TRANSITION METALS IN ORGANIC SYNTHESIS - CARBON-CARBON BOND FORMING REACTIONS AND FUNCTIONAL GROUP PREPARATIONS

ANNUAL SURVEY COVERING THE YEAR 1981 *

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CONTENTS

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*See also the article by L. Markó, p. 309; Previous review see J. Organometal. Chem., 237 (1982) 231-450.

I. General Comments

This annual survey covers the literature for 1981 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.

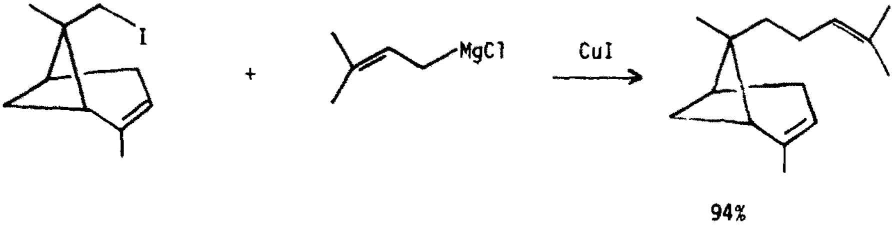
II. Carbon-Carbon Bond Forming Reactions

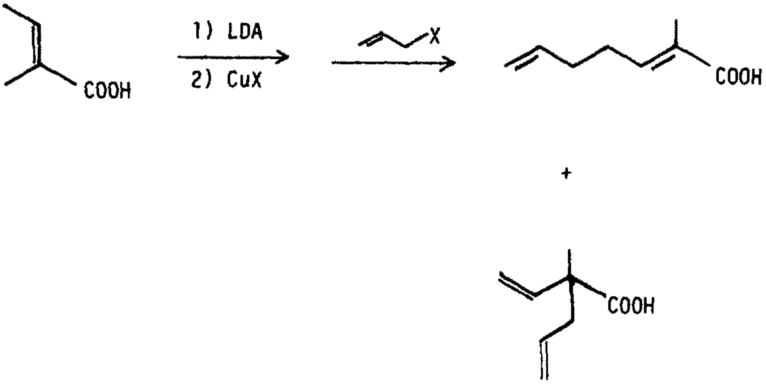
A. Alkylations

1. Alkylation of Organic Halides and Tosylates

Organocuprates continue to figure extensively in the alkylation of organic halides. cis-Bergamotene was synthesized by a copper(I)-catalyzed Grignard alkylation of the appropriate bicyclic halide (equation 1) [1]. The mixed cuprate $[R_2CuCN]Li_2$, prepared from organolithium reagents and copper(I) cyanide, was an effective reagent for the alkylation of normally unreactive secondary halides. Thus, cyclohexyl- and cyclopentyl iodide, and 2-bromo- or iodopentane were alkylated in greater than 80% yield by this reagent (R = Me, Et, n-Bu, n-Pr, vinyl) whereas the corresponding R_2CuLi reagents reacted in less than 20% yield. The $[Ph_2CuCN]Li_2$ failed to alkylate these substrates [2]. Copper tiglates reacted rapidly with allyli halides and tosylates with high γ-specificity. The epoxide underwent allylic transposition. Tiglic and crotonic acid anions were used to prepare 1,5-diene units with an E 2,3 double bond whereas senecioic acid anions gave a Z 2,3 double bond (equation 2) [3]. Aryl halides were alkylated by malonate anions in the presence of copper(I) salts (equation 3) [4]. Organocuprates alkylated aryl- and vinylmercuric halides in fair to good yield (equation 4) [5]. Chloroisopropylbiphenyls were prepared by the reaction of chloroarylcopper complexes with aryl iodides in pyridine (equation 5) [6]. Allenic copper species alkylated acetylenic iodides cleanly, whereas dialkyl cuprates gave extensive halogen-metal exchange (equation 6) [7]. Mono-copper(I) reagents were used to couple α-halosulfones with (E) and (Z)-2-iodo-1-sulfonylalkenes [8].

(1)





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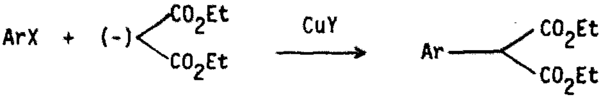


$$\mathrm{ArX} + (-)\!<\!\begin{matrix}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{matrix} \xrightarrow{\mathrm{CuY}} \mathrm{Ar}\!-\!<\!\begin{matrix}\mathrm{CO_2Et}\\ \mathrm{CO_2Et}\end{matrix} \qquad (3)$$

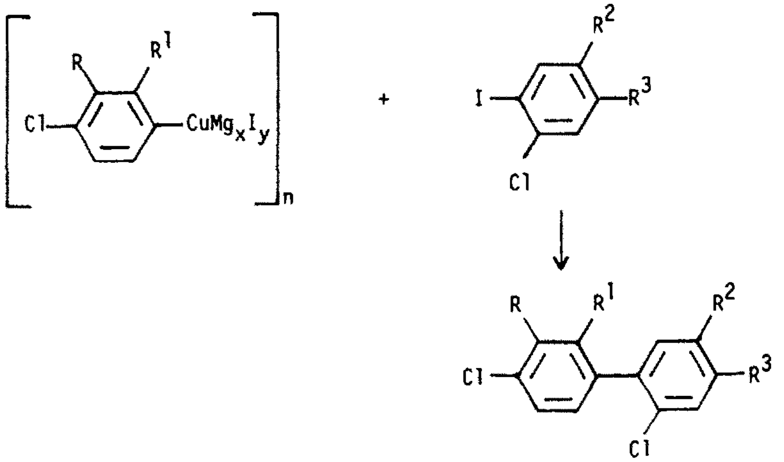
40-90% conversion

40-96% yield

Ar = Ph, o-tolyl, p-tolyl, o-OMe, p-OMe, o-NO_2, p-NO_2, o-CO_2Et, p-CO_2Et, o-Br, α-naphth

$$\mathrm{ArHgCl} + \mathrm{Li_2Cu(Me)_3} \longrightarrow \xrightarrow{\mathrm{CH_3I/O_2}} \mathrm{ArCH_3} \qquad 65\text{-}92\% \qquad (4)$$

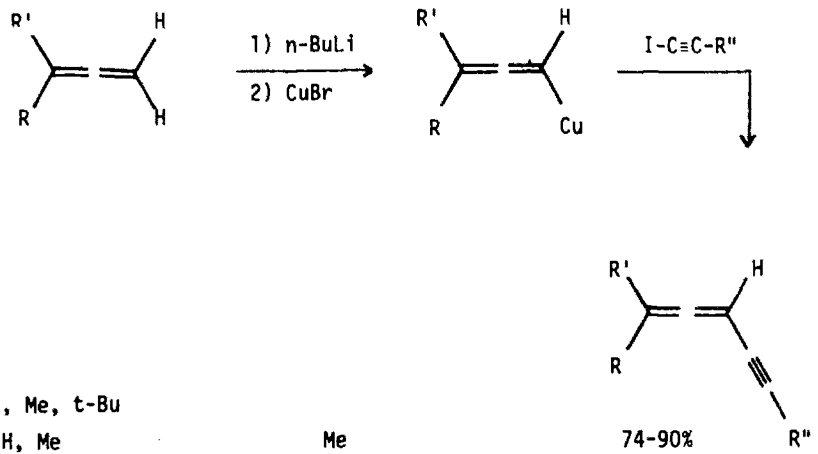
(5)



R's = H, i-Pr

24-50%

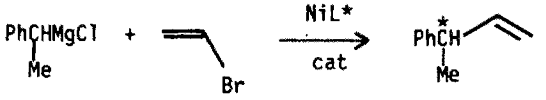
(6)



74-90%

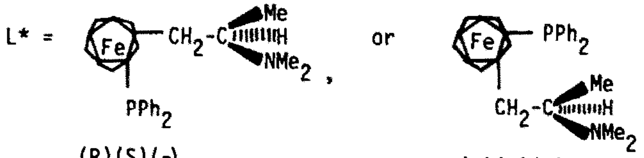
R = H, Me, t-Bu
R' = H, Me
R" = TMS, Ph, Me, H, MeC≡C, $\mathrm{H_2C{=}\overset{Me}{C}}$-

Two new chiral ferrocenylphosphines were studied as ligands for the metal-catalyzed cross-coupling of Grignard reagents with vinyl halides (equation 7). However, only low optical yields were obtained [9]. In a similar reaction, up to 67% ee was realized using a nickel(II) (-)norphos catalyst (equation 8) [10]. Halobenzenes were cross-coupled to sec-butyl Grignard reagents using chiral diphosphine ligands to give (R) or (S) 2-phenylbutenes [11]. Racemic Grignard reagents were kinetically resolved by reaction with less than one equivalent of a vinyl halide in the presence of a chiral nickel(II) catalyst (equation 9) [12]. Alkylation of a chiral vinyl bromide with methyllithium in the presence of cobalt, iron, and nickel catalysts went predominantly with retention of configuration (equation 10) [13]. Arylmagnesium halides alkylated allylic halides in the presence of nickel(II) and palladium(II) catalysts. The regiochemistry was independent of the starting halide, but was a function of the catalyst (equation 11) [14]. 2-Substituted butadienes were prepared by the palladium(0) or copper(I) catalyzed coupling of the corresponding vinyl Grignard reagent with aryl or alkyl halides (equation 12) [15].



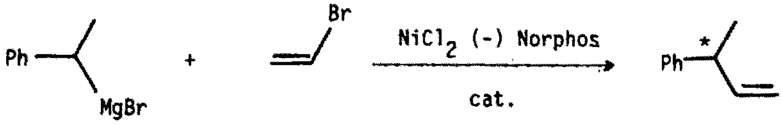
(7)

77-88% yield
14% ee



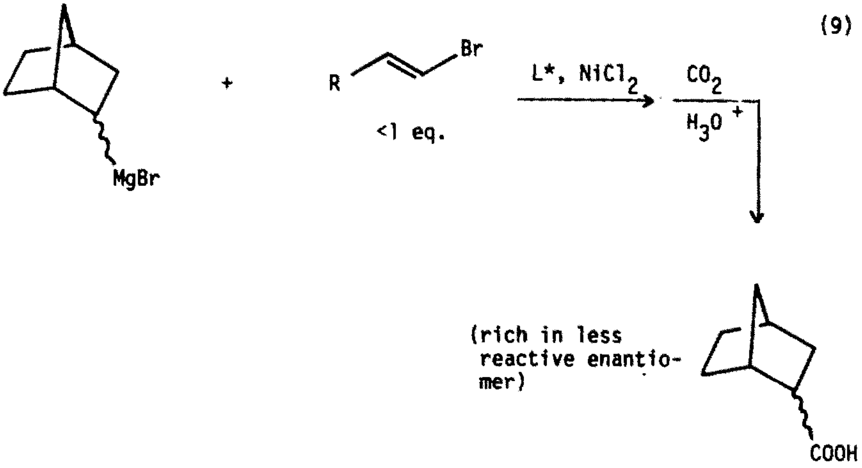
(R)(S)(-) (R)(R)(+)

(8)

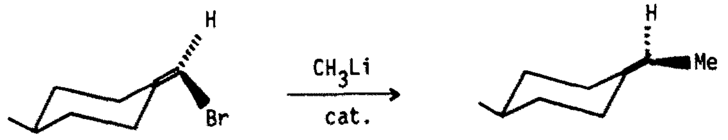


(S) 95% yield
67% ee

(9)



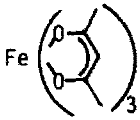
(rich in less reactive enantiomer)



(10)

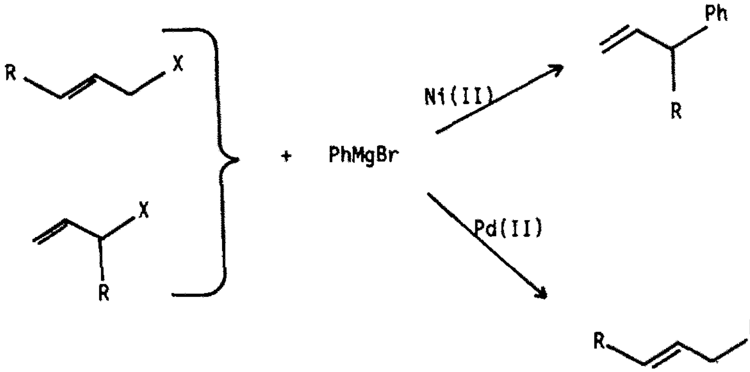
cat. = L_2CoCl_2 89% retention

$NiCl_2$ diphos 91% retention



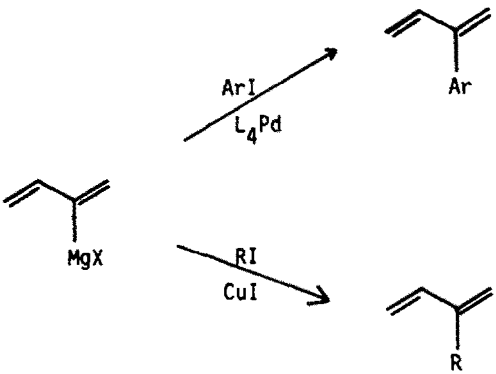
96% retention

AgBr racemic



(11)

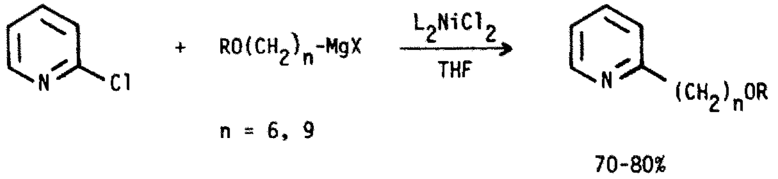
(12)



Ar = $PhCH_2$, p-tolyl, Ph,
p-OMePh 40-75%

R = n-hex, n-oct, n-dec, n-C_{16}

Grignard reagents alkylated 2-chloropyridines (equation 13) [16] and haloisoquinolines (equation 14) [17] in the presence of <u>bis</u> phosphinenickel(II) catalysts. Palladium(0) catalyzed the alkylation of allenyl and propargyl halides by alkylzinc reagents (equations 15 and 16) [18], vinyl halides by Reformatsky reagents (equation 17) [19], and iodopyrimidines by alkynyl zinc complexes (equation 18) [20]. Gemdihalides were cleanly methylated by methyltitanium complexes (equation 19) [21]. Benzyl halides, tertiary ethers, and aldehydes and ketones also reacted with these reagents.



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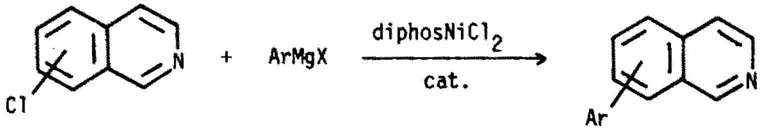
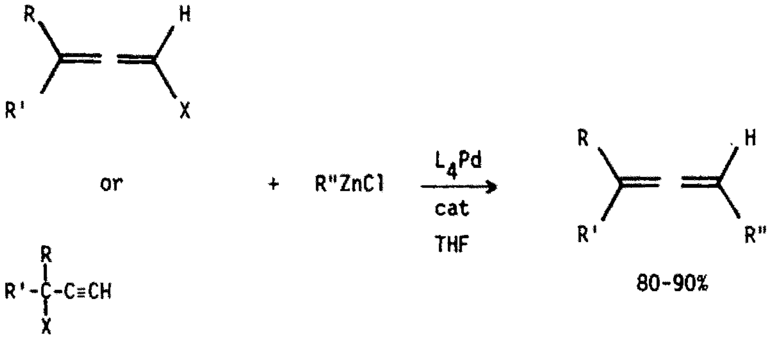


(14)



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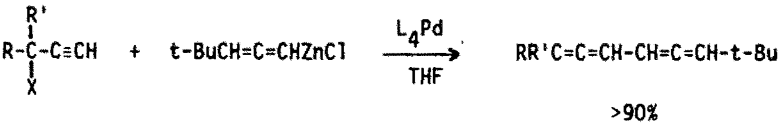
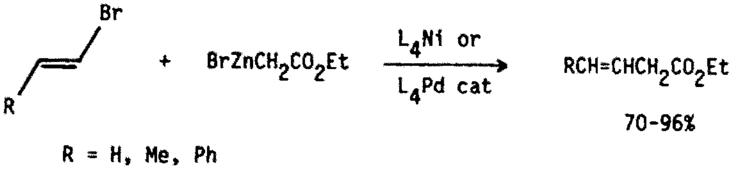


$$R\text{-}\overset{\overset{\large R'}{|}}{\underset{\underset{\large X}{|}}{C}}\text{-}C{\equiv}CH \;+\; t\text{-}BuCH{=}C{=}CHZnCl \xrightarrow[\text{THF}]{L_4Pd} RR'C{=}C{=}CH\text{-}CH{=}C{=}CH\text{-}t\text{-}Bu$$

>90%

(16)



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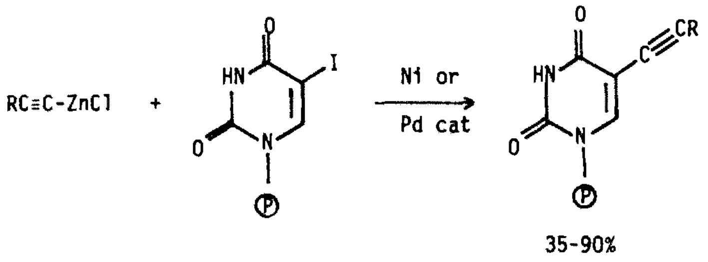

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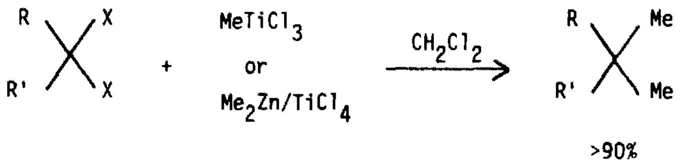
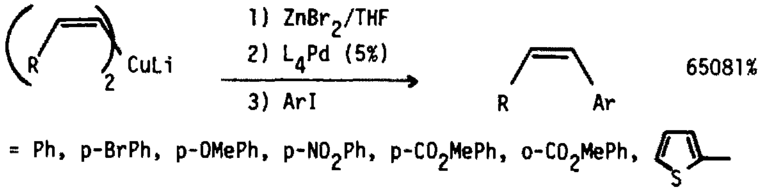


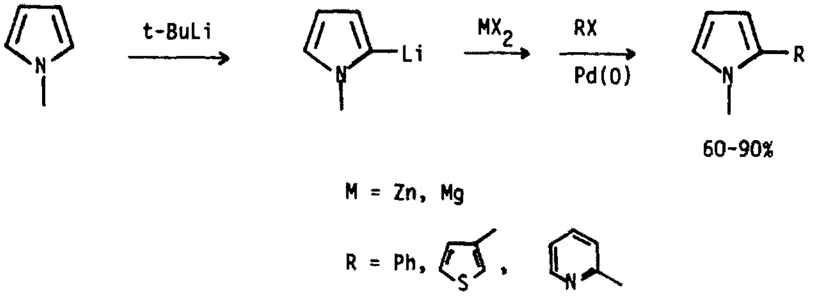
(19)

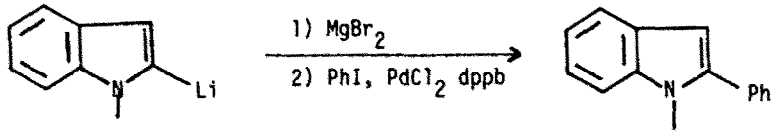
Transmetallation reactions are becoming increasingly important in organic synthesis. Aryl iodides were alkylated by vinyl cuprates through transmetallation to zinc, then to palladium (equation 20) [22]. Pyrroles were lithiated, then transmetallated to zinc or magnesium, and the resulting reagents alkylated heteroaromatic halide in the presence of a palladium catalyst (equation 21) [23]. Indoles behaved in a similar fashion (equation 22). 1,3-Dienes were synthesized by the reaction of vinyl cuprates with vinyl halides in the presence of zinc chloride and a palladium(0) catalyst (equation 23) [24]. Benzylzinc halides alkylated vinyl halides in a similar manner (equation 24) [25]. Organozinc reagents alkylated allylic substrates in the presence of palladium(0) catalysts (equation 25) [26]. Aryl phosphonates were alkylated by organometallics in the presence of nickel catalysts (equation 26) [27]. Enol ether phosphonates reacted in a similar manner (equation 27) [28]. This formed the basis for a clever ketone transposition procedure (equation 28) [29].



(20)

(21)

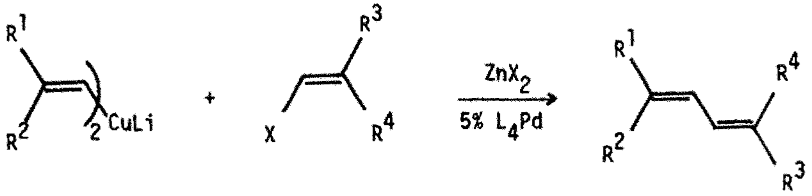




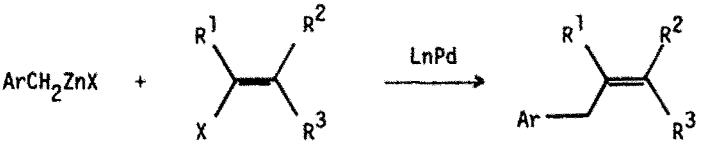
79%

(22)

(23)

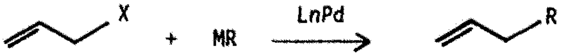


82-94%
>97% isomeric purity



~90%

(24)

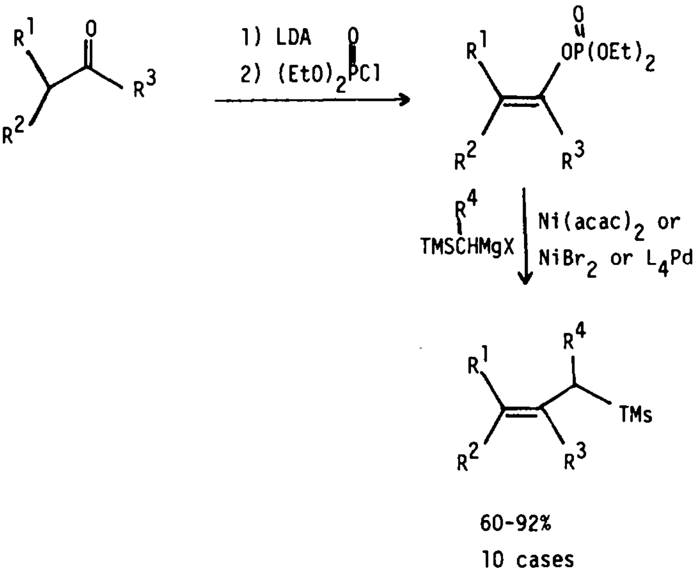


(25)

X = Cl, Br, I, OAc > $OAlR_2$ > $OPO(OR)_2$ > $OSiR_3$
M = Zn

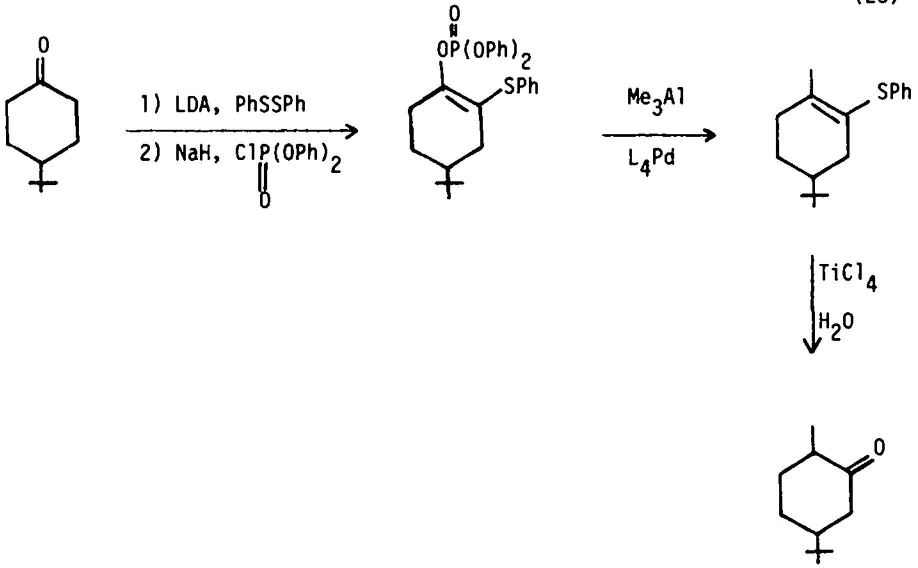
$$ArOH \longrightarrow ArOPO(OEt)_3 \xrightarrow[\text{[Ni]}]{RM} ArR \qquad (26)$$

[Ni] = $Ni(acac)_2$, $NiCl_2L_2$, $NiCl_2$dppb
RM = $TMSCH_2MgCl$, ArMgCl, $PhCH_2MgCl$, n-BuMgCl, Et_3Al,

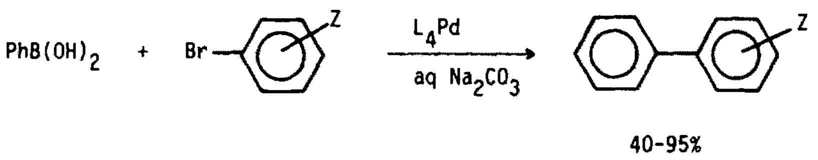


(27)

(28)



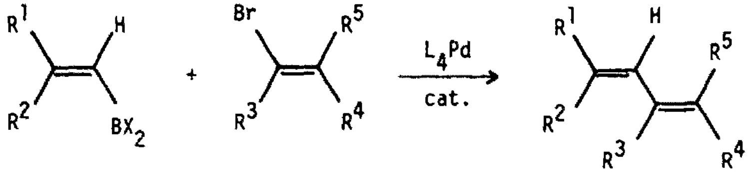
The ability to transmetallate from boron to palladium was a major advance in this area. Biphenyls were formed by the palladium(0) catalyzed coupling of aryl borates with aryl halides (equation 29) [30]. Dienes formed similarly from vinyl boranes and vinyl halides (equation 30) [31]. The regiochemistry of the reaction depended on the conditions (equation 31) [32]. Palladium-catalyzed reactions of organic halides with organotin compounds, to result in carbon-carbon bond formation, has been reported [33].



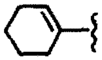
(29)

Z = Me, Cl, naphth

(30)



42-86%
>98% isomeric purity

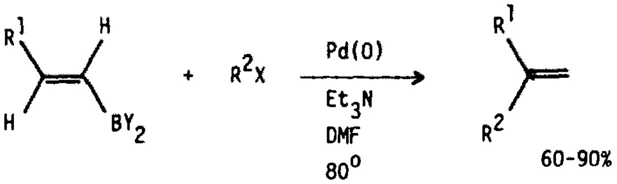
R^1 = n-Bu, H, Ph,


R^2 = H, Bu

R^3 = H, Ph

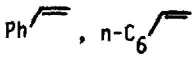
R^4 = H, Ph

R^5 = Ph, H, n-hex



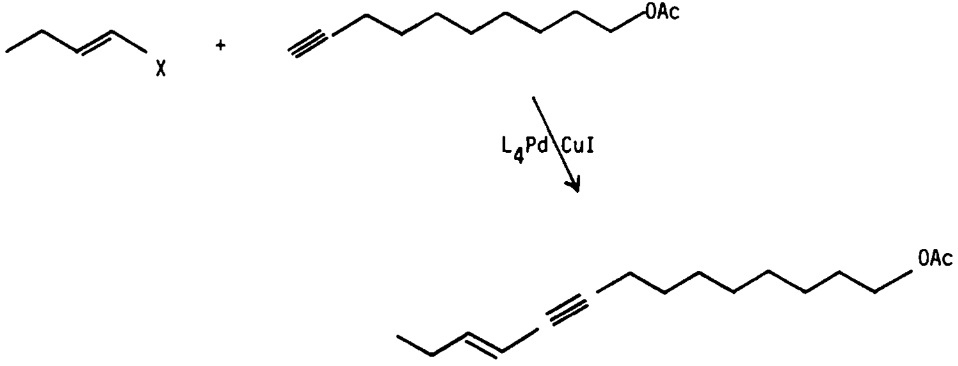
(31)

R^1 = n-Bu, Ph, n-hex

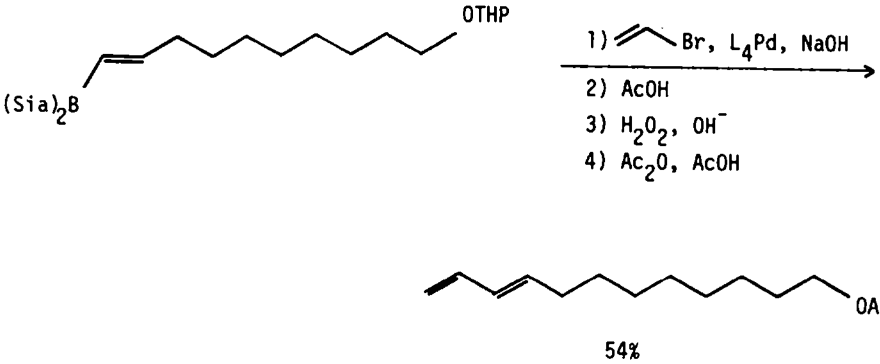
R^2 = Ph,


The sex pheremone of the Egyptian cotton leafworm was synthesized in a process the key step of which was the palladium(0) catalyzed coupling of a vinyl halide with a copper acetylide (equation 32) [34]. Dienes (equation 33) and enynes (equation 34) were prepared by related coupling reactions of vinyl halides with vinyl silanes or acetylenic Grignard reagents [35]. 5-Iodouracil was alkylated by copper acetylides in the presence of palladium catalysts (equations 35 and 36) [36].

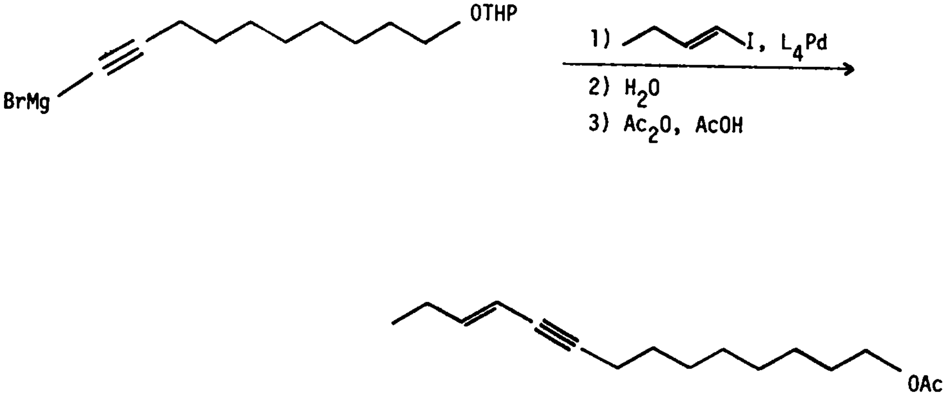
(32)

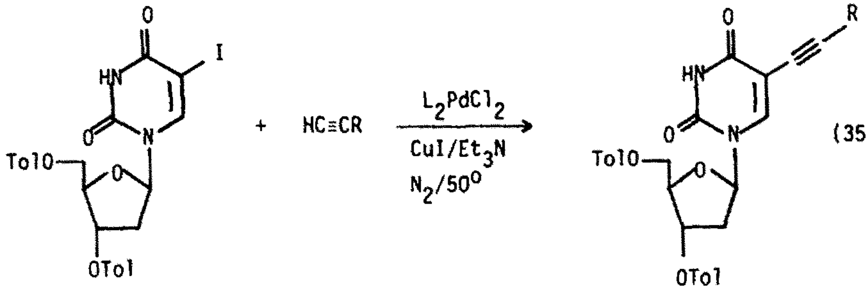

X
+
OAc
L4Pd
CuI
OAc

(33)


OTHP
(Sia)2B
1) Br, L4Pd, NaOH
2) AcOH
3) H2O2, OH−
4) Ac2O, AcOH
OAc
54%

(34)

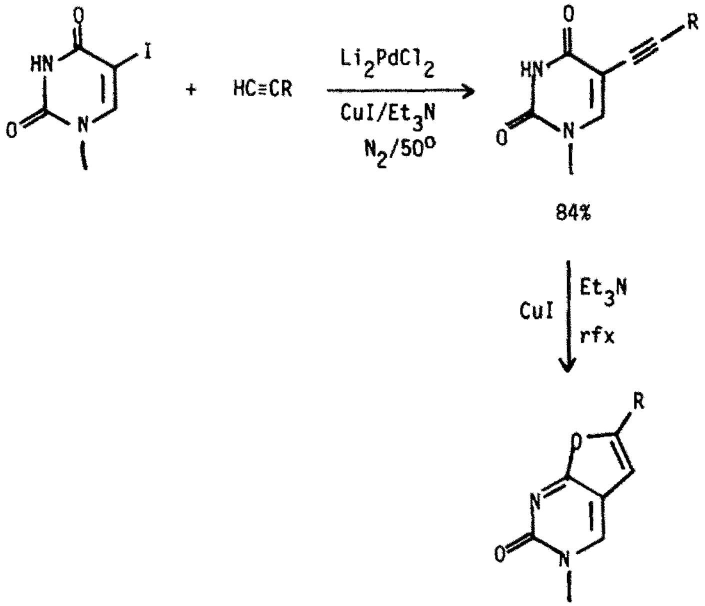

OTHP
BrMg
1) I, L4Pd
2) H2O
3) Ac2O, AcOH
OAc



(35)

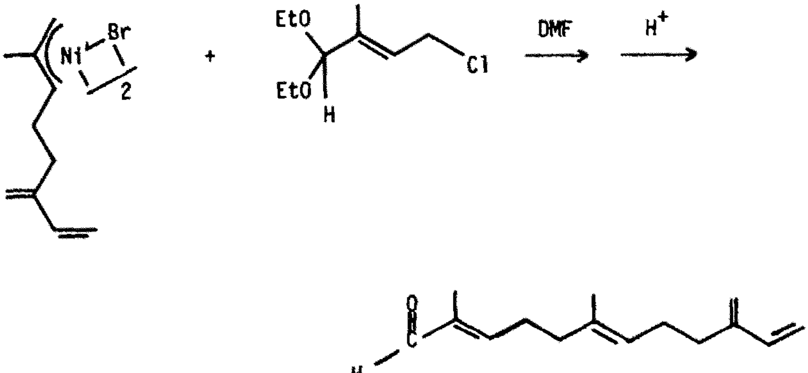
77-91%

R = Et, n-Pr, n-Bu, t-Bu, TMS, Ph, THPOCH$_2$,
n-C_2H_4O-Tol, n-C_3H_6OTol



(36)

β-Sinesal was synthesized by the alkylation of an allylic halide with a π-allylnickel halide complex (equation 37) [37].



(37)

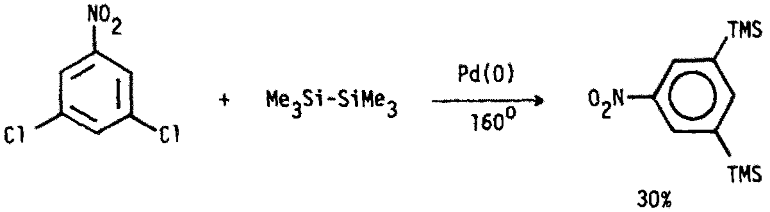
50%

Organomercuric halides were alkylated by alkylrhodium(III) complexes stoichiometrically (equation 38) [38]. Hexamethyldisilane silylated chloronitro aromatics in the presence of palladium(0) catalysts (equations 39 and 40) [39]. Benzylnitriles were alkylated by alcohols in the presence of ruthenium hydride catalysts in a process that involved catalytic transfer hydrogenation and proceeded via the aldehyde of the alcohol (equation 41) [40]. Isoprenyl cobalt complexes alkylated bromomalonates in fair yield (equation 42) [41]. Iron pentacarbonyl initiated the addition of vinyl chloride to diethyl dichloromalonate [42].

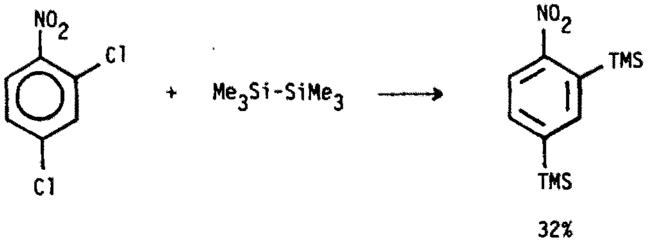
$$RRhX_2L_n \quad + \quad R'HgX \longrightarrow \underset{91\text{-}97\%}{RR'} \qquad (38)$$

R' = , Ar, t-BuC≡C

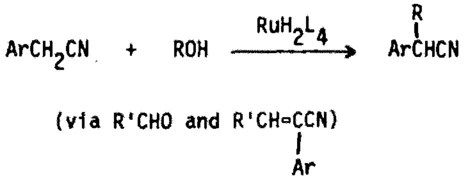
R = Me



(39)



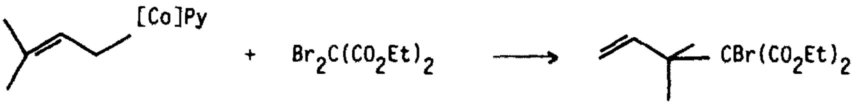
(40)



$$ArCH_2CN \quad + \quad ROH \xrightarrow{RuH_2L_4} Ar\overset{\overset{R}{|}}{C}HCN \qquad (41)$$

$$\text{(via } R'CHO \text{ and } R'CH{=}\underset{\underset{Ar}{|}}{C}CN)$$

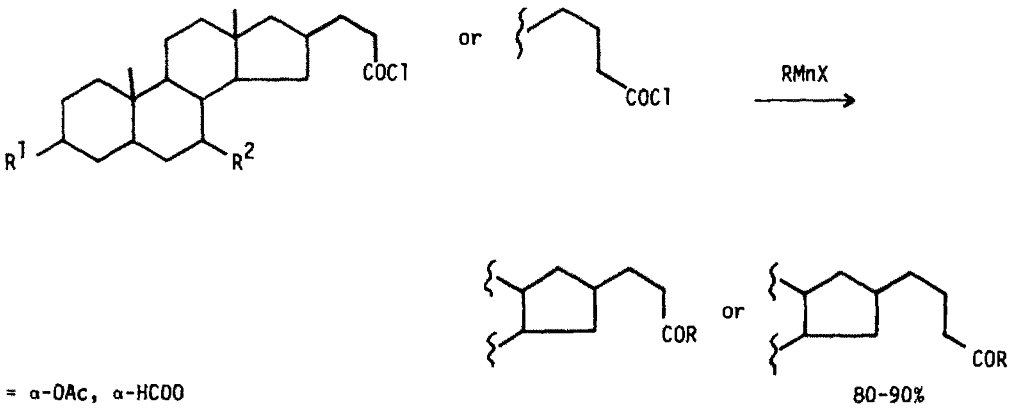
(42)



2. Alkylation of Acid Derivatives

Acid halides were cleanly converted to ketones when treated with a trialkylaluminum/copper(II)(acac)$_2$/triphenylphosphine mixture [43]. Thio esters reacted in a similar manner. Steroidal acid halides were converted to ketones by reaction with alkylmanganese complexes (equation 43) [44]. A cyclopentanone annulation scheme involving the alkylation of an α,β-unsaturated acid chloride with a vinyl copper species has been developed (equation 44) [45]. Macrocyclic conjugated enones were prepared by the palladium-catalyzed alkylation of acid halides by acetylides (equations 45 and 46) [46]. The chromium tricarbonyl complex of N-methylindole was lithiated, then acylated with ethyl chloroformate (equation 47) [47]. A number of activated esters have been converted to ketones by reaction with organometallics (equations 48 [48], 49 [49], and 50 [50]).

