43, 1011 (1978).
679. M. D. Curtis and J. Greene, J. Am. Chem. Soc., 100, 6362 (1978).
680. H. Matsumoto, T. Yako, S. Nagashima, T. Motegi and Y. Nagai, J. Organometal. Chem., 148, 97 (1978).
681. H. D. Hodes and K. M. Nickolas, Tetrahedron Lett., 4349 (1978).
682. D. Seyferth, J. S. Merola and C. S. Eschbach, J. Am. Chem. Soc., 100, 4124 (1978).
683. C. G. Kreiter and R. Aumann, Chem. Ber., 111, 1223 (1978).
684. K-H. Dotz and D. Neugebauer, Angew. Chem. IE, 17, 851 (1978).
685. J. V. Crivello and J. H. W. Lam, J. Org. Chem., 43, 3055 (1978).
686. Y. Yamaru, M. Kagolani and Z-i. Yoshida, JCS Chem. Commun., 367 (1978).
687. M. Kosugi, Y. Shimizu and T. Migita, Chem. Lett., 13 (1978).
688. H. Alper and H. N. Pack, J. Organometal. Chem., 144, C18 (1978).
689. G. L. Grunwald and D. P. Davis, J. Org. Chem., 43, 3075 (1978).
690. A. Fischli, Helv. Chim. Acta, 61, 2560 (1978).
691. M. Franch-Neumann, F. Brion and D. Martina, Tetrahedron Lett., 5033 (1978).
692. P. J. Harris and H. R. Allcock, J. Am. Chem. Soc., 100, 6512 (1978).
693. R. J. Gillespie, J. Murray-Rust, P. Murray-Rust and A. E. A. Porter, JCS Chem. Commun., 83 (1978).
694. R. Pearce, D. J. Thompson and N. V. Twigg, Annu. Rep. Prog. Chem., Sect. B, 73, 99 (1976).
695. D. J. Thompson and K. Smith, Gen. Synth. Methods, 1, 324 (1978).
696. R. M. Parlman, Diss. Abstr. Int. B, 38, 2677 (1977).
697. J-J. Lin, Diss. Abstr. Int. B, 38, 3197 (1978).
698. R. Oda, Chem. Abstr., 89, 179006u (1978).
699. R. Oda, Chem. Abstr., 89, 179005t (1978).
700. R. Noyori, Ann. N.Y. Acad. Sci., 295, 225 (1977).
701. N. M. Marinovic, Diss. Abstr. Int. B, 39, 1291 (1978).
702. L. S. Liebeskind, Diss. Abstr. Int. B, 38, 693 (1977).
703. E. W. Abel and F. G. A. Stone, Organomet. Chem., 6, 169 (1978).
704. M. I. Rybinskaya, Ann. N.Y. Acad. Sci., 295, 141 (1977).
705. M. Green, Ann. N.Y. Acad. Sci., 295, 160 (1977).
706. M. I. Rybinskaya, Chem. Abstr., 89, 24382q (1978).

707. M. Brookhart, C. R. Graham, G. O. Nelson and G. Scholes, Ann. N.Y. Acad. Sci., 295, 254 (1977).
708. G. Sartori, A. Furlani, P. Bicev, P. Carusi and M. V. Russo, Israel J. Chem., 15, 230 (1977).
709. P. L. Pauson and I. U. Khand, Ann. N.Y. Acad. Sci., 295, 2 (1977).
710. D. R. McAlister, Diss. Abstr. Int. B, 38, 5367 (1978).
711. R. F. Heck, Ann. N.Y. Acad. Sci., 295, 201 (1977).
712. S. Murahashi, Chem. Abstr., 88, 49769p (1978).
713. R. F. Heck, Pure Appl. Chem., 50, 691 (1978).
714. H. Kurosawa, Chem. Abstr., 88, 152681c (1978).
715. M. F. Farona, Organometal. React. Synth., 6, 223 (1977).
716. G. Jaouen, Ann. N.Y. Acad. Sci., 295, 59 (1977).
717. M. F. Semmelhack, Ann. N.Y. Acad. Sci., 295, 36 (1977).
718. C. M. Lentz, Diss. Abstr. Int. B, 39, 1766 (1978).
719. R. A. Amos, Diss. Abstr. Int. B, 38, 4809 (1978).
720. G. P. Chiusoli, G. Salerno, U. Bersellini, F. Dallatomasina and S. Preseglio, Transition Met. Chem., 3, 174 (1978).
721. J. F. Normant, Pure & Appl. Chem., 50, 709 (1978).
722. Y. Izumi, Chem. Abstr., 88, 61650a (1978).
723. D. Valentine, Jr., and J. W. Scott, Synthesis, 329 (1978).
724. M. Tanaka, Chem. Abstr., 88, 152682d (1978).
725. W. A. Herrmann, Angew. Chem. IE, 17, 800 (1978).
726. G. P. Pez and S. C. Kwan, Ann. N.Y. Acad. Sci., 295, 174 (1977).
727. M. P. Fleming, Diss. Abstr. Int. B, 38, 686 (1977).
728. R. C. LaRock, Angew. Chem. IE, 17, 27 (1978).
729. D. B. Carr, M. Yoshifuji, L. I. Shoer, K. I. Gell and J. Schwartz, Ann. N.Y. Acad. Sci., 295, 127 (1977).
730. C. White, Organomet. Chem., 6, 363 (1978).
731. J. L. Davison, Inorg. React. Mech., 5, 346 (1977).
732. G. Wilke, Pure & Appl. Chem., 50, 677 (1978).
733. G. Wilkinson, Chem. Aust., 44, 215 (1977).
734. G. W. Parshall, J. Mol. Catal., 4, 243 (1978).
735. P. M. Maitlis, Accts. Chem. Res., 11, 301 (1978).
736. R.L. Burwell, Jr., Surv. Prog. Chem., 8, 1, (1977).
737. G. Manecke and W. Storck, Angew. Chem. IE, 17, 657 (1978).
738. R. H. Grubbs and S-C. H. Su, Organomet. Polym., (Symp.), 129 (1978).
739. M. D. Johnson, Accts. Chem. Res., 11, 57 (1978).
740. J. K. Kochi, ACS Symp. Ser., 55, 167 (1977).
741. I. V. Kozhevnikov and K. I. Matveev, Chem. Abstr., 89, 106962t (1978).
742. K. Haage, Chem. Abstr., 88, 105428r (1978).
743. T. Nakai, Chem. Abstr., 89, 41560p (1978).
744. R. Mason and D. Meek, Angew. Chem. IE, 17, 183 (1978).

745. M. P. Laurent, Diss. Abstr. Int. B, 38, 4225 (1978).
746. J. L. Davidson, Inorg. React. Mech, 5, 333 (1977).
747. H. A. Skinner, J. Chem. Thermodyn,. 10, 309 (1978).
748. K. J. Klabunde, Ann. N.Y. Acad. Sci., 295, 83 (1977).
749. J. L. Davidson, Inorg. React. Mech, 5, 398 (1977).
750. R. Hoffmann, T. A. Albright and D. L. Thorn, Pure Appl. Chem., 50, 1 (1978).