# TRANSITION METALS IN ORGANIC SYNTHESIS
## ANNUAL SURVEY COVERING THE YEAR 1982

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CONTENTS

## I. General Comments

This annual survey covers the literature for 1982 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. This is not a critical review, but rather a listing of the papers published in the title area.

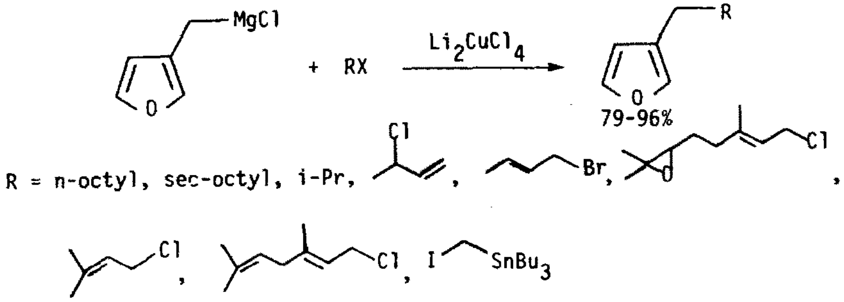
The papers in this survey are grouped primarily by reaction type rather than by organometallic reagent, since the reader is likely to be more interested in the organic transformation effected than the metal causing it. Oxidation, reduction, and hydroformylation reactions are specifically excluded, and will be covered in a different annual survey. 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.

## II. Carbon-Carbon Bond Forming Reactions

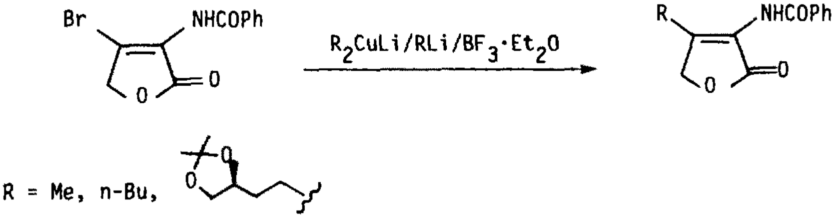
### A. Alkylation

### 1. Alkylation of Organic Halides and Tosylates

The activity in the area of new organocopper chemistry is finally abating, although several useful new procedures have been developed this year. Organic halides coupled cleanly to the appropriate Grignard reagent in the presence of $Li_2CuCl_4$ to form 3-substituted furans in quite good yield (equation 1) [1]. β-Bromobutenolides were cleanly alkylated by organocuprate reagents, with the mixture $R_2CuLi/RLi/BF_3 \cdot Et_2O$ being the most efficient reagent (equation 2) [2]. Acetoxy-β-lactams were alkylated by organocuprates stereospecifically (equations 3-5) [3]. Organocopper chemistry played an important role in the synthesis of ubiquinone 10 (equation 6) [4]. Aryl acetones were prepared by a modified Hurtley reaction (equation 7) [5]. Aryl iodides reacted with sodium trifluoroacetate in the presence of copper(I) iodide to produce trifluoromethyl aryl compounds (equation 8) [6].



(1)



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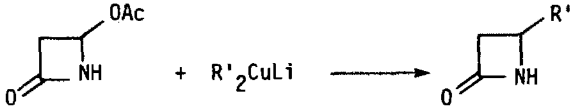

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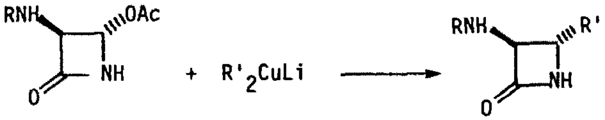

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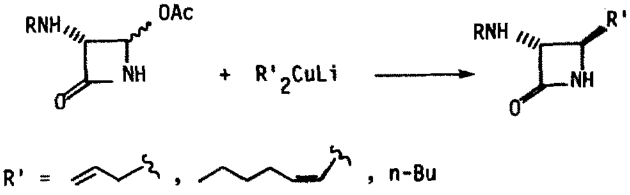

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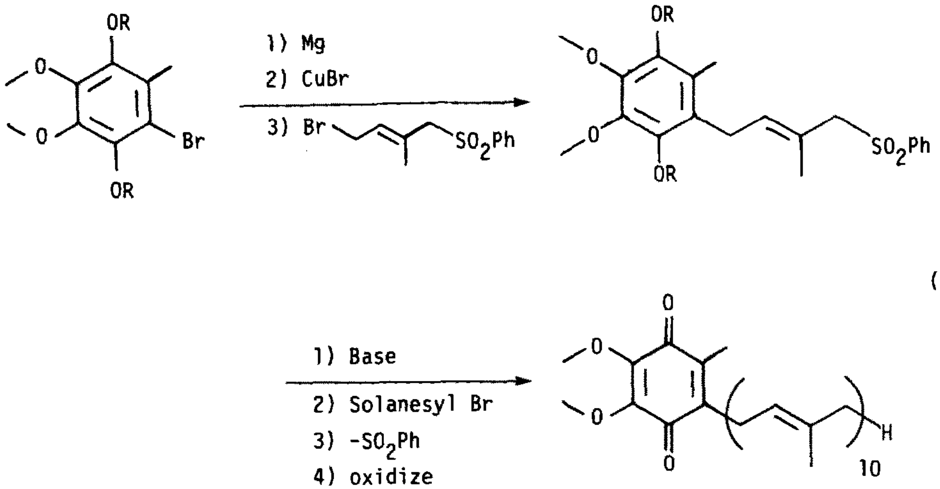
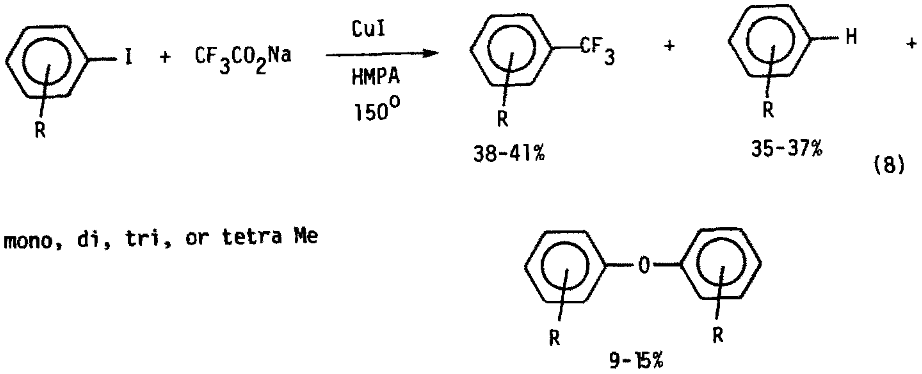


(6)

$$\mathrm{ArX} + 5\text{-}10\ \mathrm{MCH(CO_2Me)_2} \xrightarrow[\substack{\mathrm{DMF} \\ 100^{\circ}}]{\mathrm{CuX}} \mathrm{ArCH(CO_2Me)_2} \xrightarrow{\mathrm{OH^-}} \mathrm{ArCH_2COCH_3} \quad (7)$$

14 cases
40-80%

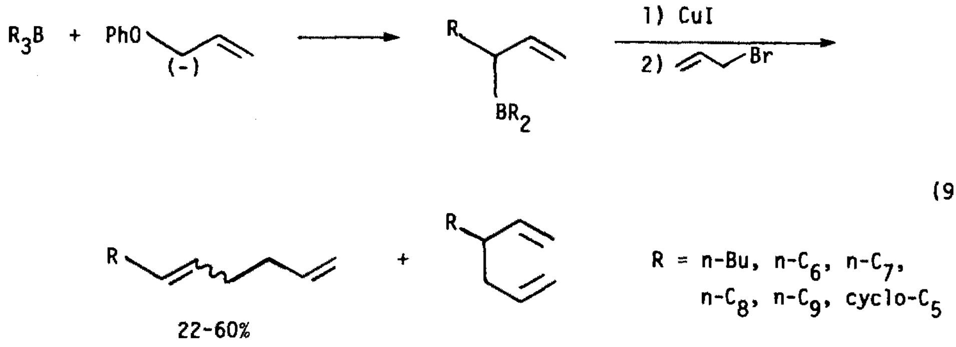
Ar contains PhCO, AcO, $NO_2$, F, Me, OMe, AcNH substituents



(8)

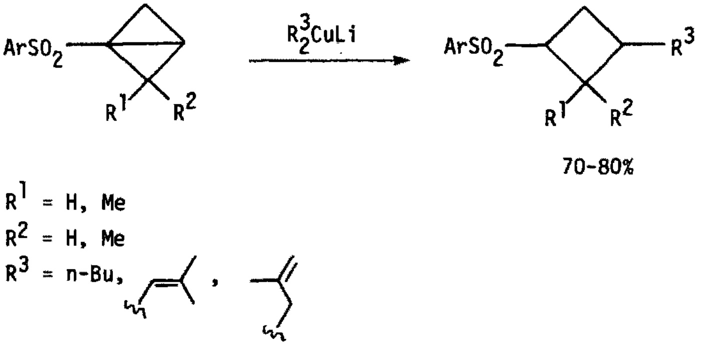
R = mono, di, tri, or tetra Me

Boron "ate" complexes were formed by the reaction of 9-borabicyclo [3.3.1] nonane (9-BBN) by reaction with lithium dialkylcuprates [7]. Allyl boranes reacted with allylic halides in the presence of copper(I) iodide to give cross-coupled products (equation 9) [8]. Bridge-head bicyclo [1.1.0] butanosulfonates underwent alkylation by organocuprates (equation 10) [9]. The new organocopper reagents $[RCuPPh_2]Li$ and $[RCuNCy_2]Li$ were thermally stable at 25°, and reacted with halides, epoxides, conjugated enones and acid chlorides in a manner similar to that of $R_2CuLi$ reagents [10].



$R$ = n-Bu, n-$C_6$, n-$C_7$, n-$C_8$, n-$C_9$, cyclo-$C_5$

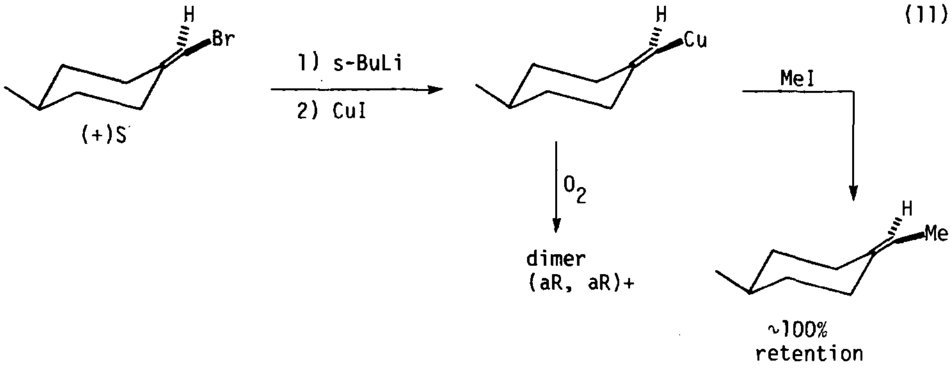
(9)



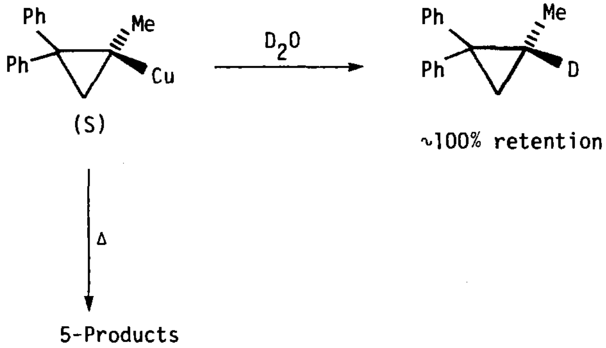
(10)

$R^1$ = H, Me
$R^2$ = H, Me
$R^3$ = n-Bu,

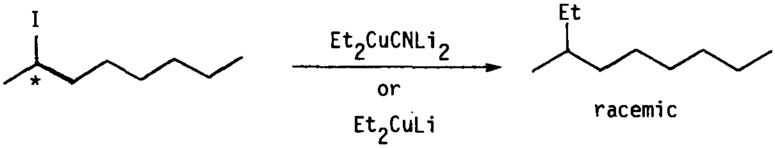
Several stereochemical and mechanistic studies regarding organocopper chemistry have been carried out. Stereochemically pure vinylcopper (equation 11) and cyclopropylcopper species (equation 12) were prepared, and reacted with methyl iodide or $D_2O$ respectively with complete retention [11]. Reaction of chiral 2-iodooctane with dialkylcuprates resulted in alkylation with racemization, whereas the same reaction with 2-bromooctane went with greater than 97% inversion, demonstrating that the stereochemistry of these processes depends on the nature of the leaving group (equations 13 and 14) [12]. Greater than 88% inversion was also observed with 2-octyl tosylate (equation 15) [13]. Evidence for electron transfer processes in the reactions of organocuprates with organic halides was obtained using both trityl chloride (equation 16) and 6-halohept-1-ene (equation 17) [14]. The "ate" complexes $Me_3CuMg$ and $Me_4Cu_2Mg$ were prepared from Grignard reagents and $[(COD)CuBr]_2$ [15].


H
Br
(+)S
1) s-BuLi
2) CuI
H
Cu
MeI
O2
dimer
(aR, aR)+
H
Me
~100%
retention

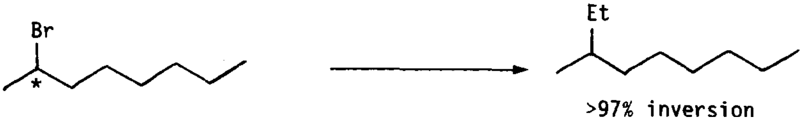
(11)


Ph
Ph
Me
Cu
(S)
D2O
Ph
Ph
Me
D
~100% retention
Δ
5-Products

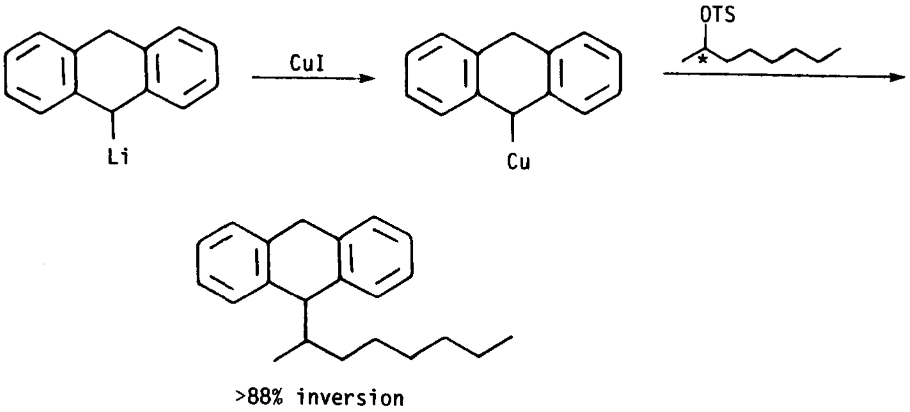
(12)


I
*
Et2CuCNLi2
or
Et2CuLi
Et
racemic

(13)

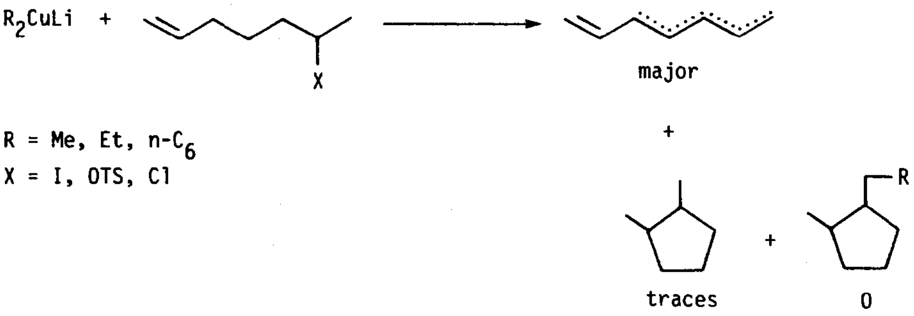

Br
*
Et
>97% inversion

(14)



(15)

$$Ph_3CCl + Me_2CuLi \longrightarrow Ph_3CCH_3 + \text{epr signal} \qquad (16)$$

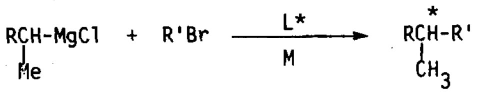


(17)

$X = I, R = Me$ 65%

$X = I, Me_3CuLi_2$ 62%

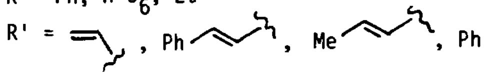
Asymmetric Grignard cross-coupling reactions involving chiral phosphine-nickel and -palladium complex catalysts was the subject of several reviews [16, 17, 18]. The full experimental details of the reaction of vinyl halides with secondary Grignard reagents in the presence of nickel and palladium-chiral ferrocenyl phosphineamine complexes (equation 18) has appeared [19]. It was found that the planar chirality of the ferrocene was more important than carbon-centered chirality; that the dialkylamino group was required; and that the bulk of the phosphine was unimportant but the bulk of the amine was crucial. This process was used to make chiral allyl silanes in high optical yield (equation 19) [20]. The same process has been carried out with achiral catalysts as well (equation 20) [21].



$$\mathrm{R\underset{Me}{C}H\text{-}MgCl} + \mathrm{R'Br} \xrightarrow[\mathrm{M}]{\mathrm{L^*}} \mathrm{R\overset{*}{\underset{CH_3}{C}}H\text{-}R'} \qquad (18)$$

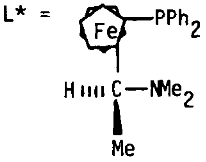
R = Ph, n-$C_6$, Et

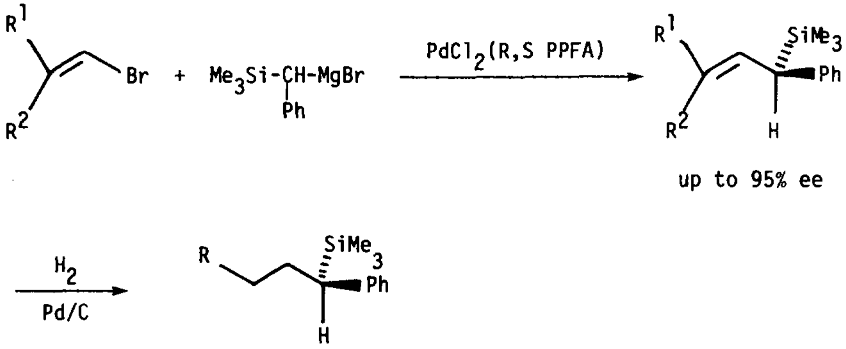
R' =



M = Ni, Pd

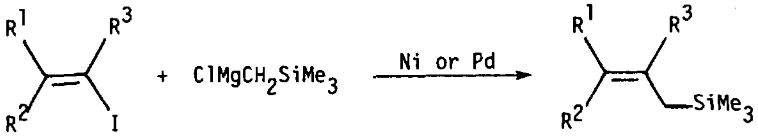
L* =





up to 95% ee

(19)

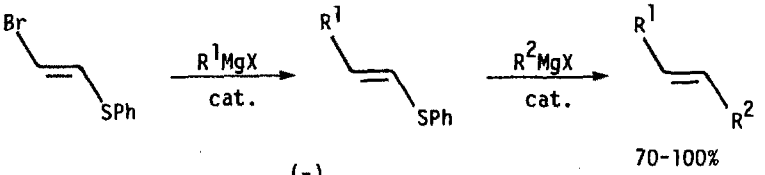


70-88%

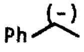
(20)

$R^1$ = n-$C_6$, n-Bu, H
$R^2$ = Me, H, n-Pr

Vinyl sulfides (equation 21) [22], sulfones (equation 22) [23], and tellurides (equation 23) [24] also underwent nickel or palladium catalyzed reactions with Grignard reagents. Biaryls were prepared by the nickel-catalyzed reaction of aryl halides with aryl Grignard reagents (equation 24) [25]. Oxazolines of halobenzoic acids were alkylated using a similar reaction (equation 25) [26]. Chloroaryl thioethers underwent a double alkylation (equation 26) [27].

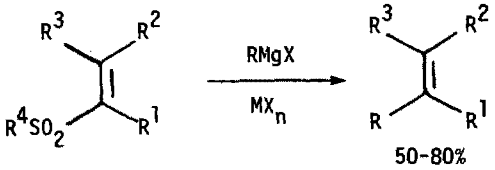


(21)

$R^1$ = Ph, n-Bu, Np, Ph

$R^2$ = Ph, Me, Np, n-Bu

cat. = $L_2PdCl_2$, diphos $NiCl_2$



(22)

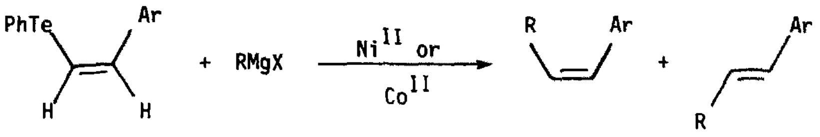
R = Ph, Me

$R^1$ = H, Me, n-Pr, n-$C_6$, i-prenyl

M = Ni, Fe

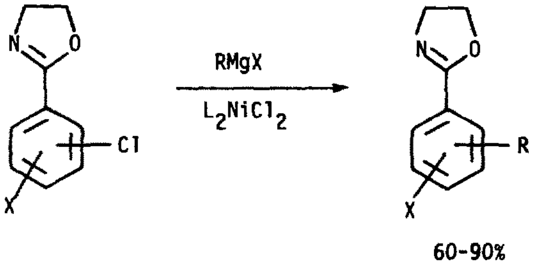
$R^2$ = Me, n-Bu, H

$R^3$ = Me, H



(23)

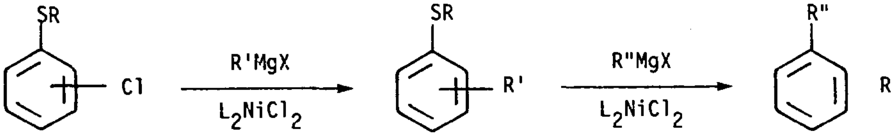
$$ArMgX + Ar'X \xrightarrow{Ni(acac)_2} ArAr' \qquad (24)$$



(25)

R = Ph, p-anisyl, Et, n-Pr, Bz

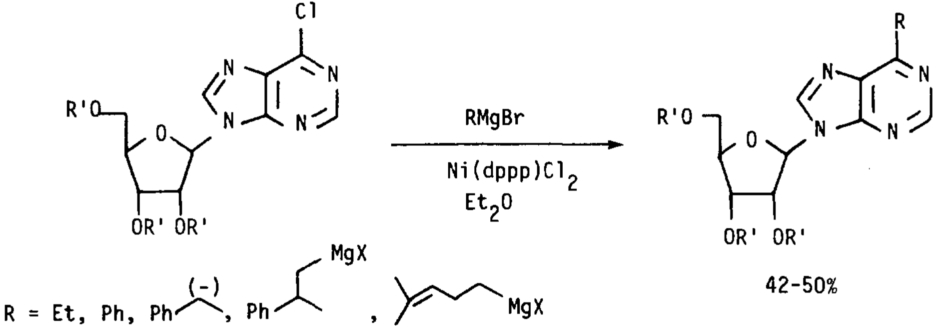
X = H, Cl, Br, $Cl_2$, SMe



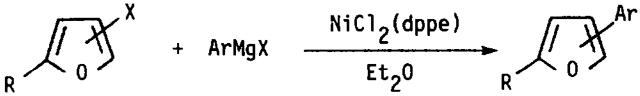
(26)

This process is especially useful for alkylation of hetero-aromatic halides. Chloronucleosides were alkylated using nickel catalyzed Grignard reactions (equation 27) [28]. Halofurans were arylated using nickel catalysts (equation 28) [29]. The full experimental details for the coupling of heteroaromatic halides with Grignard reagents (equation 29) and heteroaromatic Grignard reagents with halides (equation 30) have appeared [30].

(27)



R' = t-BuSiMe$_2$



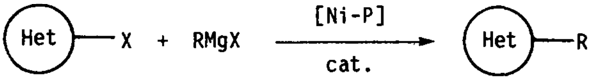
(28)

82-93%

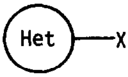
X = 2-Br, 3-Br; R = H

X = 2-SMe; R = 5-n-Bu

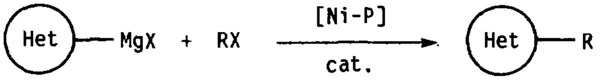
Ar = Ph, p-tolyl, 3,4-diMePh, m-tolyl, p-EtPh



(29)



= Bromothiophenes, pyridines, quinolines, isoquinolines



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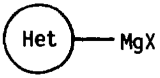
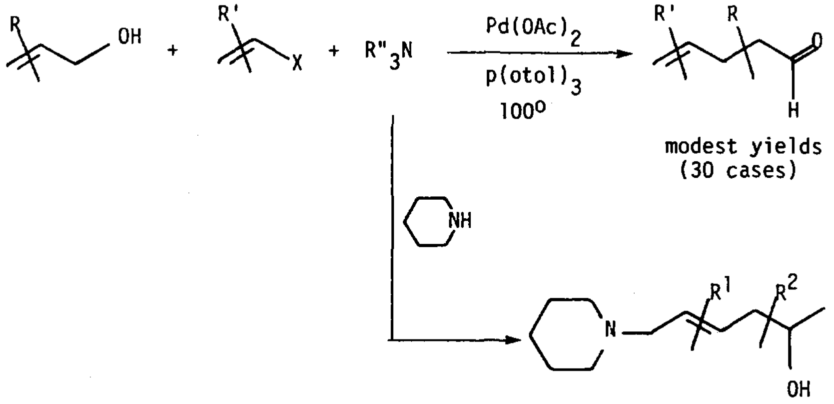


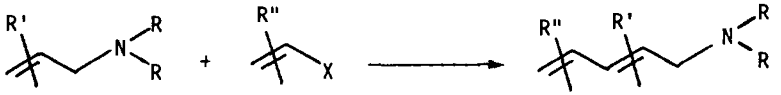
= thiophenes, pyridines

The "Heck" type reactions of vinyl halides with organopalladium species have been reviewed [31, 32, 33]. Palladium catalyzed the reactions of vinyl halides with allyl alcohols (equation 31), allylamine (equation 32), allyl OTHP compounds (equation 33), and N-allylphthalimides (equation 34) to give coupling products [34].



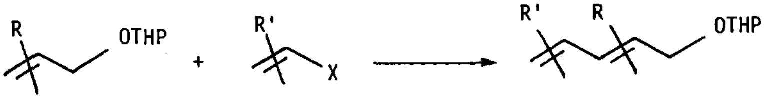
modest yields (30 cases)

(31)



(32)

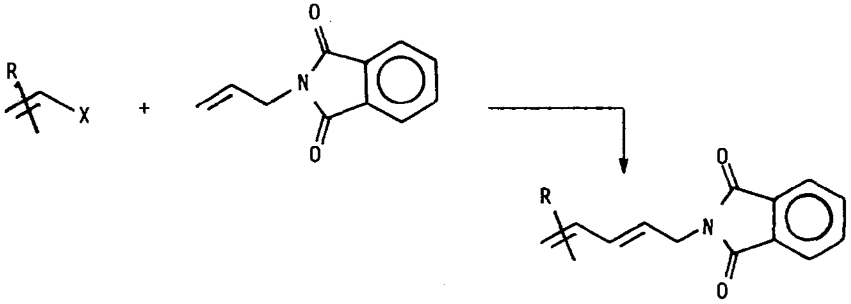
(8 cases)



(33)

(4 cases)

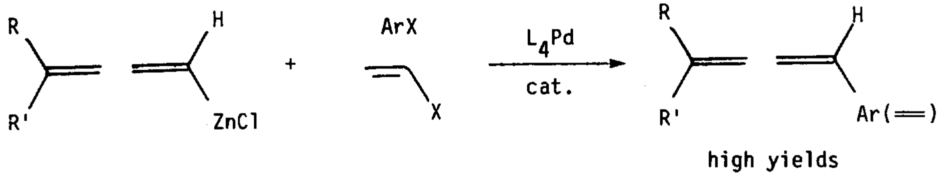
(34)



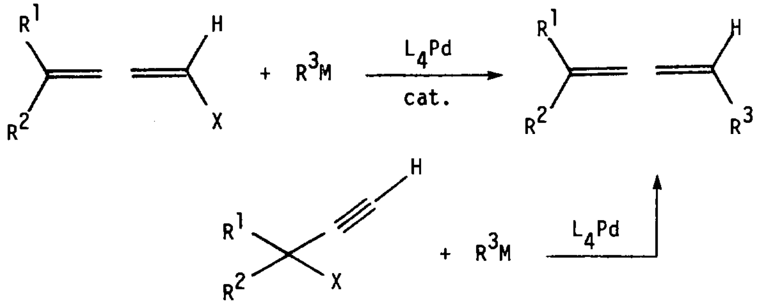
(4 cases)

Transmetallation from main group metals to organopalladium species produced by oxidative addition processes is becoming increasingly important in organic synthesis. The palladium-catalyzed cross-coupling reaction of heteroarylzinc derivatives with unsaturated organic halides as well as the palladium catalyzed coupling of heteroaryl halides with organozinc or aluminum reagents has been reported [35]. This general area has been reviewed [36]. Aryl and vinyl halides coupled with allenic zinc reagents in the presence of palladium catalysts in high yield (equation 35) [37]. Similarly, allenic halides coupled to unsaturated organozinc reagents in the presence of palladium catalysts (equation 36) [38]. Even allenic lithium reagents worked in this process (equations 37-39) [39].

(35)

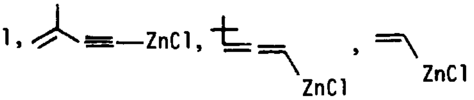


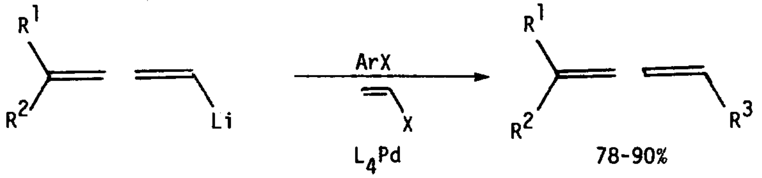
R = Me, t-Bu, H
R' = Me, H



(36)

$R^1$ = H, Me, Ph, t-Bu, i-Pr, n-$C_5$
$R^2$ = H, Me
$R^3M$ = TMSC≡C-ZnCl,





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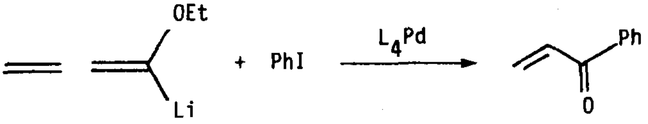
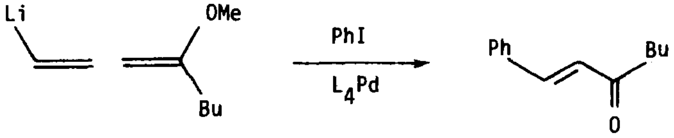


42%

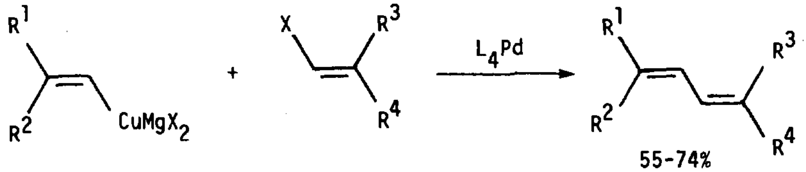
(38)



78%

(39)

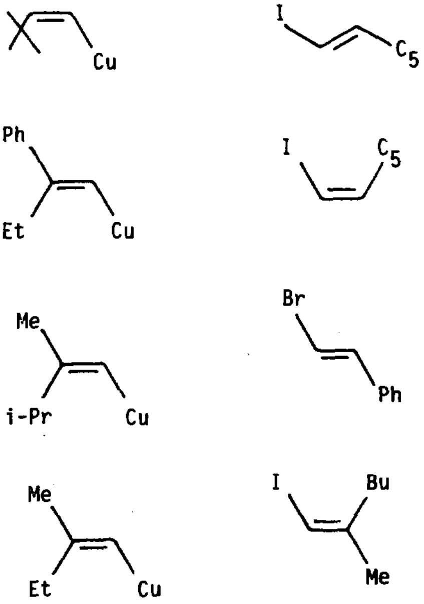
Vinyl copper reagents reacted with vinyl halides in the presence of palladium catalysts to give dienes in good yield (equation 40) [40]. Copper acetylides coupled with aryl and allyl halides (equation 41) [41], heteroaromatic halides (equation 42) [42], and vinyl halides (equation 43) [43], all in the presence of palladium catalysts.



(40)

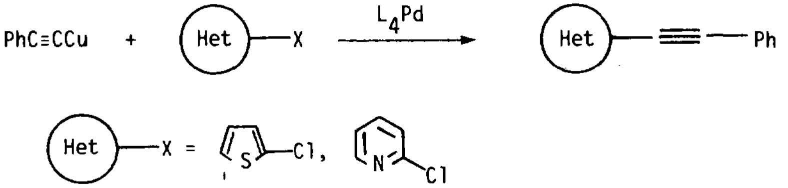
55-74%

>98% stereospecific

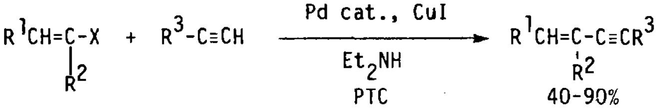


$$\mathrm{PhC{\equiv}C\text{-}Cu} \quad + \quad \mathrm{ArX} \xrightarrow{L_4Pd} \underset{84\text{-}98\%}{\mathrm{ArC{\equiv}CPh}} \qquad (41)$$

Ar = p-MeCOPh, 2,4-di$NO_2$Ph, $CO_2$MePh, NCPh



(42)



$$\mathrm{R^1CH{=}\underset{R^2}{C}\text{-}X} \quad + \quad \mathrm{R^3\text{-}C{\equiv}CH} \xrightarrow[\substack{Et_2NH \\ PTC}]{\text{Pd cat., CuI}} \underset{40\text{-}90\%}{\mathrm{R^1CH{=}\underset{R^2}{C}\text{-}C{\equiv}CR^3}} \qquad (43)$$

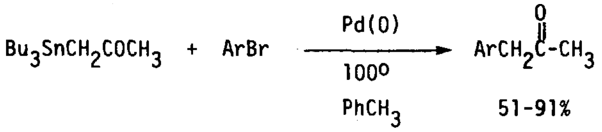
$R^1$ = H, n-Bu, n-$C_8$

$R^2$ = Me, H

X = Br, I

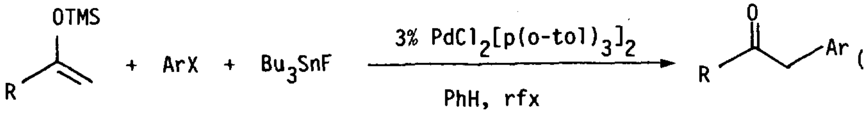
$R^3$ = n-$C_5$, $CH_2OH$, cyclo $C_6$, $(CH_2)_2OH$, $(CH_2)_8OH$

Aryl acetones were prepared by the palladium(0) catalyzed coupling of aryl halides with acetonyl tin reagents (equation 44) [44]. Trimethylsilylenol ethers alkylated aryl halides in the presence of tributyltin fluoride and a palladium catalyst (equation 45) [45]. Vinyl boranes (equation 46) [46], and vinylzirconium compounds (equation 47) [47] also coupled to aryl halides in the presence of palladium catalysts.

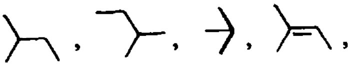


$$\mathrm{Bu_3SnCH_2COCH_3} \quad + \quad \mathrm{ArBr} \xrightarrow[\substack{100^{\circ} \\ PhCH_3}]{Pd(0)} \underset{51\text{-}91\%}{\mathrm{ArCH_2\overset{O}{\overset{\|}{C}}\text{-}CH_3}} \qquad (44)$$

Ar = Ph, p-$Me_2$NPh, p-MeOPh, o-tolyl, m-tolyl, p-tolyl, p-ClPH, p-MeCOPh

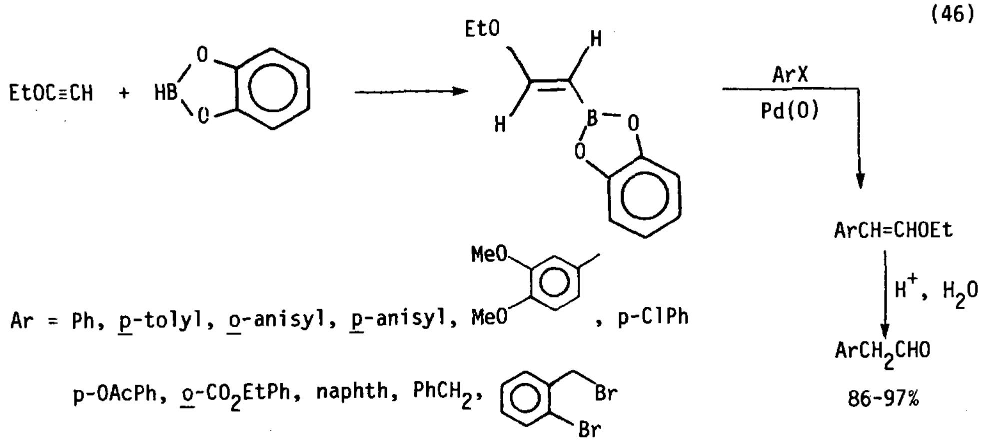


(45)

R = n-$C_7$,  , Ph

Ar = Ph, p-OMePh, p-tolyl, o-tolyl, p-$CH_3$COPh

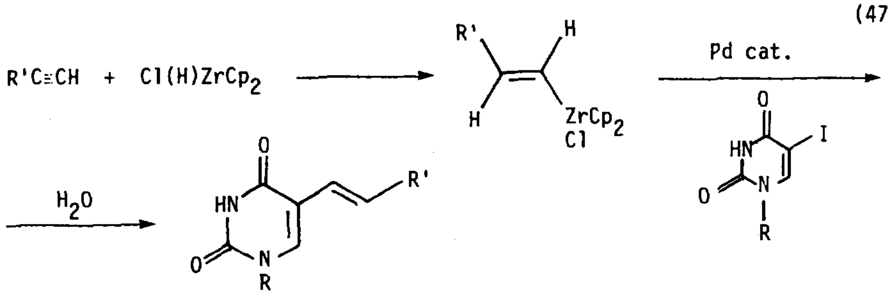
(46)



Ar = Ph, p-tolyl, o-anisyl, p-anisyl, , p-ClPh

p-OAcPh, o-$CO_2$EtPh, naphth, Ph$CH_2$,

(47)

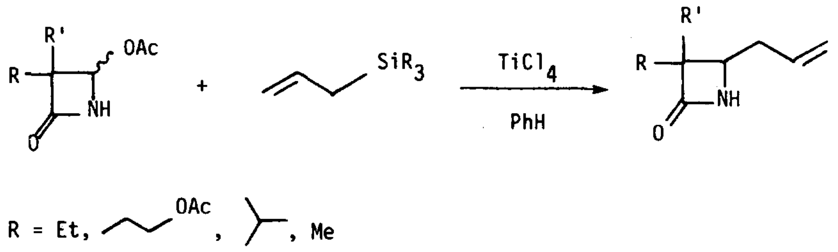


40-90%

R = Cl$(CH_2)_3$ - 89%; $CH_3(CH_2)_3$ - 95%; $CH_3(CH_2)_7$ - 76%

CN$(CH_2)_3$ - 76%; HC≡C-$CH_2$ - 80%; Ph - 85%; EtO - 49%

Finally aryl iodides coupled to 4-phenyloxazoles in the presence of palladium catalysts [48], and haloisoxazoles reacted with phenyl acetylene and styrene again in the presence of palladium catalysts [49]. Titanium(IV) chloride coupled allyl silanes to β-lactam acetates in fair yield (equation 48) [50].

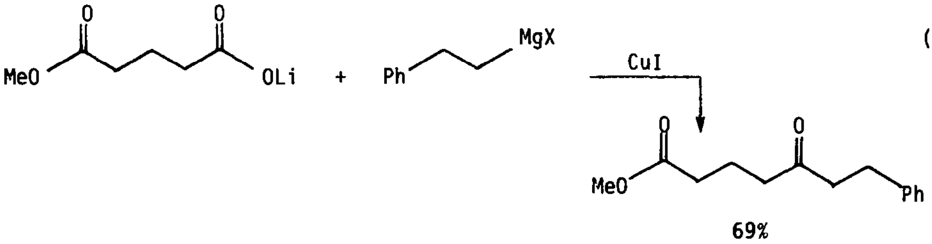


(48)

R' = H, Me

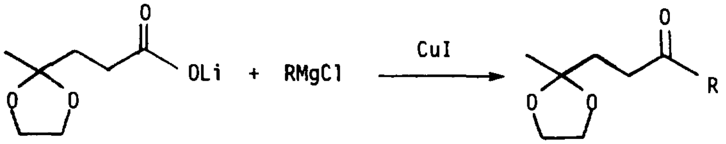
### 2. Alkylation of Acid Derivatives

Carboxylate salts reacted with Grignard reagents in the presence of a copper(I) catalyst to produce ketones (equations 49 and 50) [51]. Palladium(0) complexes catalyzed the reaction of acid halides with Reformatsky reagents (equation 51) [52], and with acetylenic tin reagents (equation 52) [53] to produce ketones in both instances. Palladium was also used to catalyze the coupling with decarbonylation of acid halides with vinyl halides (equation 53) [54]. The stereochemistry of this insertion was shown to be a cis process [55]. Titanium(IV) chloride was used to couple acid halides with trimethylsilylacetylenes (equation 54) [56].



(49)

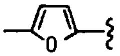
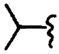
69%

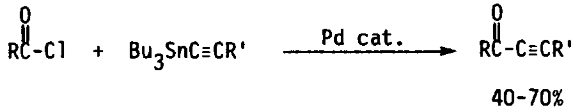


(50)

~70%

$$\mathrm{R\overset{O}{\overset{\|}{C}}\text{-}Cl} + \mathrm{BrZnCH_2CO_2Et} \xrightarrow{\mathrm{Pd(0)}} \mathrm{R\overset{O}{\overset{\|}{C}}CH_2CO_2Et} \qquad (51)$$

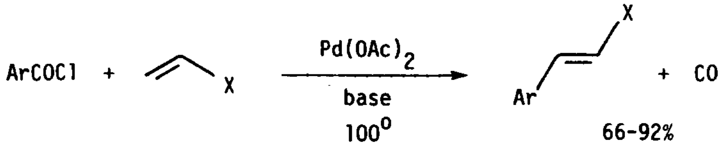
R = Ph - 80%; p-ClPh - 90%; m-ClPh - 83%; p-tolyl - 84%; p-$NO_2$Ph - 41%; p-anisyl - 51%;  - 72%; Ph - 73%;  - 89%, n-$C_8$ - 30%;  - 24%; t-Bu - 29%



$$RC(=O)\text{-}Cl + Bu_3SnC{\equiv}CR' \xrightarrow{\text{Pd cat.}} RC(=O)\text{-}C{\equiv}CR' \quad 40\text{-}70\% \qquad (52)$$

R = i-Pr, Ph, Me, p-$NO_2$Ph

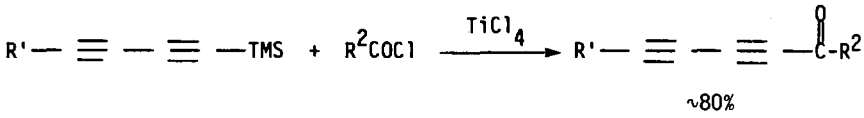
R' = Ph, $(EtO)_2CH$, TMS, $MeO_2C$



(53)

X = $CO_2Et$, Ph, $CONEt_2$, CN, COMe

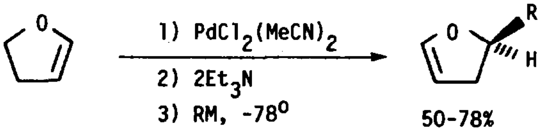
(54)



$$R'{-}{\equiv}{-}{\equiv}{-}TMS + R^2COCl \xrightarrow{TiCl_4} R'{-}{\equiv}{-}{\equiv}{-}C(=O)\text{-}R^2 \quad \sim 80\%$$

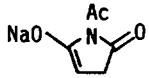
3. Alkylation of Olefins

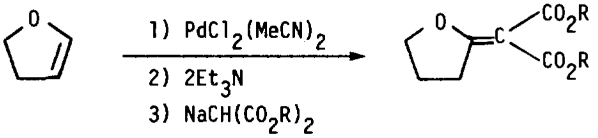
Palladium(II) assisted alkylation of olefins has found several synthetic applications recently. Dihydrofurans were selectively alkylated in the α-position with several stabilized carbanions (equation 55). The position of the olefin depended on the carbanion used (equation 56). Allylic acetates were also alkylated by stabilized carbanions, this time using palladium(0) catalysts (equation 57) [57]. A variety of olefins were alkylated by nitrile stabilized carbanions in the presence of palladium(II) species (equation 58) [58]. The least substituted terminus of the olefin was always alkylated, and the carbanion could be generated in situ using phenyllithium as the base. Asymmetry was induced in the palladium(II) assisted alkylation of olefins by using chiral amine ligands (equation 59) or better yet chiral carbanions as well [59].



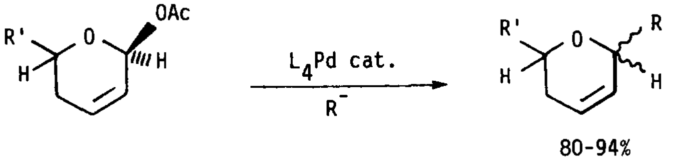
(55)

RM = $NaC(NHCHO)(CO_2Et)_2$, $NaC(NHAc)(CO_2R)_2$, $NaC(Me)(CO_2Me)_2$, NaO





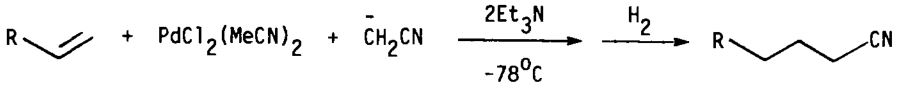
(56)



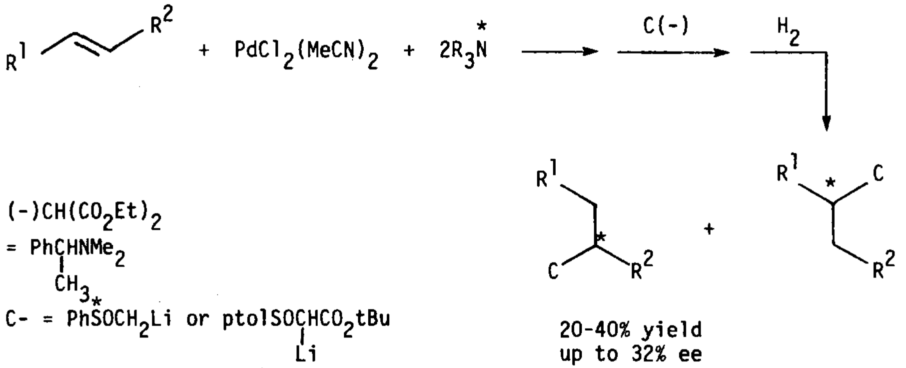
(57)

$R = (-)C(NHCHO)(CO_2Et)_2,\ (-)C(NHAc)(CO_2R)_2,$ Ph, ═

(58)



(59)



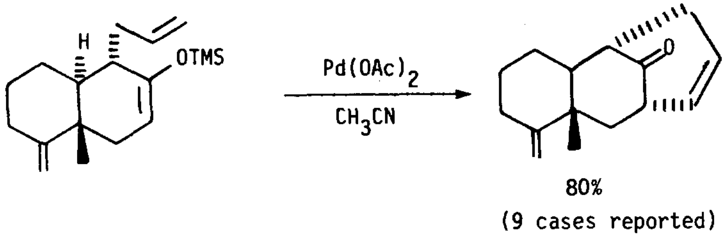
$C^- = (-)CH(CO_2Et)_2$

$R_3N^* = Ph\underset{\overset{|}{CH_3}}{C}HNMe_2$

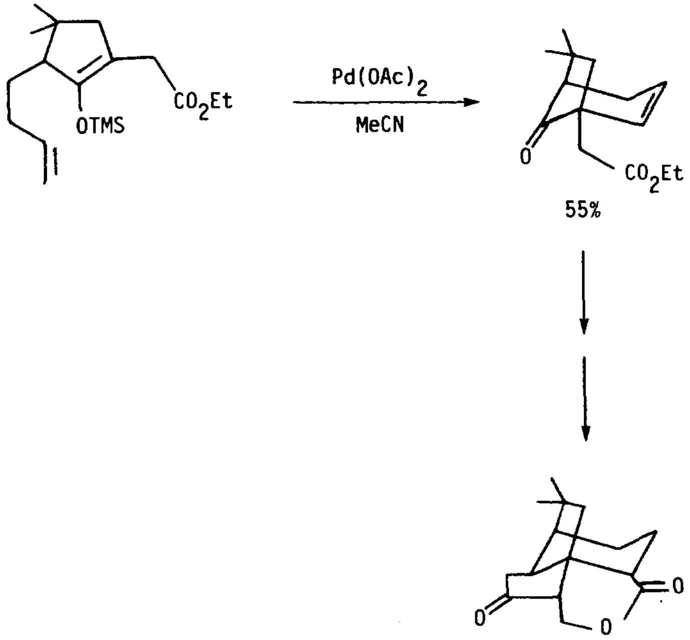
with $C^- = Ph\overset{*}{S}OCH_2Li$ or $ptolSO\underset{\overset{|}{Li}}{C}HCO_2tBu$

up to 40% optical yield

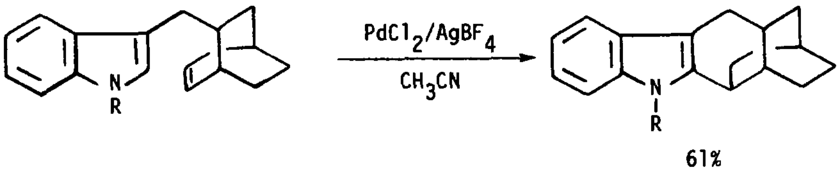
Intramolecular alkylation of olefins by trimethylsilyl enol ethers using palladium(II) catalysts has recently been developed (equation 60) [60]. This has been used in the synthesis of quadrone (equation 61) [61]. Intramolecular cyclization of olefins with indoles using palladium-silver catalysts has been studied (equations 62-65) [62]. Dissertations entitled "Addition of Enolates to Iron(0) Tetracarbonyl Complexes of Acrylates and -ylidene Malonate Esters," [63], and "Nucleophilic Addition to (Methyl α-Chloroacrylate)tetracarbonyliron - Preparation and Synthetic Applications of α-Acylacrylate and Methylene Malonate Esters" [64] have appeared.


H
OTMS
Pd(OAc)$_2$
CH$_3$CN
O
80%
(9 cases reported)

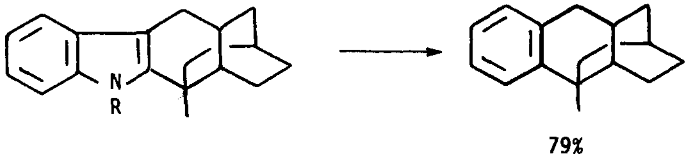
(60)


OTMS
CO$_2$Et
Pd(OAc)$_2$
MeCN
O
CO$_2$Et
55%
O
O
O

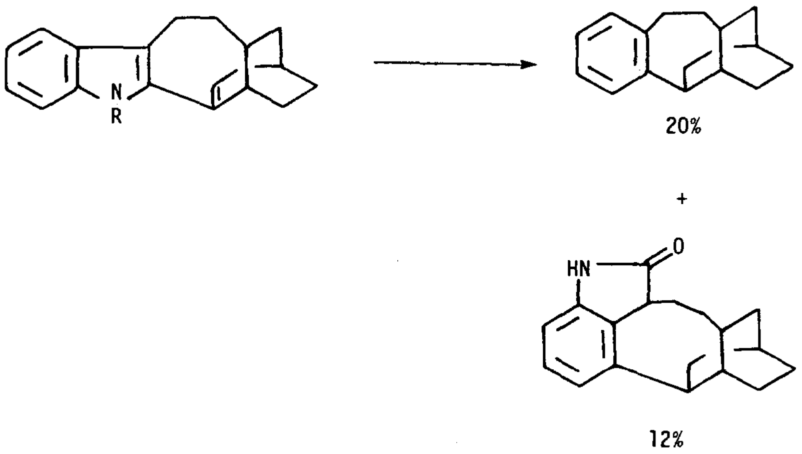
(61)


N
R
PdCl$_2$/AgBF$_4$
CH$_3$CN
N
R
61%

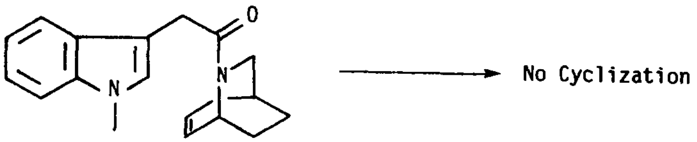
(62)


N
R
79%

(63)



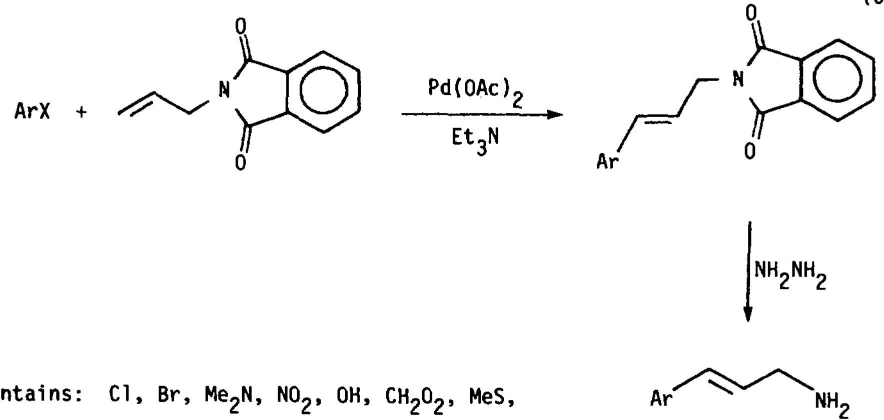
(64)



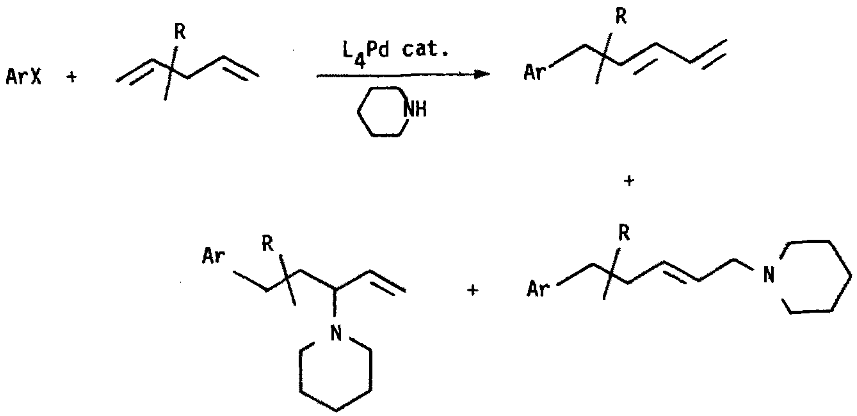
(65)

Heck type arylation of olefins was used to prepare a large number of γ-aryl allyl amines in fair to good yields (equation 66) [65]. Similar oxidative addition-insertion chemistry using aryl or vinyl halides, 1,4-dienes, and secondary amines led to the production of mixtures of allylamines (equations 67 and 68) [66]. Aryl iodides were vinylated using the palladium(0) catalyzed reaction with trimethylvinylsilane (equation 69) [67].

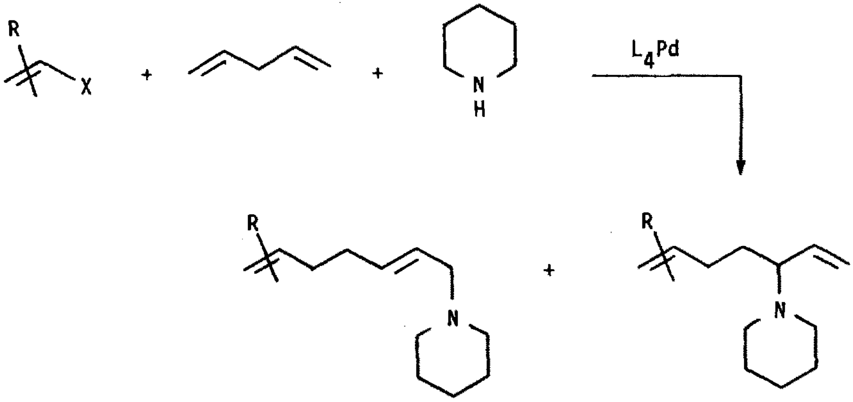
(66)



Ar contains: Cl, Br, $Me_2N$, $NO_2$, OH, $CH_2O_2$, MeS, $NH_2$, $CO_2Me$, CN

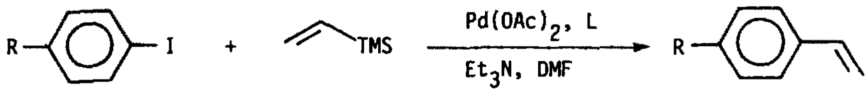


(67)



(68)

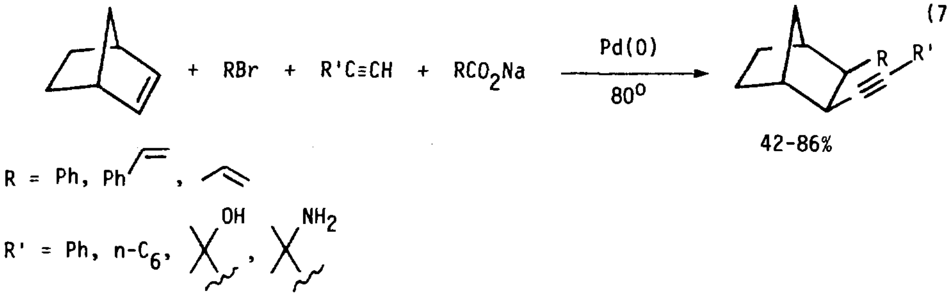
(69)



51-60%

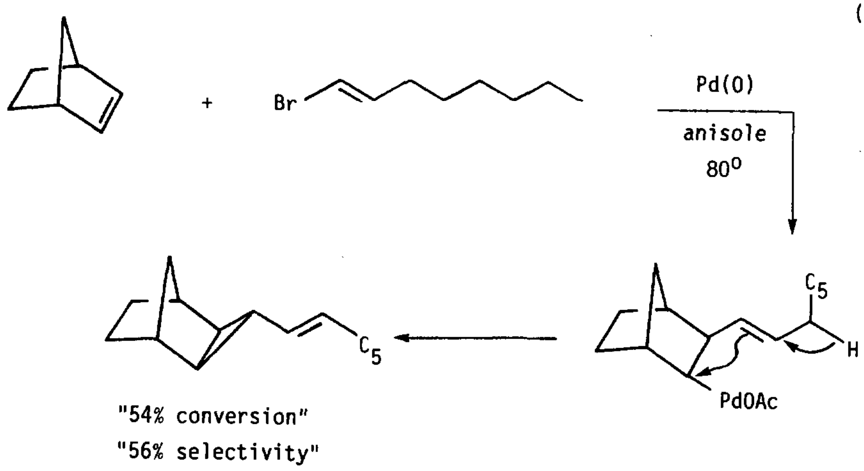
R = H, Me, MeO, $NO_2$

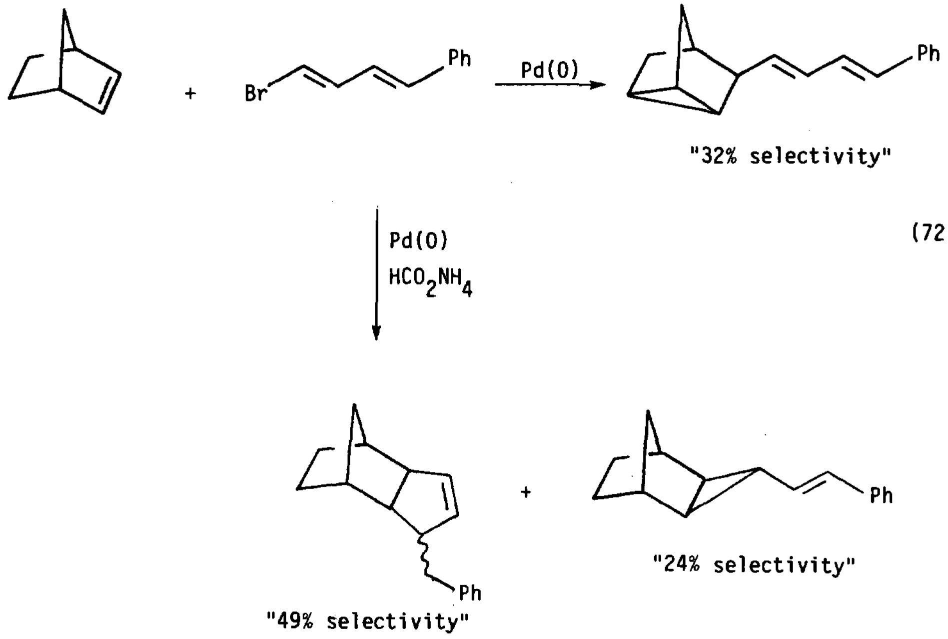
Palladium(0) catalyzed the reaction of organic halides, alkynes and norbornene to give disubstituted norbornanes (equation 70) [68]. With norbornene and simple vinyl halides cyclopropanation resulted (equation 71), while with $\alpha,\beta,\gamma,\delta$-unsaturated halides polycyclic material was obtained (equation 72) [69]. Prostaglandin analogs were made by the insertion of norbornene into $\pi$-allylpalladium complexes (equation 73) [70].


+ RBr + R'C≡CH + RCO2Na
Pd(0)
80°
R
R'
42-86%
R = Ph, Ph
R' = Ph, n-C6,
OH
NH2

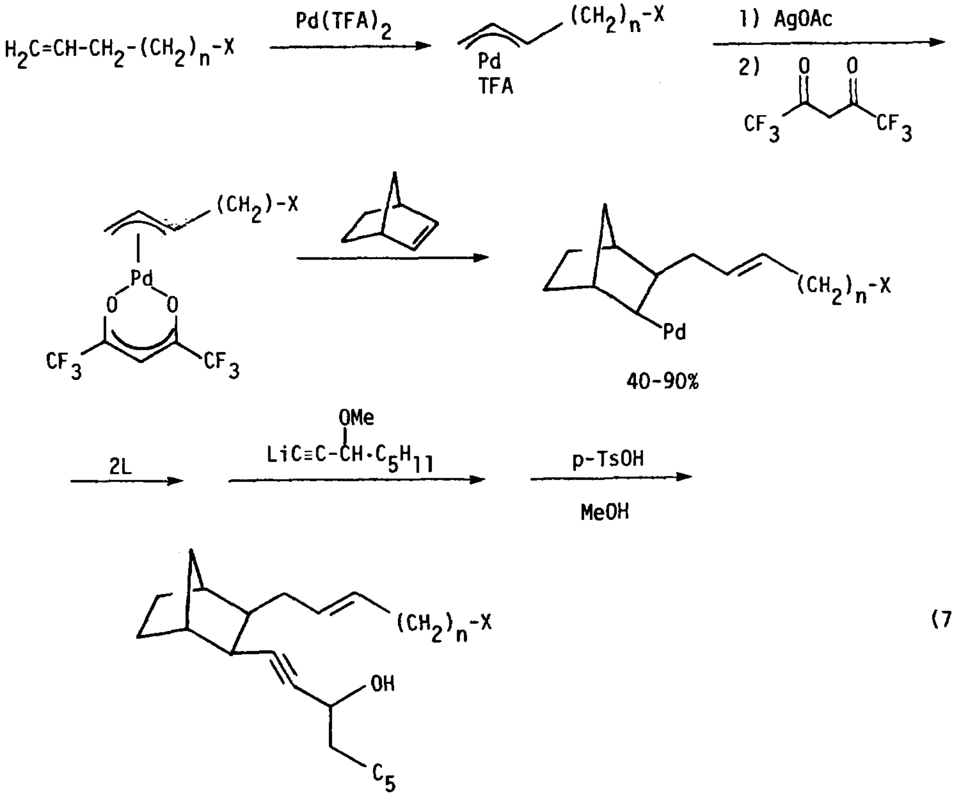
(70)

(71)


+
Br
Pd(0)
anisole
80°
C5
H
PdOAc
C5
"54% conversion"
"56% selectivity"


+
Br
Ph
Pd(0)
Ph
"32% selectivity"
Pd(0)
HCO2NH4
+
Ph
"49% selectivity"
Ph
"24% selectivity"

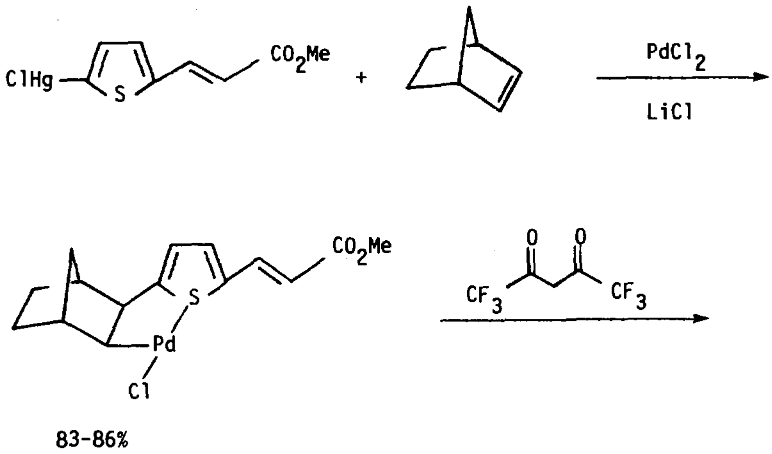
(72)



(73)

Transmetallation from mercury to palladium has been used to alkylate olefins. Again, this process has been used to make bicyclic prostaglandin derivatives (equation 74) [71], purine and pyrimidine intermediates (equations 75 and 76) [72], (equation 77) [73], and to arylate acrylic acid [74].