(43)

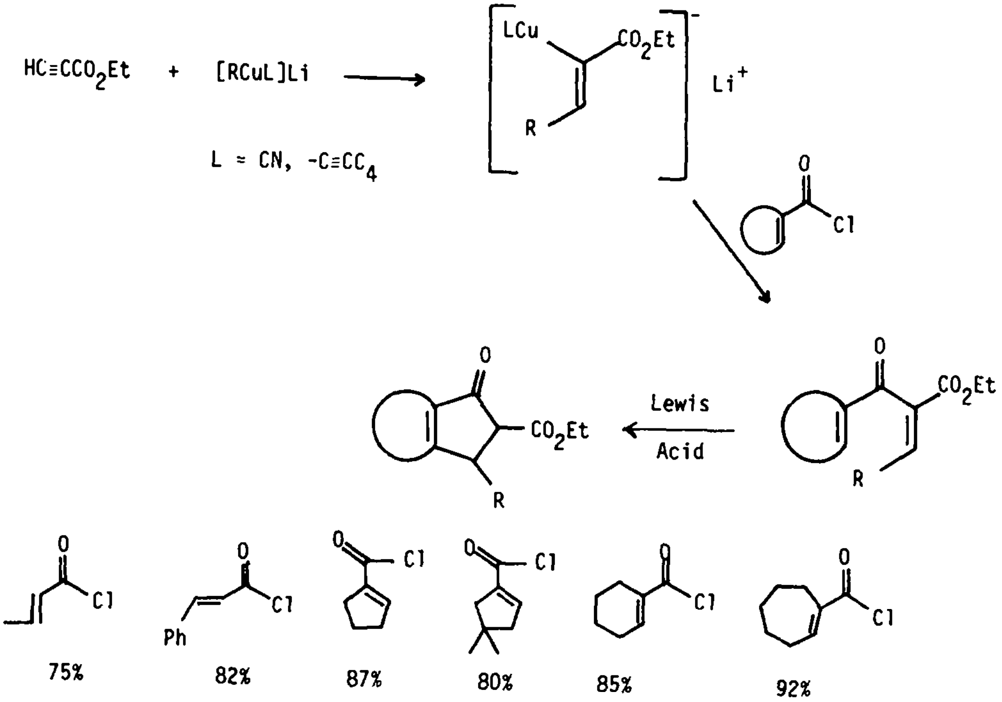


R^1 = α-OAc, α-HCOO

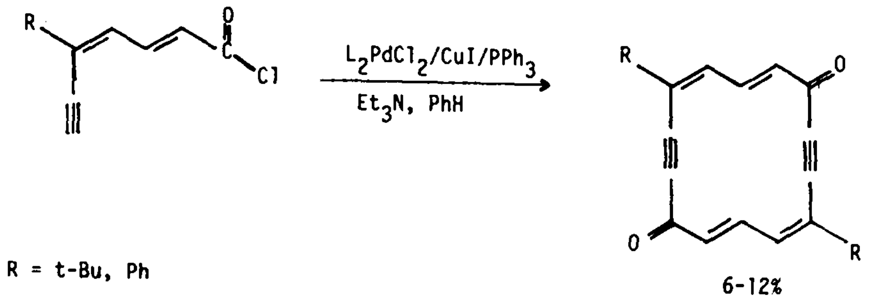
R^2 = α-OAc, β-HCOO, H

R = i-Bu

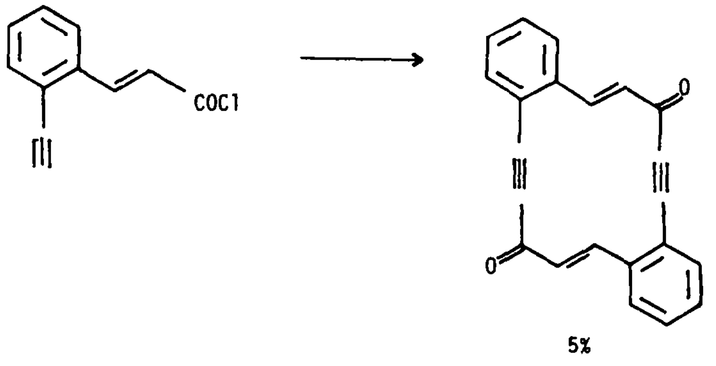
(44)

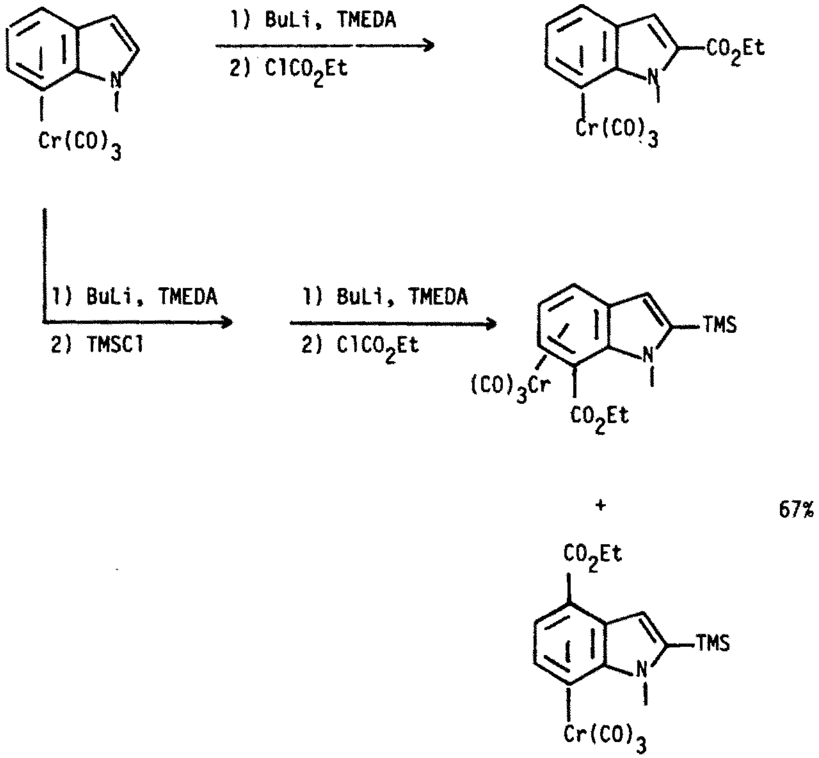

$HC\equiv CCO_2Et$ + [RCuL]Li
L = CN, $-C\equiv CC_4$
LCu
CO_2Et
R
Li^+
O
Cl
Lewis
Acid
CO_2Et
R
O
Cl
Ph
75%
82%
87%
80%
85%
92%

(45)

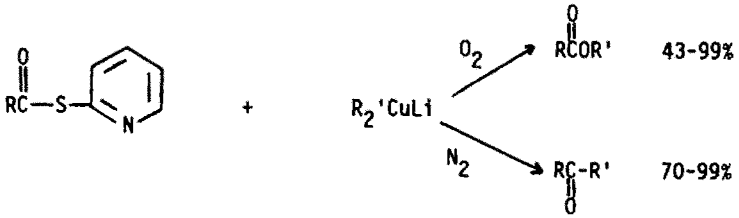

R
O
C
Cl
$L_2PdCl_2/CuI/PPh_3$
Et_3N, PhH
R
O
O
R
R = t-Bu, Ph
6-12%

(46)


COCl
O
O
5%

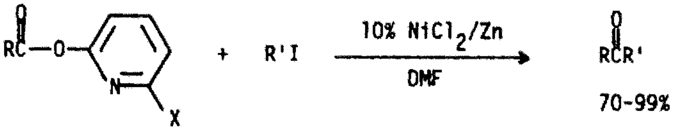


(47)

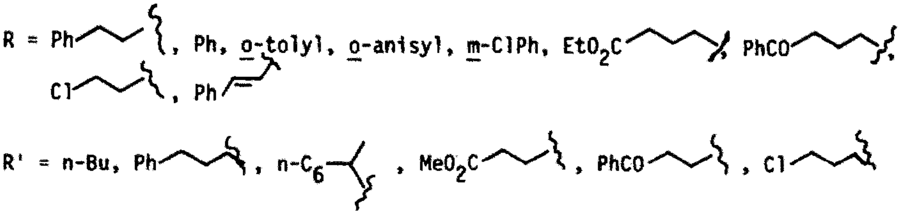


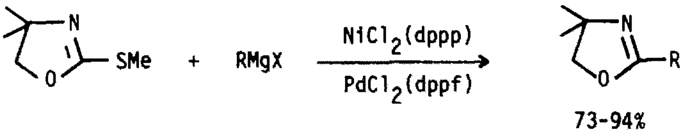
(48)

R = Ph, PhCH$_2$, n-Bu, i-Pr, t-Bu
R' = Me, n-Bu, t-Bu



(49)





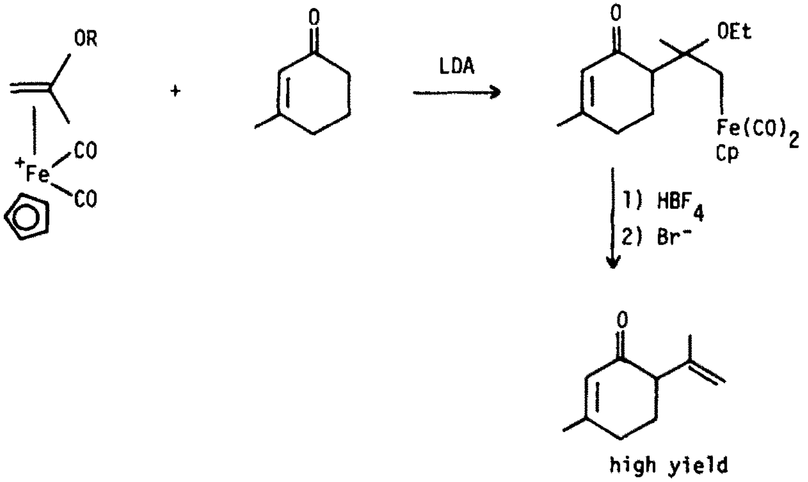
(50)

R = Ph; p-tolyl; p-anisyl; p-EtPh; 3,4-diMePh

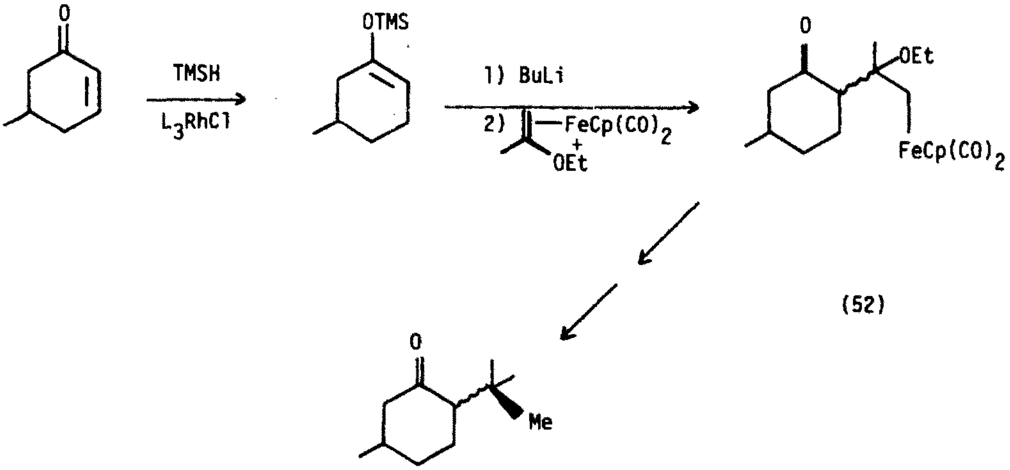
3. Alkylation of Olefins

Several approaches to the direct alkylation of olefins have been developed. The synthetic applications of the chemistry of dicarbonyl cyclopentadienyliron olefin complexes have been reviewed [51]. The cationic dicarbonyl cyclopentadienyliron complexes of enol ethers behaved as vinyl cation equivalents and were used to introduce vinyl groups α to carbonyl groups in ketones (equations 51 and 52) [52]. A synthesis of α-methylene lactones was developed using this chemistry (equation 53) [53].

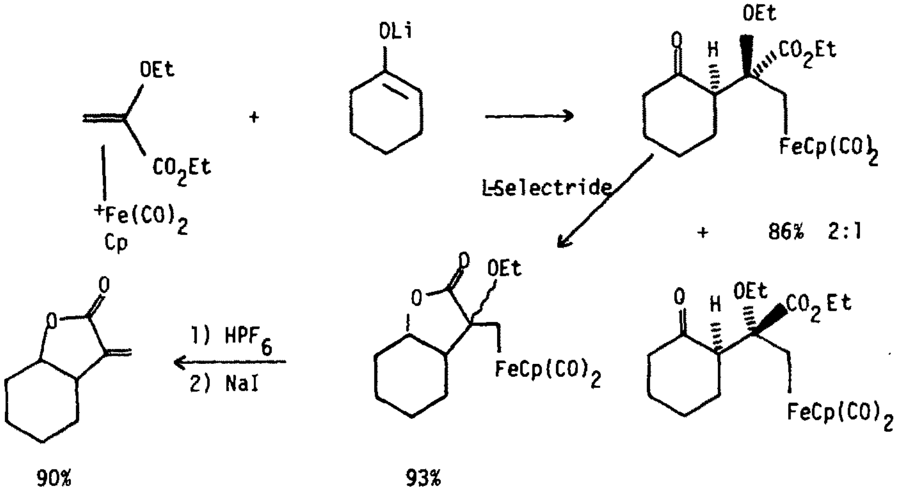
(51)



high yield

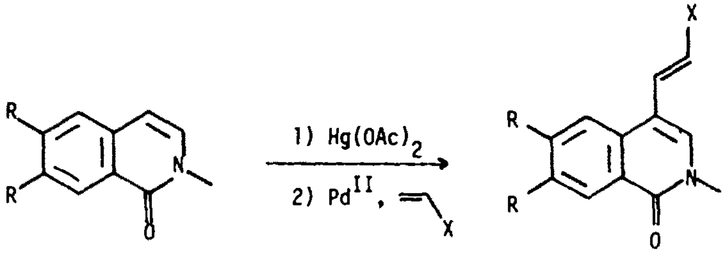


(52)



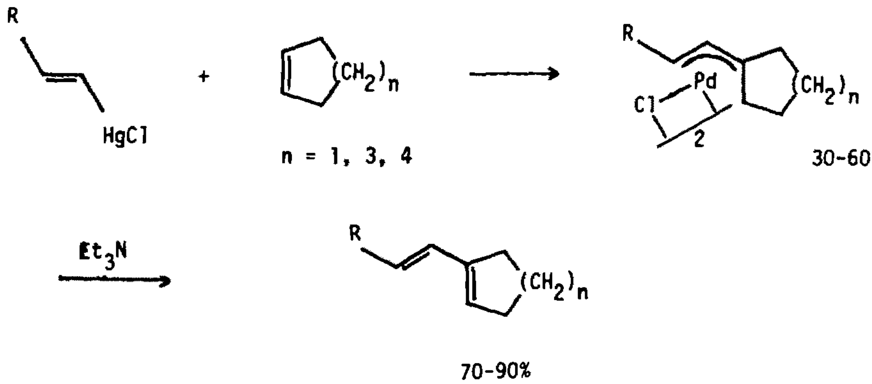
(53)

Olefins have also been alkylated by insertion into palladium-carbon σ-bonds. Mercuration of isoquinolones followed by treatment with a palladium(II) catalyst and an olefin resulted in olefination of the heterocycle (equation 54) [54]. Similar insertion chemistry was used to synthesize cyclic and bicyclic dienes (equations 55 and 56) [55]. Mercurated pyrimidines reacted with enol ethers of protected carbohydrates in the presence of a palladium(II) catalyst to effect coupling (equation 57) [56]. Allylic halides similarly inserted, leading to allylation (equation 58) [57].

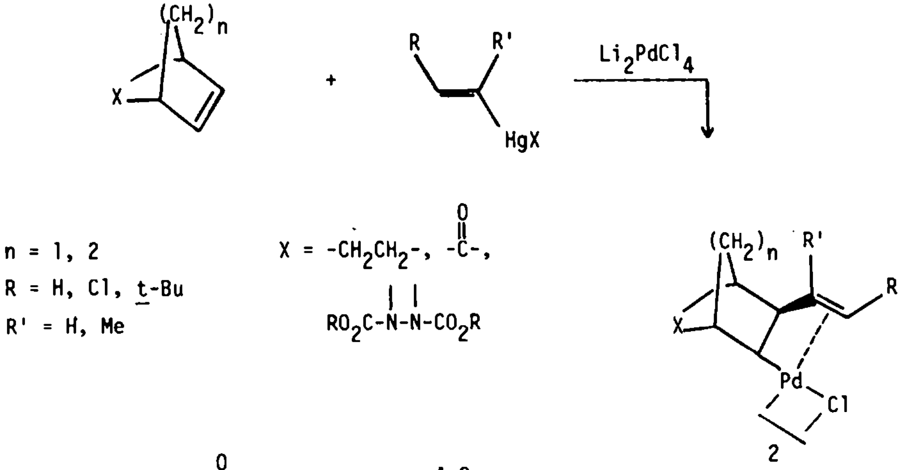


(54)

X = CO_2Me, 75% X = Ph, 57%
X = o-ClPh, 73% X - p-ClPh, 41%
X = 3,4 di OMePh, 3%



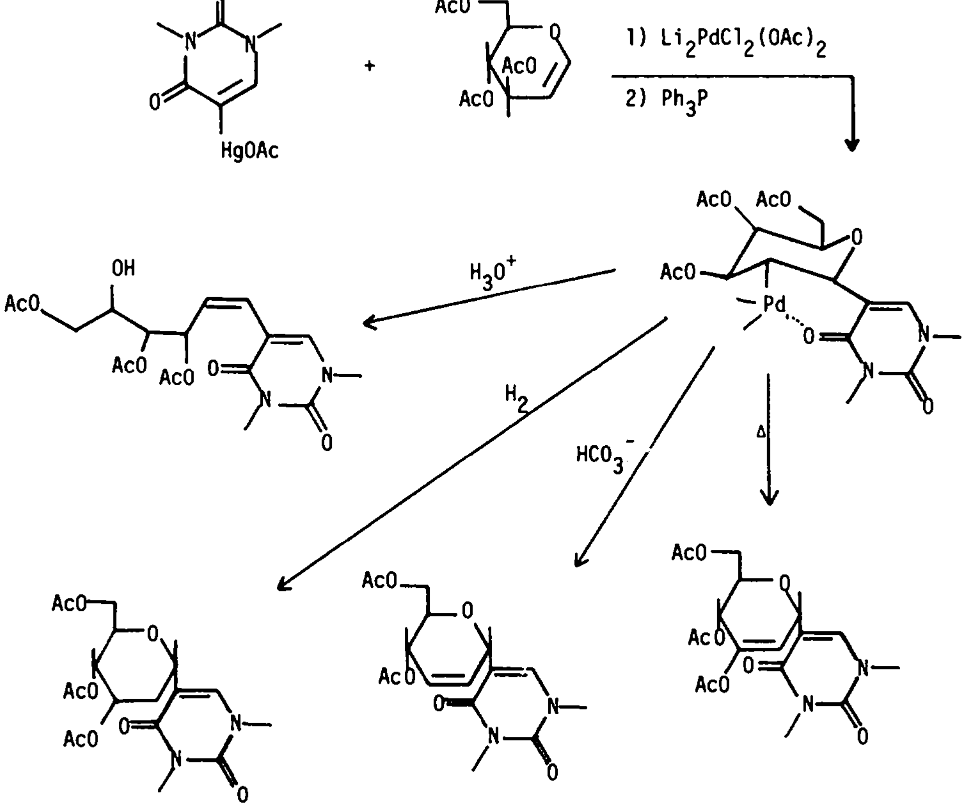
(55)



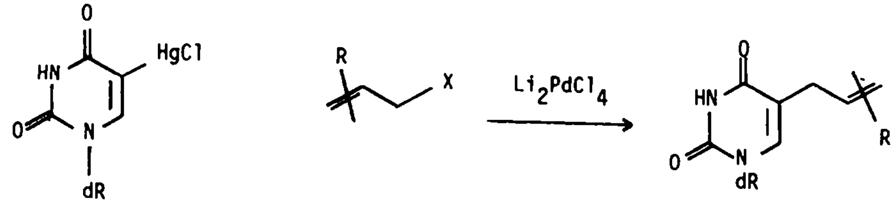
(56)

n = 1, 2
R = H, Cl, t-Bu
R' = H, Me

X = $-CH_2CH_2-$, $-\overset{O}{\overset{\|}{C}}-$,



(57)



(58)

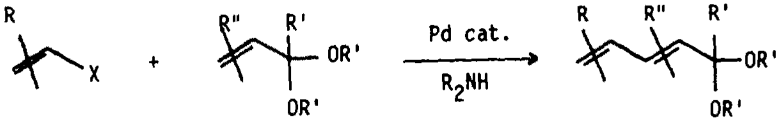
40-70%

dR = deoxyribose

X = Cl, OAc

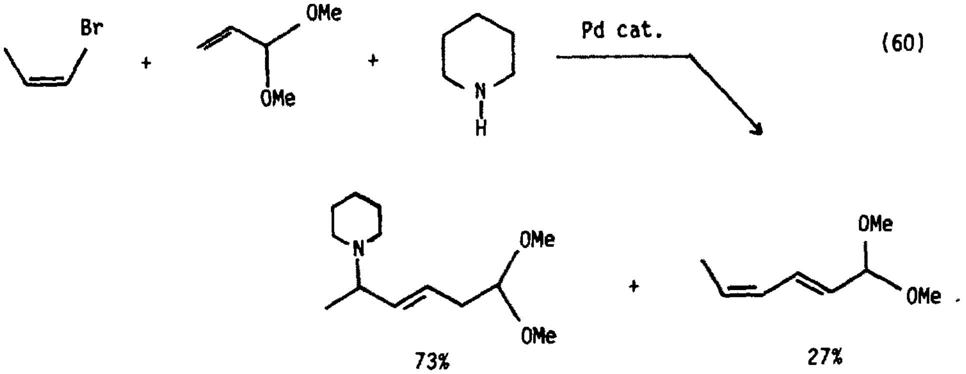
mixed regio + stereoisomer

σ-Alkylpalladium complexes from oxidative addition of organic halides to palladium(0) complexes also insert olefins. Ketals of conjugated ketones and aldehydes reacted with vinyl halides in the presence of palladium catalysts and amines to give dienyl carbonyl compounds (equation 59) [58]. With secondary amines, amination of the diene competed (equation 60). Conjugated acids, esters, amides, and nitriles also reacted with vinyl halides and palladium catalysts to produce dienes (equation 61) [59]. Aryl iodides reacted with allylic alcohols in the presence of palladium catalysts to produce β-aryl ketones by an insertion-elimination process (equation 62) [60]. Allylic carboxylic acids were alkylated by vinyl bromides in the presence of nickel(0) or rhodium(I) catalysts (equation 63) [61]. A macrocyclic lactone containing an α,β,γ,δ-dienone was synthesized using olefin insertion into a vinyl palladium complex as the key step (equation 64) [62]. Enol ethers were arylated by aryl halides in the presence of a palladium catalyst (equation 65) [63]. Aminoalkylphencyclidines were synthesized using similar chemistry (equation 66) [64]. Olefins alkylated cycloheptatrienones in the presence of palladium(0) catalysts (equation 67) [65]. Aryl amines arylated olefins when reacted with t-butylnitrite and palladium catalysts (equation 68) [66]. The vinylation of halogenated organic compounds in the presence of palladium catalysts has been reviewed [67].

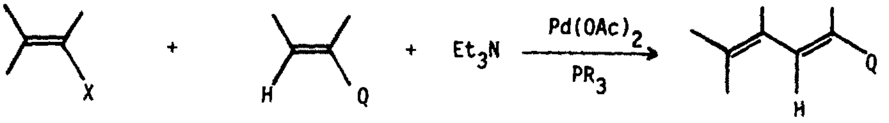


(59)

(22 cases)



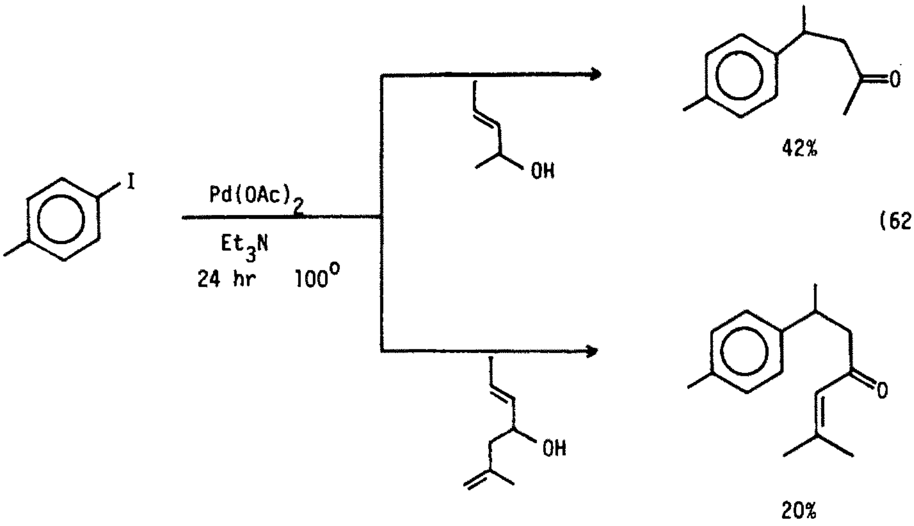
(60)



(61)

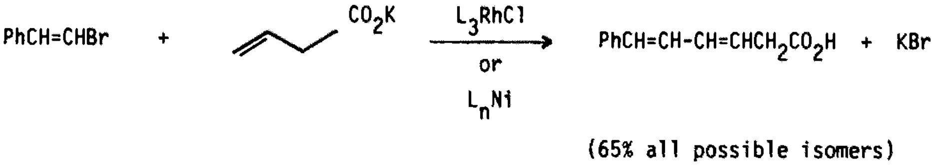
Q = COOH, CO_2Me, $CONH_2$, CN

12 cases

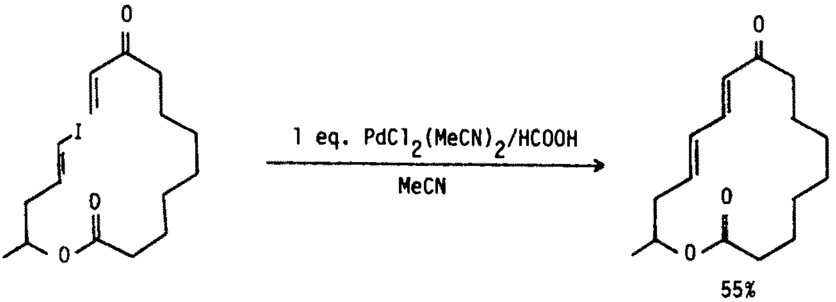

I
Pd(OAc)$_2$
Et$_3$N
24 hr 100°
OH
O
42%
OH
O
20%

(62)

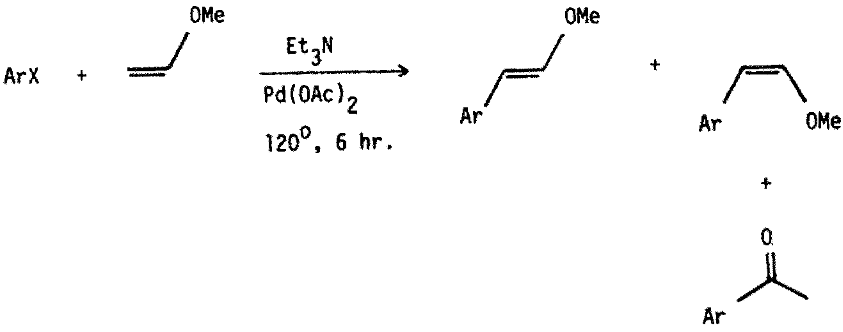
(63)


PhCH=CHBr
+
CO$_2$K
L$_3$RhCl
or
L$_n$Ni
PhCH=CH-CH=CHCH$_2$CO$_2$H + KBr
(65% all possible isomers)

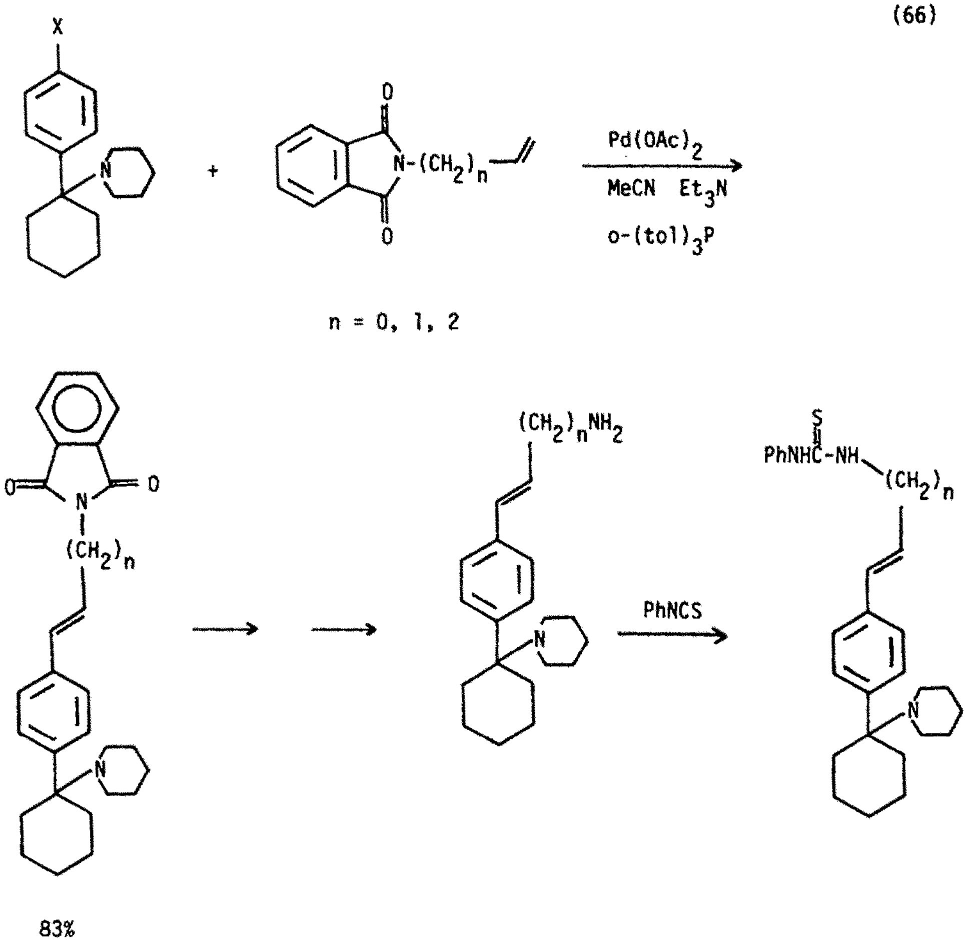
(64)


O
I
O
O
1 eq. PdCl$_2$(MeCN)$_2$/HCOOH
MeCN
O
O
O
55%

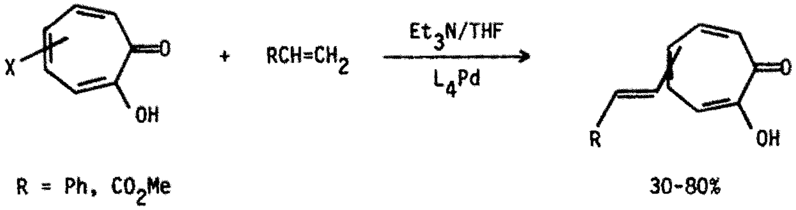
(65)


ArX
OMe
Et$_3$N
Pd(OAc)$_2$
120°, 6 hr.
Ar
OMe
Ar
OMe
O
Ar

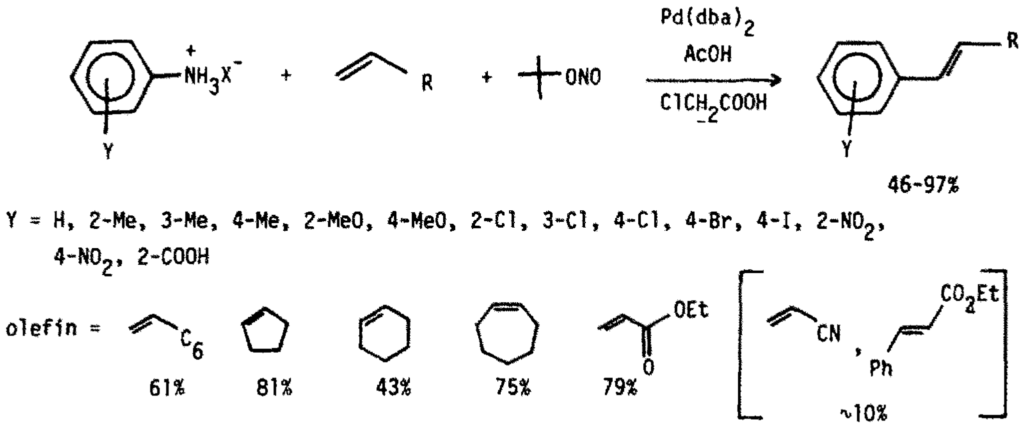
(66)


X
N
O
N-(CH$_2$)$_n$
O
Pd(OAc)$_2$
MeCN Et$_3$N
o-(tol)$_3$P
n = 0, 1, 2
O
N
O
(CH$_2$)$_n$
N
83%
(CH$_2$)$_n$NH$_2$
N
PhNCS
S
PhNHC-NH
(CH$_2$)$_n$
N

(67)

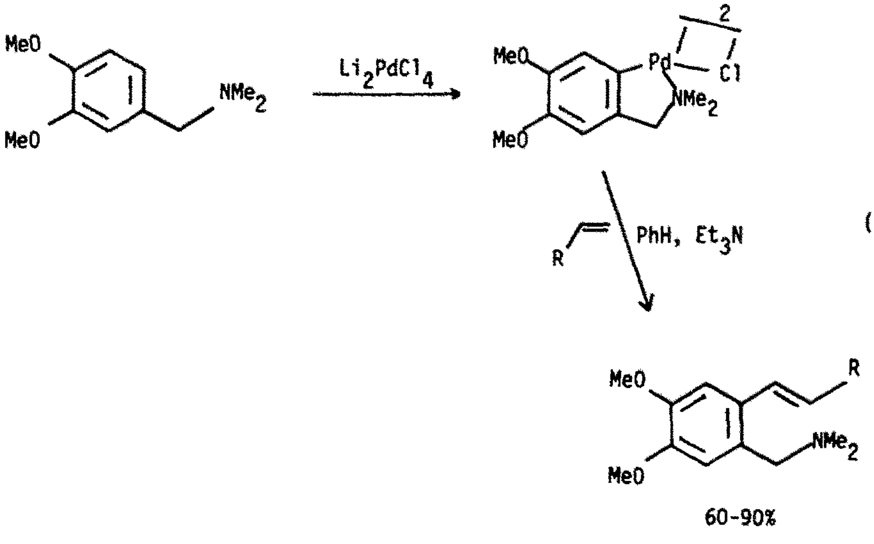

X
O
OH
RCH=CH$_2$
Et$_3$N/THF
L$_4$Pd
R = Ph, CO$_2$Me
R
O
OH
30-80%

(68)



Y = H, 2-Me, 3-Me, 4-Me, 2-MeO, 4-MeO, 2-Cl, 3-Cl, 4-Cl, 4-Br, 4-I, 2-NO_2, 4-NO_2, 2-COOH

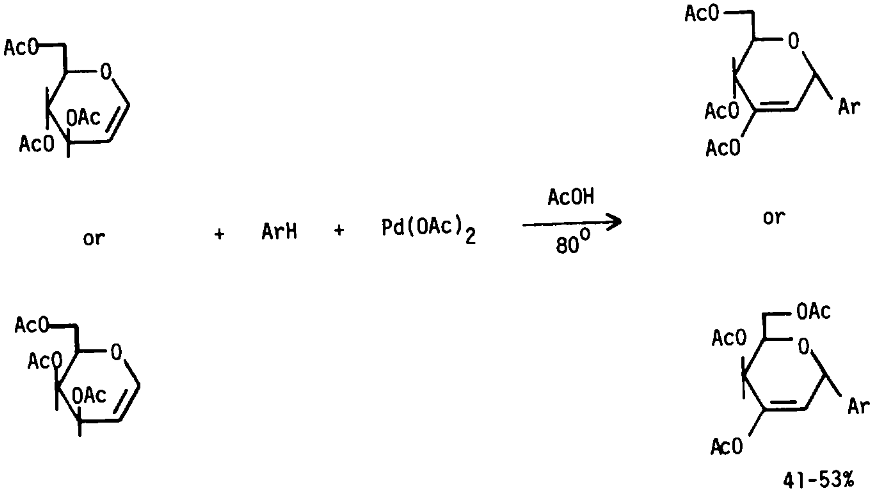
Benzylamines were o-alkylated by orthopalladation followed by olefin insertion (equation 69) [68].



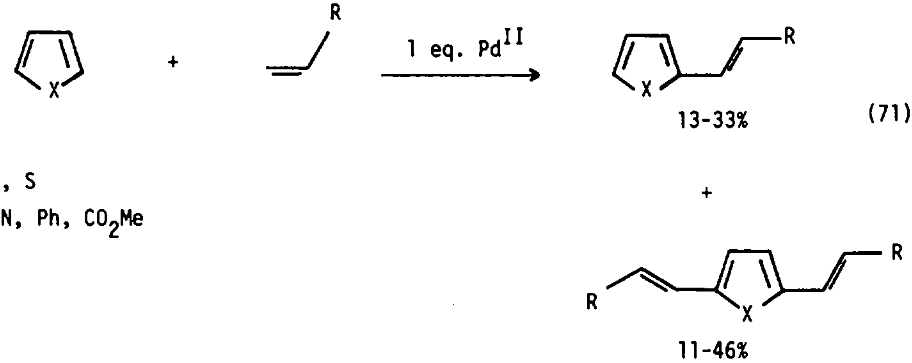
(69)

R = COMe, CO_2Et, Ph, Ar

Arylpalladium complexes are available by direct aromatic substitution (palladation), and these complexes also react with olefins. Benzene arylated protected carbohydrate enol ethers when treated with palladium(II) acetate in acetic acid (equation 70) [69]. Thiophenes and furans were alkylated at the 2-position by olefins under similar conditions (equation 71 [70] and equation 72 [71]). Quinones were arylated under similar conditions (equations 73 and 74) [72].



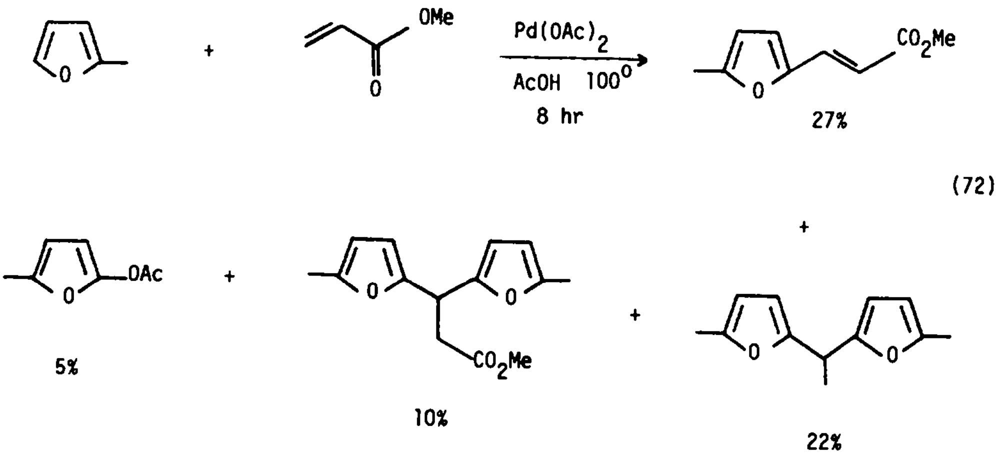
(70)



(71)

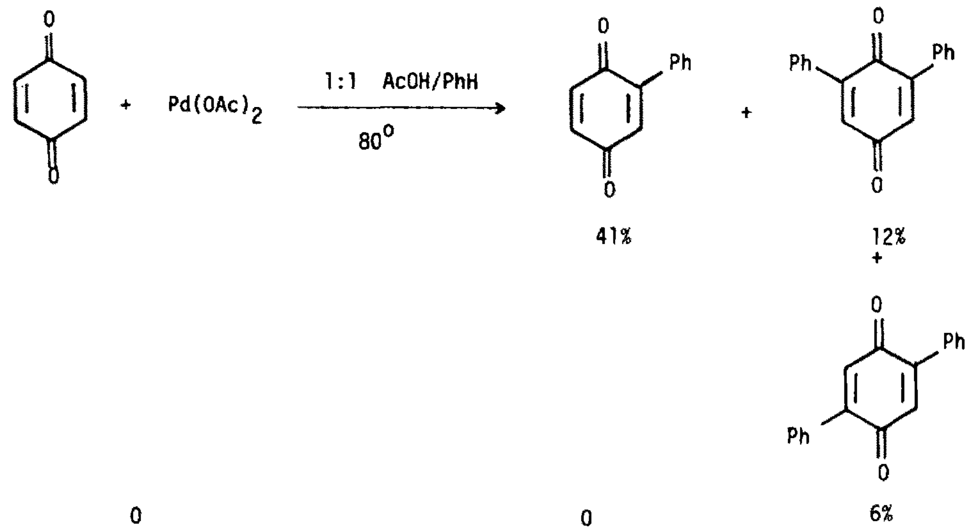
X = O, S

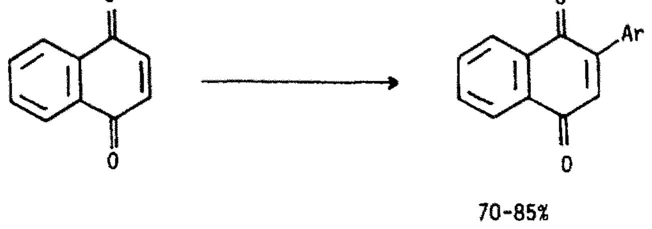
R = CN, Ph, CO_2Me



(72)

(73)

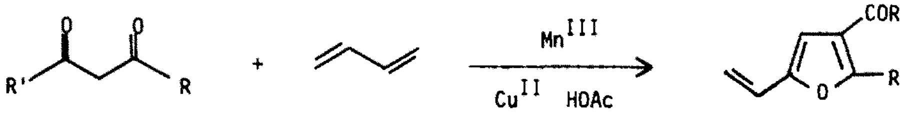




(74)

Olefins were arylated by σ-aryl complexes of platinum(IV) [73]. α-Olefins were β-alkylated by treatment with Et$_2$AlCl/M(OR)$_4$ where M = Ti, Zr, or Hf [74]. Aryl diazonium compounds reacted with 1,3-butadiene in the presence of iron(II) chloride to give 1-phenyl-4-chloro-2-butene as well as compounds containing two diene units [75]. Phenylmagnesium bromide arylated conjugated dienes at the unsubstituted terminal position in the presence of iron(III) salts [76]. Alkenyldihydrofurans resulted from the reaction of 1,3-dicarbonyl compounds with 1,3-dienes in the presence of manganese(III) and copper(II) salts (equation 75) [77].

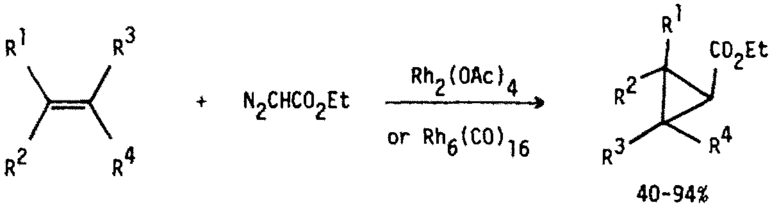
(75)



4. Decomposition of Diazoalkanes, and Cyclopropanation Reactions

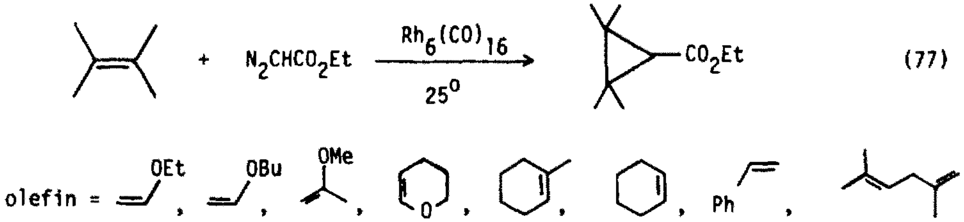
Transition-metal catalyzed decomposition of diazoalkanes to generate reactive "carbenes" continues to be developed as a synthetically useful process. A variety of metals have been used, foremost among them being rhodium. A number of olefins were cyclopropanated by ethyl diazoacetate in the presence of Rh$_2$(OAc)$_4$ or Rh$_6$(CO)$_{16}$

(equation 76 [78] and equation 77 [79]). Alkynes underwent a similar reaction, producing cyclopropenes, which were further transformed (equation 78) [80]. With allylic substrates, a competing "ylid" reaction was observed (equations 79-81) [81]. Twenty-two transition metal complexes were screened as catalysts for these processes [82]. In addition to rhodium and copper complexes, $Ru_3(CO)_{12}$ was found to be an efficient catalyst. With saturated hydrocarbon substrates, insertion into C-H bonds was observed (equation 82) [83]. Arenes were converted to cycloheptatrienes (equation 83) [84]. Terminal olefins were cyclopropanated by diazomethane in the presence of palladium(II) acetate [85].



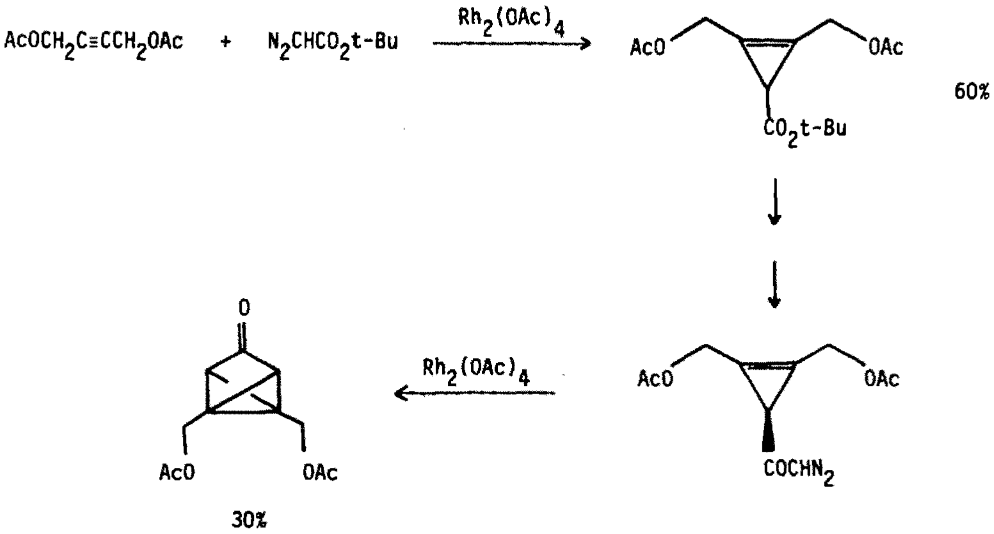
(76)

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

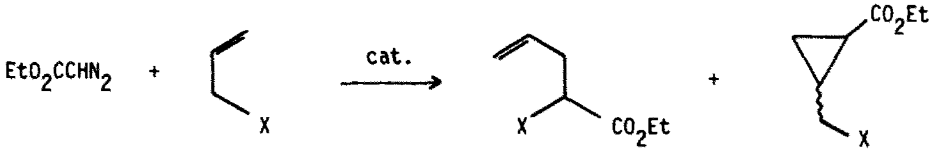


(77)

(78)

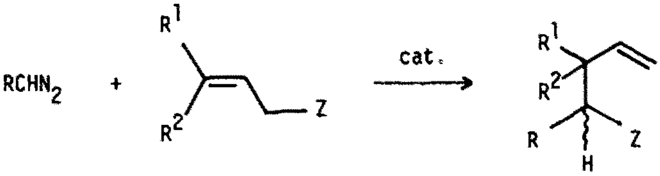


(79)



100	0	X = I
27	73	X = Br
5	95	X = Cl

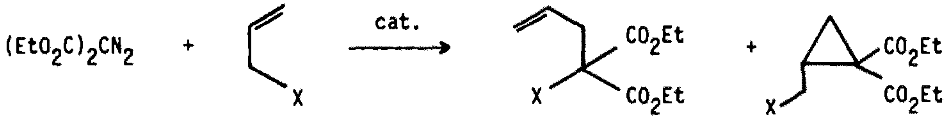
cat = $Rh_6(CO)_{16}$, $Rh_2(OAc)_4$



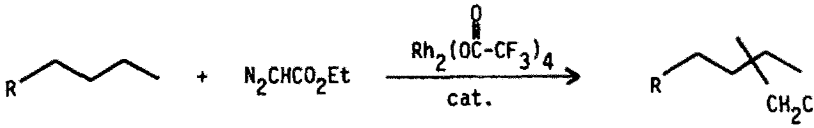
(80)

Z = SMe, 96% R^1 = H, Ph
Z = NMe_2, 82% R^2 = H, Me

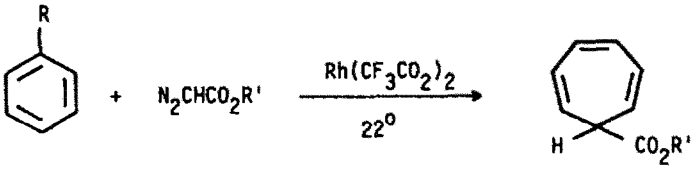
(81)



93	7	X = Br
8	92	X = Cl



(82)

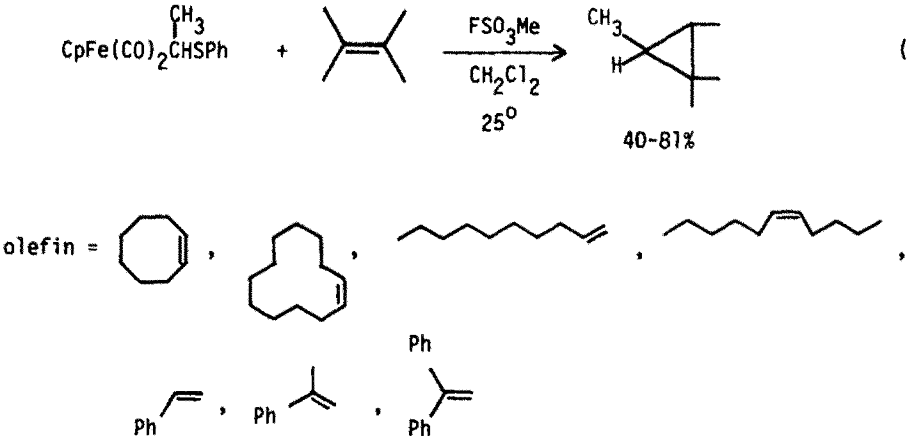


(83)

good yield

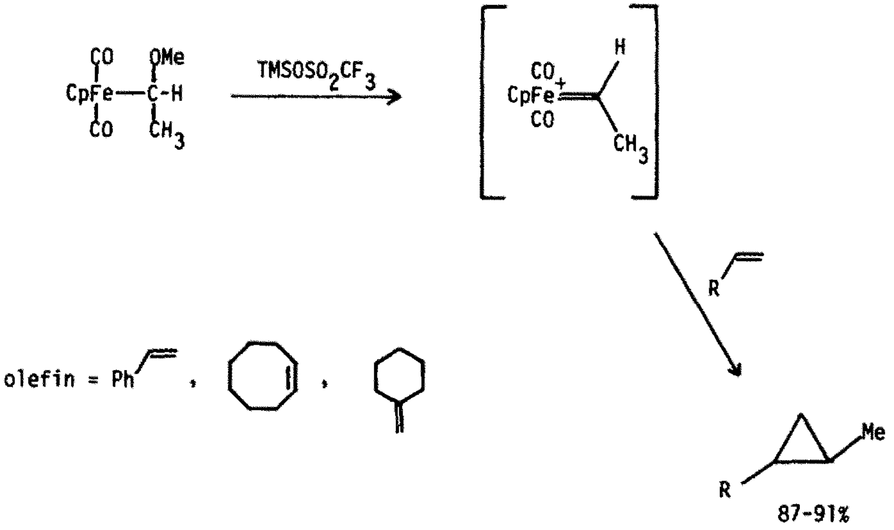
R = H; Me; 1,2-diMe; 1,3-diMe; 1,4-diMe; 1,3,5-triMe; OMe; Cl; F

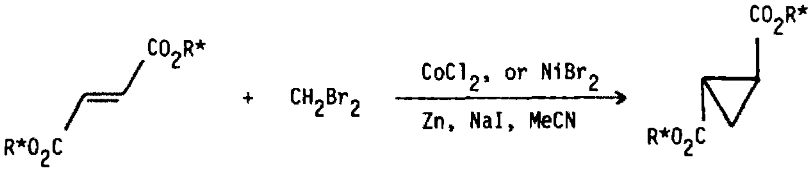
A dissertation entitled "Copper(II) catalyzed decomposition of β,γ-unsaturated diazoketones: The vinylogous Wolff rearrangement..." has appeared [86]. Olefins were arylated by aryl diazonium complexes in the presence of palladium(0) complexes [87]. Thiomethyl- (equation 84) [88] and methoxy methyl iron complexes (equation 85) [89] were stable precursors to iron-carbene complexes which cyclopropanated a variety of olefins. Chiral fumarate esters were cyclopropanated by dibromomethane and cobalt(II) or nickel(II) salts and zinc metal in fair optical yield (equation 86) [90]. Chiral cyclopropanes were obtained via resolved 1,3-dieneiron complexes (equation 87) [91].



(84)

(85)



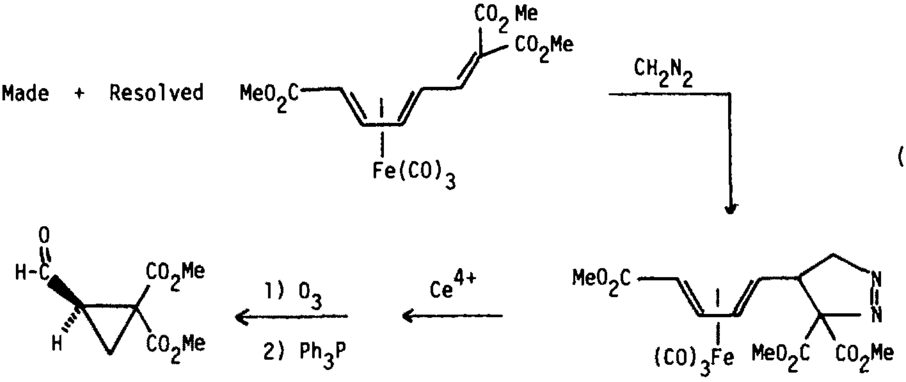


(86)

R* = (-) menthyl, (-) bornyl, (+) bornyl

18% yield
70% optical yield

Made + Resolved



(87)

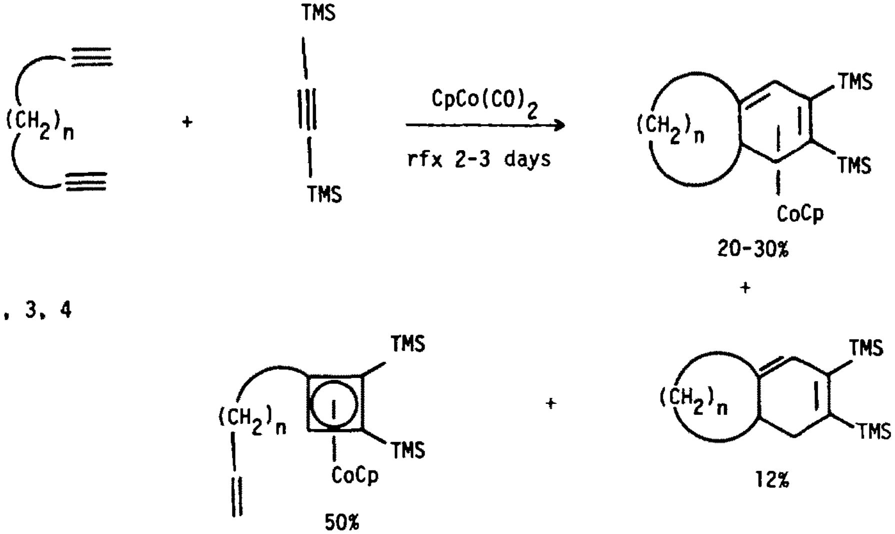
up to 90% ee

(chemical yields not reported)

5. Cycloaddition Reactions

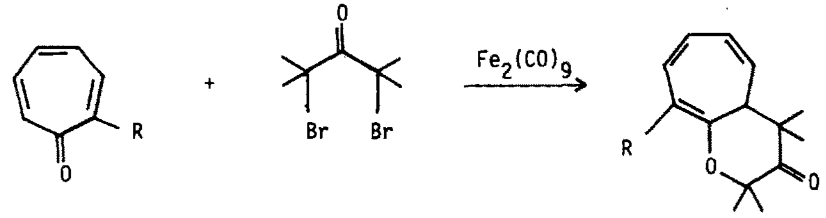
Annelated cyclohexadienes were prepared by cycloaddition of diynes to monoacetylenes using $CpCo(CO)_2$ as a catalyst (equation 88) [92] [93]. Phenylacetylene underwent a 2 + 2 cycloaddition process to triphenyl Dewar benzenes when treated with a polystyrene-supported molybdenum catalyst [94].

(88)



n = 2, 3, 4

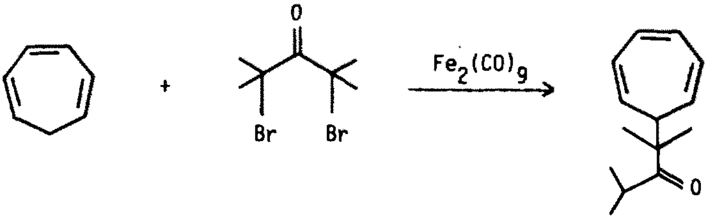
Diiron enneacarbonylcatalyzed the cycloaddition of α,α'-dibromoketones to a number of substrates (equations 89-92) [95], (equation 93) [96], (equation 94) [97]. The cycloaddition of 2,3-dimethylbutadiene to methyl acrylate produced a cyclopentenone when catalyzed by iron pentacarbonyl (equation 95) [98].



(89)

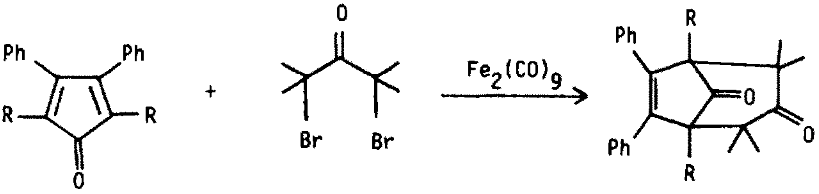
R = H, Cl, Ph

28-65%



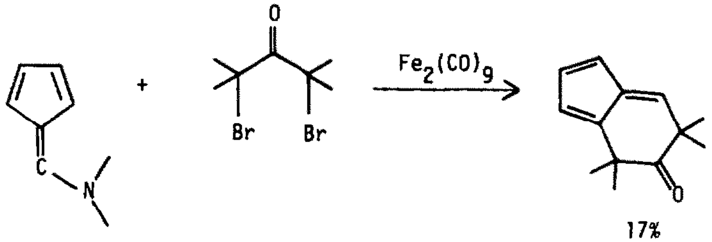
(90)

65%



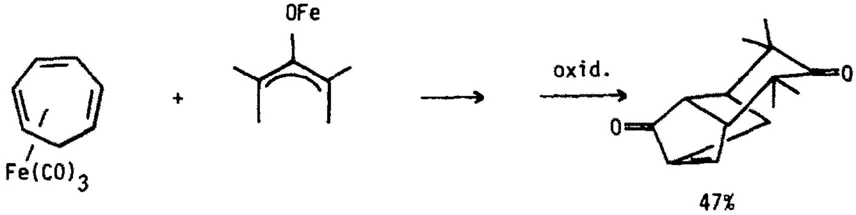
(91)

17-29%

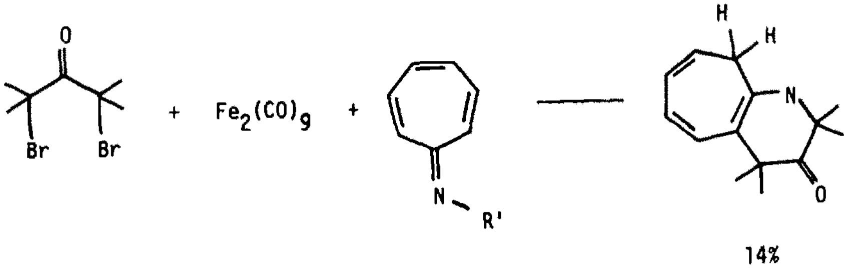


(92)

17%

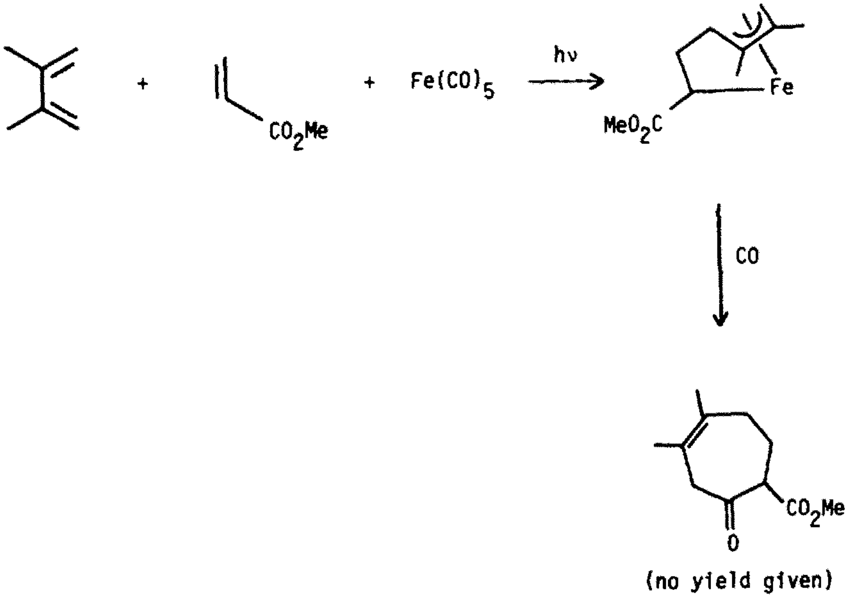


(93)

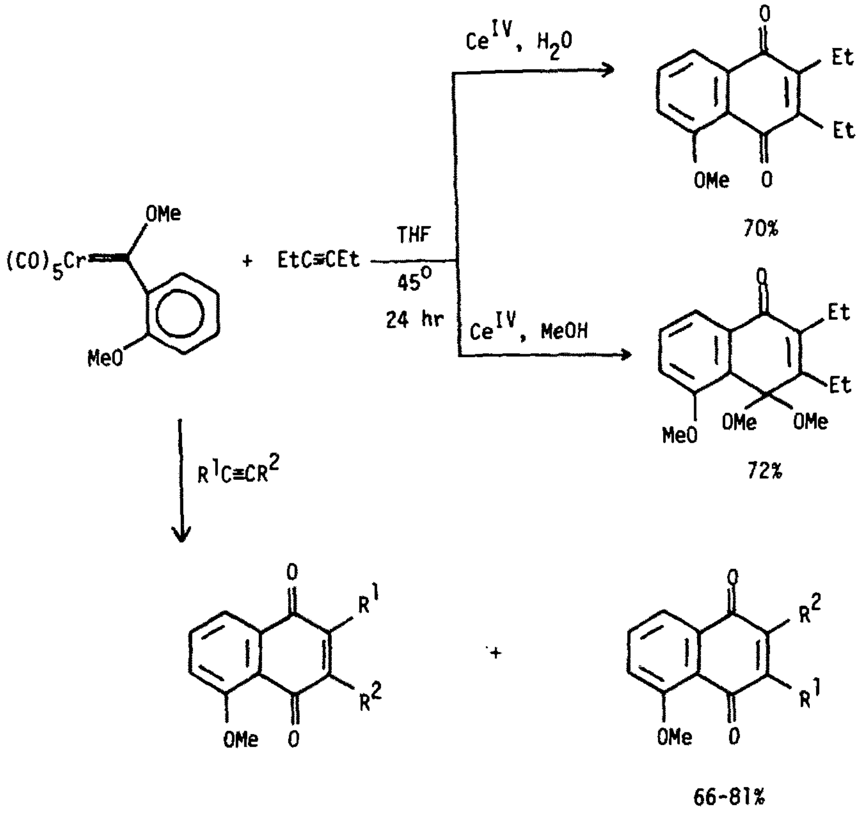


(94)

(95)

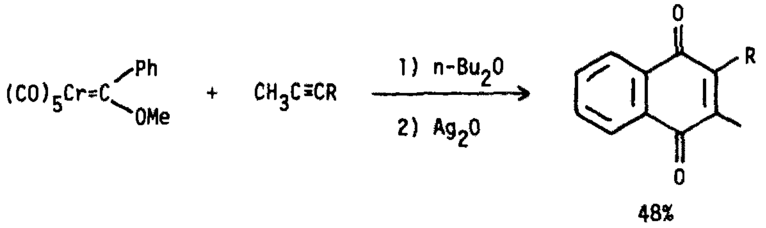


Chromium carbene complexes reacted with acetylenes to give naphthoquinones (equation 96) [99]. Vitamin $K_{(20)}$ was synthesized this way (equation 97) [100].

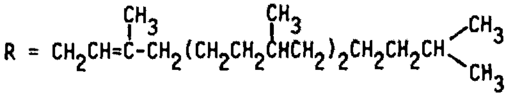


(96)

R^1 = Et, n-Pr, i-Pr, Ph, $(CH_2)_3CO_2$t-Bu, $(CH_2)_3$CONHt-Bu
R^2 = Me, H



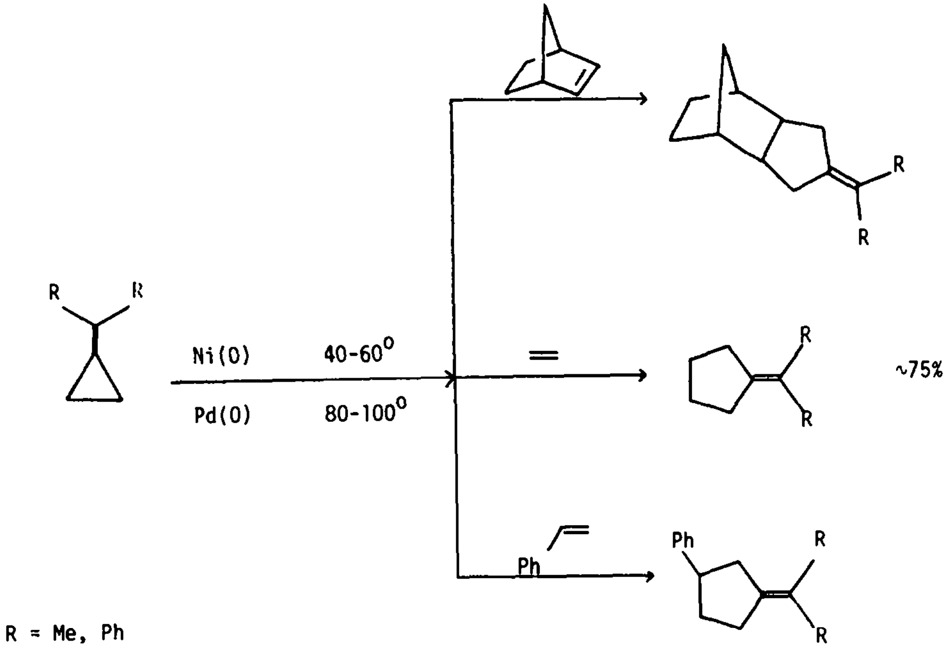
(97)



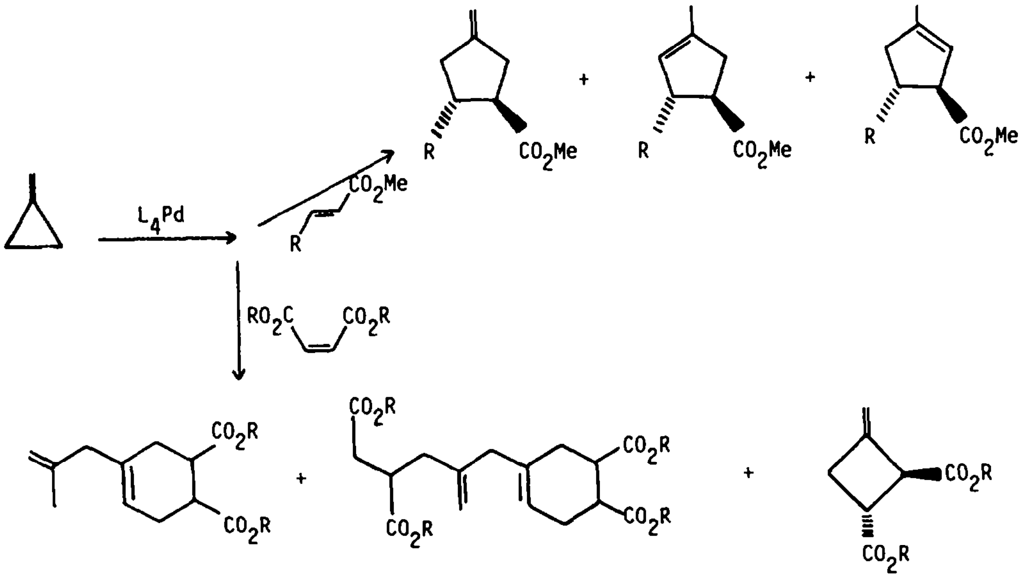
$$R = CH_2CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2(CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2)_2CH_2CH_2CH\begin{matrix}CH_3\\CH_3\end{matrix}$$

Vinylcyclopropanes underwent cycloaddition reactions to olefins (equation 98) [101] and conjugated esters (equation 99) [102] in the presence of nickel(0) or palladium(0) catalysts. Strained ring compounds also underwent nickel(0) catalyzed cycloaddition reactions to electrophilic olefins (equation 100) [103] (equation 101 and 102) [104].

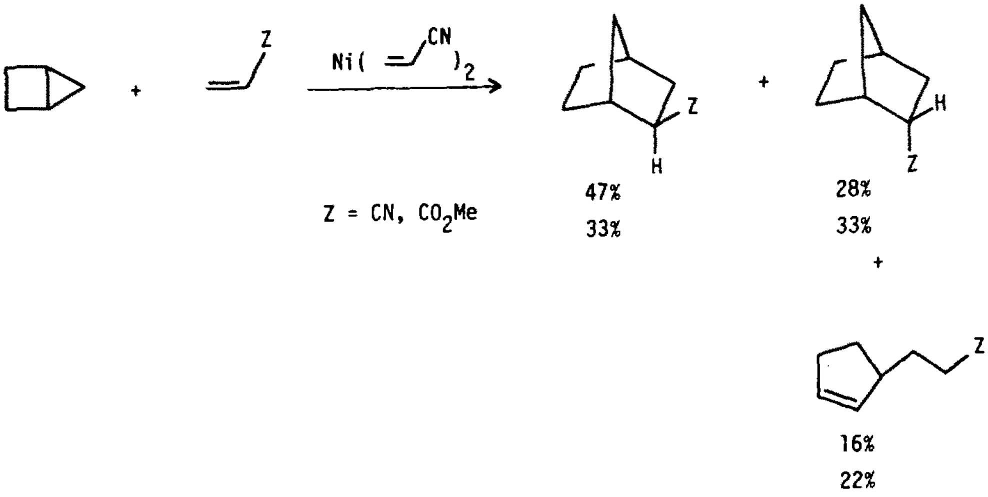
(98)

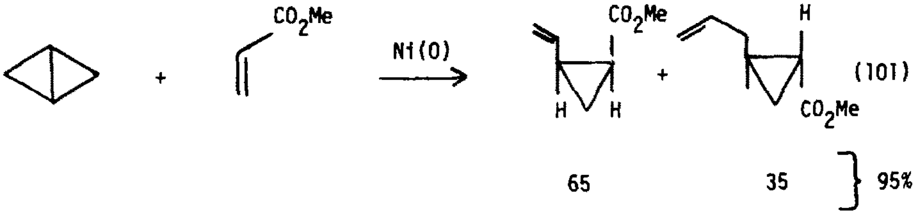


(99)

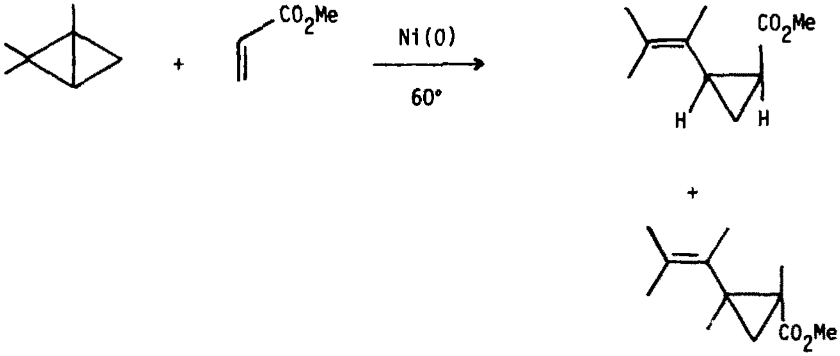


(100)





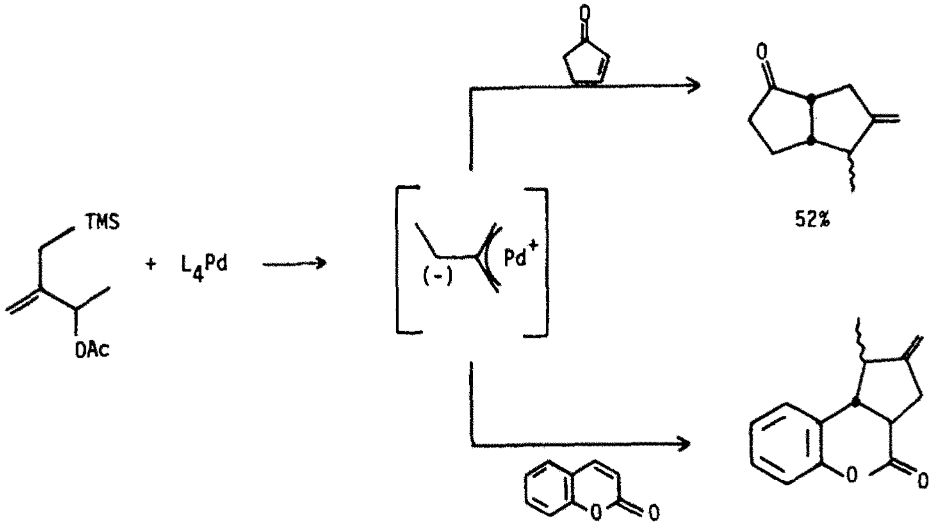
(101)

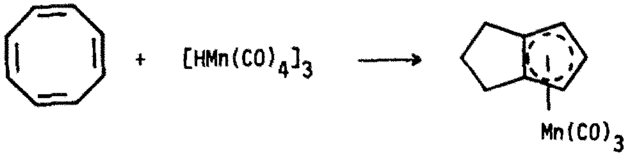


(102)

Electrophilic double bonds underwent a cycloaddition to a "trimethylene methane" species produced from an allylic substrate in the presence of a palladium(0) catalyst (equation 103) [105]. Cyclooctatetraene cyclized to a pentalene derivative when treated with $[HMn(CO)_4]_3$ (equation 104) [106].

(103)



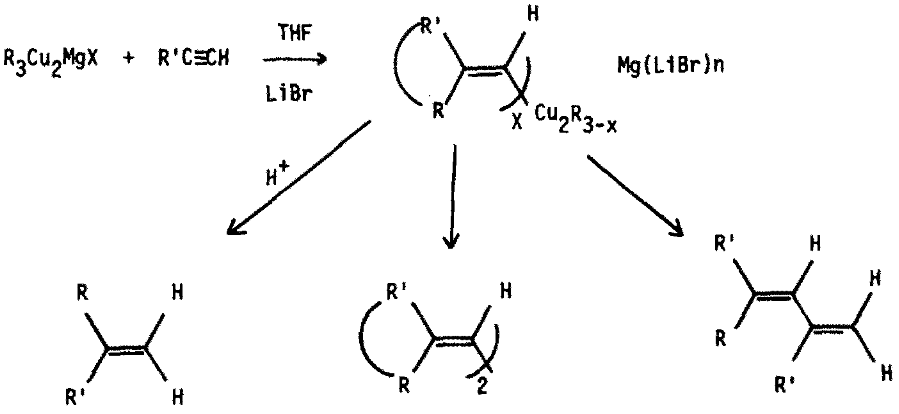


(104)

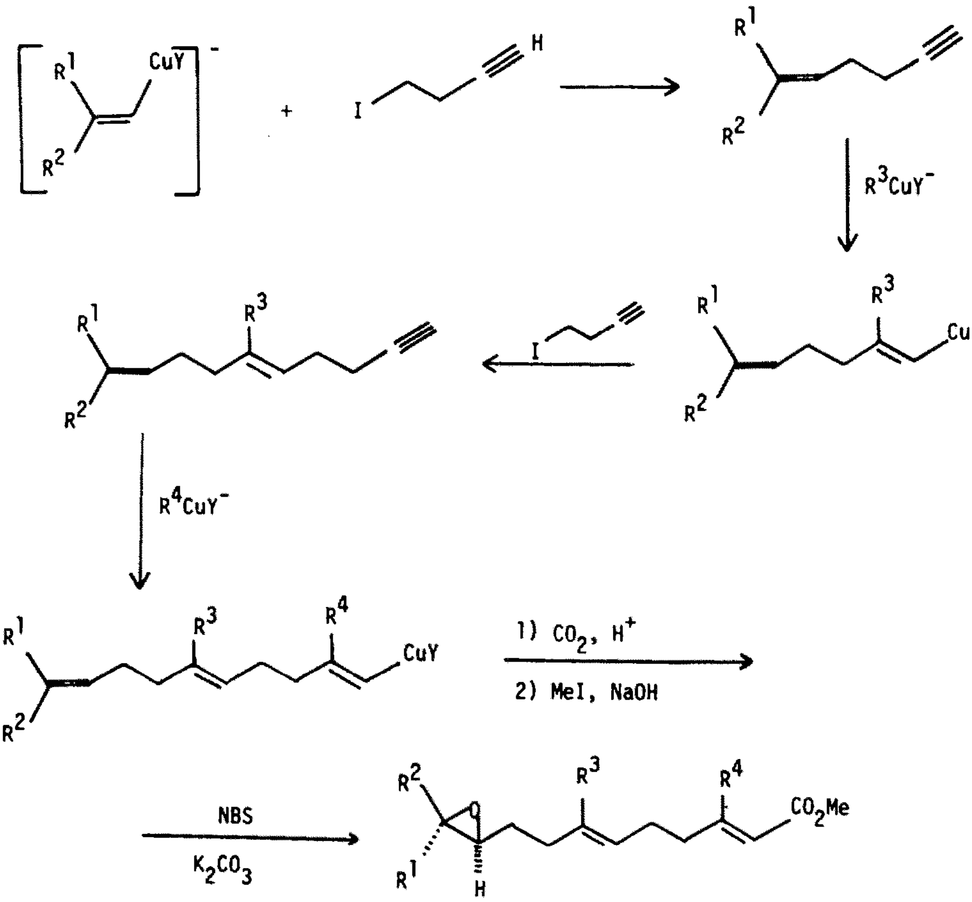
6. Alkylation of Alkynes

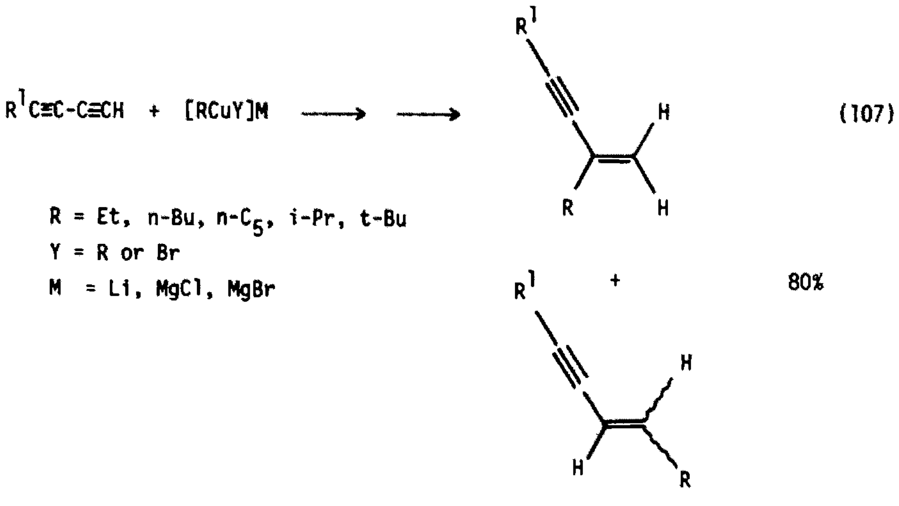
Organocuprates reacted with terminal acetylenes to produce alkylated vinylcuprates, which could be protonated or coupled (equation 105) [107]. This chemistry was used to prepare juvenile hormones (equation 106) [108] and eneynes (equation 107) [109]. Models for natural rubber were also made in this manner (equation 108) [110]. The active species in the initial "carbometallation" of the terminal alkyne appeared to be Cu_4MgR_6 or Cu_6MgR_8 [111, 112].

(105)



(106)

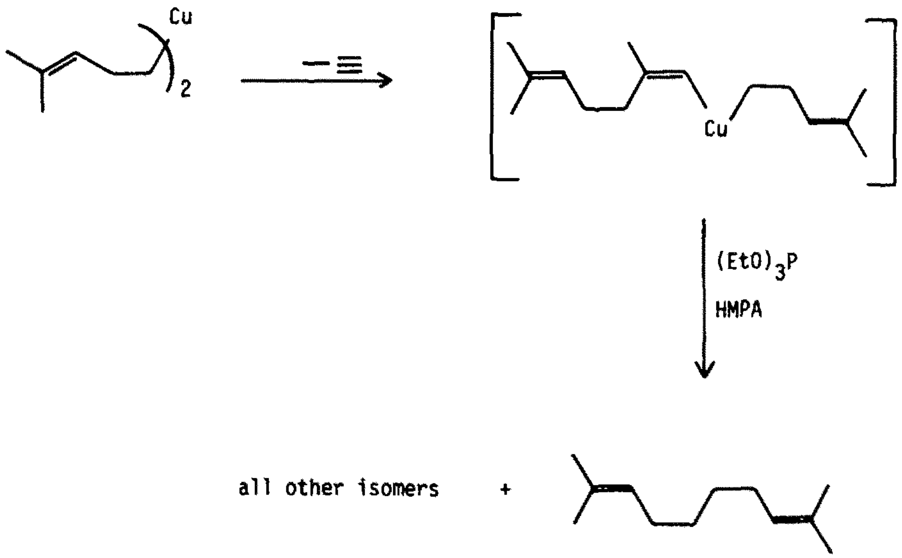




(107)

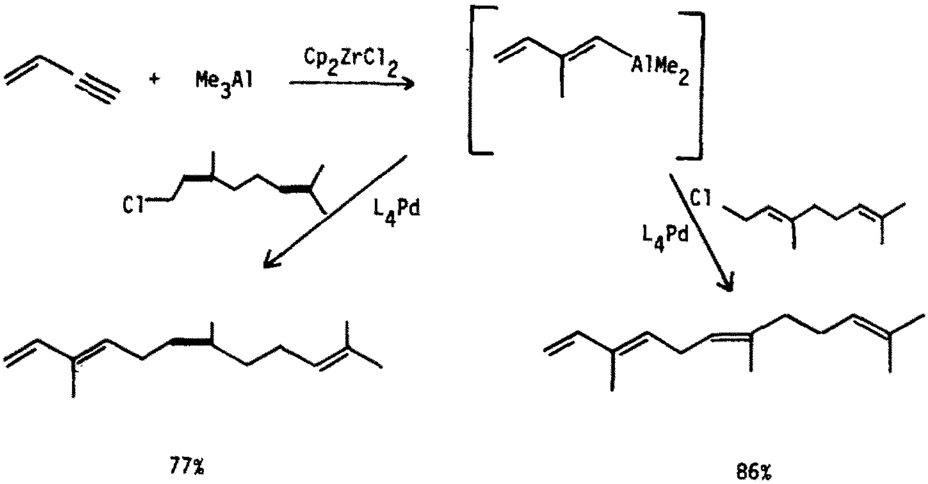
R = Et, n-Bu, n-C_5, i-Pr, t-Bu
Y = R or Br
M = Li, MgCl, MgBr

(108)

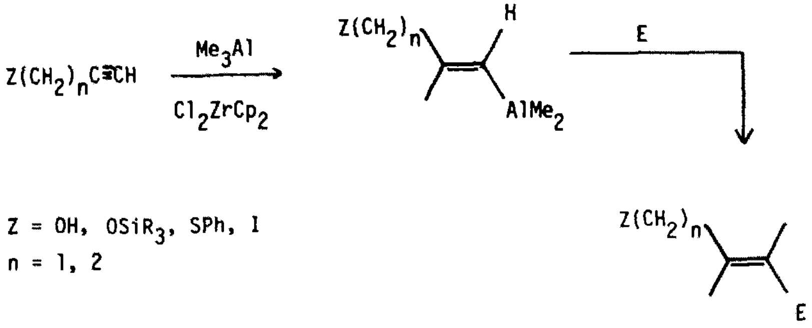


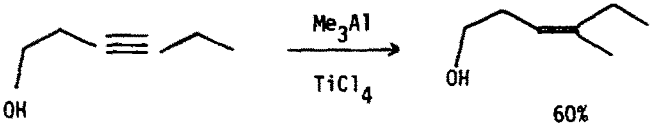
A number of early transition metals catalyze the carbometallation of alkynes. The most developed involves the use of zirconocene dichloride to catalyze the carboalumination of alkynes. A general synthesis of 1,4 dienes resulted from this procedure (equation 109) [113]. Propargyl and homopropargyl functionalized alkynes also underwent this reaction (equation 110) [114]. Titanium(IV)chloride catalyzed a similar carboalumination (equation 111) [115], and addition of Grignard reagents (equation 112) [116]. Vinyl titanium complexes added to acetylenes (equation 113) [117]. Carbometallation of alkynes has been reviewed [118].

(109)

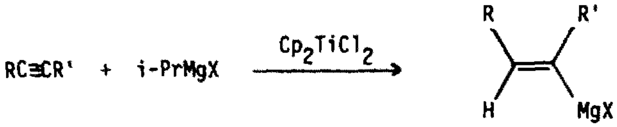


(110)

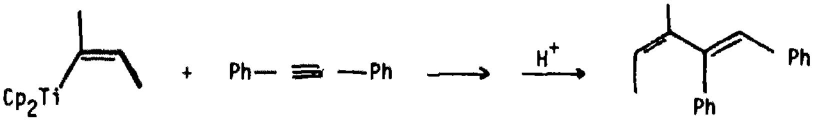




(111)

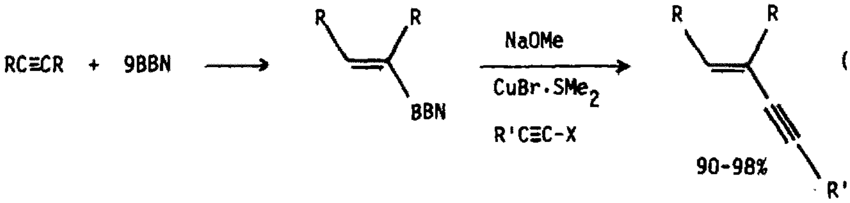


(112)



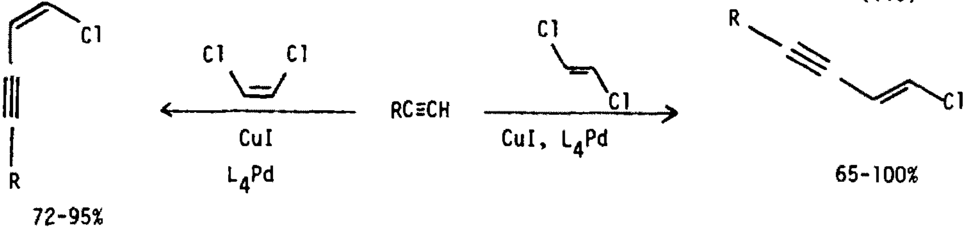
(113)

Alkynes were alkylated by reaction with 9-BBN followed by treatment with copper(I) bromide, sodium methoxide, and another halide (equation 114) [119]. Copper acetylides reacted with vinyl chlorides to produce eneynes (equation 115) [120].



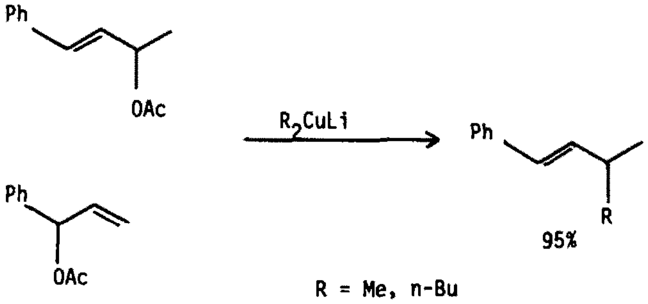
(114)

(115)



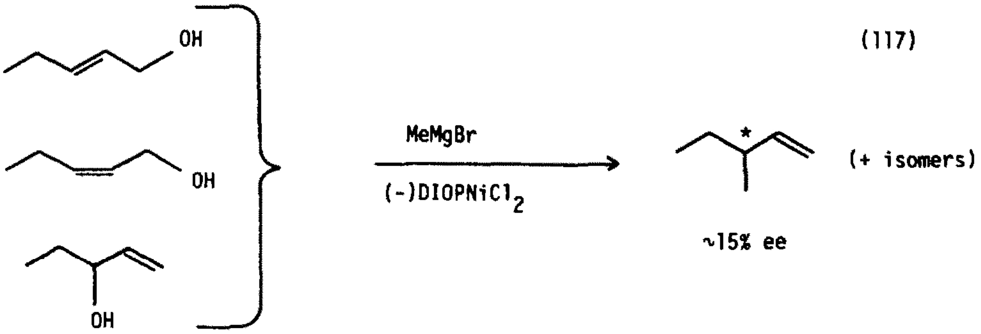
7. Alkylation of Allyl and Propargyl Alcohols and Acetates

Organocuprates alkylated allylic acetates to give the same product regardless of the position of the acetate in the starting material (equation 116) [121]. A π-allylcopper species was proposed as an intermediate. Allylic alcohols reacted with methylmagnesium bromide in the presence of a chiral nickel(II) catalyst to give alkylation product in up to 15% ee (equation 117) [122]. In a similar reaction with cyclohexenol substrates, this alkylation was shown to be stereospecific, and to occur anti to the leaving OH group (equation 118) [123]. Active methylene reagents alkylated allyl and benzyl alcohols in the presence of cobalt(II) chloride (equation 119) [124]. Grifolin and neogrifolin were made in this way. Chiral allylic alcohols reacted with aryl iodides in the presence of palladium(II) to give ketones with up to 18% optical yields from chirality transfer (equation 120) [125]. Trimethylsilyl derivatives of allyl alcohols underwent a similar arylation (equation 121) [126].

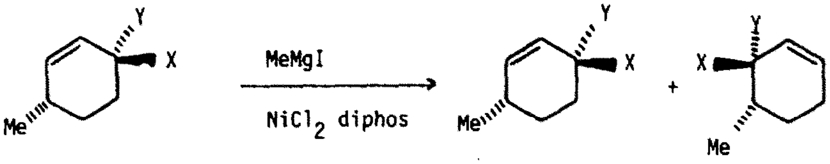


(116).

(117)



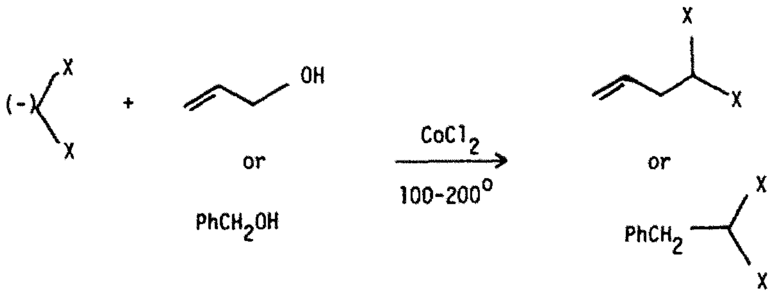
(118)



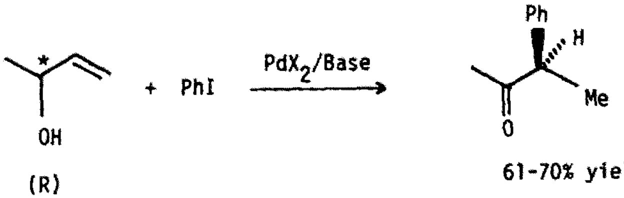
X = H, Y = OH
X = OH, Y = H

X = Me, Y = H 52%
X = H, Y = Me 88%

X = Me, Y = H 46%
X = H, Y = Me 10%

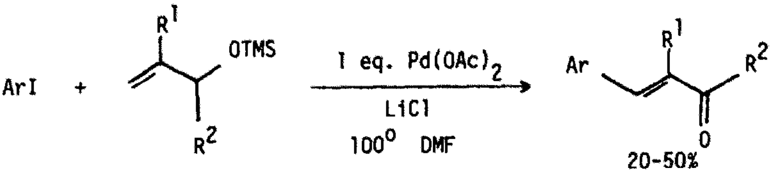


(119)



(120)

61-70% yield
18% opt. yield

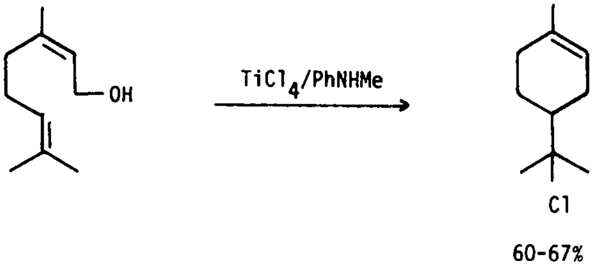


(121)

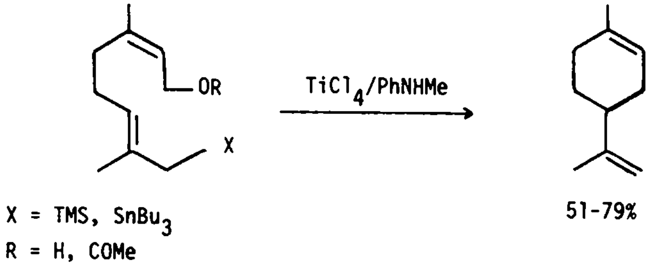
Ar = Ph, p-tolyl, p-CO_2MePh, o-CO_2MePh, 

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

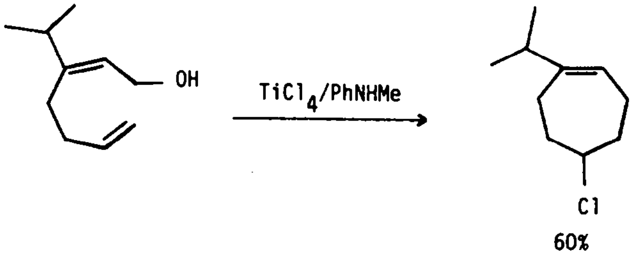
Sesquiterpene alcohols underwent halocyclization when treated with titanium(IV) chloride (equations 122-124) [127]. Propargyl alcohols were hydrometallated by Grignard reagents and the resulting vinyl Grignard reagents were reacted with electrophiles (equations 125 and 126) [128]. Cobalt stabilized-propargyl cations reacted with alkylating agents in modest yield (equation 127) [129].