(74)



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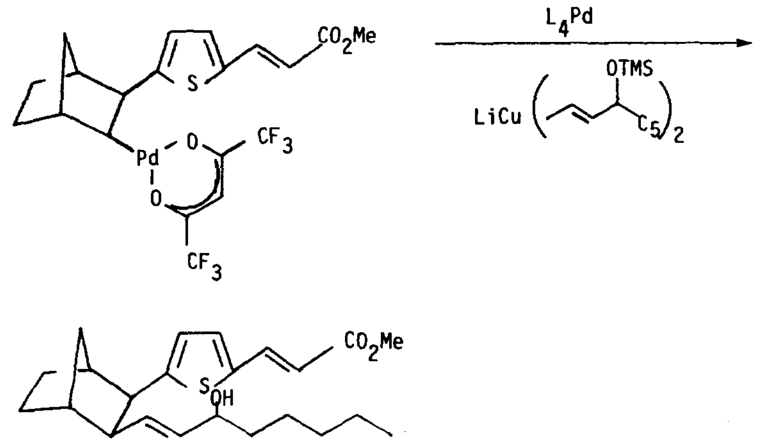
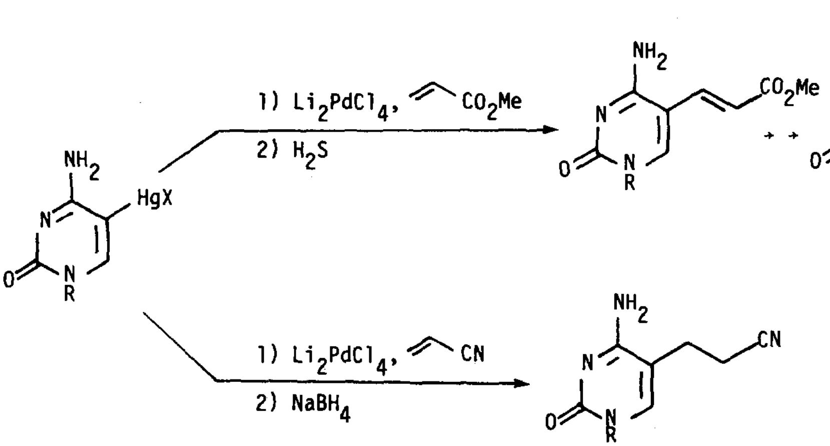
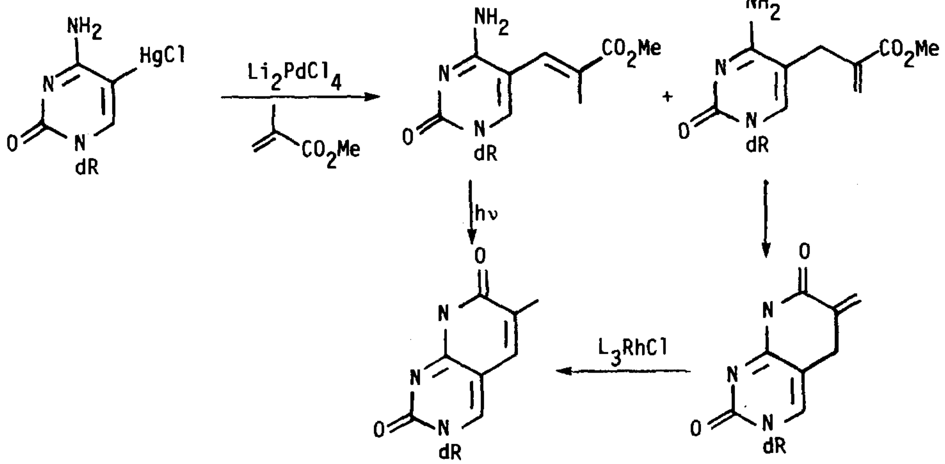

CO$_2$Me
Pd
O
CF$_3$
CF$_3$
S
L$_4$Pd
OTMS
LiCu
C$_5$
2
CO$_2$Me
S
OH

(74)

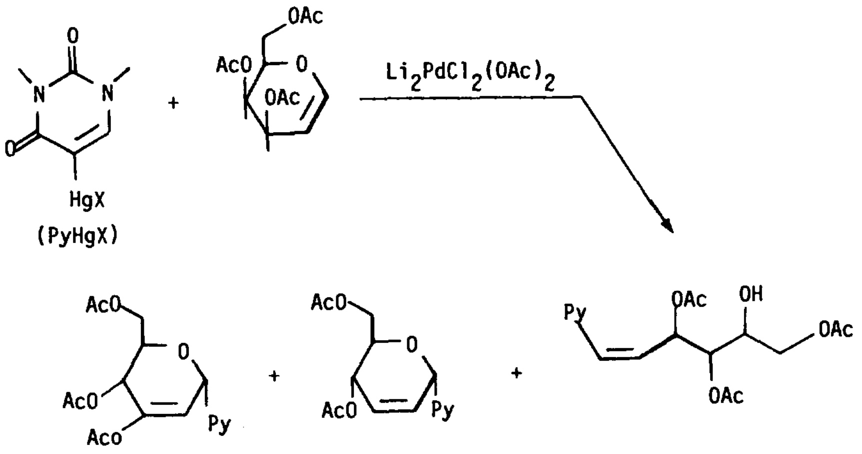

NH$_2$
HgX
N
O
N
R
1) Li$_2$PdCl$_4$, CO$_2$Me
2) H$_2$S
NH$_2$
CO$_2$Me
N
O
N
R
+
O
HN
N
O
N
R
1) Li$_2$PdCl$_4$, CN
2) NaBH$_4$
NH$_2$
CN
N
O
N
R

(75)

(76)

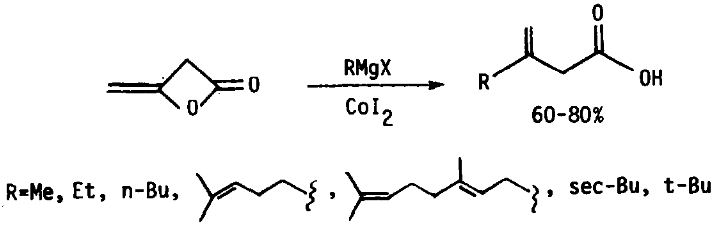

NH$_2$
HgCl
N
O
N
dR
Li$_2$PdCl$_4$
CO$_2$Me
NH$_2$
CO$_2$Me
N
O
N
dR
+
NH$_2$
CO$_2$Me
N
O
N
dR
hν
O
N
N
O
N
dR
L$_3$RhCl
O
N
N
O
N
dR

(77)

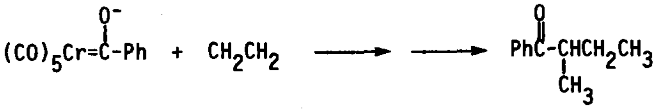


ratio depends on amounts of
$Cl^-$ and $OAc^-$

Ethene and bromobenzene were converted to 1,1-diphenylethane when electrochemically reduced in the presence of nickel(II) bromide [75]. β-Methylene-β-lactones ring-opened when treated with Grignard reagents and cobalt(II) iodide (equation 78) [76]. Chromium carbene complexes underwent a double insertion with ethylene (equation 79) [77]. ω-Olefinic alcohols were alkylated by trimethylaluminum/titanium(IV) chloride mixtures (equation 80) [78]. Unsaturated cobalt-dmg complexes cyclized when decomposed under radical conditions (equation 81) [79].



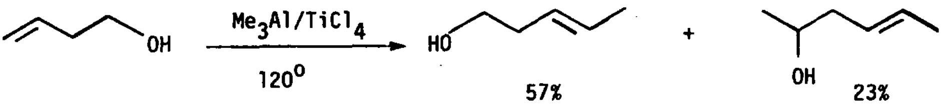
(78)

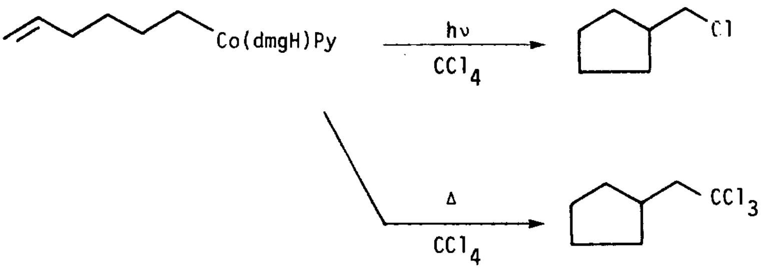


$$(CO)_5Cr{=}\overset{O^-}{C}\text{-}Ph + CH_2CH_2 \longrightarrow \longrightarrow Ph\overset{O}{\overset{\|}{C}}\text{-}\underset{CH_3}{CH}CH_2CH_3$$

(79)

(80)

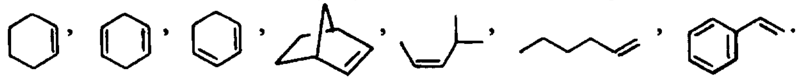




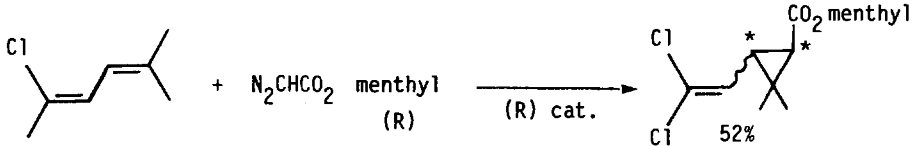
(81)

## 4. Decomposition of Diazoalkanes and Other Cyclopropanations

Transition metal catalyzed decomposition of diazoalkanes continues to be utilized to cyclopropanate olefins. Rhodium(II) porphyrin complexes were used as catalysts for the reaction between olefins and ethyl diazoacetate. High yields with large syn selectivity for cis olefins was observed, and explained by invoking the control of the direction of approach of the olefin to the carbene complex by the steric bulk of the porphyrin. The following olefins were studied [80]:

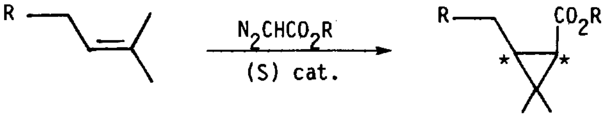


Chiral cyclopropanes were prepared by using chiral copper complexes to decompose chiral menthyl diazoacetates in the presence of olefins (equations 82 and 83) [81]. Acetylenes underwent multiple cyclopropanations when treated with diazoesters and rhodium(II) catalysts (equations 84 and 85) [82]. Diazoketones cyclopropanated olefins in the presence of molybdenum catalysts (equation 86) [83]. Metal-catalyzed decomposition of diazoketones and diazoamides of β-lactams has been studied as an approach to carbapenems [84]. The carbene species from ethyl diazoacetate and rhodium porphyrin catalysts inserts into C-H bonds of hydrocarbons (equations 87 and 88) [85]. Intramolecular cyclopropanations were observed in nickel catalyzed diazoketone decompositions (equations 89-91) [86].



1-R trans 42%

(82)



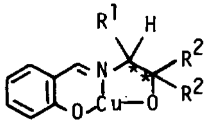
(83)

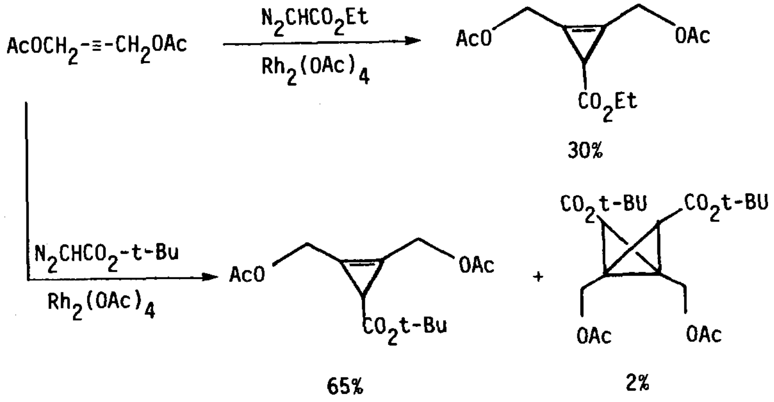
85:15 cis:trans

cis = 90% ee

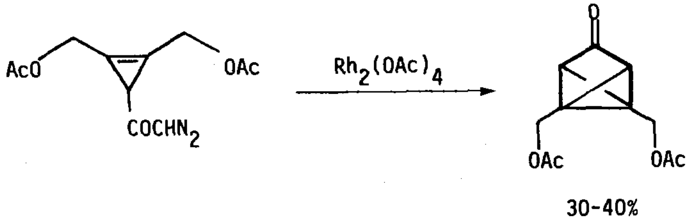
trans = 10-20% ee

cat =



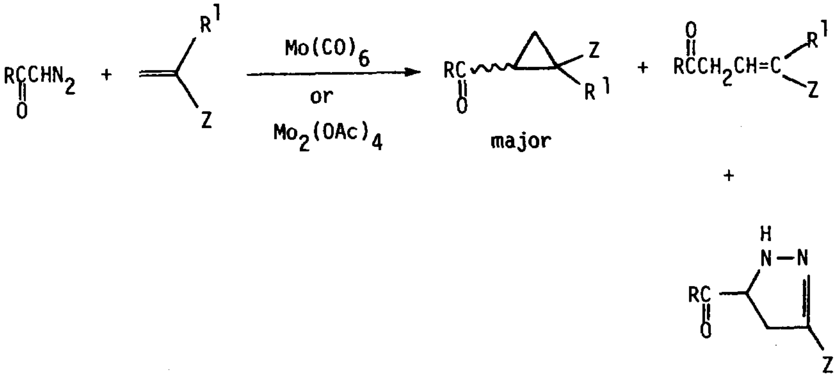

AcOCH$_2$-≡-CH$_2$OAc
N$_2$CHCO$_2$Et
Rh$_2$(OAc)$_4$
AcO
OAc
CO$_2$Et
30%
N$_2$CHCO$_2$-t-Bu
Rh$_2$(OAc)$_4$
AcO
OAc
CO$_2$t-Bu
65%
+
CO$_2$t-BU
CO$_2$t-BU
OAc
OAc
2%

(84)


AcO
OAc
COCHN$_2$
Rh$_2$(OAc)$_4$
O
OAc
OAc
30-40%

(85)

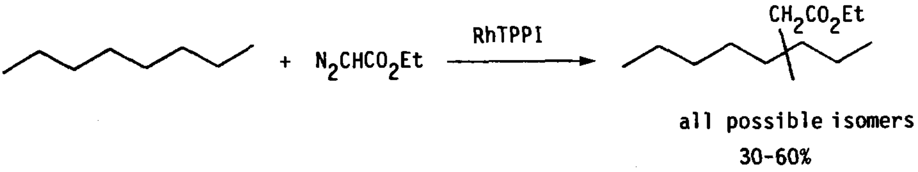
(86)


RCCHN$_2$
O
+
R$^1$
Z
Mo(CO)$_6$
or
Mo$_2$(OAc)$_4$
RC
O
Z
R$^1$
major
+
O
RCCH$_2$CH=C
R$^1$
Z
+
H
N—N
RC
O
Z

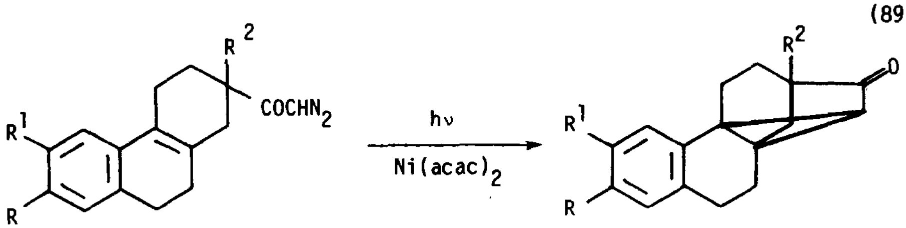

+
N$_2$CHCO$_2$Et
RhTPPI
CO$_2$Et
71%

(87)

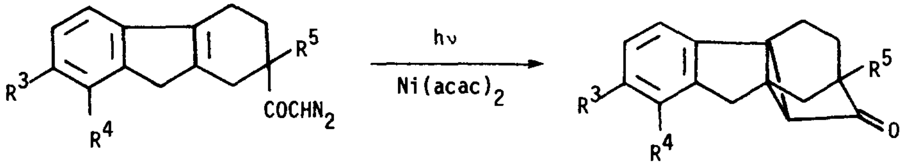
(88)


+
N$_2$CHCO$_2$Et
RhTPPI
CH$_2$CO$_2$Et
all possible isomers
30-60%

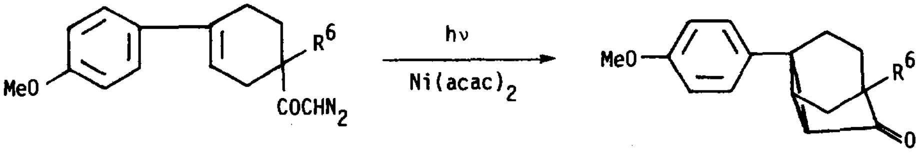
(89)



(90)

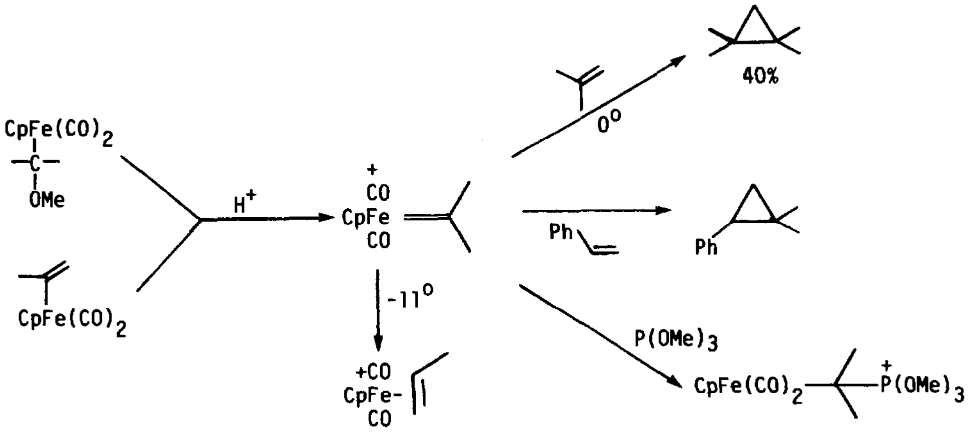


(91)

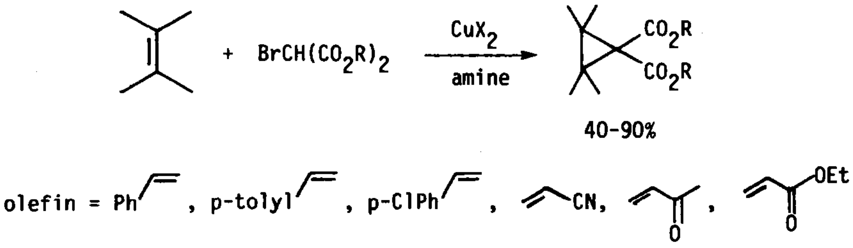


The iron carbene complex in Scheme 1 was an effective cyclopropanating agent [87].

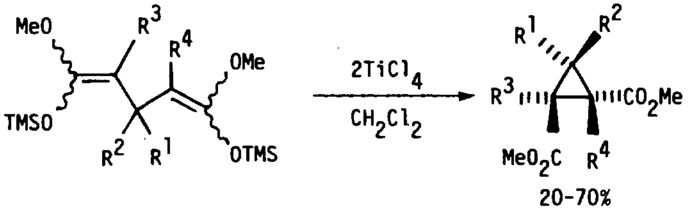
Scheme 1



Olefins were cyclopropanated by bromomalonates when treated with copper(II) halides and amines (equation 92) [88]. Bis-trimethylsilylenol ethers were converted to cyclopropanes by reactions with titanium(IV) chloride (equation 93) [89]. Allylic alcohols were cyclopropanated by ethylidene iodide and zinc/copper couple [90]. Olefins and gem dihalides produced cyclopropanes when treated with copper(I) bromide in DMSO [91].



(92)

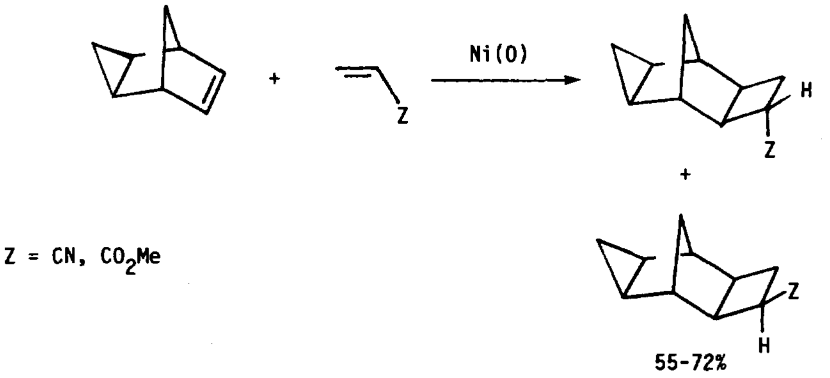


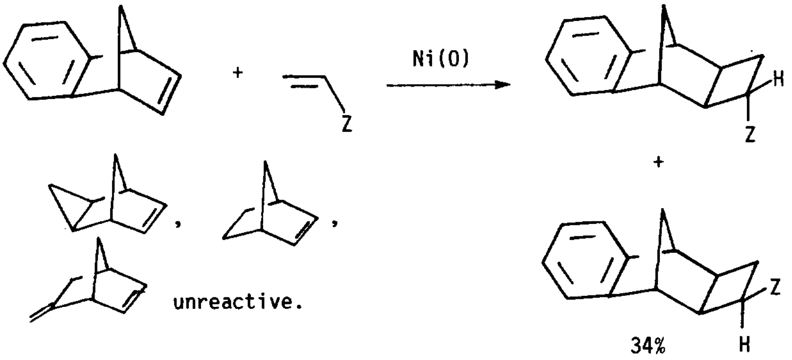
(93)

## 5. Cycloaddition Reactions

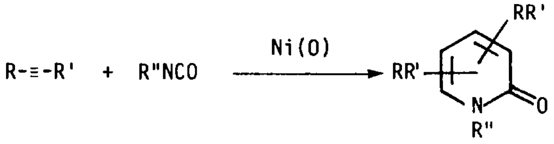
Nickel(0) complexes catalyzed the [2 + 2] cycloaddition of electrophilic olefins to strained olefins (equations 94 and 95 ) [92]. Similar complexes catalyzed the [2 + 2 + 2] cycloaddition of alkynes with isocyanates to give 2-pyridones (equation 96) [93].

(94)





(95)

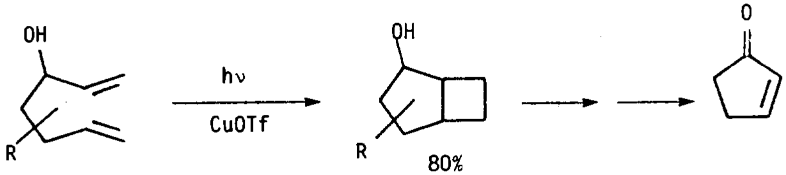


(96)

13-84%

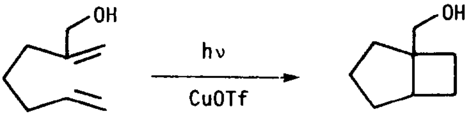
R = Ph, Et, Me
R' = Ph
R" = Me, H

Copper(I) triflate was used to catalyze a number of photolytic [2 + 2] cycloadditions (equations 97-99) [94],(equations 100-102) [95], and (equation 103) [96]. Titanocene hydride converted 1,5-hexadienes to cyclopentenes (equation 104) [97]. Palladium(II) salts catalyzed the cyclodimerization of alkoxy acetylenes, whereas cobalt carbonyl complexes cyclocarbonylated these substrates (equation 105) [98].

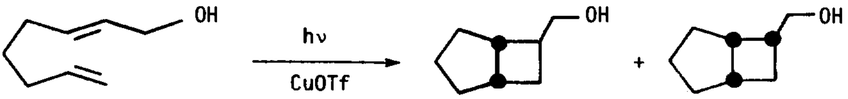


(97)

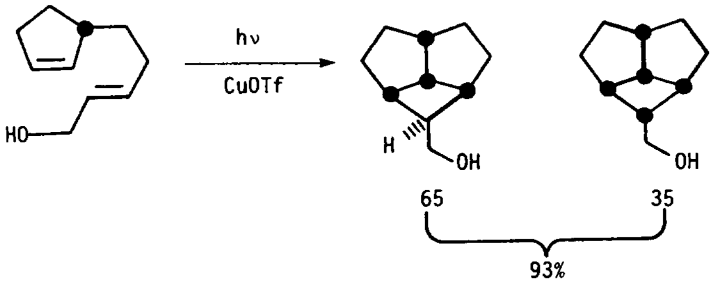
R = Me at, 2, 4, 5, 6, 3
di Me at 4, and 2,5



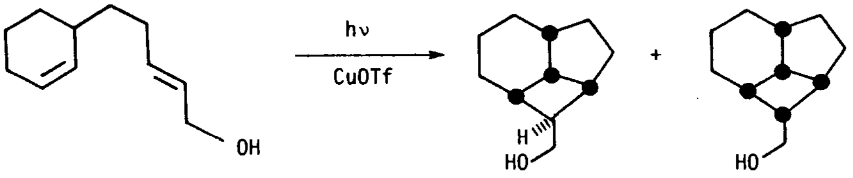
(98)



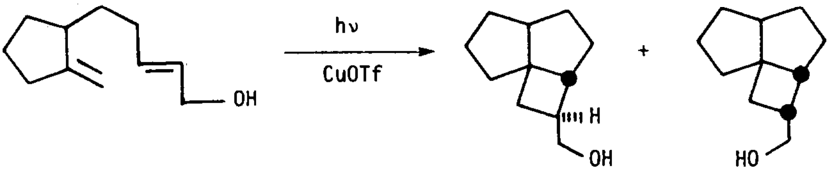
(99)



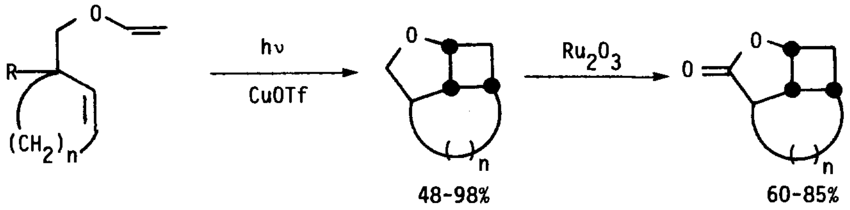
(100)



(101)



(102)

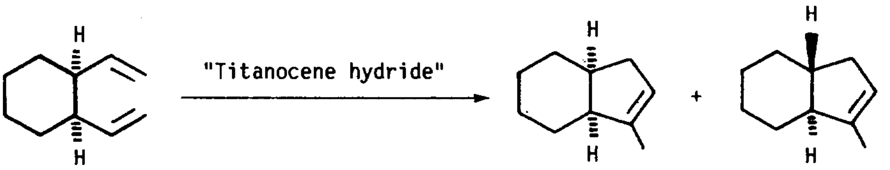


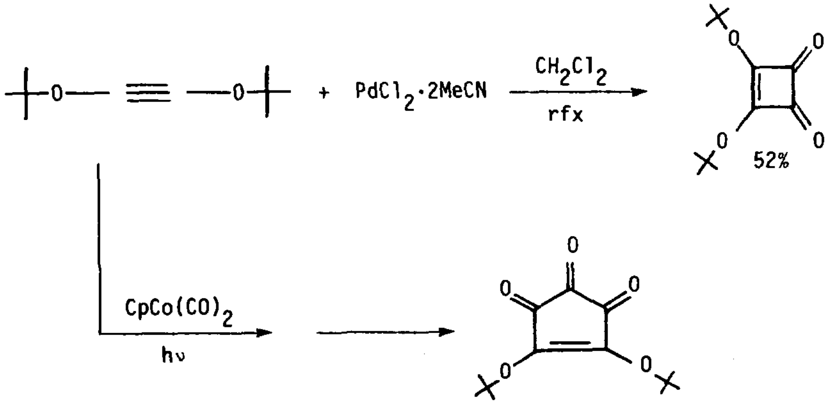
(103)

R = H, Me

n = 5, 6

(104)

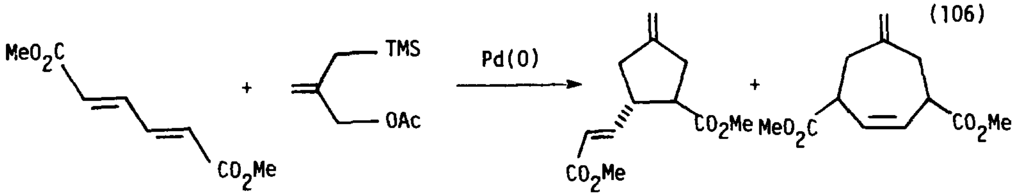




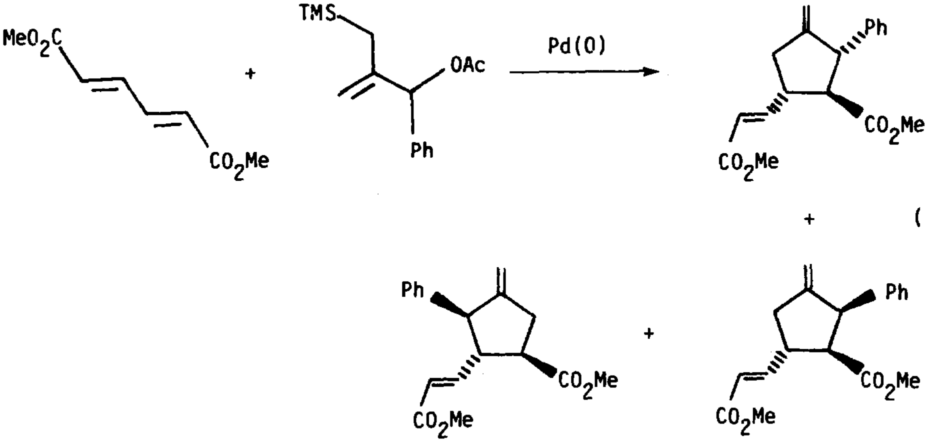
(105)

The palladium mediated "trimethylene methane" cycloaddition to α,β,γ,δ-unsaturated esters gave two cyclic products, the ratios of which depended on the palladium catalyst and the solvent (equations 106 and 107) [99]. Bicyclic material was prepared in this fashion (equation 108) [100], as was (±) albene (equation 109) [101]. Vinylcyclopropanes underwent a [3 + 2] cycloaddition to olefins to give cyclopentanes in the presence of π-allylpalladium catalysts [102].

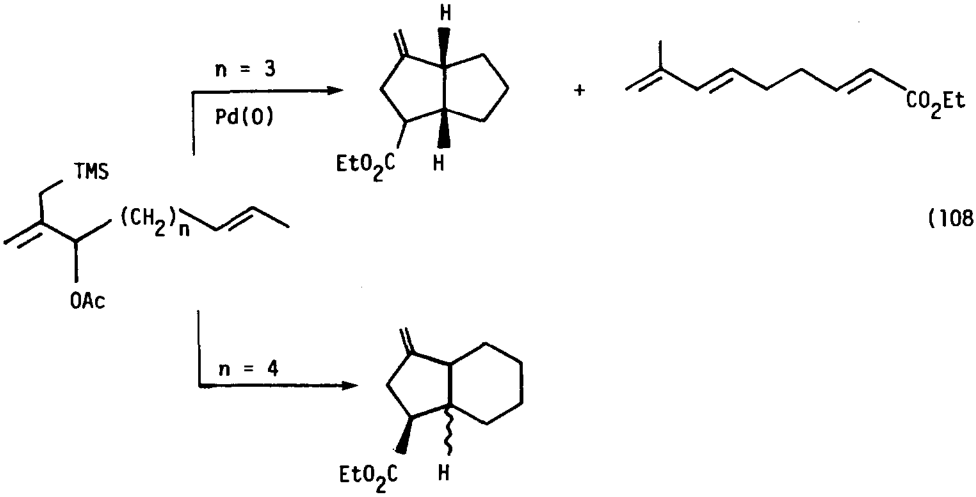
(106)



| | | | |
|---|---|---|---|
| $L_4Pd$, dppe, THF | 1.6 | 1 | 47% |
| $L_4Pd$, dppe, diox | 3.8 | 1 | 98% |
| $[(i\text{-}PrO)_3P]_4Pd$ | 1.1 | 1 | 89% |

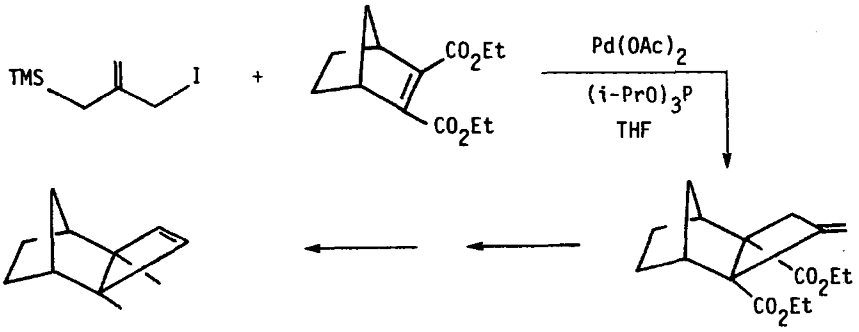


(107)

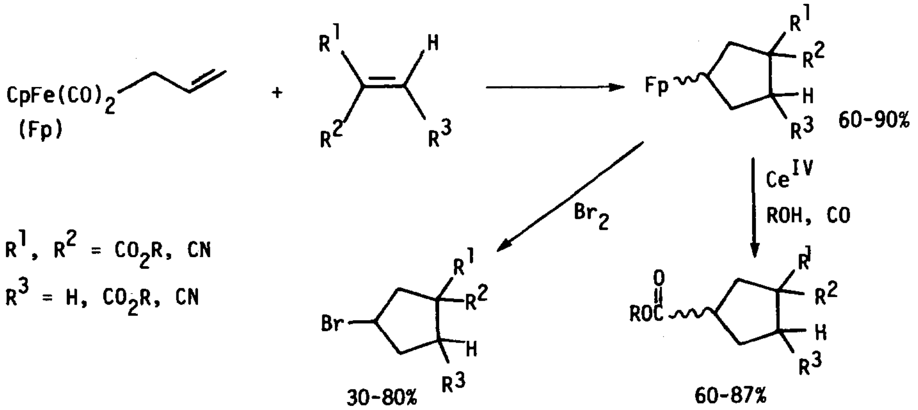


(108)

(109)

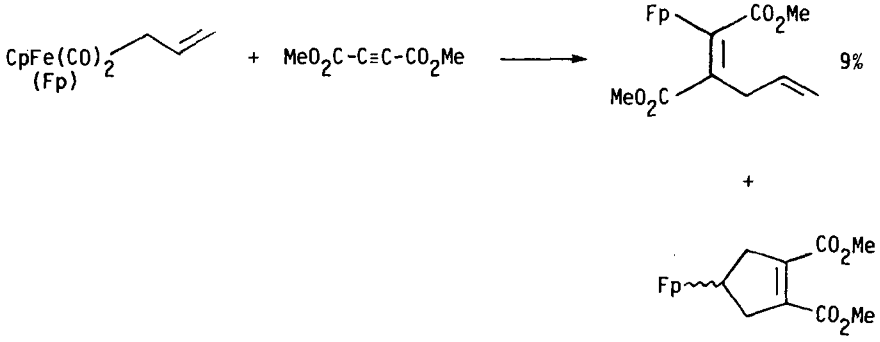


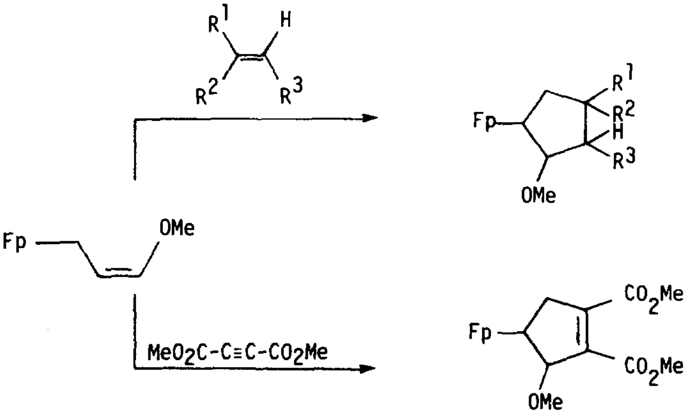
Electrophilic olefins (equation 110) and alkynes (equation 111) underwent a two step cycloaddition process when treated with $\eta^1$-allylcyclopentadienyl iron complexes [103]. Similar reactions were observed with iron complexes containing enol ethers (equation 112) [104], (equation 113) [105]. In some instances four (equation 114) and six (equation 115) membered rings were formed [106]. With cyclic enones a cyclopentane annulation procedure was developed (equation 116) [107].



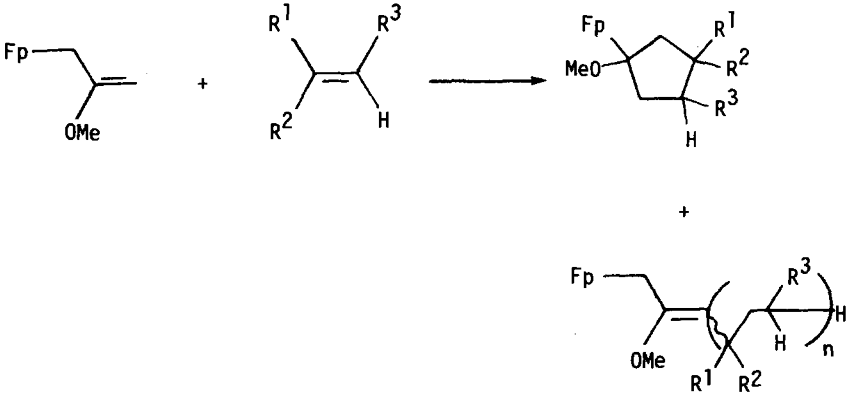
(110)

(111)

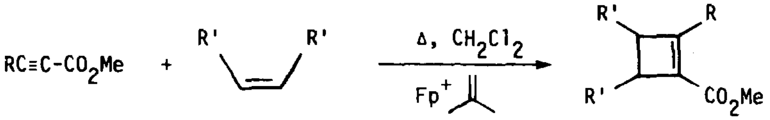




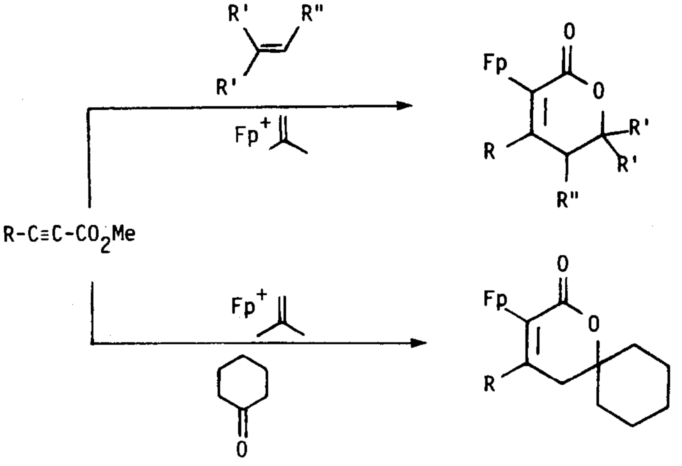
(112)



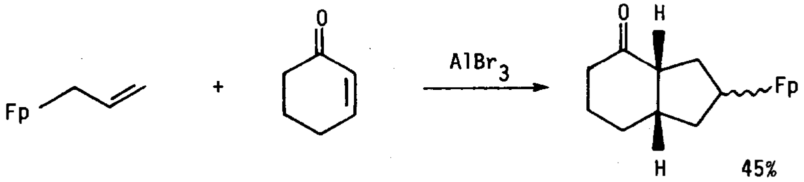
(113)



(114)

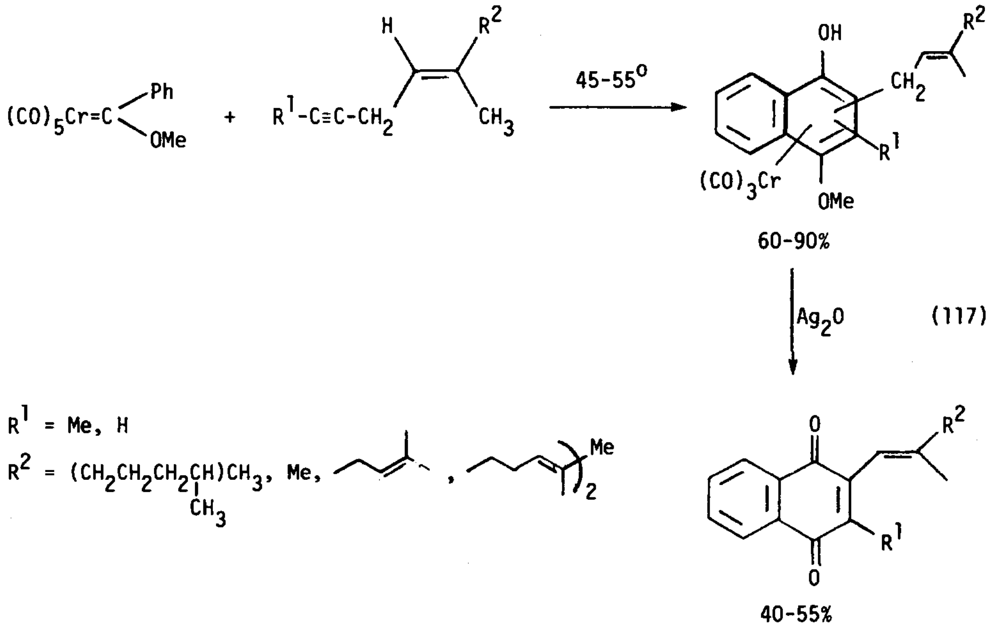


(115)



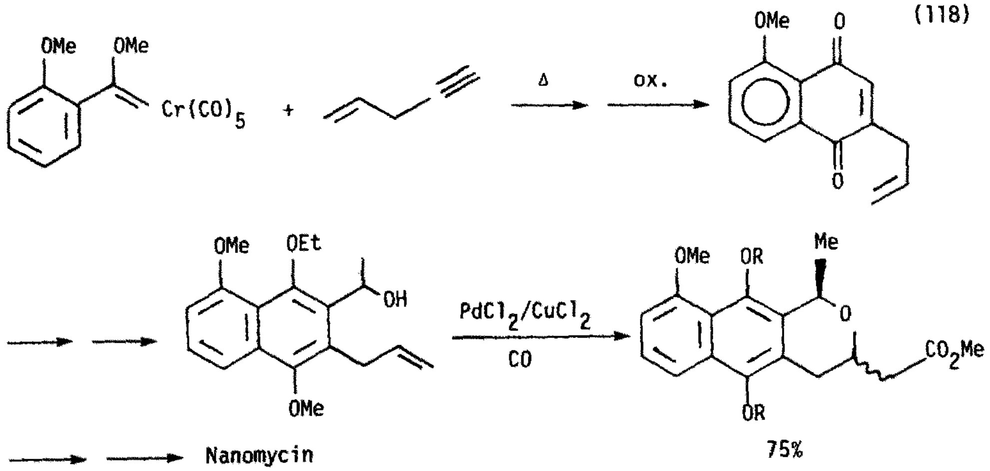
(116)

Chromium carbene complexes have finally been developed into useful reagents for organic synthesis. Reaction with enynes produced naphthoquinone vitamins after oxidative removal of the chromium (equation 117) [108]. Nanomycin (equation 118) and deoxyfrenolicin(equation 119) were prepared using this kind of chemistry [109]. The regiochemistry of addition of alkyne was controlled by incorporating it into the carbene complex (equation 120) [110].

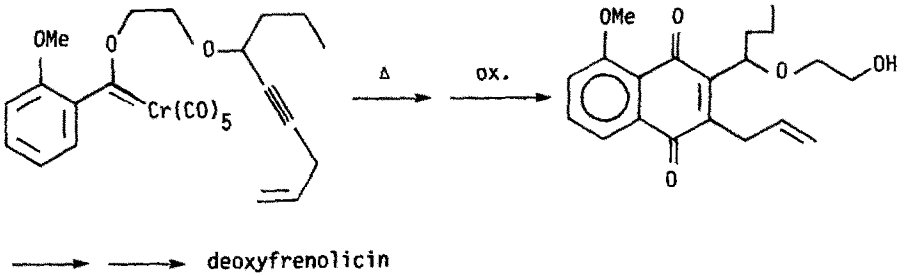


(117)

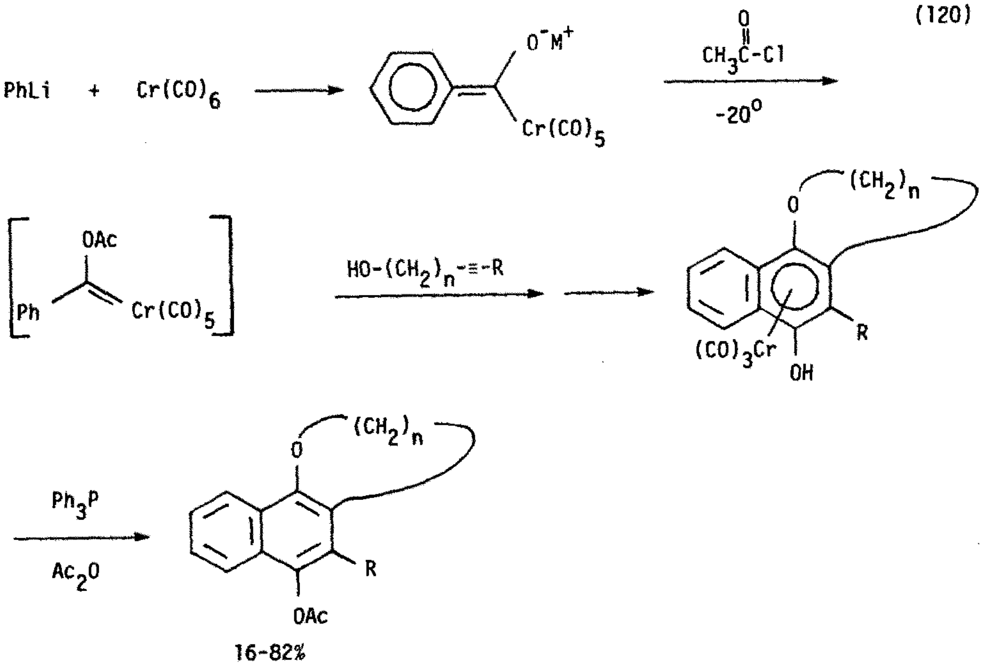
(118)


OMe
OMe
Cr(CO)$_5$
+
Δ
ox.
OMe
O
O
OMe
OEt
OH
OMe
PdCl$_2$/CuCl$_2$
CO
OMe
OR
Me
O
CO$_2$Me
OR
75%
Nanomycin

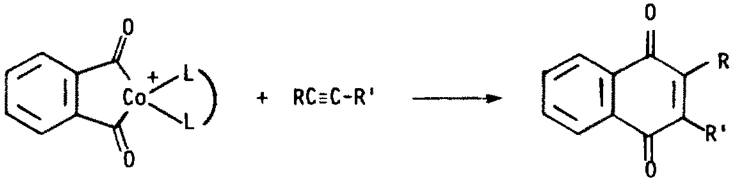
(119)


OMe
O
O
Cr(CO)$_5$
Δ
ox.
OMe
O
O
OH
O
deoxyfrenolicin

(120)


PhLi
+
Cr(CO)$_6$
O$^-$M$^+$
Cr(CO)$_5$
CH$_3$C(=O)-Cl
-20$^o$
OAc
Ph
Cr(CO)$_5$
HO-(CH$_2$)$_n$-≡-R
(CH$_2$)$_n$
O
R
(CO)$_3$Cr
OH
Ph$_3$P
Ac$_2$O
(CH$_2$)$_n$
O
R
OAc
16-82%

Naphthoquinones were synthesized by the reaction of alkynes with cobaltaphthalates (equation 121) [111]. Finally the THP ether of allyl alcohol reacted with the cobalt complex of 2-butyne to give a cyclopentenone (equation 122) [112].

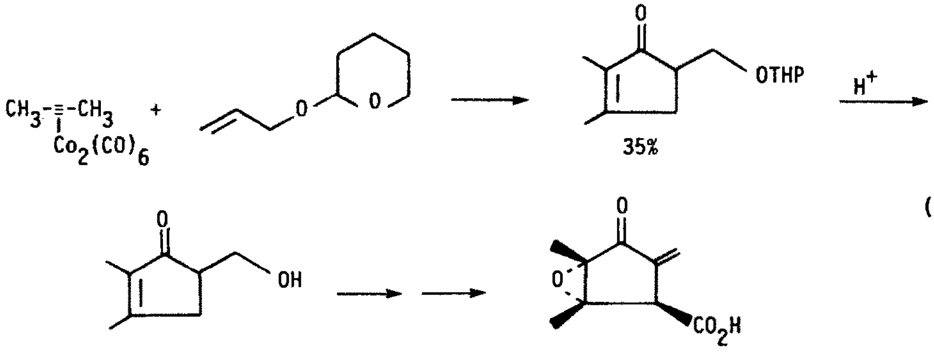


(121)

R = H, Et, TMS, Me

$R' = n\text{-}Bu, Et, CH_2OEt, CH(OEt)_2, (CH_2)_2OTHP$

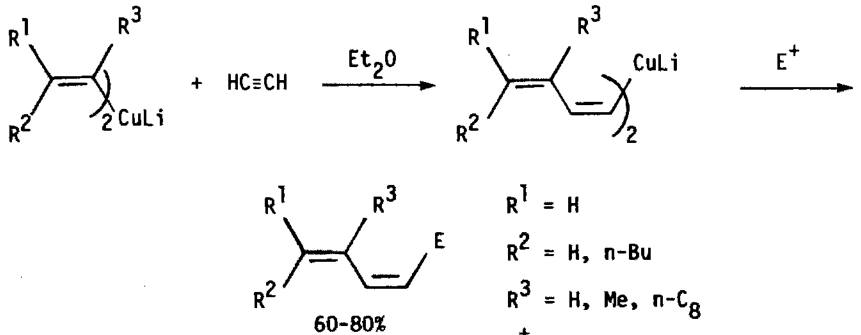
51-96%



(122)

## 6. Alkylation of Alkynes

Organocopper chemistry continues to be extensively used for the alkylation of alkynes. Vinylcuprates added to acetylene to give functionalized 1,3-dienes in excellent yield (equation 123) [113]. Similarly alkoxy containing cuprates added to alkynes to give functionalized alkenes stereo- and regiospecifically (equation 124) [114]. Triphenyltincopper reagents added to acetylene in a similar fashion (equation 125) and reacted with propargyl mesylates to give allenes (equation 126) [115].



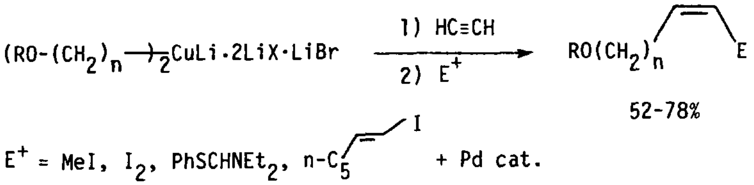
(123)

$R^1 = H$

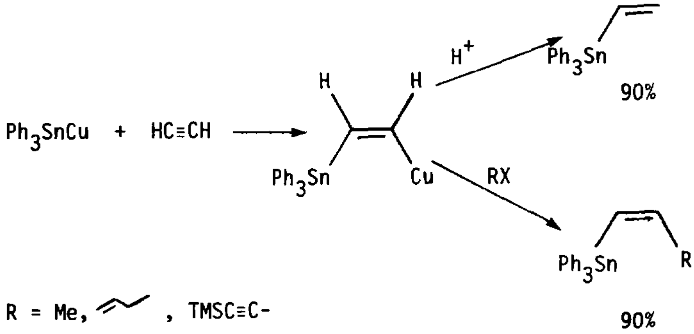
$R^2 = H, n\text{-}Bu$

$R^3 = H, Me, n\text{-}C_8$

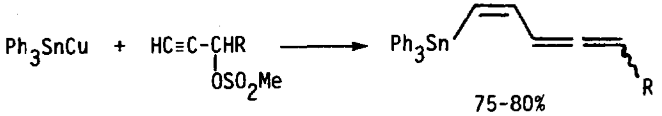
$E^+ = CO_2, BuI, MeI, PhSCH_2NEt_2$



124)

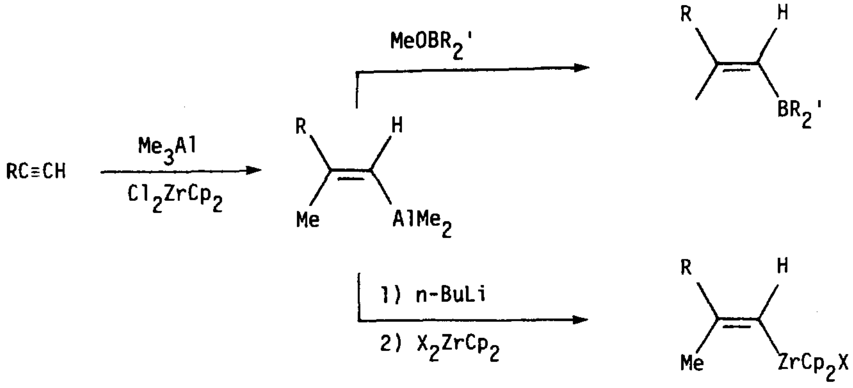


(125)

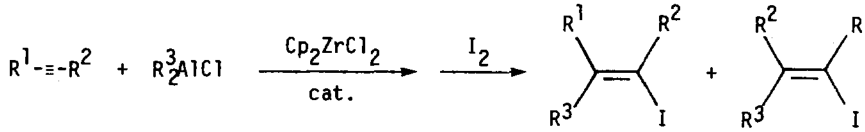


(126)

Zirconium complexes catalyzed the carboalumination of alkynes to give vinylalanes, which reacted with electrophiles to give substituted alkenes (equation 127) [116] (equation 128) [117].



(127)



(128)

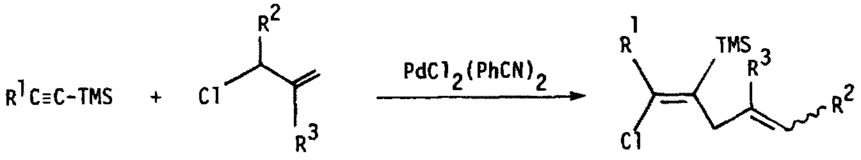
$R^1$ = n-$C_5$, n-Bu

$R^2$ = Me, Et, n-Pr, n-Bu

71-82%

from 98/2 to 76/24

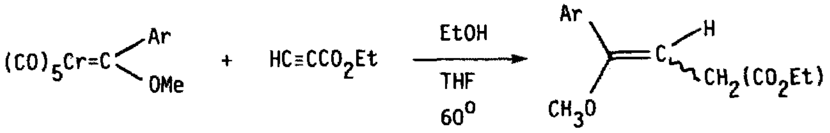
Palladium(II) complexes catalyzed the addition of allylic halides to trimethylsilylacetylenes (equation 129) [118]. Chromium carbene complexes condensed with alkynes to give unsaturated species (equation 130) [119], (equation 131) [120].



79-91%

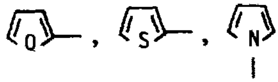
(129)

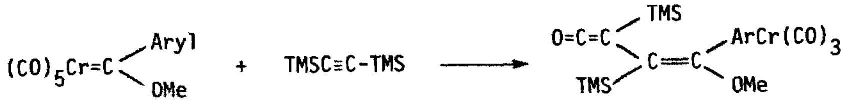
$R^1$ = n-Bu, n-$C_5$, n-$C_6$
$R^2$ = H, Me
$R^3$ = H, Me



80-87%

(130)

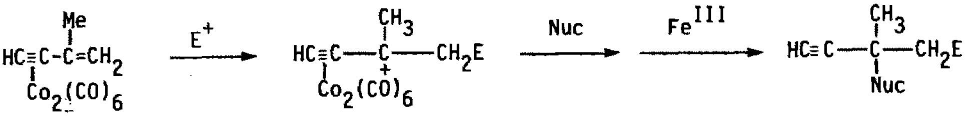
Ar = Ph,




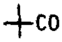
(131)

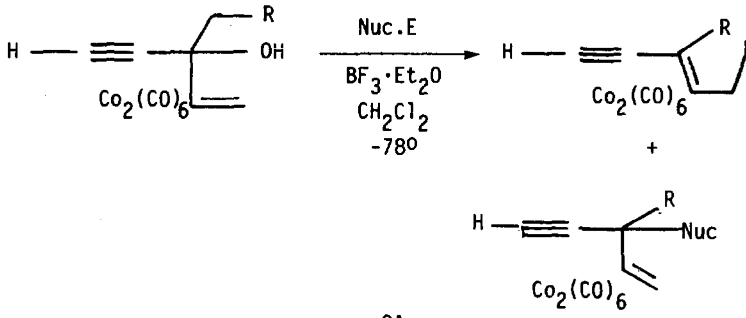
Cobalt-stabilized propargyl cations reacted with a variety of nucleophiles to produce a variety of propargyl substituted systems (equation 132) [121, 122]. With further investigation two products were obtained (equation 133) [123].

(132)

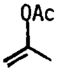
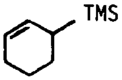


55-90%

$E^+$ = MeCO,  CO,  , t-Bu, $C_{10}H_{15}$, p-MePhS, p-ClPhS, $NO_2$
Nuc = $MeO^-$, $OH^-$

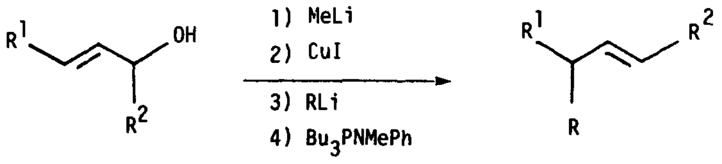


(133)

| | | | |
|---|---|---|---|
| Nuc-E = PhOMe | 82% A |  | 76% A, 6% B |
|  | 81% A | EtOH | 10% A, 70% B |
|  | 80% A | | |

### 7. Alkylation of Allyl and Propargyl Alcohols and Acetates

Allylic alcohols were alkylated with $S_N2'$ regiochemistry by sequential treatment with methyllithium, copper iodide, organolithium, and a phosphonium salt (equation 134) [124]. Allylic phosphites were alkylated by heteroaromatic Grignard reagents in the presence of copper(I) iodide (equation 135) [125]. The regiochemistry of the reaction of $Li_2Cu_3Me_5$ with allylic carbamates or acetates of terpenoid alcohols was studied [126].

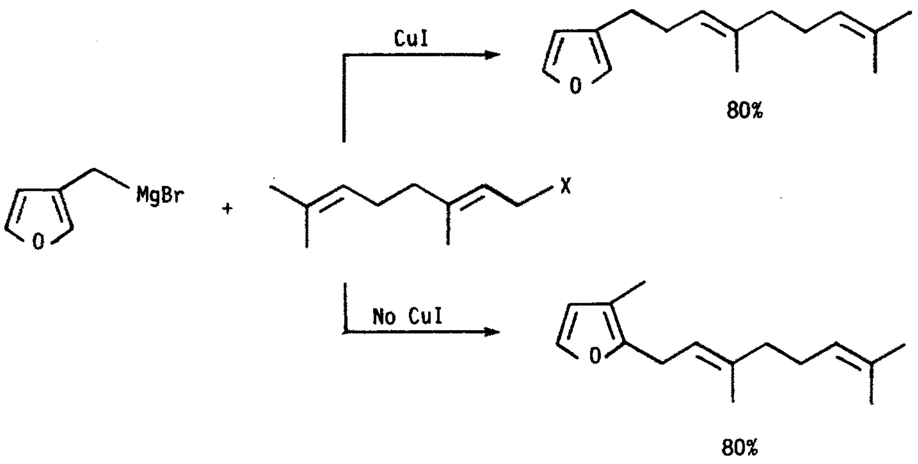


(134)

$R^1$ = TMS, $TMSCH_2$, H

$R^2$ = H, n-Bu, $TMSCH_2$

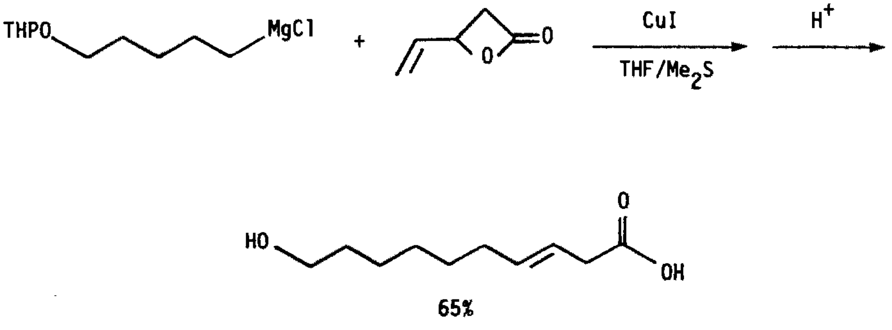
R = n-Bu, Me, Ph, Ar



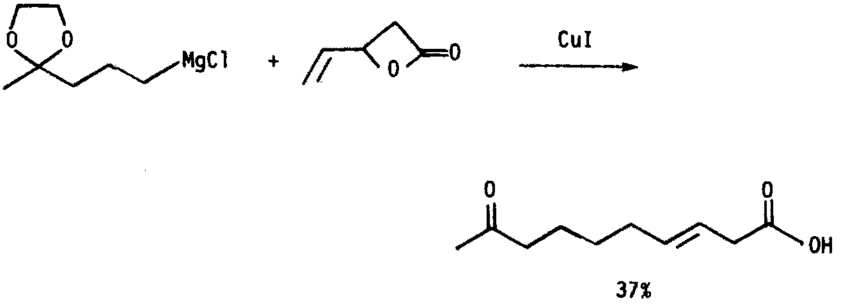
(135)

Copper-catalyzed reactions of Grignard reagents with β-vinyl-β-lactones has been used in the synthesis of a number of interesting organic compounds (equations 136 and 137) [127], (equations 138 and 139) [128], (equation 140) [129]. The five and six membered lactones reacted similarly (equations 141, 142, and 143) [130].

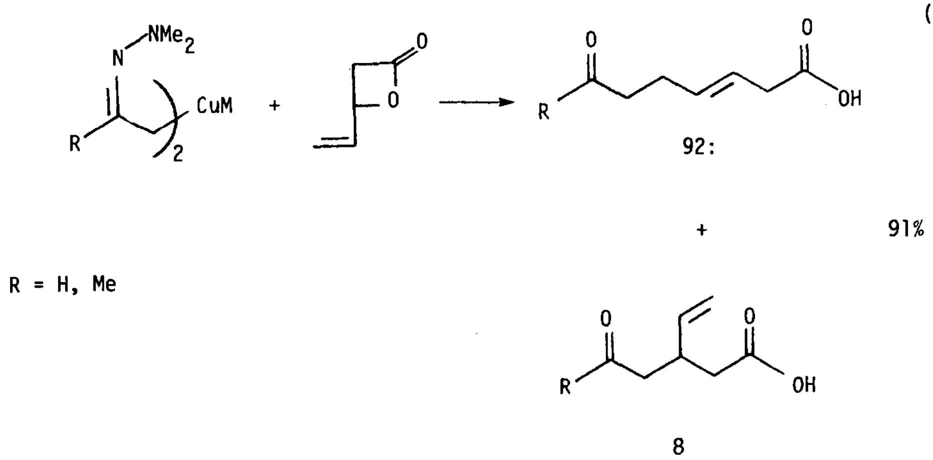
(136)



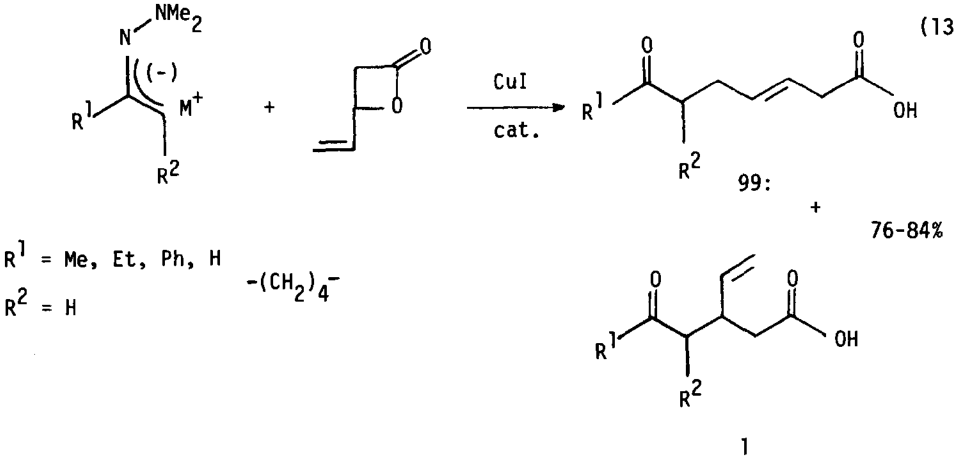
(137)



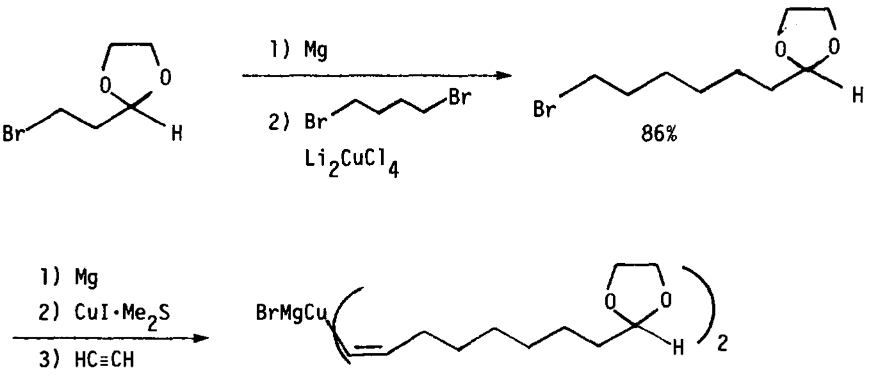
(138)



(139)



(140)



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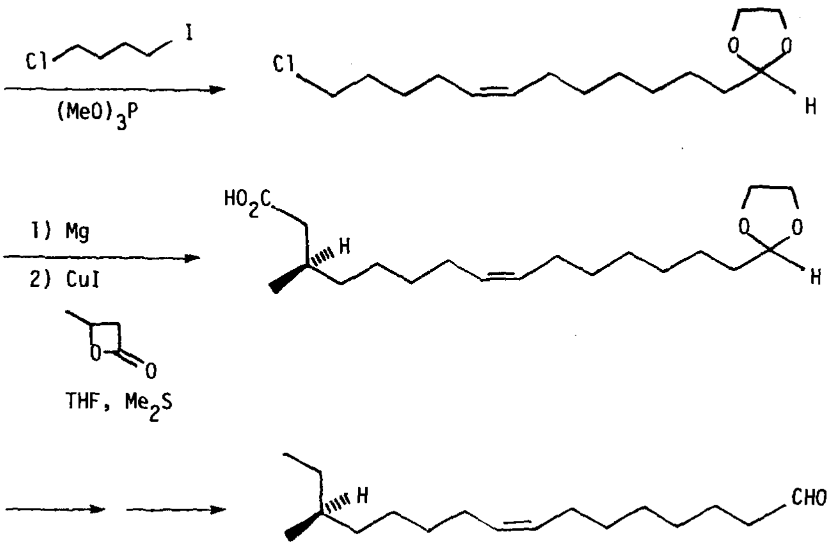
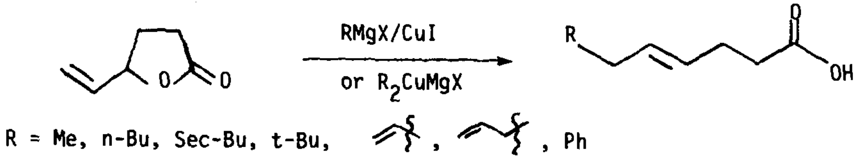
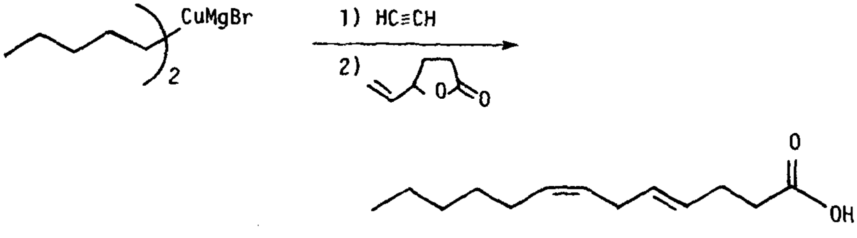
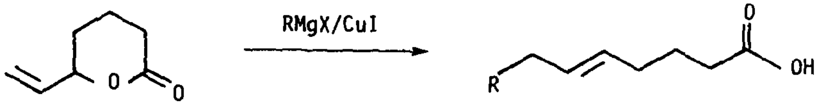




(141)

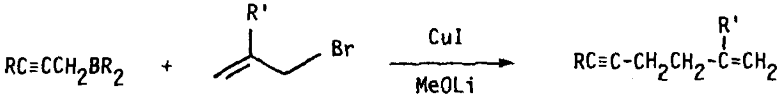
(142)





(143)

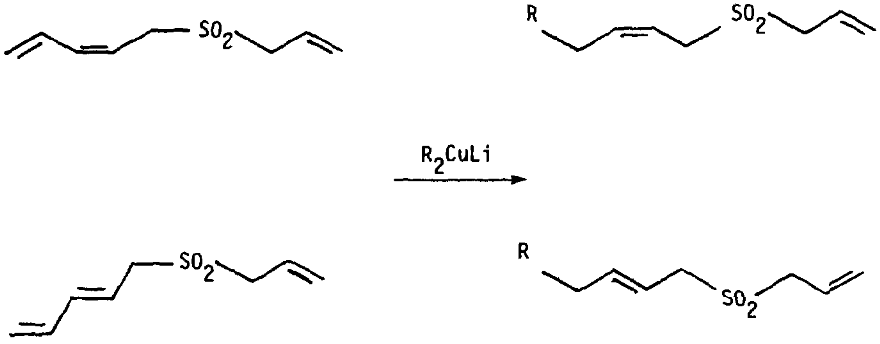
Allylic halides and propargyl boranes coupled when treated with copper(I) iodide to form eneynes (equation 144) [131]. Dienic allyl sulfones underwent 1,6-alkylation with organocopper reagents (equations 145 and 146) [132]. Organocuprates reacted with 1,4-diacetoxy-2-butenes with high regioselectivity (equations 147-149) [133]. Allylic thiocarbamates underwent $S_N2'$ alkylation when treated with organocopper reagents (equation 150) [134] (equation 151) [135].