(122)

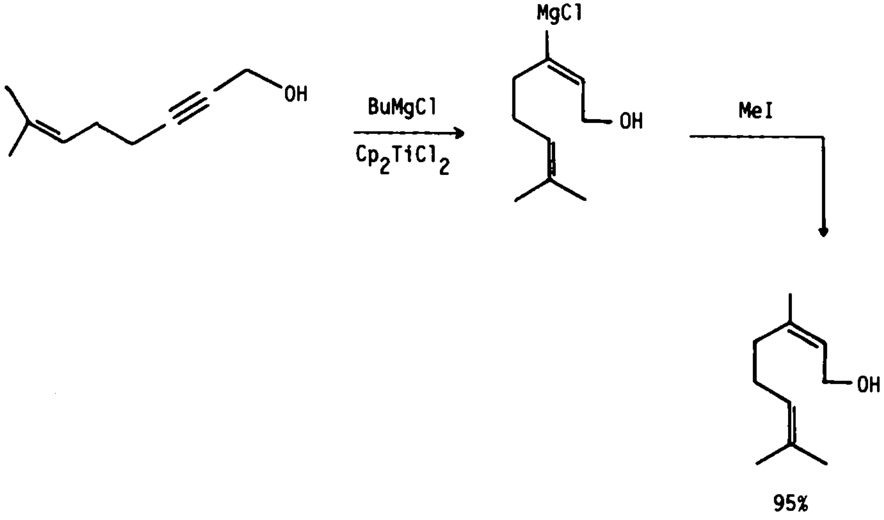


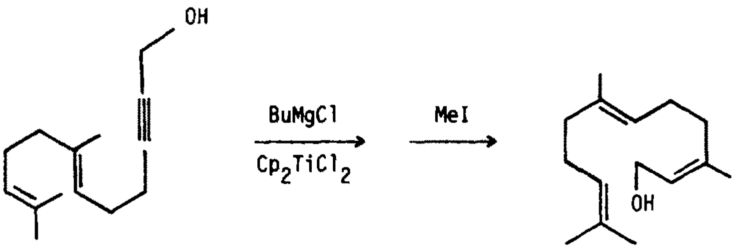
(123)



(124)

(125)

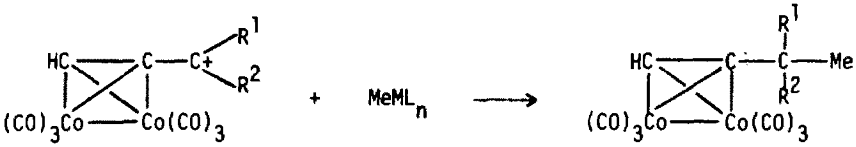




(126)

98%

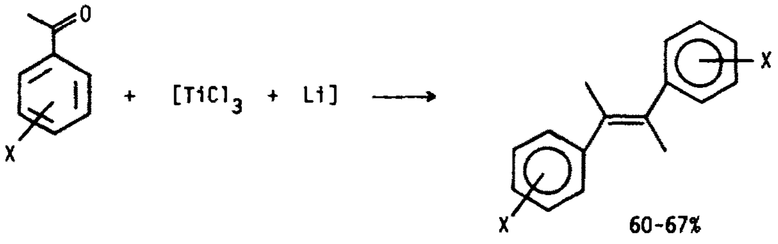
(127)



5-40%

8. Coupling Reactions

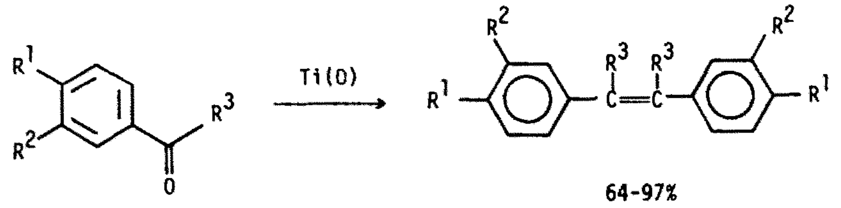
Organic reductive coupling with titanium and vanadium chlorides has been reviewed [130]. The reductive coupling of carbonyls to alkenes and its use to synthesize adamantylidenecadamantane has been described in detail [131]. Bromo- and trifluoromethyl stilbenes were synthesized by the titanium-induced coupling of the corresponding acetophenones (equation 128) [132]. A variety of highly substituted stilbenes were prepared in a similar manner (equations 129 and 130) [133]. A detailed mechanism study of the reductive coupling of ketones to olefins using $LiAlH_4/TiCl_4$ has been carried out [134]. The system $LiAlH_4/TiCl_3$ reductively coupled esters, acids, and acid chlorides as well (equation 131) [135]. Conjugated ketones coupled to a variety of products when treated with early transition metal halides and magnesium metal (equation 132) [136].



(128)

60-67%

X = p-Br, m-CF_3

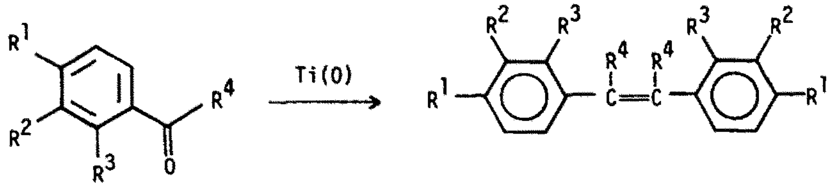


(129)

R^1 = OMe, H, AcO

R^2 = $PhCH_2O$, AcO, H, CO_2Me, $MeO_2CCH_2CH_2O\text{-}\overset{O}{\overset{\|}{C}}$

R^3 = H, Me



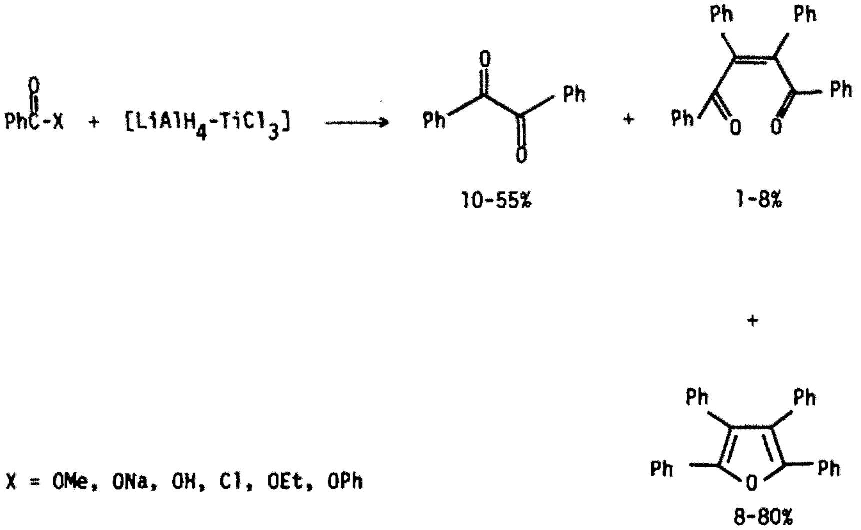
(130)

R^1 = MeO, H

R^2 = p-$MePhSO_3$, MeO, H

R^3 = H, p-$MePhSO_3$

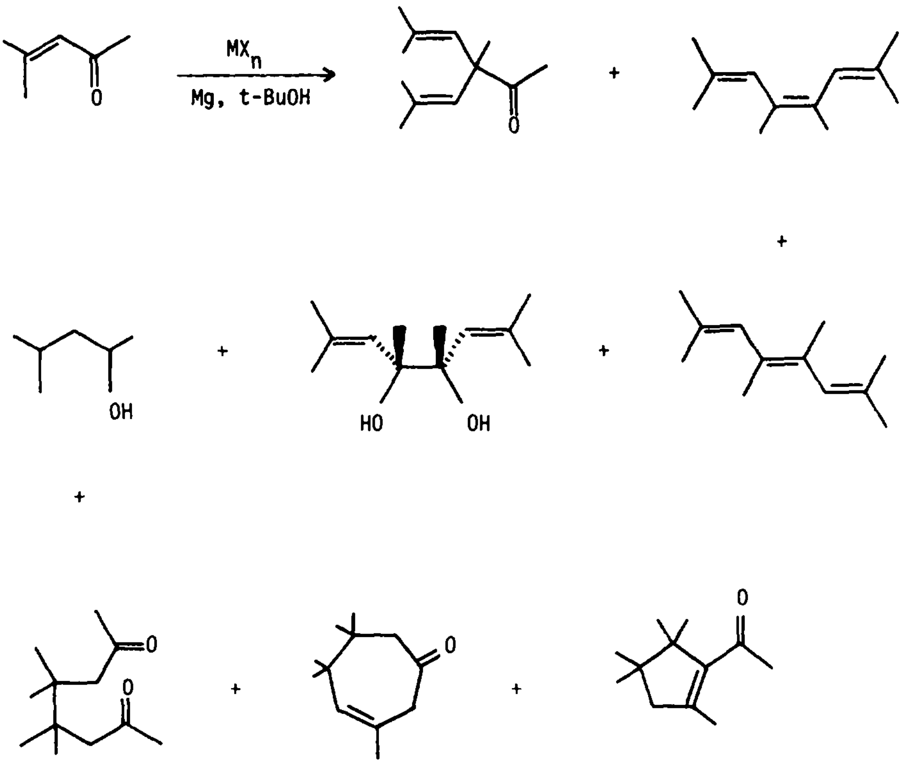
R^4 = H, Me



(131)

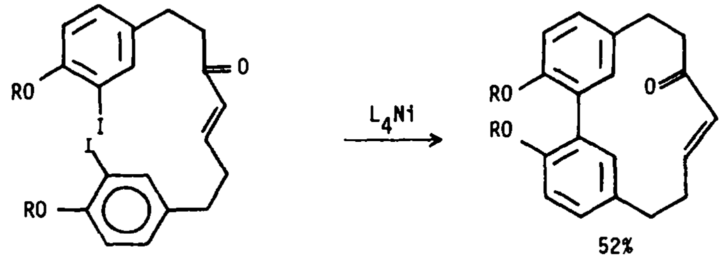
X = OMe, ONa, OH, Cl, OEt, OPh

(132)



MXn = $TiCl_3$, $TiCl_4$, VCl_3, $CrCl_3$, $FeCl_3$. $ZrCl_4$

The mechanism of the electrochemical reductive coupling of halides in the presence of nickel(II) salts has been studied [137]. The full experimental details for the nickel(0) coupling of aryl halides to diaryls, and vinyl halides to 1,3-dienes have appeared, as well as the application of this chemistry to the synthesis of alnusone (equation 133) [138]. Benzyl halides coupled to form dibenzyls when treated with L_3CoCl (equation 134) [139].

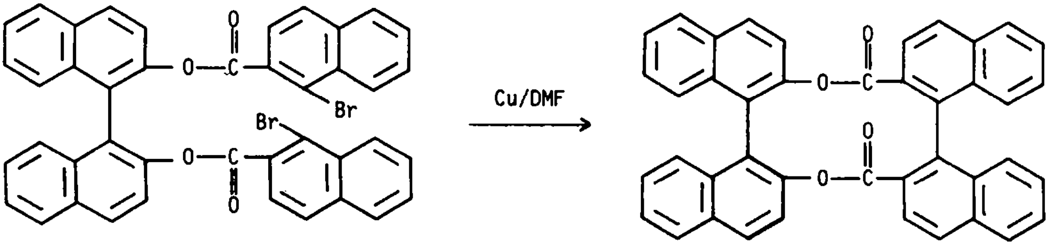


(133)

$$ArCH_2X + L_3CoCl \xrightarrow[25^{o}]{PhH} ArCH_2CH_2Ar \qquad (134)$$

The Ullmann coupling has been used to prepare macrocyclic lactones (equation 135) [140], and oligomeric anthraquinones (equation 136) [141]. The mechanism of the Ullmann condensation has been studied [142]. Furans (equation 137) [143], pyrroles (equation 138) [144], and thiophenes (equation 139) [145] were dimerized and oligomerized by lithiation followed by copper or nickel catalyzed coupling.

(135)

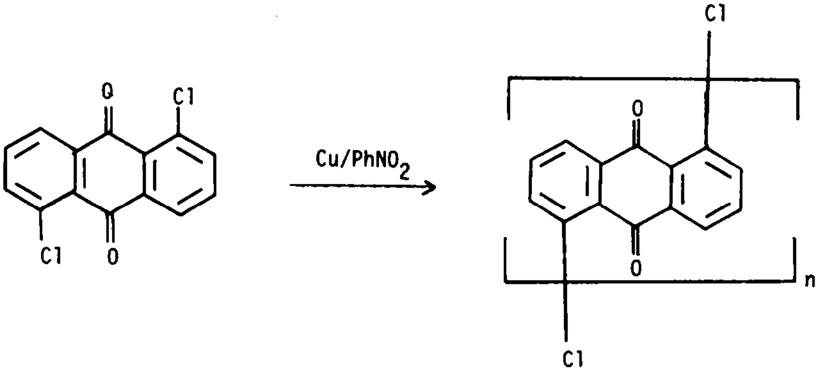


36%

+

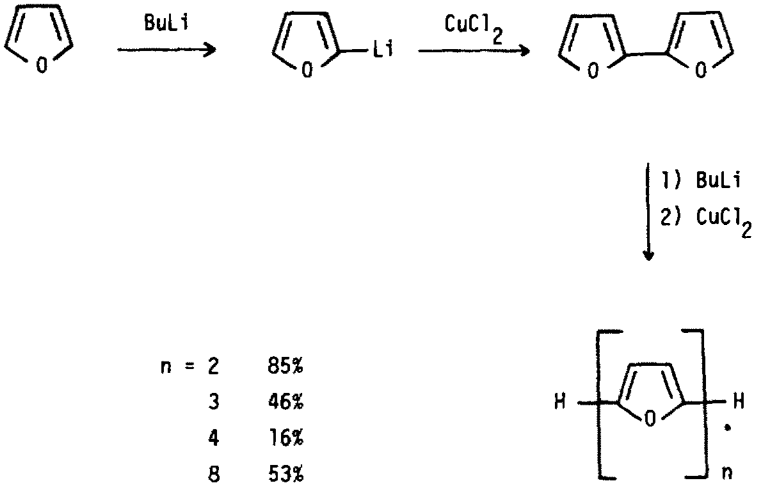
cyclic tetramer 39%

(136)



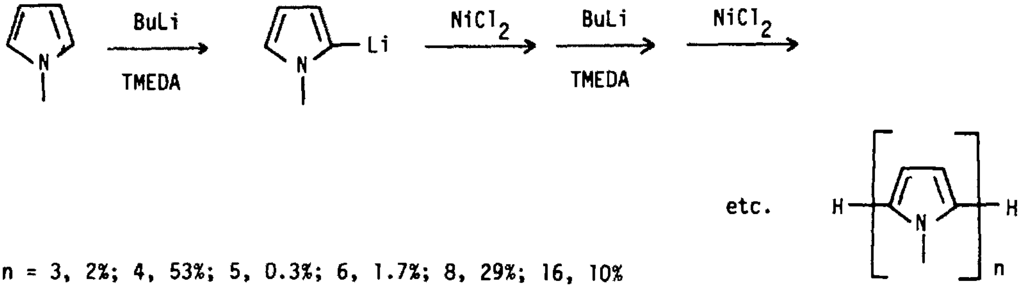
n = 2, 3, 4

(137)

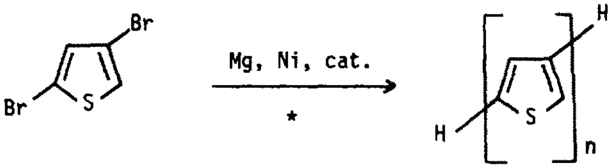


n = 2 85%
3 46%
4 16%
8 53%

(138)



n = 3, 2%; 4, 53%; 5, 0.3%; 6, 1.7%; 8, 29%; 16, 10%

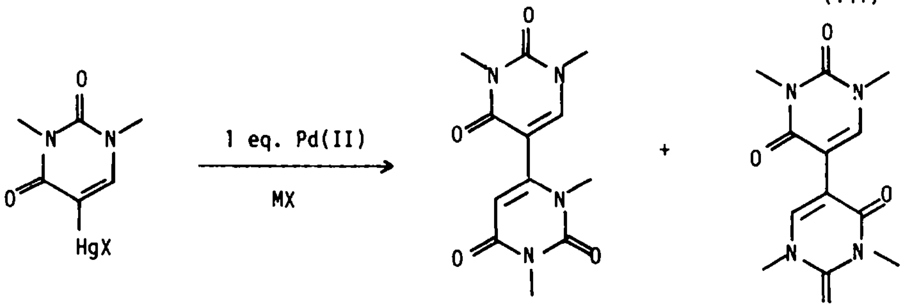


(139)

Alkyl [146] and aryl halides [147] were reductively coupled by hydrazine in the presence of palladium catalyst (equation 140). Palladium(II) salts coupled mercurated uracils to give two different dimers whose ratio depended on the counterion (equation 141) [148]. Aryl mercuric halides coupled with aryl halides in the presence of a palladium(II) catalyst [149]. Palladium on carbon catalyzed the coupling of indolizidines (equation 142) [150]. Conjugated ketones coupled to form coordinated 1,3-diketo ligands when treated with palladium(II) chloride (equation 143) [151]. Allylic alcohols coupled with aldehydes to give 1,3-dienes when treated with Pd(acac)$_2$ as a catalyst (equation 144) [152]. Biaryls were formed from aromatic hydrocarbons by thallation followed by palladium(II) acetate catalyzed coupling (equation 145) [153]. Benzene itself dimerized to biphenyl when treated with palladium(II) acetate in the presence of 18-crown-6 [154].

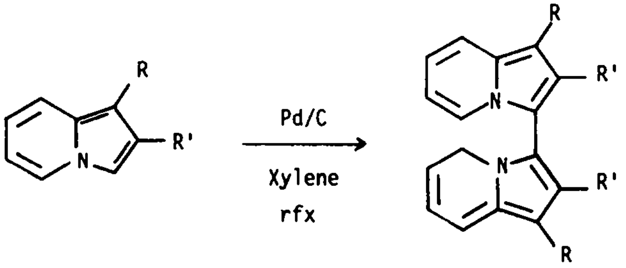
$$\begin{matrix}RX\\ \\ ArX\end{matrix} + NH_2NH_2 \xrightarrow[\Delta]{PdCl_2} \begin{matrix}RR\\ \\ ArAr\end{matrix} \qquad (140)$$

(141)



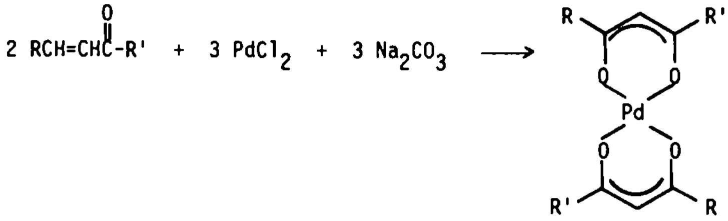
MX = NaCl 72% 2

MX = NaOAc 89% 1

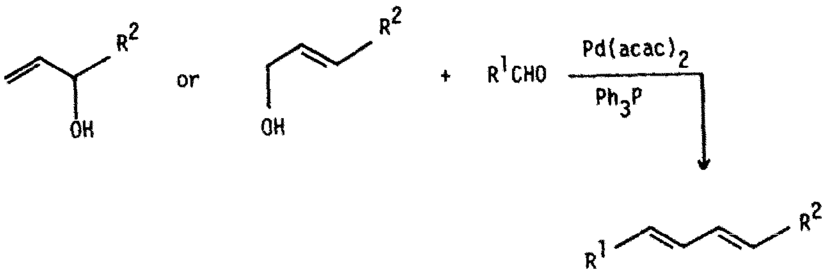


(142)

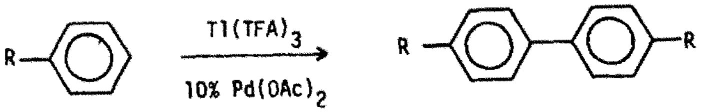
no yield reported



(143)

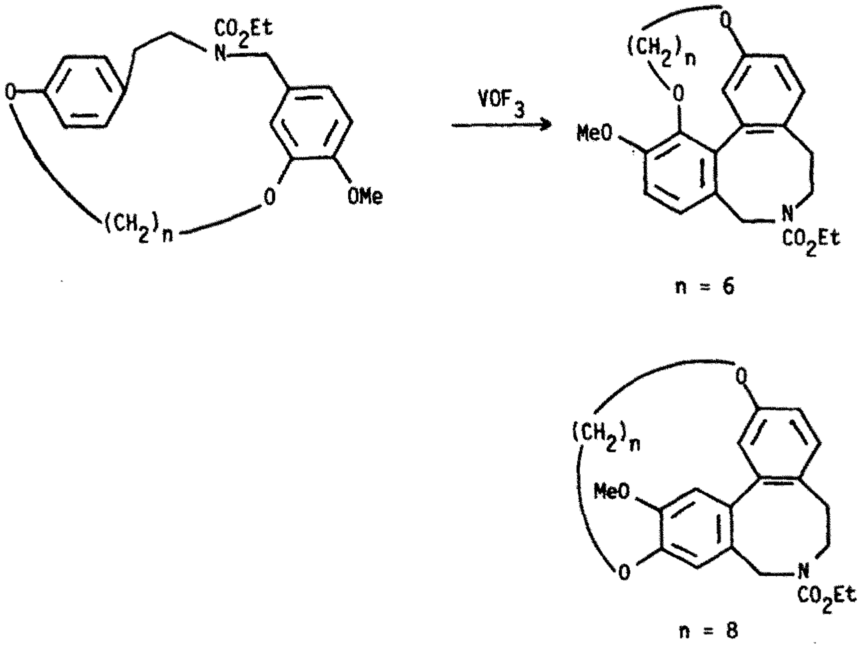


(144)

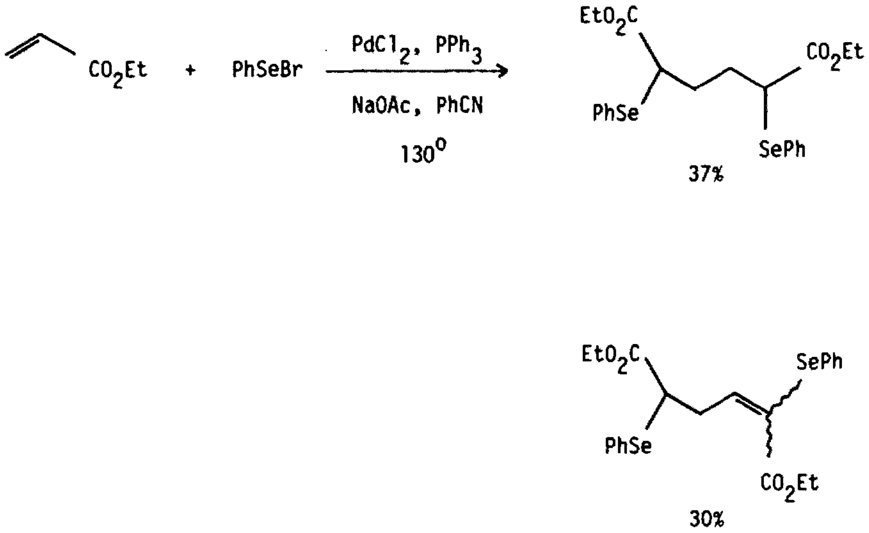


(145)

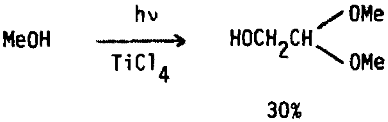
Styrene oxidatively dimerized to 1,4-diphenyl-1,3-butadiene in the presence of palladium(II) acetate [155]. Copper(II) complexes catalyzed the oxidative coupling of 2,6-dialkylphenols [156]. The VOF_3 oxidative coupling of aryls was used to synthesize unusual heterocycles (equation 146) [157]. Ethyl acrylate underwent selenation/dimerization when treated with phenyl selenium bromide and palladium(II) chloride (equation 147) [158]. Titanium(IV) chloride catalyzed the photodimerization of alcohols (equations 148-150) [159].



(146)

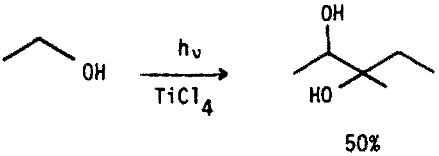


(147)

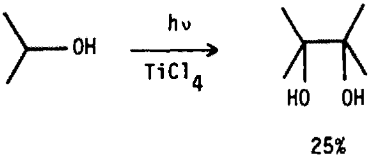


$$\mathrm{MeOH} \xrightarrow[\mathrm{TiCl_4}]{h\nu} \mathrm{HOCH_2CH(OMe)_2}$$

(148)



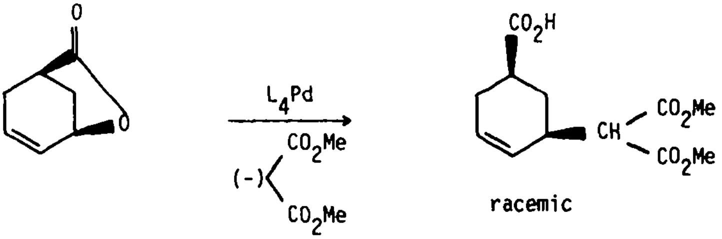
(149)



(150)

9. Alkylation of π-Allyl Complexes

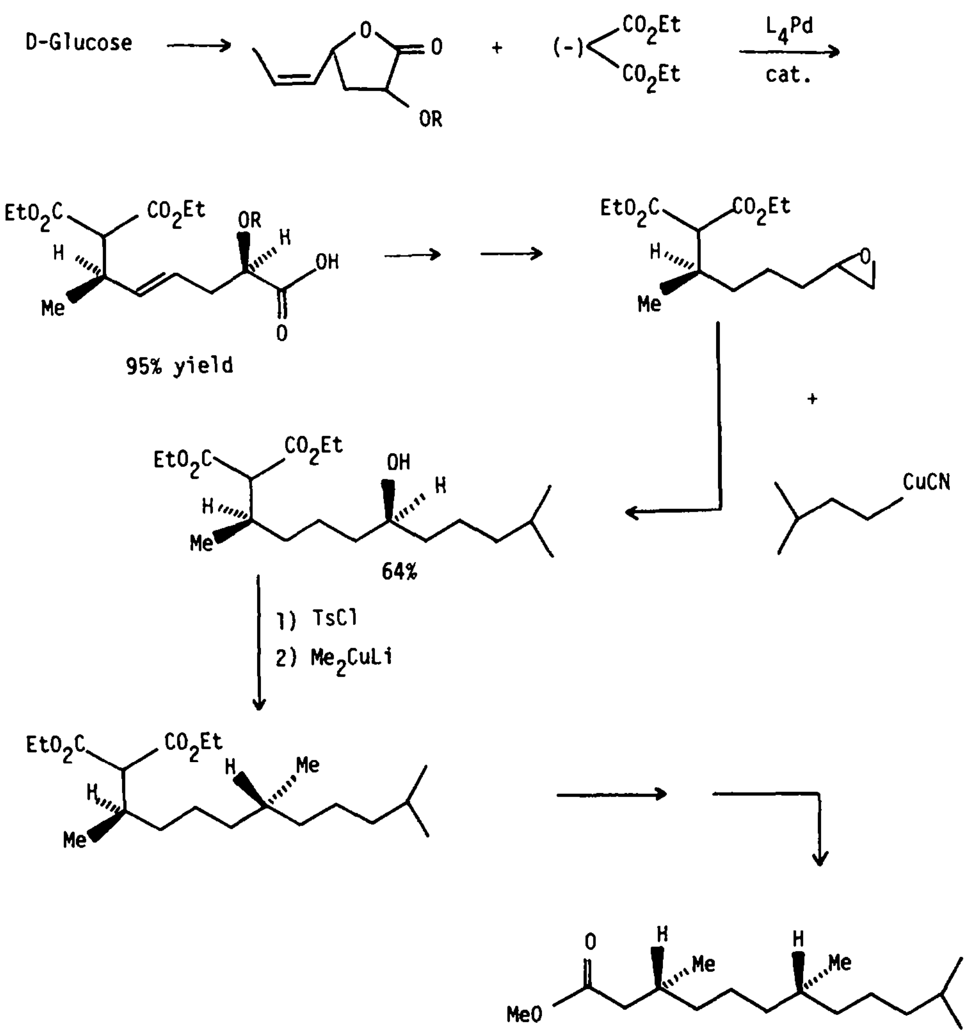
The π-allylpalladium chloride complexes of vitamins D_2 and D_3, ergosterol, 7,8-didehydrocholesterol, and 3-epi-cholesterol were prepared and subjected to oxidation and reduction reactions [160]. "Carbon-carbon bond formation through intermediate allylic complexes of palladium" was the subject of a dissertation [161]. By comparison of the reactions of a preformed [π-allylpalladium-DIOP]$^+$ cationic complex with diethyl malonate with the catalytic reaction of the corresponding allyl acetate, it was claimed that palladium-catalyzed allylic alkylation proceeded through a σ-allyl intermediate rather than a π-allylpalladium cationic species [162]. This claim has been questioned, based on the stereochemical outcome of the reaction in equation 151 [163].

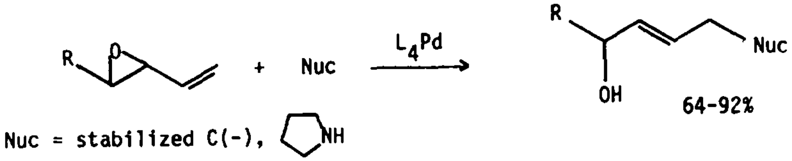


(151)

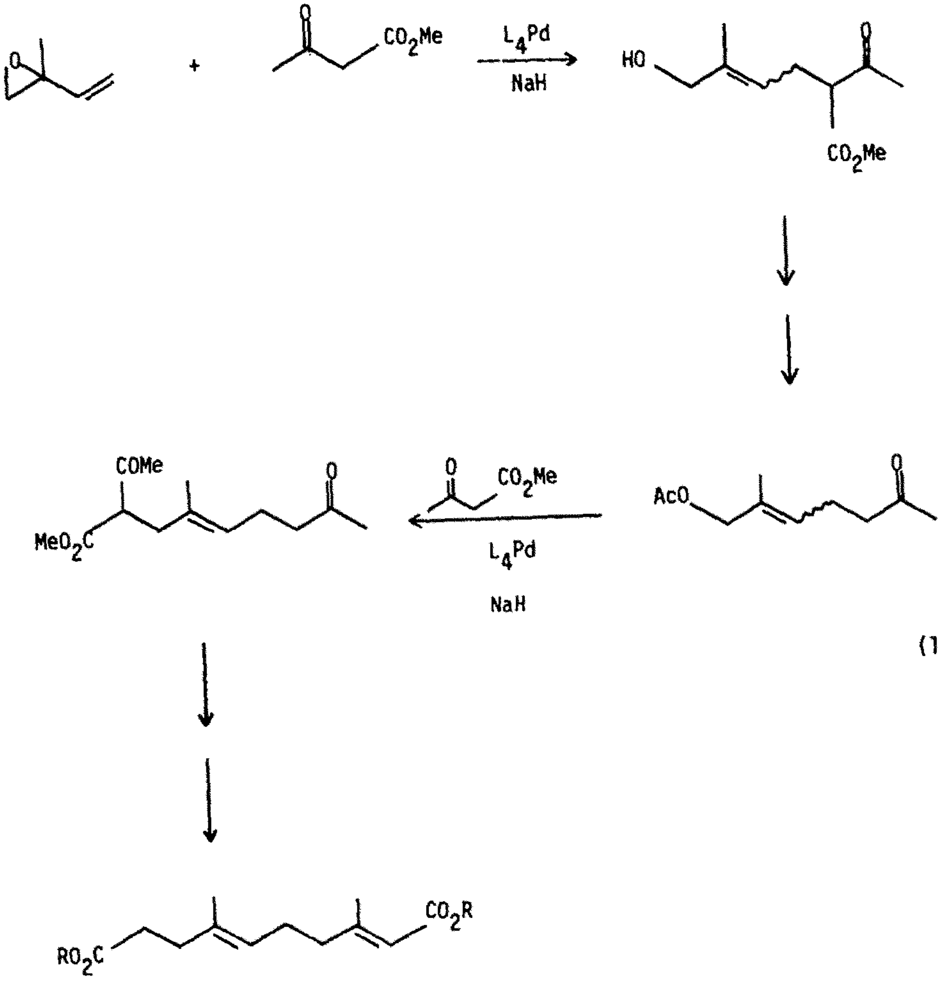
A number of new allylic substrates have found use in palladium catalyzed nucleophilic attack processes. The side chain of vitamin E was synthesized using the palladium catalyzed allylic alkylation of an allyl lactone derived from D-glucose (equation 152) [164]. High transfer of chirality was observed in this process. Allyl epoxides also underwent palladium catalyzed alkylation and amination reactions (equation 153) [165]. This process was used to synthesize terpenes (equation 154). Neutral carbanion precursors could be used since ring opening of the epoxide generated an alkoxide anion that could act as a base (equation 155) [166]. This process was complimentary to the normal alkylation process (equation 156). Acetylated allylic cyanohydrins also underwent allylic alkylation (equations 157-159) [167] as did trimethylsilyl-containing substrates (equations 160 and 161) [168]. Intramolecular allylic alkylation of an allyl phenyl ether was used to synthesize sarkomycin (equation 162) [169]. Allylic and benzylic alcohols underwent allylic alkylation by stabilized carbanions in the presence of palladium(II) acetylacetonate (equation 163) [170].

(152)

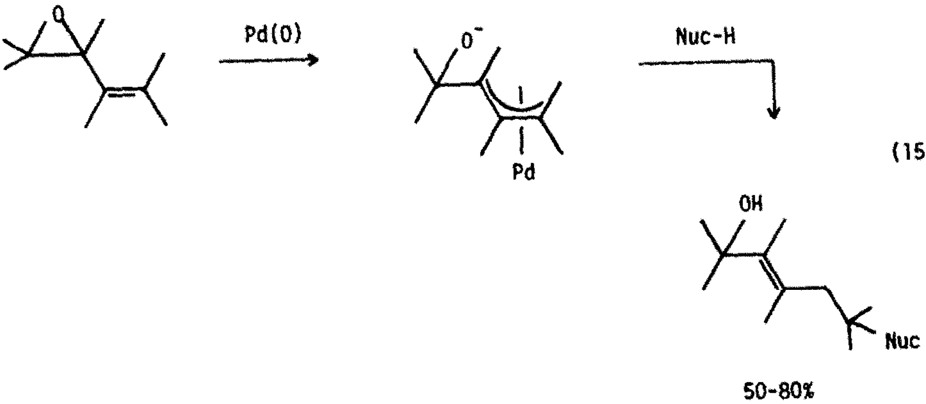

D-Glucose
O
O
OR
+
(-)
CO2Et
CO2Et
L4Pd
cat.
EtO2C
CO2Et
OR
H
OH
H
Me
O
95% yield
EtO2C
CO2Et
H
Me
O
+
CuCN
EtO2C
CO2Et
OH
H
H
Me
64%
1) TsCl
2) Me2CuLi
EtO2C
CO2Et
H
Me
H
Me
O
H
Me
H
Me
MeO


R
O
+
Nuc
L4Pd
R
Nuc
OH
64-92%
Nuc = stabilized C(-),
NH

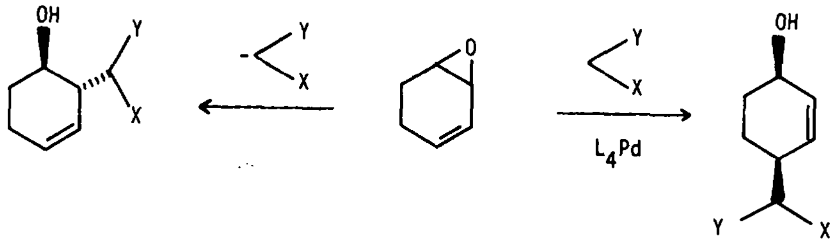
(153)


L$_4$Pd
NaH
HO
CO$_2$Me
CO$_2$Me
AcO
O
CO$_2$Me
L$_4$Pd
NaH
COMe
MeO$_2$C
RO$_2$C
CO$_2$R

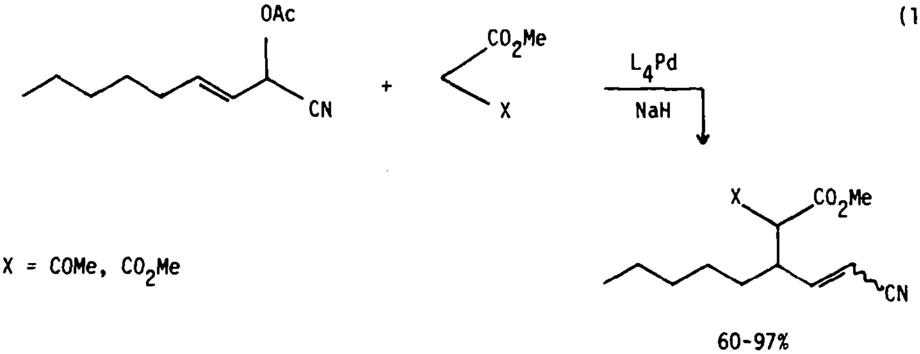
(154)


O
Pd(0)
O$^-$
Pd
Nuc-H
OH
Nuc
50-80%

(155)

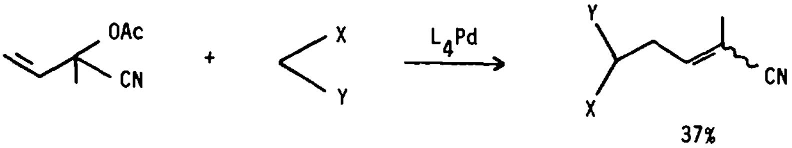


(156)

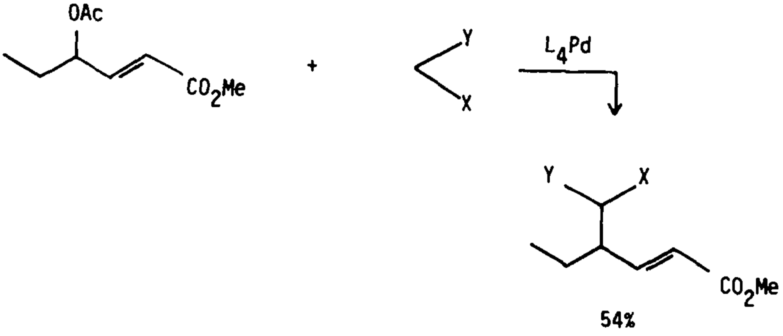


(157)

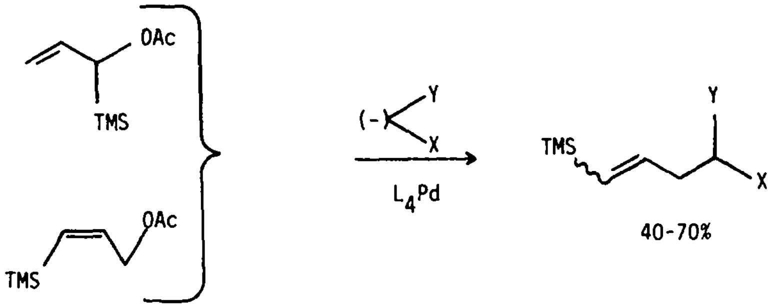
X = COMe, CO_2Me



(158)



(159)

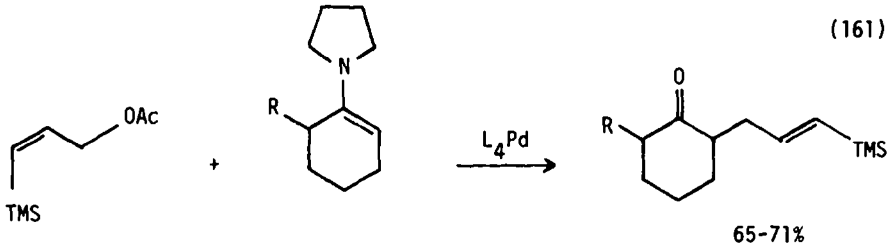


(160)

X = CO_2Et, COMe, SO_2Ph

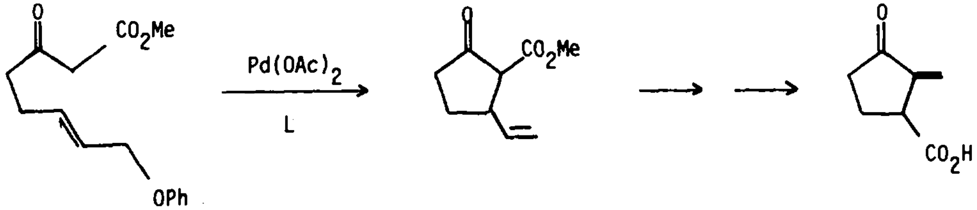
Y = CO_2Et

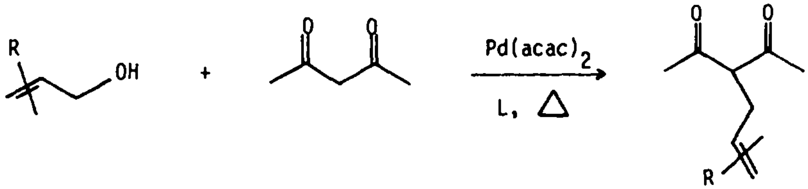
(161)



R = H, Me

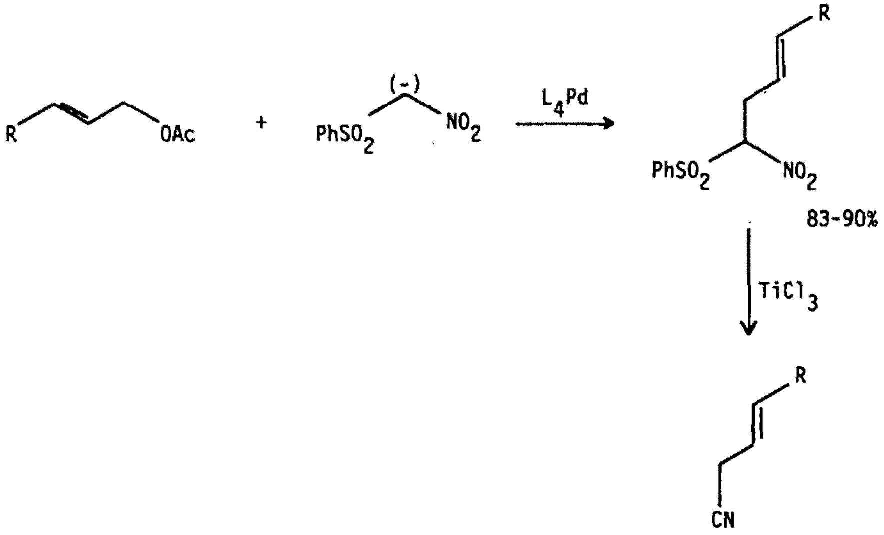
(162)



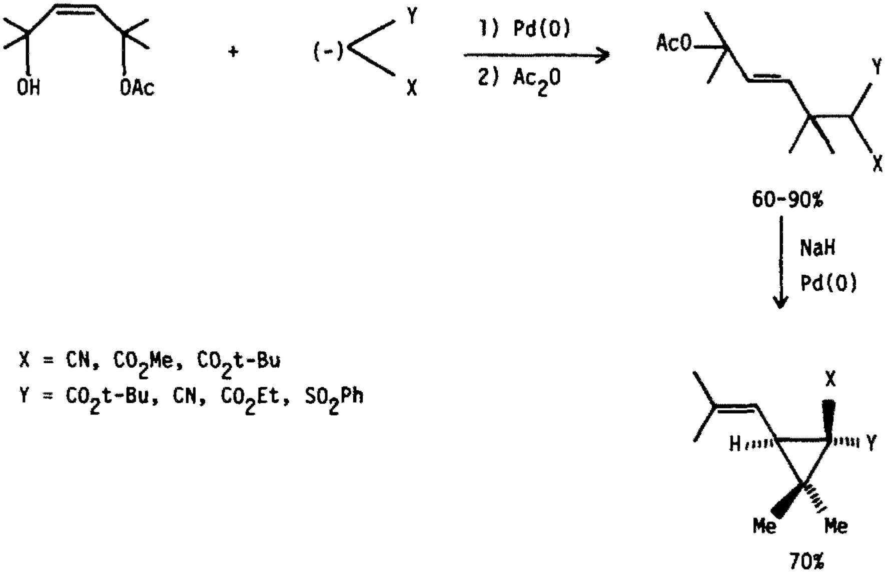


(163)

Nitro-stabilized carbanions alkylated allyl acetates in the presence of palladium(0) catalysts (equation 164) [171]. The products were converted to nitriles. Cyclopropanes, including chrysanthemic acid analogs, were prepared by allylic alkylation of a bis allylic alcohol (equation 165) [172]. Ketone enolates cleanly alkylated allylic acetates when a catalyst generated from $Pd(dba)_2$ and diphos was used (equation 166) [173]. The reaction was shown to occur by nucleophilic attack from the face opposite the metal (equation 167) [174]. Dienes were dialkylated or methoxy alkylated using palladium(II) chloride (equation 168) [175]. Vinyl zirconium species alkylated π-allylpalladium complexes through a process thought to involve initial alkylation at the metal center, followed by transfer of the alkyl group to the π-allyl ligand. The regiochemistry of alkylation could be controlled by the choice of ligands (equation 169) [176]. Steroid side chains were appended in this manner (equation 170) [177]. Photolysis of π-allyl palladium complexes produced 1,5-dienes or α,β-unsaturate ketones depending on the reaction conditions (equation 171) [178]. A series of unsaturated π-allylnickel halides were prepared and reacted with organic halides to produce dienes (equation 172) [179].



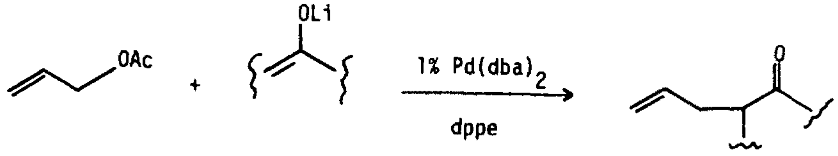
(164)



X = CN, CO$_2$Me, CO$_2$t-Bu
Y = CO$_2$t-Bu, CN, CO$_2$Et, SO$_2$Ph

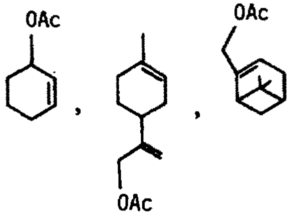
(165)

(166)

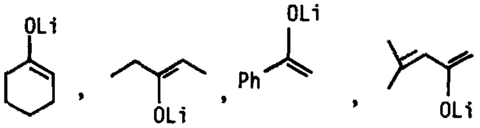


41-83%

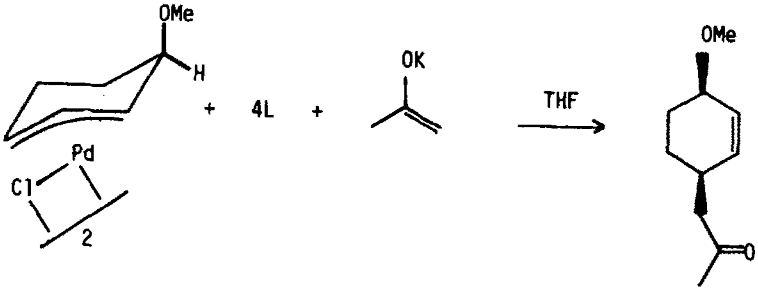
with allylic retention



worked



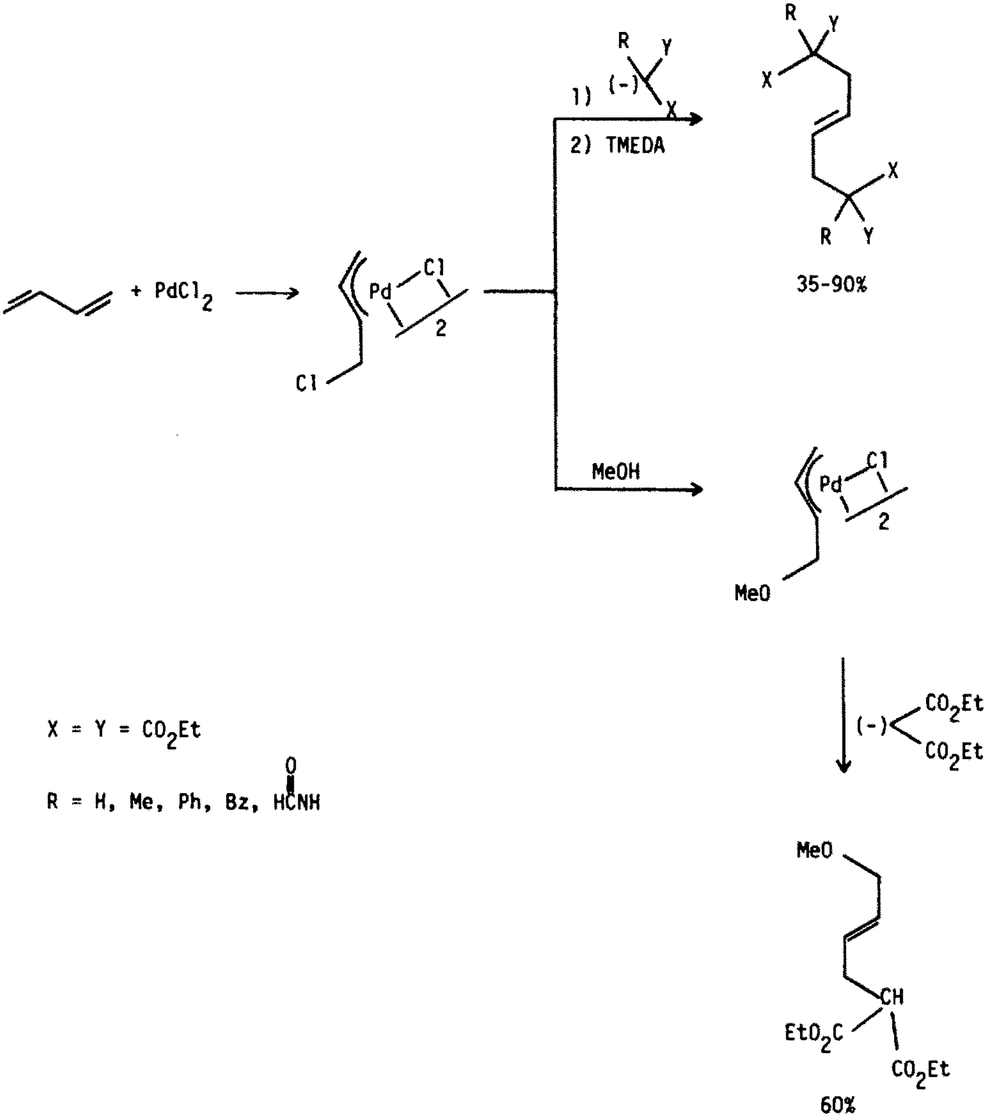
worked



(167)

60%

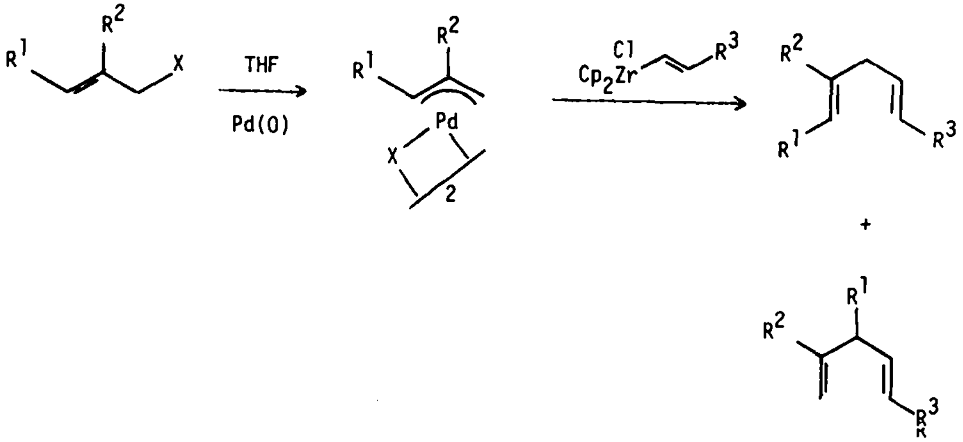
(168)



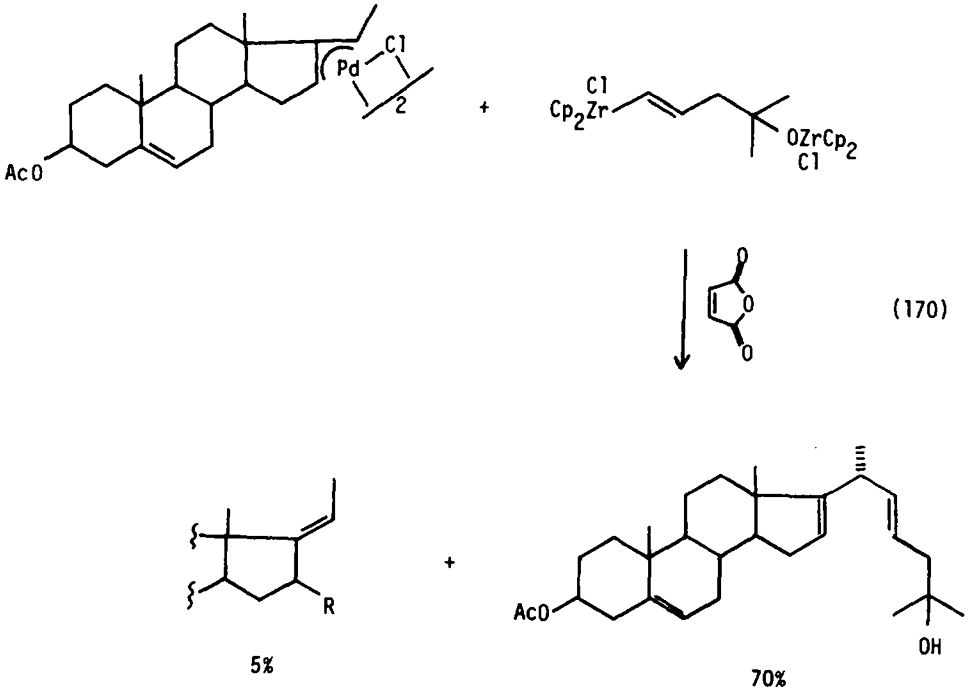
X = Y = CO$_2$Et

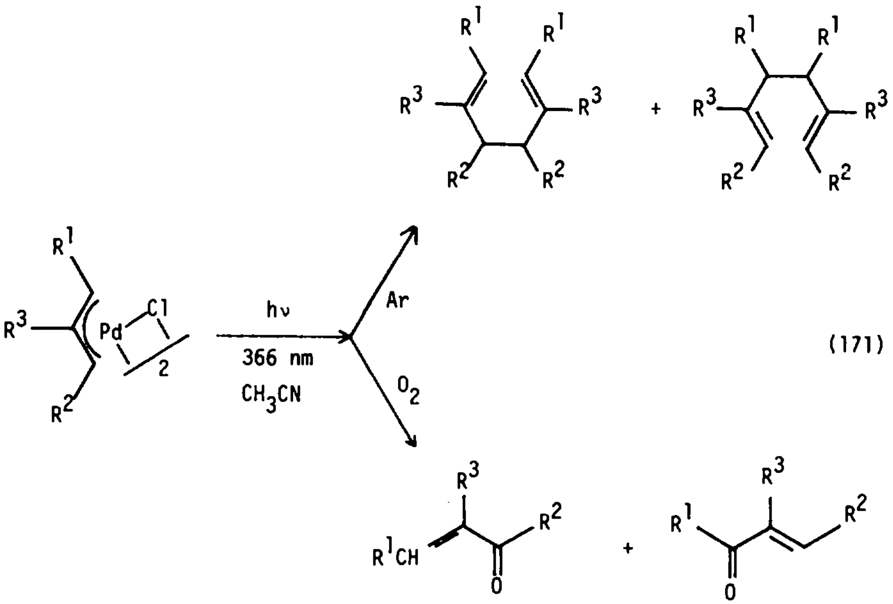
R = H, Me, Ph, Bz, $\mathrm{H\overset{O}{\overset{\|}{C}}NH}$

(169)


R1
R2
X
THF
Pd(0)
R1
R2
Pd
X
2
Cl
Cp2Zr
R3
R2
R1
R3
+
R2
R1
R3

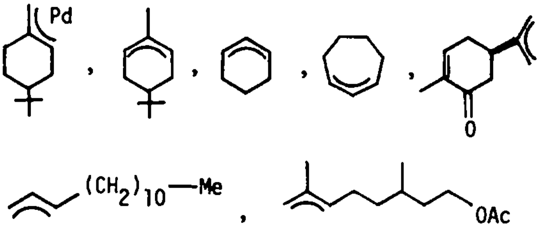
(170)


AcO
Pd
Cl
2
+
Cl
Cp2Zr
OZrCp2
Cl
O
O
O
R
5%
+
AcO
OH
70%

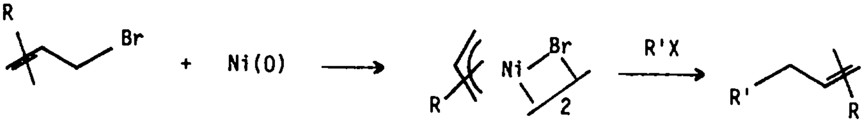


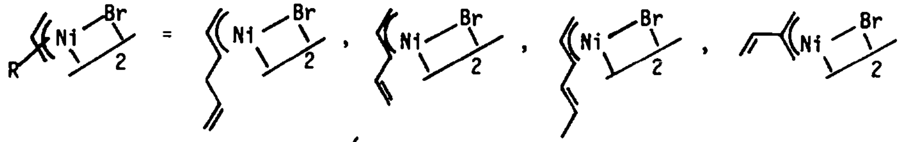
(171)

general process for:

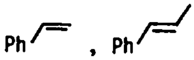


(172)



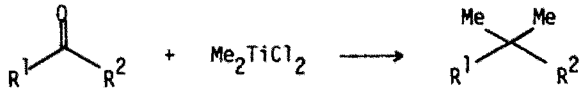


R' = Ph, PhCH$_2$,



10. Alkylation of Carbonyl Compounds

Dimethyltitanium dichloride converted ketones to dimethyl compounds in good yield (equation 173) [180]. Tertiary alcohols were similarly alkylated to give quaternary centers. The species $RZr(OBu)_3$ alkylated aldehydes in preference to ketones, but ketones did react. It had very low basicity and did not enolize ketones (equation 174) [181]. Ketones reacted with an aluminum-titanium species to give allenes (equation 175) [182]. π-Allyltitanium complexes alkylated aldehydes and ketones (equation 176) [183]. Chiral alkyltitanium (IV) complexes alkylated aryl ketones and aldehydes in up to 88% enantiomeric excess (equation 177) [184].



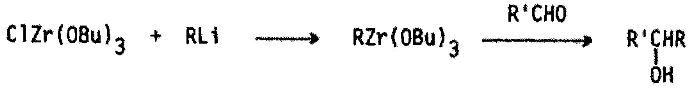
(173)

58-86%

R^1 = n-Pr, cyclo-Pr, Ph, Me

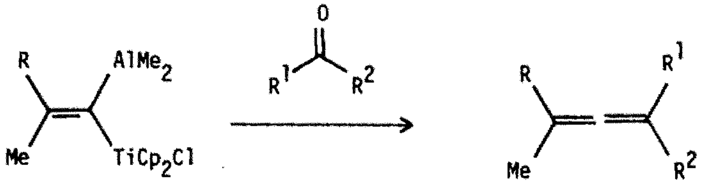
R^2 = n-Pr, cyclo-Pr, $Cl(CH_2)_3$, Ph, 1-adamantyl

$-(CH_2)_5-$



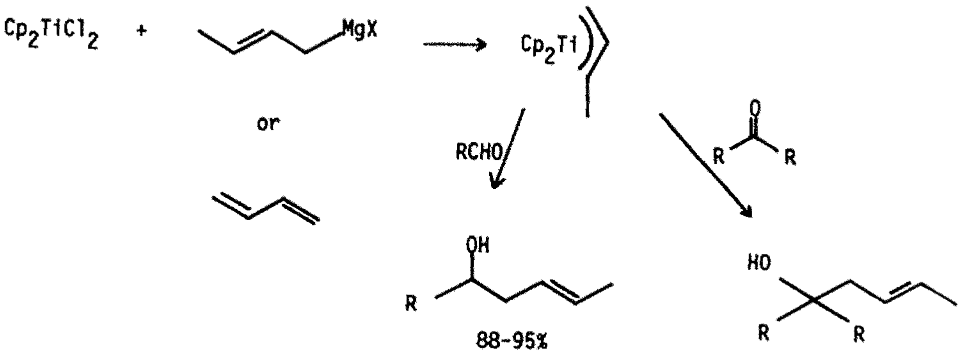
$$ClZr(OBu)_3 + RLi \longrightarrow RZr(OBu)_3 \xrightarrow{R'CHO} R'\underset{\substack{|\\ OH}}{C}HR \qquad (174)$$

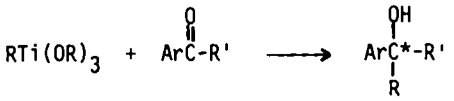
R = Me, t-Bu, , Ph



(175)

(176)

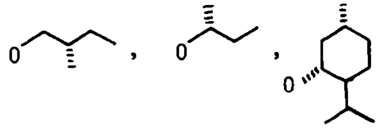




$$\mathrm{RTi(OR)_3} + \mathrm{ArC(=O)\text{-}R'} \longrightarrow \mathrm{ArC^{*}(OH)(R)\text{-}R'} \qquad (177)$$

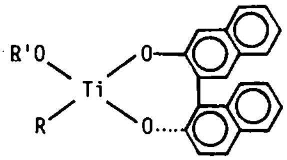
up to 88% ee

RO* =



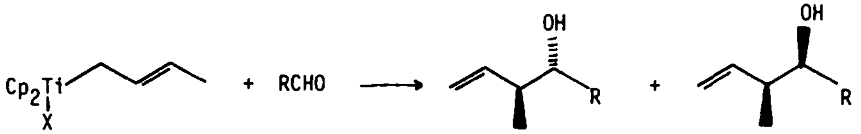
, quinine-O, chinconine-O

also

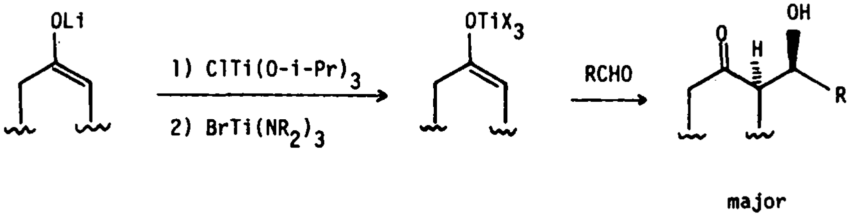


The use of early transition metal enolates to enhance erythro or threo selectivity has been studied to the point of exhaustion this year. σ-Allyltitanium compounds reacted with aldehydes with high threo selectivity (equation 178) [185]. In contrast, titanium(IV)alkoxy or amido enolates were distillable compounds, miscible with THF, ether, methylene chloride, and pentane, which reacted with aldehydes with high erythro selectivity (equation 179) [186]. Ligated methyltitanium complexes reacted similarly (equation 180) [187]. Allylzirconium complexes reacted with aldehydes with high threo selectivity (equation 181) [188], while zirconium enolates reacted with aldehydes with high erythro selectivity (equation 182) [189]. With a chiral oxazoline appended to the enolate, diastereoface selectivity within the erythro manifold ranged from 50-200 (equation 183).

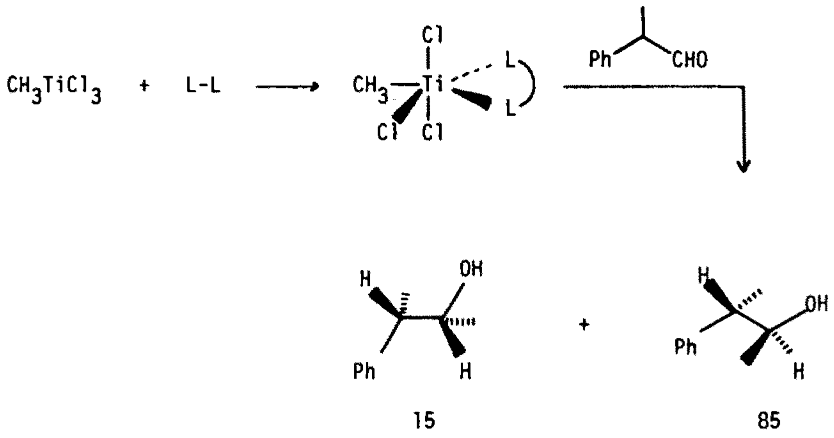
(178)



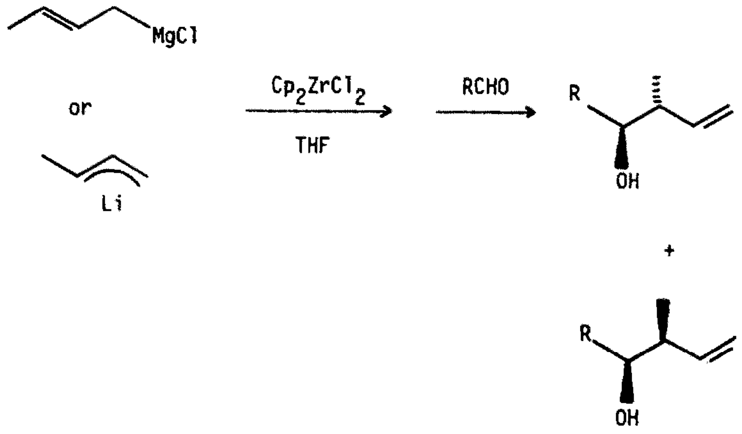
R		
R = t-Bu	90	10
R = Ph	100	0



(179)



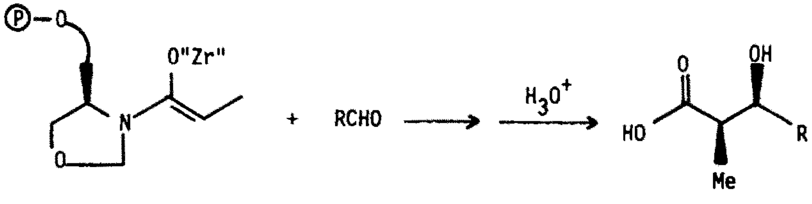
(180)



(181)

R = Ph, Me, Et, i-Pr

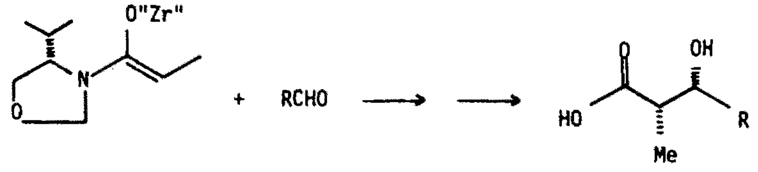
from 94:6 to 73:27



(182)

79-91%

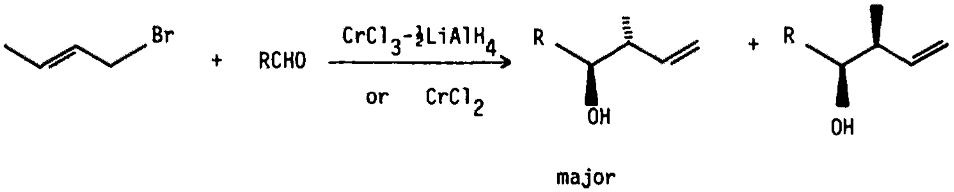
>97% *erythro*

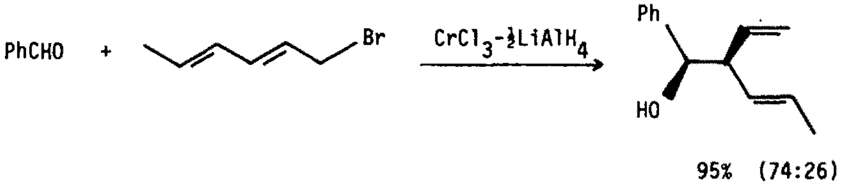


(183)

Reduction of anhydrous chromium(III) chloride with lithium aluminum hydride gave a reagent which reductively coupled allylic and benzylic halides and α-haloketones to aldehydes with high threo selectivity (equations 184 and 185) [191]. Propargyl bromides reacted with aldehydes and ketones in the presence of this chromium reagent to give α-allenic alcohols [192]. The nickel(0) promoted alkylation of ketones by halides was used to synthesize frullanolide (equation 186) [193].

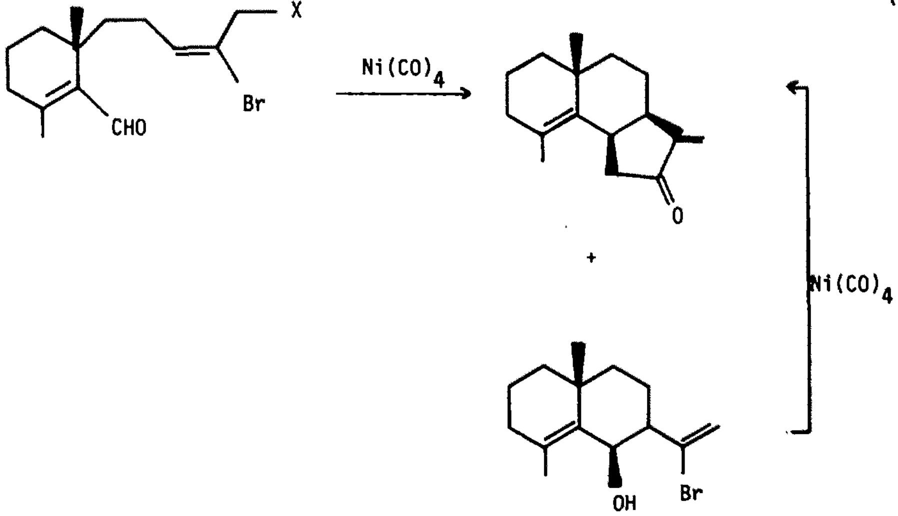
(184)





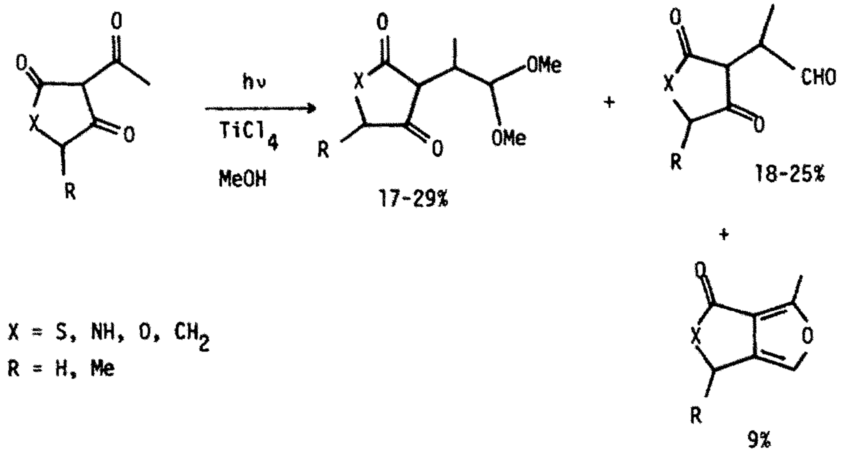
(185)

(186)



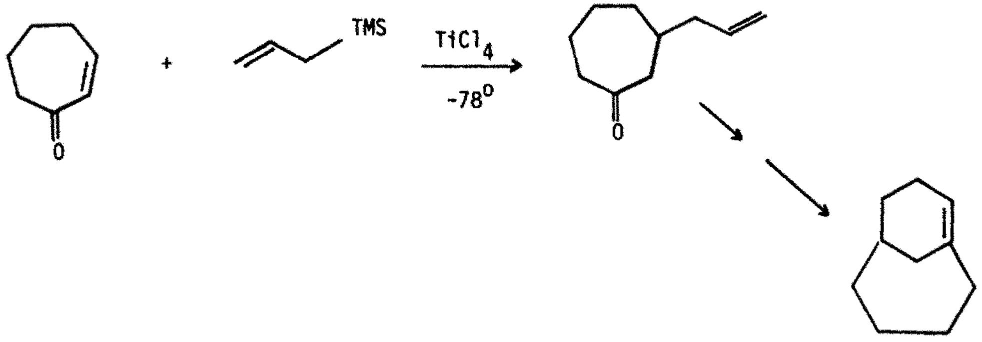
Cobalt(II) acetate/bipyridine catalysts increased the rate of aldol condensation of benzaldehyde with acetophenone by a factor of ten [194]. Titanium(IV) chloride assisted the photo process shown in equation 187 [195]. Bicyclo [4.3.1] dec-1(9)-ene was prepared by the titanium(IV) assisted reaction of cycloheptenone with allyl trimethyl silane (equation 188) [196]. Propargyl silanes alkylated ketones under similar conditions (equation 189) [197]. The chromium tricarbonyl stabilized carbanion of complexed benzyl systems alkylated aldehydes lacking enolizable hydrogens (equations 190-193) [198]. The mechanism of the nickel catalyzed addition of alkenylzirconium reagents to cyclopropyl ketones has been studied [199]. The oxime of acetaldehyde was converted to benzonitrile when treated with phenylmercuric chloride and palladium(II) and copper(II) salts [200].

(187)

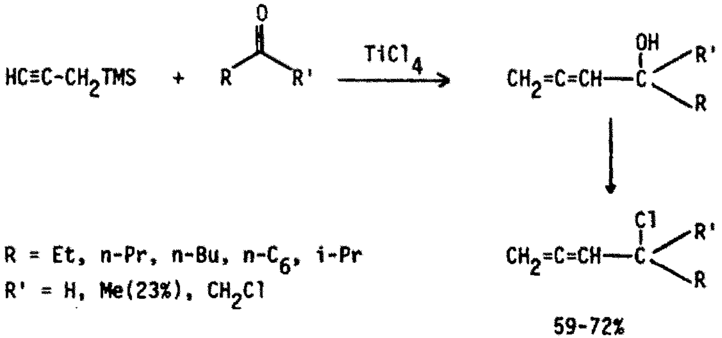


X = S, NH, O, CH_2
R = H, Me

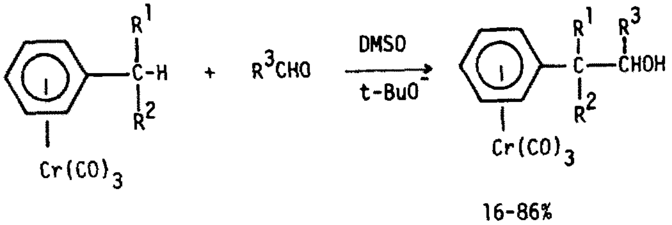
(188)



(189)

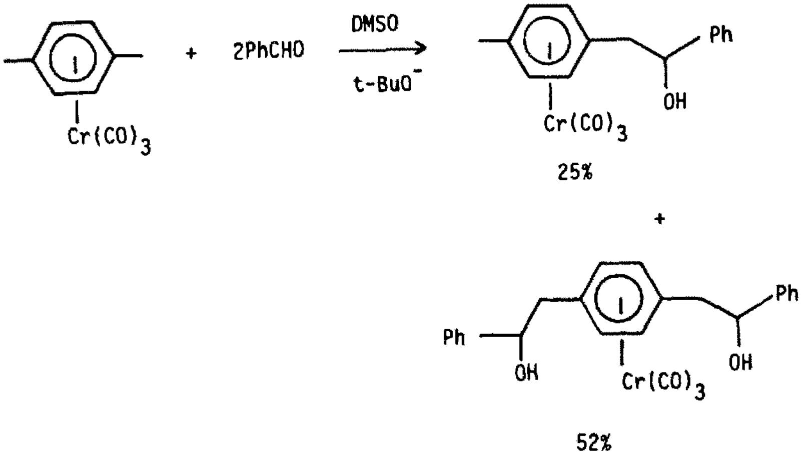


R = Et, n-Pr, n-Bu, n-C_6, i-Pr
R' = H, Me(23%), CH_2Cl

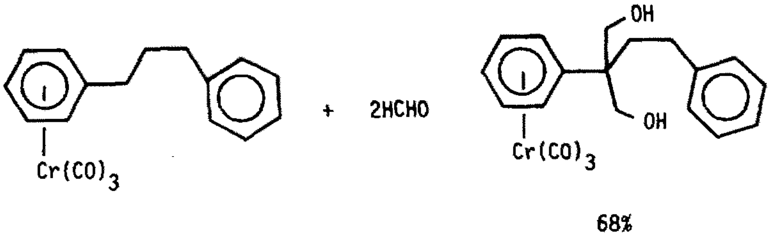


(190)

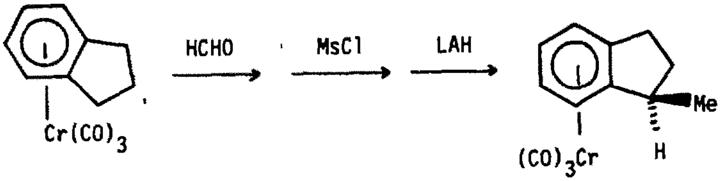
R^1 = H, Me; R^2 = H, Me; R^3 = Ph, H



(191)



(192)

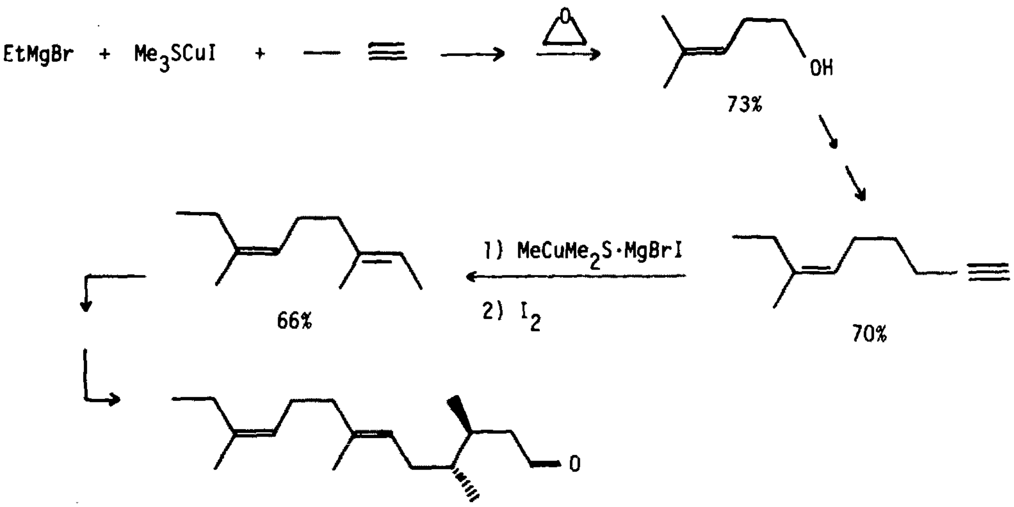


(193)

11. Alkylation of Epoxides

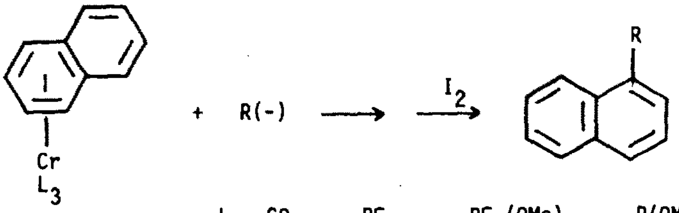
The ant pheremone faranal was synthesized by a process involving alkylation of ethylene oxide with a vinylcopper species (equation 194) [201].

(194)



12. Aromatic Substitution

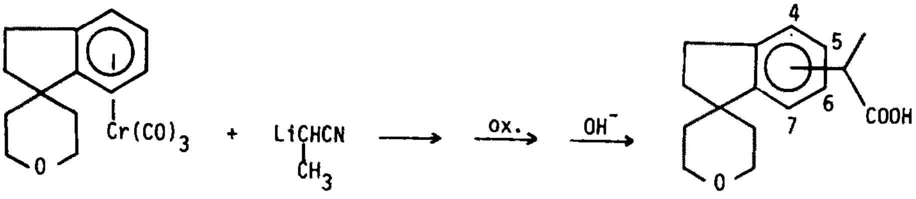
Arene-metal complexes in organic chemistry has been reviewed [202], as has addition of carbon nucleophiles to arene-chromium complexes [203]. "Metallation and cyclization of arenetricarbonylchromium complexes" was the topic of a dissertation [204]. The effects of changing ligands on the alkylation of naphthalene chromium tricarbonyl complexes by carbanions was examined (equation 195) [205]. Replacement of carbon monoxide by phosphine lowered the yield of alkylation product. The alkylation of tricyclic arene chromium (equation 196) [206] and iron complexes (equations 197 and 198) [207] has been studied. A cationic cobalt benzene complex underwent a double alkylation with cyclopentadiene anion (equation 199) [208]. Nucleophiles catalyzed aromatic substitution reactions of chromium complexed trimethylsilyl arenes (equation 200) [209].



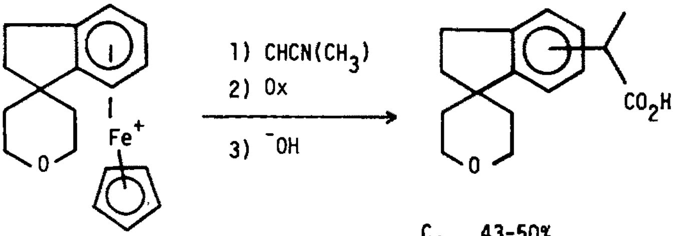
(195)

L =	CO	PF_3	$PF_2(OMe)$	$P(OMe)_3$
$LiMe_2CCN$	94	90	78	<3
$LiCH_2CN$	54	55		
$LiCHS(CH_2)_3S$	83			
LiOMe	30			

(196)

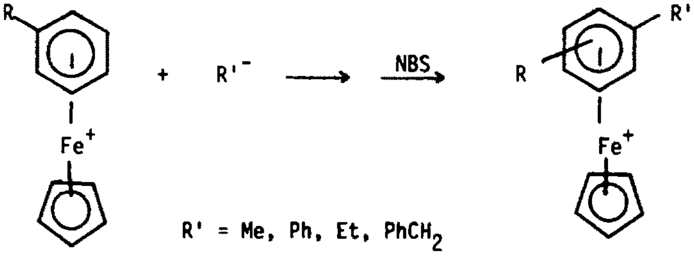


C-5	79%
C-4	3%
C-6	12%



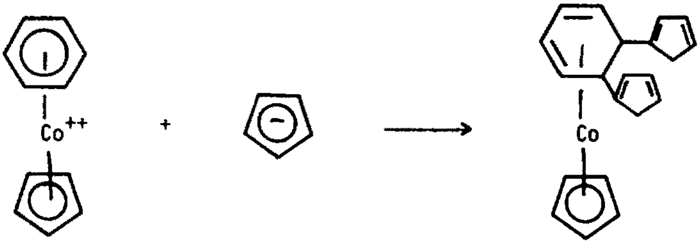
(197)

C_4	43-50%
C_5	13-14%
C_6	34-41%

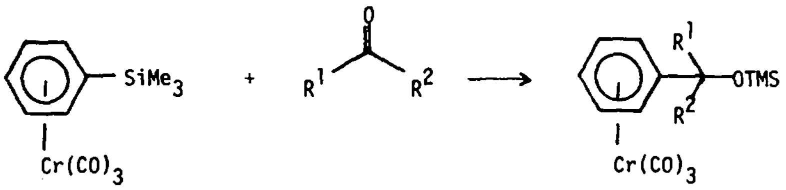


R' = Me, Ph, Et, PhCH$_2$

(198)



(199)

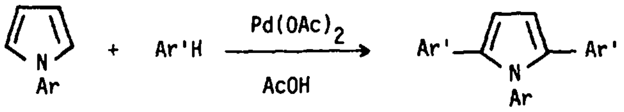


(200)

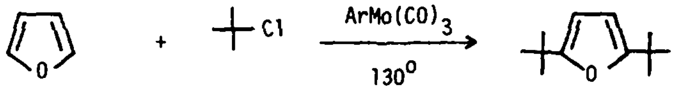
29-88%

R^1 = H, Me; R^2 = Me, n-Pr, Ph

Pyrroles underwent arylation at the α-positions when treated with benzene and palladium(II) in acetic acid (equation 201) [210]. Indoles reacted in a similar way. Furan was alkylated by t-butylchloride in the presence of a molybdenum catalyst (equation 202) [211]. Arenes were alkylated by nitromethane in the presence of manganese(III) acetate, by a radical process (equation 203) [212].



(201)



(202)

76%

$$\mathrm{ArH} + \mathrm{CH_3NO_2} + \mathrm{Mn(OAc)_3} \longrightarrow \mathrm{ArCH_2NO_2} + \mathrm{H^+} \qquad (203)$$

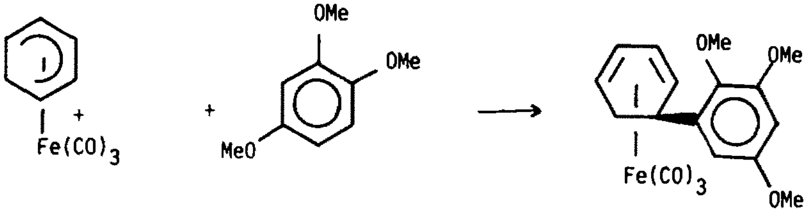
(Ce^{IV} also works) ∿70%

ArH = $PhCH_3$, PhH, naphth, PhOPh, p-MeOPhOMe

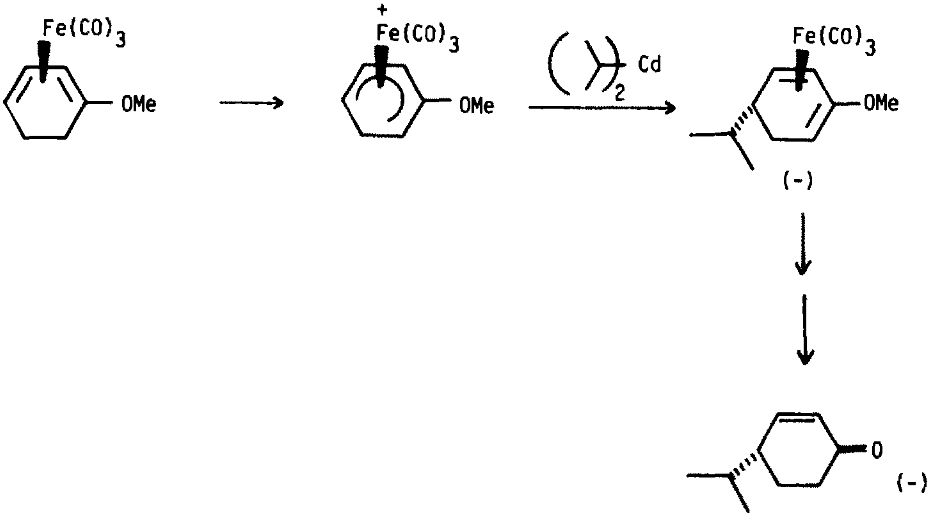
13. Alkylation of Dienyl Complexes

"Diene and dienyl complexes of iron: reactivity and synthetic utility was" the subject of a review [213], as was" the strategy of lateral control of reactivity: tricarbonyl cyclohexadiene iron complexes and their organic synthetic equivalents" [214]. The kinetics of nucleophilic attack of di- and tri-methoxybenzenes on cyclohexadienyliron tricarbonyl complexes was studied (equation 204) [215], as were the rates of reaction of pentane-2,4-dione with the same complexes [216]. Chiral dieneiron complexes were resolved and their absolute configurations were assigned through a series of chemical transformations (equation 205) [217]. A procedure to resolve some of the corresponding cyclohexadienyl complexes was devised [218].