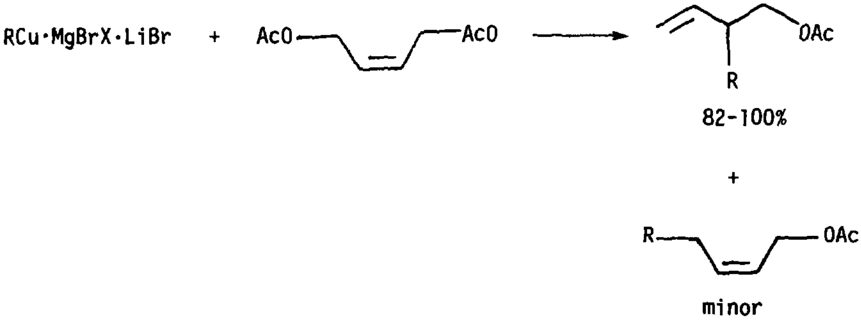
(144)

R = $n$-$C_{10}$, $n$-Bu, i-Bu, sec-Bu, cyclopentyl
R' = H, Me, Br

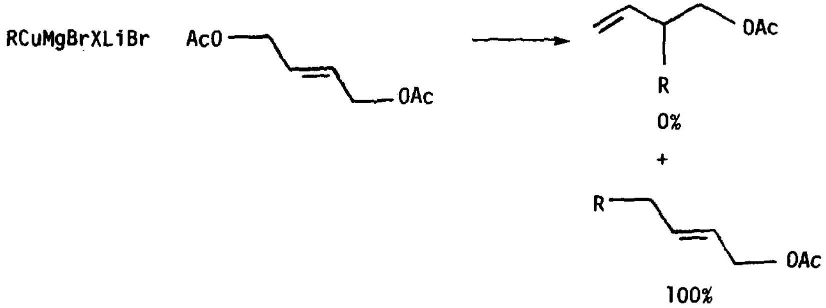
(145)



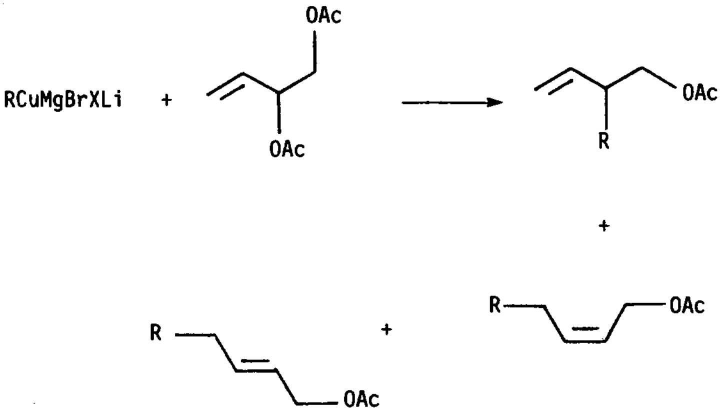
(146)



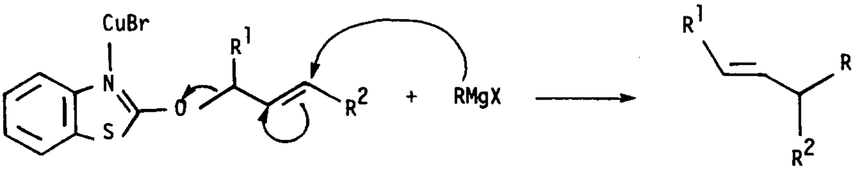
(147)



(148)



(149)



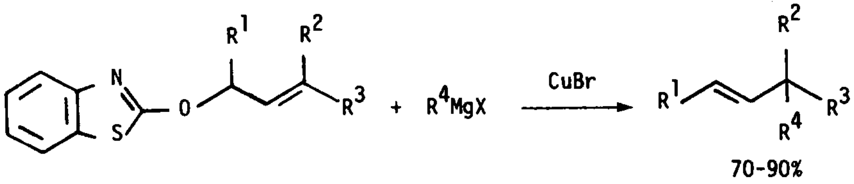
(150)

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

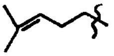
$R^1$ = Et  $R^2$ = H

R = n-Bu, Bz, n-$C_8$, -$(CH_2)_4OMgX$

(151)



$R^1$ = H, Et

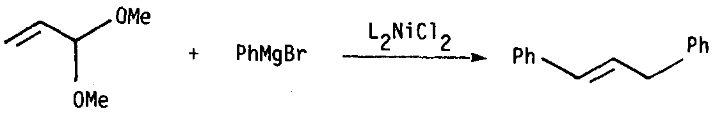
$R^2$ = Me, H, 

$R^3$ = H, Me, 

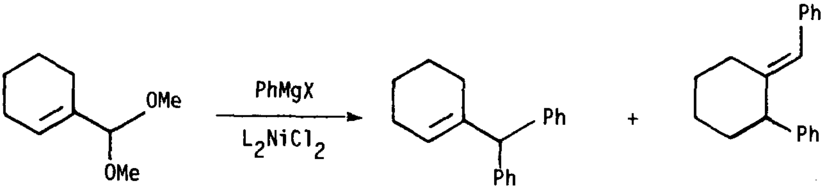
$R^4$ = n-Bu, $PhCH_2$, n-$C_8$

$ClMgO(CH_2)_3CH_2$-

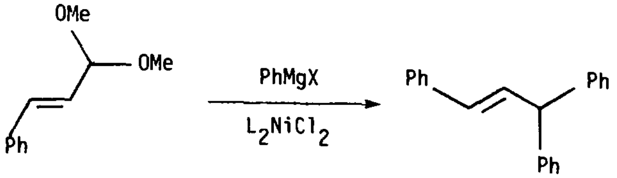
Acetals of allylic aldehydes underwent a double alkylation when treated with Grignard reagents in the presence of nickel(II) catalysts (equations 152-154) [136]. Titanium(IV) chloride coupled allyl acetates and allyl silanes (equation 155) [137]. Palladium(II) complexes were used to couple allylic halides to trimethylsilylacetylene (equation 156) [138]. Allyl acetate and benzene were reacted in the presence of palladium(II) salts to produce unsaturated aldehydes (equation 157) [139].



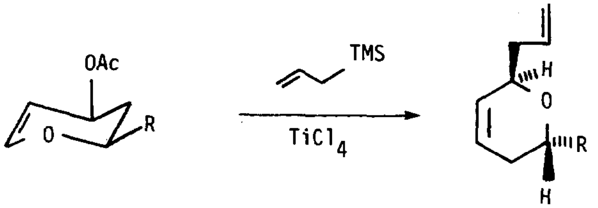
(152)



(153)



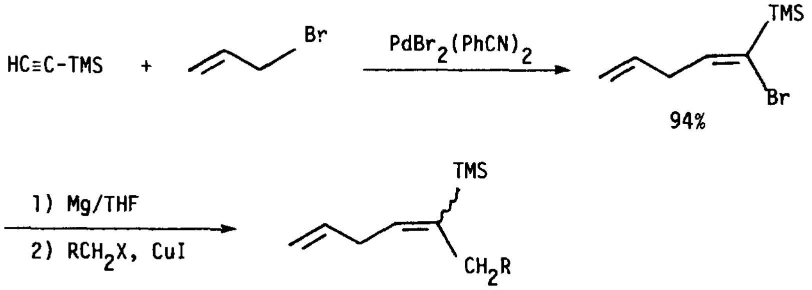
(154)



(155)

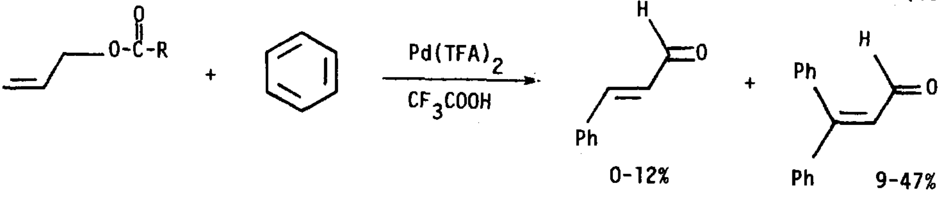
R = $CH_2OBz$, Ph, $CH_2SPh$, n-Pr

60-99%

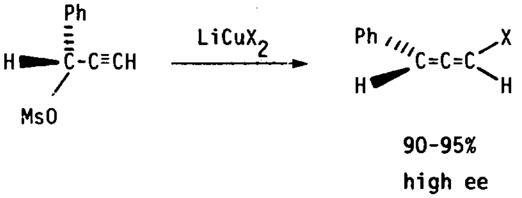


(156)

(157)

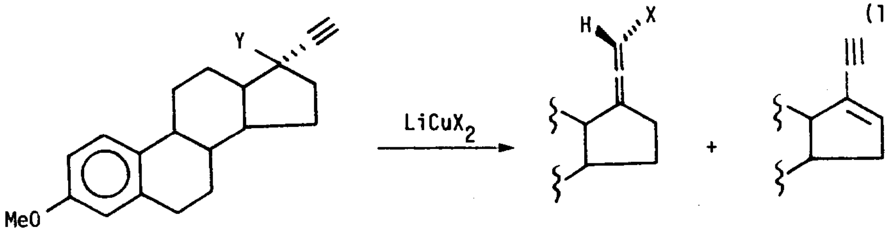


Chiral propargyl mesylates were converted to chiral haloallenes by reaction with copper halides (equations 158 and 159) [140]. Alkylcopper reagents converted propargyl tosylates or mesylates to allenes (equation 160) [141], (equation 161) [142]. More highly unsaturated propargyl systems reacted in a similar fashion (equation 162) [143]. Propargyl epoxides were converted to allenic systems when treated with organozinc reagents in the presence of palladium(0) catalysts (equations 163 and 164) [144], (equation 165) [145]. Cumulenes were produced from α-acetylenic vinyl halides and organocopper species (equation 166) [146]. Titanium(IV) chloride coupled propargylic trimethylsilanes with alkylidene malonates to produce allenes (equation 167) [147].

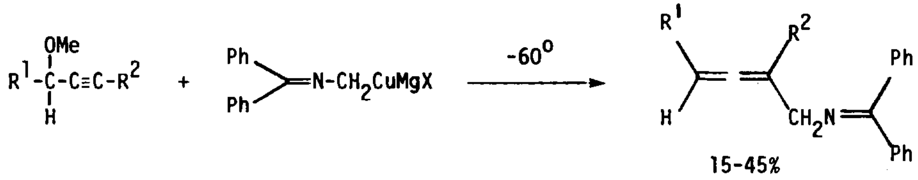


(158)

(159)

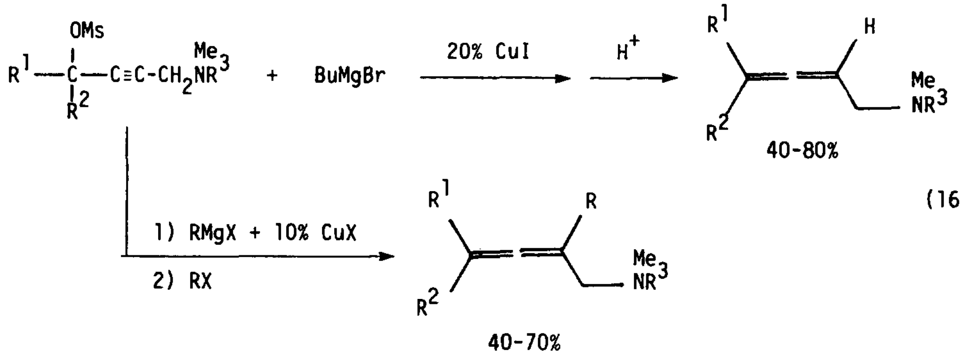


(160)



$R^1$ = Me, n-Pr, H

$R^2$ = H, Me, n-Bu, Bz, n-$C_6$



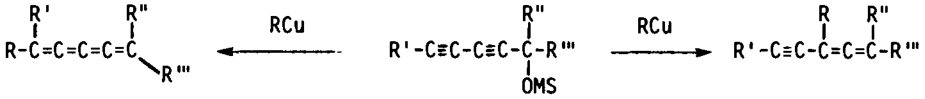
(161)

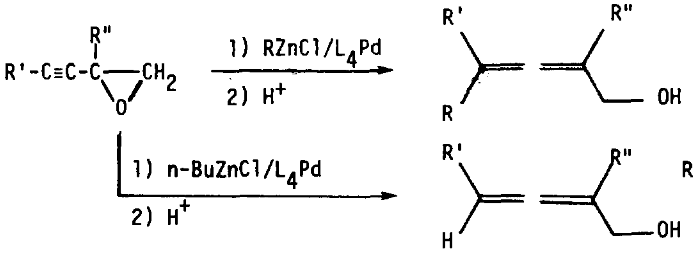
$R^1$ = H, Me, n-Pr, t-Bu

$R^2$ = H, Me

$R^3$ = $PhCH_2$, Me

(162)

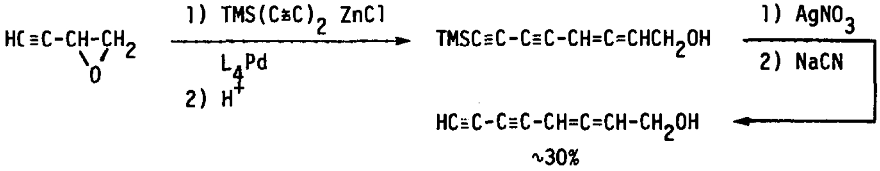




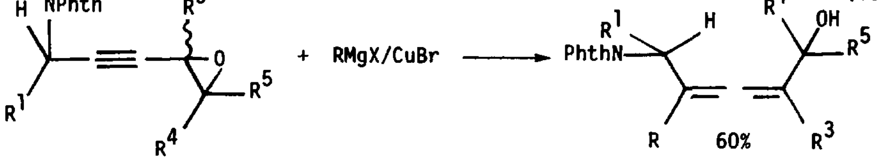
(163)

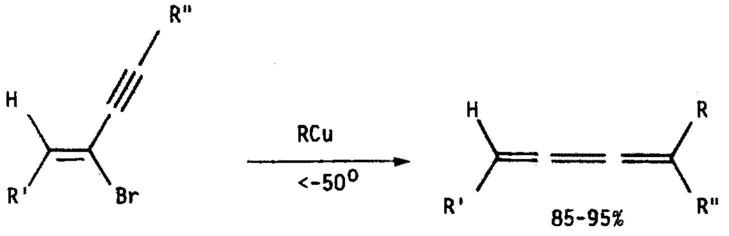
R = ═, TMSC≡C, t-Bu-CH=C=CH, TMSC≡C-C≡C

(164)



(165)

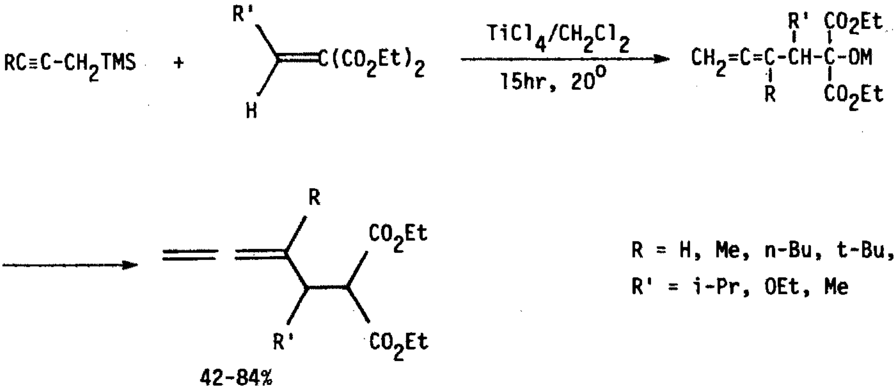




(166)

R' = n-Bu, i-Pr, t-Bu
R" = H, D, Ph
R = t-Bu, i-Pr

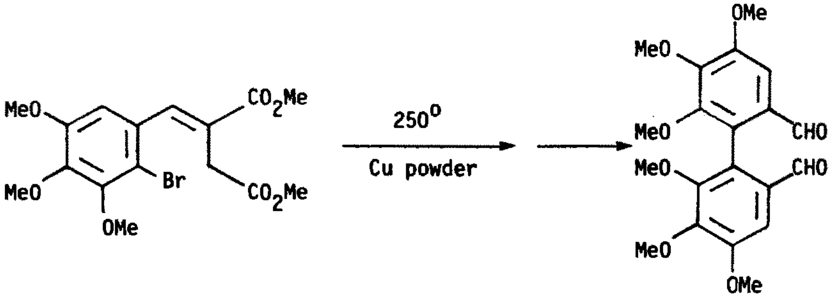
(167)



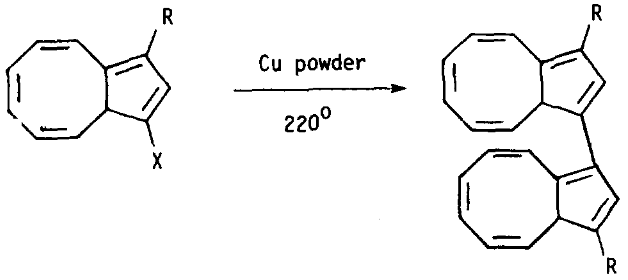
R = H, Me, n-Bu, t-Bu, Ph
R' = i-Pr, OEt, Me

## 8. Coupling Reactions

Ullmann type coupling was used to synthesize thirteen substituted biaryls in fair to good yield (for example, see equation 168) [148]. Haloazulenes were dimerized in a similar process (equations 169 and 170) [149]. Copper (equations 171 and 172) [150] and nickel salts (equations 173 and 174) [151], coupled sulfur stabilized carbanions, often with loss of the sulfur stabilizing group.

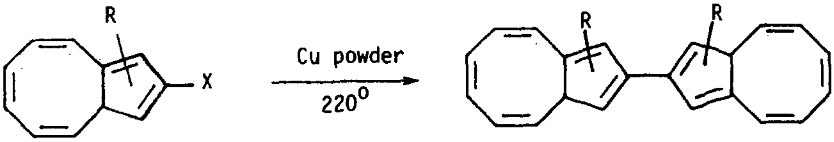


(168)

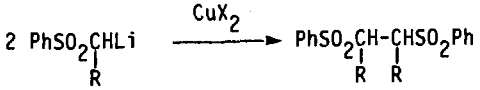


fair yield

(169)

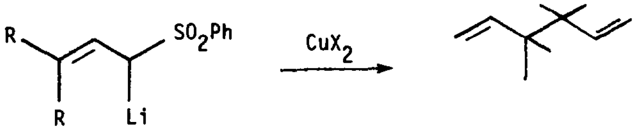


(170)

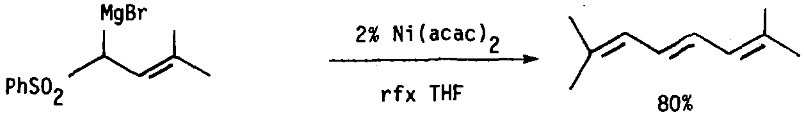


$$2\ \mathrm{PhSO_2\underset{R}{C}HLi} \xrightarrow{\mathrm{CuX_2}} \mathrm{PhSO_2\underset{R}{C}H{-}\underset{R}{C}HSO_2Ph}$$

(171)

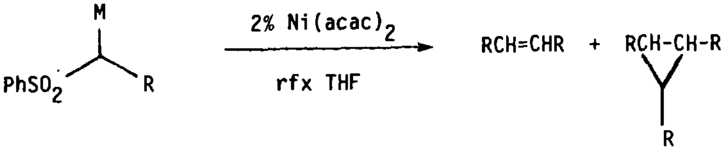


(172)



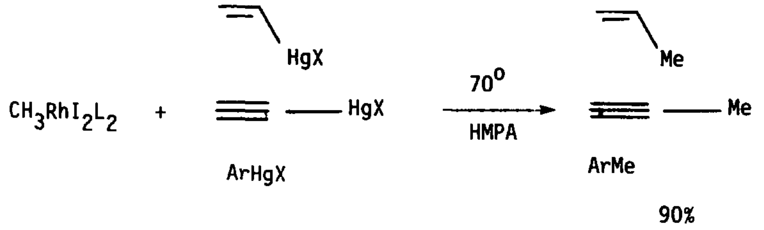
80%

(173)



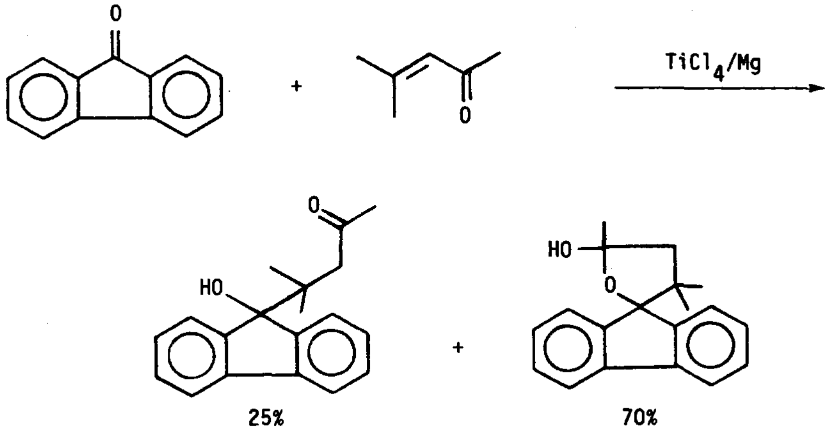
(174)

Diaryl mercury reagents cross-coupled with aryl halides to give unsymmetrical biaryls when treated with $PhPdIL_2$ in HMPA [152]. Diarylmercury compounds produced biaryls under the same conditions. Aryl, vinyl and acetylenic mercuric halides were methylated by methylrhodium(III) complexes (equation 175) [153]. A detailed study of the reaction of aryl, vinyl and alkylmercuric halides with organocopper reagents to give coupled products has been published [154]. Nickel metal coupled aryl halides to biaryls and benzyl halides to bibenzyls [155].

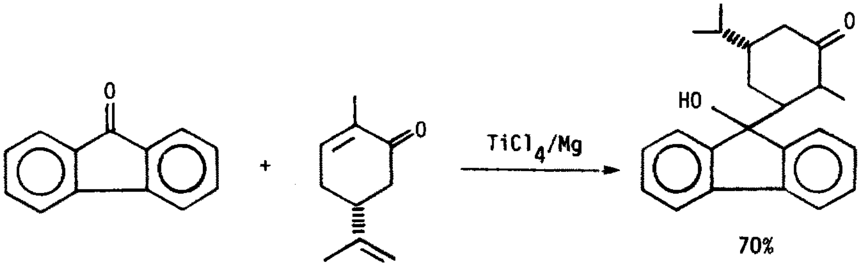


(175)

The reductive coupling of carbonyl compounds by low-valent titanium species has been reviewed (40 references) [156]. In addition to the coupling of carbonyl compounds, these reagents cause hydrogenation, isomerization and aldol condensation reactions to occur [157]. Fluorenone coupled to conjugated enones when treated with the reagent resulting from reaction of magnesium metal with titanium(IV) chloride (equations 176 and 177) [158]. The reagents produced by the reduction of $TiCl_3$, $TiCl_4$, $NbCl_5$, $MoCl_5$, and $WCl_6$, by lithium aluminum hydride were examined for their ability to couple benzophenone to tetraphenylethylene. The reagent from $TiCl_3$ proved the most efficient [159]. Reduction of $NbCl_5$ with sodium aluminum hydride gave a reagent that reductively coupled and/or deoxygenated a number of substrates (Scheme 2) [160]. The mechanism of titanium(0) coupling of ketones to olefins has been studied [161]. As the steric congestion about the parent ketone increased, the yield of substituted ethanes (from reduction of the olefin) and methanes (from reduction of the ketones) increased, at the expense of the olefin [162]. The reagent produced from the reduction of titanium(III) chloride with lithium aluminum hydride effected a number of couplings (Scheme 3) [163].

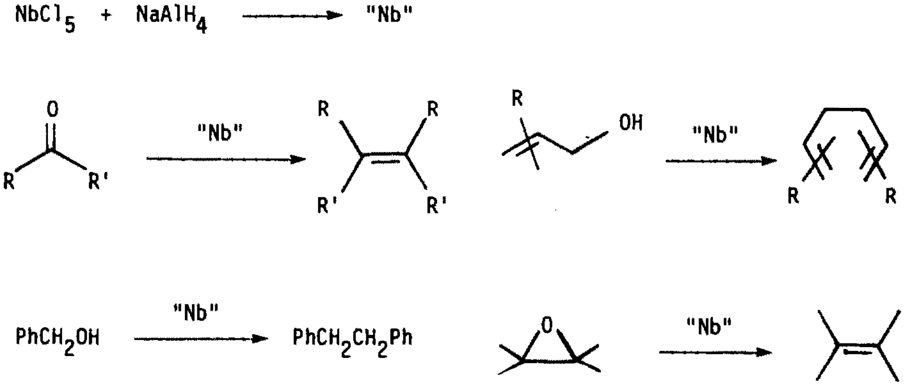


(176)



(177)

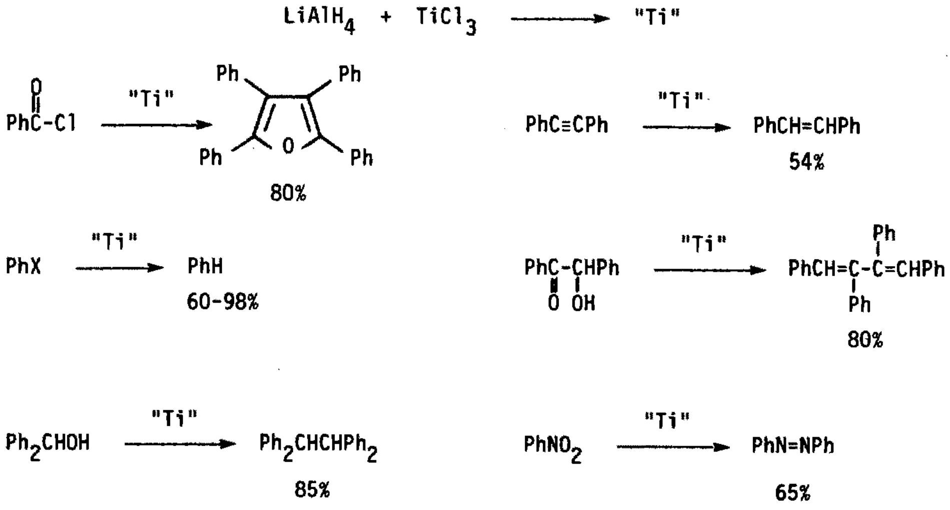
Scheme 2



$$NbCl_5 + NaAlH_4 \longrightarrow \text{"Nb"}$$

$$PhCH_2OH \xrightarrow{\text{"Nb"}} PhCH_2CH_2Ph$$

Scheme 3



$$LiAlH_4 + TiCl_3 \longrightarrow \text{"Ti"}$$

$$Ph\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow{\text{"Ti"}} \text{80\%}$$

$$PhC{\equiv}CPh \xrightarrow{\text{"Ti"}} PhCH{=}CHPh \quad 54\%$$

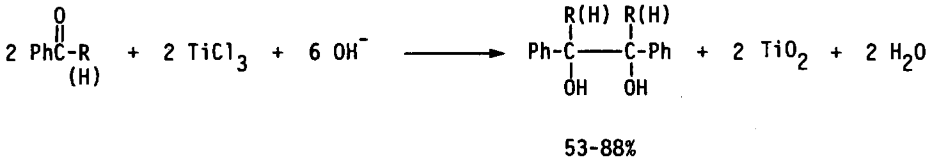
$$PhX \xrightarrow{\text{"Ti"}} PhH \quad 60\text{-}98\%$$

$$Ph\underset{O}{\underset{\|}{C}}\text{-}\underset{OH}{\underset{|}{C}}HPh \xrightarrow{\text{"Ti"}} PhCH{=}\underset{Ph}{\underset{|}{C}}\text{-}\overset{Ph}{\overset{|}{C}}{=}CHPh \quad 80\%$$

$$Ph_2CHOH \xrightarrow{\text{"Ti"}} Ph_2CHCHPh_2 \quad 85\%$$

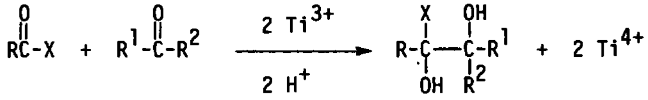
$$PhNO_2 \xrightarrow{\text{"Ti"}} PhN{=}NPh \quad 65\%$$

Ketones were dimerized to diols by titanium(III) chloride in strongly basic medium (equation 178) [164]. Carboxylic acid derivatives condensed with ketones to give diols when allowed to react with titanium(III) chloride under acidic conditions (equation 179) [165]. Ferrocenyl alcohols were dimerized when treated with titanium(III) chloride and butyllithium (equation 180) [166].



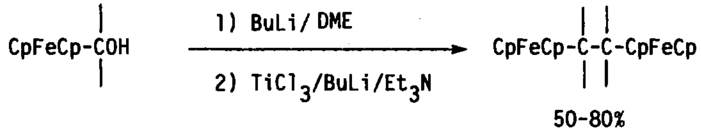
$$2\ \mathrm{Ph}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\underset{(H)}{R} + 2\ TiCl_3 + 6\ OH^- \longrightarrow \mathrm{Ph}\text{-}\underset{OH}{\overset{R(H)}{C}}\text{—}\underset{OH}{\overset{R(H)}{C}}\text{-}\mathrm{Ph} + 2\ TiO_2 + 2\ H_2O \qquad (178)$$

53-88%



$$R\overset{\overset{\displaystyle O}{\|}}{C}\text{-}X + R^1\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R^2 \xrightarrow[2\ H^+]{2\ Ti^{3+}} R\text{-}\underset{OH}{\overset{X}{C}}\text{—}\underset{R^2}{\overset{OH}{C}}\text{-}R^1 + 2\ Ti^{4+} \qquad (179)$$

X = CN, $CO_2H$, $CO_2Me$, py
R = Me, Ph
$R^1$ = Me, H
$R^2$ = H, Me, Ph

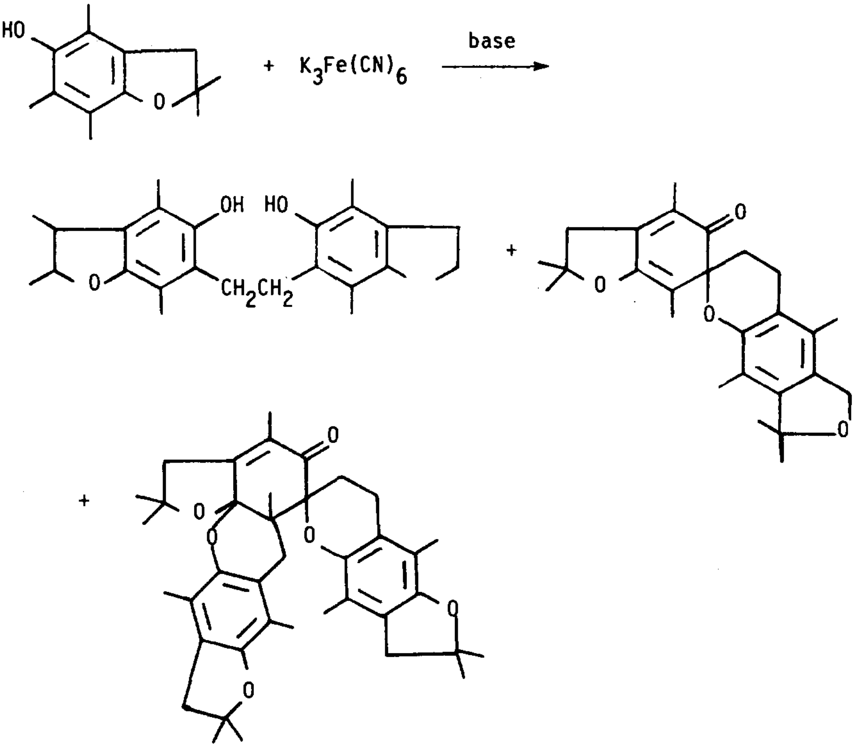


$$\mathrm{CpFeCp}\text{-}\underset{|}{\overset{|}{C}}OH \xrightarrow[2)\ TiCl_3/BuLi/Et_3N]{1)\ BuLi/DME} \mathrm{CpFeCp}\text{-}\underset{|}{\overset{|}{C}}\text{-}\underset{|}{\overset{|}{C}}\text{-}\mathrm{CpFeCp} \qquad (180)$$

50-80%

An immobilized macromolecular copper catalyst for the oxidative coupling of phenols has been developed [167]. The kinetics of the oxidative coupling of acetone with aromatic compounds in the presence of manganese(III) acetate have been studied [168]. Dihydrobenzofurans coupled when exposed to $K_3Fe(CN)_6$ and base (equation 181) [169]. Finally cobalt(II) polyvinylpyridine in DMF catalyzed aldol condensation reactions between aryl aldehydes and aryl methyl ketones. The reaction proceeded under neutral conditions and gave no sideproducts [170].

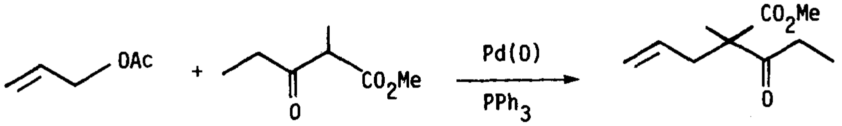
(181)



## 8. Alkylations Involving π-Allyl Complexes

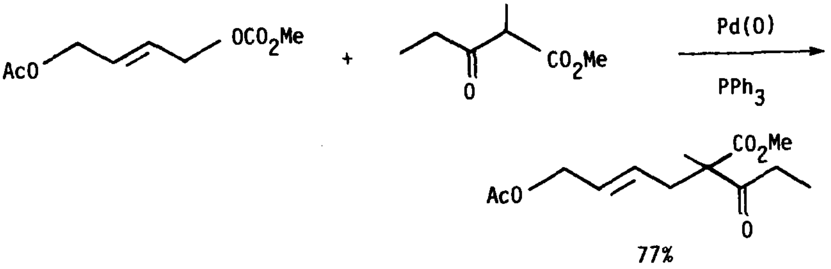
The stereochemistry of reactions of π-allyl complexes with nucleophilic reagents has been reviewed (15 references) [171]. The crystal and molecular structure of the dimeric π-allylpalladium chloride complex of testosterone has been elucidated [172]. Asymmetric catalytic allylic alkylation was the subject of a review [173]. "Cyclopentanoids: A Challenge for New Methodolgy" was the title of a review (63 references) which included a discussion of π-allylpalladium complexes in that context [174]. Catalytic reactions via π-allylpalladium complexes was also the subject of a review (14 references) [175].

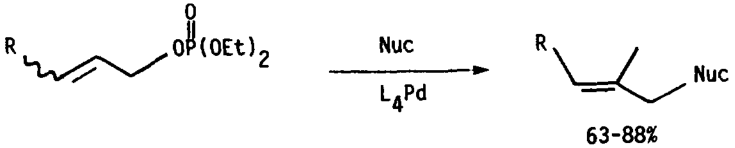
Palladium(0) complexes catalyzed the alkylation of allylic acetates with β-ketoester anions (equations 182 and 183) [176], the coupling of allyl phosphites with a wide range of nucleophiles including stabilized carbanions and amines (equations 184 and 185) [177], and the coupling of allyl ammonium salts with stabilized carbanions (equation 186) [178]. The alkylation of 1-acetoxy-4-hydroxy-2-butene at the acetoxy position was also catalyzed by palladium(0) complexes (equation 187) [179]. This type of reaction was used to make cyclopropanes (equation 188) [180]. Double alkylation of 1,4-acetoxy-2-butene using palladium(0) catalysts was also achieved (equation 189) [181]. Alkylation of allyl acetate by a β-diketone in the presence of a π-allylpalladium catalyst and a chiral ligand led to alkylation with up to 52% ee (equation 190) [182].



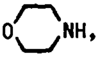
(182)

(183)

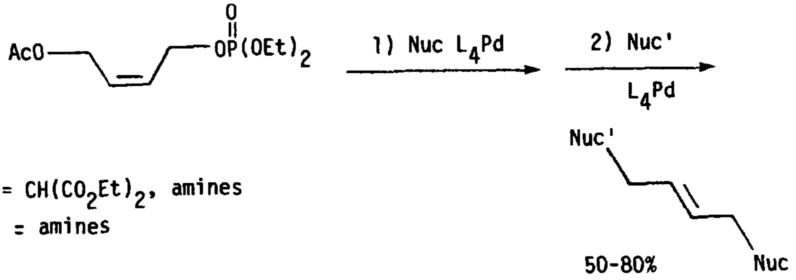




(184)

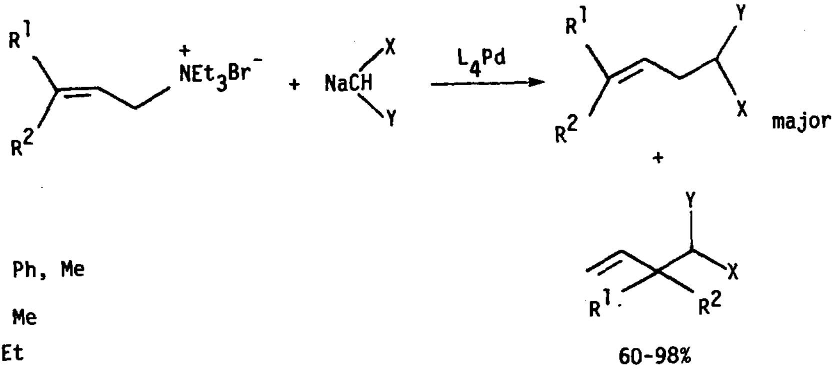
Nuc = $CH(CO_2Et)_2$, $Et_2NH$,  $PhNHMe$

(185)



Nuc = $CH(CO_2Et)_2$, amines

Nuc' = amines



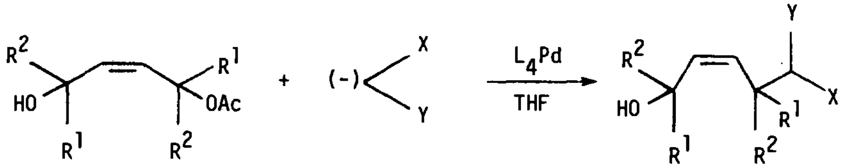
(186)

$R^1$ = H, Ph, Me

$R^2$ = H, Me

X = $CO_2Et$

Y = $CO_2Et$, $SO_2Ph$ ketone enolates also react.



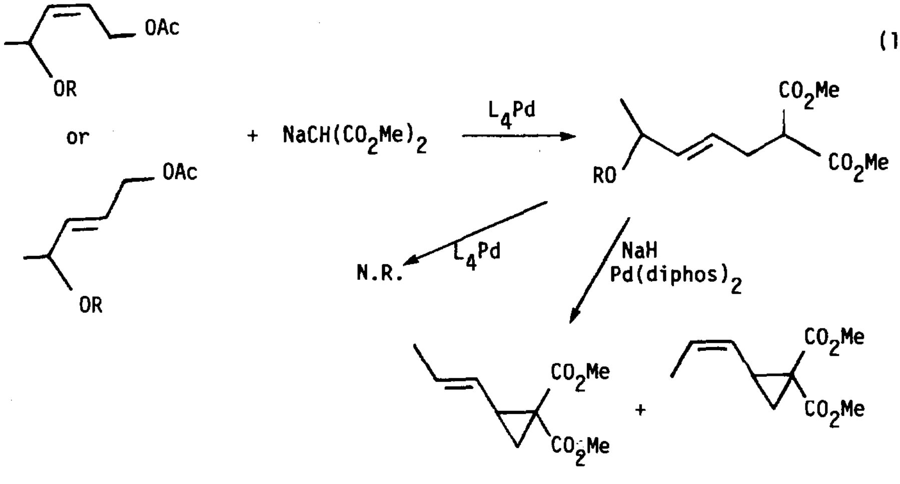
(187)

$R^1$ = H, Me

$R^2$ = H

X = $CO_2Me$, $CO_2CH_2Ph$

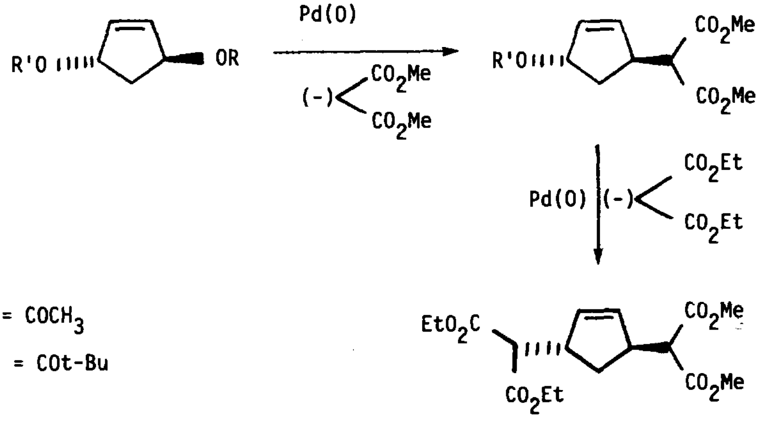
Y = $CO_2Me$, COMe, CN, $SO_2Ph$



(188)

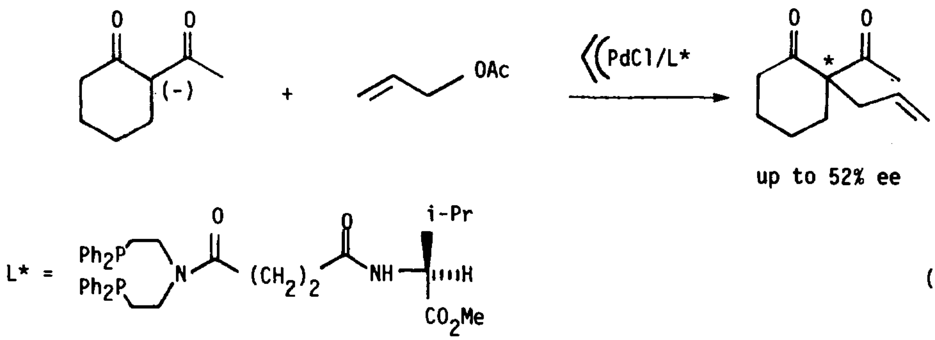
7:1 no yield

(189)



R = $COCH_3$

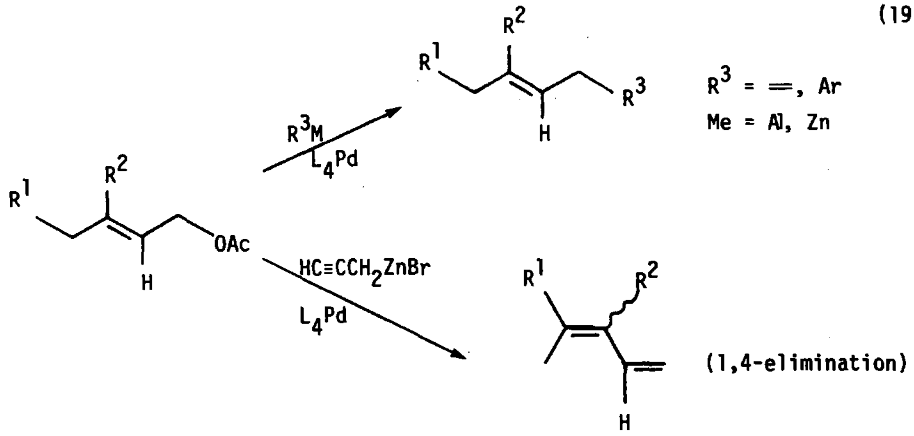
R' = COt-Bu



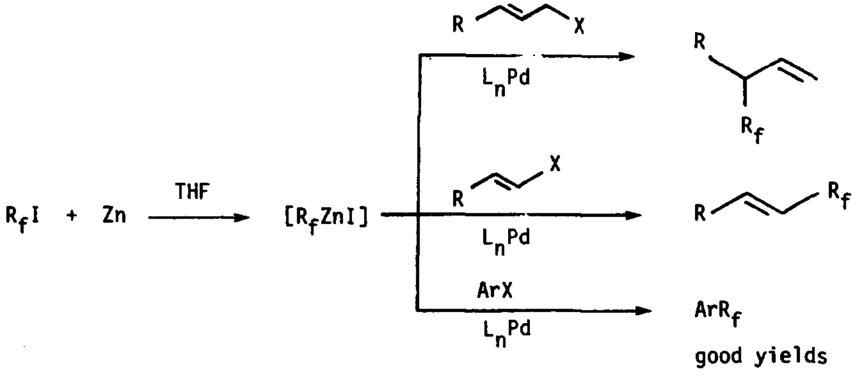
(190)

Transmetallation to π-allyl complexes continues to be a useful process. Allyl acetates were alkylated by organozinc compounds in the presence of palladium(0) catalysts (equation 191) [183]. Fluorinated alkyl groups were introduced to allyl, vinyl, and aryl halides in a similar manner, although ultrasound was required for reaction (equation 192) [184]. Palladium(0) also catalyzed the reactions of vinylalanes with allylic lactones (equation 193) [185], the reaction of boron enolates with allyl acetates (equation 194) [186], and the reaction of aryltin reagents with allyl acetates (equation 195) [187].

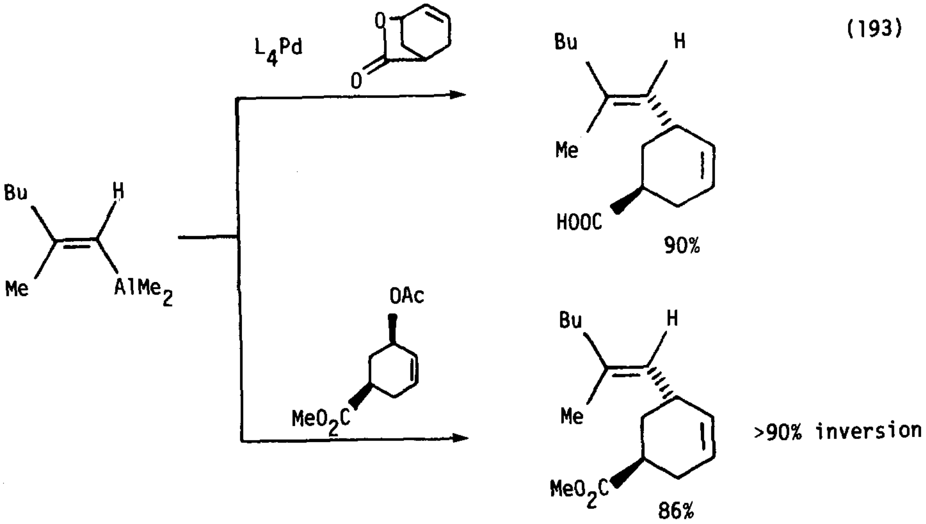
(191)



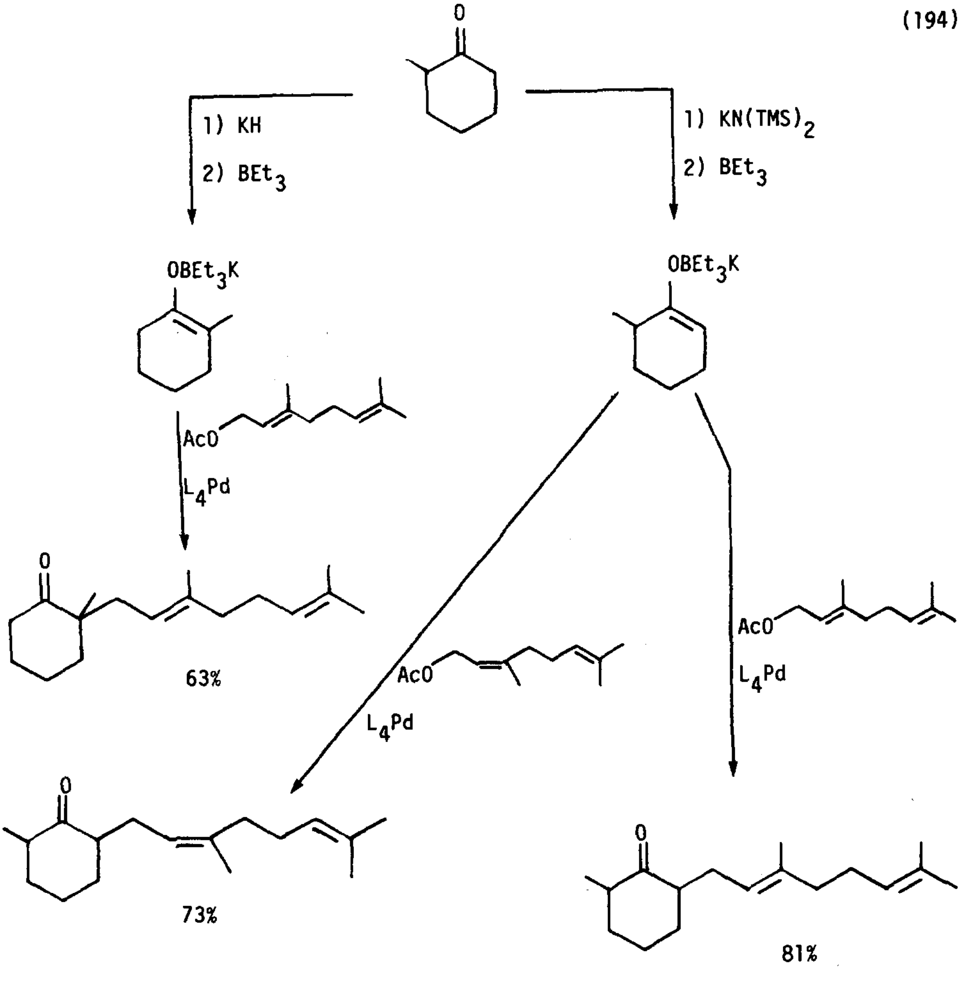
(192)

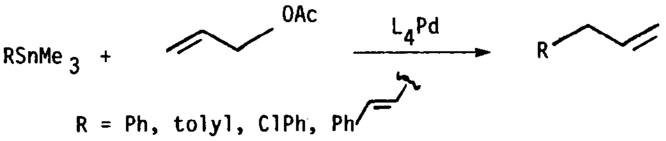


(193)


L$_4$Pd
O
O
Bu
H
Me
HOOC
90%
Bu
H
Me
AlMe$_2$
OAc
MeO$_2$C
Bu
H
Me
MeO$_2$C
86%
>90% inversion

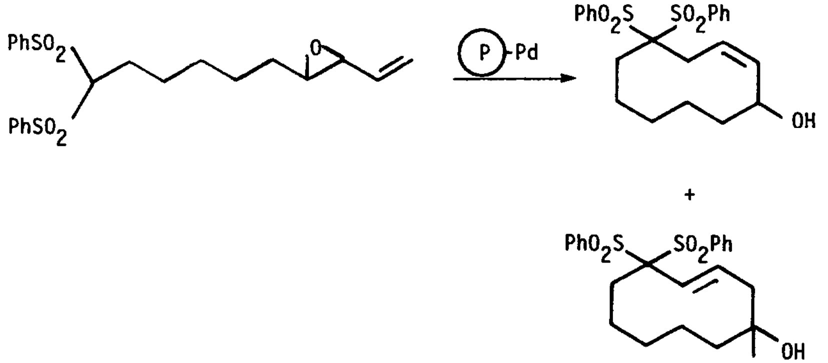
(194)


O
1) KH
2) BEt$_3$
1) KN(TMS)$_2$
2) BEt$_3$
OBEt$_3$K
OBEt$_3$K
AcO
L$_4$Pd
O
63%
AcO
L$_4$Pd
AcO
L$_4$Pd
O
73%
O
81%



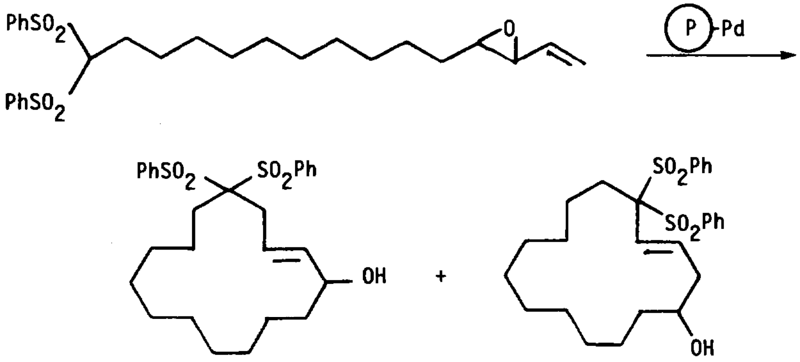
(195)

Palladium(0) catalyzed cyclization reactions have proven very useful, particularly for the synthesis of large ring compounds. By using allylic epoxides as substrates and a polymer-bound palladium(0) catalyst, large rings were synthesized efficiently without having to resort to high dilution conditions (equations 196 and 197) [188]. Although nucleophilic attack normally occurs on the <u>less</u> substituted position of a π-allyl group, the regiochemistry of the reaction depends on the leaving group. Allyl phenyl ethers underwent attack at the more substituted terminus (equation 198) [189]. Spirocyclic compounds were made by the palladium(0) catalyzed reactions of cyclohexenyl acetate. Both C (equations 199 and 200) and O (equations 201 and 202) alkylation were observed [190]. Palladium also catalyzed the reaction between allyl epoxides and vinylboranes (equation 203) [191], and the reaction of diethyl malonate with an allylic nitrile (equation 204) [192].



(196)

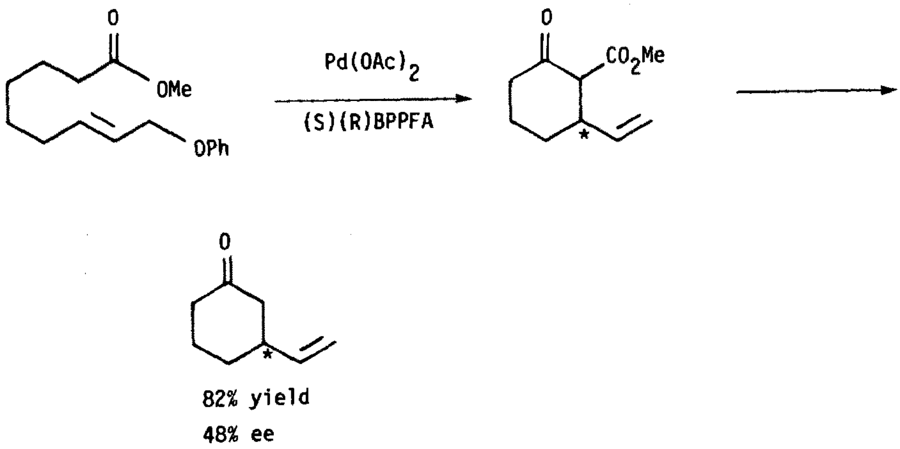
71%

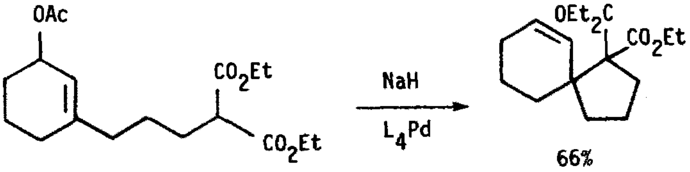


(197)

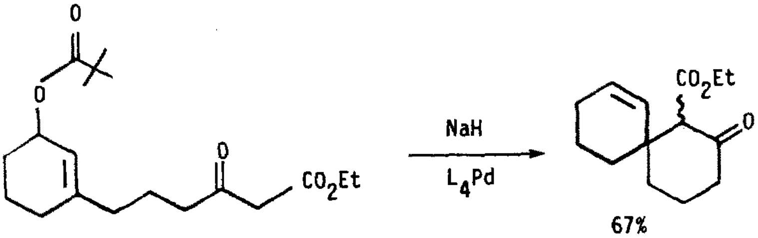
66%

(198)

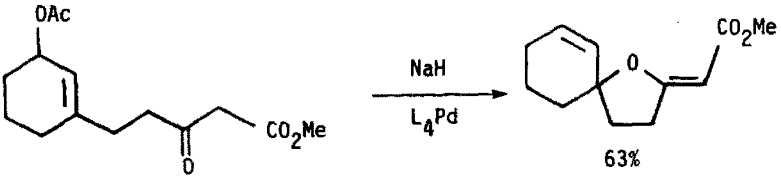




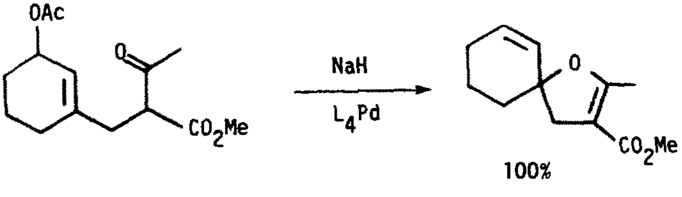
(199)



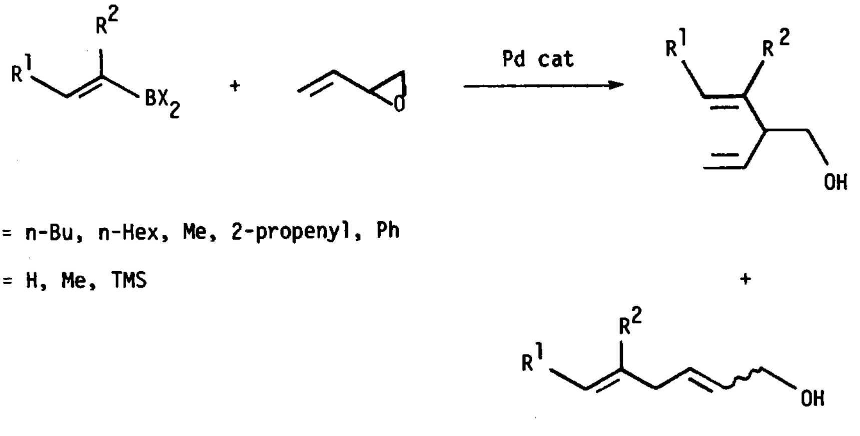
(200)



(201)



(202)



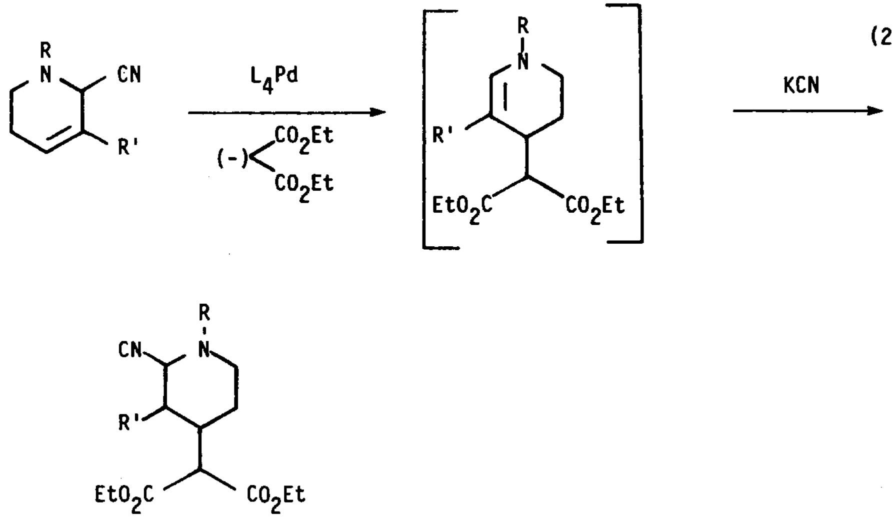
= n-Bu, n-Hex, Me, 2-propenyl, Ph

= H, Me, TMS

(203)

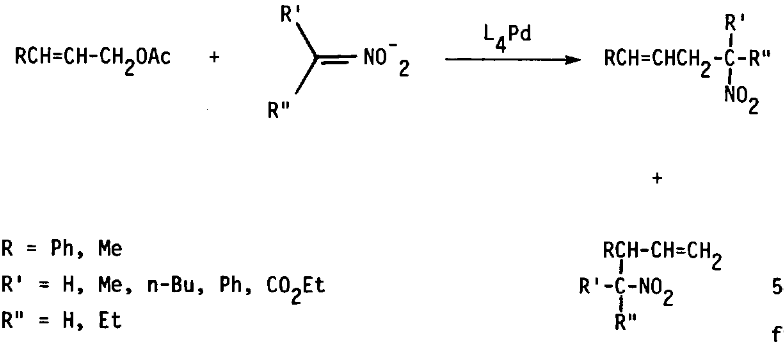
high yields

(204)



70-90%

The organometallic chemistry of nitrocompounds is beginning to be explored. Allyl acetates were alkylated by nitro stabilized carbanions (equation 205) [193]. Allyl phenyl ethers and even allyl alcohols reacted in a similar manner (equation 206) [194][195]. In contrast, allyl nitro compounds underwent alkylation with loss of the nitro group when treated with stabilized carbanions and palladium catalysts (equation 207) [196] (equation 208) [197].



(205)

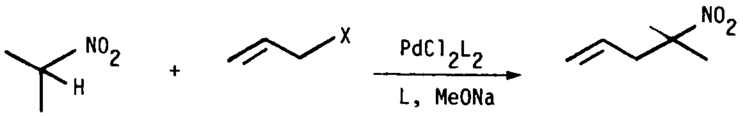
R = Ph, Me

R' = H, Me, n-Bu, Ph, $CO_2Et$

R" = H, Et

54-89%

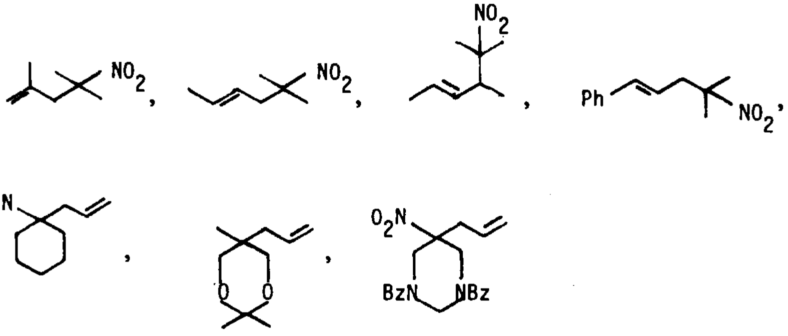
from 1:1 to 97:3

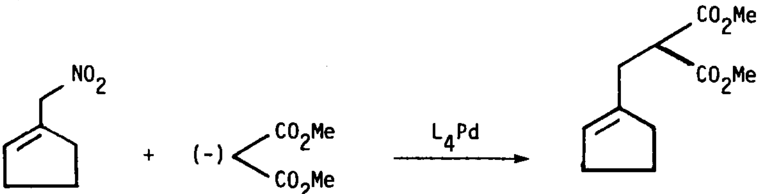


(206)

X = OAc, OPh, OH

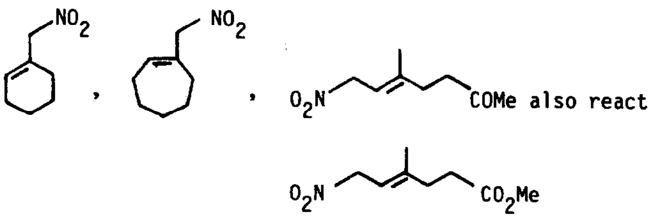
Made



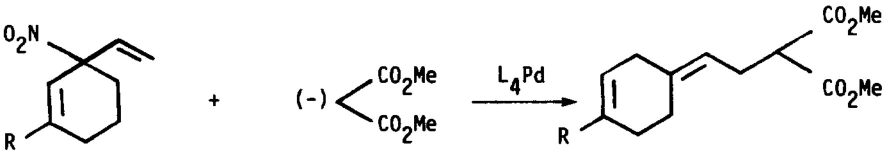


(207)

70%



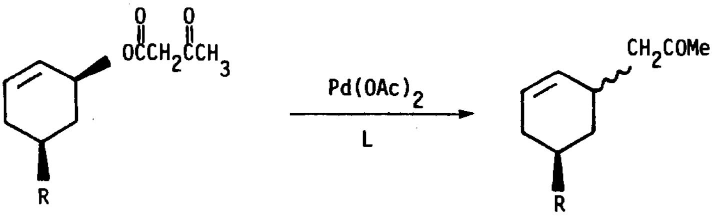
also react



(208)

40%

Allylic acetoacetates underwent a palladium catalyzed decarboxylation with some stereoselectivity (equation 209) [198]. Allylcyclopropanes underwent a palladium(II) assisted ring opening with inversion to give π-allyl complexes (equation 210) [199]. The x-ray structure and dynamic exchange process of π-allylpalladium complex ion pairs have been studied [200].



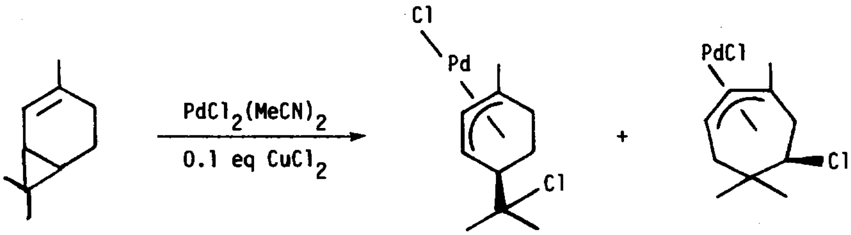
(209)

R = Ph, i-Pr

42-53%

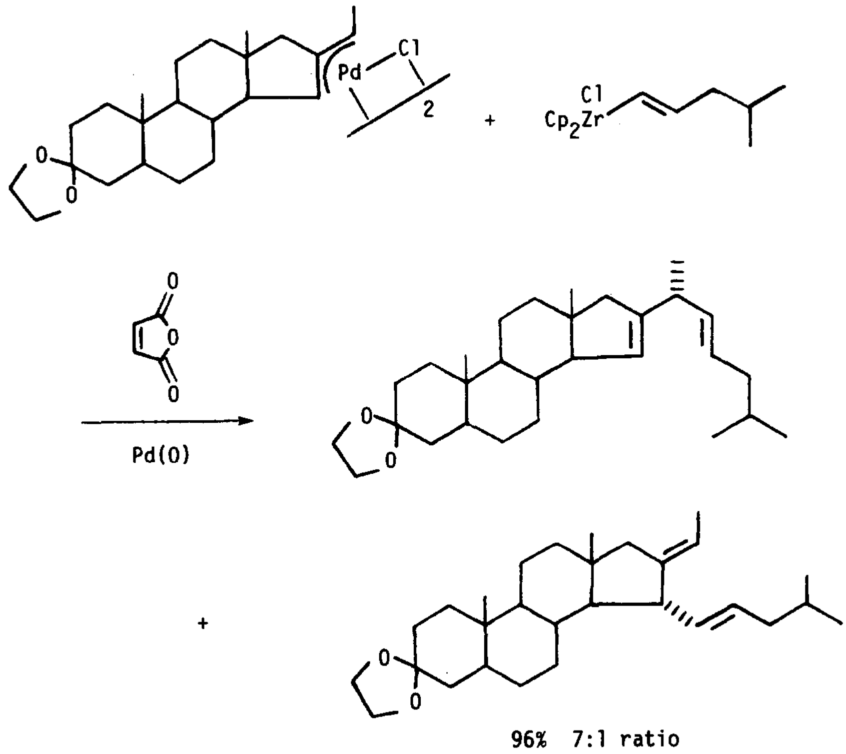
86:14 cis/trans
starting with 95:5
cis/trans

(210)

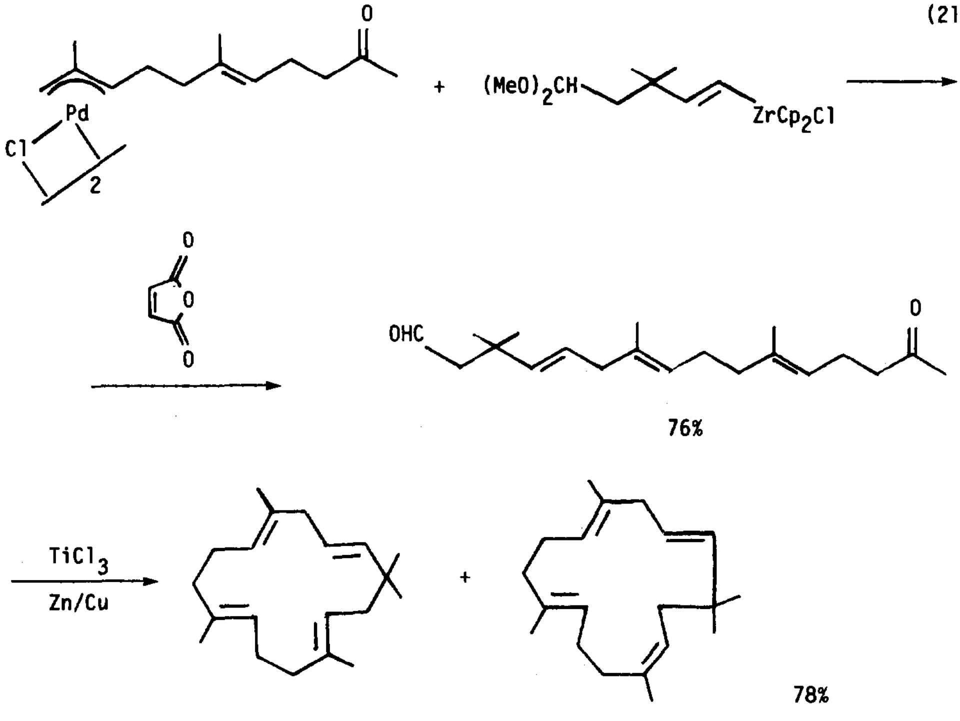


Vinylzirconium species alkylated π-allylpalladium complexes. This reaction was used to introduce steroid side chains (equation 211) [201], and to synthesize macrocyclic polyenes (equation 212) [202], (equation 213) [203].