(204)

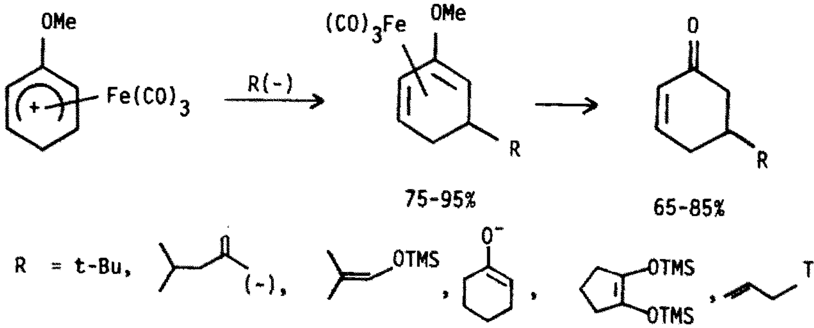


(205)



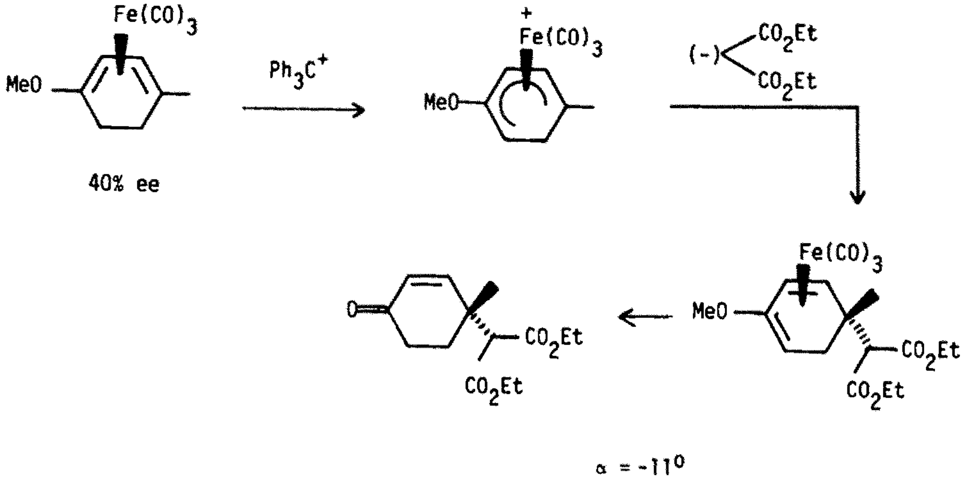
(configuration known)

A variety of substituted cyclohexadiene complexes of iron were prepared for further use in synthesis [219]. Substituted cyclohexenones were prepared by the alkylation of methoxycyclohexadienyl complexes of iron (equation 206) [220]. Starting with resolved diene complexes, optically active alkylation products were obtained (equation 207) [221]. Cyclohexadienyl complexes of iron were alkylated by nitromethane (equation 208) [222]. Complexed cyclohexadienols were prepared by alkylation of appr priate hydroxycyclohexadienyl iron complexes (equation 209) [223].

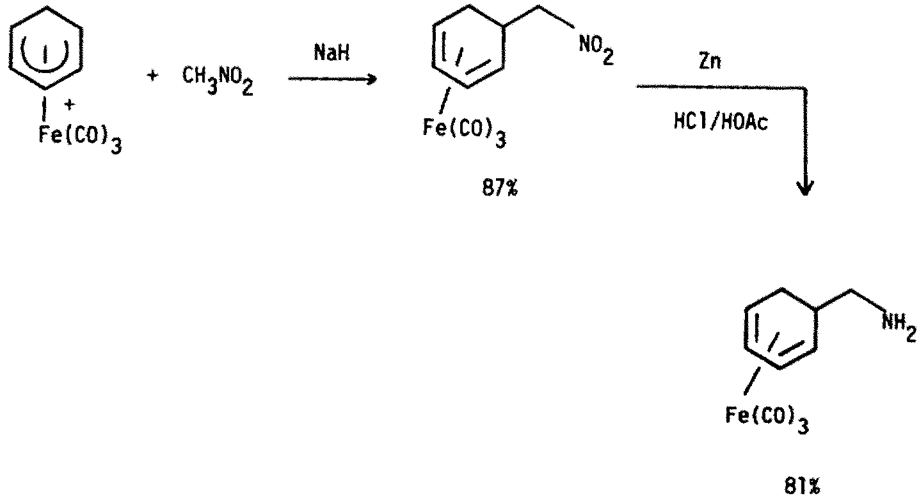

OMe
Fe(CO)$_3$
R(-)
(CO)$_3$Fe
OMe
R
O
R
75-95%
65-85%
R = t-Bu,
(-),
OTMS
O$^-$
OTMS
OTMS
TMS

(206)

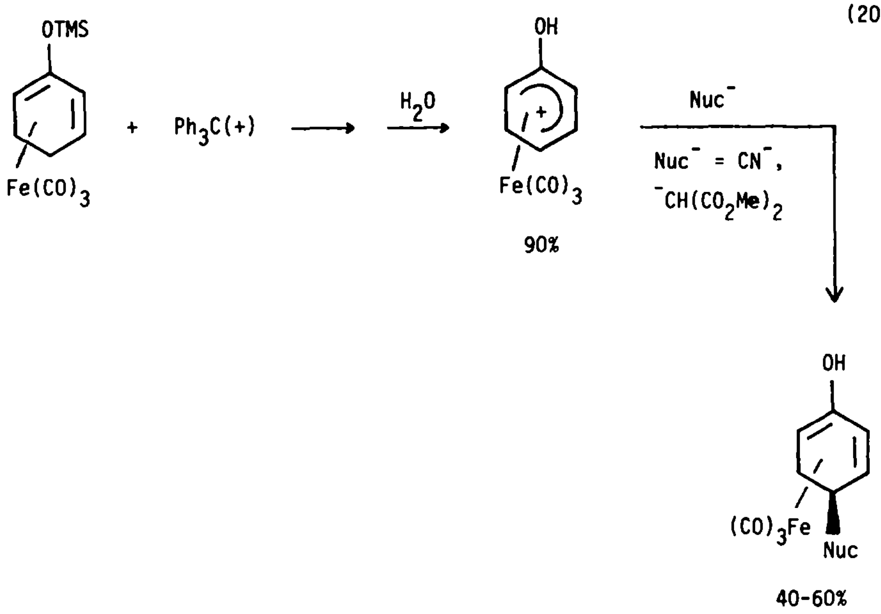
(207)


Fe(CO)$_3$
MeO
40% ee
Ph$_3$C$^+$
+
Fe(CO)$_3$
MeO
(-)
CO$_2$Et
CO$_2$Et
Fe(CO)$_3$
MeO
CO$_2$Et
CO$_2$Et
O
CO$_2$Et
CO$_2$Et
α = -11°

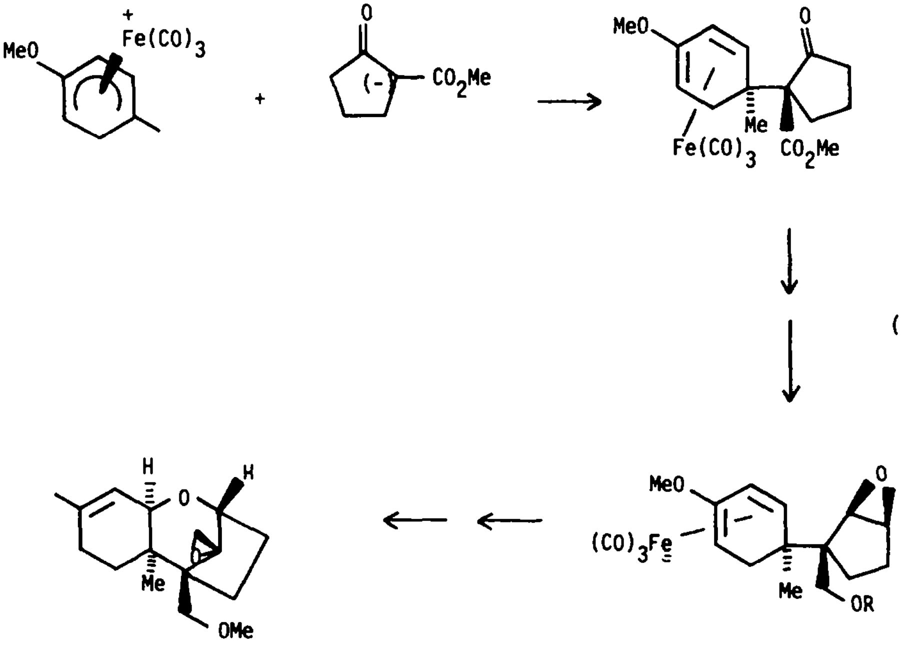
(208)


+
Fe(CO)$_3$
+ CH$_3$NO$_2$
NaH
NO$_2$
Fe(CO)$_3$
87%
Zn
HCl/HOAc
NH$_2$
Fe(CO)$_3$
81%

(209)

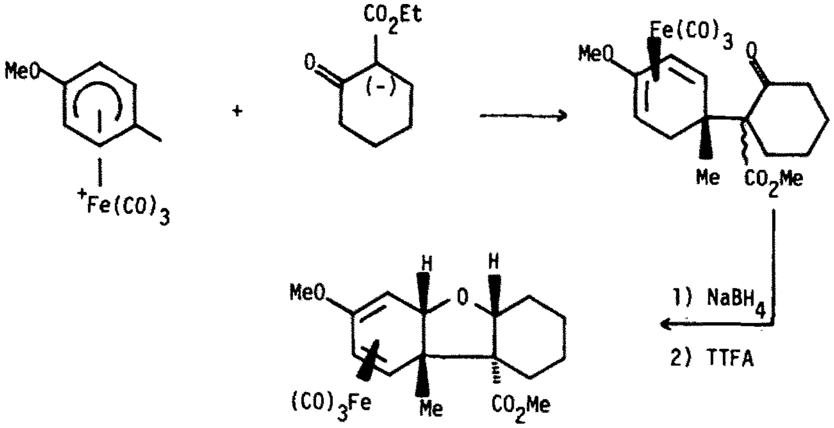


Cyclohexadienyl iron complexes have been extensively used in organic synthesis this year (equation 210) [224], (equation 211) [225], (equation 212) [226], (equation 213) [227], (equation 214) [228].

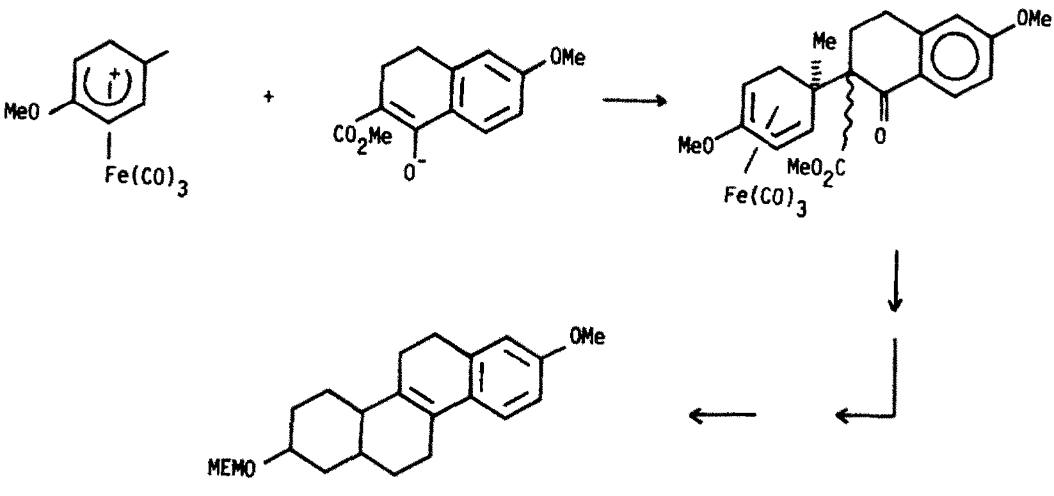


(210)

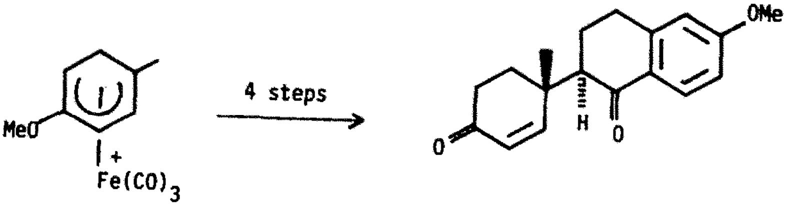
(211)

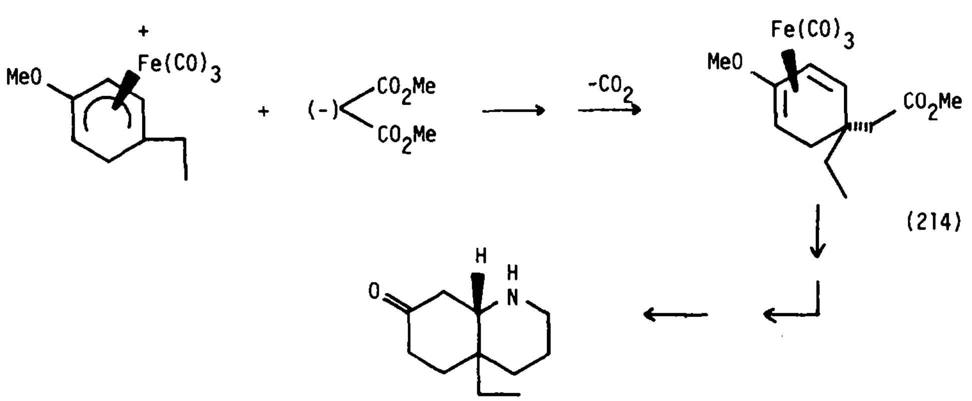

MeO
+Fe(CO)3
+
CO2Et
O
(-)
Fe(CO)3
MeO
O
Me
CO2Me
1) NaBH4
2) TTFA
H
H
MeO
O
(CO)3Fe
Me
CO2Me

(212)


MeO
Fe(CO)3
+
OMe
CO2Me
O-
Me
OMe
MeO
O
MeO2C
Fe(CO)3
OMe
MEMO

(213)

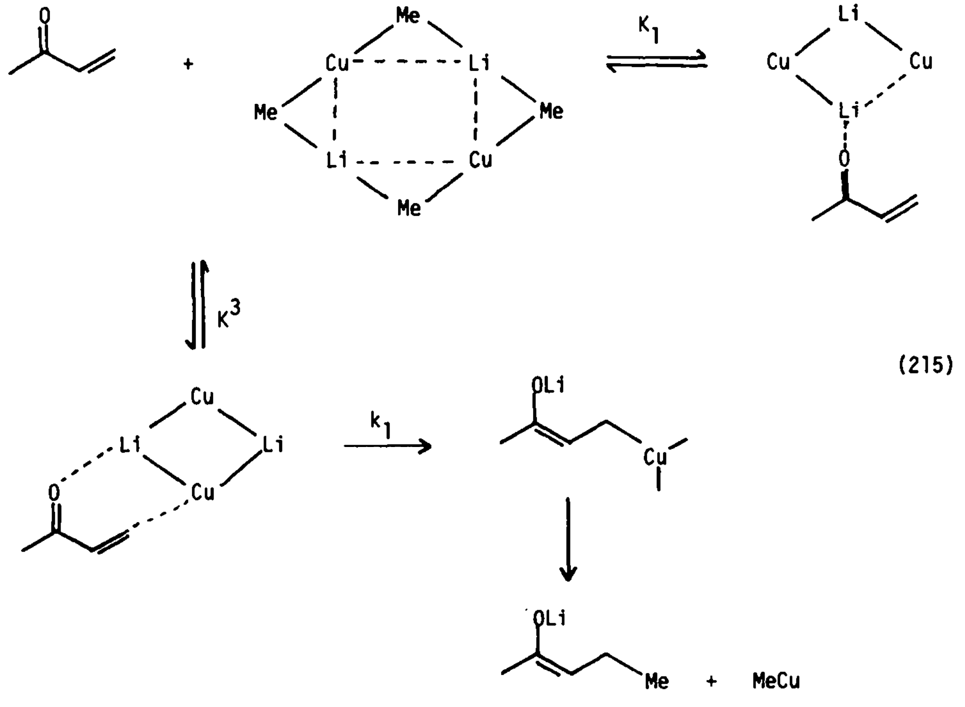

MeO
+
Fe(CO)3
4 steps
OMe
O
H
O



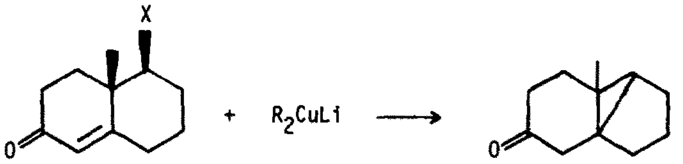
(214)

B. Conjugate Additions

Organocopper species continue to be the reagents of choice for 1,4-addition processes. Two procedures for the preparation and purification of $CuBr{\cdot}Me_2S$, an important starting material for a variety of organocopper reactions, have appeared [229][230]. Halide free "Normants" reagent $Cu_mMg_nMe_{(m+2n)}$ for which m = 1, 2, 3, 4, 6 and n = 1, 2, has been prepared [231]. Mesityl copper(I) is a stable yellow solid which has been used to provide the nontransferable alkyl group in mixed cuprate 1,4-additions and reductions [232]. The kinetics of the reaction of lithium dimethylcuprate with methyl vinyl ketone has been studied and the mechanism in equation 215 was proposed [233]. The mechanism of the reaction of dialkylcuprates with conjugated enones having leaving groups in the δ position has been studied (equation 216) [234].



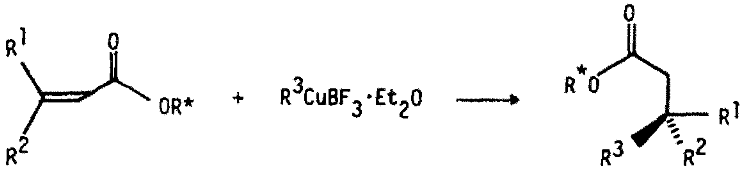
(215)



(216)

(R_2CuLi is a le-reducing agent)

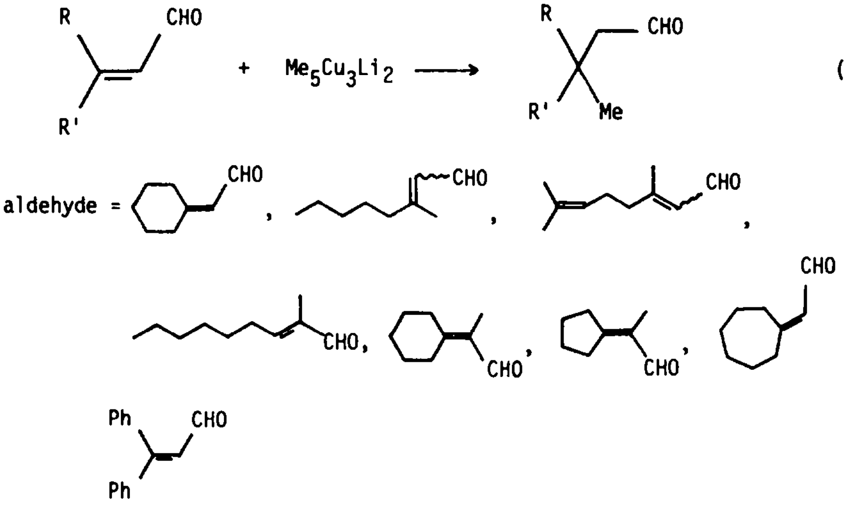
A number of attempts to induce asymmetry in the conjugate addition process have been made. Using mixed cuprates of the type [R*OCuMe]M in which the alkoxide was from a chiral amino alcohol such as 2-aminobutanol, valinol or cinchonine for 1,4-additions to chalcone, a maximum of 34% enantiomeric excess was obtained [236]. Using ℓ-prolinol as the chiral amino alcohol it was concluded that an N-H group was ten times more effective than an NMe group and that THF was a better solvent than toluene for inducing asymmetry in 1,4-addition to conjugated ketones [237]. With mixed cuprates having chiral α-phenethyl groups as the nontransferable alkyl group high chemical yields for conjugate additions to chalcones were obtained, but only 1% enantiomeric excess was observed [238]. The 1,4-alkylation of α,β-unsaturated esters of (-)-8-phenylmenthol resulted in high optical yields (equation 217) [239].



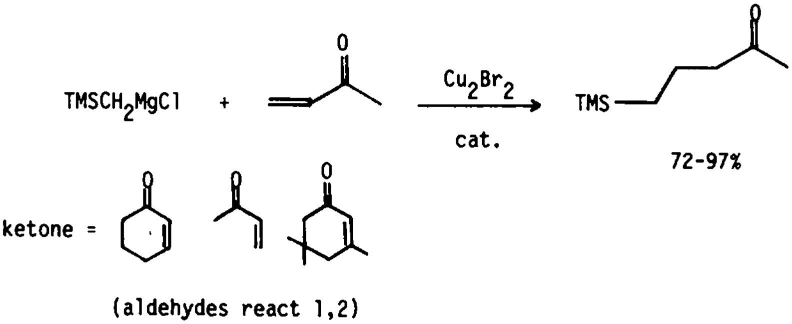
(217)

R^1	R^2	R^3	%	ee
H	Me	Ph	76	>99
H	Me	n-Bu	76	>99
Me	H	Ph	36	24
Me	H	n-Bu	76	70
H	n-Bu	Me	28	78

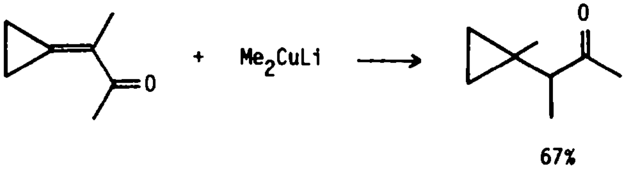
The reagent $Me_5Cu_3Li_2$ added exclusively 1,4- to conjugated aldehydes (equation 218) [240]. Copper(I) bromide catalyzed the conjugate addition of trimethylsilylmethylmagnesium chloride to conjugated enones (equation 219) [241]. β-Cyclopropyl-α,β-unsaturated ketones underwent exclusive 1,4 alkylation with Me_2CuLi (equation 220) [242]. The addition of lithium dialkylcuprates to α,β-unsaturated phosphoryl compounds has been reviewed [243]. Organocopper chemistry has been used in the synthesis of prostaglandins (equation 221) [244] and steroids (equation 222) [245].


R
CHO
R'
+
$Me_5Cu_3Li_2$
R
CHO
R'
Me
aldehyde =
CHO
CHO
CHO
CHO
CHO
CHO
CHO
Ph
CHO
Ph

(218)

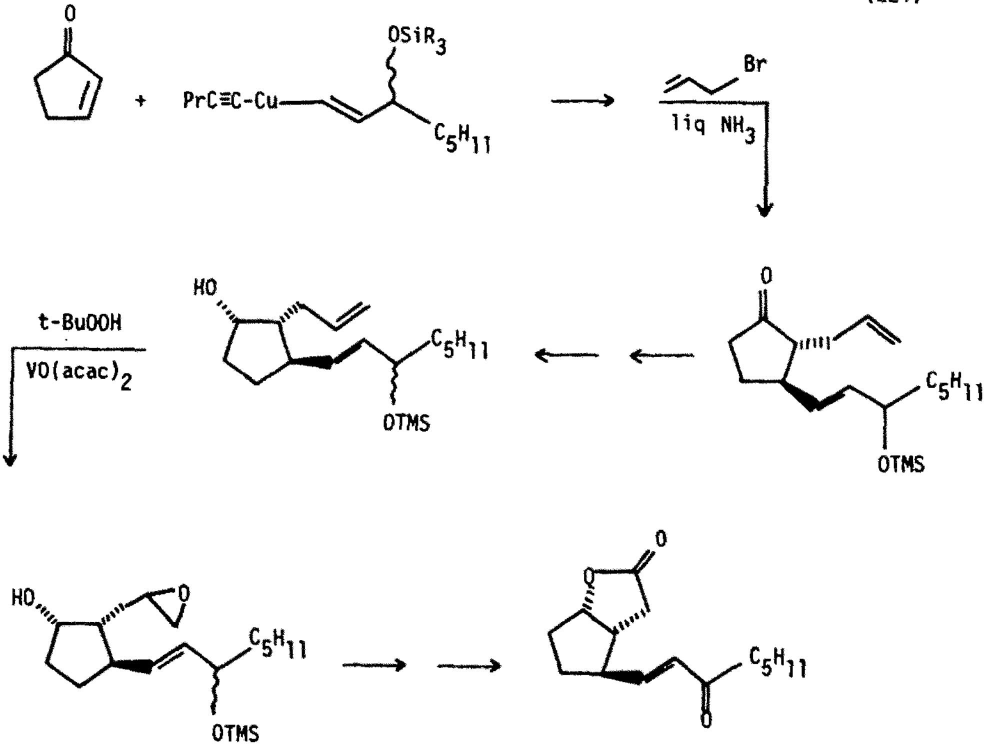

$TMSCH_2MgCl$
+
O
Cu_2Br_2
cat.
TMS
O
72-97%
ketone =
O
O
O
(aldehydes react 1,2)

(219)

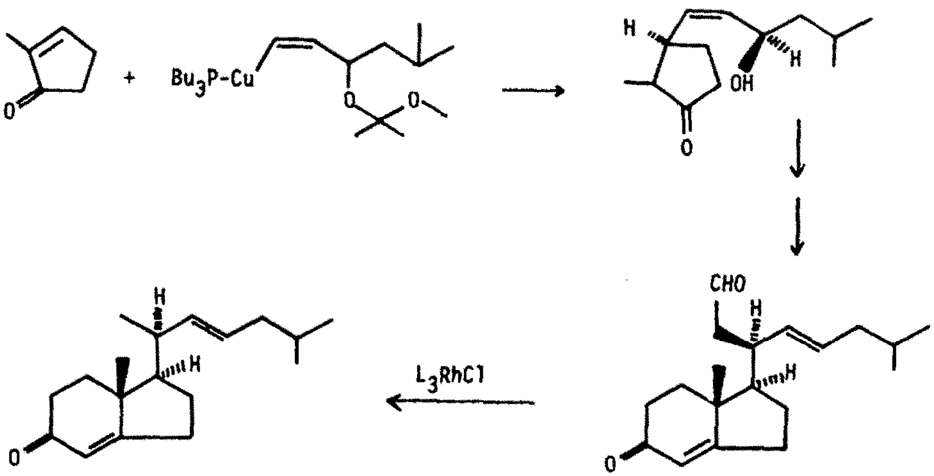

O
+
Me_2CuLi
O
67%

(220)

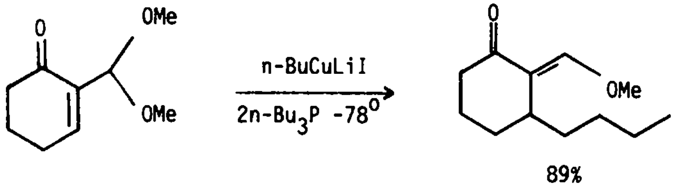
(221)



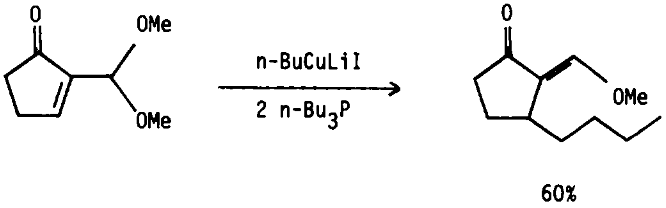
(222)



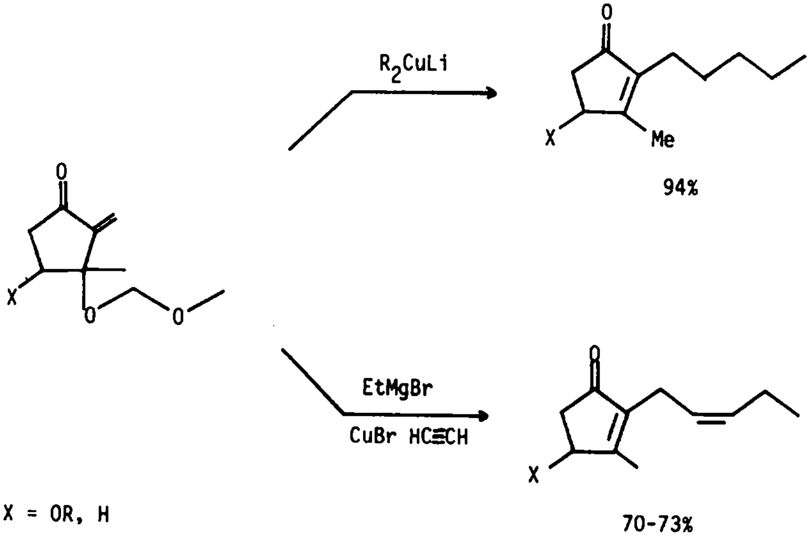
Conjugate additions to enones having appropriately located leaving groups led to olefinic products (equations 223 and 224) [246], (equation 225) [247], (equation 226) [248].



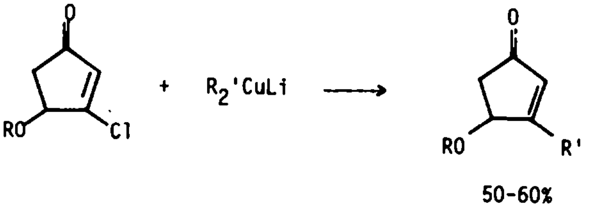
(223)



(224)

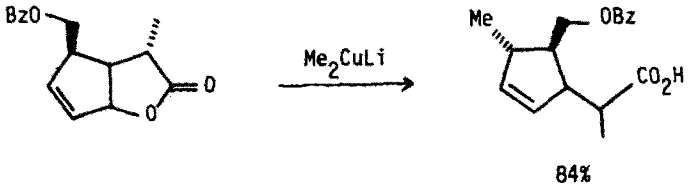


(225)



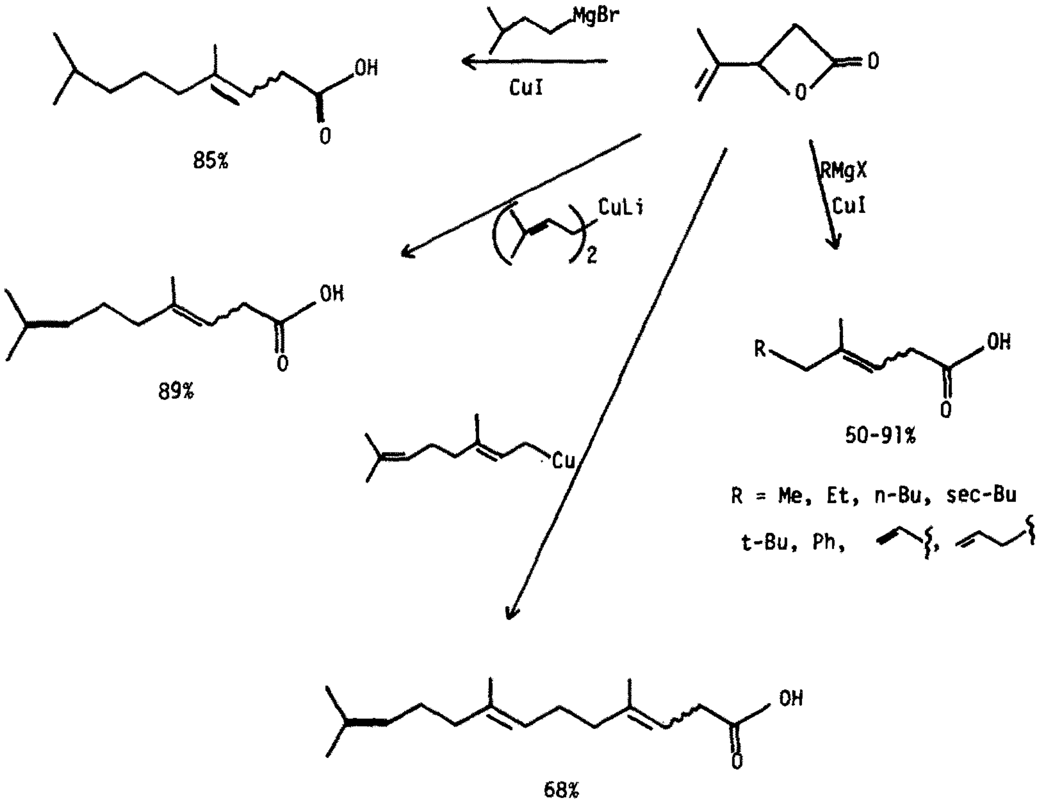
(226)

Organocuprate reagents were also very efficient in S_N2' type reactions of allyl esters and epoxides. With allylic lactones the process was shown to proceed in an S_N2' *anti* manner (equation 227) [249]. With allylic β-lactones, the copper-catalyzed Grignard addition was used to synthesize terpenes (equation 228) [250], and β,γ-unsaturated acids (equation 229) [251]. With the corresponding propargyl lactones allenic acids were obtained (equation 230). This chemistry was used to synthesize pellitorine (equation 231) [252]. Acetates of carbohydrates underwent unusual reactions with organocuprates (equations 232 and 233) [253]. Ionones (equation 234) [254] and prostaglandins (equation 235) [255] were synthesized using organocopper chemistry.

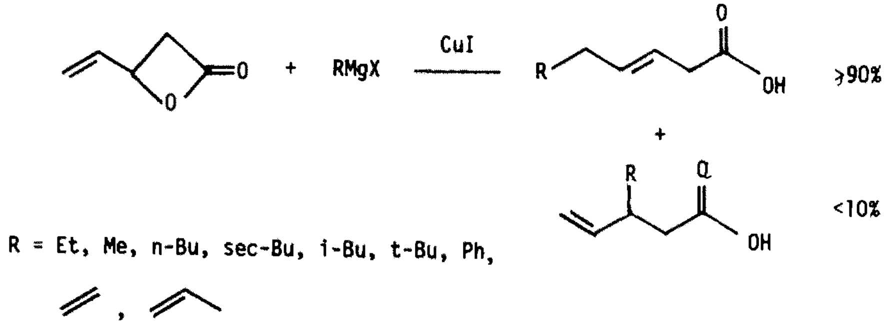


(227)

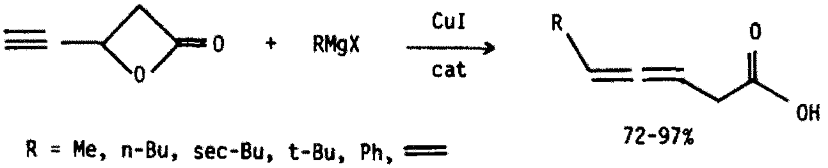
(228)



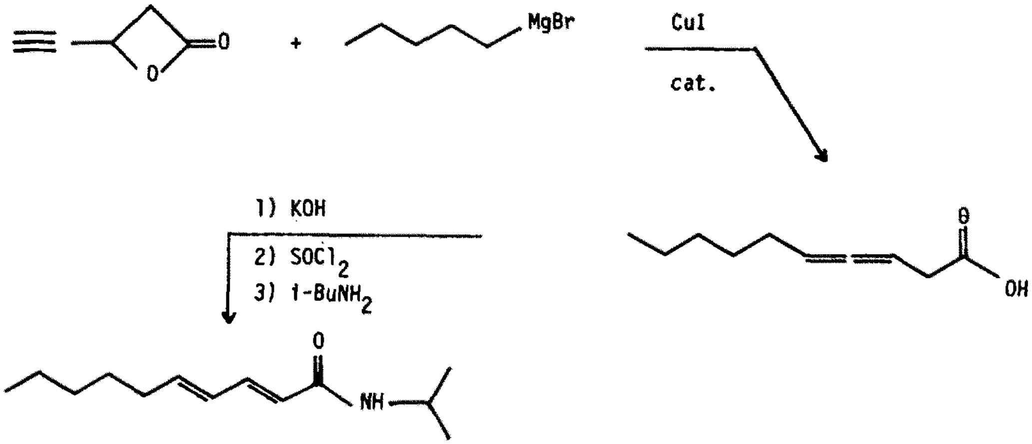
(229)

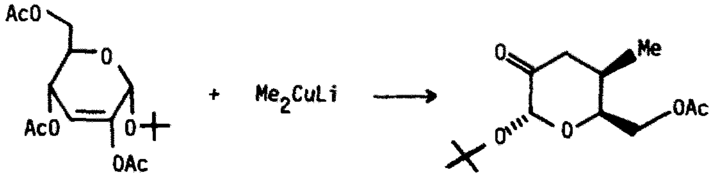


(230)

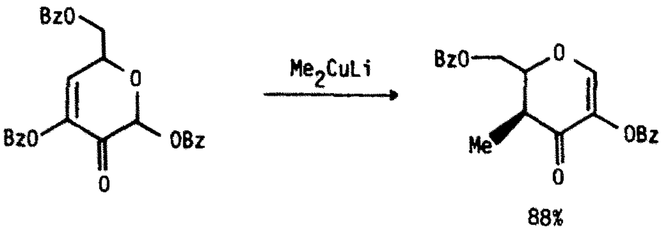


(231)



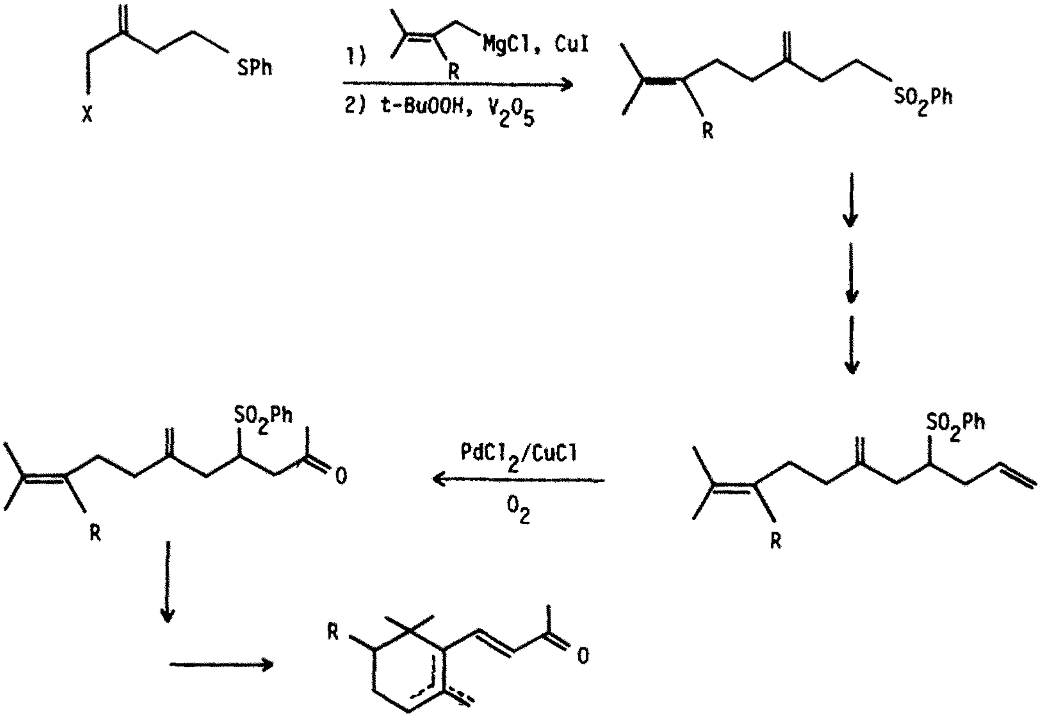


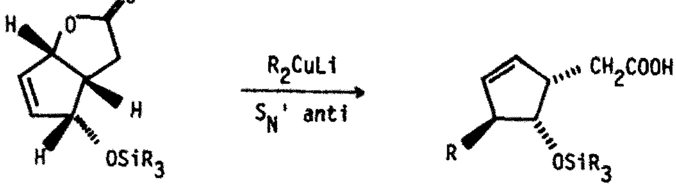
(232)



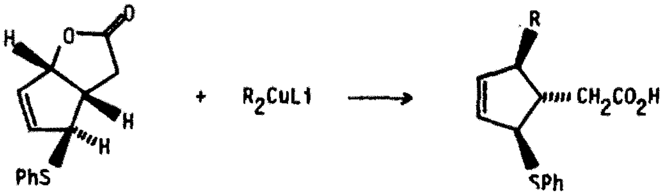
(233)

(234)





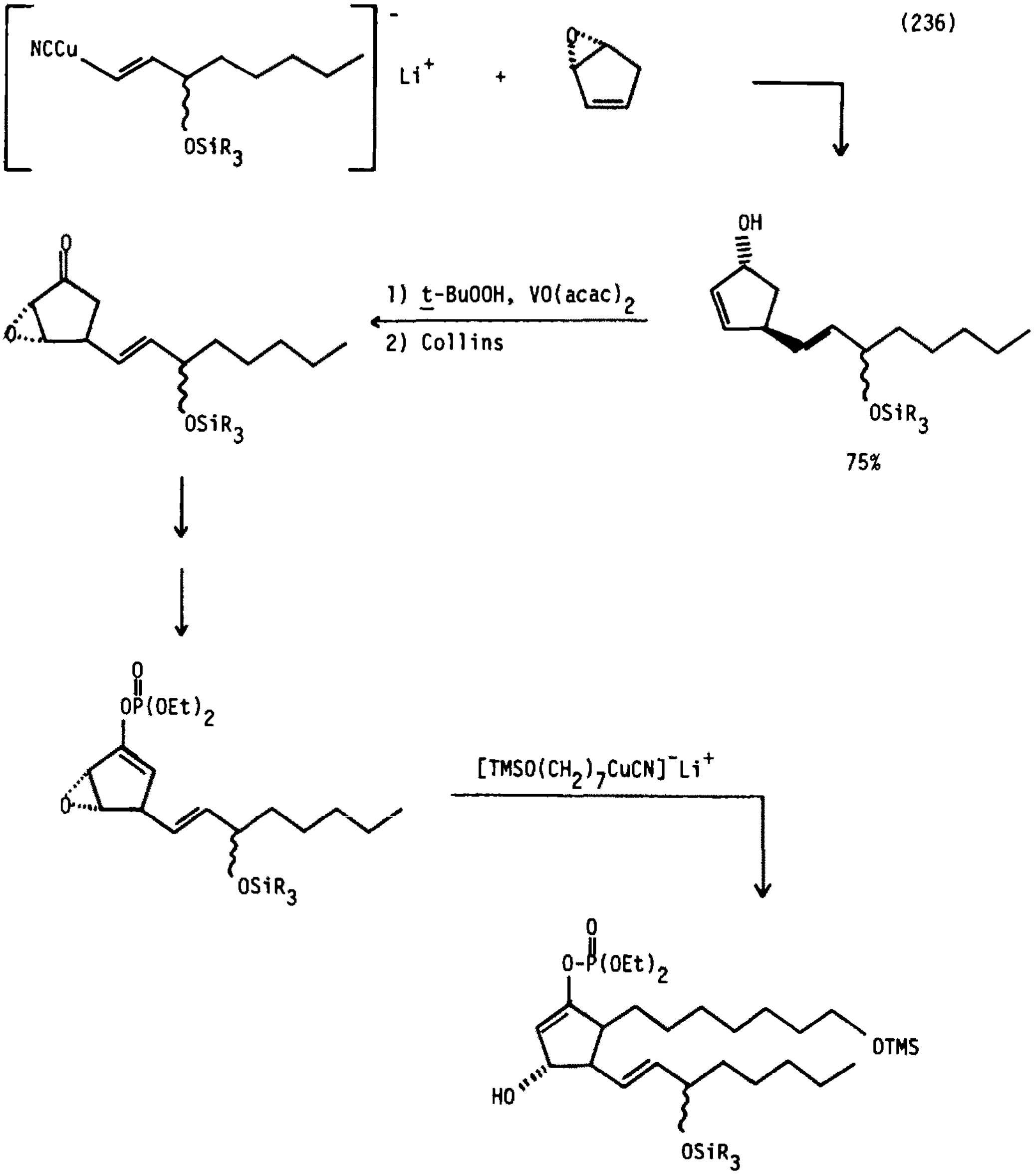
(235a)



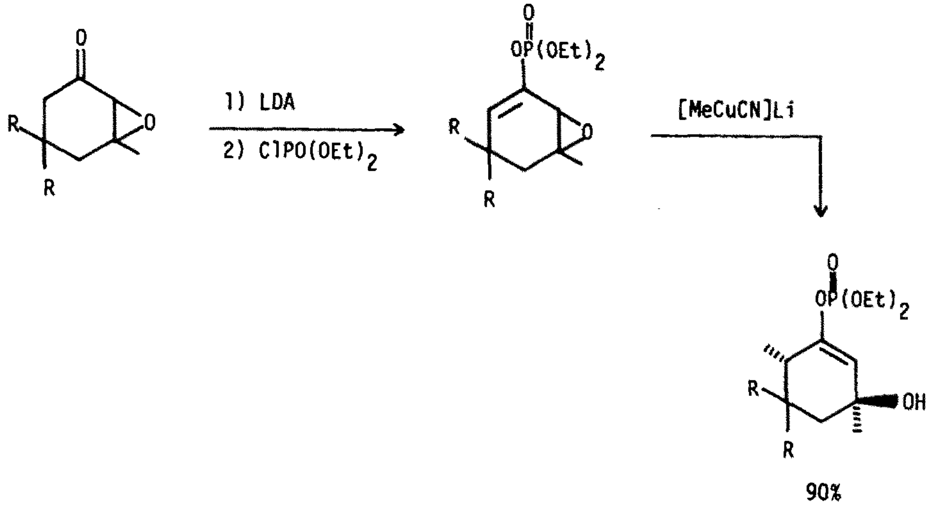
(235b)

The reaction of cyclic allylic epoxides with organocuprates was used to synthesize prostaglandin analogs (equation 236) [256]. Alkylation of enol phosphates of epoxycyclohexanones (equation 237) was used to synthesize multistriatin (equation 238) [257]. Trimethylsilylenol ethers reacted in a similar fashion (equation 239) [258]. The stereo- and regiochemistry of alkylation of exocyclic allyl epoxides depend on both the substrate and the organocopper reagent (equations 240-242) [259]. Optically active allyl epoxides underwent alkylation by organocuprates stereospecifically (equations 243 and 244) [260]. Estrenols were prepared from epoxy estrenes by alkylation with organocuprates (equation 245) [261]. Propargyl epoxides underwent alkylation to produce allenes (equation 246) [262].