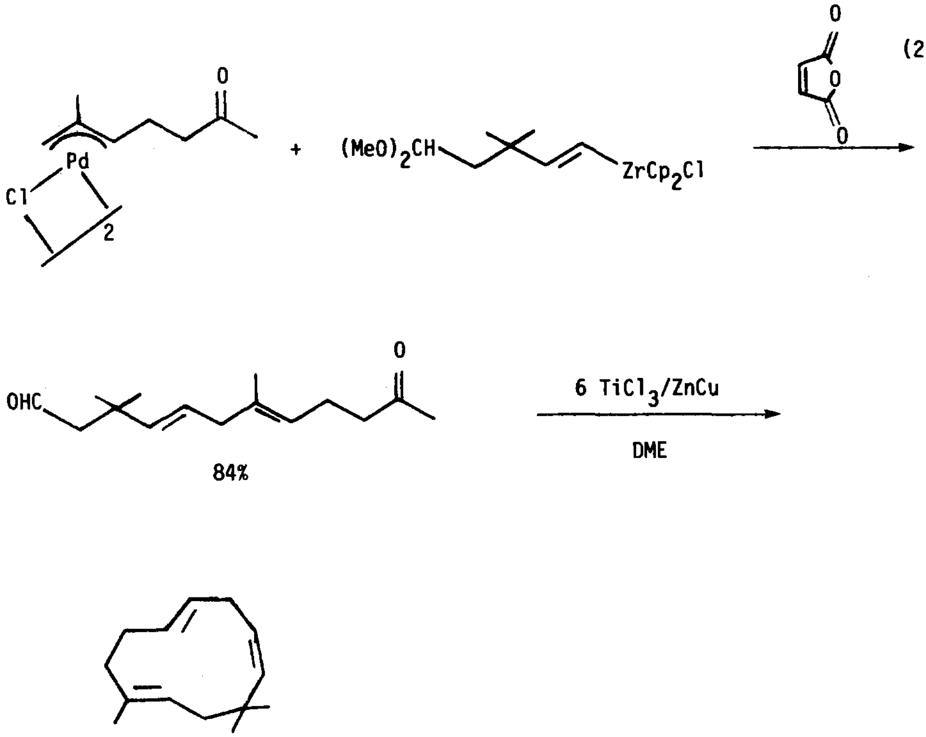
(211)


Pd
Cl
2
+
Cl
Cp$_2$Zr
O
O
Pd(0)
+
96% 7:1 ratio

(212)


O
Pd
Cl
2
+
(MeO)$_2$CH
ZrCp$_2$Cl
O
O
O
OHC
O
76%
TiCl$_3$
Zn/Cu
+
78%

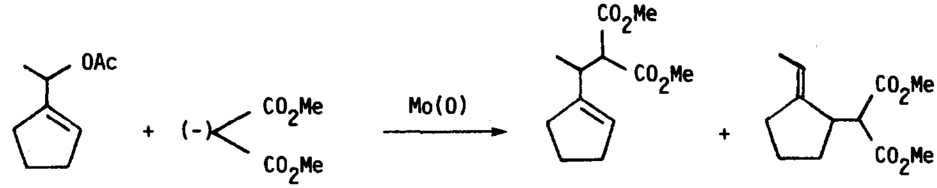
(213)



60% humulene

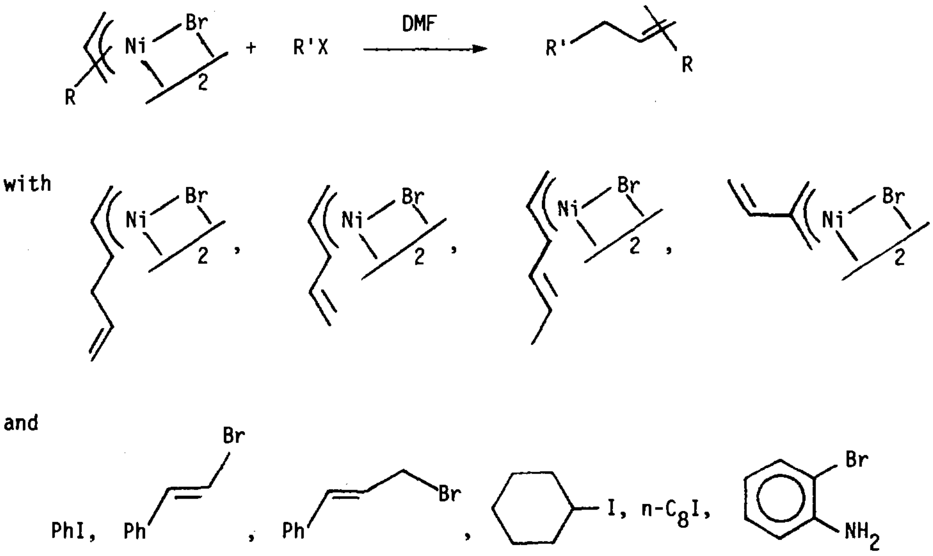
Molybdenum(0) complexes also catalyzed the allylic alkylation of allyl acetates by stabilized carbanions. The regiochemistry depended on the nature of the molybdenum reagent (equation 214) [204]. A variety of unsaturated π-allylnickel halide complexes were made and were coupled to a variety of organic halides (Scheme 4) [205].

(214)



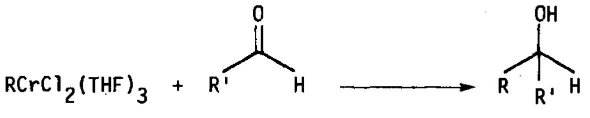
| | | | | |
|---|---|---|---|---|
| Mo(CO)$_6$ | 15 | : | 85 | 69% |
| Mo(bipy)(CO)$_4$ | 67 | : | 33 | 45% |

SCHEME 4



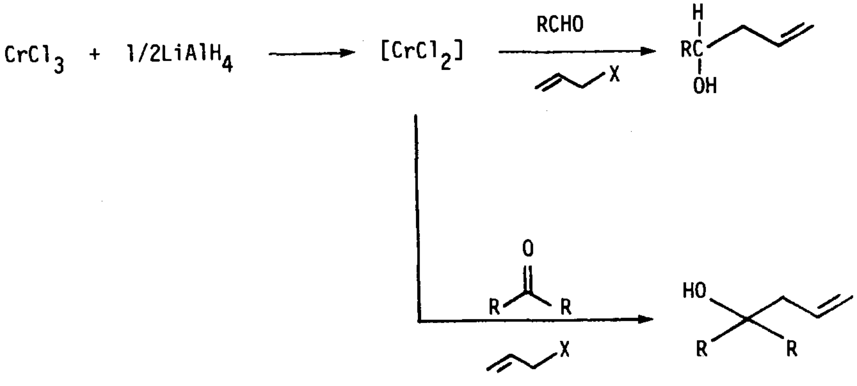
## 10. Alkylation of Carbonyl Compounds

Alkylchromium(III) reagents showed very high selectivity for aldehydes over ketones in alkylation reactions (equation 215) [206]. Chromium(II) chloride coupled aldehydes and ketones with allylic halides with strong threo selectivity (equation 216) [207]. The stereochemistry of this reaction was studied and was found to depend on the nature of the substituent on the α-carbon [208]. Manganese(0), produced by the reduction of manganese(II) chloride with lithium aluminum hydride, also coupled aldehydes and ketones to allylic halides (equation 217) [209]. Alkyl niobium and tantalum complexes of the constitution $Me_2M(O\text{-}i\text{-}Pr)_3$ and $MeMCl_4$ alkylated aldehydes exclusively in the presence of ketones [210]. Samarium(II) iodide also reductively coupled aldehydes and allylic halides (equation 218) [211].



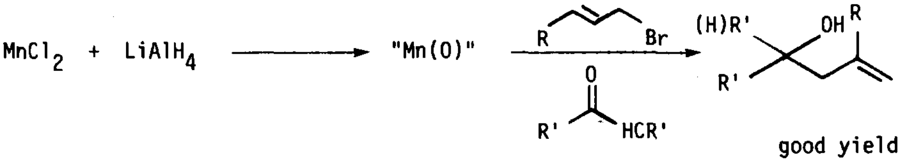
$$RCrCl_2(THF)_3 + R'CHO \longrightarrow RR'CH(OH) \qquad (215)$$

very high selectivity for aldehydes



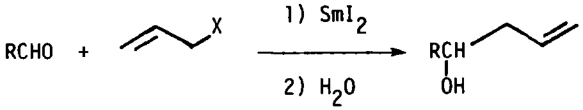
(216)

22 cases studied high yield, high threo selectivity



(217)

good yield
22 cases

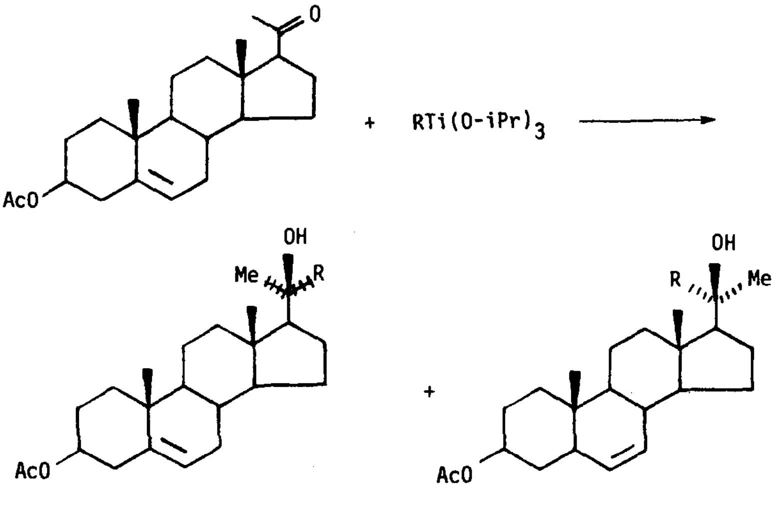


(218)

78-96%

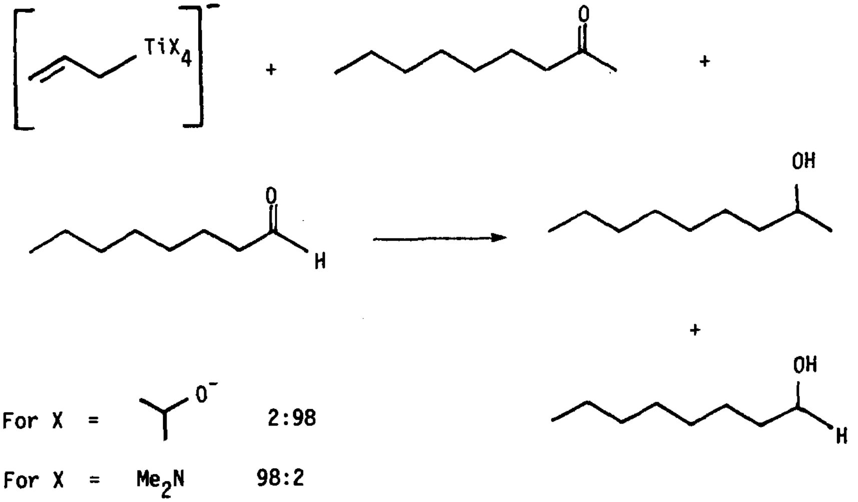
R = n-$C_7$, i-Pr, t-Bu, 
X = I > Br > Cl >> OTs

Titanium alkyls have also been studied as alkylating agents for aldehydes and ketones. Steroidal ketones were alkylated by a range of titanium alkyls and the erythro-threo ratios were determined (equation 219) [212]. Allyltitanium(IV) complexes reacted selectively with aldehydes when the anionic groups were isopropoxide, and exclusively with ketones when the anionic groups were dimethylamido (equation 220) [213]. However, a related titanium species alkylated aldehydes almost exclusively threo (equation 221) [214]. Propargyl titanium species alkylated aldehydes to give mixtures of allenic and acetylenic alcohols (Scheme 5) [215]. Titanium(IV) chloride promoted the reaction of allylic trimethyl silanes with aldehydes. The stereochemistry was determined by the geometry of the double bond (equations 222 and 223) [216]. This reaction was used to synthesize α-methylene lactones (equations 224 and 225) [217].



(219)

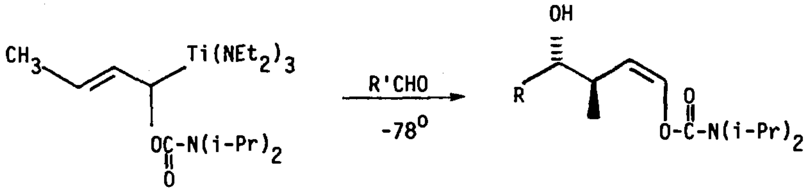
used RTi(O-iPr)$_3$, MeTi(OEt)$_3$, R$_2$Ti(O-iPr)$_2$, TiMe$_4$, MeZr(O-nPr)$_3$, ZrMe$_4$



(220)

For X = 2:98

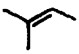
For X = Me$_2$N 98:2

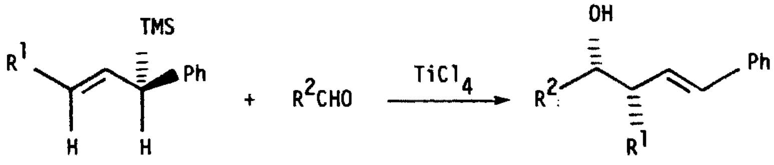


(221)

>97% threo

R' = t-Bu, Me, i-Pr,



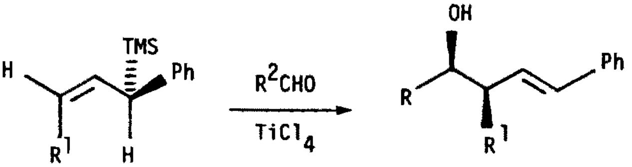


(222)

up to 86% ee

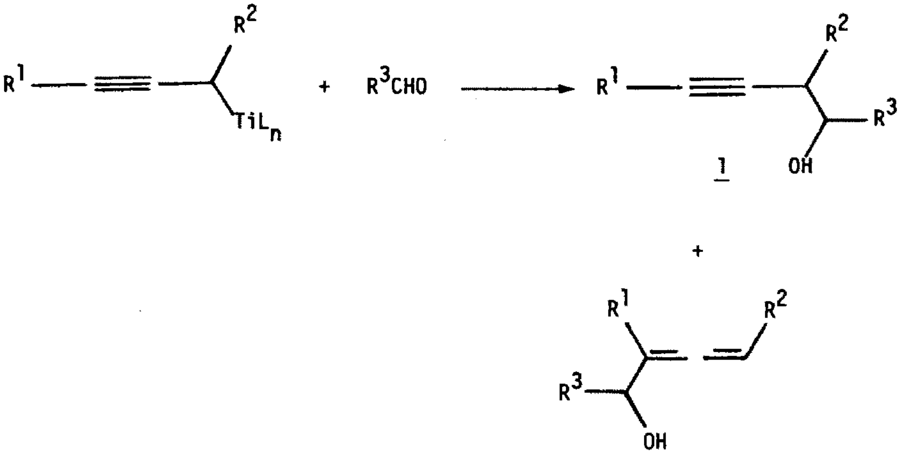
$R^1$ = Me, Ph

$R^2$ = t-Bu, i-Pr, Me



(223)

SCHEME 5



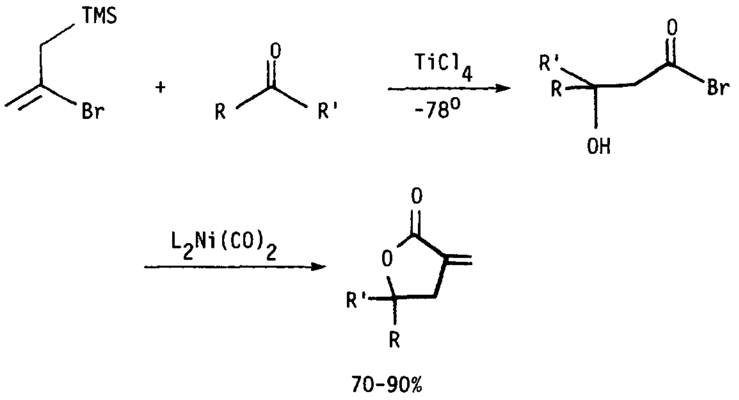
1

2

60-93%

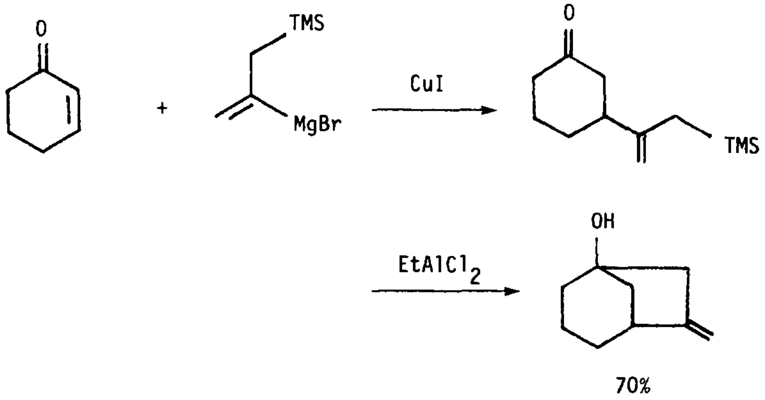
$R^1$ = TMS, Me  $R^2$ = H  $R^3$ = Ph,   1/2 = 1:99

$R^1$ = TMS, Et, Ph  $R^2$ = Me  $R^3$ = Ph,  1/2 = 99:1



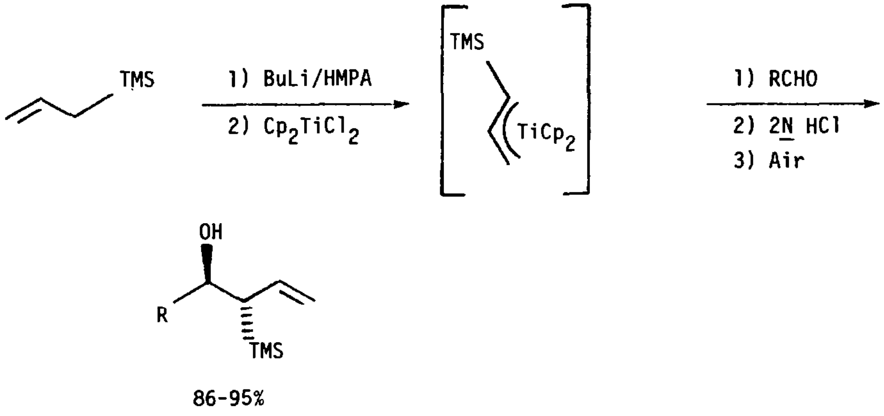
(224)

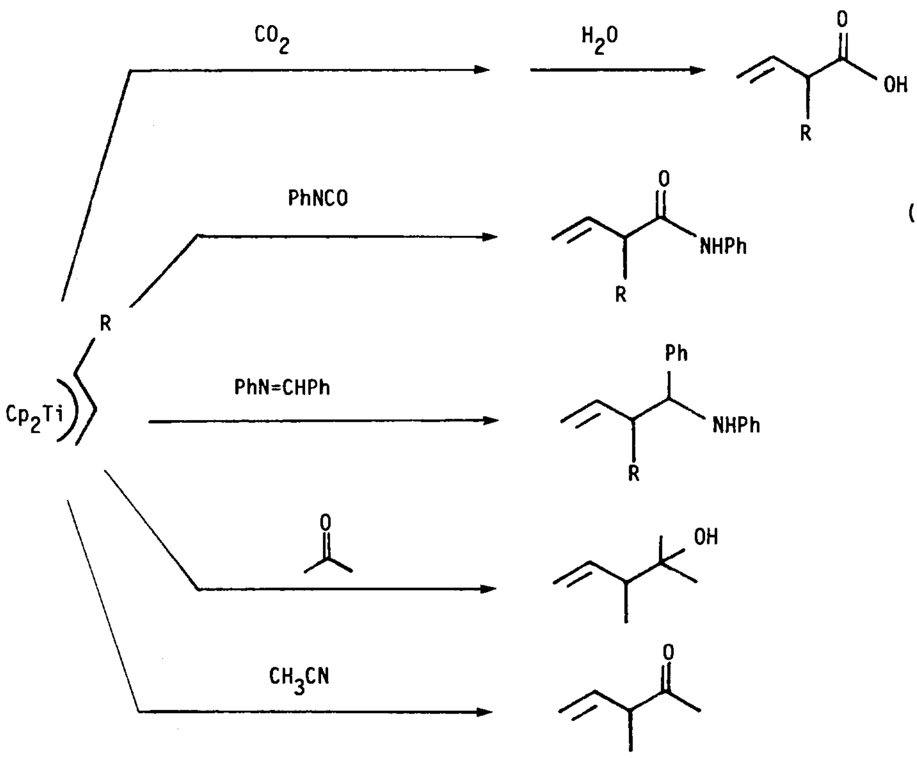
(225)



Allyltitanium complexes alkylated aldehydes (equation 226) [218]. These compounds also reacted with a wide variety of other electrophiles (equation 227) [219].

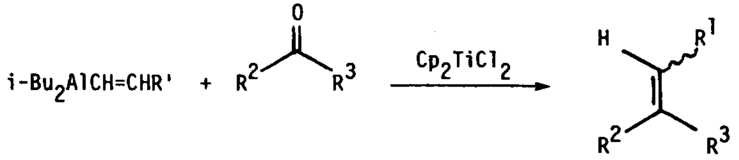
(226)





(227)

Low valent titanium complexes promoted the olefination of ketones (equation 228) [220], (equations 229, 230, and 231) [221].



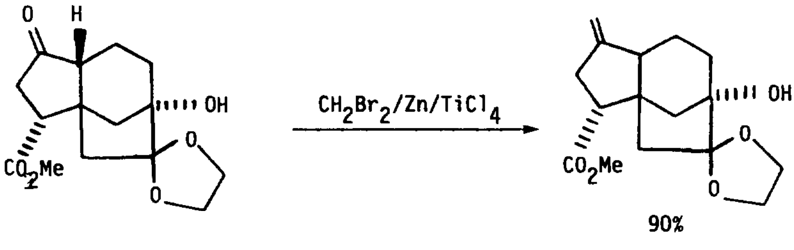
(228)

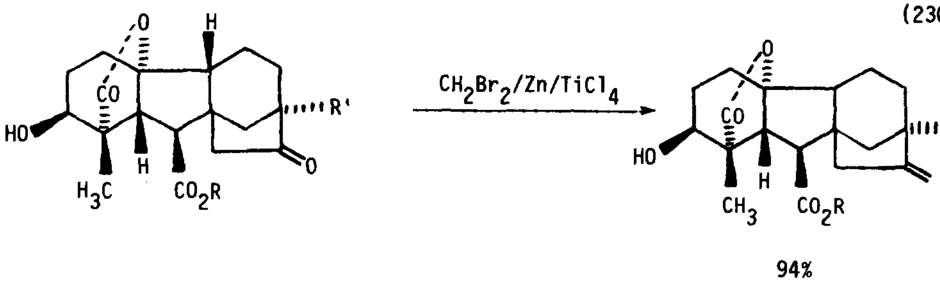
$R^1$ = n-$C_5$, n-Pr

$R^2$ = Me, Ph, -$(CH_2)_5$-

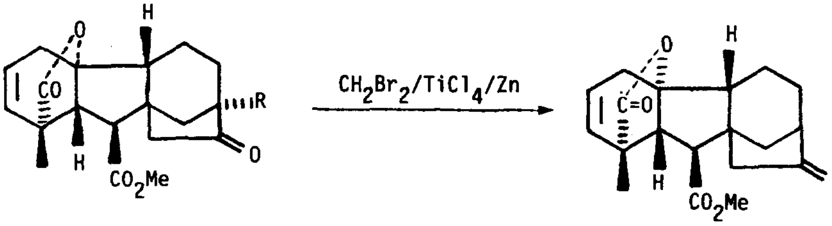
$R^3$ = Me, Et, Ph

(229)





(230)

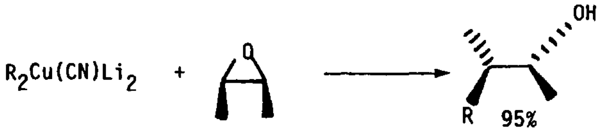


(231)

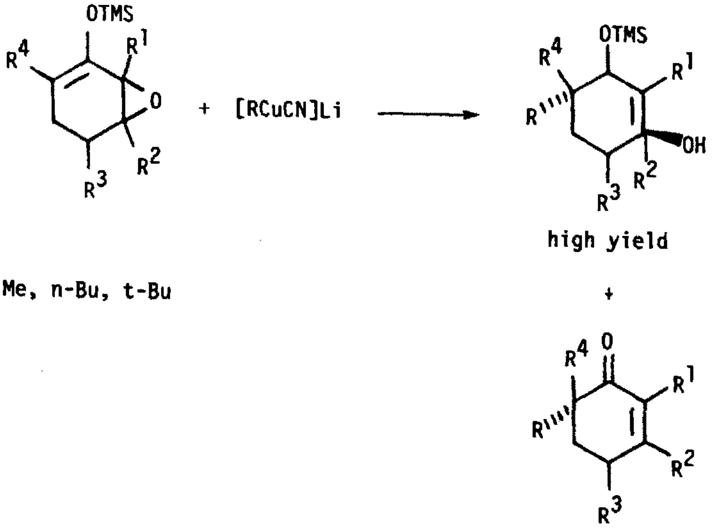
A dissertation entitled "Diastereoselective and Enantioselective Aldol Condensations with bis(Cyclopentadienyl)zirconium Enolates" has appeared [222].

## H. Alkylation of Epoxides

Organocopper compounds were extensively used to alkylate epoxides. The mixed cuprate $R_2CuCNLi_2$ was a very mild and efficient reagent for the ring opening of substituted epoxides (equation 232) [223]. The substituted cyclohexene oxide in equation 233 was studied extensively [224]. Steroidal epoxides also alkylated cleanly (equation 234) [225]. This chemistry was used to prepare a maytansine synthon (equation 235) [226]. The site of attack of allylic epoxides depended on the structure of the organocopper species (equation 236) [227]. Propargyl epoxides ring opened when treated with organozinc reagents in the presence of palladium(0) complexes (equation 237) [228].

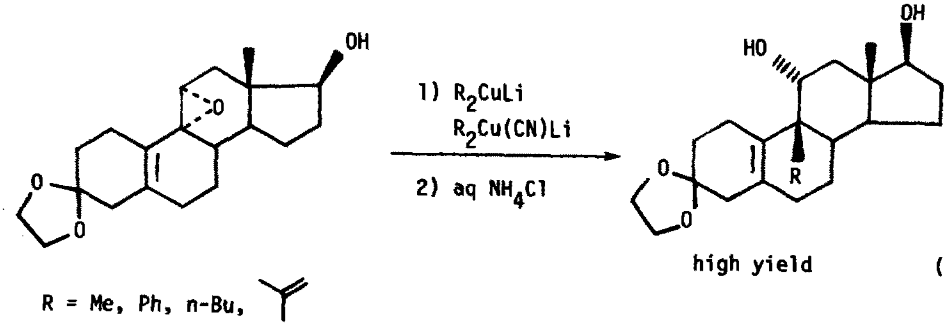


(232)



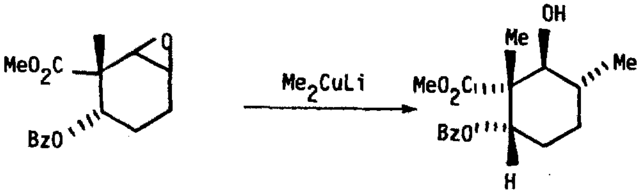
R = Me, n-Bu, t-Bu

(233)



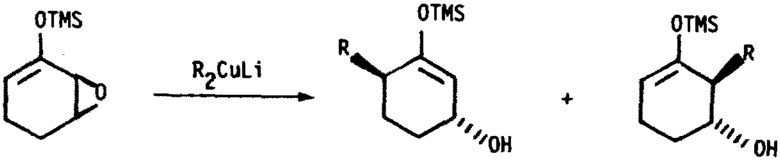
high yield (234)

R = Me, Ph, n-Bu,



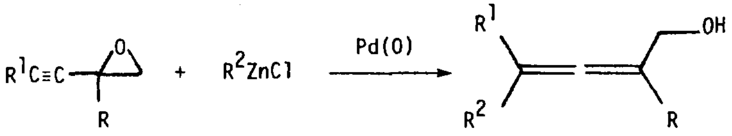
85%

(235)



(236)

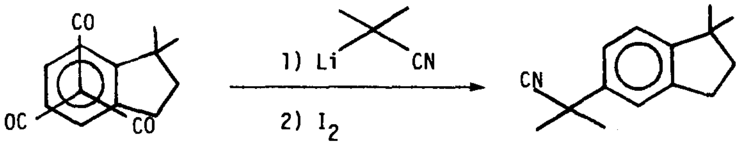
| | | | |
|---|---|---|---|
| 1.5 eq THF | 0 | 100 | 62% |
| 4 eq $Et_2O$ | 59 | 41 | 81% |
| 4 eq LiCu(CN)Me | 100 | 0 | 77% |



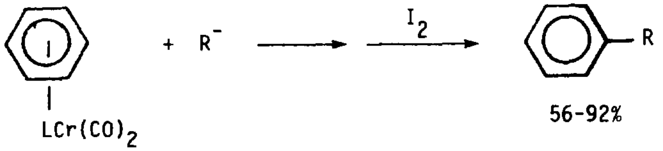
(237)

## 12. Aromatic Substitution

Selectivity in the addition of nucleophiles to $\eta^6$-(arene) tricarbonylchromium(0) complexes was the subject of a dissertation [229]. It was found that the conformation of the $Cr(CO)_3$ unit in the arenechromium tricarbonyl directed the regiochemistry of nucleophilic attack on the arene portion (equation 238) [230]. The effect of replacing the CO's of arenechromium tricarbonyl by phosphines was studied (equation 239) [231]. Cationic arene manganese complexes reacted with carbanions to give alkylated arenes. The manganese fragment could be recycled (equation 240) [232].



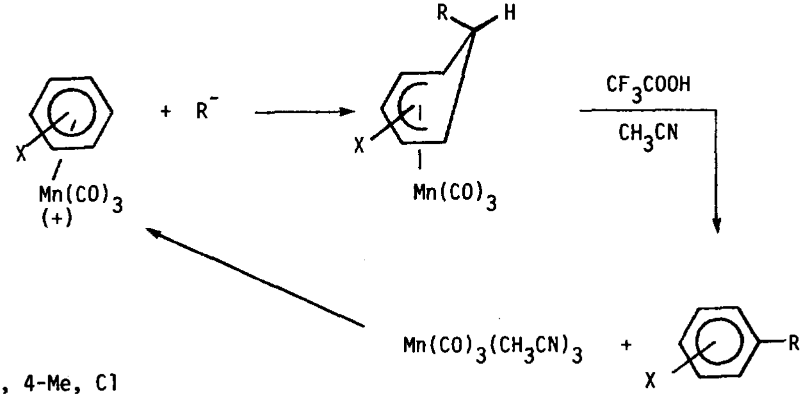
(238)



(239)

L = $PPh_3$, diphos     R = $LiC(Me)_2CN$, $CHMeCO_2R$

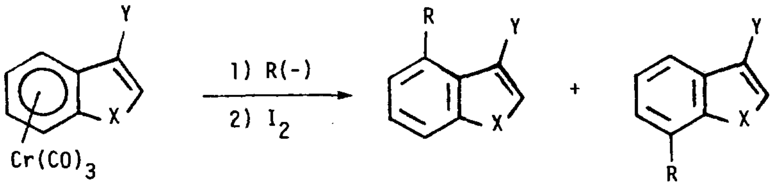
(240)



X = H, 4-Me, Cl

R = Me, Ph, $+COCH_2$-

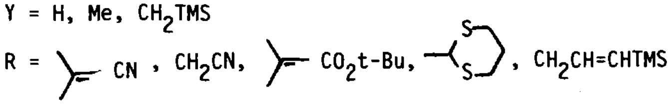
Chromium tricarbonyl complexes of indoles and benzofurans underwent alkylation at C-4 unless substituents at C-3 were large (equation 241) [233]. Chromium tricarbonyl complexes of indole were lithiated in the 4-position and treated with electrophiles to produce 4-substituted indoles (equation 242) [234]. Similar studies were carried out with aniline complexes (equation 243) [235]. Chromium tricarbonyl complexes of dihydropyridines were alkylated and dimerized by reaction with organolithium reagents (equation 244) [236]. Mixed dicyclopentadienyl cobalt complexes reacted with organolithium reagents to give mixtures of products from alkylation on either ring (equation 245) [237].

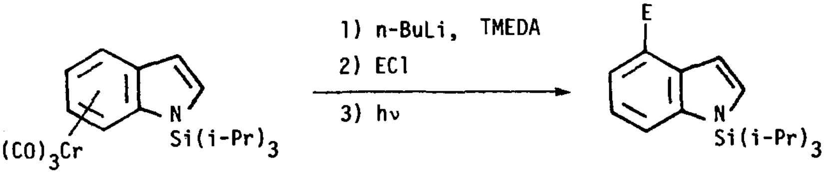


(241)

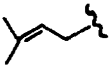
X = NH, NMe, NBz, NSiPh$_2$t-Bu, NCO$_2$t-Bu, O

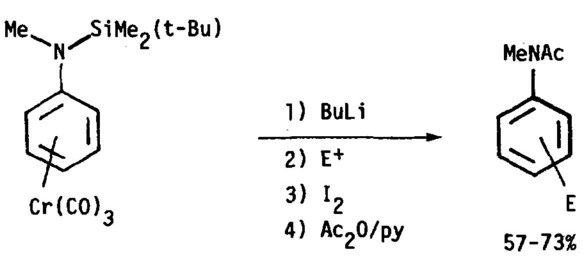
Y = H, Me, CH$_2$TMS





(242)

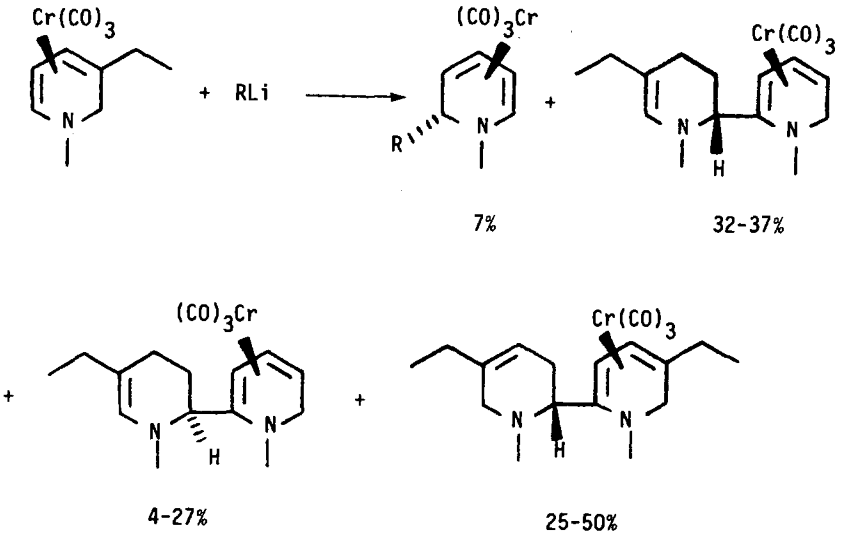
E = TMS, CO$_2$Et, CO$_2$Me, 



(243)

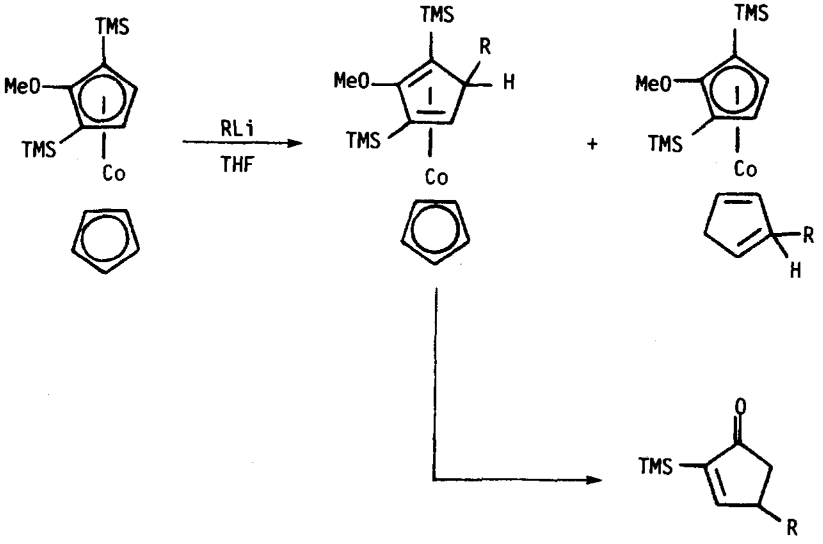
E$^+$ = PhCHO, MeCHO, HCONMe$_2$, MeI, MeSSMe, PhCN

E = CH(OH)Ph, CH(OH)Me, CHO, Me, SMe, COPh



(244)

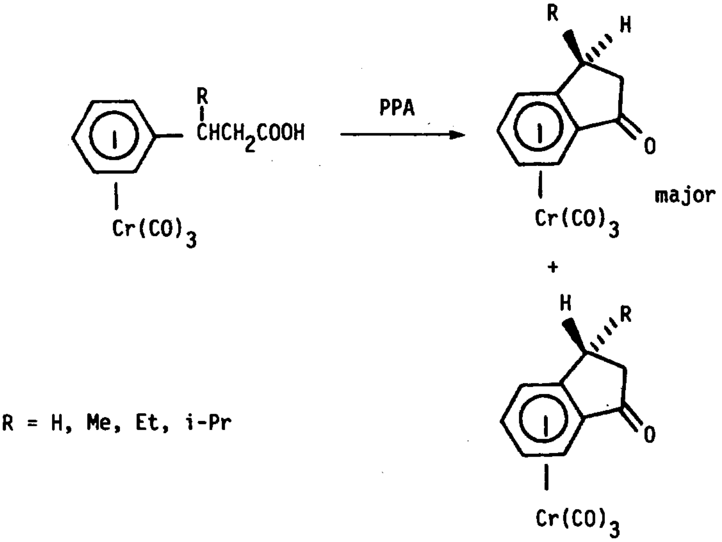
(245)



From 0:100 to 80:20 depending on R (no yields)

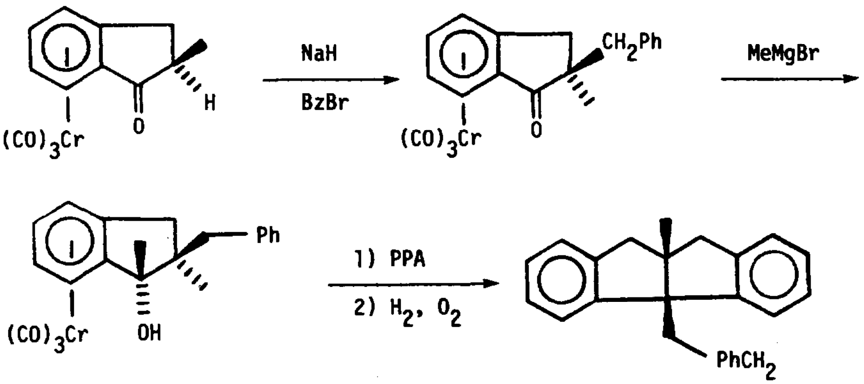
R = t-Bu, Me, n-$C_6$/═ , n-$C_6$-≡, TMS-≡, t-BuO-≡, PhS-≡, ClC≡C-, H

Chromium tricarbonyl complexes of indanones were made by acid catalyzed cyclization of the complexed corresponding phenylpropionic acid (equations 246 and 247) [238]. These complexes were alkylated and dimerized (equation 247) [239].



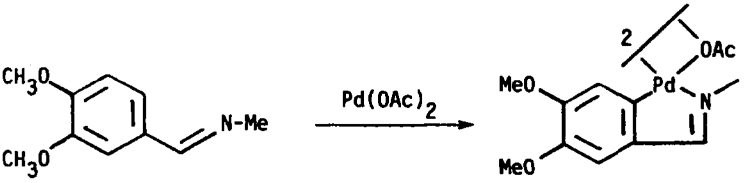
(246)

R = H, Me, Et, i-Pr

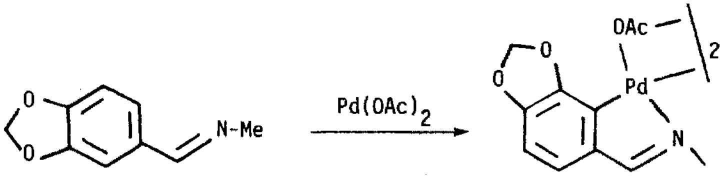


(247)

Ortho-palladation has been used to introduce alkyl substituents regiospecifically into aromatics. The regiochemistry of cyclopalladations of arylidenemethylamines was studied (equations 248 and 249) [240]. Ortho-palladation of these types of compounds was used to prepare substituted benzaldehydes (equation 250) [241], and quinolines (equation 251) [242]. Directed palladation of 2-methylaminomethylpyrrole was used to synthesize 2,3-disubstituted pyrroles [243].

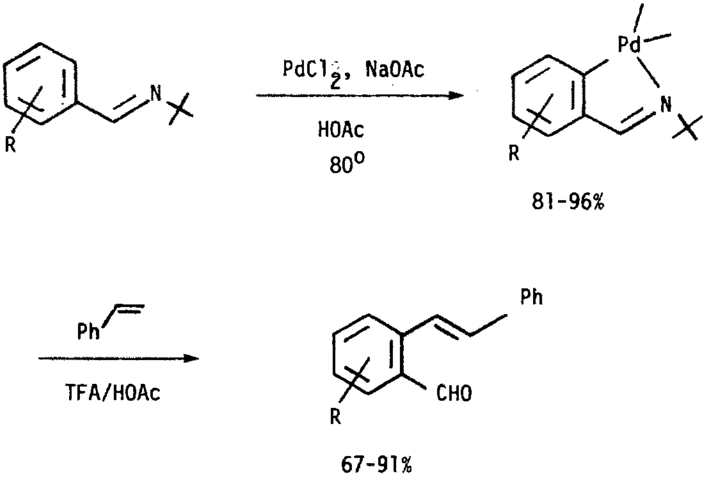


(248)

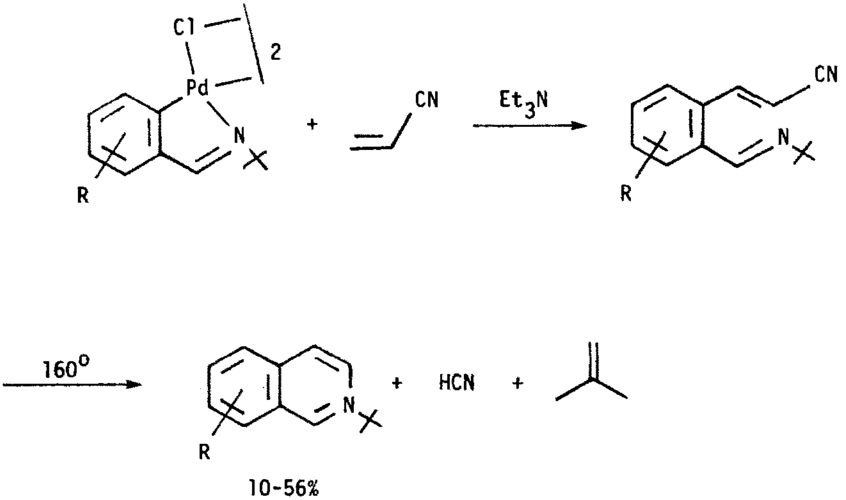


(249)

(250)



R = H, 4-Cl, 4-MeO, 3-MeO, 2-MeO, 3,4-(MeO)$_2$

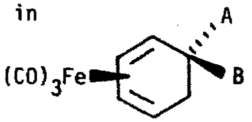


(251)

R = H, 5-Cl, 5-Me, 3,4 or 5-OMe, 4,5-diOMe

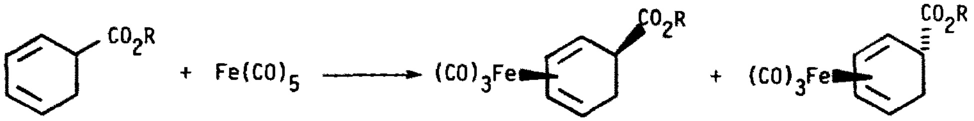
### 13. Alkylation of Dienyl Complexes

The stereoselectivity of the complexation of cyclohexadiene esters to $Fe(CO)_3$ was found to depend on the nature of the ester and the solvent (equation 252) [244]. An nmr method for determining the configuration (α or β) in if both epimers were available has been developed [245].

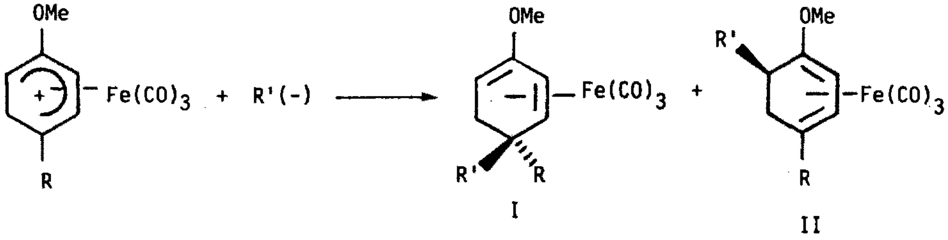


The regiochemistry of alkylation of 1-methoxy-4-substituted cyclohexadienyliron complexes depended on the counterion (cation) of the nucleophile (equation 253) [246], and was correlated to steric, coulombic, and frontier orbital factors [247].

(252)



(253)

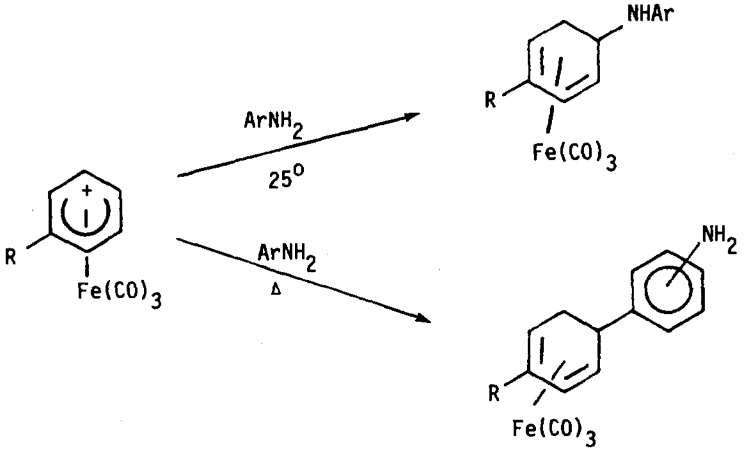


R = Me, Et, $(CH_2)_2CO_2Me$, $(CH_2)_3NPhTh$

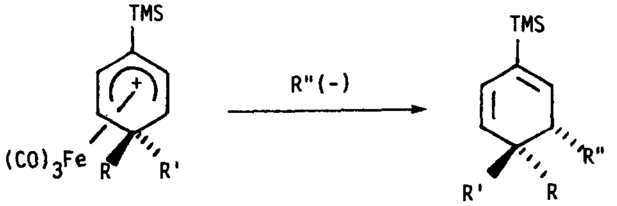
R' = $CH(CO_2Me)_2$, $CH(OMe)(CO_2Me)$, $CH(CN)_2$

For Li I:II = 3.0 Na 4.6 K 5.6 for $CH(CO_2Me)_2$

Arylamines aminated cyclohexadienyliron complexes at 25°, but alkylated them at higher temperatures (equation 254) [248]. Trimethylsilylcyclohexadienyl complexes of iron were alkylated by stabilized carbanions (equations 255 and 256) [249]. Other related alkylations are shown in equation 257 [250], equation 258, equation 259 [251], and equation 260 [252].



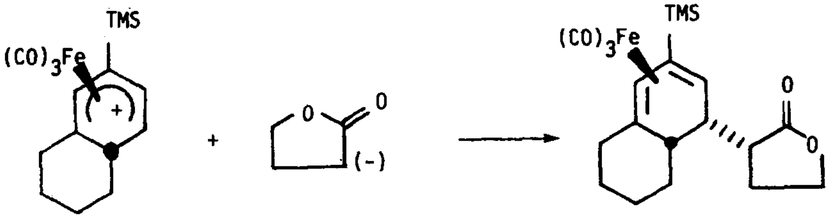
(254)



(255)

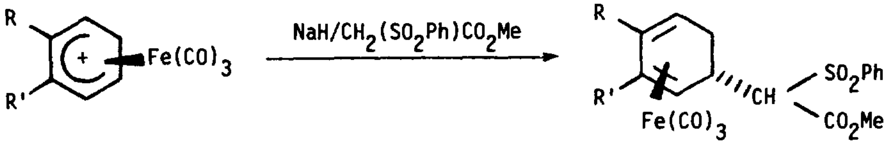
R = H, Me
R' = H, Me

R" = $CH(CO_2Et)_2$, $CH(CO_2Et)(SO_2Ph)$



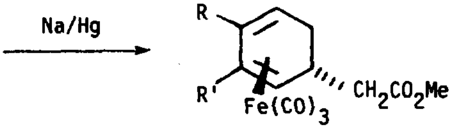
(256)

(257)



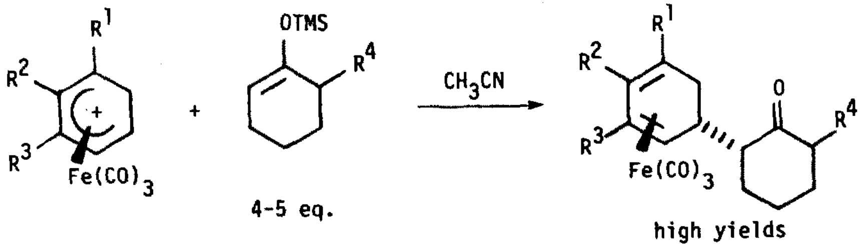
60%

R = H, OMe
R' = OMe, H



81%

(258)



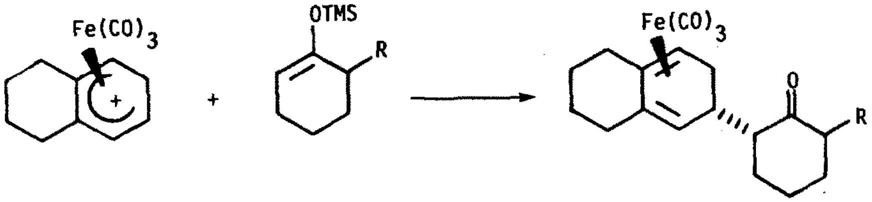
$R^1$ = H, $CO_2Me$, OMe

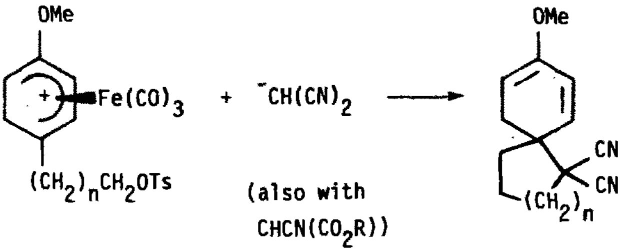
$R^2$ = H, OMe, Me

$R^3$ = H, OMe, Me

$R^4$ = H, Me

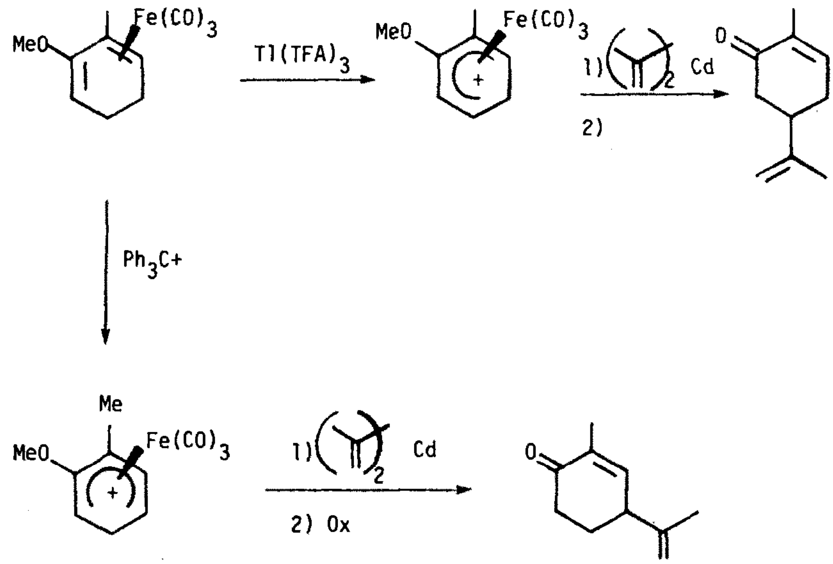
(259)





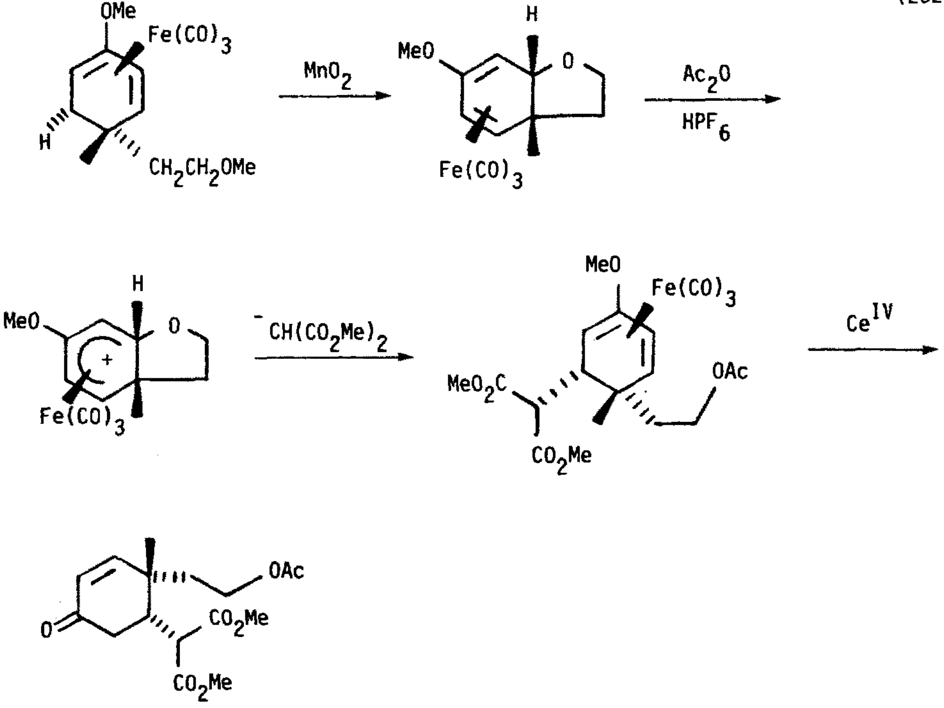
(260)

This chemistry has been used extensively in organic synthesis. Substituted cyclohexenones (equation 261) [253], (equation 262) [254], o-methyljoubertiamine (equation 263) [255], steroids (equation 264) [256], limaspermine (equation 265) [257], and aspidospermine (equation 266) [258] have been made this way. Cyclopropanes were prepared in a rather convoluted manner from dieneiron tricarbonyl complexes (equation 267) [259].

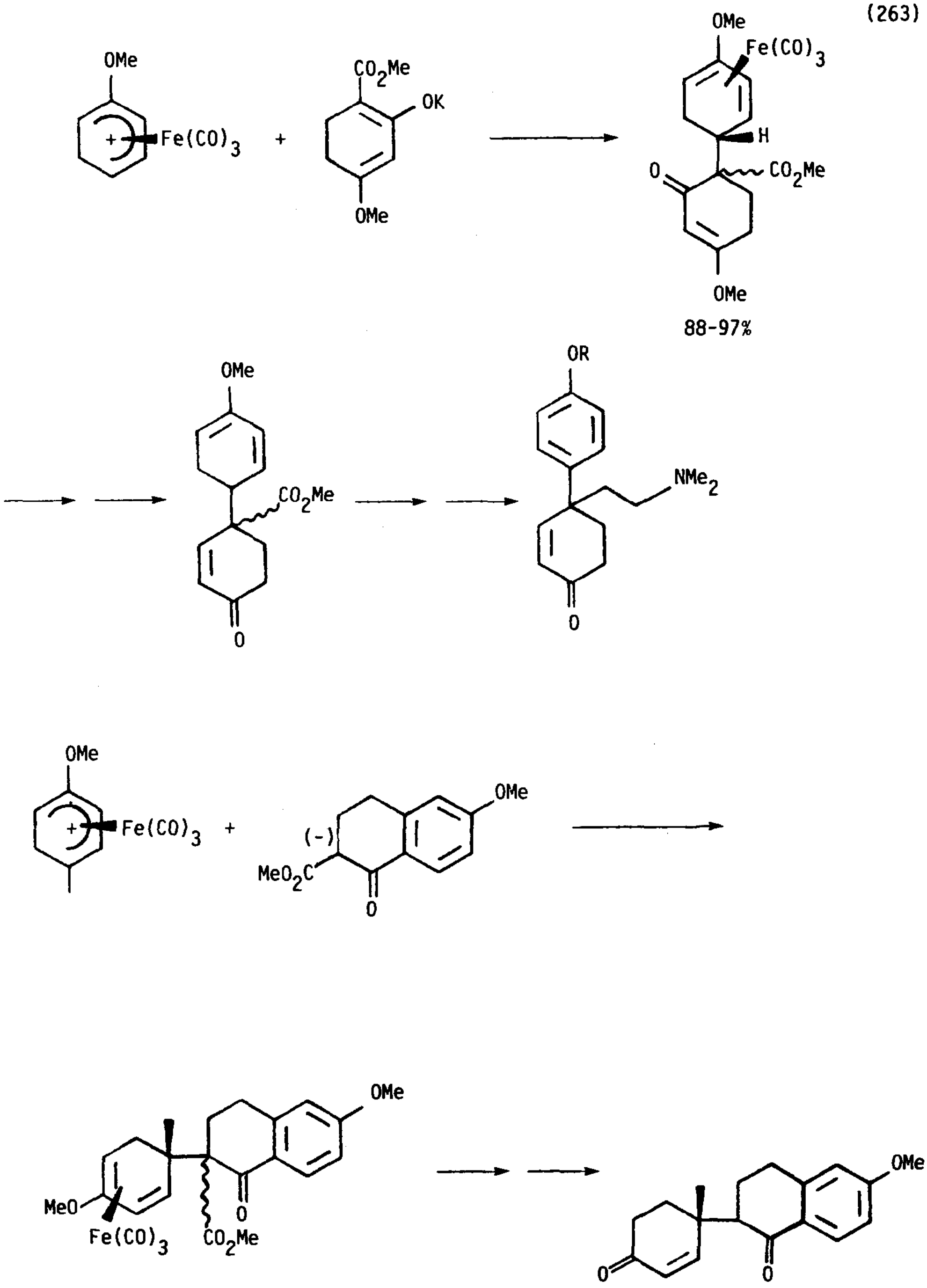

MeO
Fe(CO)$_3$
Tl(TFA)$_3$
1)
2
Cd
2)
O
Ph$_3$C+
Me
2) Ox

(261)

(262)

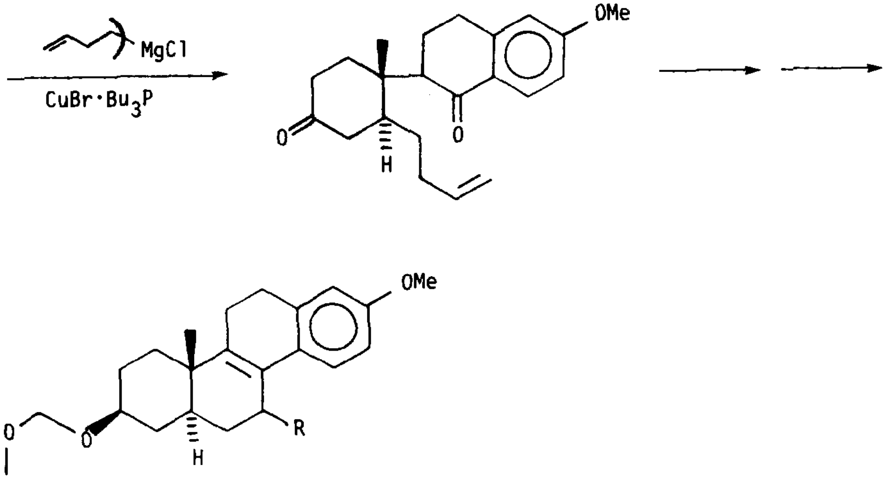

OMe
Fe(CO)$_3$
H
CH$_2$CH$_2$OMe
MnO$_2$
MeO
O
Ac$_2$O
HPF$_6$
$^-$CH(CO$_2$Me)$_2$
MeO$_2$C
CO$_2$Me
OAc
Ce$^{IV}$

(263)

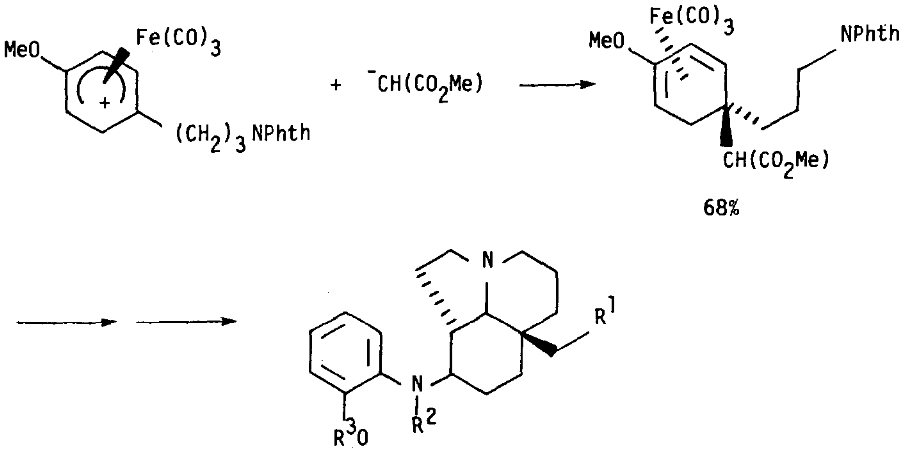


(continued on next page)

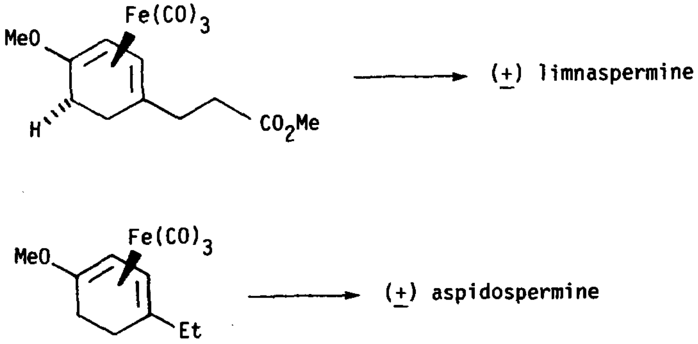
(264)


MgCl
CuBr·Bu$_3$P
OMe
O
O
H
OMe
O
O
H
R

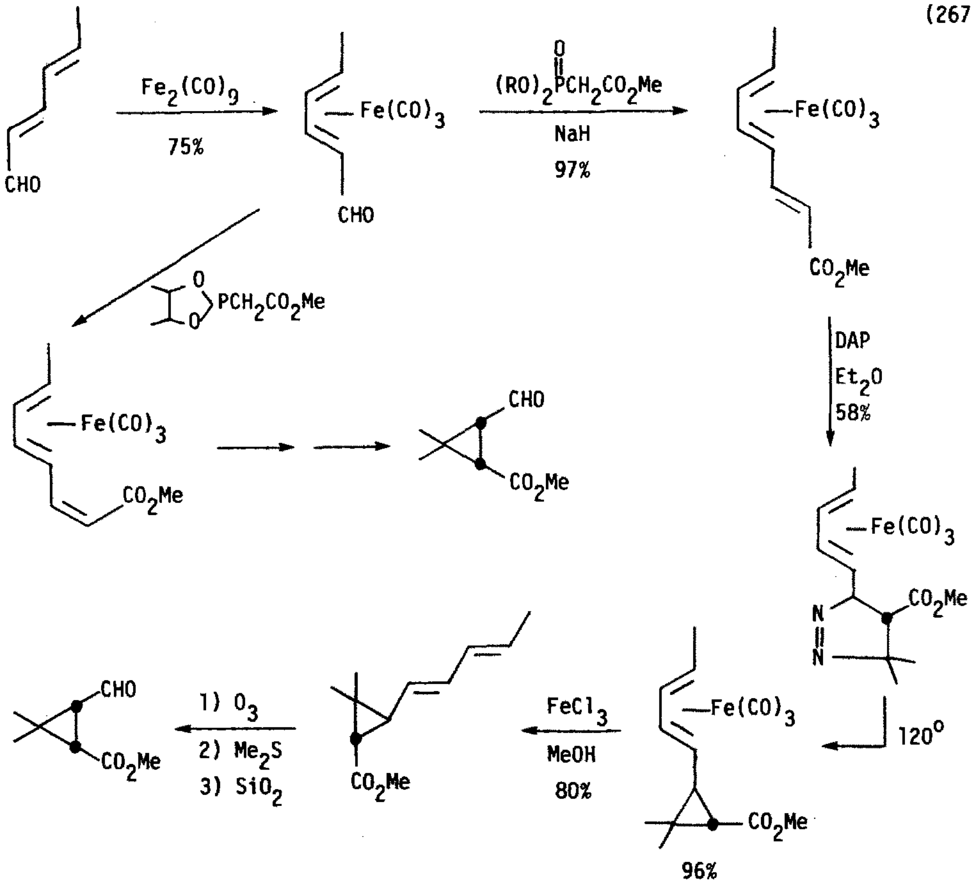
(265)


MeO
Fe(CO)$_3$
+
(CH$_2$)$_3$NPhth
+ $^-$CH(CO$_2$Me)
Fe(CO)$_3$
MeO
NPhth
CH(CO$_2$Me)
68%
N
R$^1$
N
R$^2$
R$^3$O

(266)

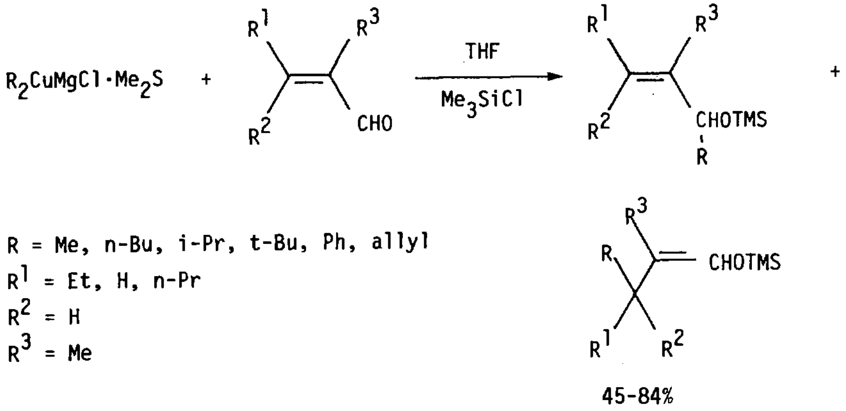

Fe(CO)$_3$
MeO
H
CO$_2$Me
(±) limnaspermine
Fe(CO)$_3$
MeO
Et
(±) aspidospermine

(267)



B. Conjugate Addition

Organocuprates continue to be the reagents of choice for conjugate alkylation of α,β-unsaturated carbonyl systems. The reagent $Me_5Cu_3Li_2$ was the best reagent for the 1,4-alkylation of aldehydes without concommitant 1,2-addition. Other reagents tried were $Me_2CuLi$, MeLi, $MeCuBF_3$, $Me_3CuLi_3$, $R_4(Me)Cu_3^-(MgBr)_2$, $Me_3Cu_2Li$, MeCu(R)MgX, and MeCu [260]. The reagent $R_2CuMgCl\cdot Me_2S$ reacted with α,β-unsaturated aldehydes to give mixtures of 1,2- and 1,4-addition (equation 268) [261]. The reagent $RCu\cdot BF_3$ was efficient for the 1,4-alkylation of sterically crowded α,β-unsaturated ketones, esters, and even a number of acids. With α,β,γ,δ-unsaturated systems, 1,4-addition again predominated (equation 269) [262]. The reagent $R_2CuCNLi_2$ was also effective in 1,4-alkylation reactions (equation 270) [263]. Reagents of the type $RSO_2CH_2CuR'$ were efficient mixed cuprates for conjugate addition reactions. The $RSO_2CH_2$ group did not transfer [264]. Finally 1,4-alkylation was effected by irradiating with ultrasound, mixtures of conjugated enone, organic halide, lithium sand, and copper(I) iodide (equation 271) [265].



(268)

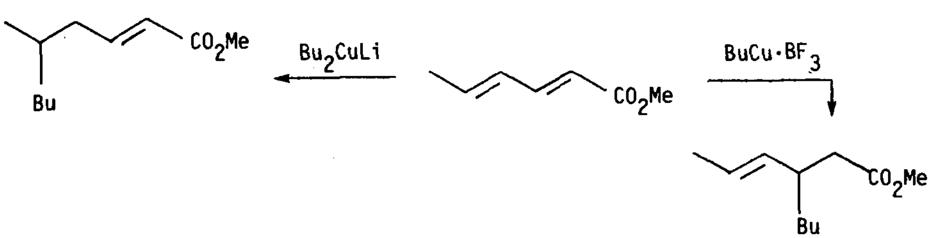
R = Me, n-Bu, i-Pr, t-Bu, Ph, allyl

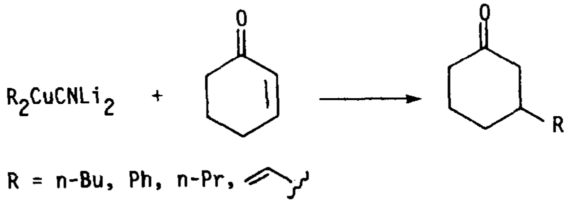
$R^1$ = Et, H, n-Pr

$R^2$ = H

$R^3$ = Me

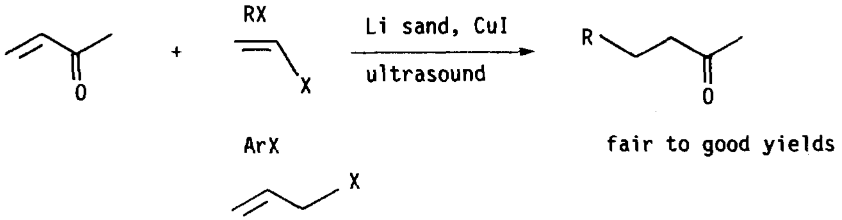
(269)





(270)

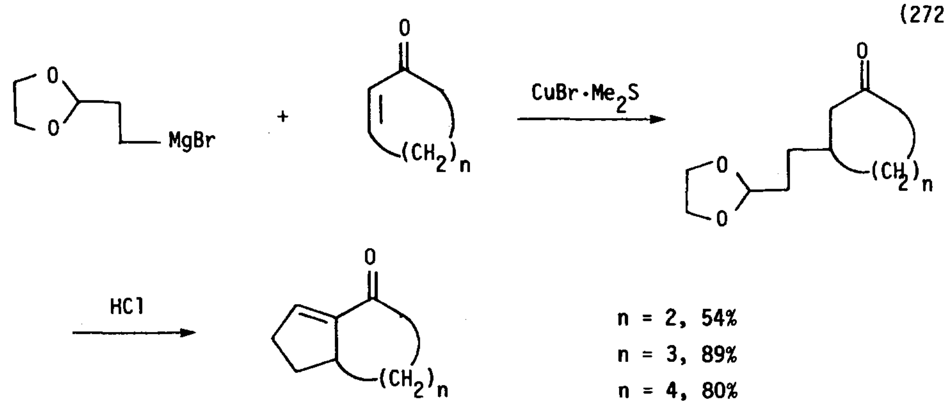
R = n-Bu, Ph, n-Pr,

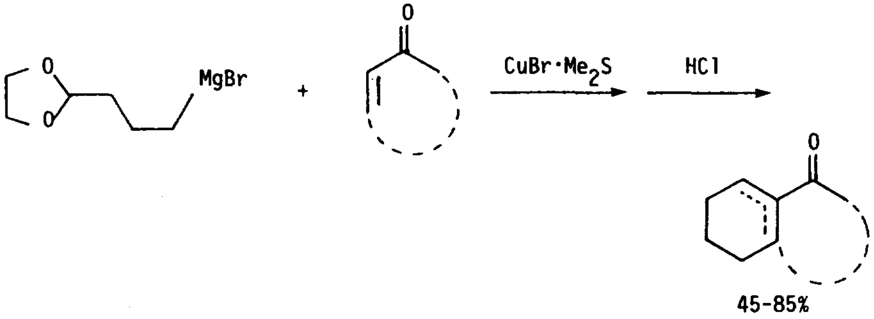


(271)

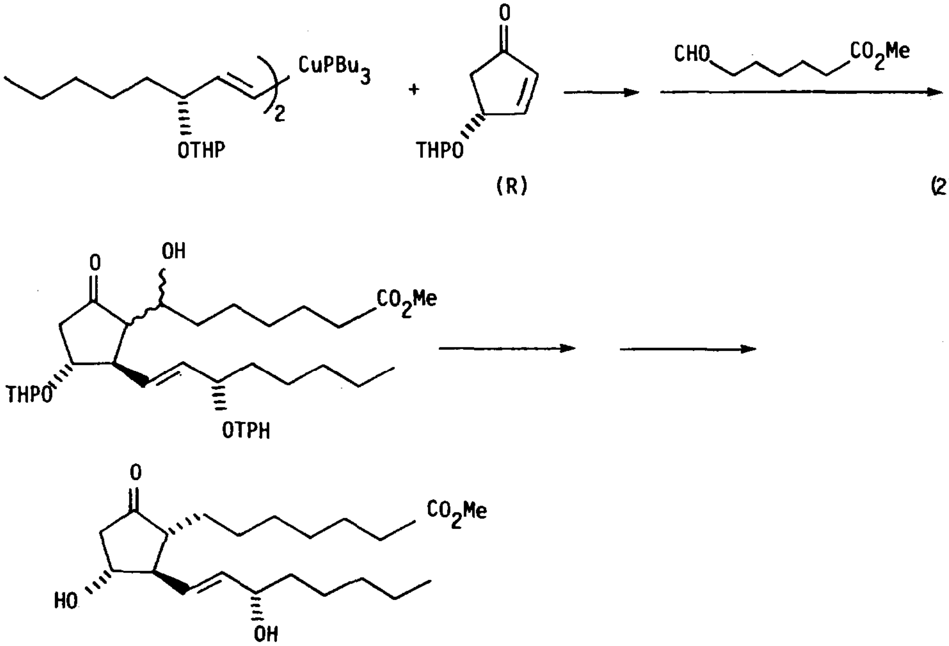
Conjugate addition was a key step in a new annelation procedure (equations 272 and 273) [266]. Prostaglandins were synthesized using conjugate addition of organocuprates to cyclopentenones (equation 274) [267]. This topic has been reviewed (20 references) [268]. Chiral alkylcuprates underwent conjugate addition to cyclic enones to give chiral products in up to 75% optical yield (equation 275) [269].

(272)

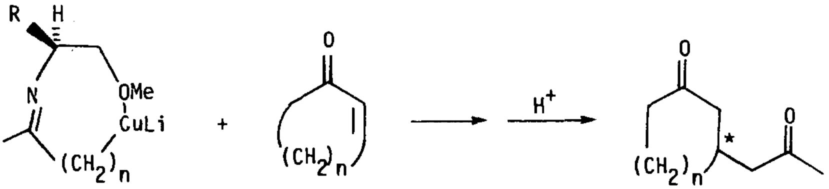




(273)



(274)



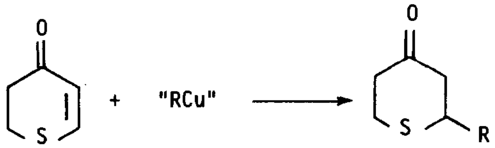
n = 2, 1

30-89%

16-75% opt. yield

(275)

Other more exotic conjugated enones also undergo 1,4-alkylation when treated with organocuprates (equation 276) [270], (equation 277) [271], and (equation 278) [272].

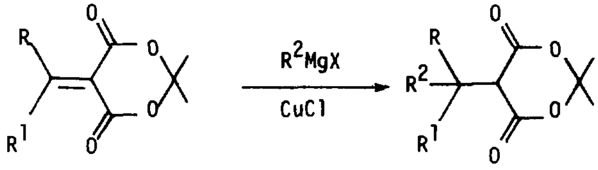


(SO, $SO_2$ compounds react similarly

(276)

"RCu" = [RCu-C≡CPr]Li

R = Me, Bu, t-Bu, Ph, 



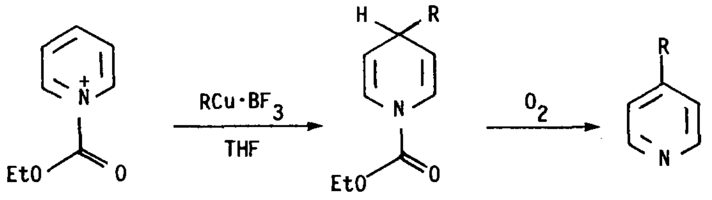
(277)

83-86%

R = H, Me

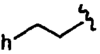
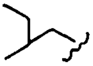
$R^1$ = Me, Ph

$R^2$ = Me, Et, Ph

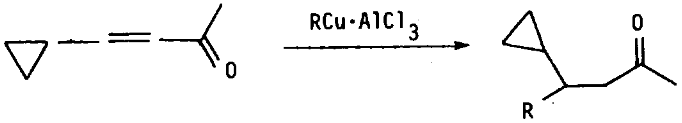


(278)

81-94%

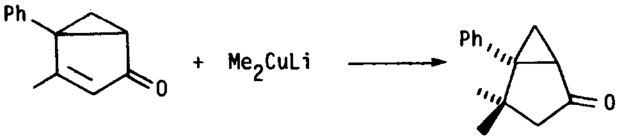
R = n-Pr, n-$C_6$, Ph, Ph, 

Depending on conditions cyclopropanes conjugated to carbonyl groups either survive intact (equation 279) [273], or ring open (equations 280-283) [274].



70-90%
15 cases

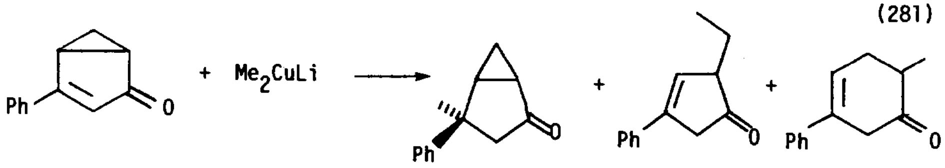
(279)



100%

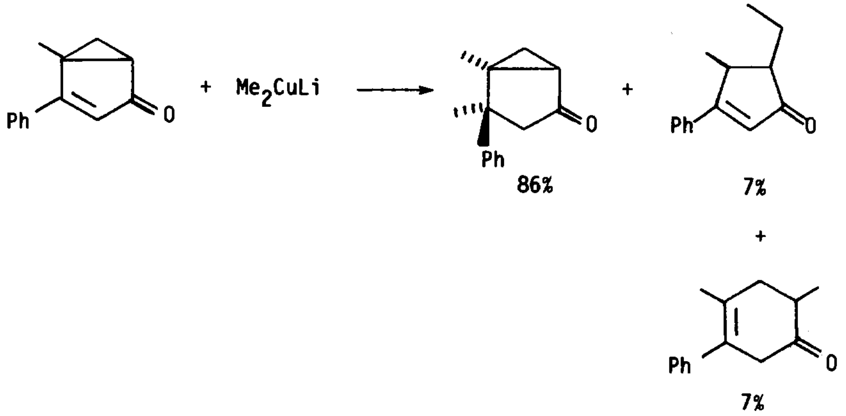
(280)

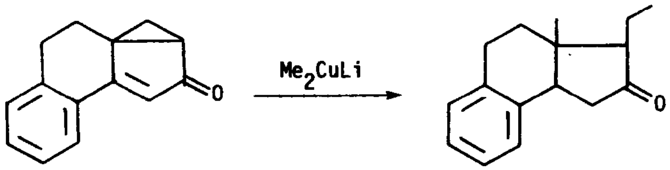
(281)



92% 2% 6%

(282)

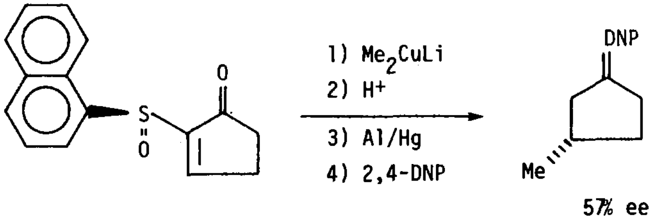




100%

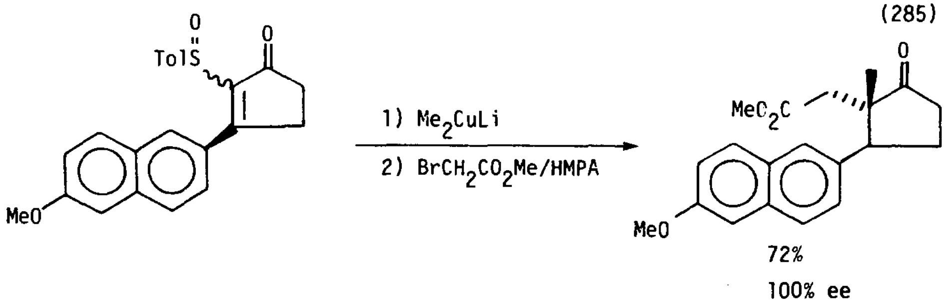
(283)

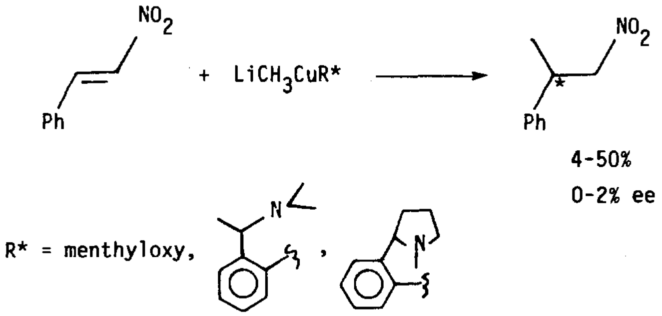
Chirality was induced into the conjugate addition process by introducing a chiral sulfoxide in the α-position (equations 284 and 285) [275], or by using a chiral alkyl group on the copper (equation 286) [276], (equation 287) [277].



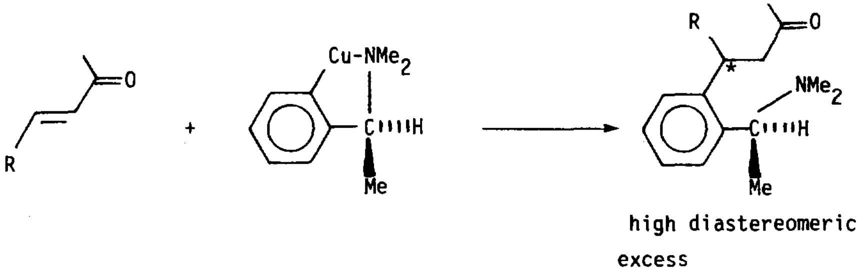
(284)

(285)



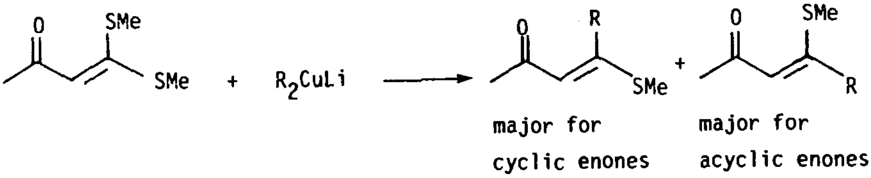


(286)

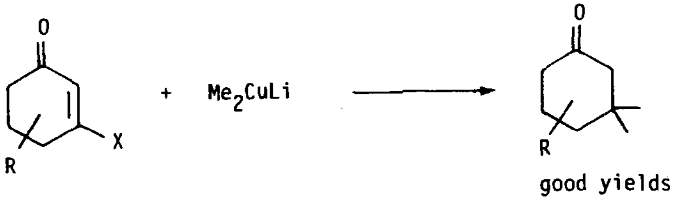


(287)

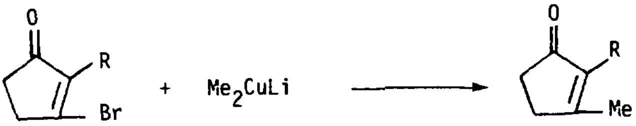
β-Substituted conjugated enones underwent conjugate alkylation by organocuprate reagents to give unsaturated products (equation 288) [278], or doubly alkylated products (equations 289 and 290) [279]. Heteroaryl cuprates also added 1,4 to conjugated enones (equation 291) [280].



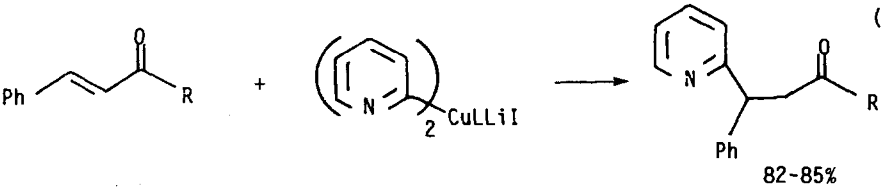
(288)



(289)

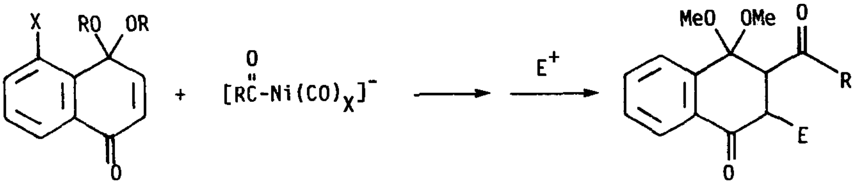


(290)

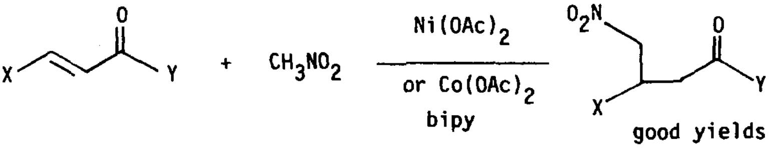


(291)

Quinone monoketals were 1,4-acylated when treated with acylnickel carbonylates (equation 292) [281]. Nitromethane added 1,4 to conjugated ketones in the presence of nickel(II) or cobalt(II) salts (equation 293) [282].



(292)

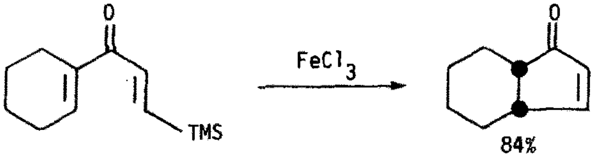


(293)

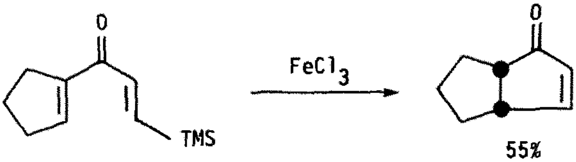
X = Ph, p-$NO_2$Ph, p-ClPh, styryl, H

Y = Ph, p-$NO_2$Ph, p-ClPh, Me, CN

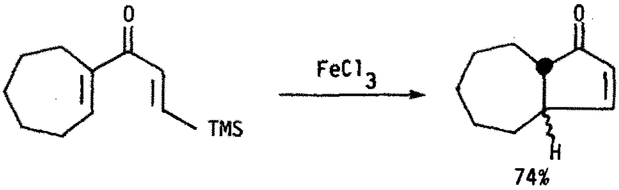
Iron pentacarbonyl and iodine catalyzed the 1,4 addition of diethyl malonate to acrylic compounds [283]. Iron(III) chloride promoted the cyclization of dienones to cyclopentenones (equations 294-299) [284]. Titanium(III) chloride and t-butylhydroperoxide promoted the addition of ethers to conjugated enones (equation 300) [285]. Titanium(IV) chloride catalyzed the hydrocyanation of conjugated enones by isonitriles (equation 301) [286].



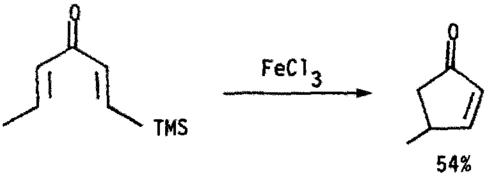
(294)



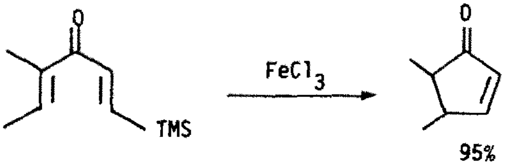
(295)



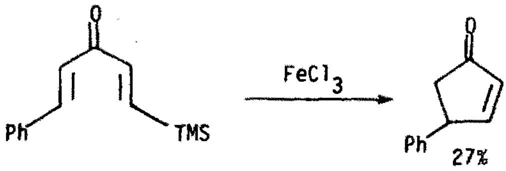
(296)



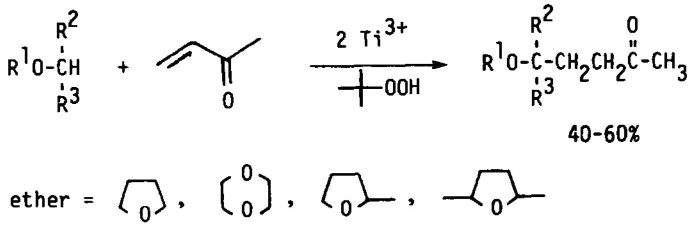
(297)



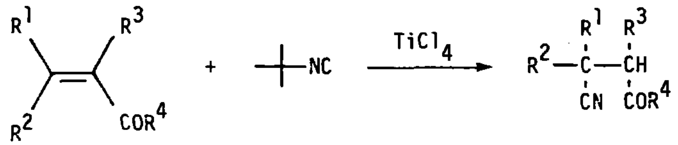
(298)



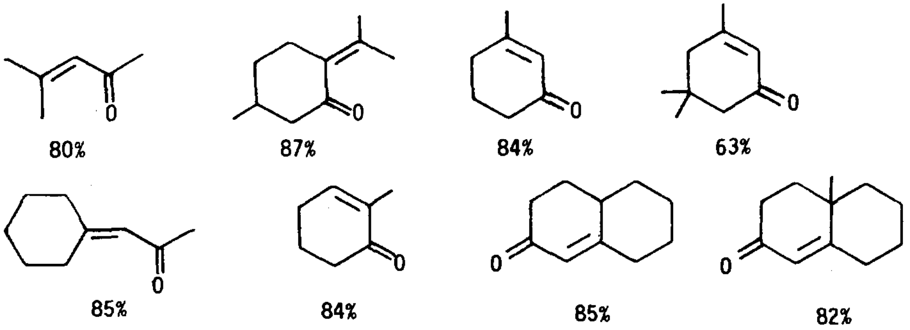
(299)



(300)



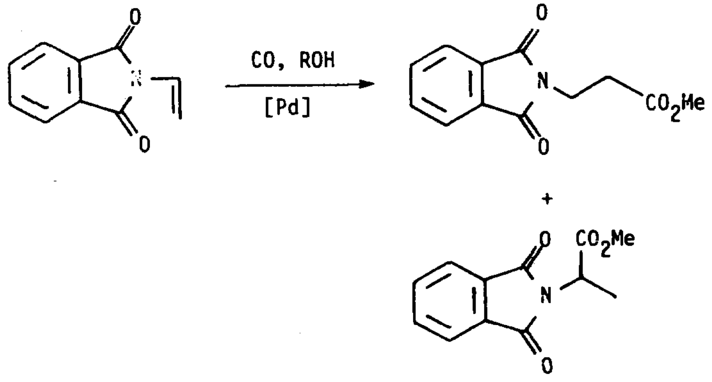
(301)



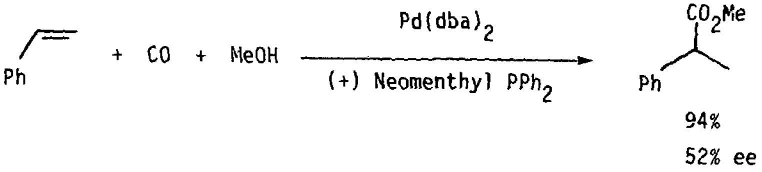
## C. Acylation Reactions (Excluding Hydroformylation)

### 1. Carbonylation of Alkenes and Alkynes

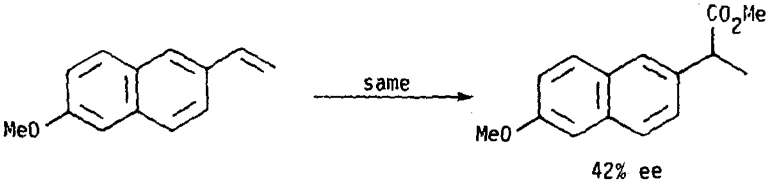
N-Vinylphthalimide was carbonylated using palladium catalysts (equation 302) [287]. The regiochemistry depended on the solvent and the presence of added ligands and ranged from 98.5/1.5 linear to branched to 8.7/91.3. Carbonylation of styrene or vinyl naphthalene in the presence of palladium(0) catalysts and a chiral phosphine ligand produced chiral esters (equations 303 and 304) [288]. Indole was carboxylated at the 3-position using palladium(II) catalysts under oxidizing conditions (equation 305 and 306) [289]. Immobilized palladium catalysts were used in the hydrocarboxylation of 1-nonene [290].



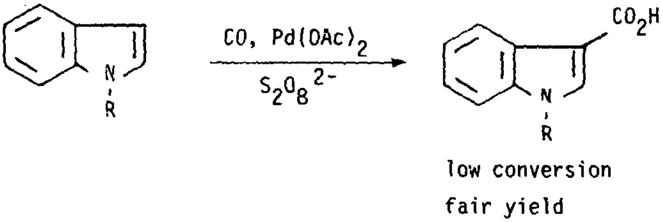
(302)



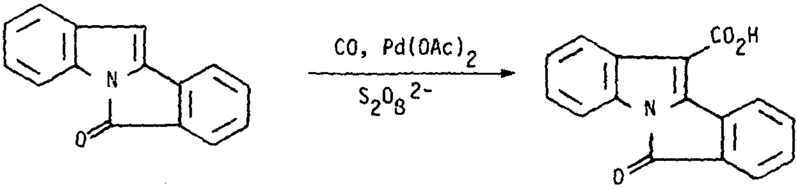
(303)



(304)

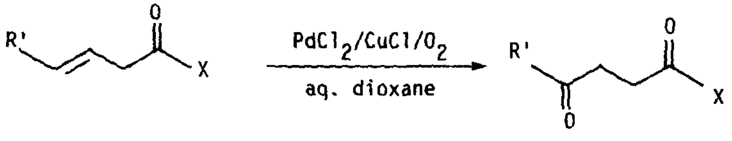


(305)



(306)

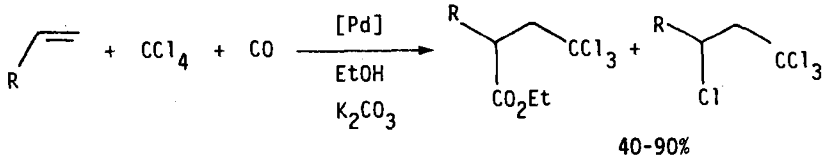
β,γ-Unsaturated ketones were converted to γ-diketones when oxidized in the presence of palladium(II) salts (equation 307) [291]. Palladium also catalyzed reaction of olefins and carbon tetrachloride with carbon monoxide to give β-trichloromethyl esters (equation 308) [292]. π-Allylpalladium complexes carbonylated when treated with sodium butyrate and carbon monoxide (equations 309 and 310) [293]. A dissertation concerning the rhodium catalyzed hydroacylation of ethylene with unsaturated aldehydes has appeared [294].



(307)

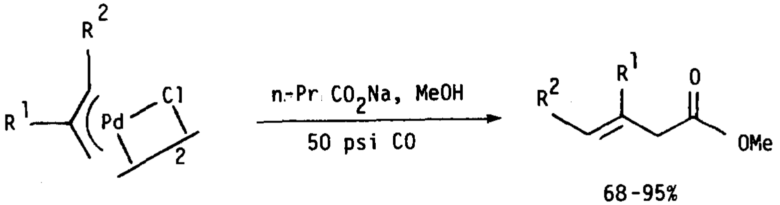
R' = Et, $n$-$C_6$
X = OMe, Me

45-61%



(308)

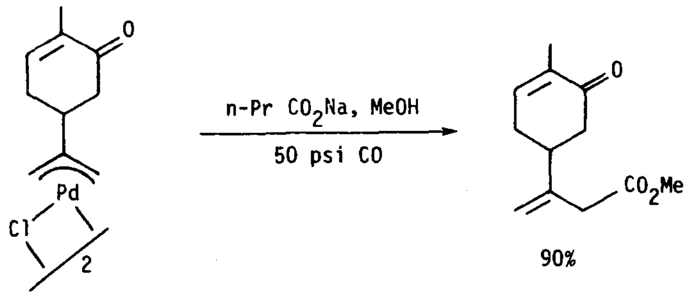
R = n-$C_6$, $ArCH_2$, $(CH_2)_2CO_2Et$, $(CH_2)_8CO_2Me$



(309)

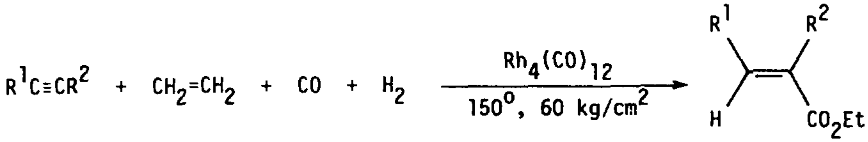
$R^1$ = H, Me

$R^2$ = H, Me



(310)

Alkynes were carbonylated to conjugated esters when treated with carbon monoxide, hydrogen, and ethylene in the presence of a rhodium catalyst (equation (311) [295]. Under other conditions, furanones were formed (equation 312) [296]. Acetylene itself was carbonylated in solutions of palladium(II) bromide in the presence of triphenylphosphite and tosic acid [297].



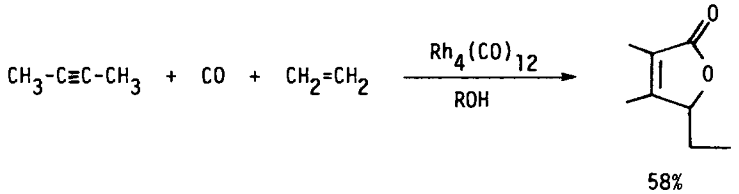
(311)

$R^1=R^2=Ph$ 75%
$R^1=Bu$, $R^2=H$ 42%
$R^1=Ph$, $R^2=CO_2Me$ 40%

$R^1=Ph$, $R^2=H$ 48%
$R^1=Me$, $R^2=CO_2Me$ 76%

$R^1=Ph$, $R^2=Me$ 49%
$R^1=t\text{-}Bu$, $R^2=H$ 61%

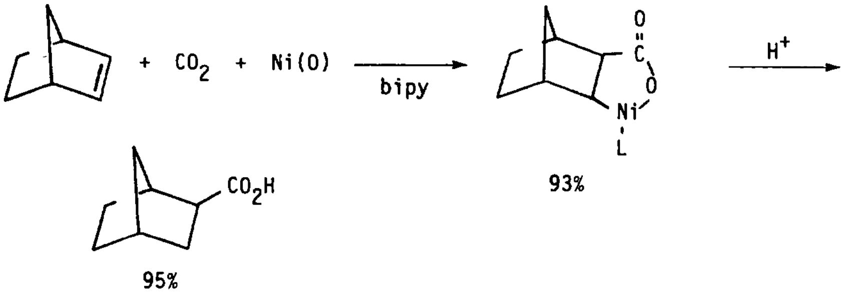
$R^1=R^2=Me$ 25%
$R^1=R^2=MeO_2CH_2$ 76%

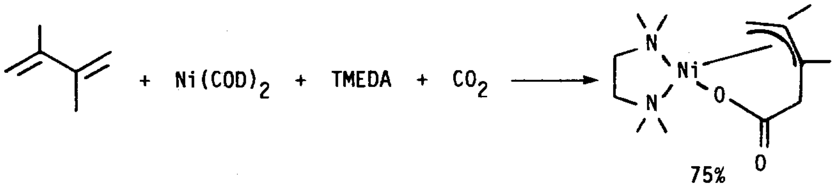


(312)

Transition metals were used to activate carbon dioxide in a number of systems. Norbornene was carboxylated when treated with carbon dioxide and a nickel(0) catalyst (equation 313) [298]. 2,3-Dimethylbutadiene reacted with carbon dioxide in the presence of nickel(0) complexes (equation 314) [299]. The intermediate complex from alkynes was converted to acids or anhydrides (equation 315) [300][301]. Furanones were produced by the palladium(0) catalyzed reaction of carbon dioxide with methylenecyclopropanes (equation 316) [302]. Group VIII metals catalyzed the carboxylation of ethylene by carbon dioxide [303].

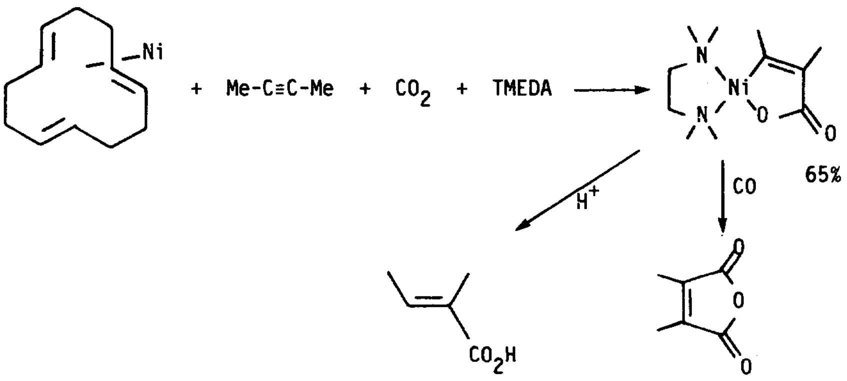
(313)

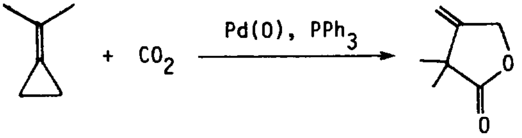




(314)

(315)

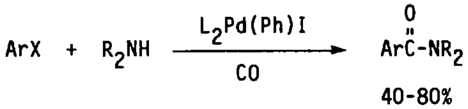




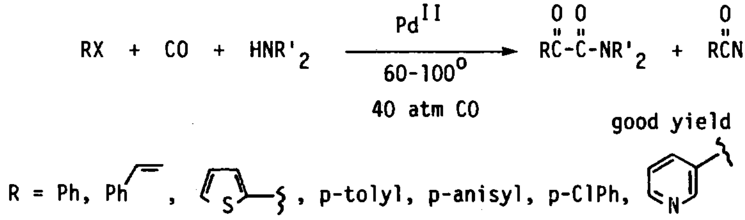
(316)

## 2. Carbonylation of Halides

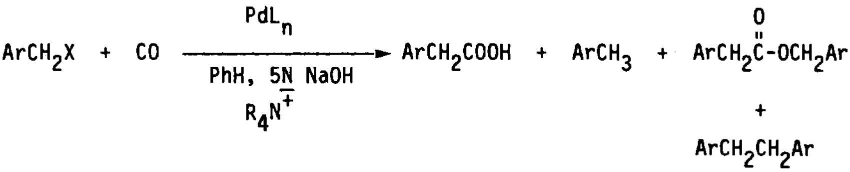
Aryl and vinyl halides were converted to their corresponding amides when treated with carbon monoxide and palladium catalysts in the presence of secondary amines (equation 317) [304]. Under appropriate conditions a double insertion occurred giving α-ketoamides in good yield (equation 318) [305][306][307]. Benzyl halides reacted with carbon monoxide and a palladium catalyst under phase transfer conditions to give several products (equation 319). With $L_4Pd$ as catalyst the carboxylic acid was the major product, whereas $Pd(dba)_2$ resulted in reduction and coupling, and $Pb(diphos)_2$ produced esters [308]. Diaryliodonium salts were carbonylated to benzoates by carbon monoxide and palladium(II) or palladium(0) catalysts [309], as were aryl halides [310]. Acid anhydrides were produced in the reaction of arenes and 1,2-dibromoethane with carbon monoxide and palladium(II) complexes (equation 320) [311].



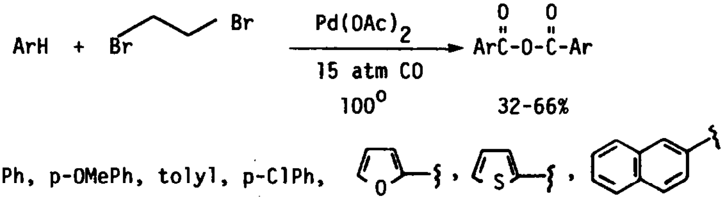
$$ArX + R_2NH \xrightarrow[CO]{L_2Pd(Ph)I} \underset{40\text{-}80\%}{Ar\overset{O}{\overset{\|}{C}}\text{-}NR_2} \qquad (317)$$



$$RX + CO + HNR'_2 \xrightarrow[\substack{60\text{-}100^{o} \\ 40\ atm\ CO}]{Pd^{II}} R\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NR'_2 + R\overset{O}{\overset{\|}{C}}NR'_2 \qquad (318)$$

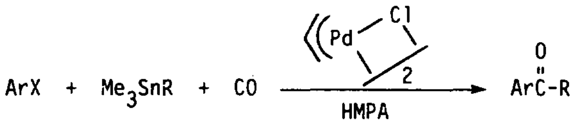


$$ArCH_2X + CO \xrightarrow[\substack{PhH,\ 5\underline{N}\ NaOH \\ R_4N^+}]{PdL_n} ArCH_2COOH + ArCH_3 + ArCH_2\overset{O}{\overset{\|}{C}}\text{-}OCH_2Ar + ArCH_2CH_2Ar \qquad (319)$$



$$ArH + BrCH_2CH_2Br \xrightarrow[\substack{15\ atm\ CO \\ 100^{o}}]{Pd(OAc)_2} \underset{32\text{-}66\%}{Ar\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ar} \qquad (320)$$

Ketones were produced in the reaction of aryl halides with aryl trimethyltin reagents and carbon monoxide in the presence of a palladium catalyst (equation 321)[312][313]. Iron pentacarbonyl acylated sulfur stabilized carbanions (equation 322) [314].



(321)

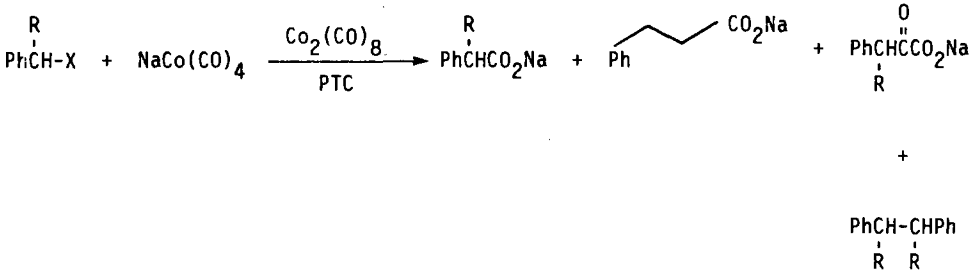
$$\underset{R'}{RSCH}\text{-Li} + Fe(CO)_5 \longrightarrow \xrightarrow{R''X} \underset{R'}{RSCH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R'' \qquad (322)$$

modest yields

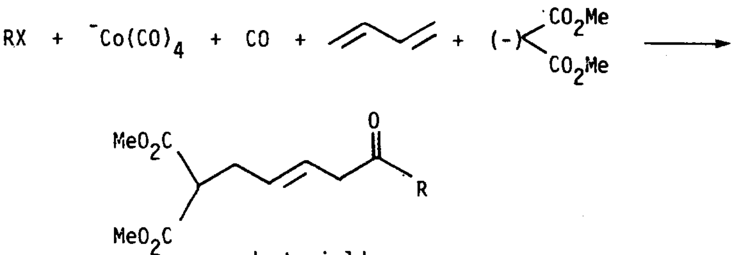
R = PH, vinyl
R" = Me, RCO

Cobalt carbonyl converted benzyl halides into a number of products under phase transfer conditions. The product distribution depended on the conditions (equation 323) [315]. Organic halides, carbon monoxide, 1,3-dienes, and stabilized carbanions combined to give β,γ-unsaturated ketones when sodium tetracarbonyl cobaltate was treated sequentially with these reagents (equation 324) [316]. 1,3-Diiodopropane was converted to a cobaltacyclopentanone, which behaved like a cyclic ketone in that it could be α-alkylated (equation 325) [317]. Benzyl bromide was converted to dibenzylketone by $Ni(CN)_2(CO)_2^{=}$ in aqueous acetone [318]. Electrochemical reduction of $NiL_2X_2$ in the presence of aryl halides and carbon dioxide gave arene carboxylates in good yield [319]. These same nickel complexes catalyzed the production of ketones by the reaction of aryl halides, carbon monoxide, and Grignard reagents [320].

(323)

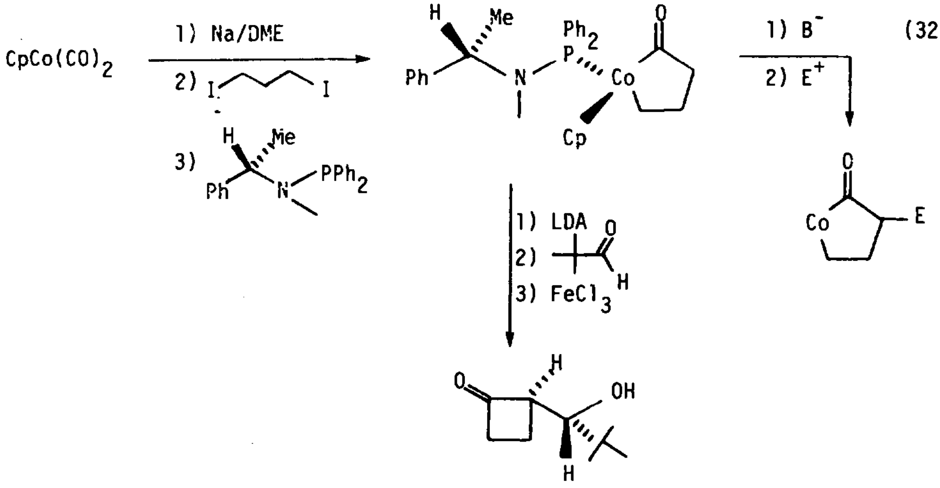


(324)



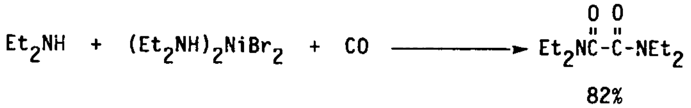
modest yields

(325)

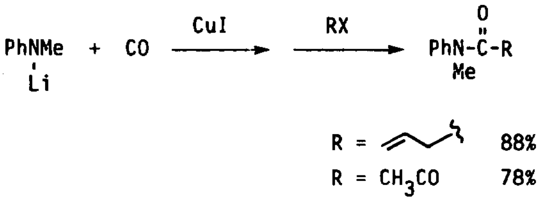


3. Carbonylation of Nitrogen Compounds

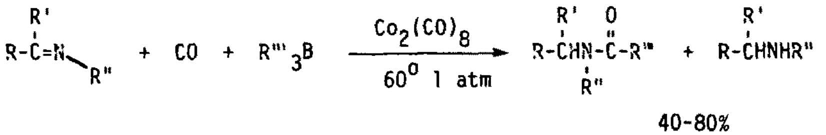
Diethylamine was converted to diethyl oxamide by reaction with carbon monoxide and nickel(II) amine complexes (equation 326) [321]. Amides were also produced in the reaction of lithium amides with carbon monoxide and alkyl halide and copper(I) iodide (equation 327) [322]. Metal complexes oxidatively carbonylated amines [323]. Imines were acylated and reduced by carbon monoxide and trialkylboranes in the presence of dicobalt octacarbonyl (equation 328) [324]. Ketones were produced from alkyl tin reagents, carbon monoxide and aryl diazonium salts in the presence of palladium(II) catalysts (equation 329) [325].



$$Et_2NH + (Et_2NH)_2NiBr_2 + CO \longrightarrow \underset{82\%}{Et_2N\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-NEt_2} \quad (326)$$



$$\underset{\underset{Li}{|}}{PhNMe} + CO \xrightarrow{CuI} \xrightarrow{RX} Ph\underset{Me}{N}-\overset{O}{\overset{\|}{C}}-R \quad (327)$$



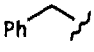
$$\mathrm{R{-}\overset{R'}{C}{=}N{-}R''} + \mathrm{CO} + \mathrm{R'''_3B} \xrightarrow[60^0\ 1\ \mathrm{atm}]{\mathrm{Co_2(CO)_8}} \mathrm{R{-}\overset{R'}{C}H{-}\underset{R''}{N}{-}\overset{O}{\overset{\|}{C}}{-}R'''} + \mathrm{R{-}\overset{R'}{C}HNHR''} \qquad (328)$$

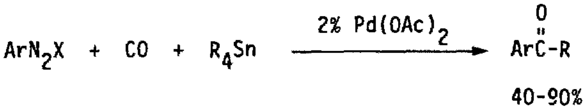
40-80%

R = PhCO, p-tolCO

R' = Ph, p-tolyl, H

R" = Ph, p-anisyl

R''' = Et, n-Bu, n-$C_7$, Ph 



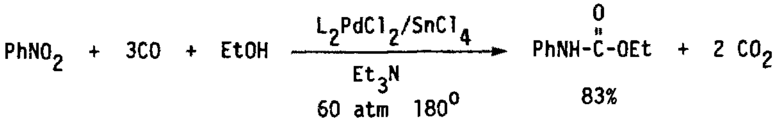
$$\mathrm{ArN_2X} + \mathrm{CO} + \mathrm{R_4Sn} \xrightarrow{2\%\ \mathrm{Pd(OAc)_2}} \mathrm{Ar\overset{O}{\overset{\|}{C}}{-}R} \qquad (329)$$

40-90%

R = Me, Et, Ph

Ar = Ph, o-tolyl, m-tolyl, p-tolyl, 2-ClPh, 4-ClPh, 4-BrPh, 4-IPh, 3-$NO_2$Ph, 4-$NO_2$Ph

Nitrobenzene was carbonylated to its corresponding ethyl carbamate by carbon monoxide in the presence of mixed platinum/tin catalysts (equation 330) [326]. Palladium catalysts anchored to silica gel by nitrogen and sulfur containing ligands were effective catalysts for the carbonylation of nitroaromatics to carbamates and isocyanates [327]. Rhodium on alumina catalyzed the same process and a mechanism for this system was proposed [328]. The additives $Ca(VO_3)_2$, $Al(VO_3)_3$, $Pd(VO_3)_2$, $H_2MoO_4$, $(NH_4)_2MoO_4$, and $CdMoO_4$ promoted the palladium(II) chloride-pyridine catalyzed carbonylation of nitroarenes, azobenzenes and azoxybenzenes to isocyanates [329]. A catalyst prepared by impregnating γ-alumina with $Pd_2Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6(PPh_3)_2$ followed by heating at 300° for 16 hrs converted nitrobenzene into phenylisocyanate at 240° and 100 atmospheres carbon monoxide, in 80% yield and 100% conversion [330].

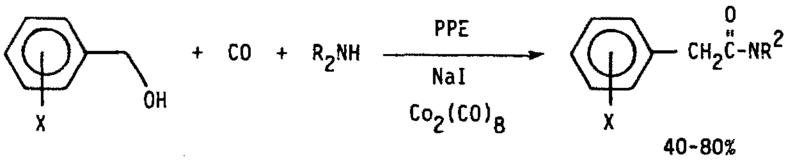


$$\mathrm{PhNO_2} + 3\mathrm{CO} + \mathrm{EtOH} \xrightarrow[\substack{\mathrm{Et_3N} \\ 60\ \mathrm{atm}\ \ 180^0}]{\mathrm{L_2PdCl_2/SnCl_4}} \mathrm{PhNH{-}\overset{O}{\overset{\|}{C}}{-}OEt} + 2\ \mathrm{CO_2} \qquad (330)$$

83%

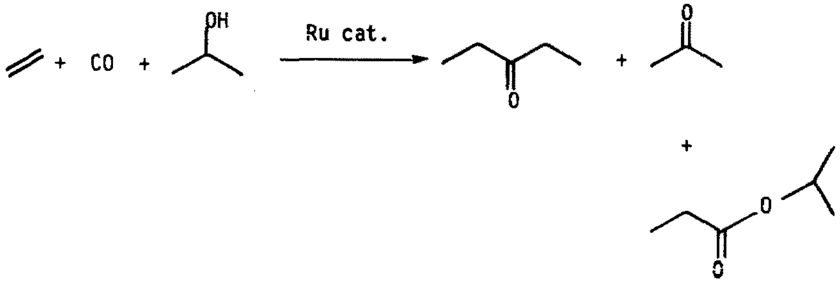
## 4. Carbonylation of Oxygen Compounds

Carbonylation of benzyl alcohols and acetates has been reviewed (36 references) [331]. The full details of the synthesis of phenylacetic acid from benzyl alcohol and carbon monoxide, catalyzed by rhodium complexes has appeared [332]. Cobalt catalyzed a similar conversion of benzyl alcohols to phenylacetic acid amides (equation 331) [333]. A variety of ketones and esters were produced by the reaction of ethylene, carbon monoxide, and isopropanol in the presence of ruthenium catalysts (equation 332) [334]. Palladium(II) catalyzed the conversion of allyl carbonates to allyl esters in the presence of carbon monoxide (equation 333) [335]. Methanol was reductively carbonylated over $FeCo_3(CO)_{12}^-$ catalysts [336]. Rhodium zeolites were used to catalyze the carbonylation of ethanol to ethyl propionate [337]. Formaldehyde was carbonylated by copper- or silver carbonyl catalysts in 85% sulfuric acid [338].

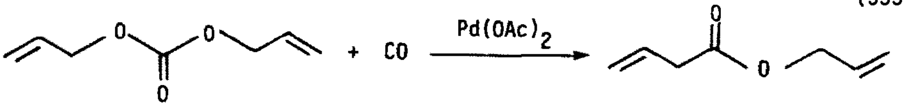


(331)

X = H, p-OMe, p-Cl, p-Br, p-NO$_2$, o-Cl
R = i-Pr, cyclohexyl, Et



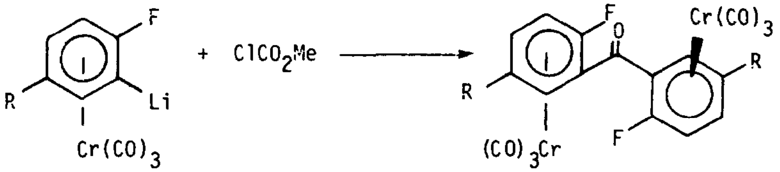
(332)

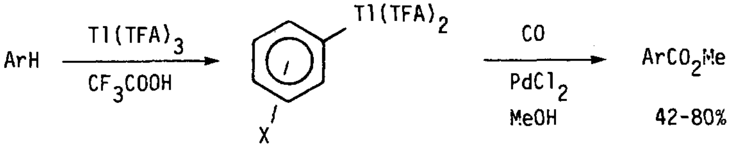


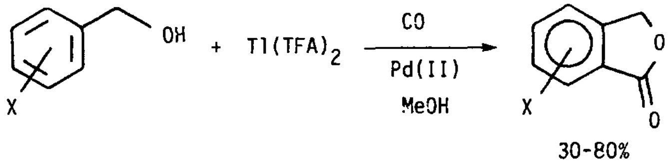
(333)

5. Miscellaneous Carbonylations

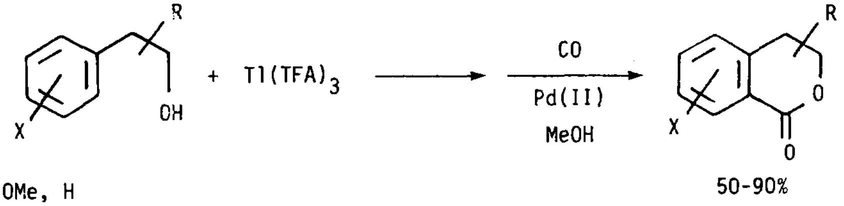
Reviews dealing with carbonylation (43 references) [339], cyclocarbonylation of organic unsaturated substrates with carbon monoxide (24 references) [340], organic synthesis with carbon dioxide (153 references) [341], and carbon monoxide in organic synthesis by organotransition metal complexes (60 references) [342] have appeared. Lithiated arenechromium tricarbonyl complexes reacted with methyl chloroformate to produce carbonyl-bridged dimers (equation 334) [343]. Arylthallium complexes were carbonylated by treatment with carbon monoxide and palladium(II) catalysts (equations 335-337) [344]. Grignard reagents were carbonylated to aldehydes by reaction with iron pentacarbonyl [345].


(334)


(335)


(336)

X = H, MeO, OH, Me


(337)

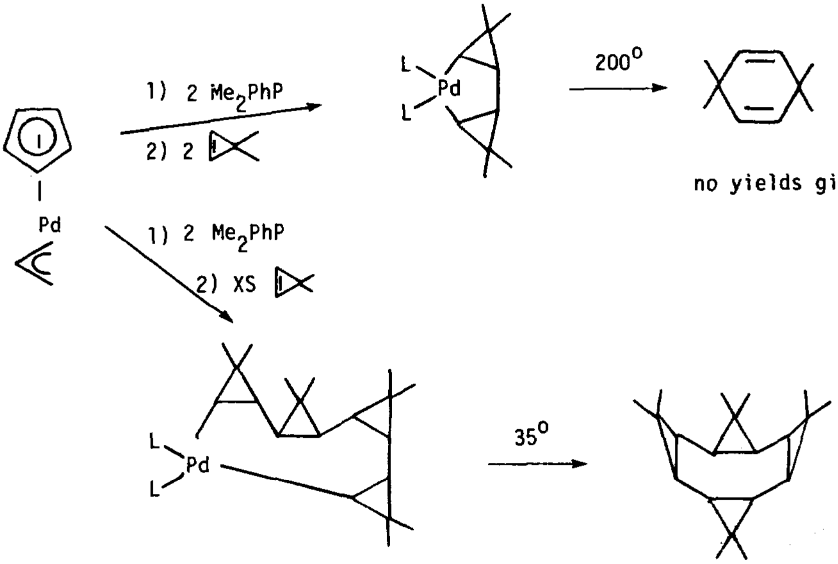
X = OMe, H

6. Decarbonylation

Aryl acid chlorides were decarbonylated to aryl halides by treatment with 1% palladium on carbon at 360°C [346]. Catalytic decarbonylation of aldehydes using chelating diphosphine complexes of rhodium (I) has been studied [347]. The complex $[Rh(dppp)_2]BF_4$ was $10^2$ faster than $Rh(PPh_3)_3Cl$, under mild conditions (150°) with turnovers in excess of 100,000 being observed.

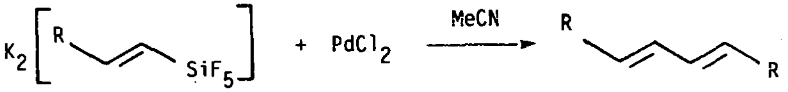
## D. Oligomerizations

The mechanism of the Fischer-Tropsch synthesis was claimed to involve methylene polymerization, but a carbon monoxide insertion mechanism was equally well supported by the data [349]. Dimethylsulfoxide complexes of palladium(II) such as $(DMSO)_2PdCl_2$ and $K^+[DMSO\ PdCl_3]^-$ were efficient catalysts for the dimerzation of ethylene [350], as were tetrabutyl titanate/triethylaluminum systems in ether in the presence of hydrogen [351]. Propylene was dimerized by complex nickel catalysts fixed on phosphorylated polystyrene [352]. A dissertation dealing with metallacyclopentanes as catalysts for the linear and cyclodimerization of olefins has appeared [353]. Dimethylcyclopropene was dimerized and tetramerized by π-allylpalladium catalysts (equation 338) [354]. 1,3-Dienes were prepared by the palladium-catalyzed dimerization of vinyl pentafluorosilicon species (equation 339) [355]. Methyl acrylate dimerized with incorporation of carbon monoxide when treated with carbon monoxide and dicobalt octacarbonyl (equation 340) [356]. Methyl acrylate was hydrodimerized to dimethyl adipate by cobalt(0)/alkali halide/zinc catalysts [357]. The mechanism of the cobalt-catalyzed dimerization of acrylonitrile to adiponitrile was studied (equation 341) [358].



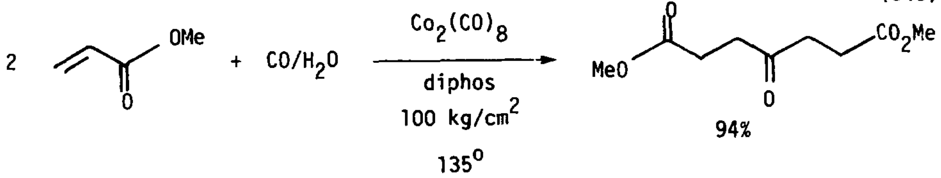
no yields given

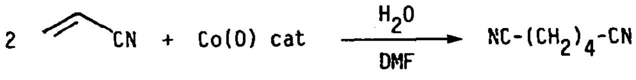
(338)



(339)

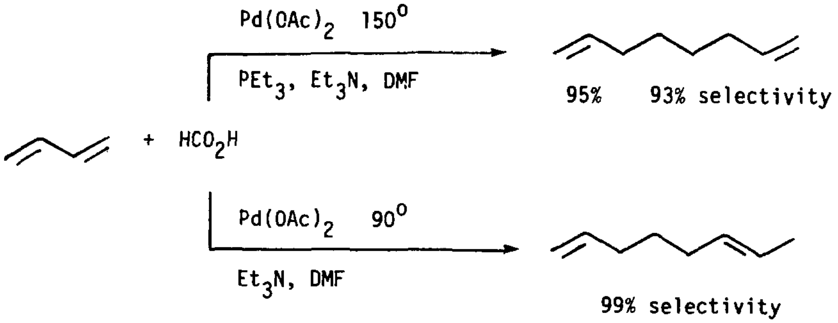
(340)



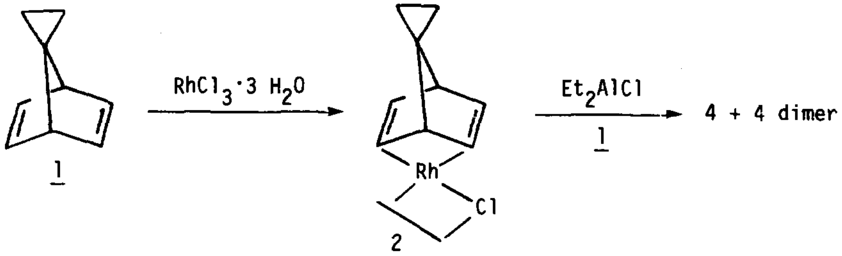


(341)

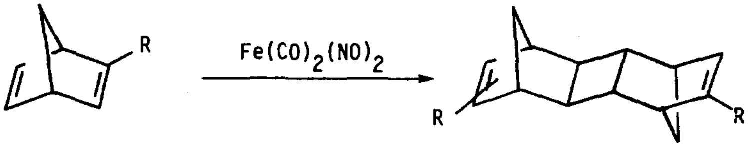
Butadiene was dimerized to 1,7- or 1,6-octadiene by palladium(II) catalysts in the presence of formic acid (equation 342) [359]. Bisphenoxytitanium catalysts dimerized isoprene [360]. Substituted norbornadienes were dimerized by rhodium(III) complexes (equation 343) [361] and by iron carbonyl nitrosyl complexes (equation 344) [362]. Iron carbonyls promoted the dimerization shown in equation 345 [363].



(342)

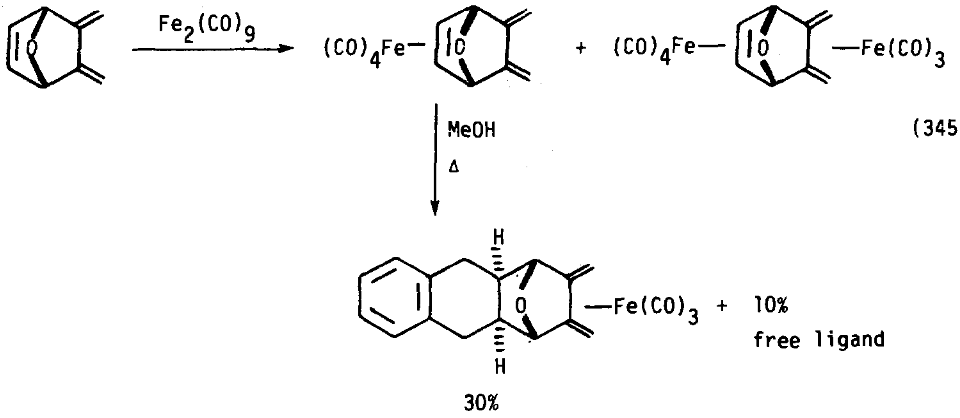


(343)



(344)

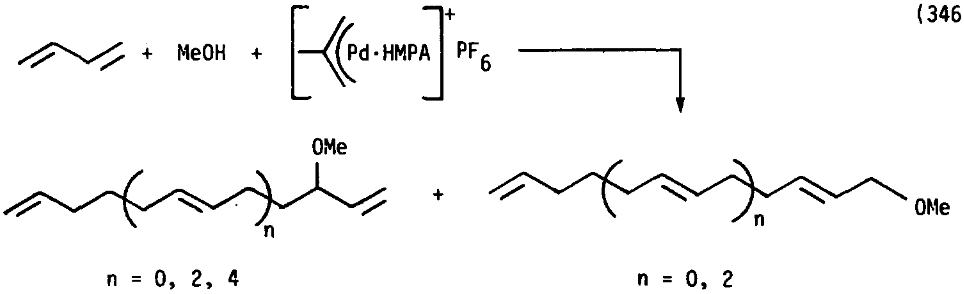
R = Me, $CH_2OH$, $CH_2OMe$, $CO_2Me$



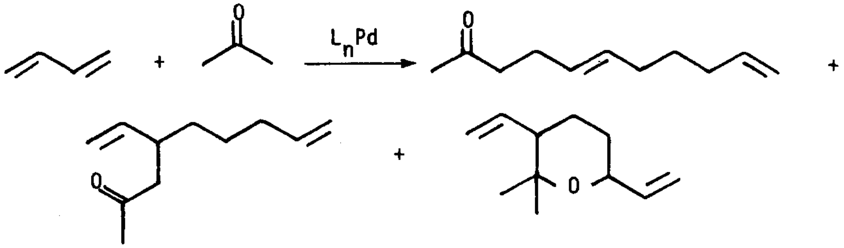
(345)

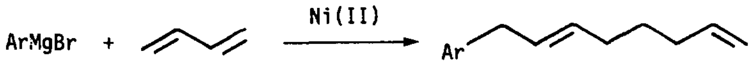
With cationic π-allylpalladium complexes as catalysts, higher telomers of butadiene and methanol were obtained than when neutral complexes were used (equation 346) [364]. Pheremones were prepared from a telomer of butadiene and phenol, produced in a palladium-catalyzed process [365]. Alkylphosphine complexes of palladium catalyzed the telomerization of butadiene with acetone to give a number of products (equation 347) [366]. Nickel(II) salts catalyzed the telomerization of aryl grignard reagents with butadiene (equation 348) [367]. Isoprene and phenol telomerized over Pd(dba)$_2$ catalysts (equation 349) [368]. In the presence of chiral phosphines, palladium complexes telomerized isoprene and methanol to give chiral products (equation 350) [369]. The kinetics of the telomerization of ethylene with carbon tetrafluoride catalyzed by chromium hexacarbonyl or its monophosphine derivative have been studied [370].

(346)



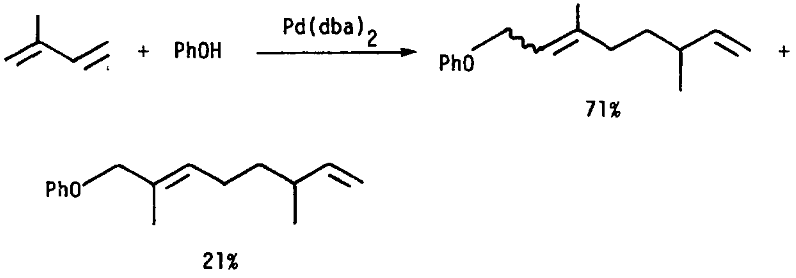
(347)

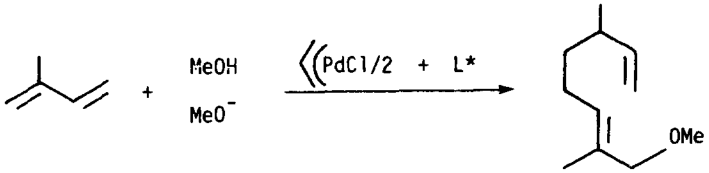




(348)

(349)



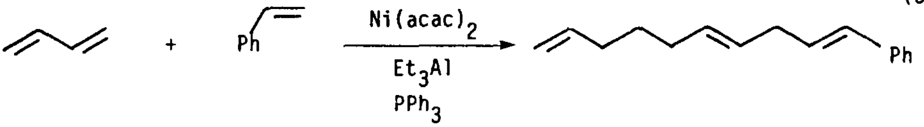


100% conversion
up to 35% ee

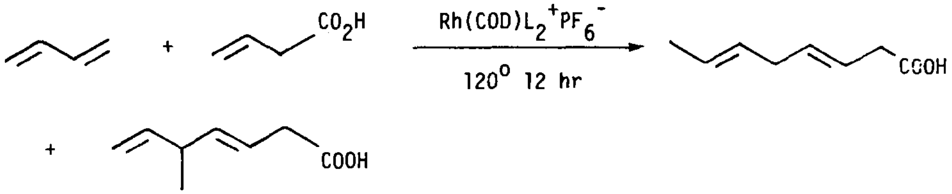
(350)

The kinetics of the cotrimerization of butadiene with styrene over nickel catalysts (equation 351) have been studied [371]. Rhodium(I) complexes catalyzed the codimerization of dienes with unsaturated acids (equations 352 and 353)[372]. Nickel(0) complexes with chiral aminophosphine ligands such as (-)(R)-$Ph_2PNMeCHMePh$ catalyzed the asymmetric codimerization of ethylene with 1,3-cyclohexadiene [373]. Palladium(0) complexes catalyzed the codimerization of norbornene with bromobenzene (equation 354) [374], and vinyl cyclopropanes with almost everything (equation 355) [375].

(351)

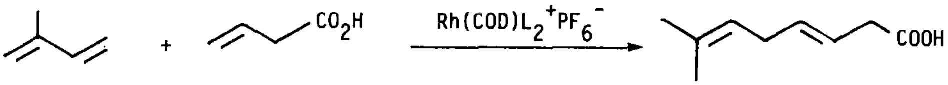


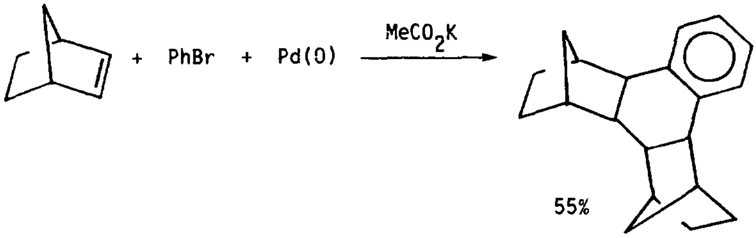
(352)



66%

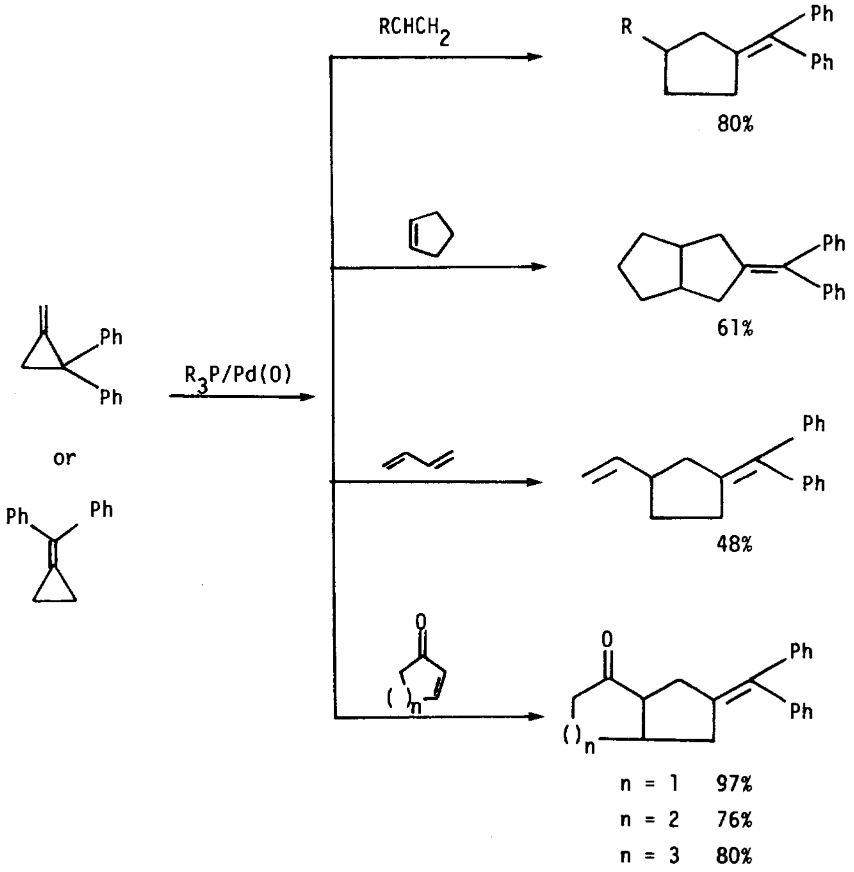
(353)





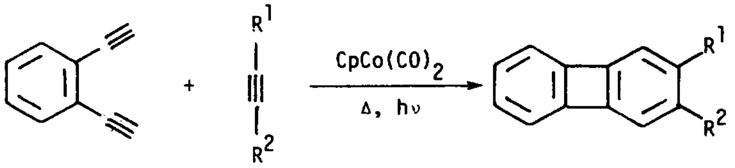
55%

(354)



(355)

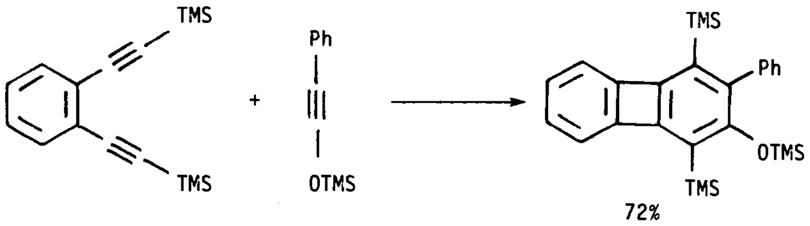
A dissertation on the subject "organonickel intermediates in alkyne oligomerization reactions by nickel(0) complexes" has appeared [376]. Niobium(V) and tantalum(V) halides catalyzed the polymerization of 3-octyne and phenyl methyl acetylene to polymers exceeding molecular weight 1 x $10^6$ [377]. Dibenzocyclobutanes were produced by the cobalt-catalyzed CO-cyclotrimerization of diynes with alkynes (equation 356) [378] (equation 357) [379]. Estrone (equation 358) [380] and other polycyclic compounds (equation 359) were made this way. Rhodium(I) catalyzed a similar process (equations 360-362) [381].