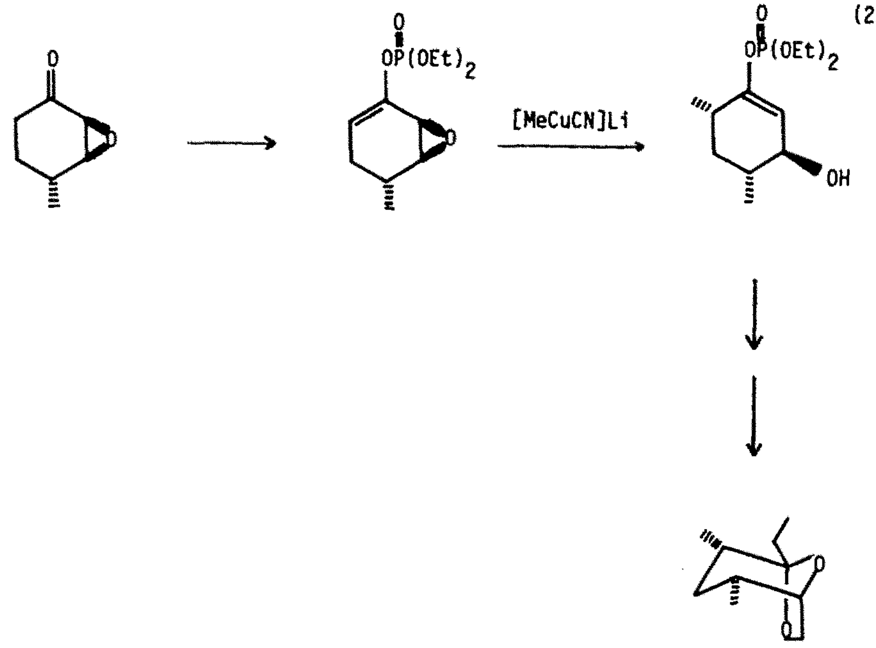
(236)

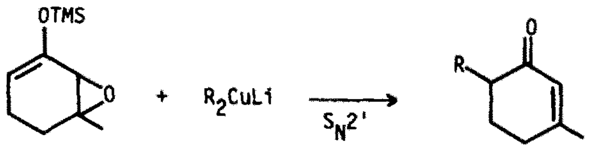


(237)



(238)





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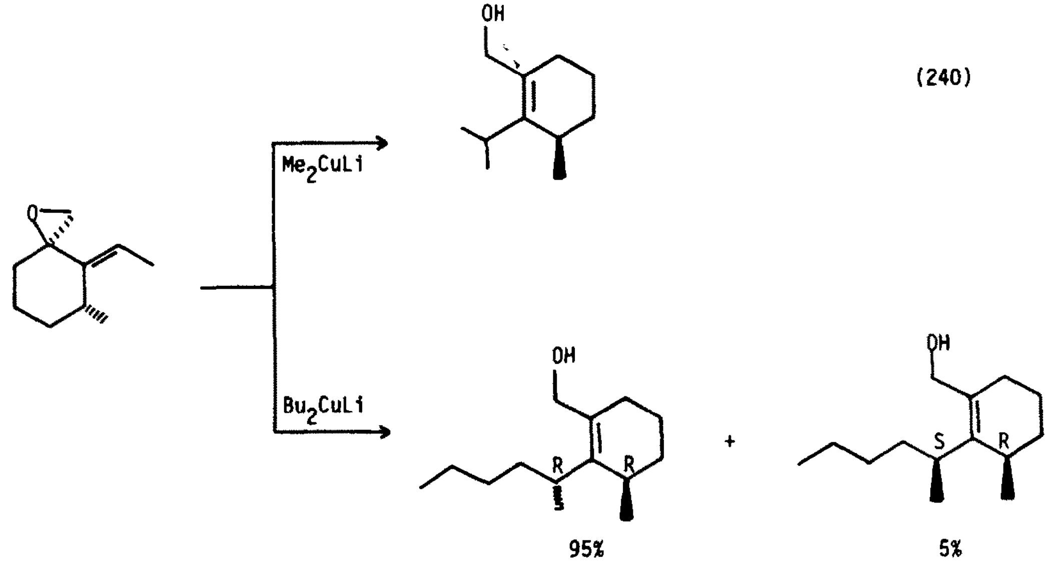

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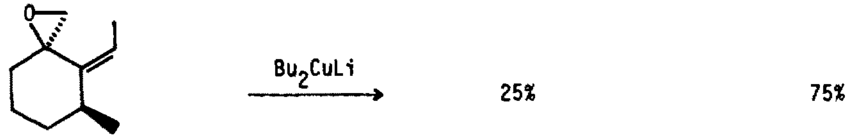
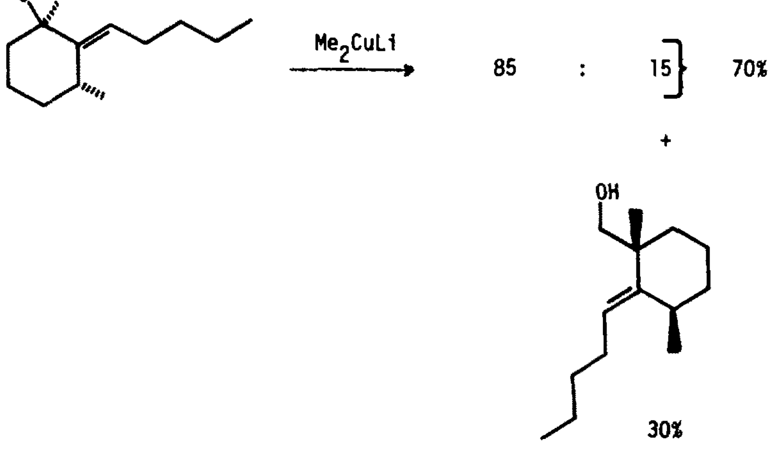
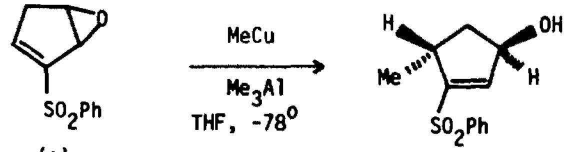


(241)

(242)

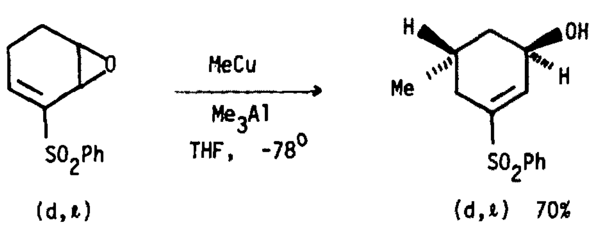




(ℓ)

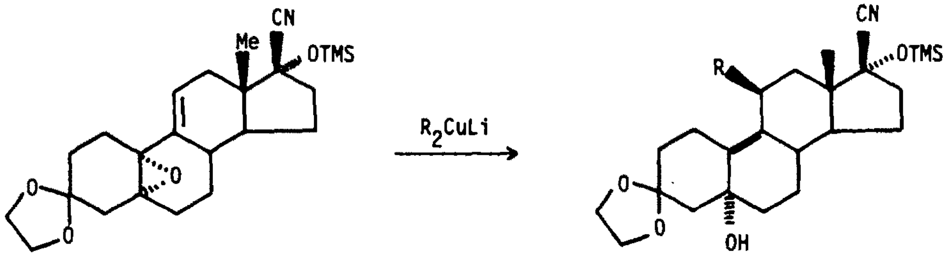
(d) 80%

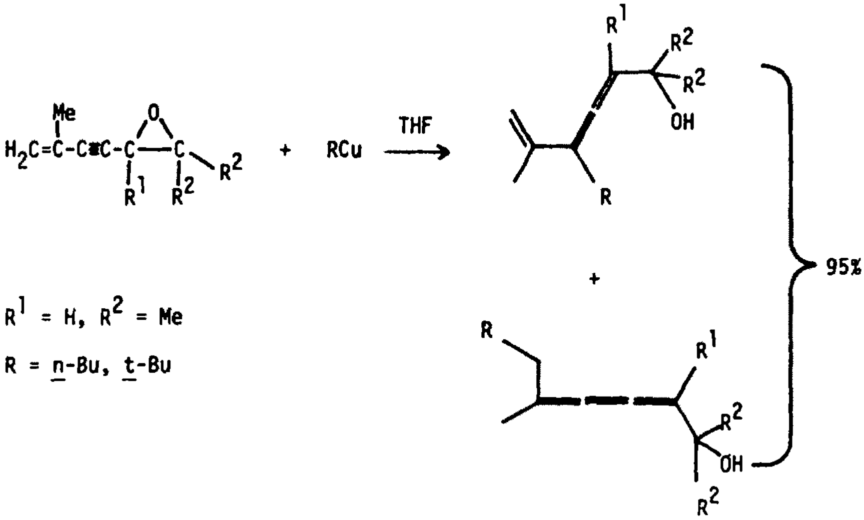
(243)



(244)

(245)





(246)

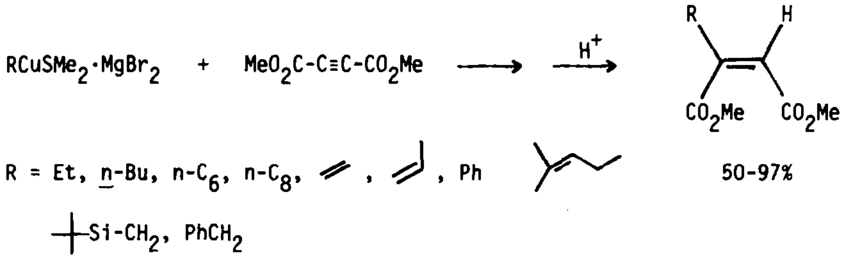
$R^1 = H$, $R^2 = Me$

R = n-Bu, t-Bu

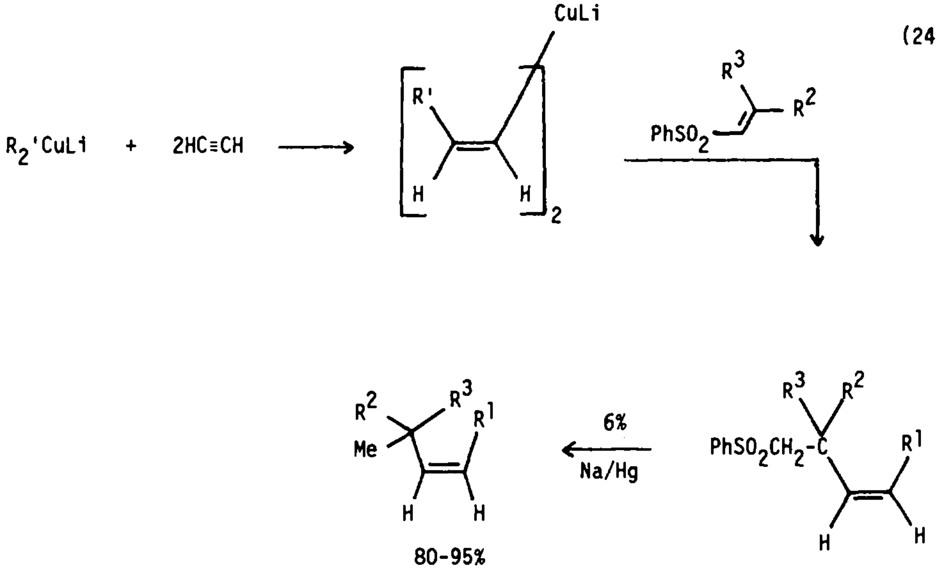
R = n-Bu 99:1

R = t-Bu 60/40

The conjugate addition of $[Me_3SnCuSPh]Li$, $[Me_3SnCuSnMe_3]Li$, $[Me_3SnCuC{\equiv}CCMe_2OMe]Li$, and $Me_3SnCuLiBrMe_2S$ to acetylenic esters was studied in detail [263]. The stereochemistry of the reaction depended on both the reagent and the substrate. Organocuprates added cis to dimethyl acetylene dicarboxylate (equation 247) [264]. Vinylcuprates reacted with vinyl sulfenes (equation 248) [264]. Cumulated trienes resulted from the reaction of t-butylcopper with eneynes (equation 249) [266].

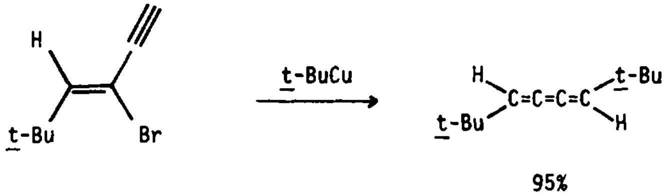


(247)



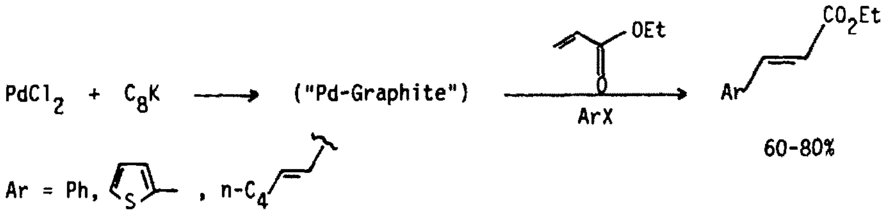
(248)

R^1 = n-Bu, sec-Bu, t-Bu; R^2 = Me, Ph, H; R^3 = H, Me

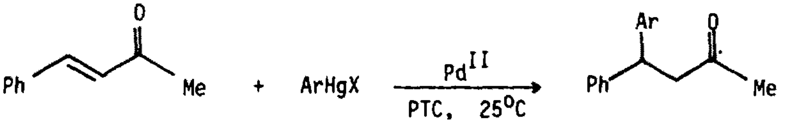


(249)

Dissertations entitled "Applications and Scope of Tetracarbonyliron Mediated Michael Reactions of Acrylate Esters" [267] and "Michael Reactions of Highly Stabilized Enolate Anions to Iron(0) Tetracarbonyl Complexes of Acrylate Esters" [268] have appeared. Enol phosphates of 1,3-dicarbonyl compounds underwent nickel-catalyzed conjugate alkylations with trialkylaluminums [269]. Ethyl acrylate was alkylated by aryl or vinyl halides in the presence of a "palladium-graphite" catalyst (equation 250) [270]. Arylmercuric halides arylated benzalacetone in the presence of palladium(II) salts under phase transfer conditions (equation 251) [271]. The mechanism of the nickel(0) catalyzed 1,4-addition of vinyl-zirconium complexes to cyclohexenone was proposed to involve an electron transfer process [272].

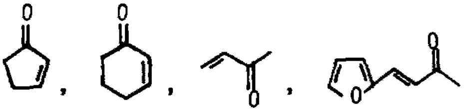


(250)



(251)

Ar contains NO_2, CHO, OH, NHAc, NH_2, CO_2Me, COMe, OMe, Cl, Me



also reacted

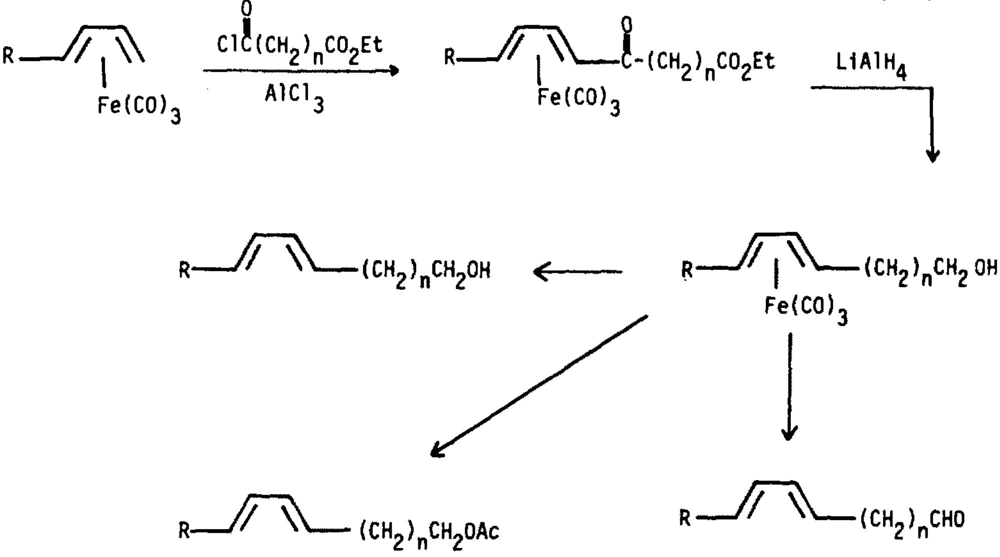
C. Carbonylation Reactions

1. Carbonylation of Alkenes and Alkynes

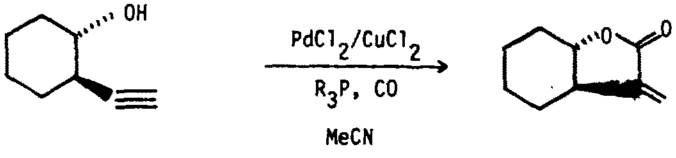
Homogeneous catalysis of carbonylation has been reviewed [273], as have the mechanistic pathways of olefin hydrocarboxylation by rhodium, iridium, and cobalt catalysts [274]. The solvent effect on the hydrocarboalkoxylation of propene promoted by a $[PdCl_2(PPh_3)_2]$-PPh_3 catalyst has been studied [275]. Propene was converted to dipropyl ketone by reaction with water and carbon monoxide at 100 kg/cm^2 pressure in the presence of dicobalt octacarbonyl [276]. The same catalyst also effected the hydroesterification of acrylonitrile and methyl acrylate under different conditions [277].

The kinetics of the palladium(II) chloride catalyzed conversion of styrene to methyl cinnamate and dimethyl phenylsuccinate have been studied [278]. A variety of insect pheremones were synthesized by the Friedel-Crafts acylation of butadieneiron tricarbonyl complexes (equation 252) [279]. The synthetic scope of the palladium-catalyzed cyclocarbonylation of unsaturated alcohols to α-substituted lactones has been reported (equation 253) [280]. The rhodium-catalyzed carbonylation of acetylenes in alcohol solvent produced furanones (equation 254) [281]. A variety of cyclic carbonyl-containing compounds were synthesized from acetylenes and carbon monoxide, using a nickel(0) complex as a template (equation 255) [282][283]. Friedel-Crafts acylation of a bis iron complex of butadiene produced 2-acylbutadienes (equation 256) [284]. Alkynes were hydroborated and the resulting vinyl boranes were carbonylated by treatment with carbon monoxide and methanol in the presence of a palladium(II) catalyst (equation 257) [285].

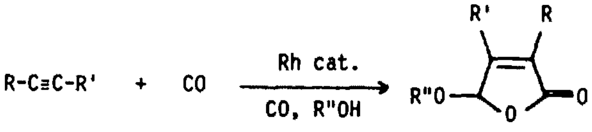
(252)



R = H, MeCO, Et, Me, EtCO, n-Pr
n = 6, 7, 8



(253)

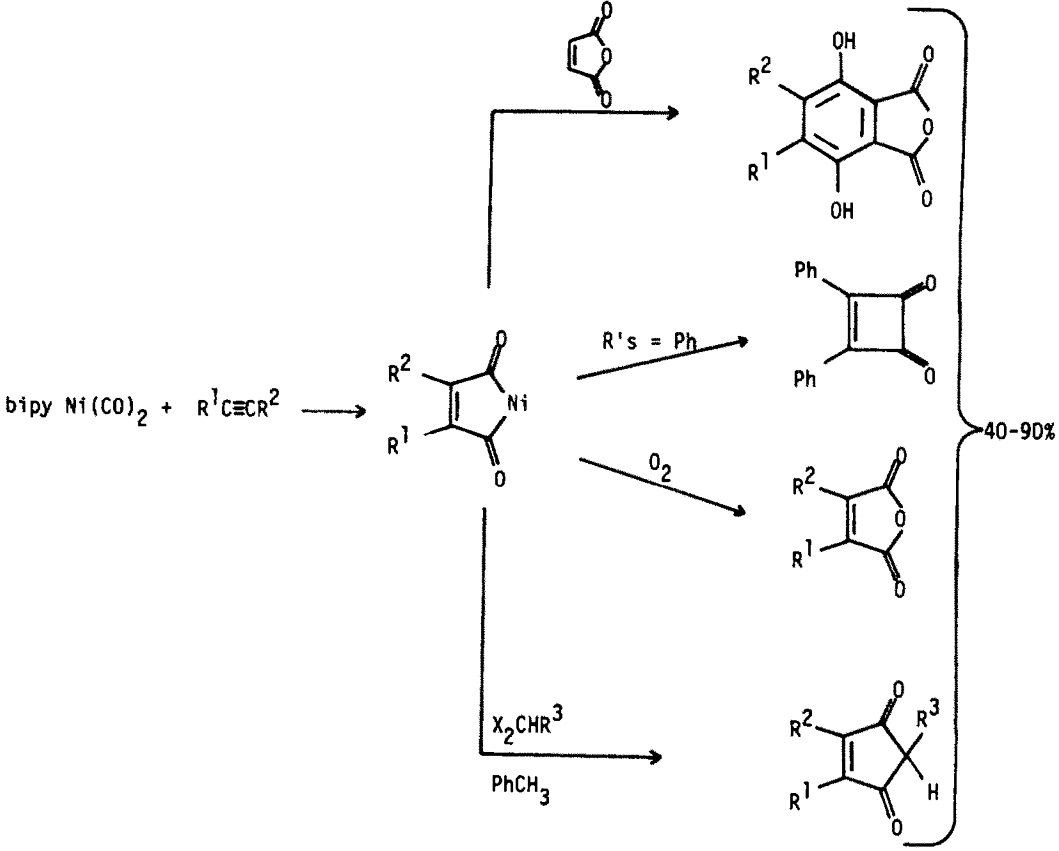


(254)

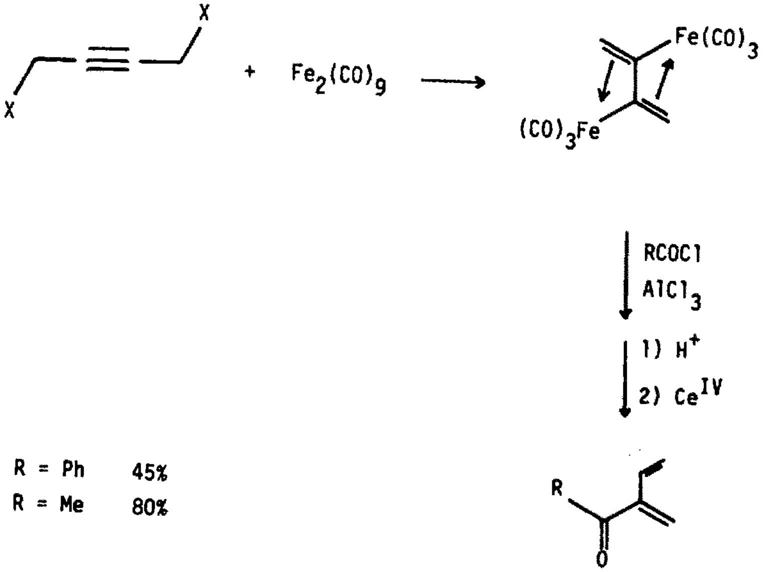
R, R' = Ph, Me

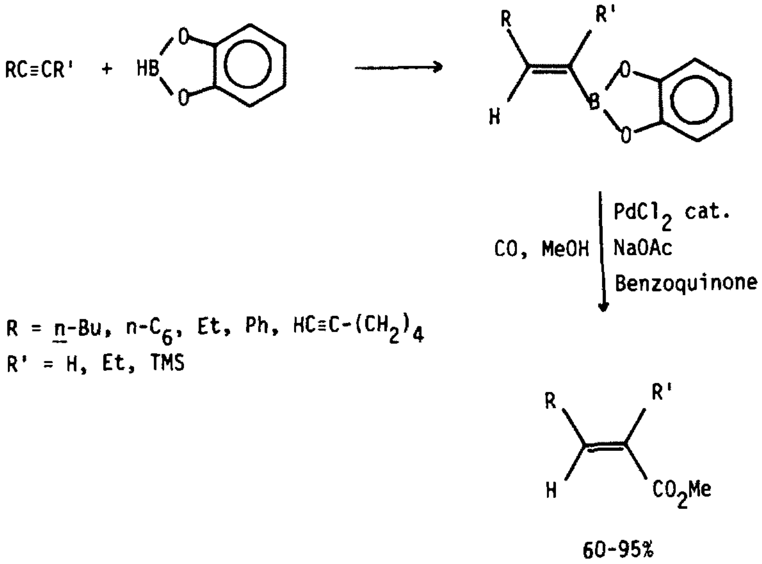
R" = Me, Et, Pr, i-Pr, n-C_8

(255)


bipy Ni(CO)$_2$ + R^{1}C≡CR^2
R^2
R^1
Ni
O
O
OH
OH
R's = Ph
Ph
Ph
O$_2$
X$_2$CHR^3
PhCH$_3$
R^3
H
40-90%

(256)

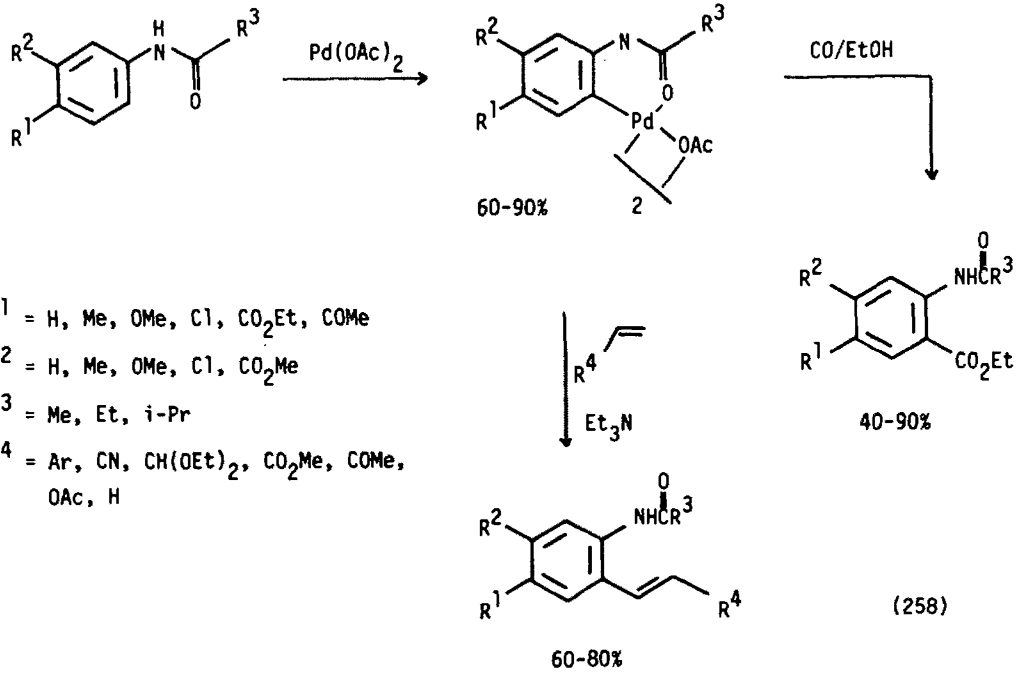

X
X
+ Fe$_2$(CO)$_9$
Fe(CO)$_3$
(CO)$_3$Fe
RCOCl
AlCl$_3$
1) H$^+$
2) Ce^{IV}
R
O
R = Ph 45%
R = Me 80%



(257)

R = n-Bu, n-C_6, Et, Ph, $HC{\equiv}C{-}(CH_2)_4$
R' = H, Et, TMS

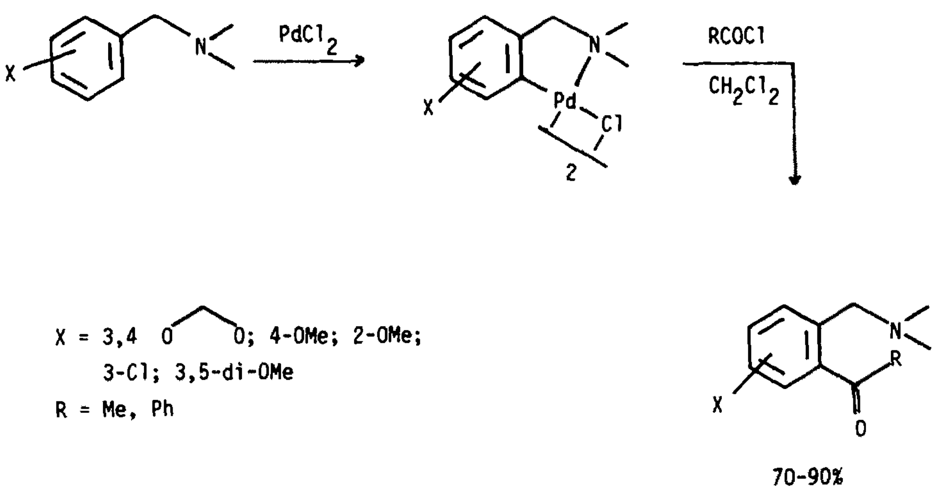
Benzene was converted to benzophenone by $PdCl_2/CuCl_2$ at 180° under 40 atmospheres of carbon monoxide [286]. N-Acylated anilines underwent orthopalladation readily. The resulting palladium complexes were carbonylated in high yield (equation 258) [287]. Benzylamines underwent a similar orthopalladation, the product of which was acylated by treatment with acid halides (equation 259) [288]. Mercurated pyrrolo [2,3-d]pyrimidine systems were carbonylated by carbon monoxide in the presence of a palladium catalyst (equation 260) [289]. The total synthesis of aphidicolin and cyclocarbonylation with disodium iron tetracarbonyl was the subject of a dissertation [290].

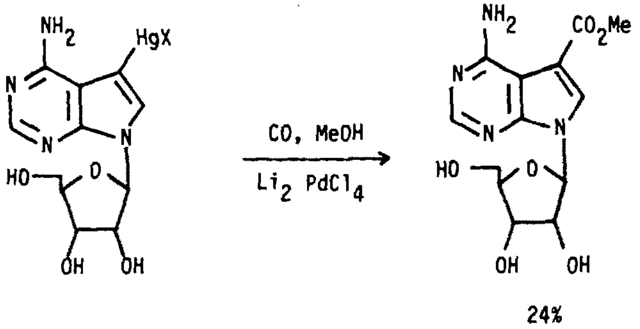


R^1 = H, Me, OMe, Cl, CO_2Et, COMe
R^2 = H, Me, OMe, Cl, CO_2Me
R^3 = Me, Et, i-Pr
R^4 = Ar, CN, $CH(OEt)_2$, CO_2Me, COMe, OAc, H

(258)

(259)



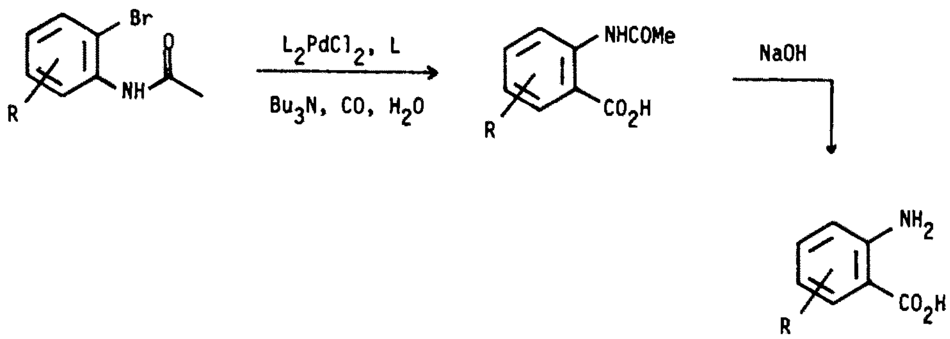


(260)

2. Carbonylation of Halides

Anthranilic acids were synthesized by the palladium-catalyzed carbonylation of o-haloacetanilides (equation 261) [291]. Aryl and vinyl halides were converted to carboxylic acids by dicobalt octacarbonyl under phase-transfer conditions (equation 262) [292]. Cobalt acetate/sodium hydride effected a similar transformation (equation 263) [293]. Benzyl halides were carbonylated to phenylacetic acids by $Co(CO)_3NO$ (equation 264) [294], and were acylated by acid halides in the presence of palladium(0) catalysts (equation 265) [295]. Benzyl bromides having α-hydrogens were converted to methyl ketones by reaction with tetramethyltin, carbon monoxide, and a palladium catalyst (equation 266) [296]. Palladium also catalyzed the conversion of aryl halides to acylnitriles (equation 267) [297].

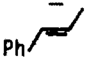
(261)



$$ArX + CO + 2NaOH \xrightarrow[Bu_4N^+Br^-,\ h\nu]{NaOH/H_2O/PhH/Co_2(CO)_8} ArCOONa \qquad (262)$$

>95%

Ar = Ph, o-tolyl, p-tolyl, p-OMePh, o-OMePh, 1-Naphth



, cyclooctenyl

(263)

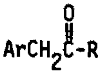
$$PhBr + CO\ (1\ atm) \xrightarrow[THF,\ rfx,\ 24\ hr]{NaH/t\text{-}AmONa/Co(OAc)_2} PhCOOH + PhCO_2\text{-}t\text{-}Am + PhCHO$$

1250 turns

$$ArCH_2\text{-}X + CO \xrightarrow[\substack{5\underline{N}\ NaOH,\ PhH \\ R_4N^+Cl^-}]{Co(CO)_3NO} ArCH_2COOH \qquad (264)$$

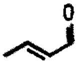
Ar = Ph, p-CNPh, β-Naphth o-MePh, p-MePh

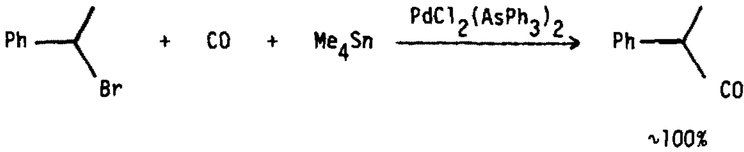
$$ArCH_2Br + RCOCl \xrightarrow[DME,\ 25^0]{L_4Pd\ cat/2\ eq\ Zn}$$



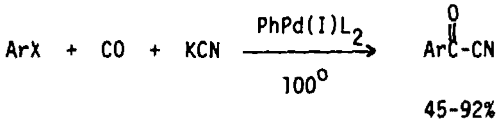
$$ArCH_2\overset{O}{\overset{\|}{C}}\text{-}R \qquad (265)$$

60-80%

Ar = Ph, p-tolyl, p-ClPh, p-NO_2Ph R = Ph, alkyl,




(266)



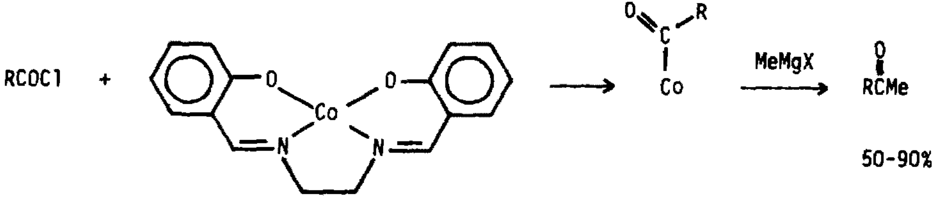
$$\mathrm{ArX\ +\ CO\ +\ KCN\ \xrightarrow[100^{o}]{PhPd(I)L_2}\ Ar\overset{O}{\overset{\|}{C}}\text{-}CN}$$

(267)

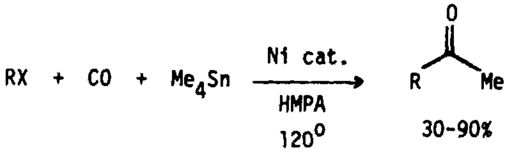
Ar = Ph, p-OMePh, p-tolyl, 

Acid chlorides were converted to methyl ketones by forming an acylcobalt complex and reacting this complex with methyl magnesium halides (equation 268) [298]. Aryl halides were converted to acetophenones by reaction with carbon monoxide and tetramethyltin in the presence of nickel catalysts (equation 269) [299] or π-allylpalladium catalysts [300]. Acyl halides were converted to ketones by reaction with alkyltins and the same catalyst [301].

(268)



R = $PhCH_2$, 1-Naph, 1,3,5-mesityl, cyclohexyl



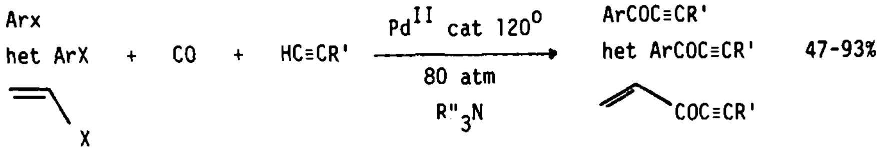
(269)

R = Ph, p-tolyl, p-OMePh, p-EtO_2CPh, p-CN-Ph, 

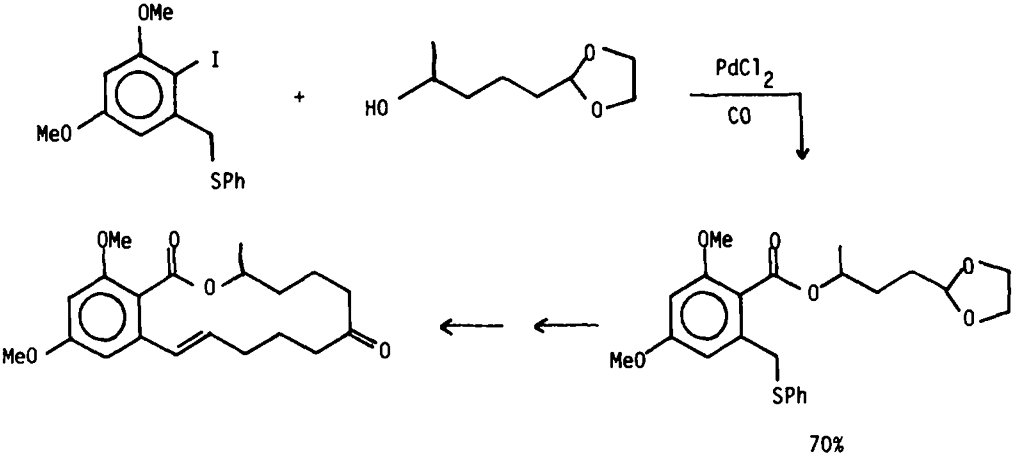
cat = $Ni(CO)_4$, $LNi(CO)_3$, $L_2Ni(CO)_2$, L_2NiCl_2

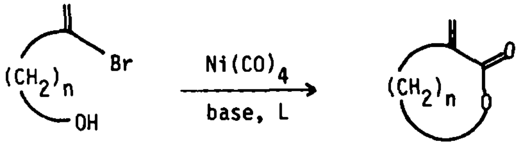
Aryl and vinyl halides were converted into acetylenic ketones by reaction with carbon monoxide and an alkyne in the presence of a palladium(II) catalyst (equation 270) [302]. (±)-Zearalenone was synthesized by a process involving acylation of an aryl halide with a palladium catalyst as a key step (equation 271) [303]. α-Methylene lactones were synthesized by a nickel-promoted cyclocarbonylation (equations 272-274) [304]. Lactams were formed in a similar process using a palladium catalyst (equation 275) [305].

(270)



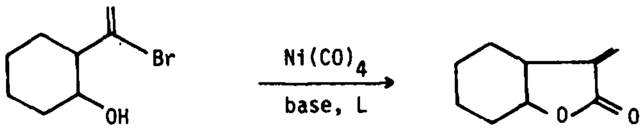
(271)





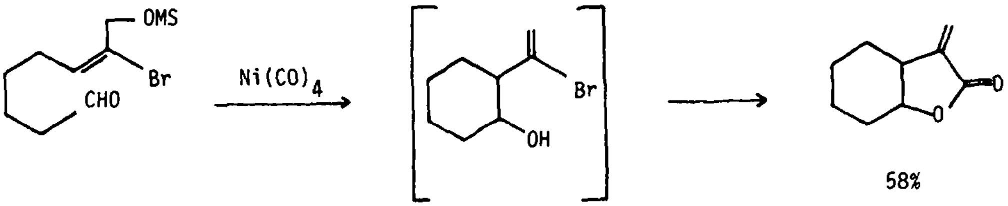
(272)

n = 2, 3
good yields

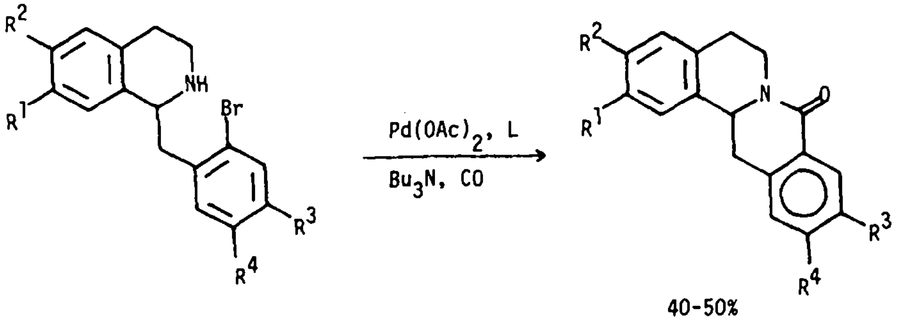


(273)

(274)

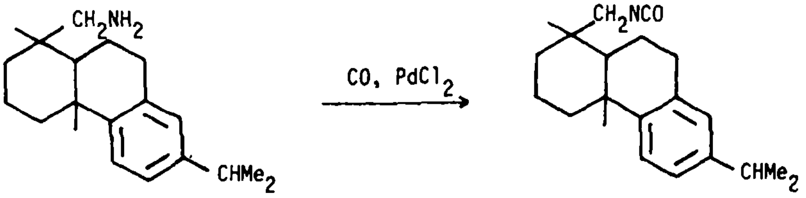


(275)

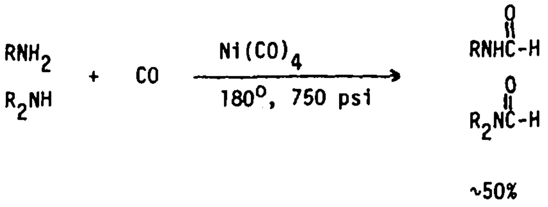


3. Carbonylation of Nitrogen Compounds.

Dehydroabietylamine was carbonylated to the isocyanate by reaction with carbon monoxide in the presence of a palladium(II) catalyst (equation 276) [306]. Amines were carbonylated to formamides by nickel carbonyl (equations 277 and 278) [307]. Imines were converted to enamides by reaction with $Cp_2Zr(H)Cl$ followed by acetyl chloride (equation 279) [308]. Phenyl azides were converted to phenyl isocyanates in high yield when treated with carbon monoxide in the presence of $L_2Rh(CO)Cl$ as a catalyst [309].