(356)

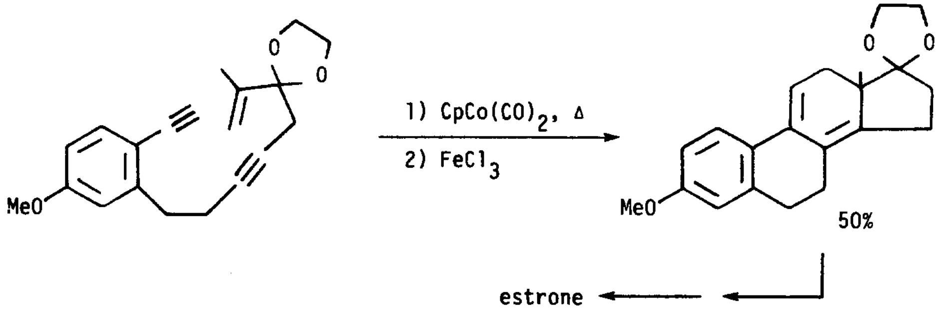
$R^1 = R^2 =$ TMS 96%

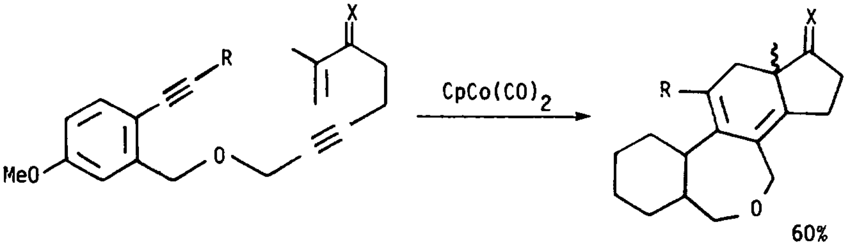
$R^1 =$ TMS, H, n-Bu, Ph, $CO_2Me$
$R^2 =$ n-$C_5$, n-Bu, Ph, $CO_2Me$
} 25-58%



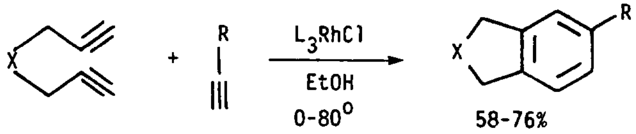
(357)

(358)



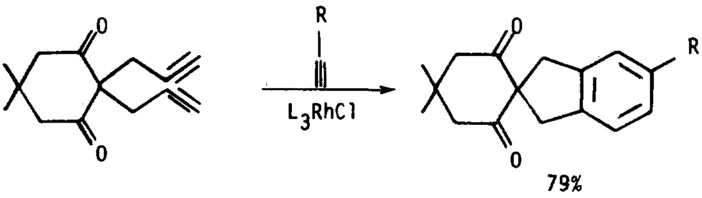


(359)

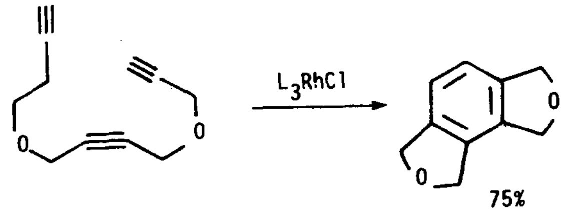


(360)

X = $CH_2$, O, $SO_2$, NHCOMe, $C(CO_2Me)_2$
R = H, n-Pr, $CH_2OH$, Ph, TMS

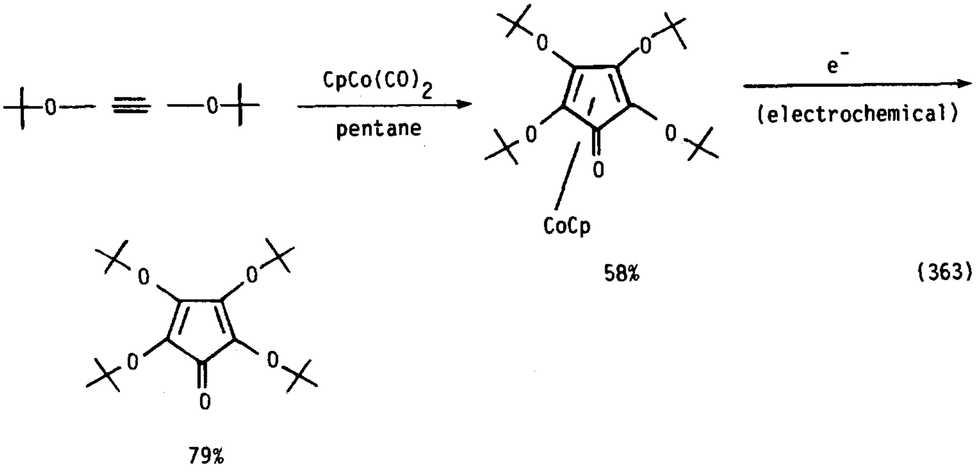


(361)



(362)

Cobalt complexes cyclodimerized di-t-butoxyacetylene with carbon monoxide to make the tetrasubstituted cyclopentadienone (equat. 363) [382]. Theoretical calculations concerning the role of cobaltacyclopentadienes in the cobalt-catalyzed oligomerization of alkynes have been carried out [383]. Nickel(0) complexes catalyzed the reaction of alkynes with carbon dioxide (equation 364) [384] and isocyanates (equation 365) [385] to give a variety of products.



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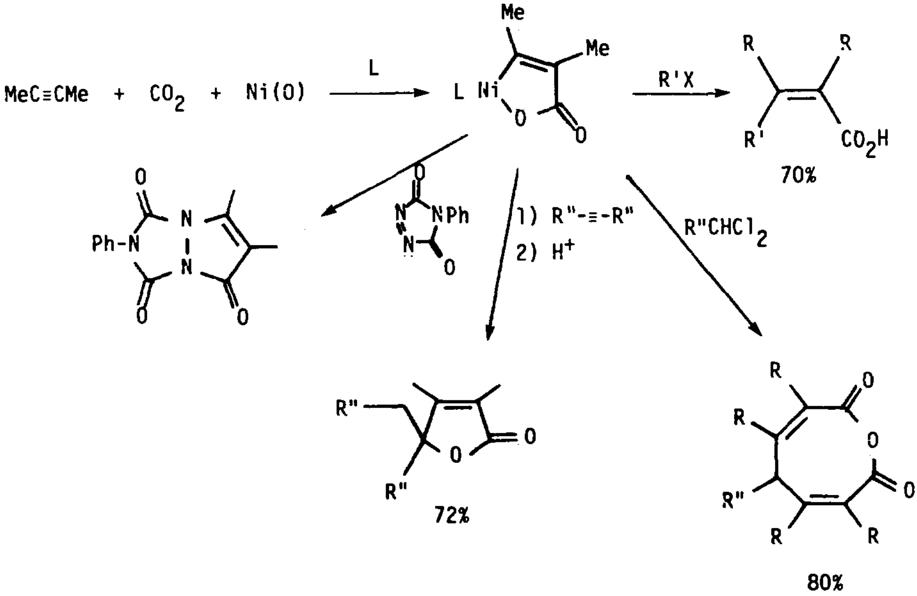
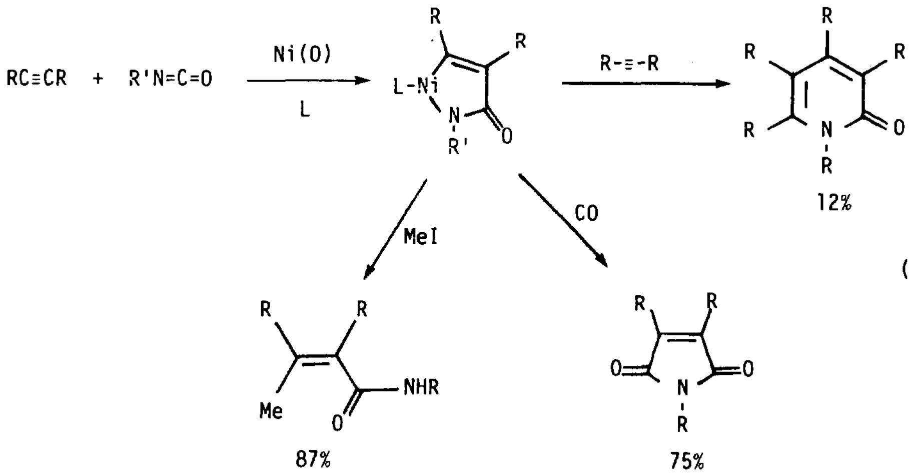
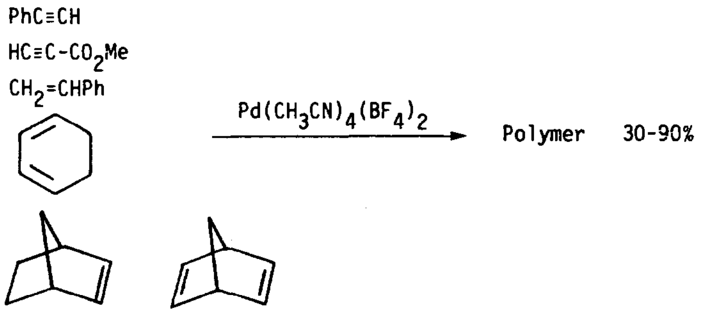


(364)

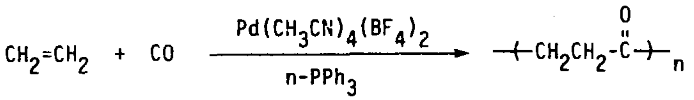


(365)

Condensation of diphenylacetylene with chromium vapor produced tetraphenylcyclobutadiene, hexaphenyl benzene, and the bis-arene chromium complex of the starting acetylene [386]. The influence of ligands on the rhodium catalyzed oligomerization of terminal hydroxyacetylenes has been studied [387]. Alkynes were oligomerized by polymeric organostannylphosphphenyl(tricarbonyl)nickel complexes [388]. A review (24 references) entitled "Carbon-carbon Bond Formation II. Oligomerization, Isomerization, Metathesis, and Hydrocyanation" has appeared [389]. The cationic palladium(II) complex $Pd(CH_3CN)_4(BF_4)_2$ polymerized (equation 366) [390] and polymerized with carbonylation (equation 367) [391] a number of unsaturated substrates. The tantalum-carbene complex $Ta(CHCMe_3)(H)L_3I_2$ polymerized ethylene to polyethylene [392]. Benzene was polymerized to polybenzene (equation 368) [393] by $Cu(AlCl_4)_2$. Cationic molybdenum and tungsten complexes polymerized olefins via a cationic process (equation 369) [394].

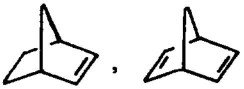


(366)

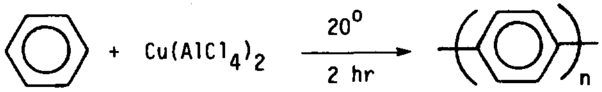


$$CH_2{=}CH_2 + CO \xrightarrow[n\text{-}PPh_3]{Pd(CH_3CN)_4(BF_4)_2} \left[CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\right]_n \qquad (367)$$

high molecular weight



also react

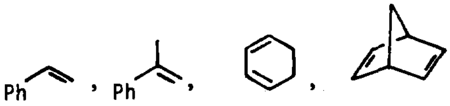


(368)

92%

$$M(CO)_6 + 2\ NOBF_4 \xrightarrow{MeCN} [M(NO)_2(CH_3CN)_4](BF_4)_2 \qquad (369)$$

M = W, Mo

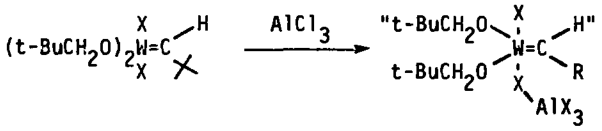


are polymerized by this catalyst

## E. Rearrangements

### 1. Metathesis

New metathesis catalysts continue to be developed and refined. Homogeneous metathesis of internal alkynes was catalyzed by $MoO_2(acac)_2/Et_3Al/PhOH$ systems, which are more efficient than previous $L_nMo(CO)Y$ phenol systems [395]. The methathesis of cis-2-butene over $MoO_3Al_2O_3$ catalysts of varying degrees of reduction was studied [396]. Tungsten hexacarbonyl was attached to an ion exchange resin, reduced with $EtAlCl_2$, and thereafter functioned as a metathesis catalyst for 1-octene [397]. The technetium complex $(Ph_3P)_2Tc(CO)_3Cl$ was a moderately active metathesis catalyst for 2-pentene [398]. Tungsten phenoxides in combination with $EtAlCl_2$ active catalysts for the metathesis of olefins [399]. Tungsten carbene complexes became very active metathesis catalysts when treated with aluminum trichloride (equation 370) [400]. The molybdenum complex $Mo(NO)(CO)_4(AlCl_4)$ was an active long-lived metathesis catalyst for 2-pentene [401]. The metathesis of 1,7-octadiene was catalyzed by tungsten complexes such as $W(CO)_4(NO)X$, $W(CO)_3(NO)LX$, and $W(CO)_2(NO)L_2X$ [402]. Active centers for metathesis of alkenes on tungsten oxide-silica centers were studied [403].



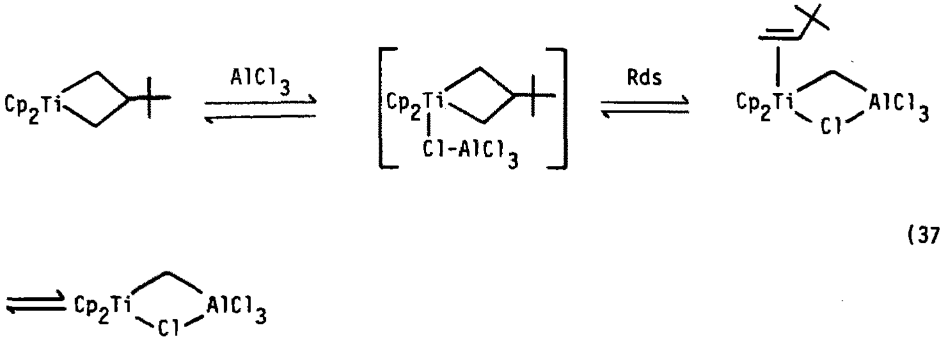
$$(t\text{-}BuCH_2O)_2WX_2{=}C(H)(t\text{-}Bu) \xrightarrow{AlCl_3} \text{"}(t\text{-}BuCH_2O)_2W(X)(X{\cdot}AlX_3){=}C(H)R\text{"} \qquad (370)$$

1-Hexadecene metathesized to produce 80% 15-triacontene and ethylene over a $Bu_4N[Mo(CO)_5Cl]/EtAlCl_2$ catalyst system [404]. Small amounts of phenylacetylene initiated the tungsten hexachloride catalysted metathesis of cis-2-pentene, cyclopentene, cycloheptene, and cyclooctene [405,406]. The ring opening metathesis of norbornene using group VI metal catalysts was studied [407]. Evidence for metallacycles in the metathesis reaction was gained by studying the metathesis of labeled alkynes (equation 371) [408]. A mechanism for Lewis acid promoted metathesis reactions has been proposed (equation 372) [409]. The mechanism of olefin metathesis was subjected to a theoretical treatment, and it was concluded that oxoalkylidene species were chain carrying [410].

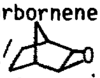
$$Ph\overset{*}{C}\equiv C\text{-p-tolyl} \xrightarrow[25^0]{W(N\text{-}i\text{-}Pr_2)_3t\text{-}BuC} Ph\overset{*}{C}\equiv C\text{-p-tolyl} + Ph\overset{*}{C}\equiv\overset{*}{C}Ph +$$

(371)

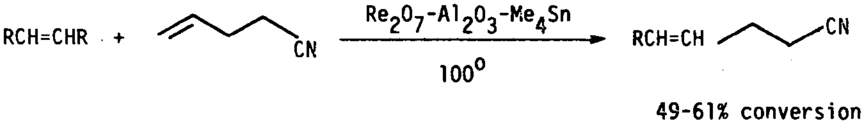
$$\text{p-tolyl-}C\equiv C\text{-p-tolyl}$$



(372)

The origin of the stereochemistry of metathesis of cyclic and acyclic olefins has been addressed [411]. Dimethyl norbornene metathesized to a trans isotactic polymer over a $EtAlCl_2/(Ar)W(CO)_3/$ catalyst [412]. The stereochemistry of olefin metathesis on heterogeneous oxide catalysts was explained by a model based on a metallacyclobutane intermediate [413]. The metathesis of norbornene and cis-2-pentene over a number of group VI metal catalyst/promoter combinations have been compared [414].

The metathesis of functionalized olefins has been reviewed (42 references) [415]. The metathesis of technical grade methyl oleate over $WCl_6/Me_4Sn$ produced numerous side products [416]. Monoolefins were metathesized with 4-pentene-1-nitrile in reasonable yield over a supported rhenium catalyst (equation 373) [417]. A tungsten-tin catalyst system metathesized ω-olefins tosylates (equation 374) [418]. Functionalized alkynes also metathesized, but over molybdenum catalysts (equation 375) [419].



(373)

R = Pr, Bu, n-$C_6$

$$RCH{=}CH\text{-}(CH_2)_n\text{-}OTs \xrightarrow[60^\circ,\ PhCl]{WCl_6/Me_3SnCl} TsO(CH_2)_n\text{-}CH{=}CH\text{-}(CH_2)_n\text{-}OTs \qquad (374)$$

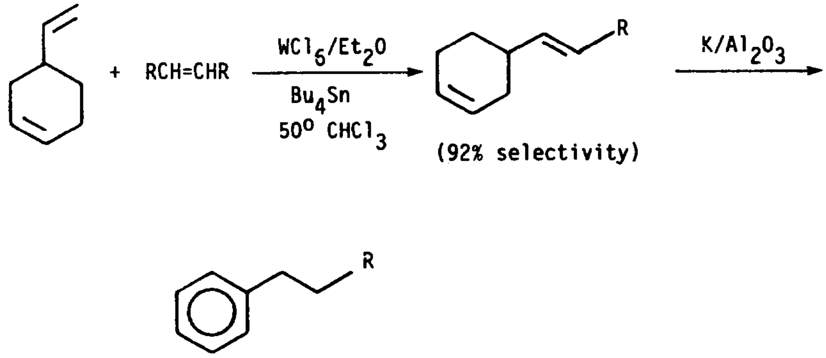
n = 7, 8, 9

>90% yields

$$PhC{\equiv}C\text{-}(CH_2)_2Y \xrightleftharpoons{Mo(CO)_6} PhC{\equiv}CPh + Y(CH_2)_2\text{-}C{\equiv}C\text{-}(CH_2)_2\text{-}Y \qquad (375)$$

Y = OH, OAc, Br, COOH, $CO_2Me$, CN

Internal alkenes metathesized with vinylcyclohexene to produce alkyl benzenes, ultimately (equation 376) [420]. The catalyst system consisting of $Re_2O_7$ or $Al_2O_3$ rapidly metathesized 1,5-hexadiene and 1,6-heptadiene [421]. Alkynes metathesized over tungsten(VI) alkylidyne complexes [422]. A molybdenum catalyst also metathesized alkynes (equation 377) [423].



(376)

$$RC{\equiv}CR' \xrightarrow[\substack{Et_3Al\\ PhCH_3\ rfx}]{MoO_2(acac)_3} RC{\equiv}CR + R'C{\equiv}CR' \qquad (377)$$

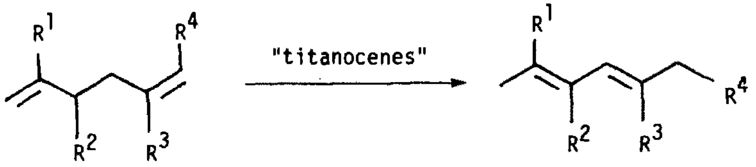
statistical

R = Bu, Ph, $CH_2CHCH_2$, $Cl(CH_2)_3$, $MeO_2C(CH_2)_2$

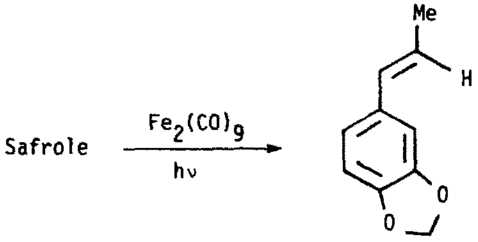
R' = Pr, p-tolyl, Bu, Et

## 2. Olefin Isomerization

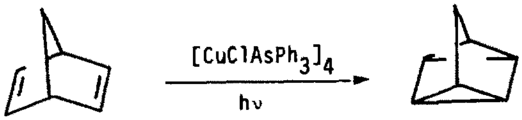
Titanocenes rearranged nonconjugated dienes to conjugated dienes (equation 378) [424]. A review (15 references) dealing with the use of ruthenium hydride complexes to catalyze double bond migration has been published [425]. The complex $HCo_3(CO)_9$, produced from the reaction of $HCo(CO)_4$ with $Co_2(CO)_8$ was an active catalyst for the isomerization of hexene [426]. Triosmium clusters such as $H_2Os_3(CO)_9PPh_3$ and $H_2Os_3(CO)_{10}$ were attached to phosphine functionalized supports and used to catalyze olefin isomerization [427]. Zirconium dioxide catalyzed a similar process [428]. Irradiation of safrole and eugenol in the presence of iron carbonyls led to isomerization (equation 379) [429]. The copper complex $[CuClAsPh_3]_4$ was a catalyst for the photoisomerization of norbornadiene to quadricyclene (equation 380) [430].



(378)



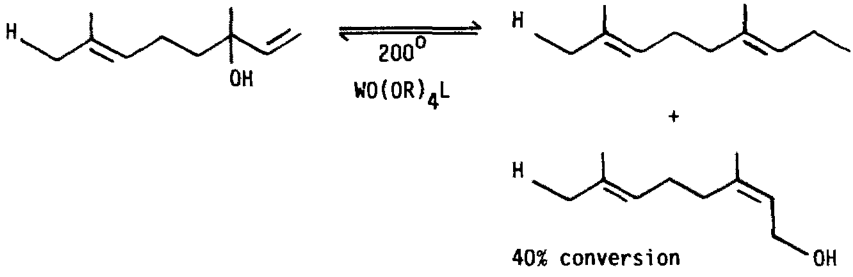
(379)



(380)

## 3. Rearrangements of Allylic and Propargylic Oxygen and Nitrogen Compounds

Tertiary allyl alcohols rearranged to primary allyl alcohols when treated with a tungsten oxide catalyst (equation 381) [431]. Allyl alcohol rearranged to propanol over Raney nickel [432]. Chiral allyl acetates underwent allylic transposition when treated with palladium(II) catalysts (equations 382 and 383) [433]. Reduced titanium species rearranged bicyclic oxides to aromatics or cyclohexadienes (equation 384) [434][434a].



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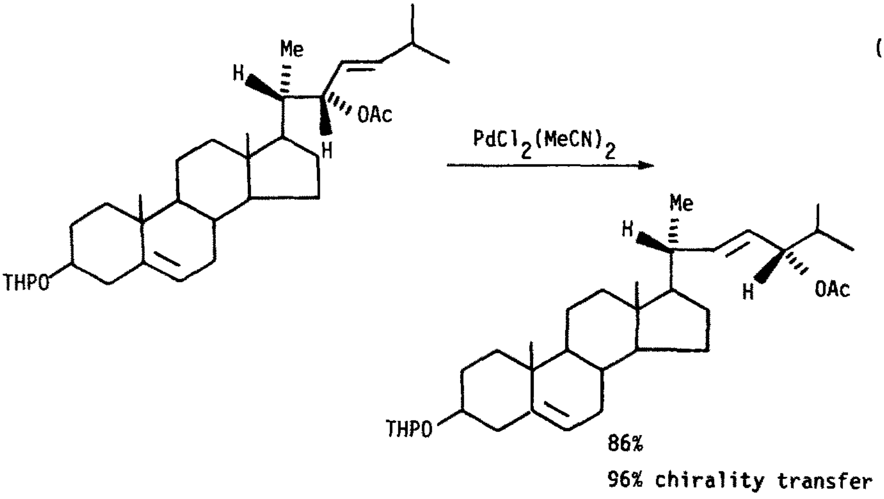
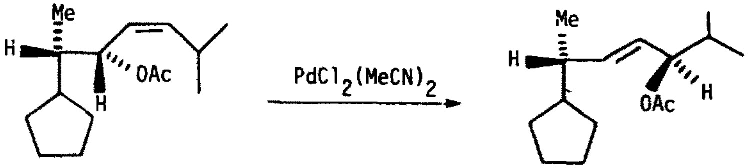


(382)



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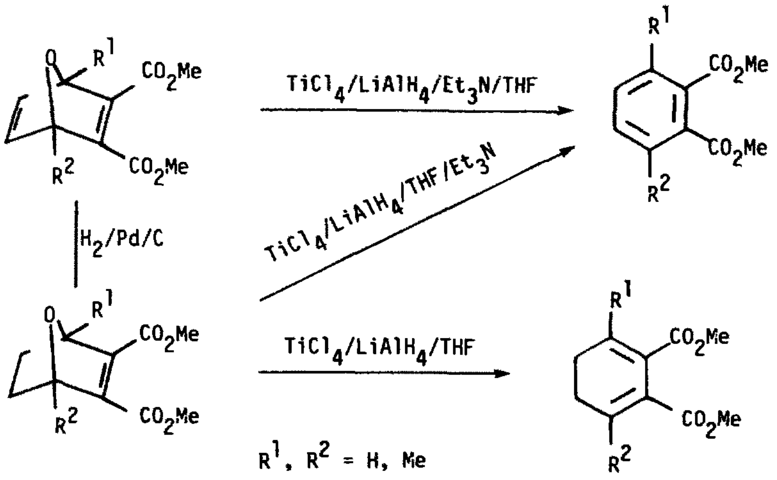
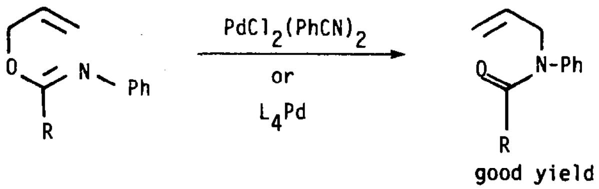


(384)

Allyl ethers of amides rearrange to N-allylamides in the presence of palladium(II) or palladium(0) catalysts (equations 385-387) [435]. β-Keto-allyl ester rearranged to α-allylketones of enones under palladium(II) catalysis (equation 388) [436]. Allyl esters were converted to allyl vinyl ethers by reaction with a titanium carbene complex, and subsequently rearranged (equation 389) [437]. Allylamines rearranged to enamines with high enantioselectivity when treated with chiral rhodium(I) complex catalysts (equation 390) [438].



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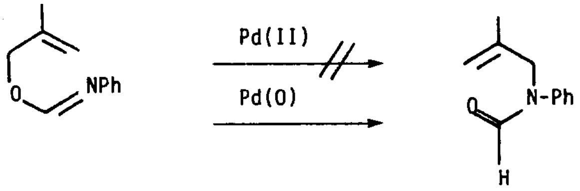
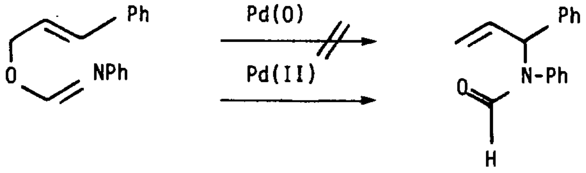
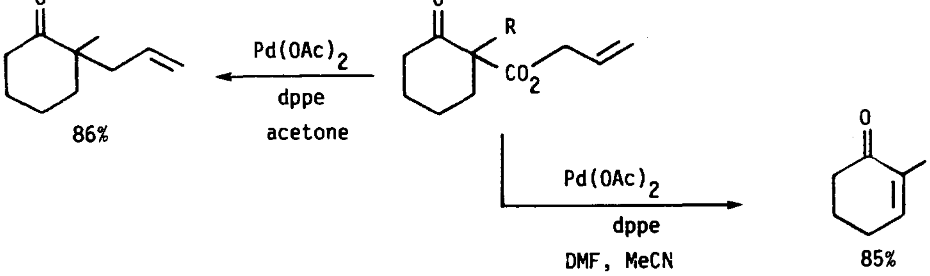


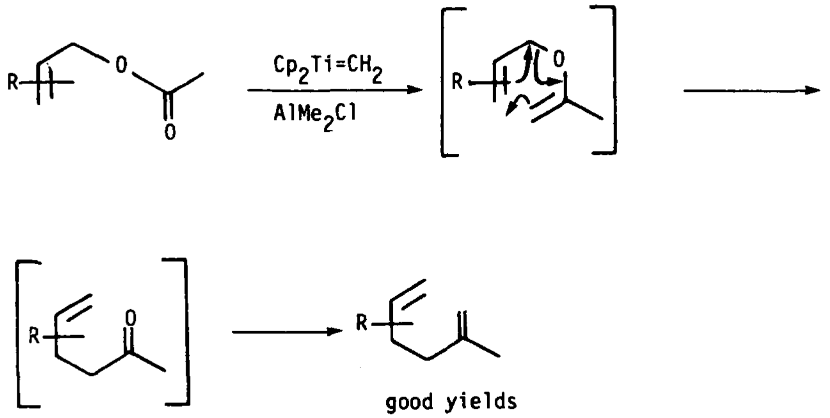
(386)



(387)

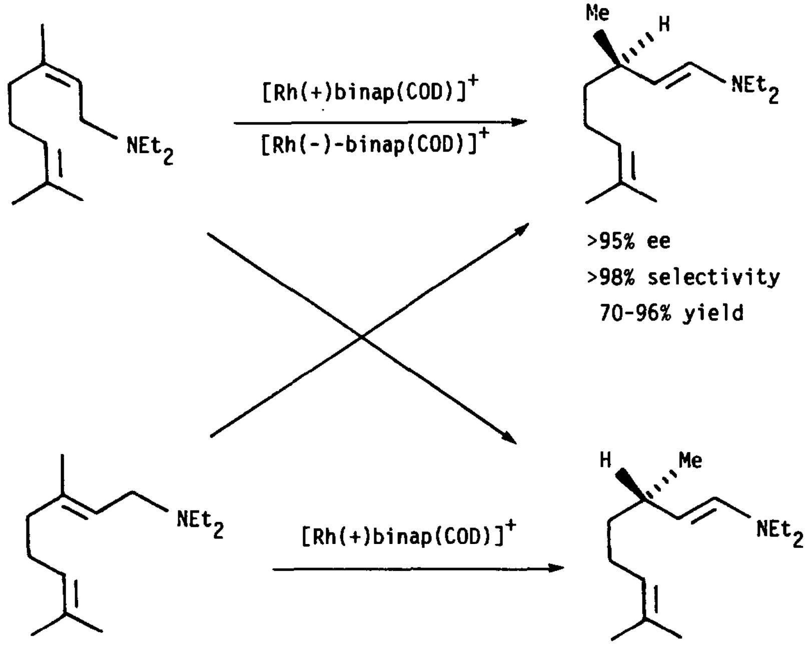
(388)





(389)

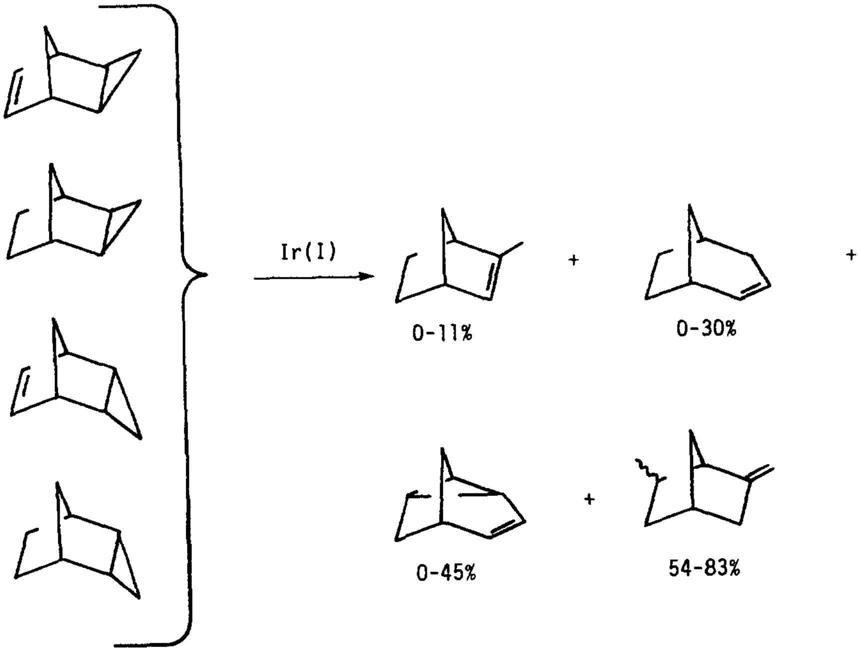
(390)



### 4. Skeletal Rearrangements

A dissertation dealing with transition metal promoted rearrangements of sterically hindered derivatives of bicyclo[1.1.0]butane has appeared [439]. Iridium(I) catalyzed the skeletal rearrangements of a variety of cyclopropylnorbornyl systems (equation 391) [440]. α,β,γ,δ-Unsaturated cyclopropanes bearing two ring ester groups rearranged when treated with palladium(0) complexes (equations 392 and 393) [441]. Rhodium, ruthenium, and platinium catalysts all promoted cyclopropane ring opening (equations 394-397) [442]. Cope rearrangements with complete chirality transfer were observed using palladium(II) catalysts (equation 398) [443]. Iron pentacarbonyl catalyzed the disproportionation shown in equation 399) [444].

(391)



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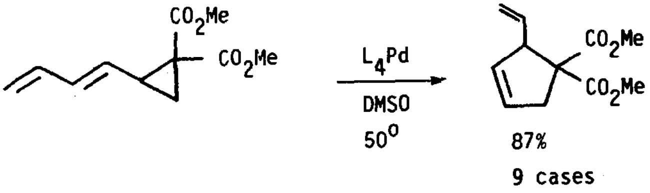

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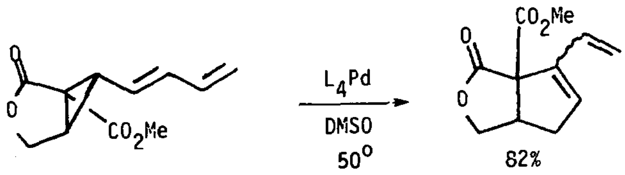

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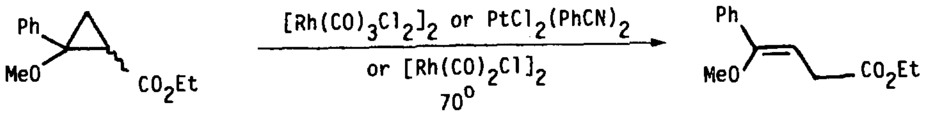

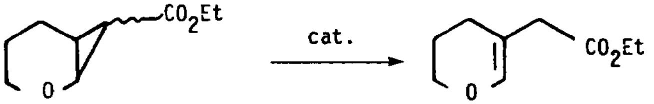

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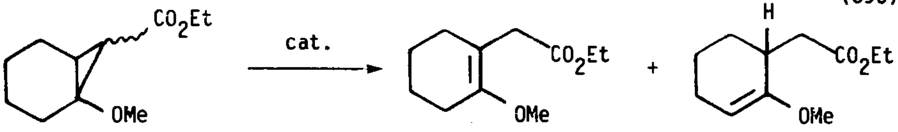

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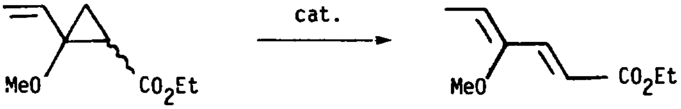
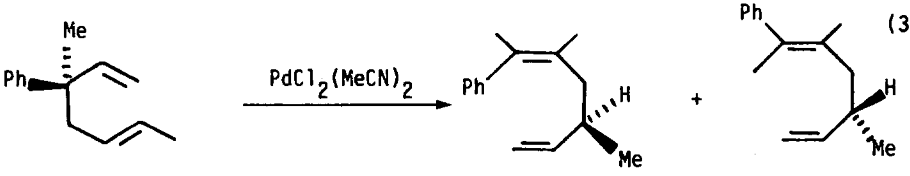


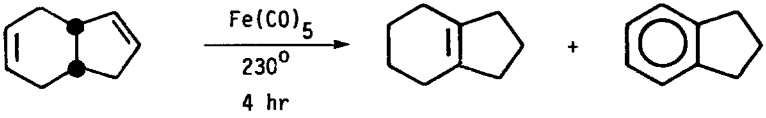
(397)



(398)

7:3 86%

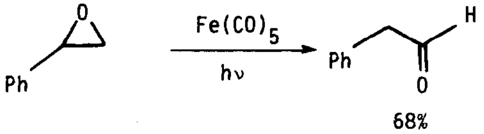
complete chirality transfer

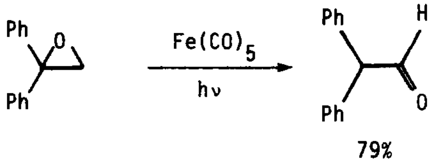


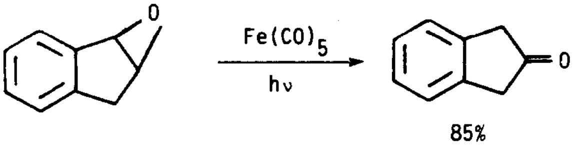
(399)

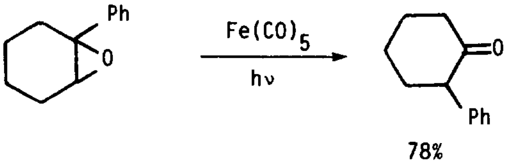
## 5. Miscellaneous Rearrangements

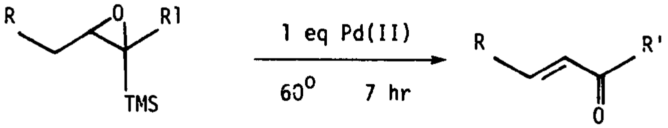
Platinum racemized chiral 1,1'-binaphthyls [445]. Iron pentacarbonyl rearranged epoxides to carbonyl compounds (equations 400-403) [446]. Trimethylsilyl epoxides were converted to conjugated enones by one equivalent of a palladium(II) complex (equation 404) [447]. Prostaglandin endoperoxide rearranged to a variety of prostaglandin methyl esters when treated with $RuCl_2(PPh_3)_3$ or $Pd(PPh_3)_4$ [448]. Oxazoles rearranged to vinologous amides when irradiated in the presence of iron pentacarbonyl (equation 405) [449]. Some glucopyranosides were anomerized by titanium(IV) chloride (equation 406) [450]. Rhodium(I) complexes catalyzed the reaction shown in equation 407 [451]. Alkyl groups on amines scrambled when treated with $RuCl_2L_3$ at 180° (equations 408 and 409) [452]. Primary amines were methylated by methanol under similar conditions (equation 410) [453].


(400)

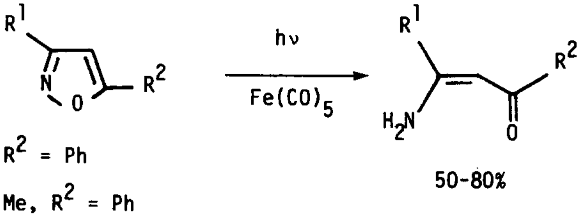

(401)


(402)

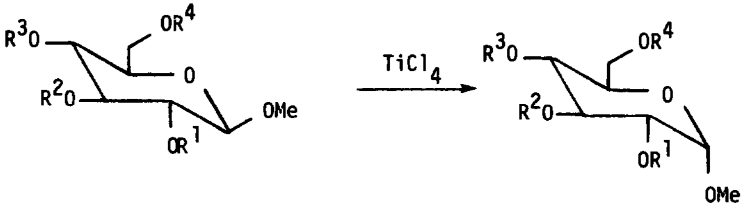

(403)


(404)

R' = H, n-Pr
R = n-Pr, n-$C_5$, Et


(405)

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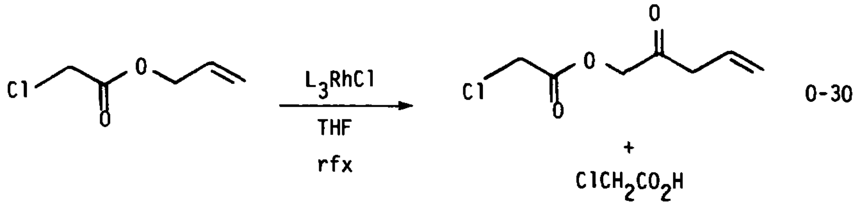


(407)

$$2\ RCH_2NHCH_3 \xrightarrow[180^0]{RuCl_2L_3} (RCH_2)_2NCH_3 + CH_3NH_2 \qquad (408)$$

$$2\ RCH_2N(CH_3)_2 \xrightarrow{RuCl_2L_3} \underset{71\text{-}96\%}{(RCH_2)_2NCH_3} + CH_3NH_2 \qquad (409)$$

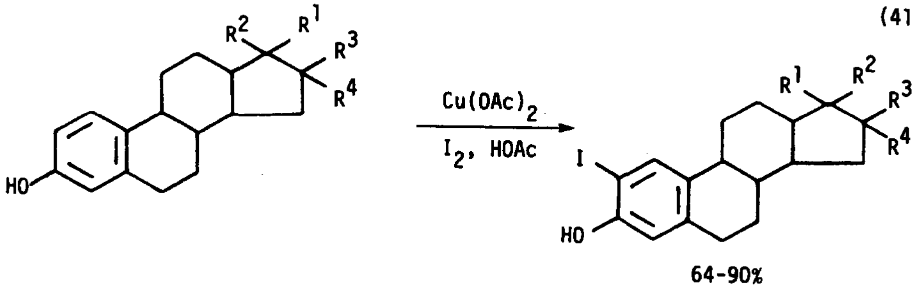
$$RCH_2NH_2 + CH_3OH \xrightarrow[180^0\ 7\ hr]{RuCl_2L_3} RCH_2NMe_2 + (RCH_2)_2NMe \qquad (410)$$

## III. Functional Group Preparation

### A. Halides

The aromatic ring of steroids was iodinated by reaction with copper (II) acetate and iodine in acetic acid (equation 411) [455]. A related system, using aluminum trichloride as well, iodinated a variety of arenes (equation 412) [456]. Dienes were chloropalladated to produce chloro-π-allylpalladium complexes, which were subsequently further functionalized (equation 413) [457]. Palladium(II) assisted ring opening of allylcyclopropanes involved a trans chloropalladation (equation 414) [458]. π-Allylpalladium chloride complexes were converted to allyl halides by treatment with copper(I) halides (equation 415) [459]. Cyclic ethers were cleaved to γ-chloroesters by palladium(II) complexes and trialkyltin halides (equation 416) [460]. The cobalt tetracarbonyl enolate of ethyl acetate was cleaved in low yield to ethyl iodoacetate by iodine [461]. Cyclohexane was converted to chlorocyclohexane by reaction with carbon tetrachloride and a variety of transition metal complexes (equation 417) [462]. Ruthenium(II) catalyzed the addition of trichloroacetyl chloride to olefins (equation 418) [463].

(411)



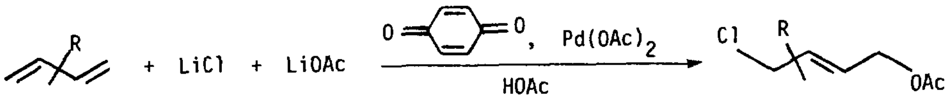
R's = H, OH, =O

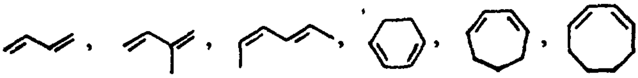
$$2\ ArH + I_2 + 2\ CuCl_2 \xrightarrow{AlCl_3} 2\ ArI + 2\ HCl + Cu_2Cl_2 \qquad (412)$$

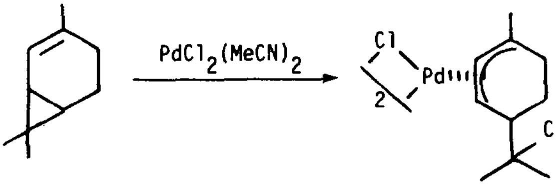
good yields

Ar = Ph, p-tolyl, mesityl, p-ClPh, p-BrPh, p-IPh, p-OMePh, napht, BiPh

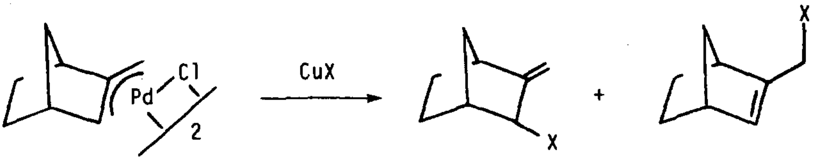
(413)



 worked.

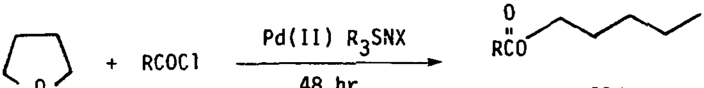


(414)



(415)

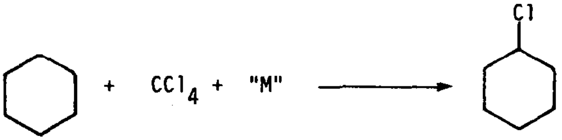
X = Cl, Br, OAc



(416)

63%

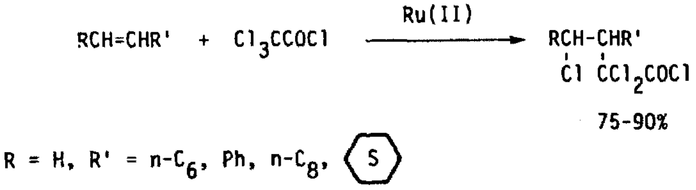
 also cleave.



(417)

up to 78%

"M" = $Mo(CO)_6$, $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_2(CO)_4Cp_2$,
$Cr(CO)_6$, $Re_2(CO)_{10}$

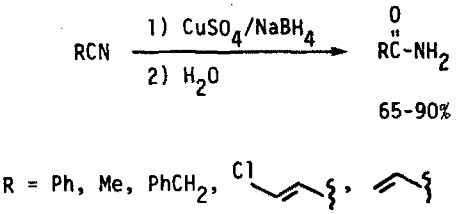


$$\mathrm{RCH{=}CHR' + Cl_3CCOCl \xrightarrow{Ru(II)} \underset{Cl\;\;CCl_2COCl}{RCH\text{-}CHR'}}$$

(418)

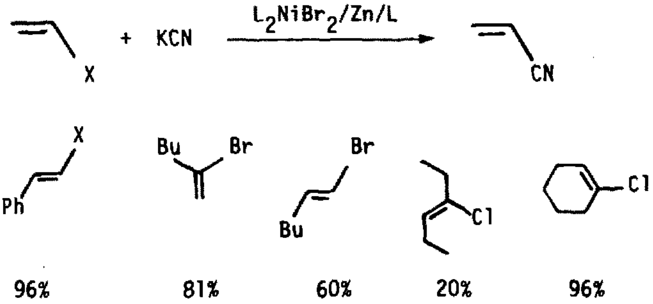
## B. Amides, Nitriles

Copper(II) sulfate reduced by sodium borohydride, promoted the hydrolysis of nitriles to amides (equation 419) [464]. Copper salts catalyzed the N-phenylation of amides such as pyrrolidin-2-OMe with aryl halides [465]. Benzylamine was oxidized to benzonitrile by ruthenium complexes such as $RuCl_2(PPh_3)_3$ [466]. Vinyl halides were converted to vinyl cyanides (nitriles) by reaction with potassium cyanide and reduced nickel salts (equation 420) [467]. The cobalt complex $[Co(CN)_4]^{3-}$ effected the same transformation, and a detailed mechanistic study of this process was undertaken [468].



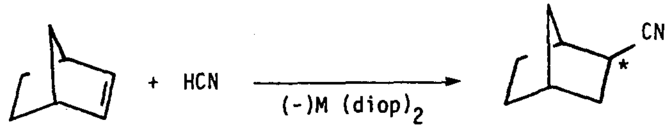
$$\mathrm{RCN \xrightarrow[2)\ H_2O]{1)\ CuSO_4/NaBH_4} R\overset{O}{\overset{\|}{C}}\text{-}NH_2}$$

(419)



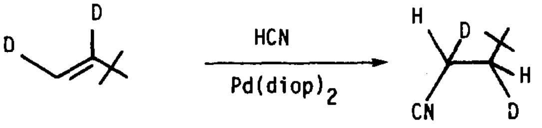
(420)

Chiral nickel(II) and palladium(II) complexes catalyzed the hydrocyanation of norbornene in high yield with up to 32% optical yield (equation 421) [469]. Similar results obtained with DCN showed this to be a stereospecific cis addition (equations 422 and 423) [470]. Nickel(0) and palladium(0) complexes catalyzed the hydrocyanation of alkynes (equation 424) [471], as well as dienes and trienes [472]. Cyanohydrin acetates (equation 425) and γ-amino acrylonitriles (equation 426) were converted to allyl cyanides by reaction with a trialkyltin hydride and a palladium(0) catalyst [473].



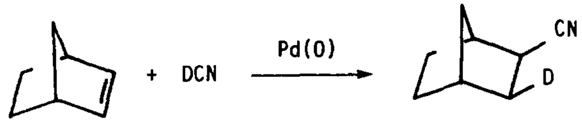
95% yield
32% ee

(421)

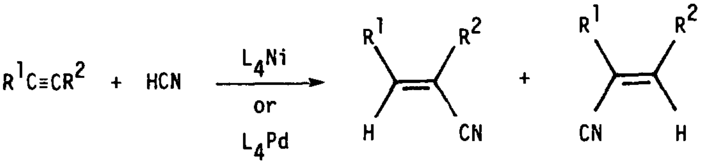


cis addition

(422)



(423)

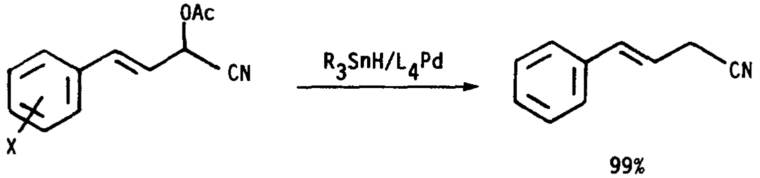


(424)

$R^1$ = Ph, t-Bu, $CO_2Me$, n-Pr

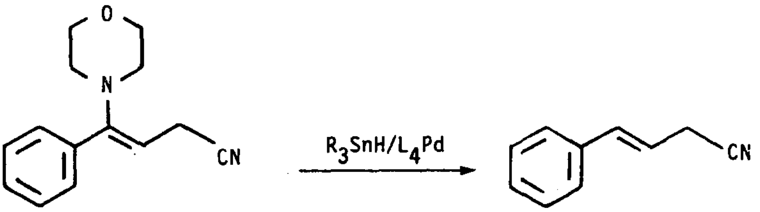
$R^2$ = Ph, Me, $CO_2Me$, H

fair to high yield



99%

(425)

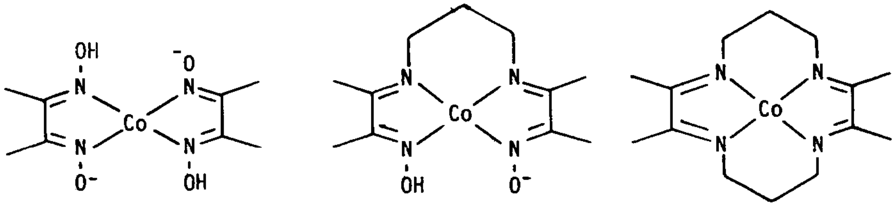


68%

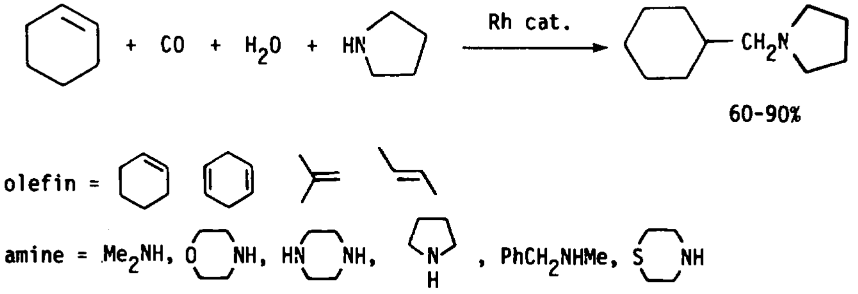
(426)

## C. Amines, Alcohols

Research continues into the development of new catalysts for the reduction of aromatic nitro compounds to amines. These included copper-modified platinum catalysts [474], palladium/aluminum phosphate/silica dioxide with triethylammonium formate as the hydrogen source [475], the complex $Pd_2(PPh_3)_2Cl_4$ in basic ethanol [476], the complex trans-$Pd(py)_2Cl_2$ in ethanol [477], and the cobalt chelates shown below [478]. Nitriles were reduced to amines over cobalt catalysts [479].

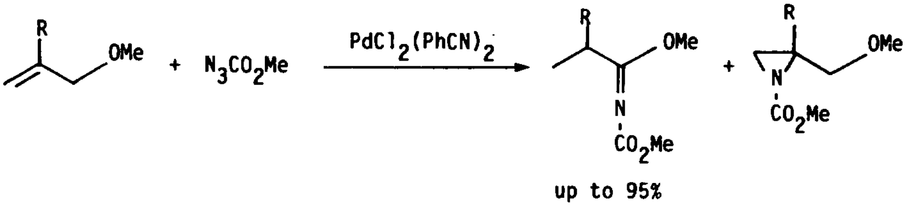


Olefins were aminomethylated by hydroformylation in the presence of an amine and a rhodium(I) catalyst (equation 427) [480]. The reduction of nitrobenzene in the presence of aldehydes over chloranilic acid platinum catalysts gave aromatic amines having the aldehyde group as a substituent on nitrogen [481]. Similarly reduction of mixtures of aniline and aldehydes with platinum complexes of Alizarine Red S as catalysts produced alkylated anilines [482]. Isobutyraldehyde was reductively aminated over group VIII metal complexes supported on alumina [483]. Imines were produced as in equation 428 [484].

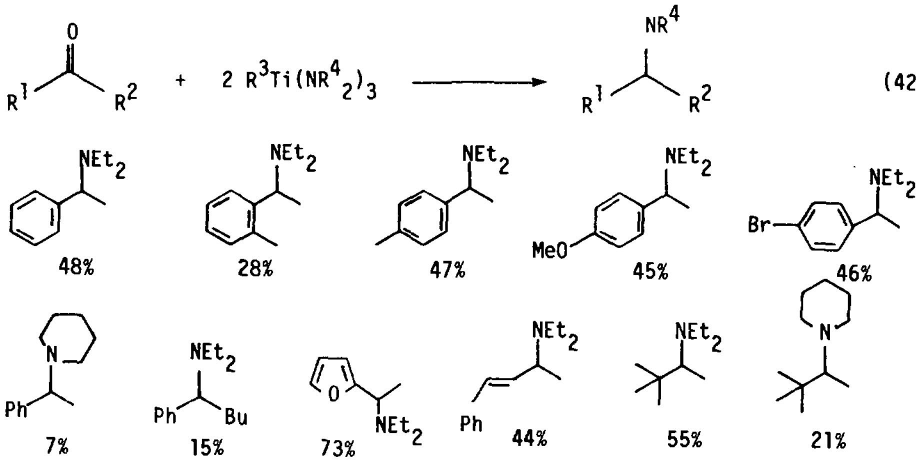


(427)

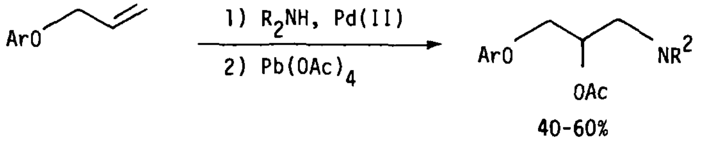
(428)



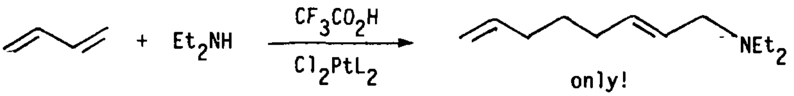
Nonenolizable ketones and aldehydes were aminated by titanium(IV) amide complexes (equation 429) [485]. Allyl aryl ethers were oxaminated over palladium(II) salts (equation 430) [486]. Butadiene telomerized with diethylamine in the presence of platinum(II) catalysts (equation 431) [487]. Cationic bis chloroarene chromium complexes were aminated by nucleophilic substitution of one or both of the halogens [488].



(429)

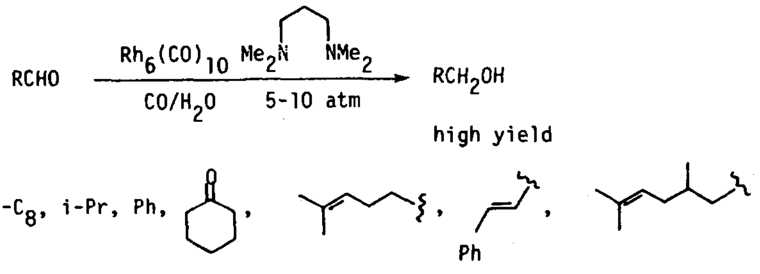


(430)

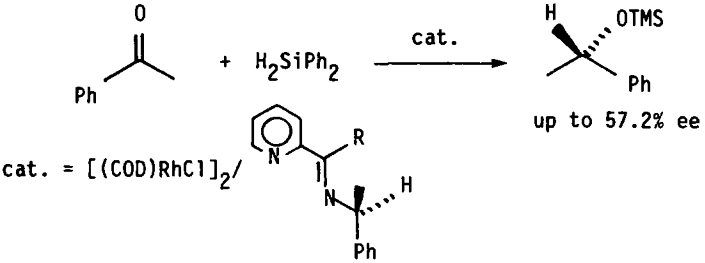


(431)

Aldehydes were reduced to alcohols by carbon monoxide and water over a rhodium catlayst (equation 432) [489]. Acetophenone was reduced to chiral phenethylalcohol using catalytic hydrosilation in the presence of a chiral rhodium catalyst (equation 433) [490]. Conjugated enones were completely reduced by reaction with $HFe(CO)_4^-$ (equation 434) [491] whereas 1,4-reduction was the major product from the use of DIBAH and nickel(II) salts (equation 435) [492].

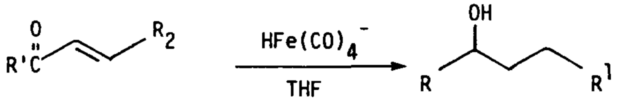


(432)



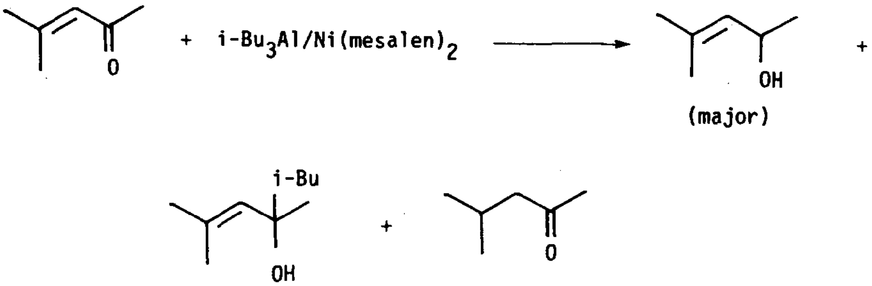
up to 57.2% ee

(433)

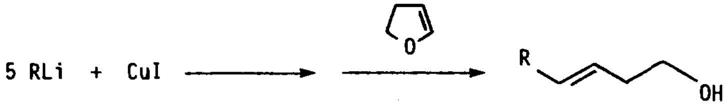


>98%

(434)



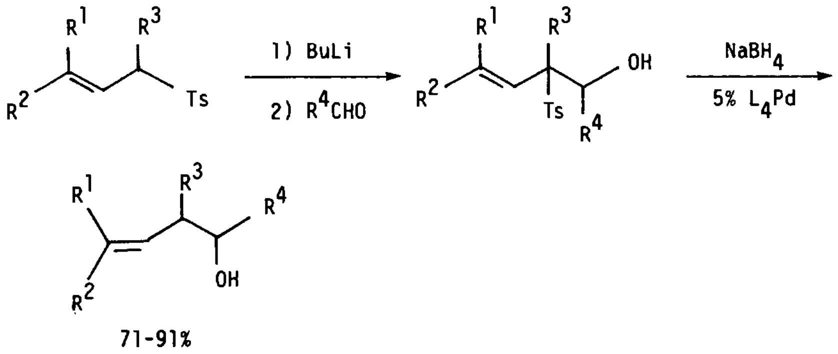
(435)



(436)

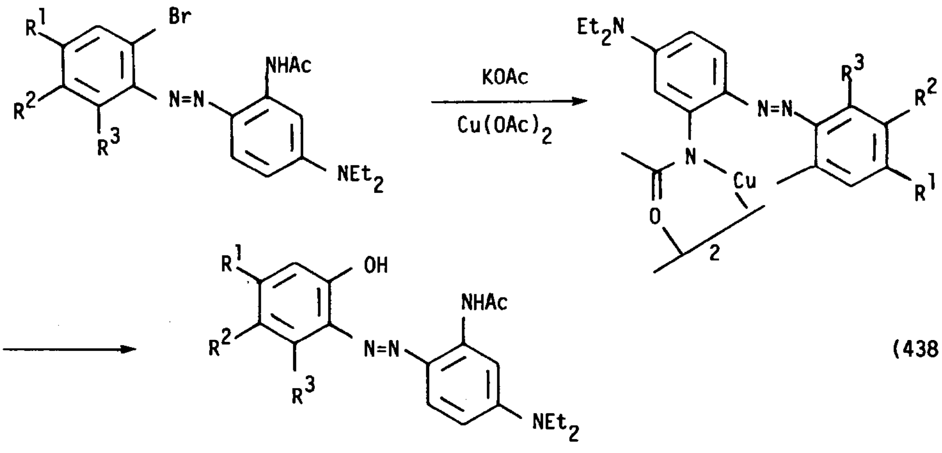
R = Et, 59%; n-Bu, 83%; n-$C_6$, 83%; n-$C_8$, 62%; Ph, 30%

Dihydrofuran underwent a ring opening reaction when treated with alkyllithium reagents in the presence of copper(I) iodide (equation 436) [493]. Allylic tosylates were lithiated, condensed with aldehydes, and the tosylate group removed by reduction in the presence of palladium(0) compounds (equation 437) [494]. Copper(II) acetate promoted the production of the phenol shown in equation 438 [495].



(437)

$R^1$ = H, Me; $R^2$ = Ph, H, Me; $R^3$ = H, $PhCH_2$; $R^4$ = Ph, n-$C_8$



(438)

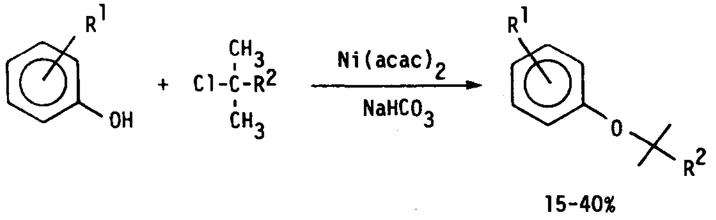
Long chain internal olefins were hydrozirconated and oxidized to produce terminal long-chain alcohols (equation 439) [496]. A similar procedure was applied to long chain fatty acids whose carboxyl group had been protected as an oxazoline [497]. Sterically hindered olefins were converted to vicinal diols by using trimethylamine oxide and a catalytic amount of osmium tetroxide as an oxidizing agent in refluxing t-butanol [498]. 1,3-Butadiene was acetoxylated over palladium catalysts, reduced, and hydrolyzed to give 1,4-dihydroxybutane [499]. Benzene was oxidized to phenol over a silica-supported iron(III)-catechol complex [500]. Iron compounds and hydrogen peroxide were used for a similar purpose [501].

$$C_{14}H_{29}CH{=}CHC_{14}H_{29} \xrightarrow[2)\ \underline{t}\text{-BuOOH}]{1)\ Cp_2ZrHCl} (CH_3)(CH_2)_{29}OH \qquad (439)$$

triacontanol

### D. Ethers, Esters, Acids

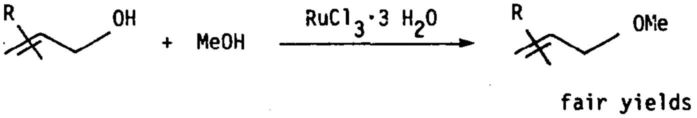
Tertiary ethers of phenols were prepared by the nickel(II) promoted reaction of phenols with tertiary alkyl chlorides (equation 440) [502]. Allyl alcohols were converted to allylmethyl ethers by reaction with methanol and ruthenium(III) chloride (equation 441) [503]. Alcohols reacted with ethyl diazoacetate to produce α-carboethoxyethers (equation 442) [504].



(440)

$R^1$ = H, 2-OMe, 3-OMe, 4-OMe, 2-Me, 3-Me, 4-Me, 4-$NO_2$, 2-Cl, 3-F, 4-Cl

$R^2$ = Me, Et



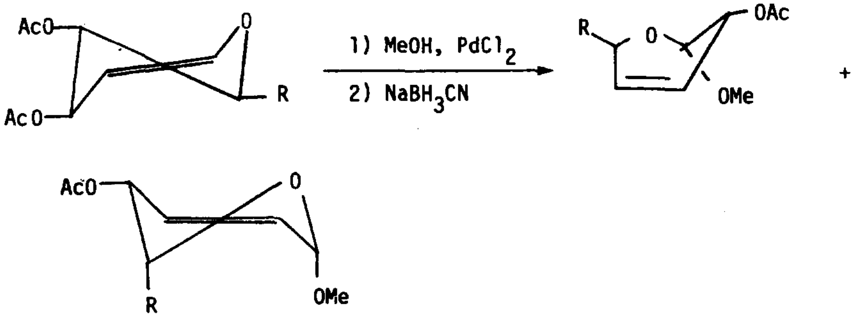
(441)

$$ROH + N_2CHCO_2R' \xrightarrow[\text{or } Cu(OTf)_2]{Rh_2(OAc)_4} ROCH_2CO_2R + N_2 \qquad (442)$$

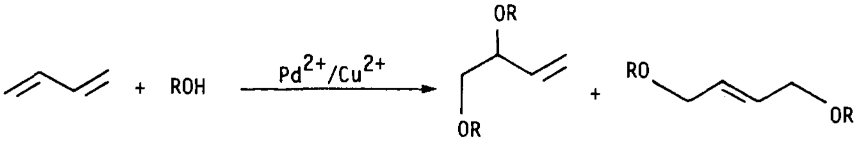
up to 97%

R = Et, i-Pr, t-Bu,

Cyclic enol ethers were methoxylated by methanol and palladium(II) chloride (equation 443) [505]. Reaction of 1,3-butadiene with alcohols in the presence of palladium(II) and copper(II) halides gave diethers (equation 444) [506]. 1-Hexene was converted to di-2-hexyl ether over a copper(II)-smectic catalyst [507].

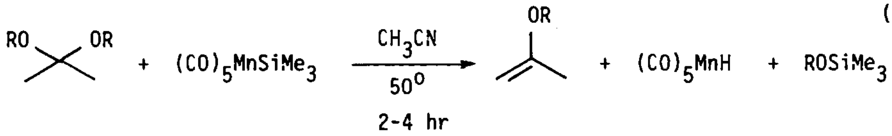


(443)

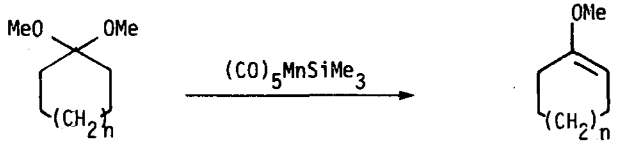


(444)

Ketals were converted to enol ethers by reaction with $(CO)_5MnSiMe_3$ (equations 445-450) [508][509]. Trimethylsilylenol ethers were converted to α-alkoxyketones by treatment with mercuric oxide/palladium(0) (equations 451-454) [510].

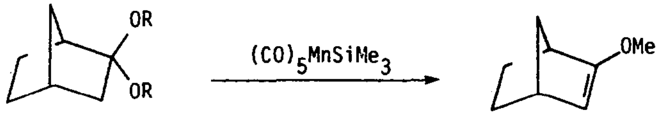


(445)



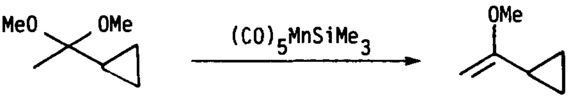
(446)

| | |
|---|---|
| n = 0 | 95% |
| n = 1 | 98% |
| n = 3 | 85% |



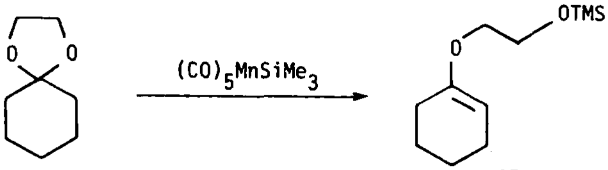
(447)

60%



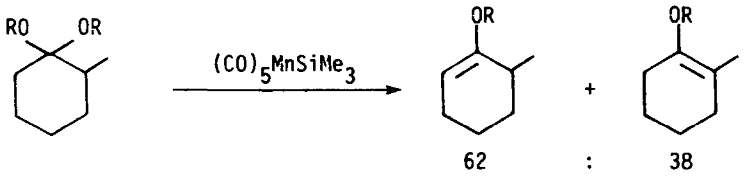
(448)

78%

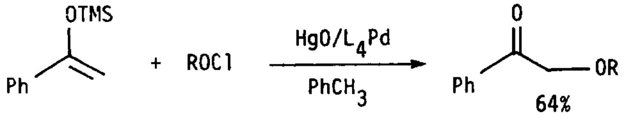


(449)

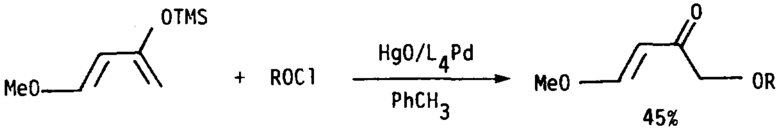
87%



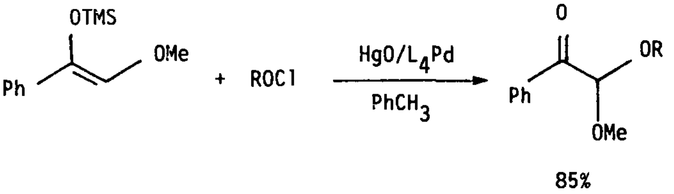
(450)



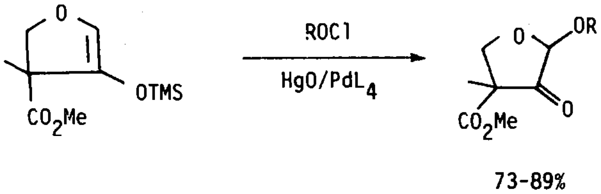
(451)



(452)

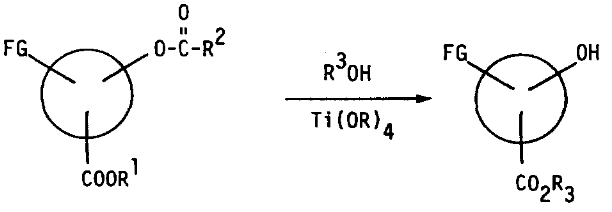


(453)

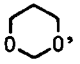


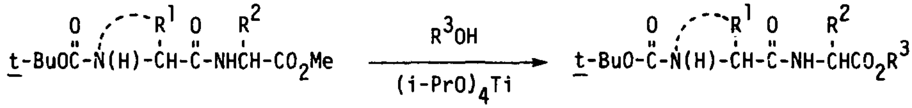
(454)

Titanium(IV) alkoxides promoted a very mild transesterification process (equation 455) [511]. Aminoacids chelated to cobalt(III), molybdenocene, and platinum(II) were esterified by treatment with dimethyl sulfate or methanol and acid [512]. Dipeptides were transesterified without racemization by treatment with alcohol and titanium(IV) alkoxides (equation 456) [513].



(455)

FG = TMS, $NO_2$, CN, Br, OH,  , RCONH, RCO

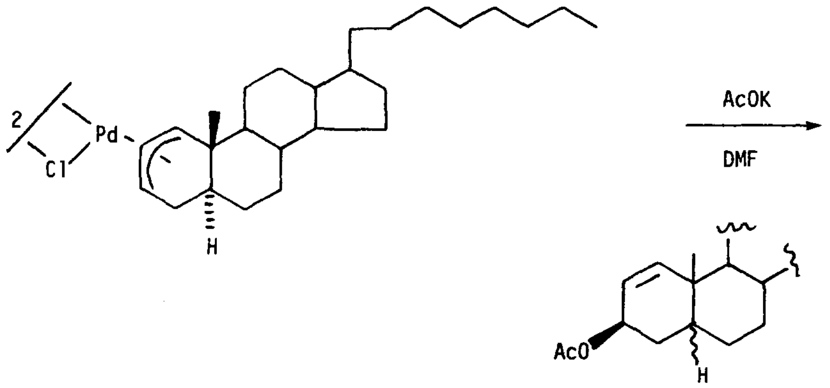


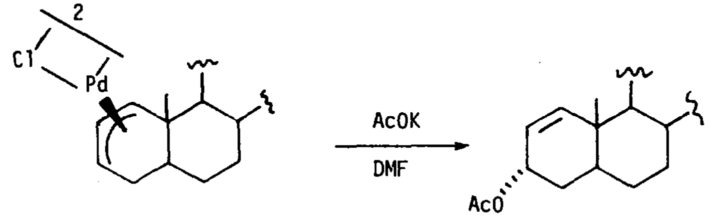
$$\underline{t}\text{-BuO}\overset{O}{\overset{\|}{C}}\text{-}N(H)\text{-}\overset{R^1}{C}H\text{-}\overset{O}{\overset{\|}{C}}\text{-NH}\overset{R^2}{C}H\text{-CO}_2Me \xrightarrow[(i\text{-PrO})_4Ti]{R^3OH} \underline{t}\text{-BuO-}\overset{O}{\overset{\|}{C}}\text{-}N(H)\text{-}\overset{R^1}{C}H\text{-}\overset{O}{\overset{\|}{C}}\text{-NH-}\overset{R^2}{C}HCO_2R^3 \qquad (456)$$

without racemization

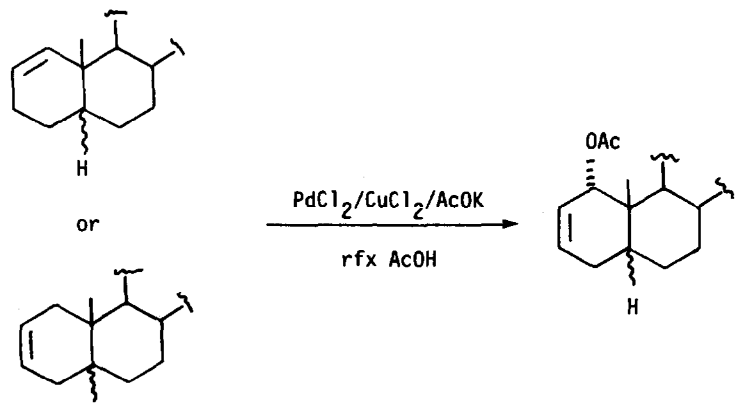
π-Allylpalladium complexes were converted to allyl acetates by reaction with potassium acetate (equations 457-459) [514]. The stereochemistry of acetoxylation of dienes using palladium(II) complexes depended on reaction conditions (equation 460) [515]. Allyl esters and carbamates were converted to the acid salt by reaction with a catalytic amount of a palladium(0) complex (equation 461) [516].

(457)

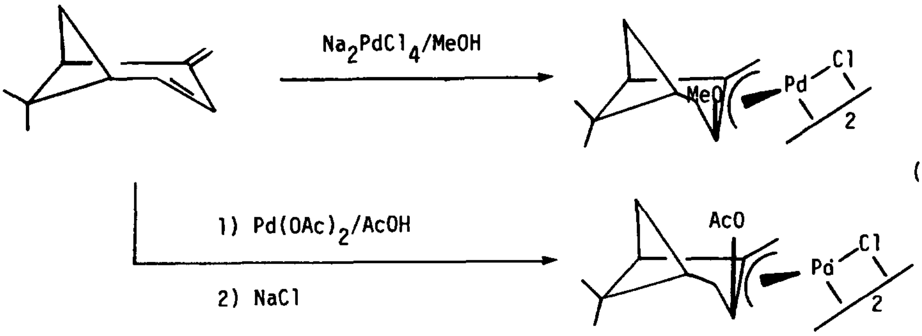




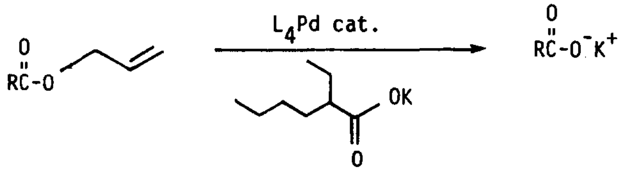
(458)



(459)

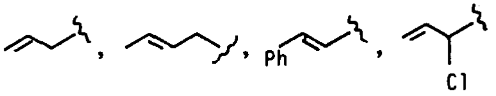


(460)

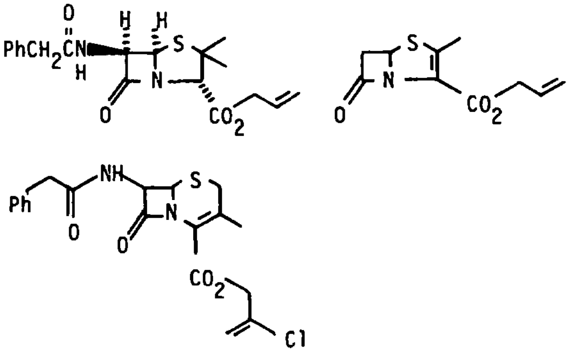


(461)

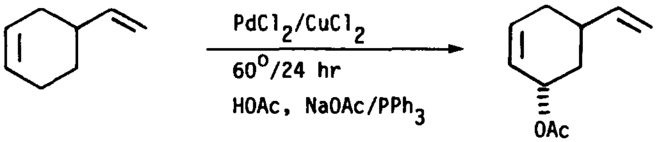
R =



substrates included

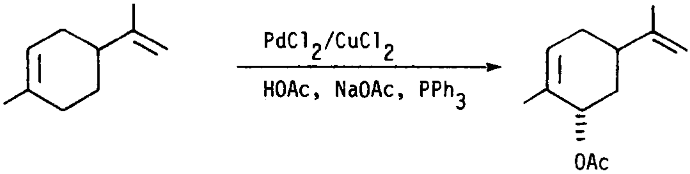


1,5-Dienes were allylically acetoxylated by reaction with palladium(II) salts in acetic acid (equations 462 and 463) [517]. Olefins were oxaminated in the presence of chiral ligands to give reasonable amounts of asymmetric induction (equation 464). This chemistry was used to make β-blockers (equation 465) [518]. Aryl acetates were produced from the air oxidation of aryl cuprates in acetic acid (equation 466) [519].



(462)

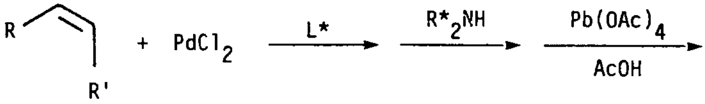
36%



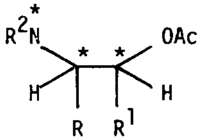
63%

(463)

(464)



L* = chiral $3^\circ$ amine

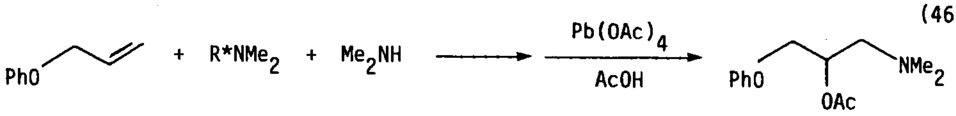


20-50%

up to 60% ee

(3-11% ee if achiral $2^\circ$ amine used)

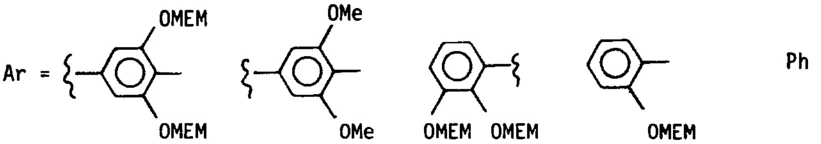
(465)



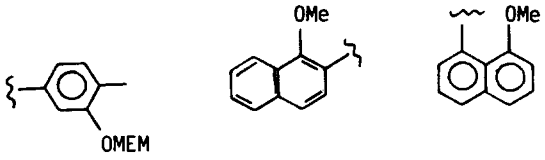
45% yield

11% ee

$$\mathrm{ArCuLiBr} \xrightarrow[\text{THF}]{\text{air, }0^\circ} \xrightarrow[25^\circ]{\mathrm{Ac_2O}} \mathrm{ArOAc} + \mathrm{Ar{-}Ar} \qquad (466)$$

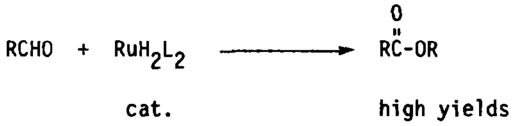


29-67% 65% 58% 46% 19%



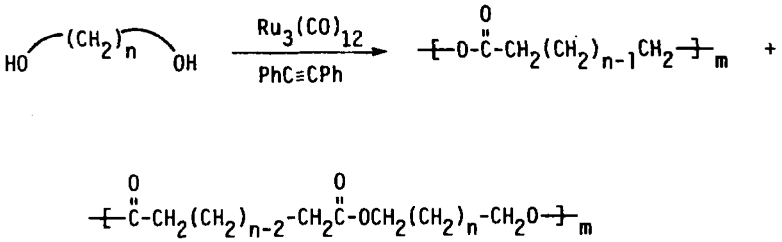
35% 37% 24%

Aldehydes were oxidized to esters using ruthenium(II) hydrides as catalysts (equation 467) [520]. Diols were oxidized to polyesters by $Ru_3(CO)_{12}$ (equation 468) [521]. Methyl acetate was homologated to ethyl acetate (as well as many other products) in the presence of mixed ruthenium/cobalt catalysts (equation 469) [522]. A review (39 references) dealing with the production of esters and acids from carbon monoxide over metal cluster catalysts has appeared [523]. Phenanthraquinone was oxidized to the diacid using copper(I) chloride, oxygen, and pyridine (equation 470) [524].



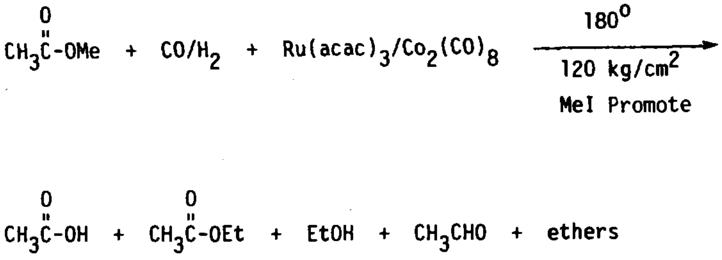
$$\mathrm{RCHO} + \underset{\text{cat.}}{\mathrm{RuH_2L_2}} \longrightarrow \underset{\text{high yields}}{\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{-}\mathrm{OR}} \qquad (467)$$

R = Me, Et, i-Pr, n-Bu, i-Bu, Ph



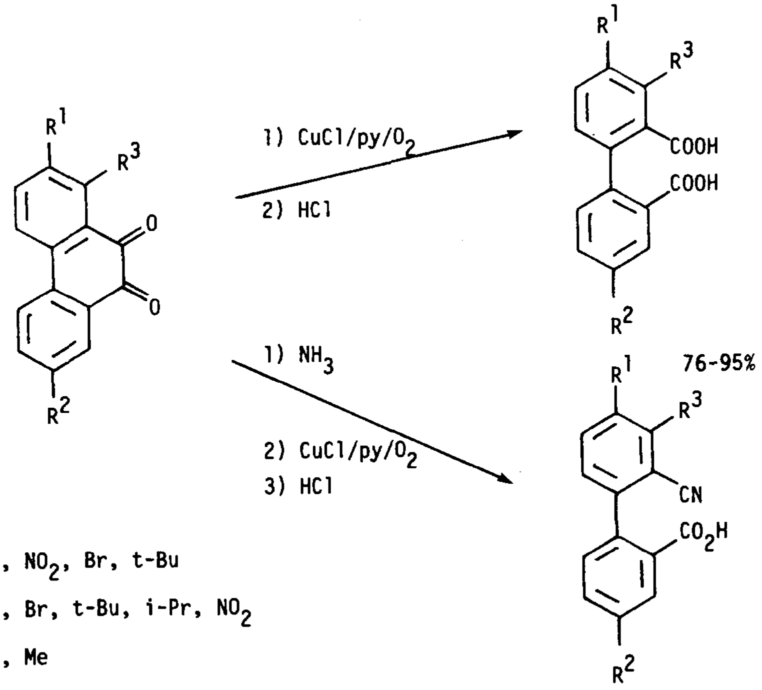
$$\mathrm{HO{-}(CH_2)_n{-}OH} \xrightarrow[\mathrm{PhC{\equiv}CPh}]{\mathrm{Ru_3(CO)_{12}}} \mathrm{-\!\!\left[O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2(CH_2)_{n-1}CH_2\right]\!\!-_m} + \qquad (468)$$

$$\mathrm{-\!\!\left[\overset{O}{\overset{\|}{C}}\text{-}CH_2(CH_2)_{n-2}\text{-}CH_2\overset{O}{\overset{\|}{C}}\text{-}OCH_2(CH_2)_n\text{-}CH_2O\right]\!\!-_m}$$



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}\text{-}OMe} + \mathrm{CO/H_2} + \mathrm{Ru(acac)_3/Co_2(CO)_8} \xrightarrow[\substack{\text{120 kg/cm}^2 \\ \text{MeI Promote}}]{180^{\circ}} \qquad (469)$$

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}\text{-}OH} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}\text{-}OEt} + \mathrm{EtOH} + \mathrm{CH_3CHO} + \text{ethers}$$



$R^1$ = H, $NO_2$, Br, t-Bu

$R^2$ = H, Br, t-Bu, i-Pr, $NO_2$

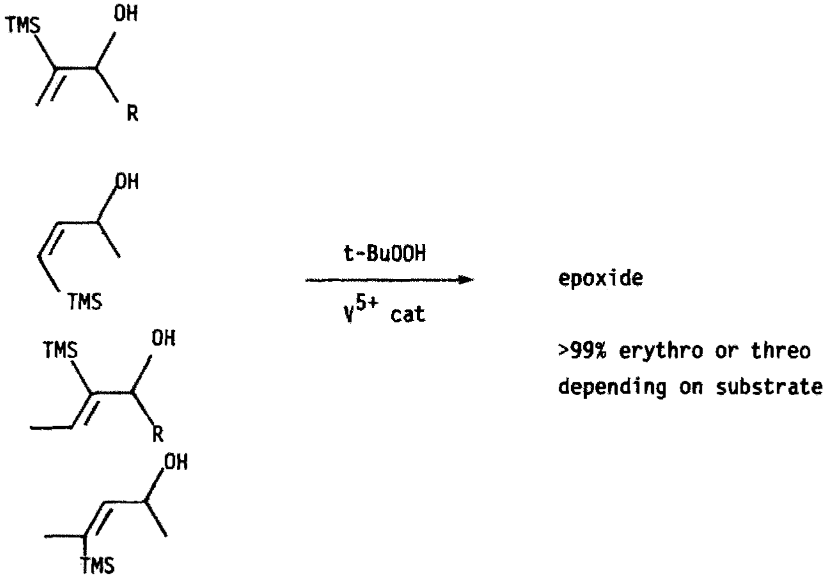
$R^3$ = H, Me

(470)

E. Heterocycles

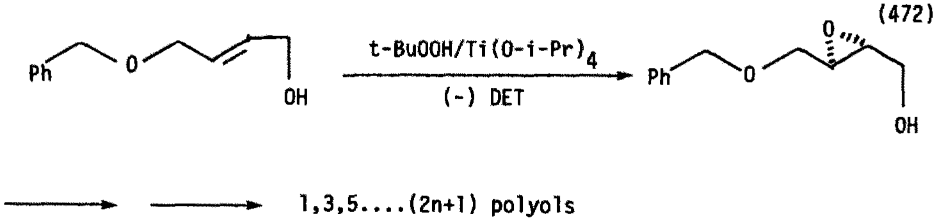
Reviews entitled "New Organometallic Approaches to Heterocycles" (24 references) [525], and "Use of Transition Metal Organometallic Compounds in Heterocyclic Synthesis" (250 references) [526] have appeared. Transition metal catalyzed epoxidation of olefins has been extensively studied. Reviews entitled "Transition Metal-Catalyzed Stereocontrolled Epoxidations" (23 references) [527], "Catalytic Epoxidation of Olefins" (74 references) [528], "Recent Advances in Metal-Complex-Catalyzed Epoxidation of Olefins with Organic Hydroperoxides - A Mechanistic Approach" (20 references) [529], and "New Developments of Sharpless Reaction" (27 references) [530] have appeared. Dissertations dealing with new reagents for olefin epoxidation [531], and epoxidation and hydroxylation catalyzed by ferric porphyrins [532] have appeared.

The epoxidation of vinyltrimethylsilanes having allylic alcohol groups using vanadium(V) catalysts and t-butylhydroperoxide produce very high yields of epoxides with high erythro or threo selectivity (equation 471) [533]. Double bonds allylic to both ether and alcohol functional groups were epoxidized by t-butylhydroperoxide/$Ti(O\text{-}i\text{-}Pr)_4$/(-) diethyl tartrate with high stereospecificity (equation 472) [534]. C-Glucopyranosides were synthesized using this chemistry (equation 473) [535]. The vanadium/t-butylhydroperoxide epoxidation of sterically encumbered allyl aclohols gave predominately erythro epoxides (equation 474) [536]. Epoxidation of allyl alcohols with t-butylhydroperoxide/titanium(IV) alkoxide gave mainly syn epoxide wherein MCPBA gave mainly anti epoxides (equation 475) [537]. This reaction, in the presence of (+)-L-diethyltartrate resulted in epoxide of high optical purity.

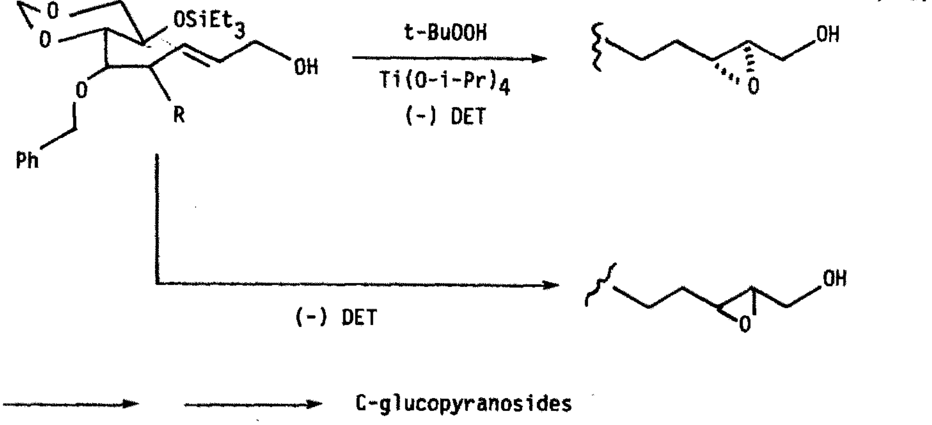


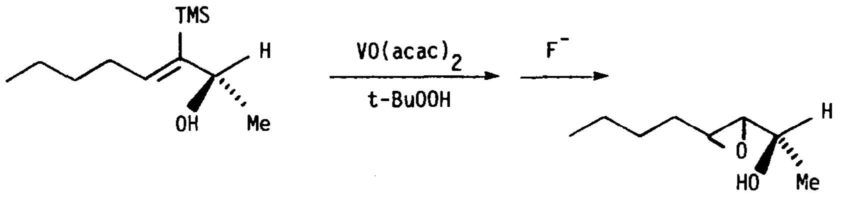
(471)

(472)



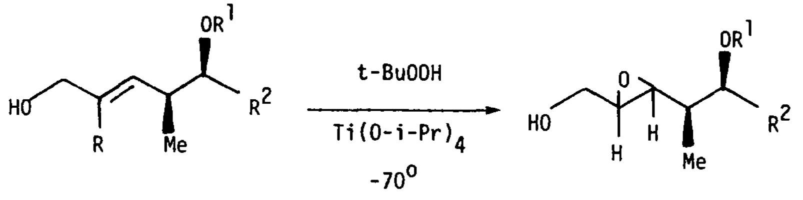
(473)





(474)

erythro

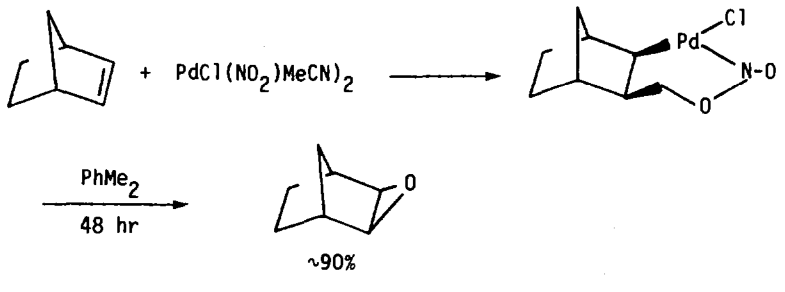


(475)

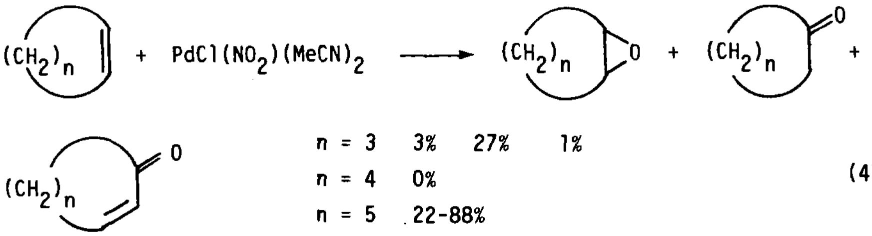
$R = Me, R^1 = SiMe_2\text{-t-Bu}, R^2 = (CH_2)_4OSiMe_2\text{-t-Bu}, CH_2C(OMe)_2CH(OMe)CH_2OAc$

Diepoxides of diolefins were prepared by the $Cp_2MoX_2$ catalyzed epoxidation of these substrates by t-butylhydroperoxide [538]. Molybdenum naphthenate catalyzed the epoxidation of styrene by hydroperoxides [539]. Cyclohexene and allyl chloride were epoxided by t-butylhydroperoxide in the presence of $MoO_4$(8-quinolol)$_2$ [540]. Cyclohexene was also epoxidized using $MoO_2Cl_2L_2$ complexes as catalysts ($L_2 = Ph_2P(O)CH_2CH_2P(O)Ph_2$, bipy, 1,10-phen) [541]. Molybdenum carbide catalyzed the epoxidation of 1-octene by t-butylhydroperoxide [542]. Propylene epoxidation was catalyzed by $MoO_2Cl_2$ on Amberlite IRC-84 resin [543]. Cyclohexene was epoxidized in fair yield by hydrogen peroxide using molybdenum blue on charcoal as a catalyst, in the presence of trialkyltin halides [544].

Cyclic alkenes were epoxidized by palladium(II) nitrite compounds (equations 476 and 477) [545]. Cobalt nitrite compounds epoxidized acyclic olefins (equation 478) [546]. Complex iron species catalyzed the air epoxidation of polyolefinswith remarkable specificity for the most highly substituted alkene (equations 479-485) [547]. 1,4-Epoxy-1,4-dihydroarenes were converted in high yields to the corresponding arenes by reaction with $Fe_2(CO)_9$ in refluxing benzene [548].

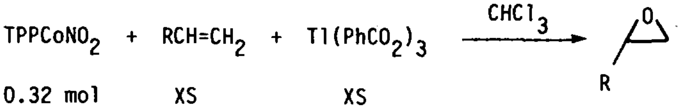


(476)



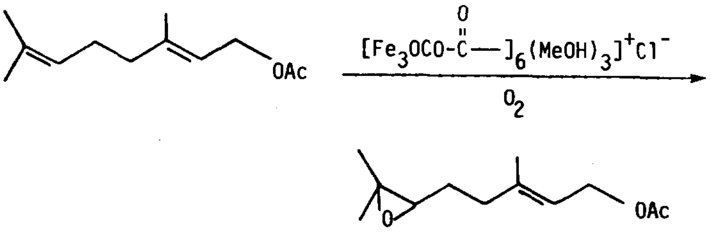
(477)

n = 3 3% 27% 1%
n = 4 0%
n = 5 22-88%
n = 6 34%
n = 7 32%
n = 8 69%
n = cis 6 12%
n = trans 6 4%



(478)

up to 0.18 mol
(50% based on Co)

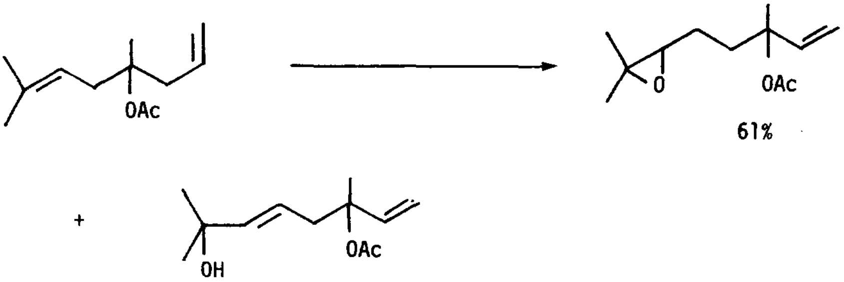


(479)

87%

(480)

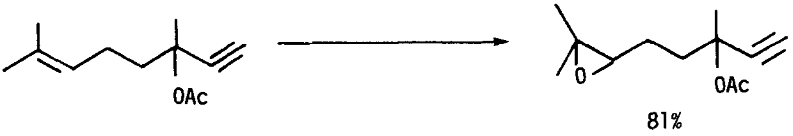
74%



61%

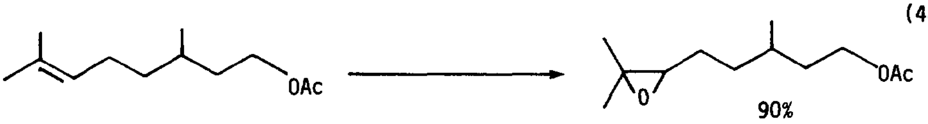
(481)

21%

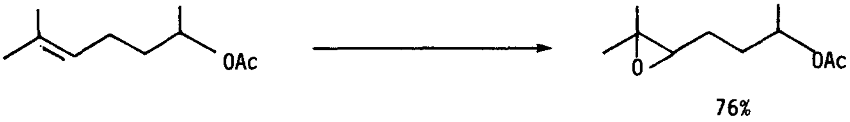


(482)

(483)

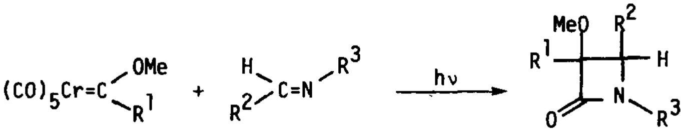


(484)



(485)

A dissertation on metal assisted β-lactam formation has appeared [549]. Irradiation of imines and chromium carbene complexes in ether solution produced β-lactams in good yield (equations 486-488) [550]. Azirines reacted with carbon monoxide in the presence of a palladium(0) catalyst to produce bicyclic β-lactams (equation 489) [551]. β-Lactams were functionalized by reaction with dimethyl diazomalonate and rhodium(II) catalysts (equation 490) [552]. Intramolecular carbene insertions led to more complex β-lactam systems (equation 491) [553], (equations 492 and 493) [554]. β-Lactams containing allylic ester groups were converted to the free acid by treatment with palladium(0) complexes (equation 494) [555].

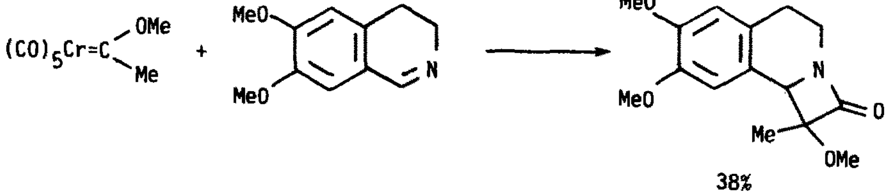


(486)

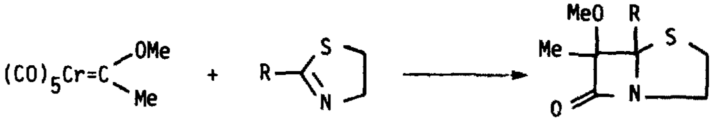
$R^1 = R^3 = Me, R^2 = Ph$ 76%

$R^1 = Me, R^2 = R^3 = Ph$ 52%

$R^1 = R^2 = Ph, R^3 = Me$ 72%



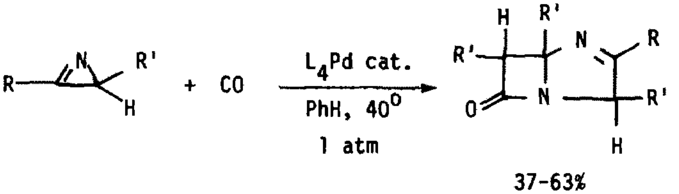
(487)



(488)

R = H 81%

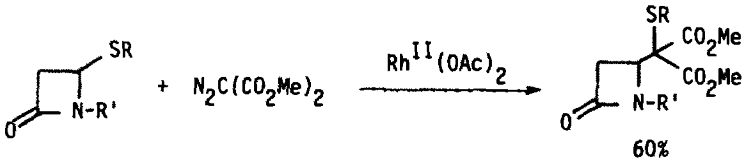
R = Ph 52%



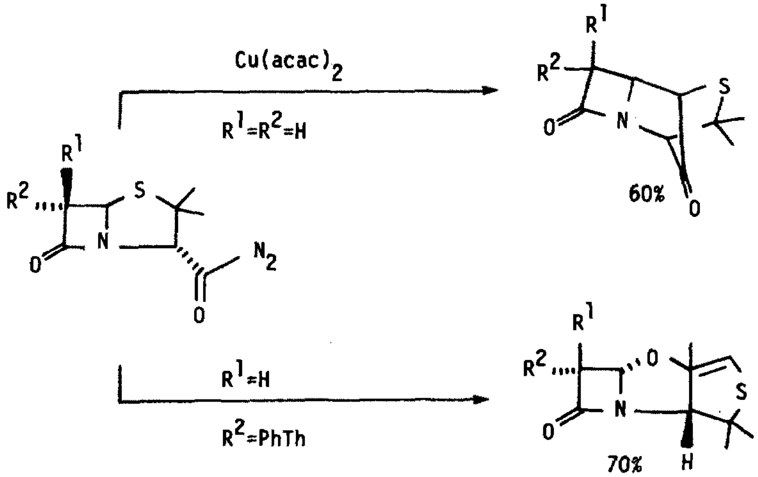
(489)

R = p-tolyl, Ph, p-ClPh, p-BrPh

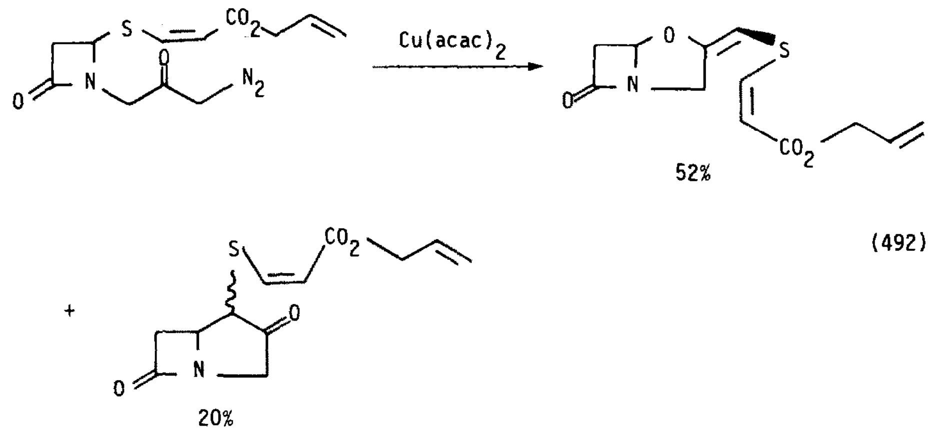
R' = H, Me



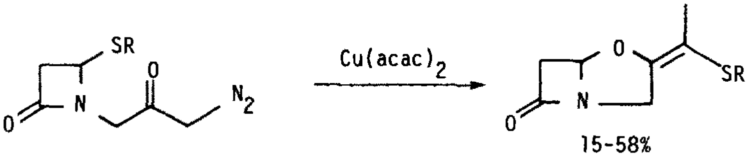
(490)



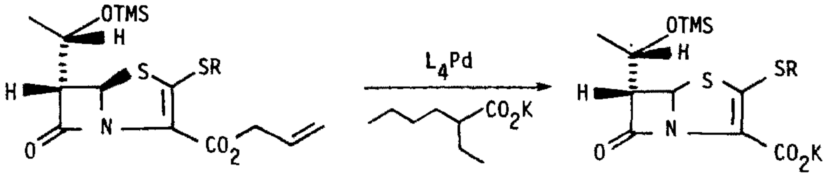
(491)



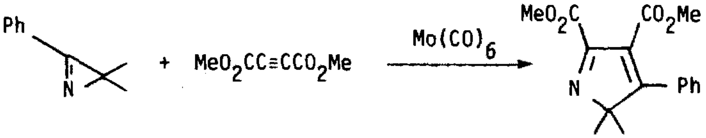
(492)



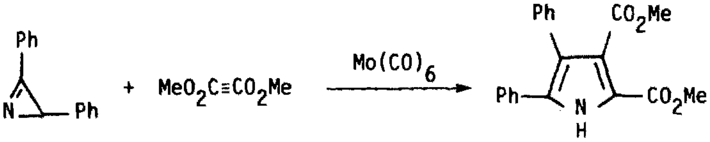
(493)



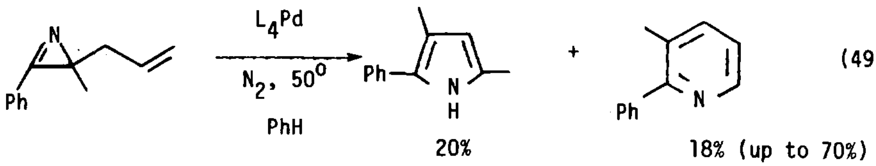
Azirines reacted with alkynes in the presence of molybdenum hexacarbonyl to give pyrroles (equation 495 and 496) [556]. Pyrroles and pyridines formed from azirines when treated with palladium(0) complexes (equations 497-499) [557]. Pyrroles also formed from β-dicarbonyl compounds and azocompounds in the presence of copper(II) chloride (equation 500) [558].



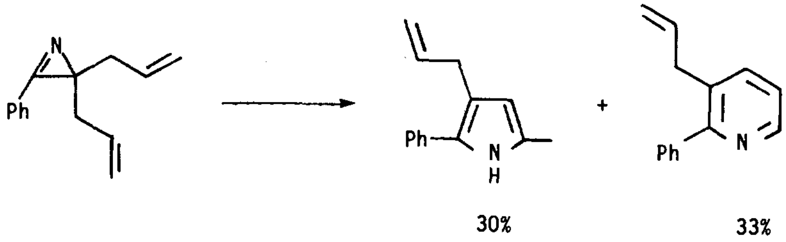
(495)



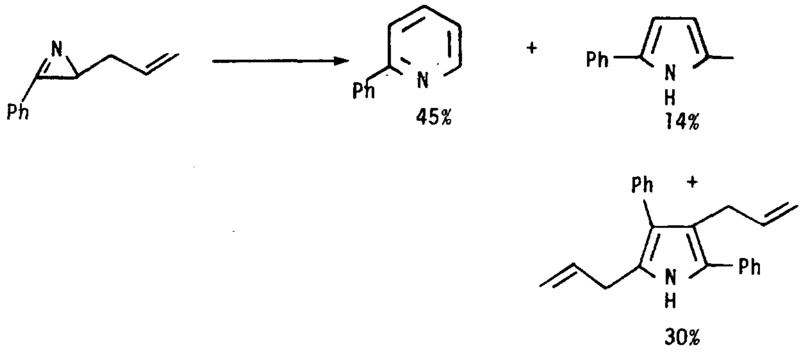
(496)



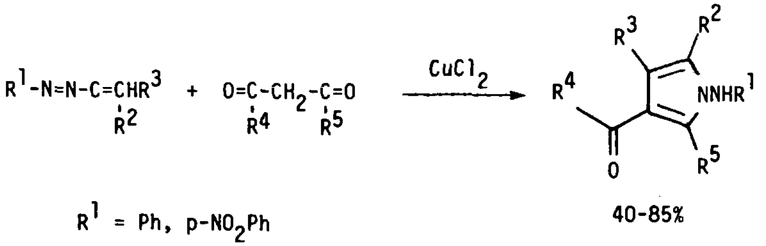
(497)



(498)



(499)



(500)

$R^1$ = Ph, p-$NO_2$Ph

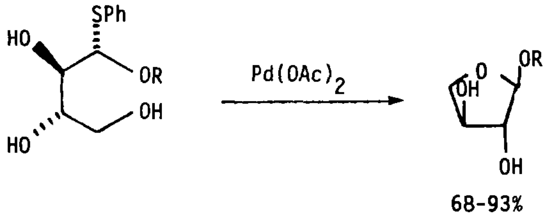
$R^2$ = Ph, $PhCH_2$-, -$(CH_2)_4$-

$R^3$ = Ph

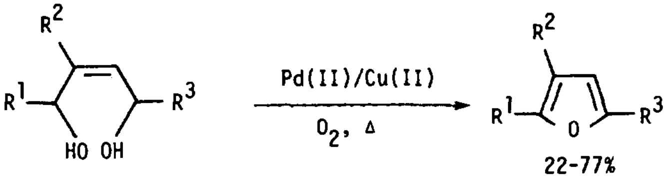
$R^4$ = Me, EtO

$R^5$ = Me, -$(CH_2)_3$-

Thiohemiacetals cyclized to tetrahydrofurans when treated with palladium(II) acetate (equation 501) [559]. But-2-ene-1,4-diols cyclized to furans when treated with palladium(II) and copper(II) under oxidizing conditions (equation 502) [560].



(501)

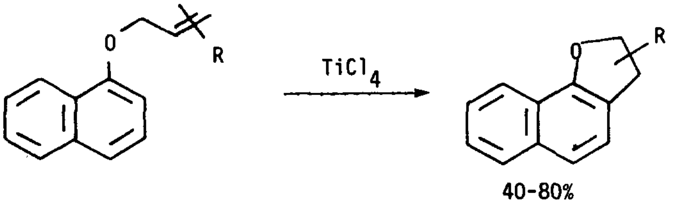


$R^1$ = H, Et, n-Pr, Ph

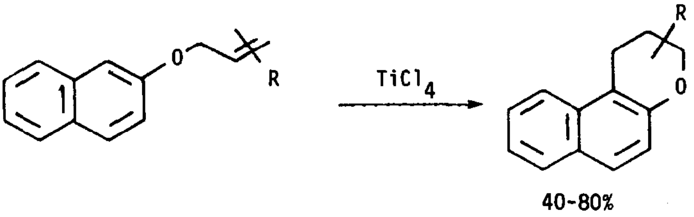
$R^2$ = H, Me

$R^3$ = H, n-Pr

O-Allylnaphthols cyclized to dihydronaphthofurans when treated with titanium(IV) chloride (equations 503 and 504) [561]. Acetylacetone and 1-hexene oxidatively cyclized to the dihydrofuran in equation 505 in the presence of manganese(III) acetate [562]. Dihydrobenzofurans were prepared by nucleophilic attack on dienyliron complexes (equation 506) [563]. Enol ethers reacted with diazo acetoacetate to give dihydrofurans in the presence of a copper(II) catalyst (equation 507) [564]. Butadiene and formaldehyde combined to give ketals when treated with ruthenium acetate species (equation 508) [565].

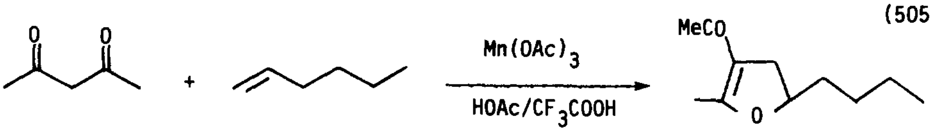


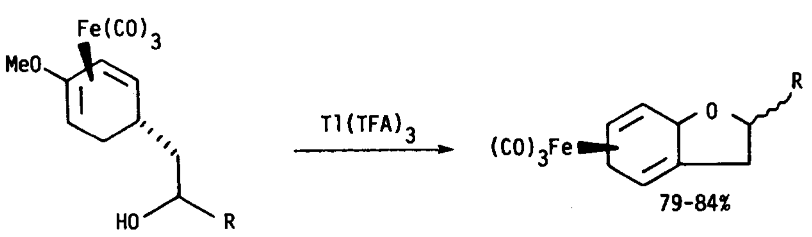
(503)



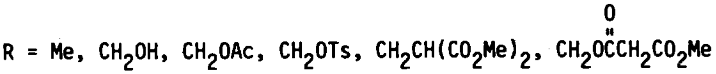
(504)

(505)

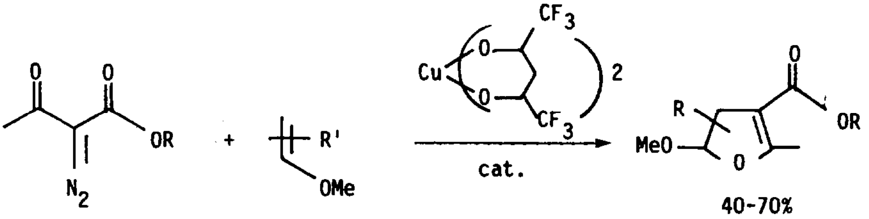




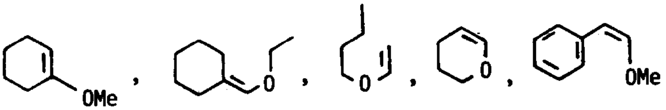
(506)



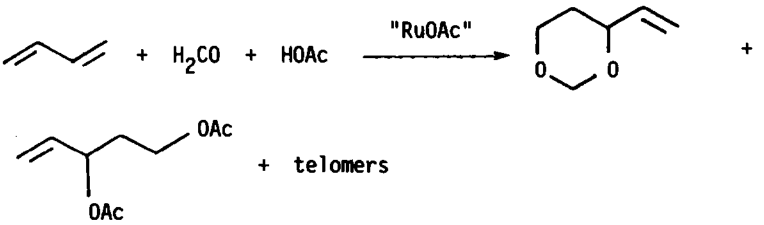
$R = Me, CH_2OH, CH_2OAc, CH_2OTs, CH_2CH(CO_2Me)_2, CH_2O\overset{O}{\overset{\|}{C}}CH_2CO_2Me$



(507)

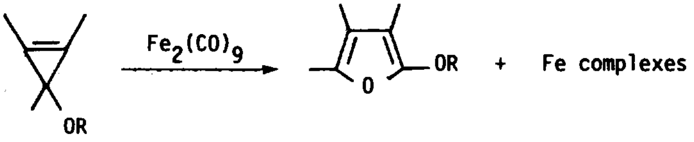


work

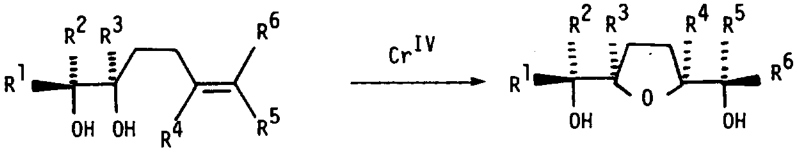


(508)

Methoxycyclopropenes opened to methoxyfurans when treated with $Fe_2(CO)_9$ (equation 509) [566]. Chiral homoallylic alcohols oxidatively cyclized to furans with very high stereospecificity (equation 510) [567]. Vinyltetrahydrofurans and α-methylenelactones were made as in equation 511 [568]. Titanium(IV) chloride cyclized protected hydroxy vinyl silanes to tetrahydrofurans (equation 512) or tetrahydropyrans (equation 513) [569]. Palladium(II) coupled o-aryl mercuric halides with conjugated enones to give products which cyclized to pyrans (equation 514) [570].



(509)

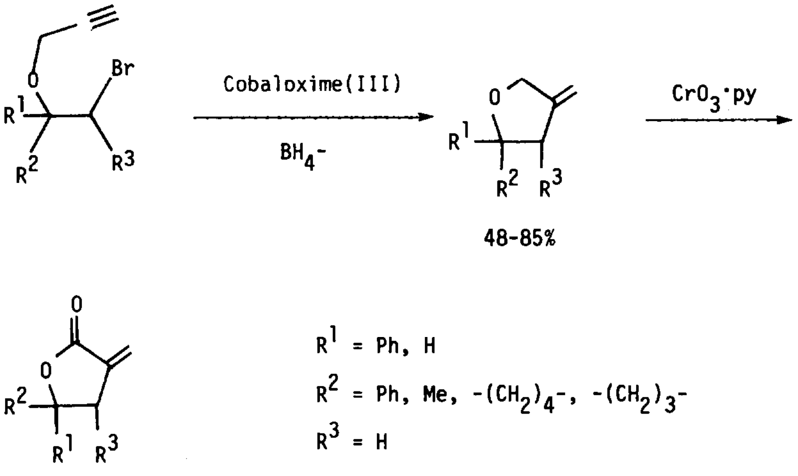


(510)

45-50%

>99.5% stereospecific

(511)



48-85%

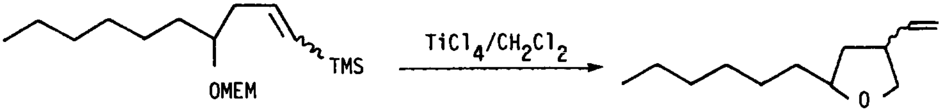
33-61%

$R^1$ = Ph, H

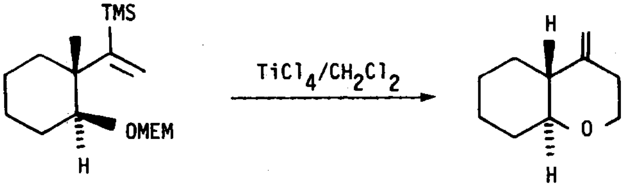
$R^2$ = Ph, Me, $-(CH_2)_4-$, $-(CH_2)_3-$

$R^3$ = H

(512)



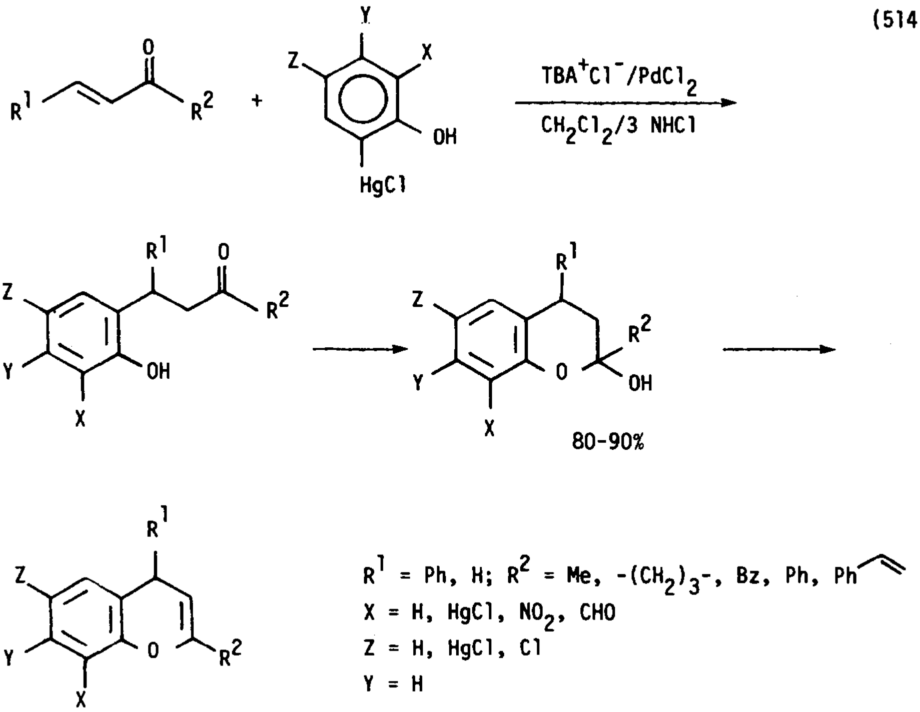
96%



(513)

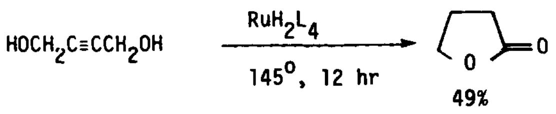
88%

(514)

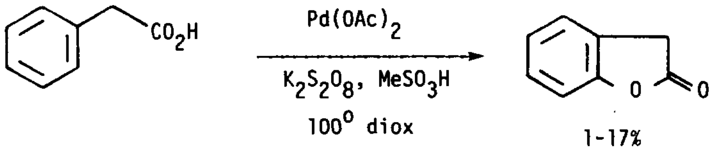


$R^1$ = Ph, H; $R^2$ = Me, $-(CH_2)_3-$, Bz, Ph, Ph
X = H, HgCl, $NO_2$, CHO
Z = H, HgCl, Cl
Y = H

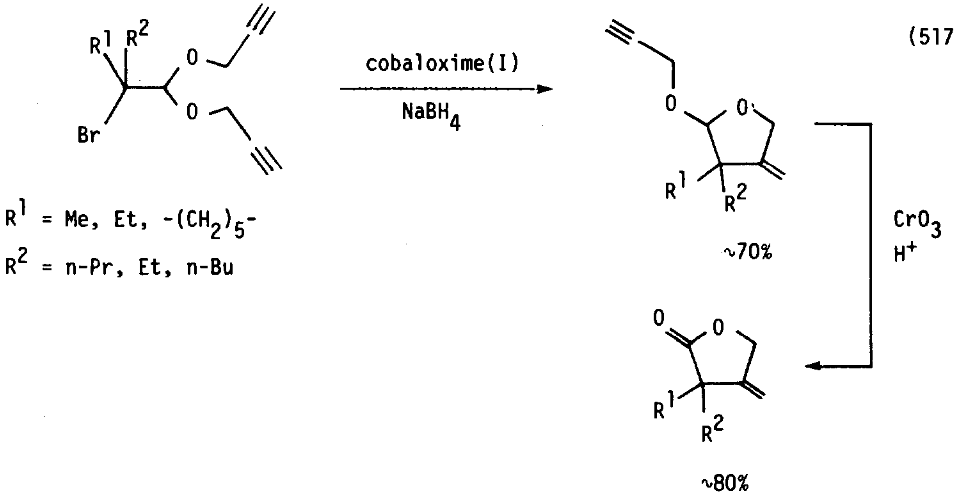
A dissertation entitled "Synthesis and Reactions of 3(2H)-Furanones - Novel Chromium(II) Induced Cyclizations" has appeared [572]. But-2-yne-1,4-diol cyclized to butyrolactone when treated with $RuH_2L_4$ (equation 515) [573]. Phenylacetic acid cyclized to the lactone when treated with palladium(II) acetate under oxidizing conditions (equation 516) [574]. Bis-Propargylic ethers cyclized to furans in the presence of low valent chromium (equation 517) [575]. These were converted to β-methylene lactones by oxidation.. α-Methylene-α-butyrolactones were synthesized by the palladium(0) catalyzed cyclization carbonylation of β-hydroxyvinyl bromides (equation 518-520) [576]. Butane-1,4-diols cyclized to lactones when treated with copper(I) carbonyls in 100% sulfuric acid (equation 521) [577]. Alkynes reacted with carbon dioxide in the presence of nickel(0) complexes to produce α-pyrones or butenolides (equation 522) [578]. Methoxyfurans were converted to α-pyrones by reaction with $Fe_2(CO)_9$ (equation 523) [579]. Di-tert-butyl-o-hydroquinones were oxidized to the seven membered anhydride by vanadium(V) reagents (equation 524) [580].



(515)



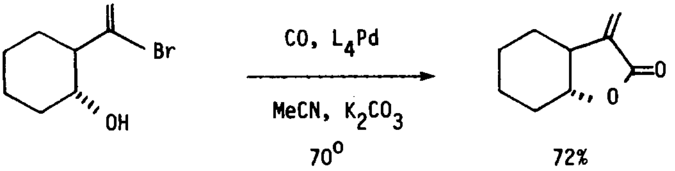
(516)



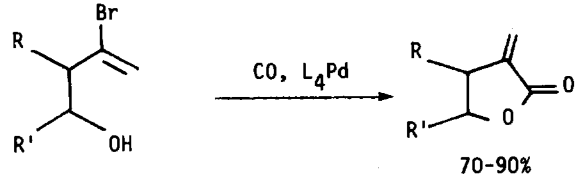
(517)

$R^1$ = Me, Et, -(CH$_2$)$_5$-

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

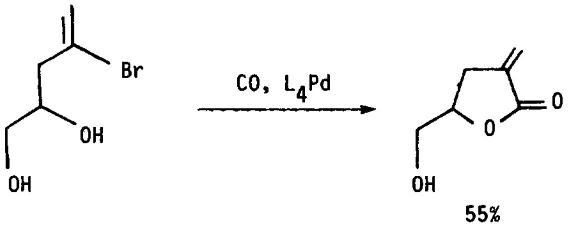


(518)

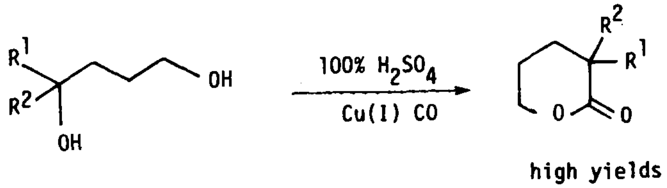


(519)

R's = H, Me, Et



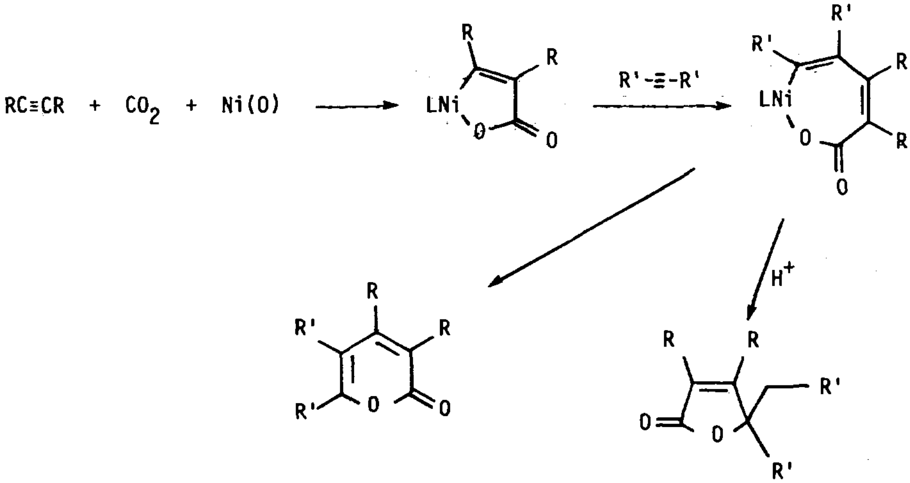
(520)



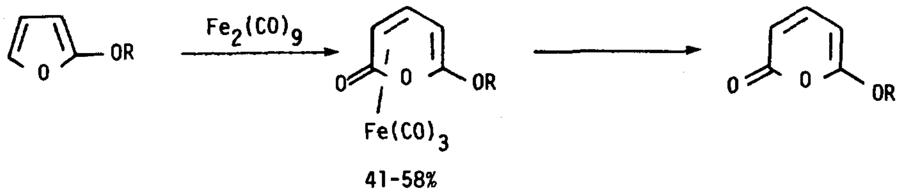
(521)

$R^1$ = Me, $-(CH_2)_4-$, $-(CH_2)_5-$

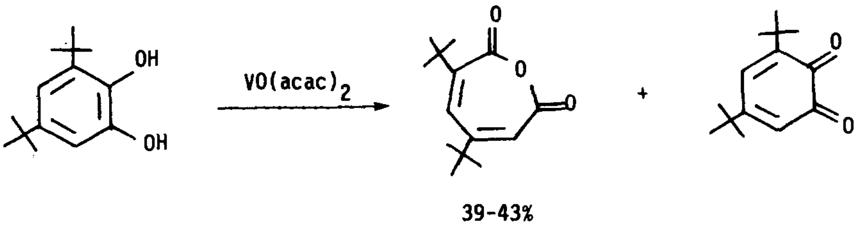
$R^2$ = Me, Et, n-Pr, n-Bu, n-$C_5$, n-$C_6$, n-$C_7$, n-$C_8$



(522)

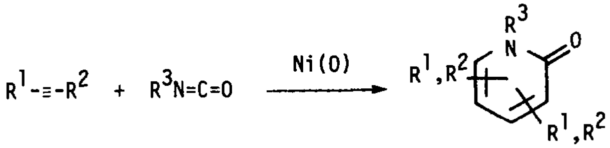


(523)



(524)

Alkynes reacted with isocyanates in the presence of nickel(0) catalysts to produce 2-pyridones (equation 525) [581]. Pyridines were made by the cobalt-catalyzed cyclotrimerization of alkynes with nitriles (equation 526) [582]. Acrylonitrile reacted with trichloroacetaldehyde in a copper-catalyzed free radical reaction to produce 2,3,5-trichloropyridine [583]. Trimethylstannyl pyridines, quinolines, and isoquinolines reacted with acid chlorides in the presence of palladium(0) catalysts to produce acylated products [584].



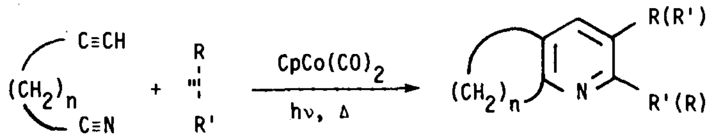
(525)

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

$R^3$ = Ph, Me, 

~80%, if one R = Ph

~16% if not



(526)

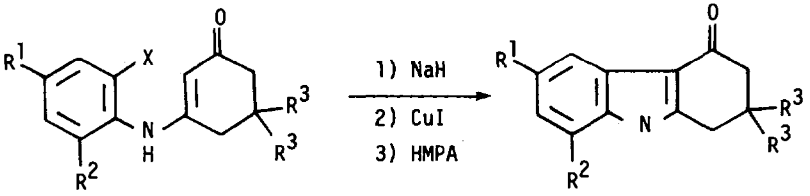
40-90%

n = 3, 4, 5

R = TMS, $CO_2Me$, Me, $CH_2OMe$, Ph, Me, H, n-Bu

R' = TMS, $CO_2Me$, CHOMe, Ph, n-Bu, $CO_2Et$

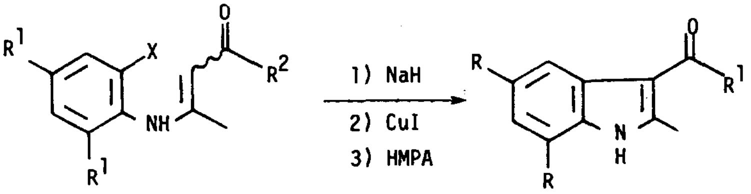
Carbazoles were prepared by the copper(I) assisted cyclization of haloarenes containing conjugated enone side chains (equations 527-530) [585]. Indoles were reduced to indolines by treatment with formic acid over palladium on carbon (equation 531) [586]. Nitroarenes reacted with aldehydes and carbon monoxide in the presence of rhodium/palladium catalysts to produce quinoline (equation 532) [587] (equation 533) [588]. Ureas condensed with vinyl halides and carbon monoxide in the presence of palladium(II) catalysts to produce pyrimidines (equation 534) [589].



(527)

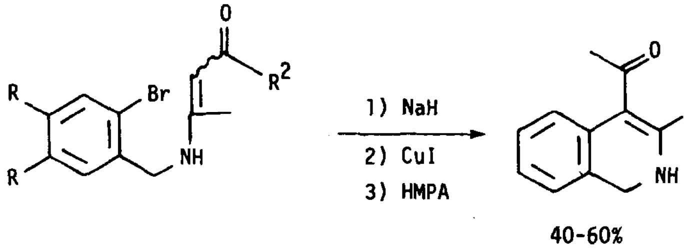
80-90%

R's = H, Me

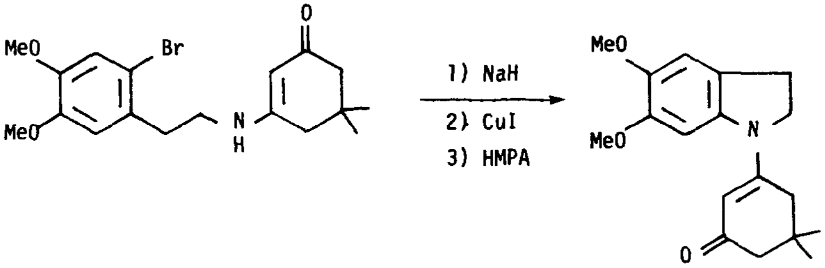


(528)

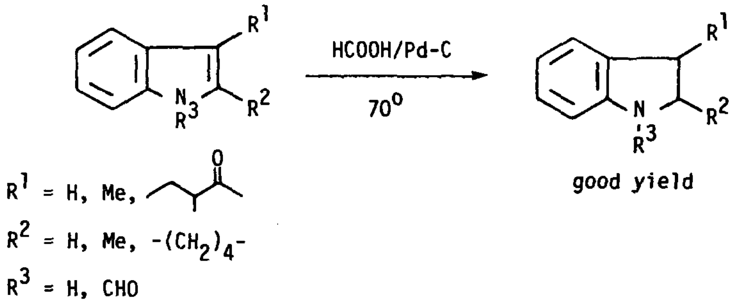
40-60%



(529)

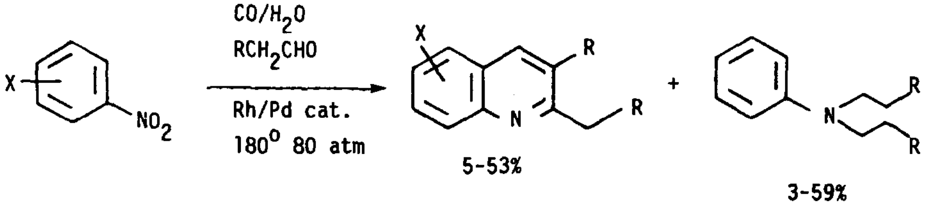


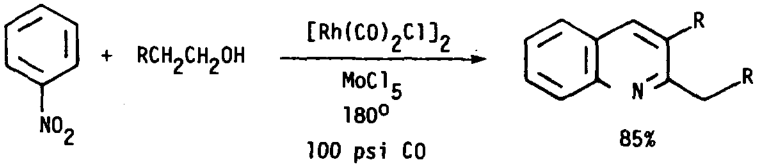
(530)



(531)

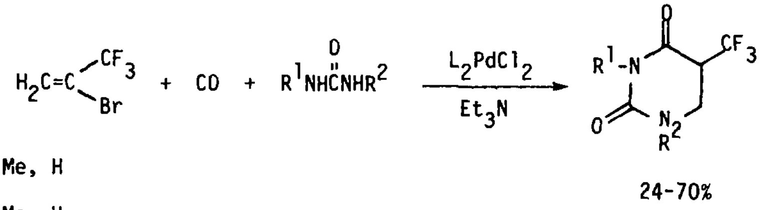
(532)





(533)

R = Me, Et

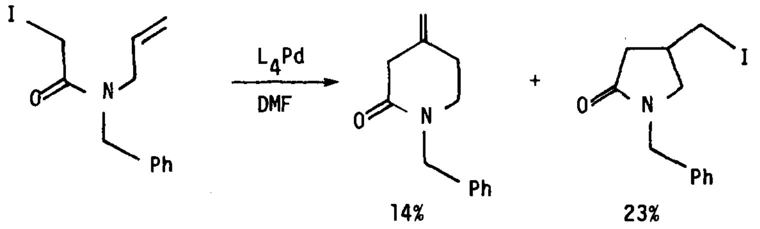


(534)

$R^1$ = Me, H

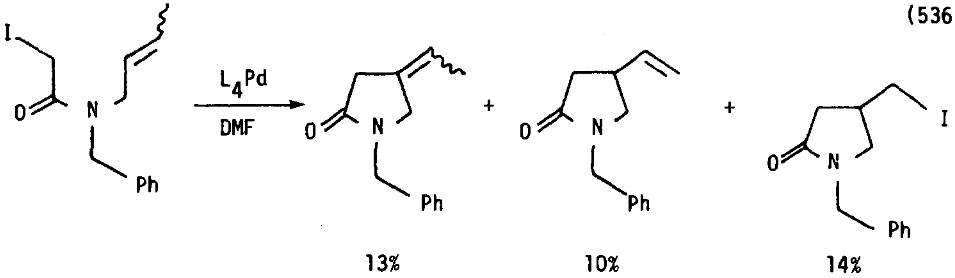
$R^2$ = Me, H

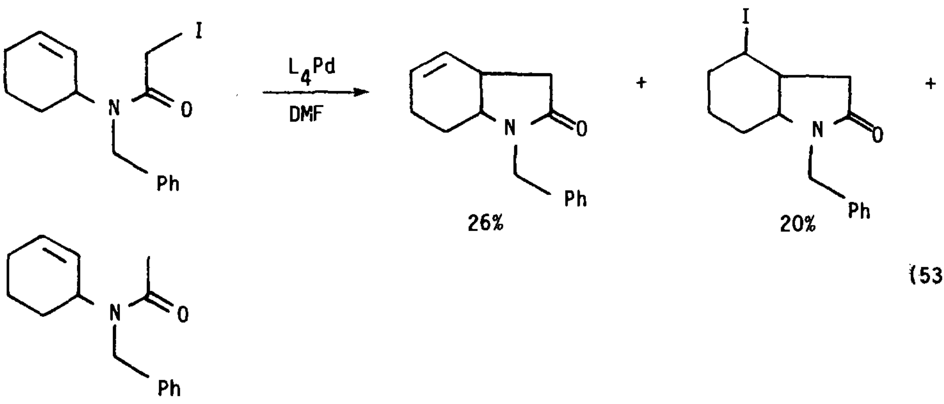
A variety of lactams were prepared by the palladium(0) catalyzed cyclization of olefinic α-iodoamides (equations 535-537) [590]. A variation of this chemistry was used to synthesize anthramycin (equation 538) [591], diazepam (equation 539) [592], and other lactams (equations 540 and 541) [592]. A macrocyclic lactam was prepared by the palladium(0) catalyzed intramolecular amination of an allyl acetate (equation 542) [593]. Metal-catalyzed reduction of N-imidotryptamines prdocued β-carbolines (equation 543) [594].



(535)

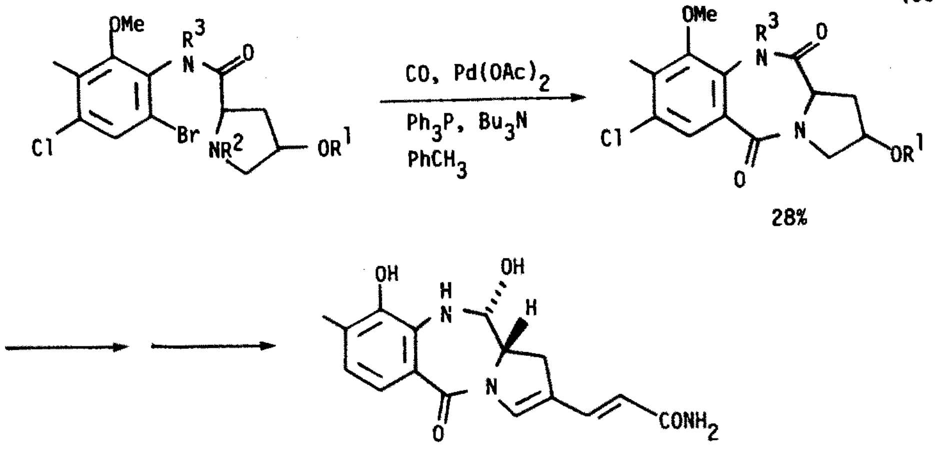
(536)

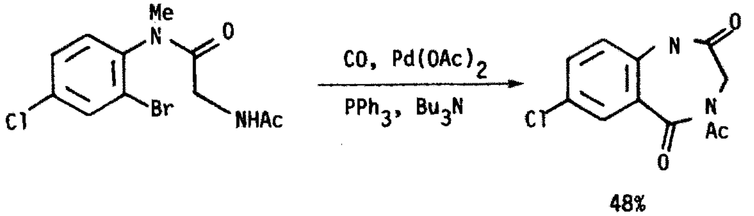




(537)

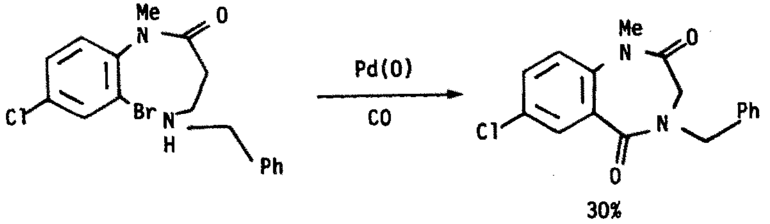
(538)



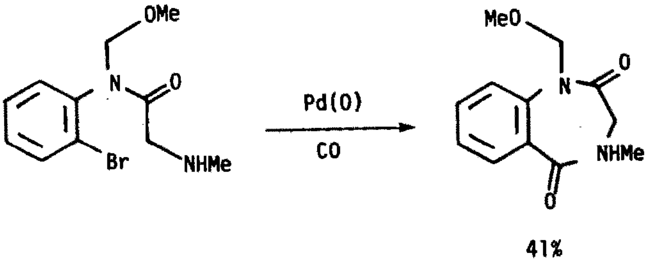


(539)

$\xrightarrow{\text{PhLi}}$ diazepam

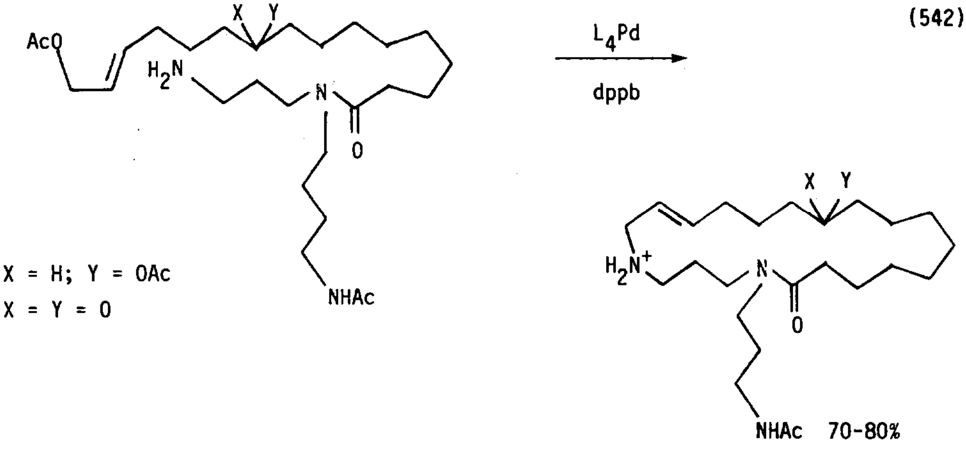


(540)

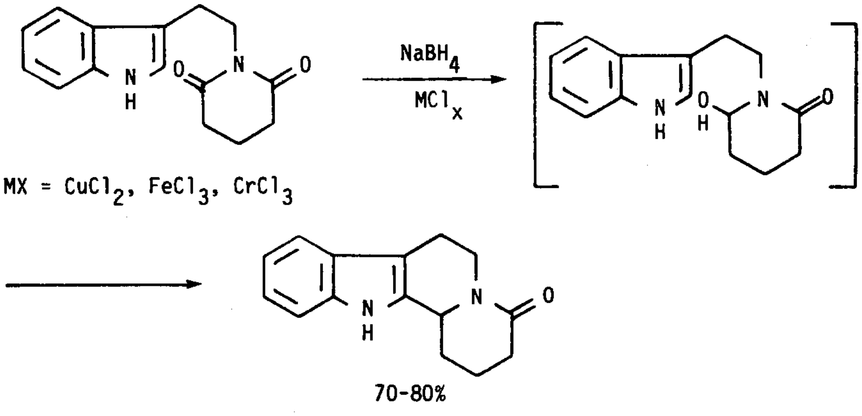


(541)

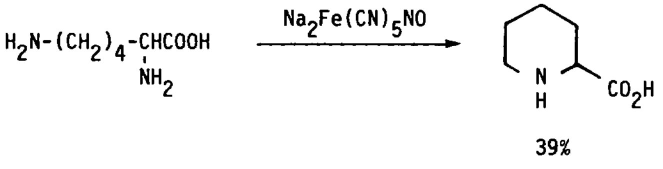
(542)



(543)

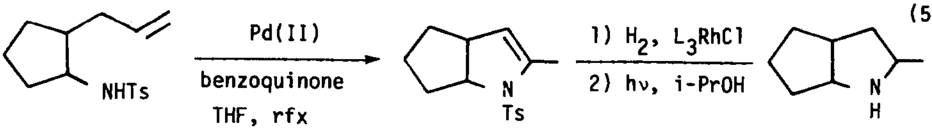


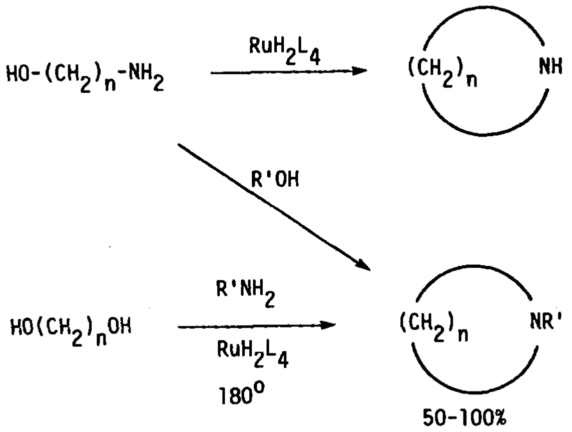
α,e-Diaminoacids cyclized when treated with $Na_2Fe(CN)_5NO$ (equation 544) [595]. The palladium catlayzed cyclization of olefinic tosamides was the topic of a dissertation [596], and a full paper (equation 5450 [597]. Amino alcohols cyclized to nitrogen heterocycles when treated with ruthenium(II) complexes (equations 546-548) [598]. Oxidative dimers of p-dimethylaminoanisole were formed by treatment with palladium(II) acetate (equation 549) [599].



(544)

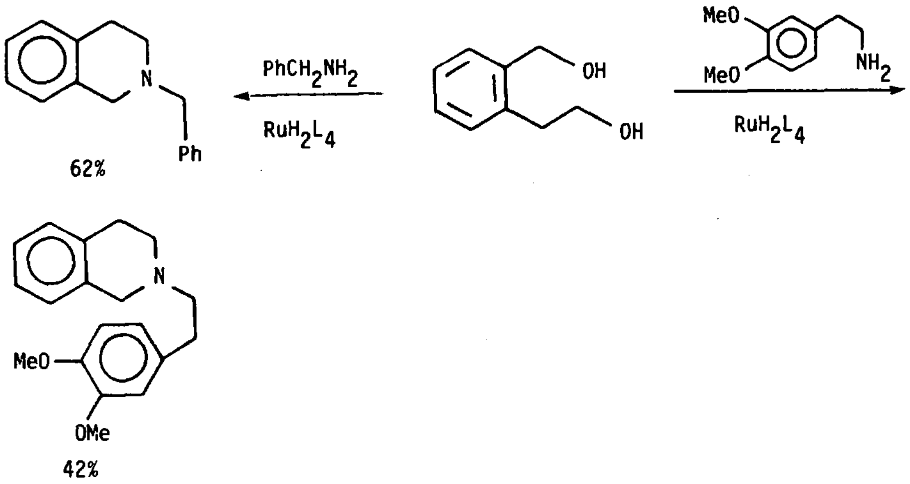
(545)

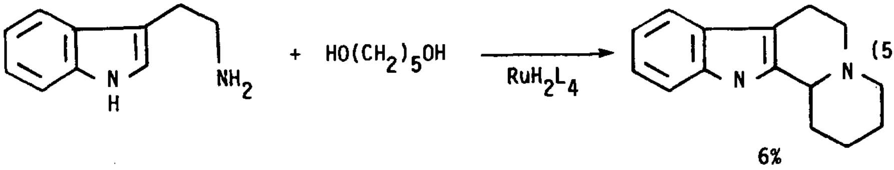




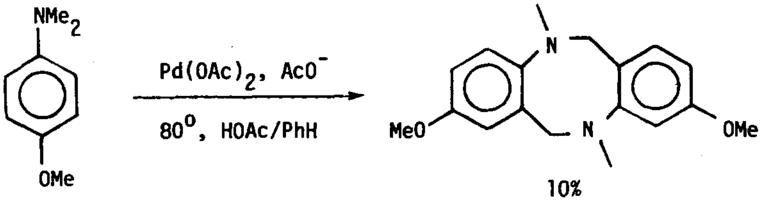
(546)

(547)



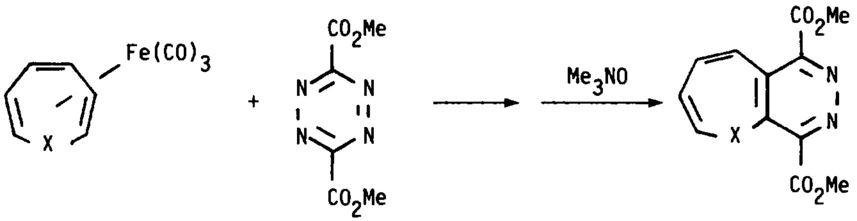


(548)



(549)

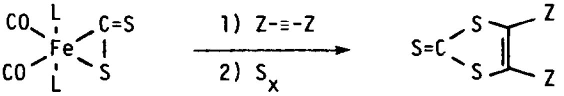
Miscellaneous heterocyclic syntheses are shown in equation 550 [600], equations 551 and 552 [601], and equation 553 [602].



good yields

(550)

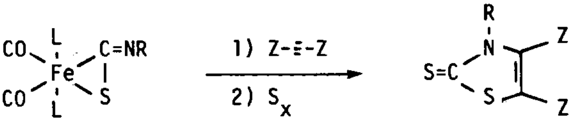
X = $NCO_2Me$, $CH_2$, C=O, C=N-$C_6H_4$-Me



22-64%

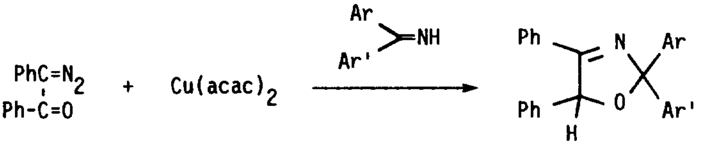
(551)

Z = $CO_2Me$, Ph, COMe, CHO



18-32%

(552)



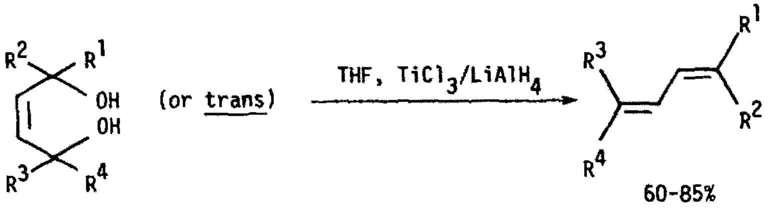
20-36%

(553)

Ar = Ph, p-MePh
Ar' = Ph, p-MePh, p-ClPh

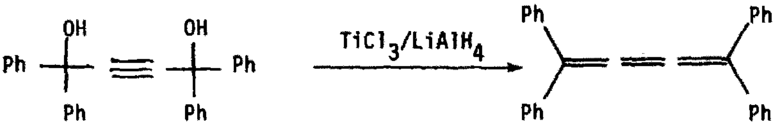
## F. Alkenes

But-2-ene-1,4-diols eliminated to 1,3-dienes when treated with titanium(III) chloride/lithium aluminum hydride (equation 554 and 555) [603]. Vicinial dihalides were debrominated to olefins with a similar reagent (equation 556) [604], as were thioacetals (equation 557) [605]. Propargyl halides were converted to allenes and alkynes by reaction with chromium(II) chloride (equation 558) [606]. Diaminoglyoximes were converted to alkynes by oxidation over cobalt catalysts (equation 559) [607]. Cyclic olefins were produced from linear olefins by reaction with rhenium hydrides (equation 560) [608]. Aryl and vinyl thiols were desulfurated to the hydrocarbon by reaction with isopropylmagnesium chloride and nickel(II) salts in the presence of triphenyl phosphine [609]. Alkynes were reduced to alkenes by mixed copper-aluminum hydrides (equation 561) [610]. Cyclopentanones were converted to cyclopentenones by air oxidation in the presence of iron(III) chloride (equation 562) [611]. Palladium on carbon catalyzed a similar oxidation of 2-aminocyclopentanones to 2-aminocyclopentenones (equation 563) [612]. Allyl acetates were reduced to the parent olefin by tributyltin hydride/palladium(0) catalyst systems [613].

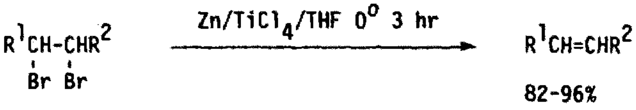


(554)

$R^1$ = Me, Ph, $-(CH_2)_5-$
$R^2$ = Me, Ph, H
$R^3$ = Me, Ph, $-(CH_2)_5-$
$R^4$ = Me, Ph, H

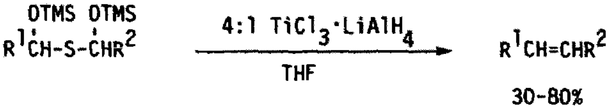


(555)

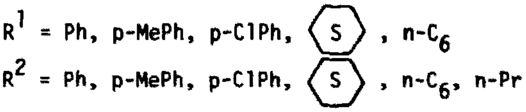


$$\underset{Br}{R^1CH}-\underset{Br}{CHR^2} \xrightarrow{Zn/TiCl_4/THF\ 0^o\ 3\ hr} \underset{82-96\%}{R^1CH{=}CHR^2} \quad (556)$$

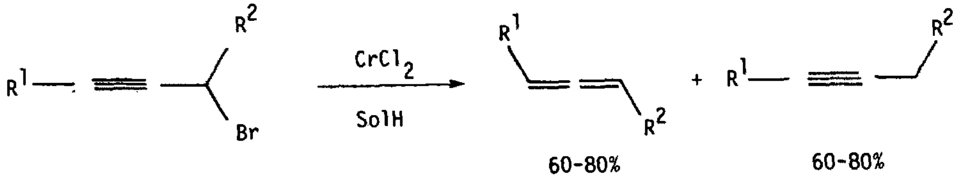
$R^1$ = n-$C_8$, n-Pr, H
$R^2$ = H, n-Bu, $CH_2COEt$, $CH_2CH(OH)C_2H_5$



$$R^1\overset{OTMS}{CH}-S-\overset{OTMS}{CHR^2} \xrightarrow[THF]{4:1\ TiCl_3\cdot LiAlH_4} \underset{30-80\%}{R^1CH{=}CHR^2} \quad (557)$$

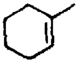


$R^1$ = Ph, p-MePh, p-ClPh, S, n-$C_6$
$R^2$ = Ph, p-MePh, p-ClPh, S, n-$C_6$, n-Pr

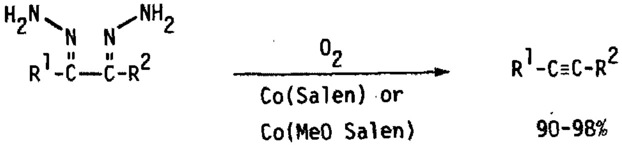


SolH = carboxylic acid

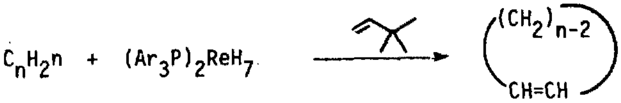
SolH = alcohol

$R^1$ = Ph, , , n-$C_6$, t-Bu (558)

$R^2$ = Me, n-Pr, n-$C_5$



(559)



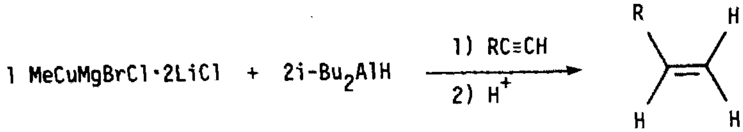
(560)

n = 6, 7, 8

$C_6$ = 25%

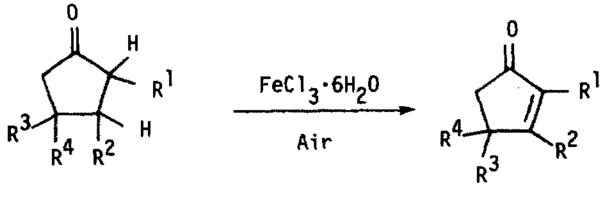
$C_7$ = 35%

$C_8$ = 60%



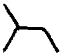
(561)

R = n-$C_6$, Ph, $PhS(CH_2)_3$, PhS, $(EtO)_2\overset{O}{\overset{\|}{P}}\text{-}\underset{|}{N}CH_2C{\equiv}CH$ ~100%

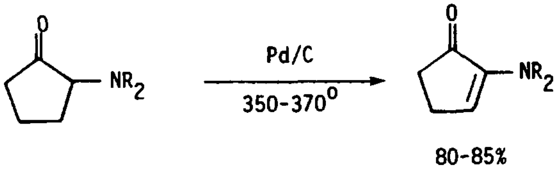


(562)

~40%

$R^1$ = H, , n-$C_5$, n-$C_6$, n-$C_7$, n-$C_{10}$, Me, $MeO_2C(CH_2)_6$

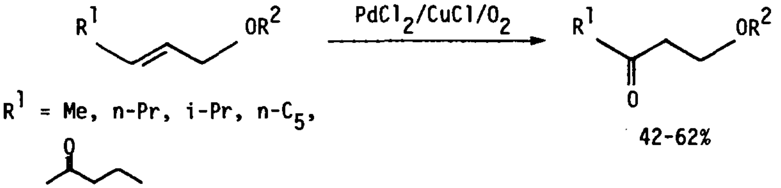
$R^2$, $R^3$, $R^4$ = H, Me



(563)

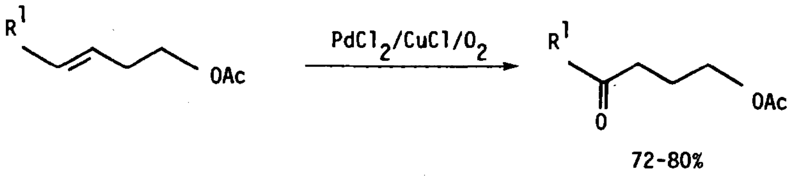
## G. Ketones, Aldehydes

A dissertation entitled "Synthesis of Optically Active α-Deuterio Ketones. Investigation of Tricarbonylchromium Derivatives of Aromatic Compounds" has appeared [614]. Ethylene and propylene were oxidized to ketones over $PdCl_2/CuCl_2/NaY$ zeolite catalysts [615] and $PdCl_2/CuCl_2$ on $Al_2O_3$ or $SiO_2$ [616]. Allyl ethers and acetates were oxidized to β-alkoxyketones by $PdCl_2/CuCl/O_2$ (equations 564-567) [617]. Palladium nitrite complexes oxidized olefins to ketones in fair yield (equation 568). Strained olefins such as norbornenes were epoxidized instead (equation 569) [618]. Steroid precursors were made by Wacker-type oxidation of olefins (equation 570) [619]. Olefins underwent allylic oxidation by irradiation in the presence of oxygen and palladium(II) trifluoroacetate (equation 571) [620]. Other allylic oxidations were effected by t-butylhydroperoxide in the presence of rhodium(II) catalysts (equation 572) [621][622]. 1-Hexene was oxidized to 2-hexanone by oxygen and cobalt (salen) catalysts (equation 573) [623]. Alkoxy- and aminoalkynes oxidized to α-ketoesters or amides when treated with PhI=O in the presence of ruthenium(II) catalysts (equation 574) [624].

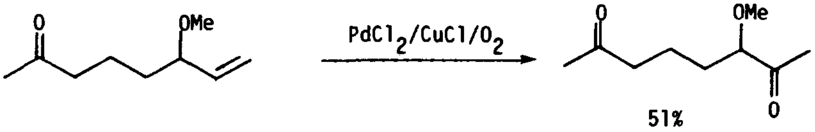


(564)

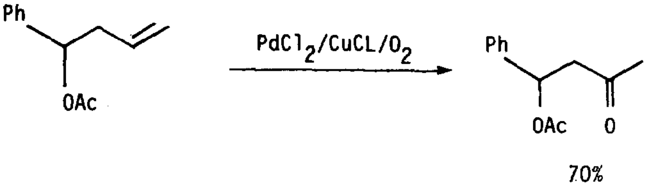
$R^1$ = Me, n-Pr, i-Pr, n-$C_5$,



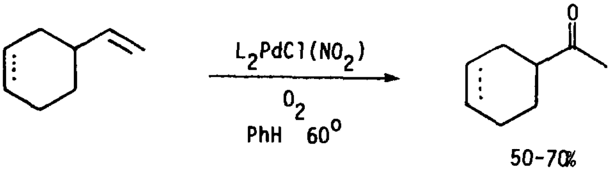
(565)



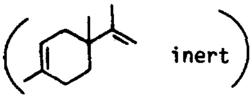
(566)

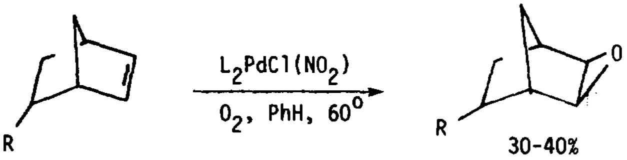


(567)

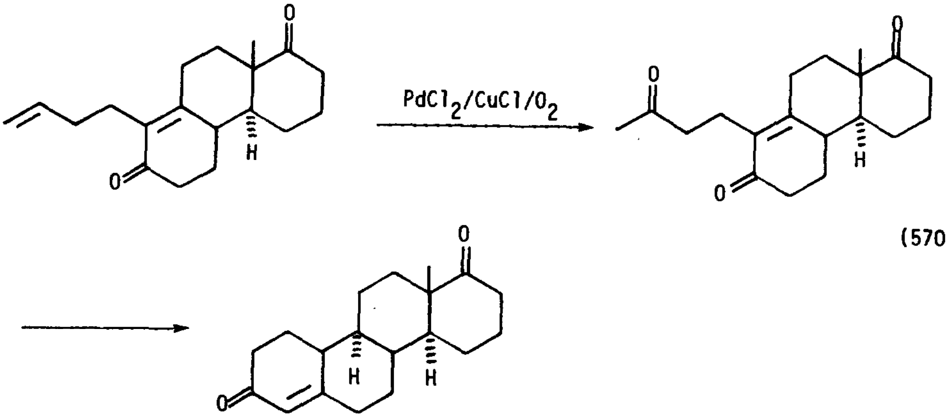


(568)



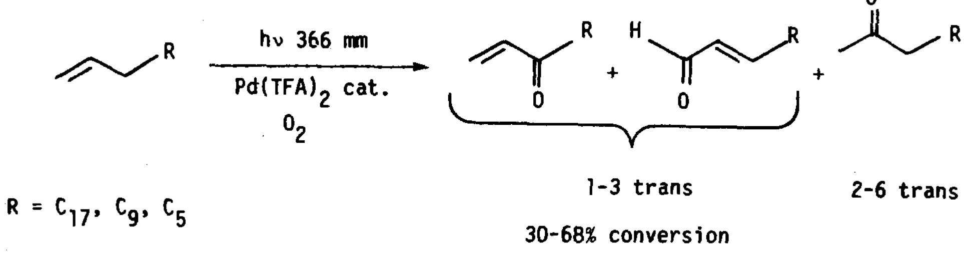


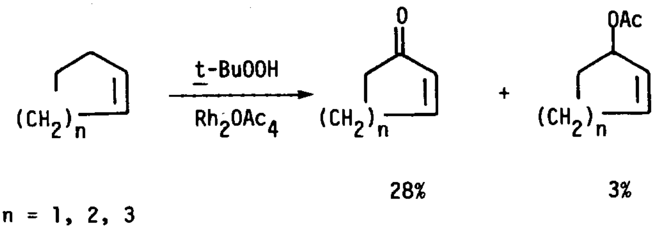
(569)



(570)

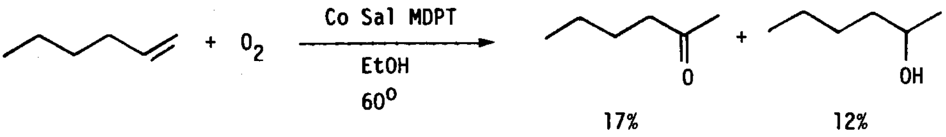
(571)

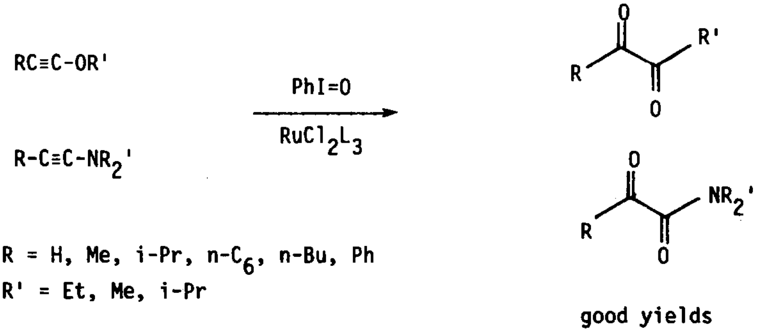




(572)

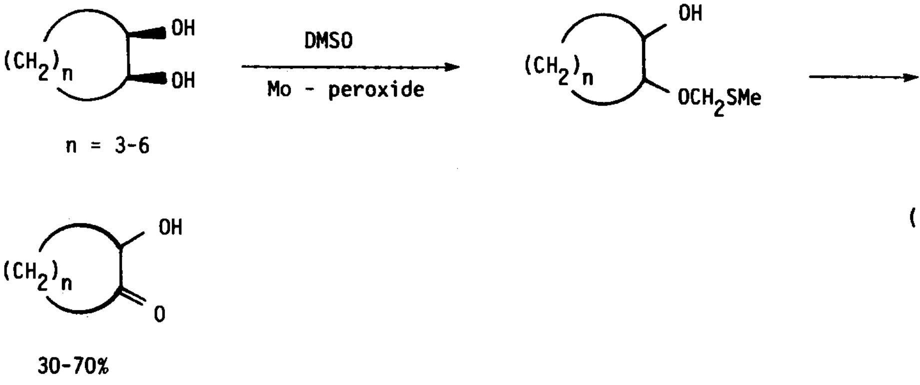
(573)



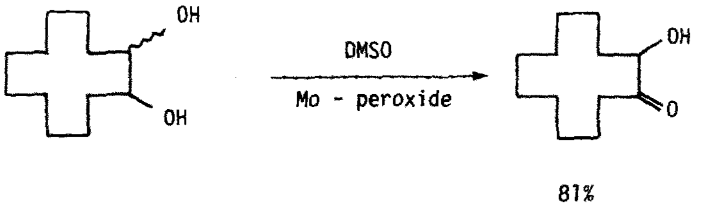


(574)

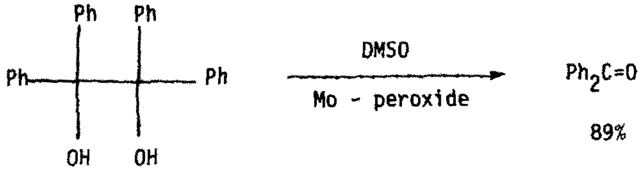
Vicinal diols were oxidized to α-hydroxyketones when treated with molybdenum peroxides (equation 575-577) [625]. Chromium tricarbonyl complexes of benzylic alcohols were oxidized to the corresponding aldehydes by DMSO in acetic anhydride (equation 578) [626]. Similar chemistry occurred with substituted iron tricarbonyl diene complexes (equation 579) [627]. Indanones were oxidized to a variety of products by oxygen and a cobalt salen complex (equation 580) [628].



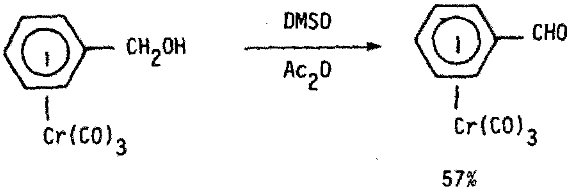
(575)



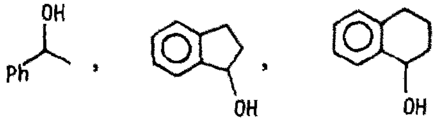
(576)



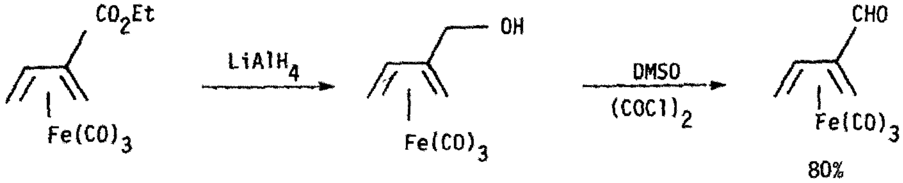
(577)



(578)

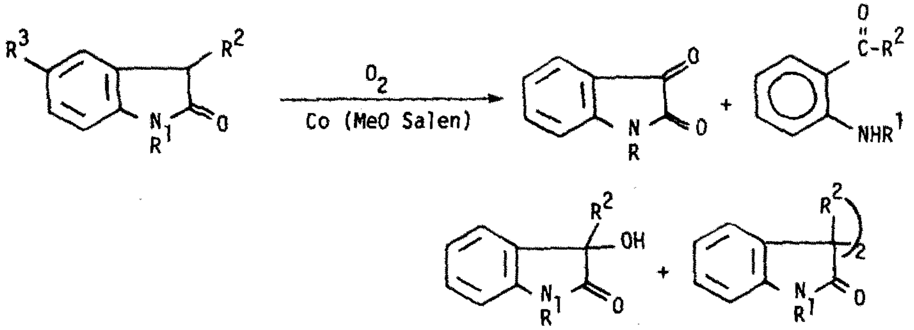


also worked.

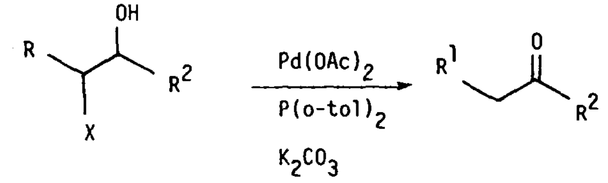


(579)

(580)

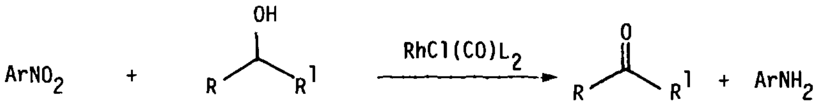


Alcohols were oxidized to ketones by palladium(II) salts (equation 581) [629] or by nitro aromatics in the presence of rhodium catalysts (equation 582) [630]. Trimethylsilylenol ethers were converted to α-hydroxyketones by chromyl chloride (equation 583) [631]. 1,4-Dicarbonyl compounds were prepared as in equation 584 [632].

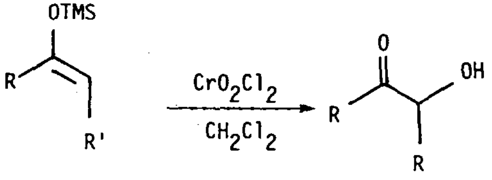


(581)

X = Br, Cl, I

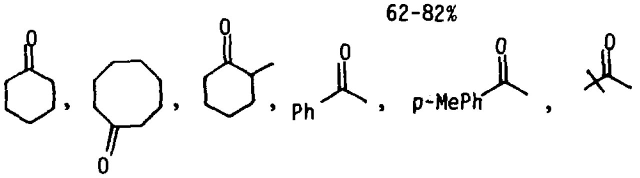


(582)



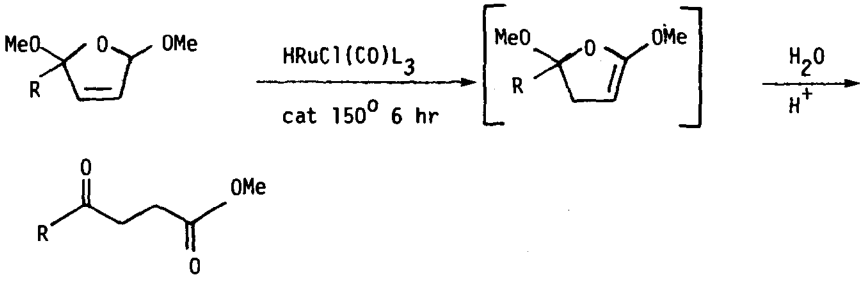
(583)

62-82%



work.

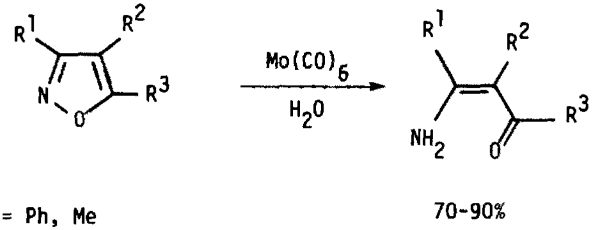
(584)



90-100%

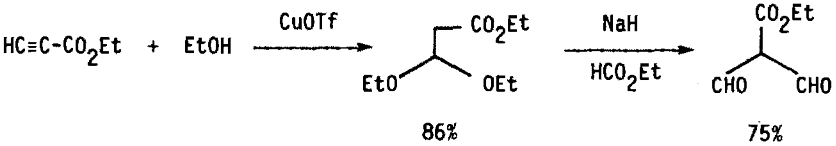
R = H, Me, n-Bu, n-$C_6$, n-$C_7$, $CH_2OH$, $\underset{CH_3}{CHOH}$

Oxazoles were converted to vinylogous amides by reaction with molybdenum carbonyl (equation 585) [633]. Acetylenic esters were converted to dialdehydes as in equation 586 [634]. Tributyltin hydride reduced α,β-unsaturated aldehydes and ketones to saturated carbonyls in the presence of palladium(0) catalysts (equation 587-590) [635].

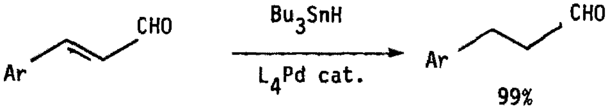


(585)

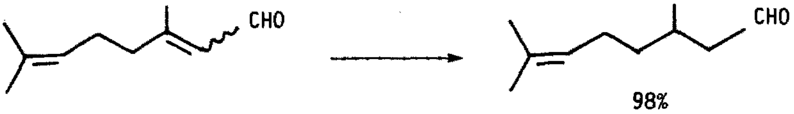
$R^1$ = Ph, Me
$R^2$ = H
$(CH_2)_4$
$R^3$ = Ph, Me



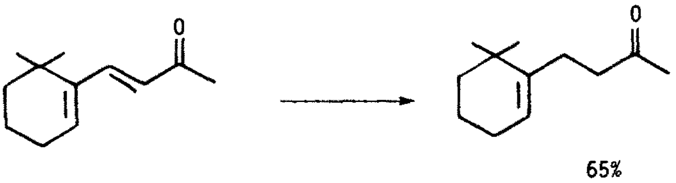
(586)



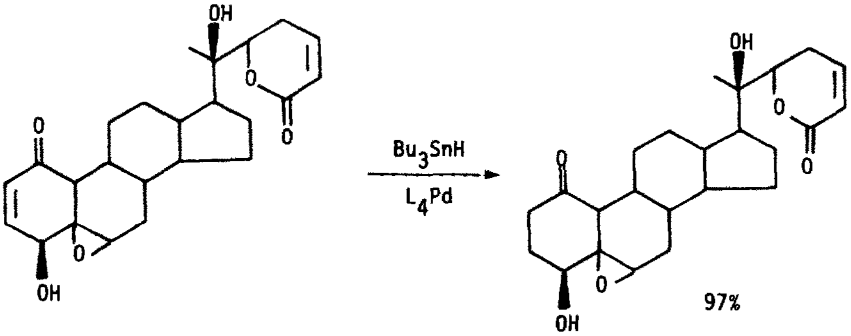
(587)



(588)

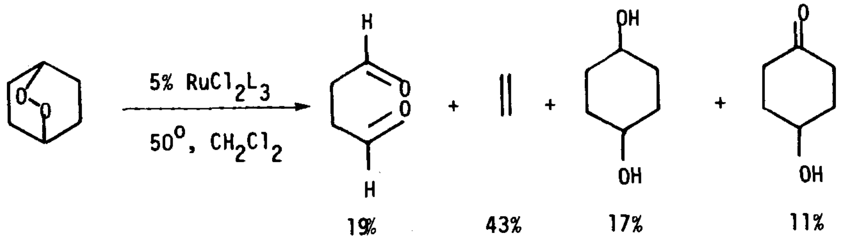


(589)

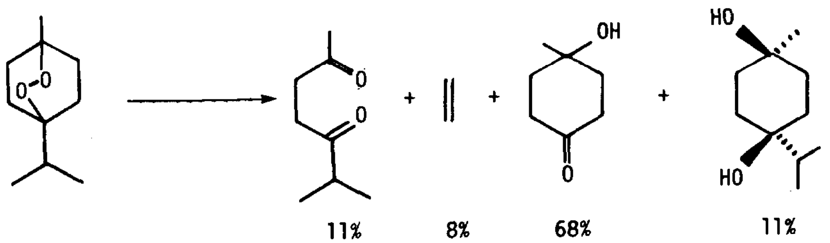


(590)

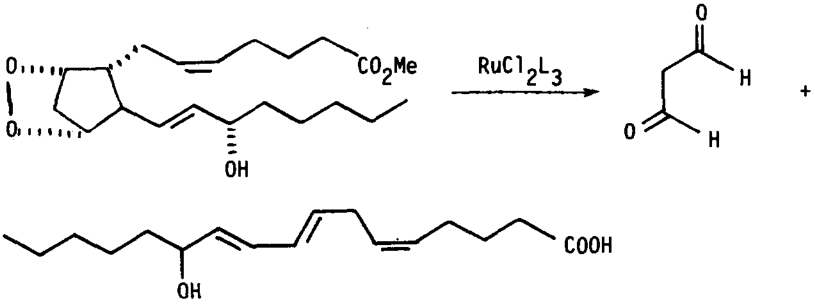
Ruthenium(II) catalyzed the opening of endoperoxides to a variety of carbonyl compounds (equations 591-593) [636]. Rhodium(I) complexes catalyzed a similar process (equations 594 and 595) [637]. Aldehydes were homologated to ketones by reaction with olefins and ruthenium(II) catalysts (equation 596) [638].



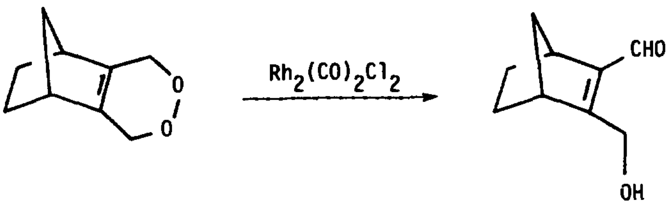
(591)



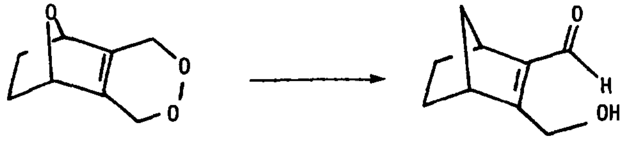
(592)



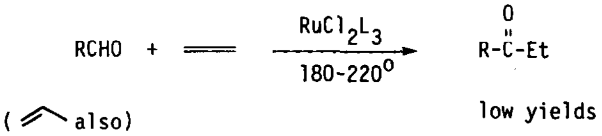
(593)



(594)



(595)

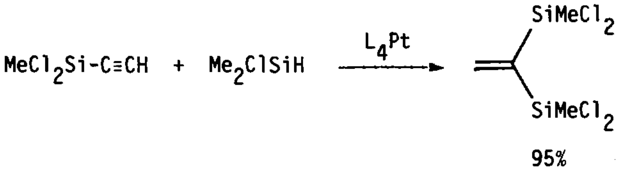


$$RCHO + CH_2{=}CH_2 \xrightarrow[180\text{-}220^{\circ}]{RuCl_2L_3} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Et \qquad (596)$$

low yields

### H. Organosilanes

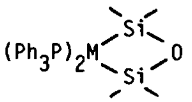
A review dealing with the synthesis of vinylsilanes from olefins and hydrosilanes with the aid of transition metal catalysts (23 references) has appeared [639]. Polymeric organosilicon supported rhodium phosphine complexes catalyzed the hydrosilation of olefins [640]. Platinum(0) catalyzed the hydrosilation of silylacetylenes (equation 597)[641]. Polysiloxanes were made over platinum, palladium, and iridium complexes (equation 598) [642]. Silyl cyclopropanes dimerized when treated with palladium(II) catalysts (equation 599) [643]. A review dealing with new polymer-supported metal catalysts for hydrogenation and hydrosilation (23 references) has appeared [644]. Silylated enamines resulted from the reaction of nitriles with (dimethylsilyl) benzene in the presence of rhodium(I) catalysts (equation 600) [645]. Intact cobalt clusters catalyzed the hydrosilation of acetophenone (equation 601) [646]. Chiral rhodium catalysts hydrosilylated conjugated enones to give chiral allyl alcohols (equations 602-606) [647]. α-Haloesters, ketones, and nitriles were reduced by hexamethyldisilane and palladium(0) catalysts (equation 607) [648]. Benzyl chlorides were converted to benzyl silanes by reaction with chlorosilanes and a palladium(0) catalyst (equation 608) [649].



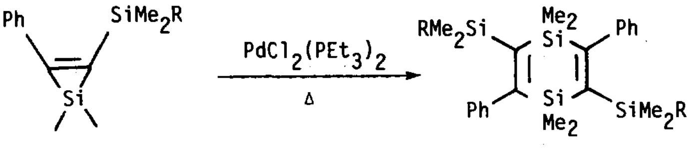
(597)

$$(HSiMe_2)_2O \xrightarrow{\text{cat.}} HMe_2Si(OSiMe_2)_nOSiMe_2H \qquad (598)$$

cat =



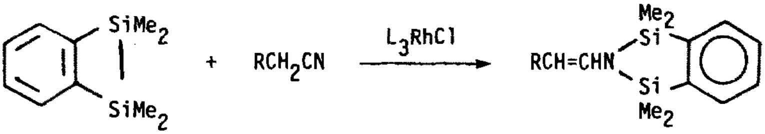
M = Pd, Pt, Ir(CO)H



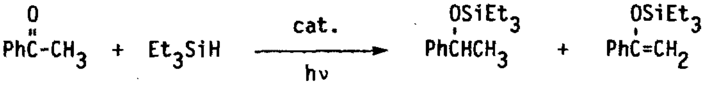
(599)

R = Me, Et, t-Bu, Ph

70%



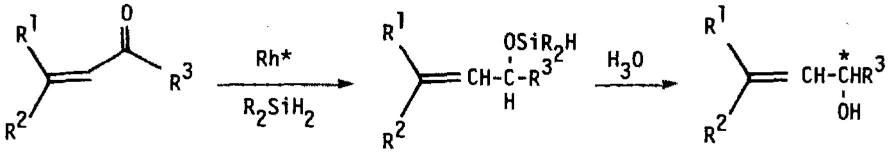
(600)



$$\mathrm{Ph\overset{O}{\overset{\|}{C}}-CH_3 + Et_3SiH \xrightarrow[h\nu]{cat.} Ph\overset{OSiEt_3}{C}HCH_3 + Ph\overset{OSiEt_3}{C}=CH_2}$$

(601)

cat. = Co-Ni Co-Ni-Mo Co-Mo-Fe clusters
Co-Mo



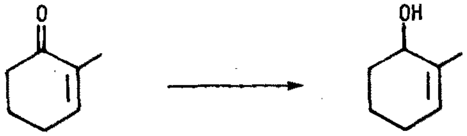
(602)

up to 69% ee

Rh* = Rh(I) DIOP, Rh(I) BMPP

(603)

70% yield
27% ee

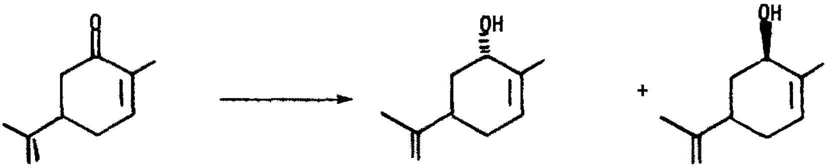


(604)

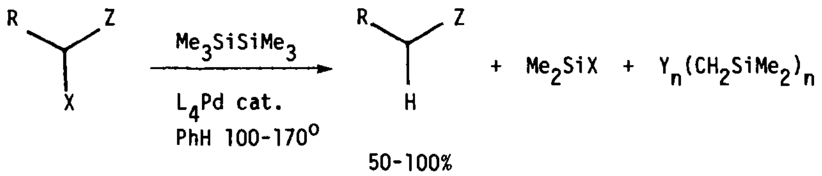
83% yield
52% ee

(605)

60% 38% ee



(606)



(607)

X = Br, Cl

Z = COR, $CO_2R$, CN

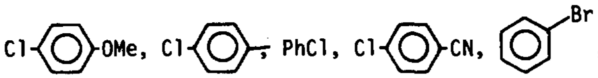
$$ArCH_2Cl + Me_nSi_2Cl_{6-n} \xrightarrow[130^\circ]{L_4Pd} \underset{61\text{-}100\%}{ArCH_2SiMe_nCl_{3-n}} \qquad (608)$$

I. Miscellaneous

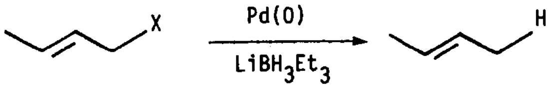
Aryl halides were reduced to the hydrocarbon by zinc and a nickel(II) catalyst (equation 609) [650]. Halides were also reduced to hydrocarbons by isopropylmagnesium chloride and $Cp_2TiCl_2$ [651]. The process was shown to be a radical process. Allylic systems were reduced to olefins by $LiBHEt_3$ and a palladium(0) catalyst (equation 610) [652]. Aryl halides were reduced to arenes by formic acid and palladium on carbon [653]. Nitriles were reduced to hydrocarbons by $[CoL_2N_2]Li(Et_2O)_3$ [654] and ammonium formate and palladium on carbon (equation 611) [655].

$$ArX + Zn + H_2O \xrightarrow[\text{cat.}]{L_2NiX_2} ArH \qquad (609)$$

ArX =



, 1-Br adamantane



(610)

X = OPh, OMe, SPh, $SO_2Ph$, SePh, OTMS, Cl

stereo- and regiochemistry maintained

$$ArCN + HCOONH_4 \xrightarrow{10\%\ Pd/C} \underset{40\text{-}100\%}{ArCH_3} \qquad (611)$$

Sulfoxides were reduced to sulfide by $CoCl_2/NaBH_4$ (equation 612) [656]. Molybdenum(VI) complexes catalyzed the deoxygenation of a variety of substrates by triphenylphosphine (equations 613-616) [657]. Sulfides were oxidized to sulfoxides by t-butylhydroperoxide and titanium(IV) catalysts [658]. Oxygen oxidized isocyanides to isocyanates and nitrosobenzene to nitrobenzene over cobaloxime(II) catalysts [659]. Cyclohexenones with unsaturated side chains were converted to aromatic compounds by reaction with rhodium(III) chloride (equations 617-619) [660].

$$\mathrm{RSOR'} + \mathrm{CoCl_2(H_2O)_6/NaBH_4} \xrightarrow{\mathrm{EtOH}} \underset{44\text{-}96\%}{\mathrm{RSR'}} \qquad (612)$$

$$\mathrm{Ph_3P} + \mathrm{Ph_3M{=}O} \xrightarrow[\mathrm{(Et_2NCS_2)MoO_2}]{} \mathrm{Ph_3P{=}O} + \mathrm{Ph_3M} \qquad (613)$$

M = As, Sb

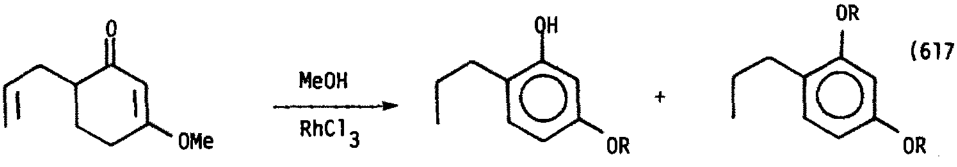
$$\mathrm{Me_2SO} \longrightarrow \underset{63\%}{\mathrm{Me_2S}} \qquad (614)$$

100%

(615)

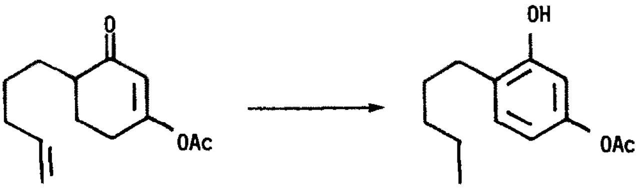
88%

(616)

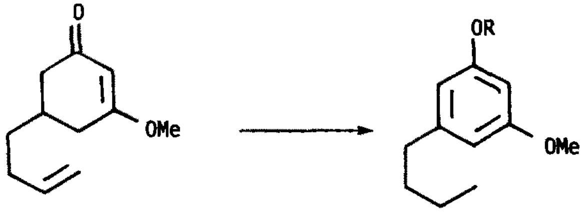


81%

(617)

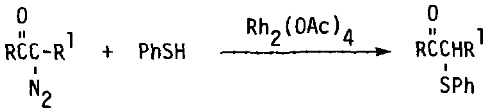


(618)



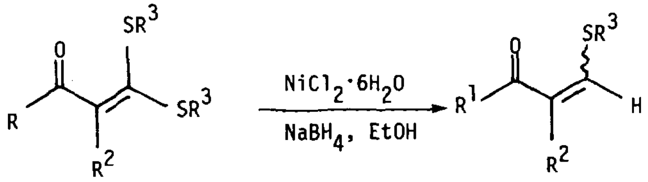
(619)

Diazoketones were converted to α-thioketones by reaction with thiophenol and rhodium(II) acetate (equation 620) [661]. β,β-Dithio-α,β-unsaturated ketones were monodesulfurated by borohydride in the presence of nickel(II) salts (equation 621) [662]. Terminal alkynes were selenated by reaction with PhSeCN and a copper catalyst (equation 622) [663]. Allyl ethers were treated with ethylazidacarbonate to give insertion products (equation 623) [664]. Two new systems for hydrocarbon activation have been developed (equation 624) [665], (equation 625) [666].



$$\mathrm{R\overset{O}{\overset{\|}{C}}\underset{N_2}{C}\text{-}R^1} + \mathrm{PhSH} \xrightarrow{\mathrm{Rh_2(OAc)_4}} \mathrm{R\overset{O}{\overset{\|}{C}}\underset{SPh}{C}HR^1} \qquad (620)$$

70-90%



(621)

$R^1$ = Ar

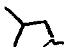
$R^2$ = H, Me, Et, n-Pr

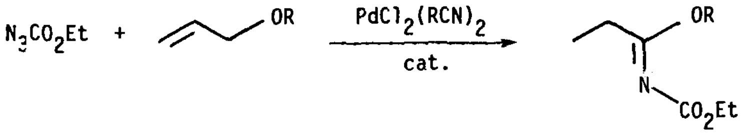
$R^3$ = Me, Et

40-80%
14 cases

$$\mathrm{HC{\equiv}CR} \xrightarrow[\mathrm{CuX/Et_3N/CH_2Cl_2}]{\mathrm{PhSeCN}} \mathrm{PhSeC{\equiv}CR} \qquad (622)$$

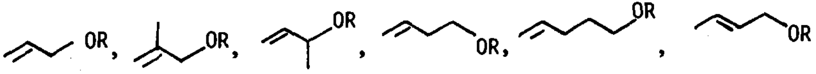
89-96%

R = n-Bu,  , n-$C_6$, n-$C_7$, $CH_2OH$, $C(OH)(Me)CH_2Me$

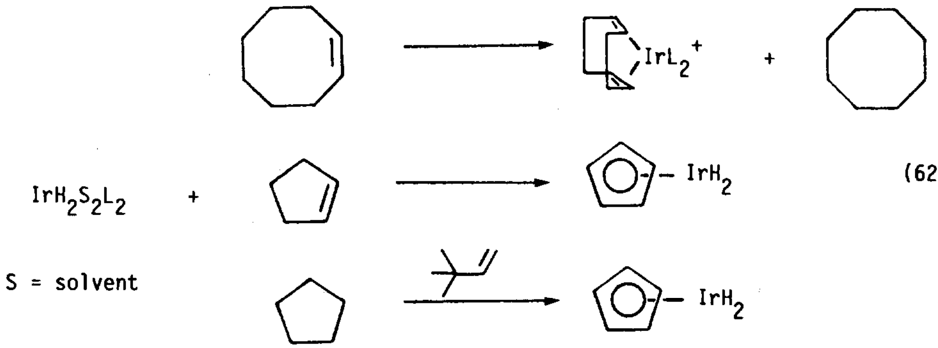


(623)

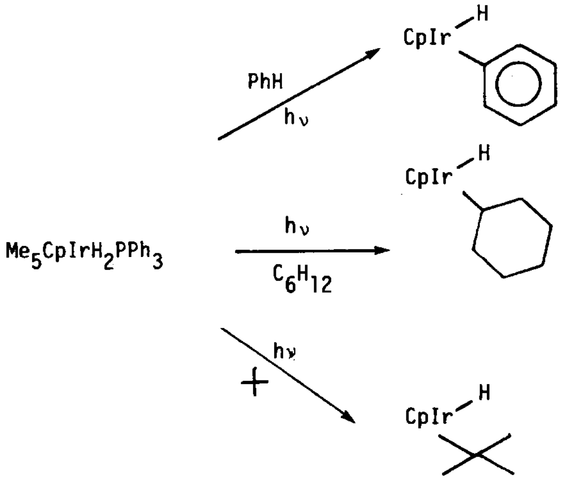
40-80%



all work.

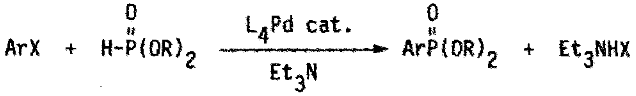


(624)



(625)

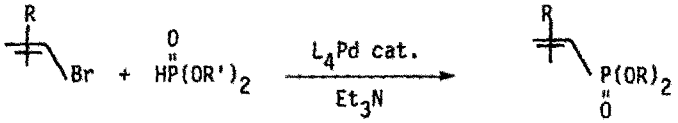
Aryl (equation 626) and vinyl halides (equation 627) were converted to phosphites by reaction with $HP(O)(OR)_2$ and a palladium(0) catalyst [667]. Reaction of iron(III) chloride with potassium graphite produced a reagent that converted vic dihalides to olefins, α-haloketones to ketones, and promoted the cycloaddition of α,α'-dihaloketones to enamines (equation 628) and furans (equation 629) [668]. Phosphorous stabilized ylides were silylated or stannated by chlorosilanes or stannanes in the presence of copper(I) iodide (equation 630) [669]. α-Amidoacids were prepared by the dicobalt octacarbonyl catalyzed reaction of amides with allyl alcohols (equation 631) [670]. Allyl acetates were converted to allyl tosylates by reaction with the sodium salt of tosic acid in the presence of a palladium catalyst (equation 632) [671]. Diphenylamine was oxidatively dimerized to tetraphenylhydrazine by oxygen and a copper(I) chloride-pyridine catalyst [672]. The o-hydrogens of benzoic acid and the β-hydrogens of acrylic acid exchanged with $D_2O$ in the presence of rhodium(III) chloride (equation 633) [673].



$$\mathrm{ArX} + \mathrm{H\text{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(OR)_2} \xrightarrow[\mathrm{Et_3N}]{\mathrm{L_4Pd\ cat.}} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(OR)_2} + \mathrm{Et_3NHX}$$

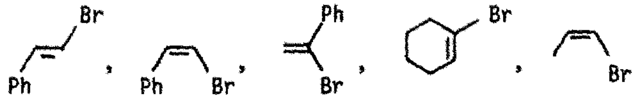
(626)

20 cases - good yields

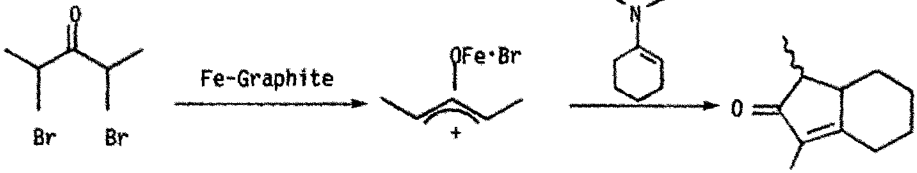


(627)

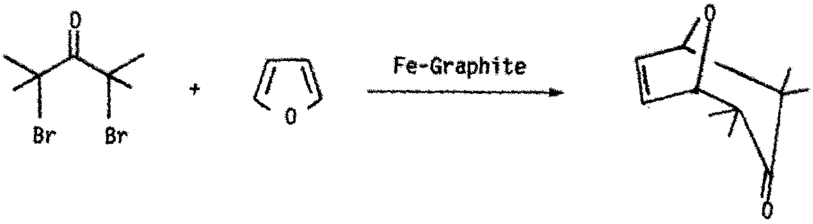
66-99%



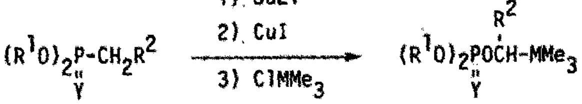
(628)



high yield



(629)



$$\mathrm{(R^1O)_2}\underset{\mathrm{Y}}{\underset{\|}{\mathrm{P}}}\mathrm{\text{-}CH_2R^2} \xrightarrow[\mathrm{3)\ ClMMe_3}]{\substack{\mathrm{1)\ BuLi}\\ \mathrm{2)\ CuI}}} \mathrm{(R^1O)_2}\underset{\mathrm{Y}}{\underset{\|}{\mathrm{P}}}\mathrm{O}\overset{\mathrm{R^2}}{\mathrm{C}}\mathrm{H\text{-}MMe_3}$$

(630)

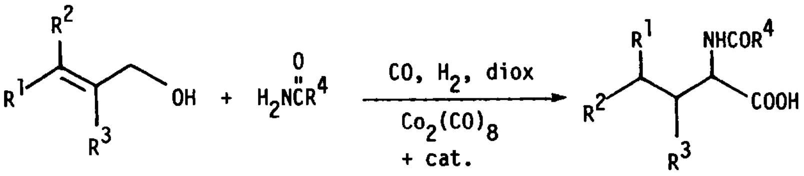
M = Si, Sn

40-80%

Y = O, S

$R^1$ = Me, Et, i-Pr

$R^2$ = H, Me, Et



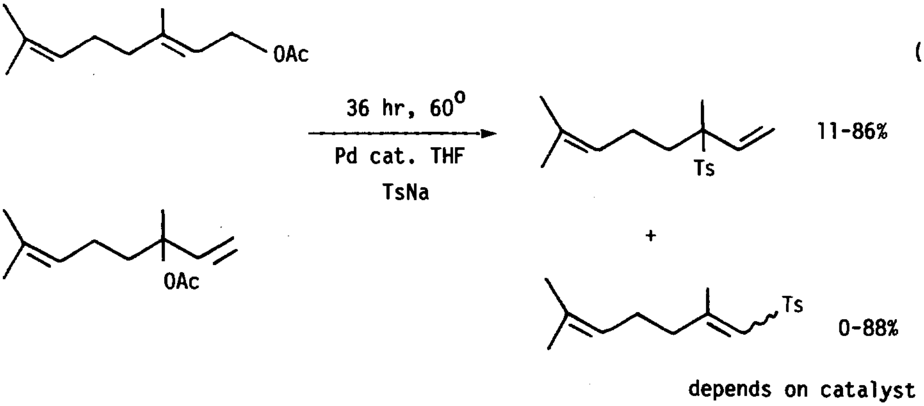
(631)

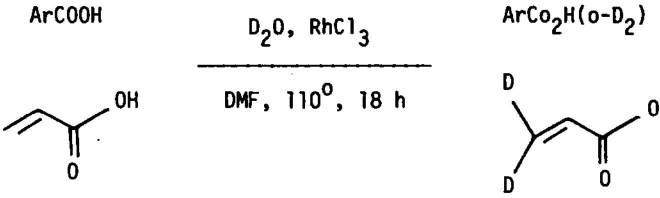
$R^1, R^2, R^3$ = H, Me

$R^4$ = Me, Ph

cat = $HRh(CO)_2L_3$, $Fe_2(CO)_9$, $PdCl_2L_2$, $HRuCl(CO)L_3$

(632)





(633)

VI. Reviews

The following reviews have appeared.

Transition metal chemistry review. [675]

Transformation of organic substrates on metal cluster complexes. (23 references) [676]

Metal-carbon and carbon-carbon bond formation from small molecules and one carbon functional groups. (21 references) [677]

Organometallics in synthesis. Part I. (60 references) [678]

Organometallics in synthesis. Part II. (217 references) [679]

Inorganic enzymes? Transition metal atoms as assembly and control centers in organic synthesis. (2 references) [680]

Metal atoms in synthesis and related aspects. (38 references) [681]

Organometallics in synthesis. (270 references) [682]

Synthetic organic reactions by means of copper complexes. Preparation and characterization of novel copper(I) complexes and their utilization in organic synthesis. (35 references) [683]

Common metals and transition metals - the skill of combining them for organic synthesis. (53 references) [684]

Actinide organometallic chemistry. (62 references) [685]

Transition metals in organic synthesis -- Annual Survey, 1980. (1045 references) [686]

Organometallics in synthesis. (270 references) [687]

Control of metal-catalyzed organic syntheses. Part I. Introduction of models and methods in examples. (40 references) [688]

Organoborates in new synthetic reactions. (71 references) [689]

Transition-metal complexes of organoaluminum phosphides. (Dissertation) [690]

New applications of organotitanium compounds in precision organic synthesis during recent years. (2 references) [691]

Synthetic applications of bis($\eta$-cyclopentadienyl)titanium compounds. (46 references) [692]

Titanium compounds - their application to organic syntheses. (many references) [693]

Organomercurials in organic synthesis. (398 references) [694]

Organomercury, -palladium, -rhodium, and -thallium intermediates in organic synthesis. (39 references) [695]

Organomercurials in organic synthesis. (398 references) [696]

Syntheses using 1,3-dienetricarbonyliron complexes. (27 references) [697]

Cobalt-mediated bond forming and bond breaking reactions: synthetic and mechanistic perambulations. (19 references) [698]

Synthesis and reactions of 2-azidooxiranes. Polymer attachment and cobalt complexes of phosphine macrocycles. (Dissertation) [699]

Cobalt mediated cyclopentanoid synthesis. (Dissertation) [700]

The reaction of alkylcobalt complex. (51 references) [701]

Reactions of alkyl ligands coordinated to cobalamins and cobaloximes. (97 references) [702]

Nickel - a knack of its use. (102 references) [703]

Zerovalent-nickel catalyzed carbon-carbon and carbon-hydrogen bond formation. (Dissertation) [704]

Syntheses of some terpenoids via nickel tetracarbonyl induced cyclization. (11 references) [705]

Rhodium - a knack of its use. (52 references) [706]

Organometallic intramolecular $\pi$-olefin metal coordination complexes. (171 references) [707]

Nucleophilic addition to $\pi$-olefin, $\pi$-allyl, and $\sigma$-alkyl-palladium complexes. Examples of "unpoling" by the use of organometallic reagents. (57 references) [708]

Application of palladium catalysts to natural products syntheses. (26 references) [709]

Palladium - a knack of its use. (39 references) [710]

Some metal-catalyzed reactions of acetylenes and allenes. (Dissertation) [711]

New synthetic method of isocyanates and aliphatic amines. (5 references) [712]

Organic synthesis via catalytic activation of carbon-hydrogen bonds of aromatic compounds by rhodium carbonyls. (25 references) [713]

Copper salt in catalytic reactions of organic compounds. (343 references) [714]

The coordination chemistry of acrylonitrile. (315 references) [715]

The synthetic possibilities of addition reactions between common organometallic compounds and conjugated enzymes. (54 references) [716]

Oxygen transfer from inorganic and organic peroxides to organic substrates: A common mechanism. (145 references) [717]

Electron transfer catalysis applied to organometallics. Part I. Application to the activations of $C_{sp^3}X$ bonds and other $\sigma$ bond species. (439 references) [718]

Recent applications of homogeneous catalysis to organic synthesis. (140 references) [719]

Recent results on the heterogeneous catalytic transformations of carbon compounds. (42 references) [720]

Asymmetric catalysis with transition metal complexes. (33 references) [721]

Asymmetric synthesis catalyzed by transition-metal complexes with functionalized chiral ferrocenylphosphine ligands. (32 references) [722]

Stereoselective synthesis of diastereomeric amino alcohols from chiral aminocarbonyl compounds by reduction or by addition of organometallic reagents. (245 references) [723]

Asymmetric synthesis mediated by transition metal complexes. (82 references) [724]

Some asymmetric syntheses catalyzed by chiral phosphine-transition metal complexes. (40 references) [725]

Organometallic compounds for stereoregulated synthesis of acyclic systems. Their application to the synthesis of the Prelog-Djerassi lactonic acid. (68 references) [726]

Chirality transfer involving organopalladium and organocopper intermediates. (Dissertation) [727]

Synthetic use of heavy metal catalysts in organic chemistry. Asymmetric oxidation. [728]

Asymmetric reaction of olefins with nucleophiles via metal complex. (32 references) [729]

Organometallic aspects of the Fischer-Tropsch synthesis. (48 references) [730]

Metal-carbon and carbon-carbon bond formation from small molecules and one-carbon functional groups. (26 references) [731]

$C_1$ chemistry and metal complex catalyst. II. Hydrogenation of carbon monoxide. (no references) [732]

Structure and reactivity in organometallic chemistry. An applied MO approach. (132 references) [733]

Insertion reactions [of organometallic compounds]. (27 references) [734]

Metal-carbon bond formation and cleavage, including oxidative addition and reductive elimination. (64 references) [735]

Reductive elimination. (17 references) [736]

The cyclometalation of ketones and quinones by alkylmanganese pentacarbonyl complexes: Mechanistic and synthetic studies. (Dissertation) [737]

Metallacyclic pathways in organometallic reactions. (43 references) [738]

Palladium(0) olefin complexes and their role in homogeneous catalyses by way of metallacycle intermediates. (31 references) [739]

The photochemistry of transition-metal organometallic compounds, carbonyls, and low-oxidation-state compounds. (150 references) [740]

Novel reduction and oxidation using transition metal salts. (38 references) [741]

Oxidation of organometallic compounds by transition-metal salts. (244 references) [742]

Carbon monoxide in organic synthesis by organotransition metal complexes. (57 references) [743]

Activation of alkyl halides by $d^8$ complexes. Complex-metal nucleophilic catalysis. [744]

Cycloaddition reactions of transition metal-$\eta^1$-allyl, -propargyl, and related complexes. (69 references) [745]

Metal-assisted terpenoid synthesis. (103 references) [746]

$\pi$-Cyclopentadienyl, $\pi$-arene, and related complexes. (382 references) [747]

Catalytic aromatization reactions of low-molecular-weight olefins and alkanes. (24 references) [748]

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