(276)

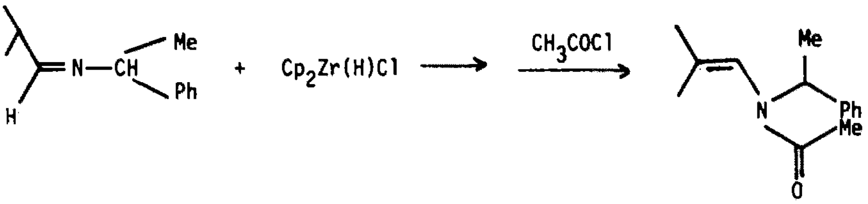


$$\begin{matrix} RNH_2 \\ R_2NH \end{matrix} + CO \xrightarrow[180^{\circ},\ 750\ psi]{Ni(CO)_4} \begin{matrix} RNH\overset{O}{\overset{\|}{C}}\text{-}H \\ R_2N\overset{O}{\overset{\|}{C}}\text{-}H \end{matrix}$$

∿50%

(277)

(278)



30%

Nitrobenzene was converted into methyl-N-phenylcarbamate by reaction with carbon monoxide in methanol with $ClIr(CO)(PPh_3)_2$, $ClH_2Ir(PPh_3)_3$, $HIr(CO)(PPh_3)_3$, $HRh(CO)(PPh_3)$ and $ClRh(CO)(PPh_3)_2$ as catalysts. The yields were low [310]. The synthesis of nitrogen-containing compounds by the reaction of nitro compounds with carbon monoxide has been reviewed (128 references) [311]. p-Methylnitrobenzene was carbonylated to p-methyl phenylisocyanate using palladium(0) or palladium(I) catalysts in the presence of iron halide cocatalysts [312]. The best results (83% conversion) were obtaine with $PdCl_2$-$(pyH)_2Fe_2Cl_8(py)_2$ as catalyst [313]. The carbonylation of nitrobenzene to phenyl isocyanate was accelerated by addition of MoO_3 or MoO_3/Al_2O_3 to the normal $PdCl_2$-pyridine catalyst [314]. The effect of pyridine and pyridinium hydrochloride on the activation of $[Pd(CO)Cl]_n$ for carbonylation of nitrobenzene was assessed [315]. The effect of solvent and added transition metal oxides and chlorides on the $PdCl_2$ or $RhCl_3$-catalyzed carbonylation of nitrobenzenes to aryl isocyanates was studied [316]. The effects of added $FeCl_3$ and Fe_2O_3 on this reaction were also studied [317].

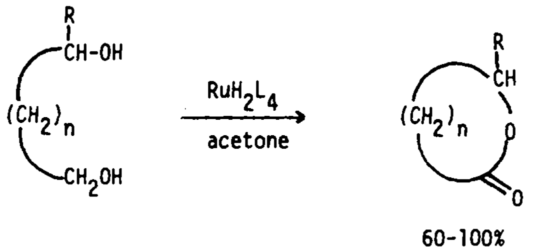
4. Carbonylation of Oxygen Compounds

Alcohols were converted to esters (equations 279) and diols to lactones (equat 280) when treated with ruthenium catalysts at high (180°) temperatures [318]. Lactones were converted to dicarboxylic acids when treated with carbon monoxide and rhodium(III) chloride as a catalyst (equation 281) [319]. A variety of carbonyl compounds were produced by the reduction of cationic iron carbonyl compounds with sodium cyanoborohydride (equation 282) [320].

$$RCH_2OH \xrightarrow[180^{o},\ PhCH_3]{RuH_2L_4} R\overset{O}{\overset{\|}{C}}\text{-}OCH_2R \qquad (279)$$

78-93%

R = n-Pr, n-C_5, Ph, $PhCH_2$, cyclohexyl, EtCHMe



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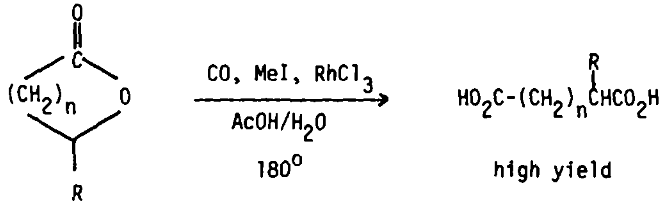

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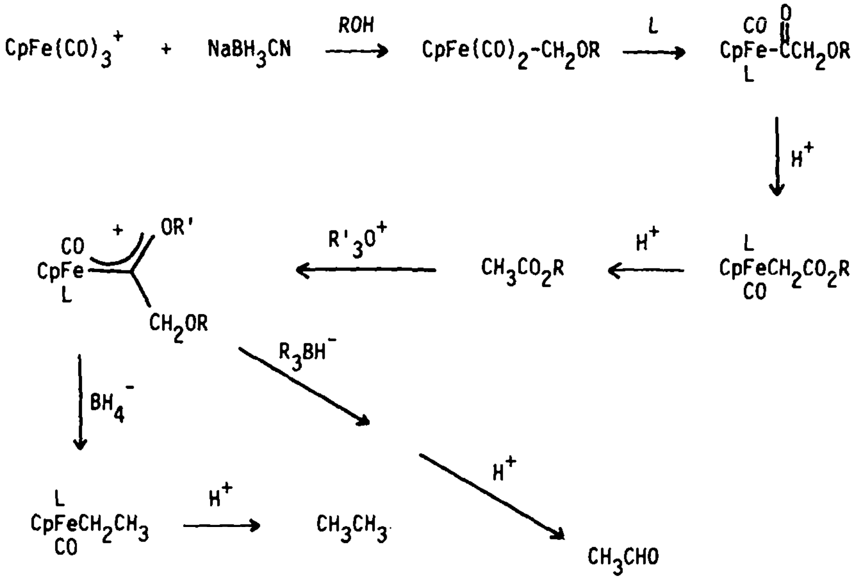
(282)

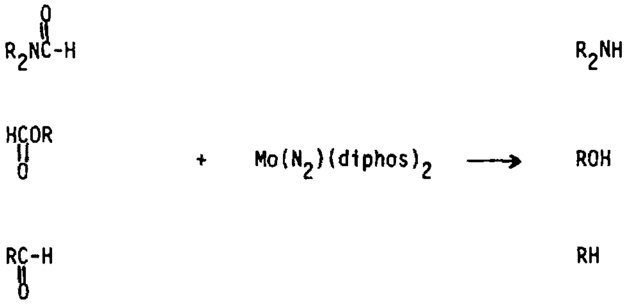


5. Miscellaneous Carbonylations

The following reviews concerning carbonylation have appeared: "Carbonylations Catalyzed by Metal Carbonyls Reppe Reactions" (289 references) [321]. "Catalytic Reactions Induced by Transition Metal Complexes Solvated in Zeolite Matrices: Oxidation, Carbonylation, and Related Reactions" (76 references) [322]. "A Series of New Catalytic Reactions with Carbon Monoxide and Hydrosilane" (27 references) [323].

6. Decarbonylation Reactions

Formamides, formate esters, and aldehydes were decarbonylated stoichiometrically using $Mo(N_2)(diphos)_2$ (equation 283) [324]. Aldehydes were decarbonylated to hydrocarbons by ruthenium(II) porphyrin catalysts [325]. The mechanism of reductive deacylation of 2-alkylidene-1,3-diones by $KHFe(CO)_4$ was studied [326]. The deacylation of acryloyl acid chlorides by rhodium(I) complexes led to vinylphosphonium salts not vinyl halides (equation 284) [327]. A review (32 references) entitled "Catalysis by Platinum-Group Metals- Decarbonylation and Desulfonylation" has appeared [328].



$$\left.\begin{array}{l} R_2N\overset{O}{\overset{\|}{C}}\text{-}H \\ H\underset{O}{\underset{\|}{C}}OR \\ R\underset{O}{\underset{\|}{C}}\text{-}H \end{array}\right. \quad + \quad Mo(N_2)(diphos)_2 \longrightarrow \begin{array}{l} R_2NH \\ ROH \\ RH \end{array} \qquad (283)$$

$$R^1R^2C{=}CHCOCl \quad + \quad L_3RhCl \longrightarrow R^1R^2C{=}CH\overset{+}{P}Ph_3Cl^- \qquad (284)$$

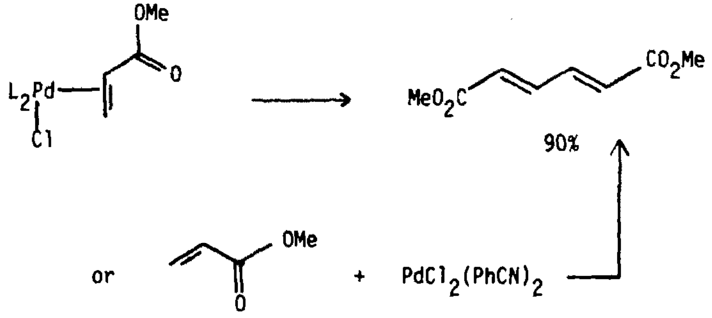
R^1 = Ph, Me, n-Bu, H

R^2 = H, Me

D. Oligomerization

Ethylene dimerization was efficiently catalyzed by a mixed $Ni(acac)_2/Et_2AlCl/PPh_3$ catalyst supported on alumina or silica gel-alumina [329]. The kinetics of the conversion of ethylene to butenes on a π-allylnickel halide/alumina/$Et_3Al_2Cl_3$ supported catalyst was studied [330]. A bis carbene complex of tantalum $RTaL_2(=CHCH_3$ was an efficient olefin dimerization catalyst [331]. The physical and structural properties of the olefin dimerization catalyst $Ni(acac)_2/Et_2AlCl/PPh_3$ have been studied [332], as have nickel(II) catalysts grafted to polymers [333]. Perfluoropropene was converted to dimers and trimers when treated with bis (benzene)chromium as a catalyst [334]. Ethylene and propene were codimerized by gel-immobilized nickel(II) catalysts [355]. Similar codimerization catalysts were made by gel-immobilizing nickel complexes of poly(4-vinylpyridine) containing phosphorous ligands [336].

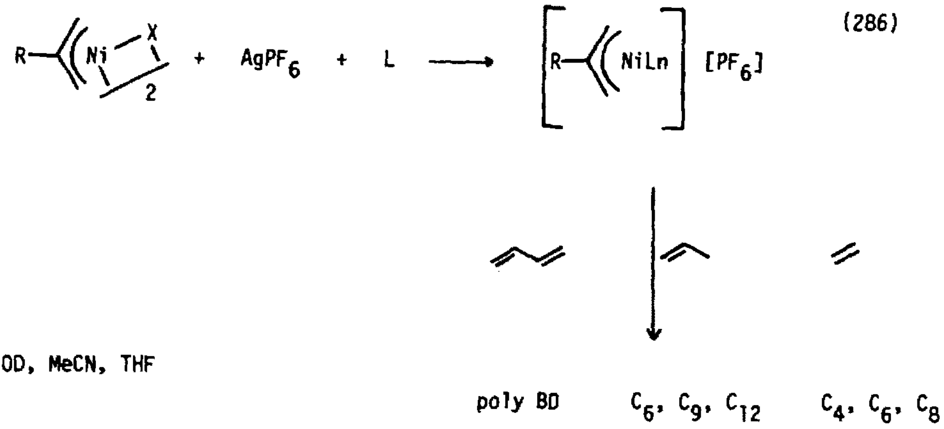
The kinetics of the oxidative dimerization of styrene in the presence of palladium(II) have been studied [337][338]. Methyl acrylate dimerized when treated with palladium(II) salts (equation 285) [339]. Methyl vinyl ketone was hydrodimerized to 2,7-octanedione by cobalt(I)-bipyridyl complexes [340]. The system $ZrCl_4/Et_2AlCl$ at 120° codimerized C_6 to C_{10} α olefins with butadiene [341].



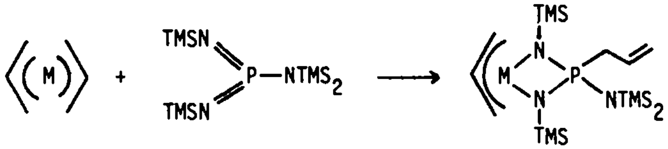
(285)

Isobutene was trimerized by a catalyst prepared from $SnCl_2$ and $RuCl_3 \cdot H_2O$ in nitromethane [342]. Cationic π-allylnickel complexes catalyzed the polymerization of olefins (equation 286) [343]. Styrene and methyl acrylate were polymerized by *tetrakis* (neopentyltitanium(IV)) by a free radical process. Irradiation of the mixture increased the rate of reaction [344]. Ethylene was polymerized by the π-allylnickel complex in equation 287, but the corresponding palladium complex was inert [345]. Cyclopentene, cyclohexene and cycloheptene were polymerized by metathesis-type polymerization and by normal olefin oligomerization processes when treated with zirconium salts/$EtAlCl_2$ catalysts [346]. The cationic palladium(II) complex $Pd(CH_3CN)_4^{2+}$ polymerized styrene to polystyrene, ethylene to C_4, C_6, C_8, and C_{10} oligomers, but only isomerized butenes [347]. Heating the copper(I) triflate complex of *trans* cycloheptene with cycloheptene produced the cyclic trimer (equation 288) [348]. The effects of the nature of catalyst components on the Ziegler-Natta type copolymerization of styrene with propylene have been examined [349]. Styrene was polymerized by an $IrCl(CO)(PPh_3)_2$/*t*-butylhydroperoxide catalyst system [350]. *Bis*-π-arene chromium(0) complexes catalyzed the oligomerization of perfluoropropene [351][352].

(286)



L = COD, MeCN, THF



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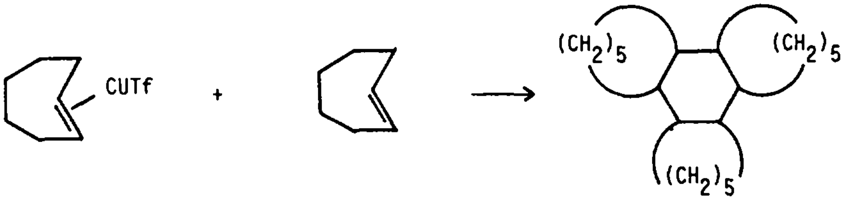
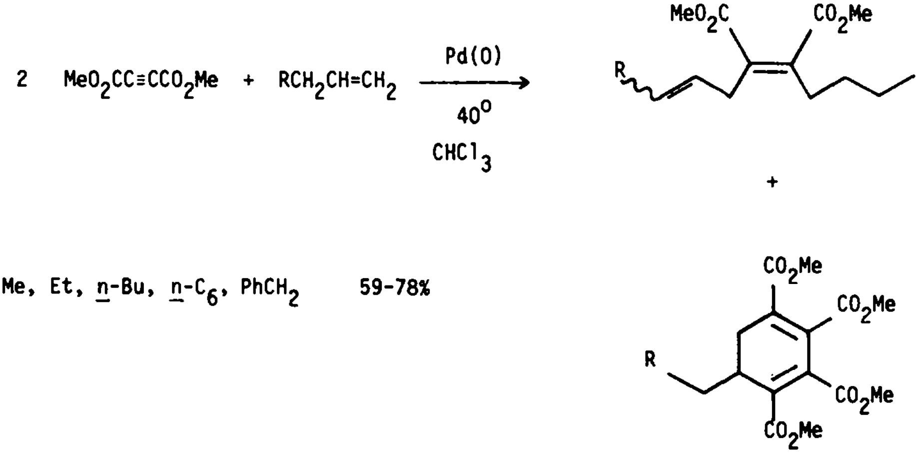
(288)



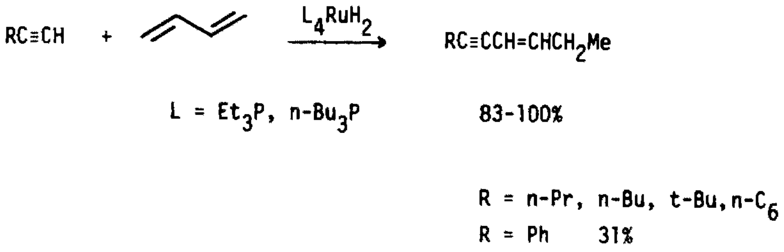
80%

Acetylene was cyclotrimerized to benzene by $TaCl_5/EtAlCl_2$ catalyst systems [353]. In contrast $Pd(Al_3Cl_7)_2 \cdot 2PhH$ cyclotrimerized acetylene to fulvenes [354]. Linear trimers of $HC{\equiv}CCMe_2OH$ were obtained from the reaction of this substrate, in aqueous solution, with $Cl_2Pd(PPh_2C_6H_4SO_3Na)_2$ as a catalyst [355]. The linear and cyclotrimerization of 1-ethynyl-1-cyclohexanol was catalyzed by nickel(II) salts and nickel(II) alkyne complexes [356]. The mechanism of the cyclotetramerization of acetylene to cyclooctatetraene was shown to be "zipper-wise" [357]. Olefins cooligomerized with dimethyl acetylenedicarboxylate in the presence of palladium(0)catalysts (equation 289) [358]. Butadiene and terminal alkynes codimerized over a ruthenium catalyst (equation 290) [359]. Eneynes dimerized when treated with $\underline{i}$-Bu_3Al and manganese or nickel salts (equation 291) [360]. Palladium(II) salts cooligomerized acetylene and allyl chloride [361]. Zirconium complexes of butadiene reacted with olefins, alkynes, and 1,3-dienes to produce co-dimers (equation 292) [362].

(289)

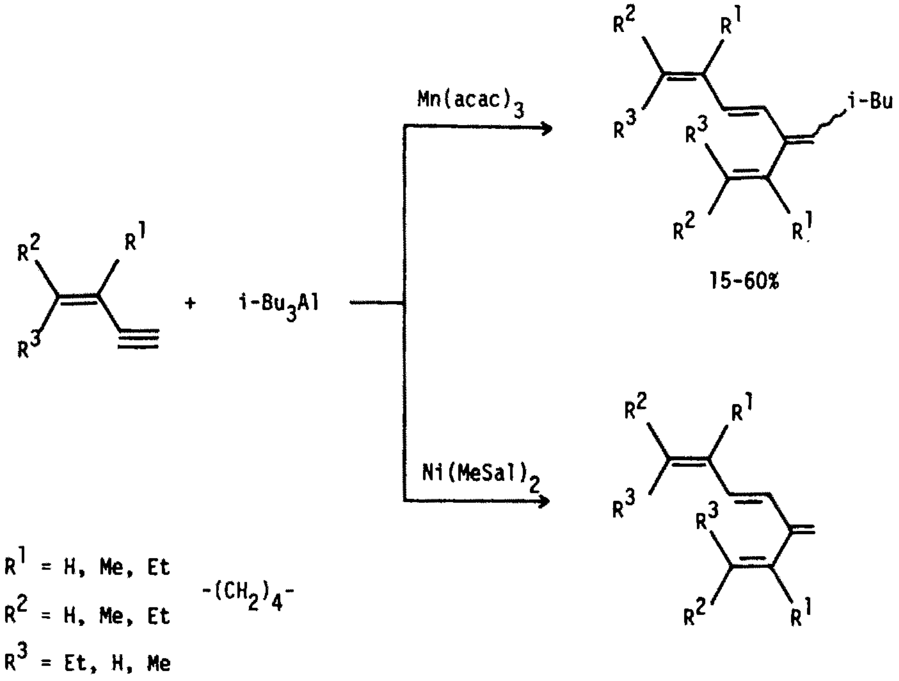


R = Me, Et, $\underline{n}$-Bu, $\underline{n}$-C_6, $PhCH_2$ 59-78%

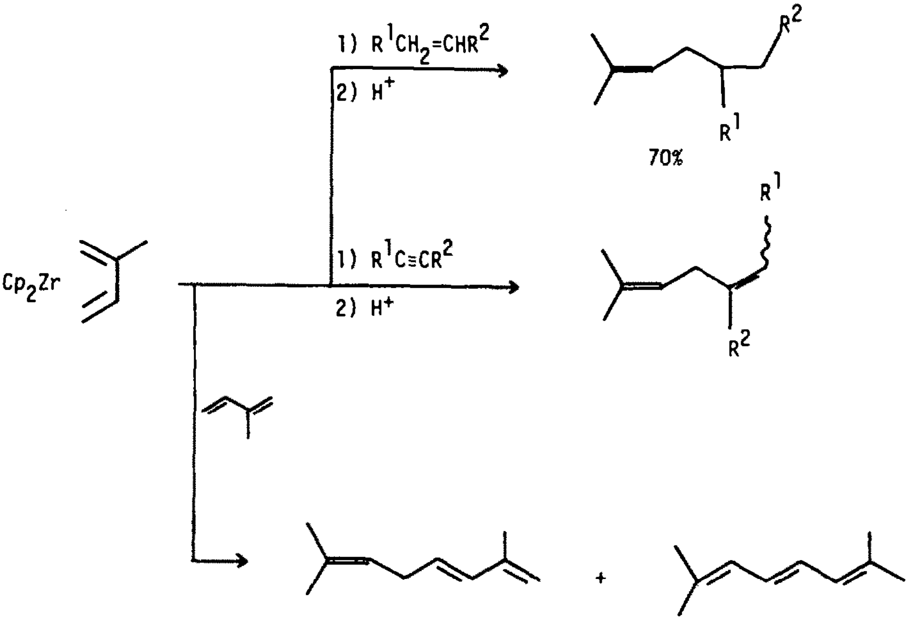

RC≡CH
+
L4RuH2
RC≡CCH=CHCH2Me
L = Et3P, n-Bu3P
83-100%
R = n-Pr, n-Bu, t-Bu, n-C6
R = Ph 31%

(290)

(291)

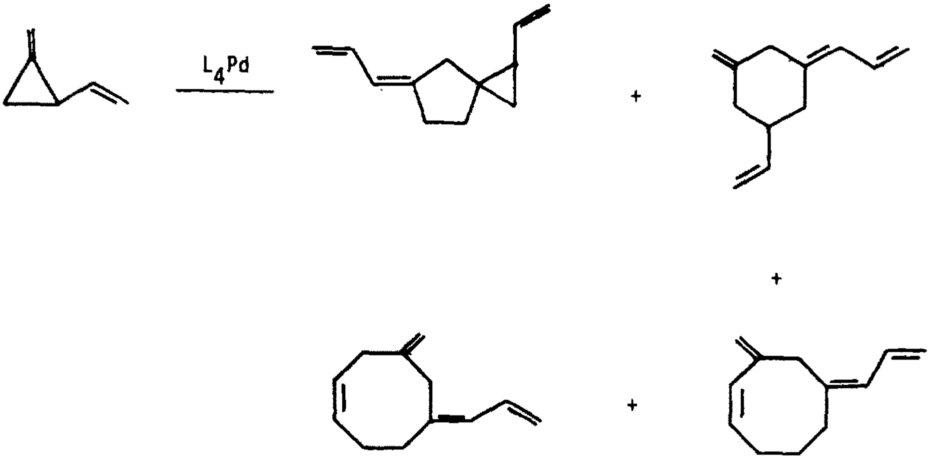

R2
R1
R3
+
i-Bu3Al
Mn(acac)3
i-Bu
15-60%
Ni(MeSal)2
R1 = H, Me, Et
R2 = H, Me, Et
R3 = Et, H, Me
-(CH2)4-

(292)



Palladium(0) complexes catalyzed the cycloaddition reactions of 1-methylene-2-vinylcyclopropane with itself (equation 293), with strained olefins (equation 294) [363] and the cycloaddition of methylenecyclopropane to acrylic esters (equation 295) [364].

(293)



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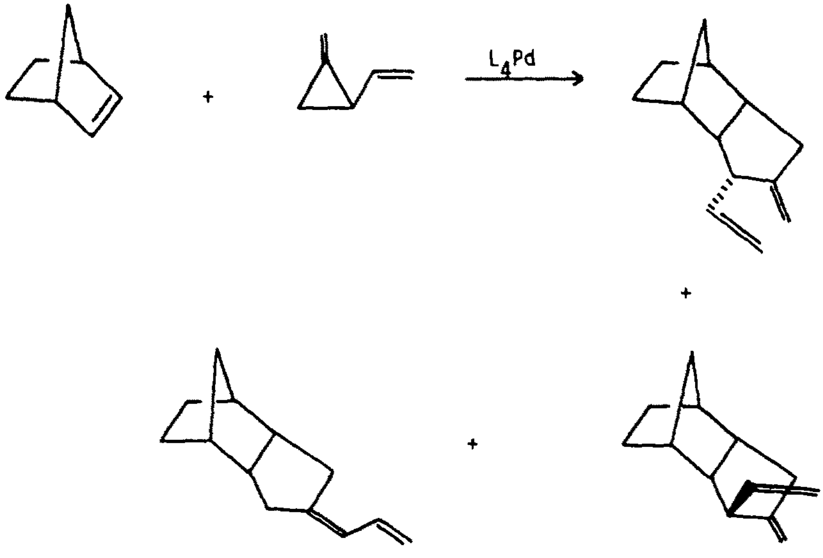
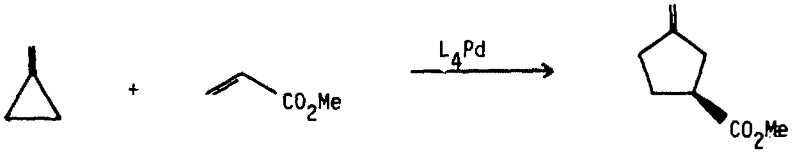




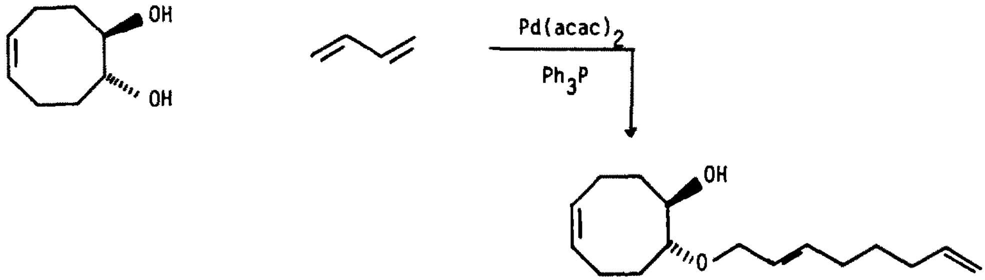
(295)

The catalyst system $Zr(OBu)_4/PPh_3/Et_2AlCl$ dimerized and codimerized conjugated dienes and trienes [365]. Butadiene was polymerized to <u>cis</u> and <u>trans</u> polybutadienes when treated $L_2Rh(CO)Cl/Et_2AlCN$ catalysts in ethanol. In DMF or pyridine, cyclooctadiene, and vinylcyclohexene were formed instead [366]. The complex $[(EtO)_3P]_4NiH^+$ reacted with ethylene [367] and propylene [368] and mixed octatrienes to give all possible codimers. Palladium complexes were studied as catalysts for the linear dimerization of isoprene [369]. Optically active phosphine or phosphonite complexes of nickel(0) species catalyzed the conversion of butadiene to 4-vinylcyclohexene with up to 35% epimer excess [370]. The mechanism of the nickel-catalyzed regioselective cyclodimerization of isoprene was studied [371]. Bicyclo[2.2.1]hepta-2,5-diene dimerized and codimerized with norbornadiene in the presence of rhodium complexes [372]. Butadiene reacted with 2,5-dihydrothiepine 1,1-dioxide in the presence of a $Pd(acac)_2/Ph_3P/AlEt_3$ catalyst to give 2-vinyl-5-butadienylsulfolanes in 80% yield [373]. Complexation of methyl benzoylacrylate to a nickel(0) species followed by reaction with butadiene produced linear addition products, rather than the normal Diels-Alder cycloaddition products [374]. The kinetics and mechanism of the cotrimerization of butadiene with styrene in the presence of $Ni(acac)_2/Ph_3P/Et_3Al$ catalysts have been studied [375]. Butadiene was polymerized over f-transition metal catalysts [376], $Co(acac)_3/RAlCl_2$ catalysts [377] and $Mo(butadiene)_3$ and $W(butadiene)_3$

catalysts [378]. Cycloocta-1,4-diene and various methyl and dimethylcyclooctadienes underwent metathesis type polymerization over a $WCl_6/EtAlCl_2$ catalyst system [379].

Butadiene and isoprene cotelomerized with water in the presence of palladium(II) acetylacetonate, triphenyl phosphine, and carbon dioxide to give nonadienols [380], while octadienols were obtained from telomerization of butadiene with water [381]. Palladium-phosphine complexes catalyzed the telomerization of butadiene with glycols (equation 296) [382]. The telomer of butadiene and acetate was used to synthesize macrocyclic lactones (equation 297) [383]. Isoprene (equation 298) [384] and butadiene [385] underwent telomerization with ammonia to give mixtures of alkylamines. Nickel(0) complexes catalyzed the telomerization of butadiene and methylamine (equation 299) [386]. When chiral phosphines were used as ligands in the telomerization of dialkylamines with butadiene amine telomers with optical activity resulted [387]. Polystyrene-supported palladium(0) complexes catalyzed the telomerization of butadiene with amines and carboxylates (equations 300 and 301) [388]. Palladium(0) complexes catalyzed the telomerization of N,N-dimethyl allylamine with butadienes (equations 302-304) [389]. The synthesis of medium to large ring lactones and ketones from butadiene telomers has been reviewed (62 references) [390], as has nickel catalyzed reactions of olefins with carbon-nitrogen double bond systems (18 references) [391].

(296)



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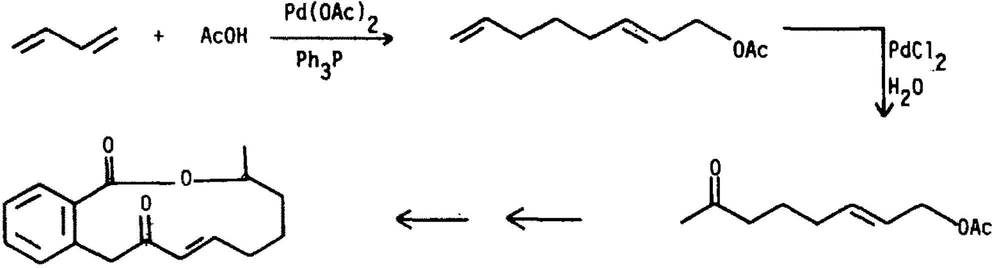

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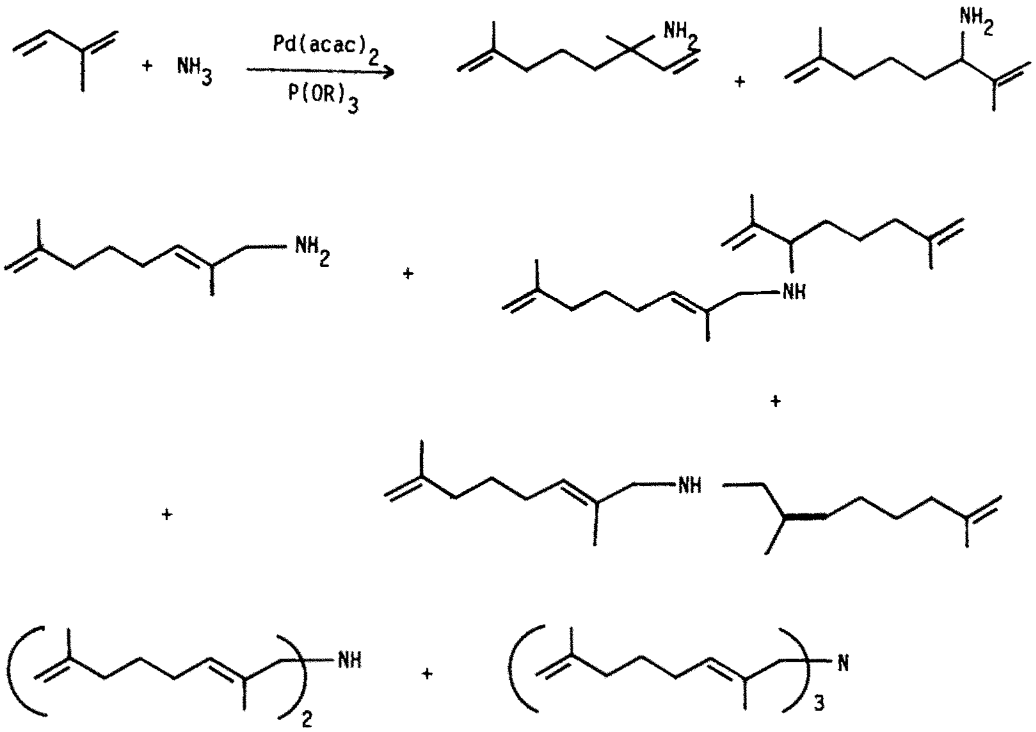
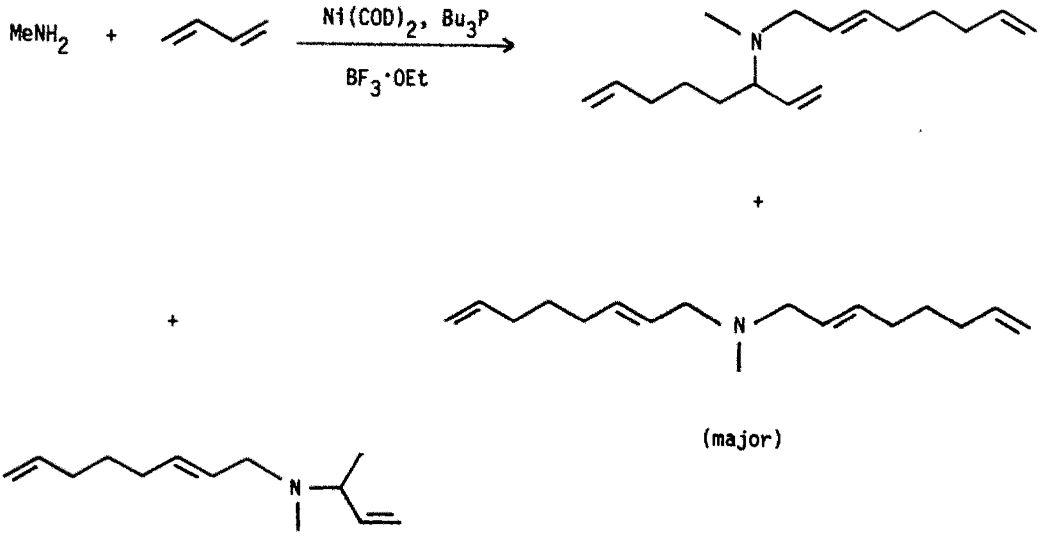


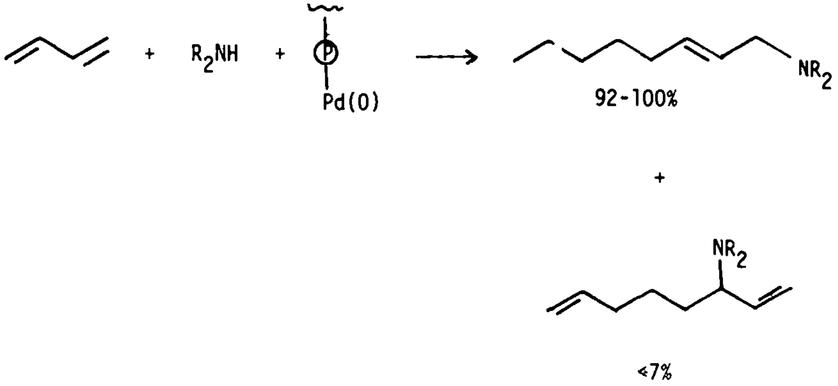
+ NH3
Pd(acac)2
P(OR)3
NH2
+
NH2
NH2
+
NH
+
+
NH
NH
2
+
N
3

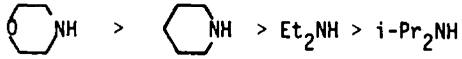
(299)

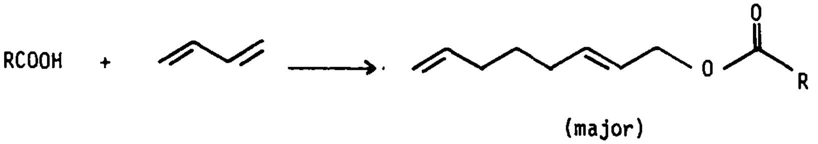


MeNH2
+
Ni(COD)2, Bu3P
BF3·OEt
N
+
+
N
(major)
N

(300)



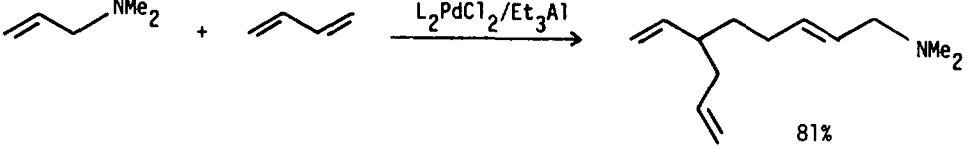




(301)

R = Me, Et, n-C_5

(302)



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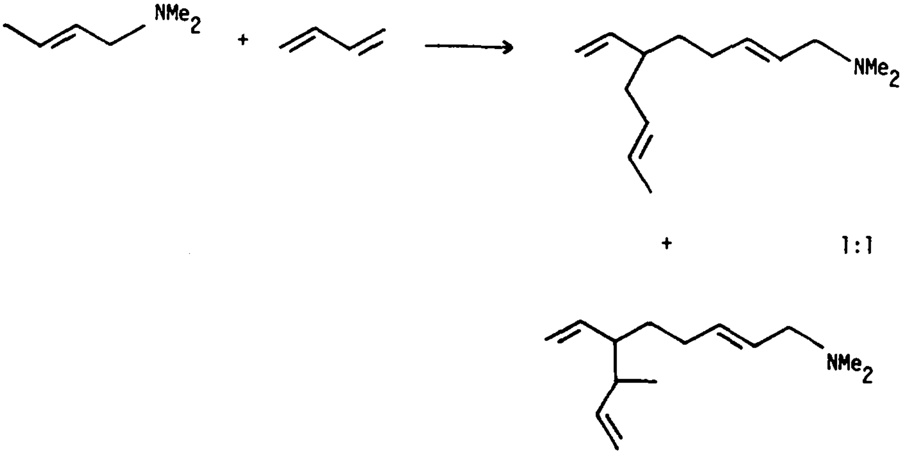

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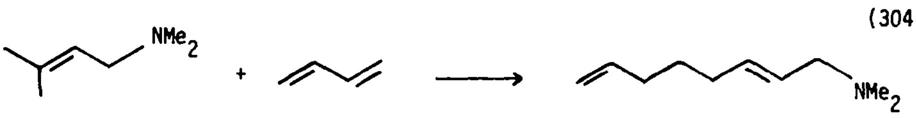
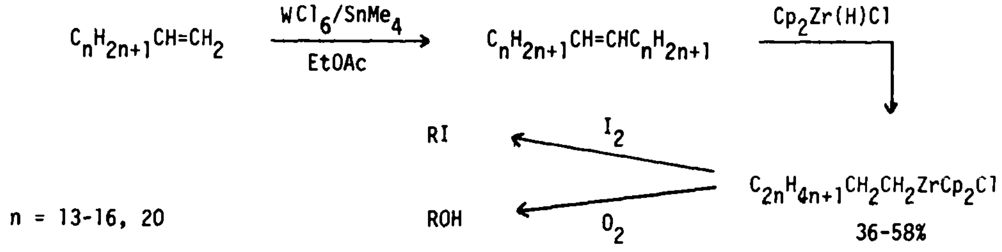


E. Rearrangements

1. Metathesis

Olefin metathesis continues to be intensively studied, although it is becoming increasingly difficult to tell the difference among many of the studies. Reviews dealing with the mechanism of olefin metathesis (40 references) [392], metal-carbene complexes as reactive intermediates (110 references) [393], catalysts for disproportionation of olefins (49 references) [394], and metathesis of olefins having functional groups (47 references) [395] have appeared. Long chain iodides and alcohols were synthesized by a combined olefin metathesis/hydrozirconation process (equation 305) [396]. The metathesis of ω olefinic esters (equation 306) [397] and nitriles (equation 307) [398] was studied. Long chain diesters (equations 308-310) and macrocyclic lactones (equations 311 and 312) were made by a metathesis process [399]. The influence of basicity and steric effects on the metathesis of olefinic amines over $W(CO)_5L$ or $W(CO)_3$ arene catalysts was studied [400]. The olefin metathesis of a cyclooctatetraene iron complex produced the dimer shown in equation 313 [401].

(305)



$$C_nH_{2n+1}CH{=}CH_2 \xrightarrow[EtOAc]{WCl_6/SnMe_4} C_nH_{2n+1}CH{=}CHC_nH_{2n+1} \xrightarrow{Cp_2Zr(H)Cl} \underset{36\text{-}58\%}{C_{2n}H_{4n+1}CH_2CH_2ZrCp_2Cl}$$

$$C_{2n}H_{4n+1}CH_2CH_2ZrCp_2Cl \xrightarrow{I_2} RI \qquad C_{2n}H_{4n+1}CH_2CH_2ZrCp_2Cl \xrightarrow{O_2} ROH$$

n = 13-16, 20

(306)

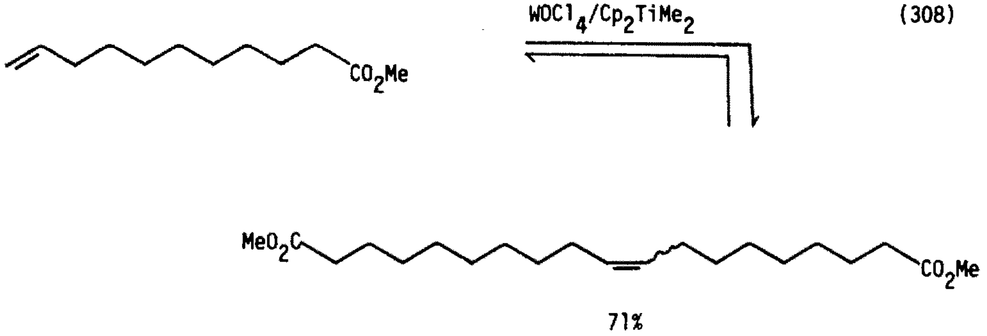
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me + H_2C{=}CH_2 \xrightleftharpoons[Me_4Sn]{Re_2O_7\text{-}Al_2O_3} CH_2{=}CH(CH_2)_7CO_2Me + CH_2{=}CH(CH_2)_7Me$$

39-75% co metathesis

$$CH_2{=}CH(CH_2)_nCN \underset{SnMe_4}{\overset{WCl_6}{\rightleftharpoons}} NC(CH_2)_nCH{=}CH(CH_2)_nCN + CH_2CH_2 \qquad (307)$$

$1 \leq n \leq 4$ best for $n = 2$

(308)



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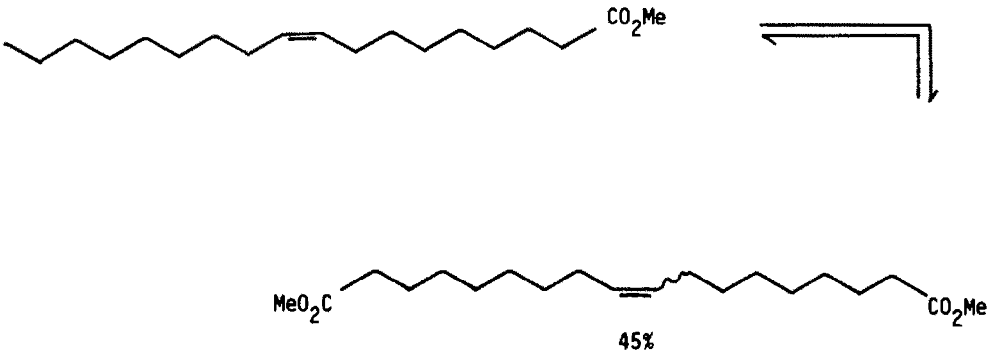

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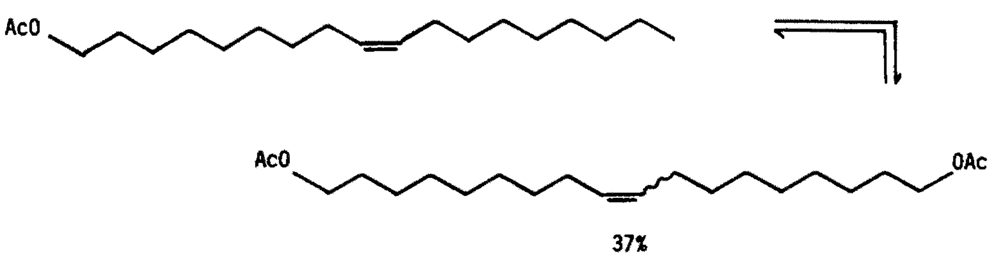
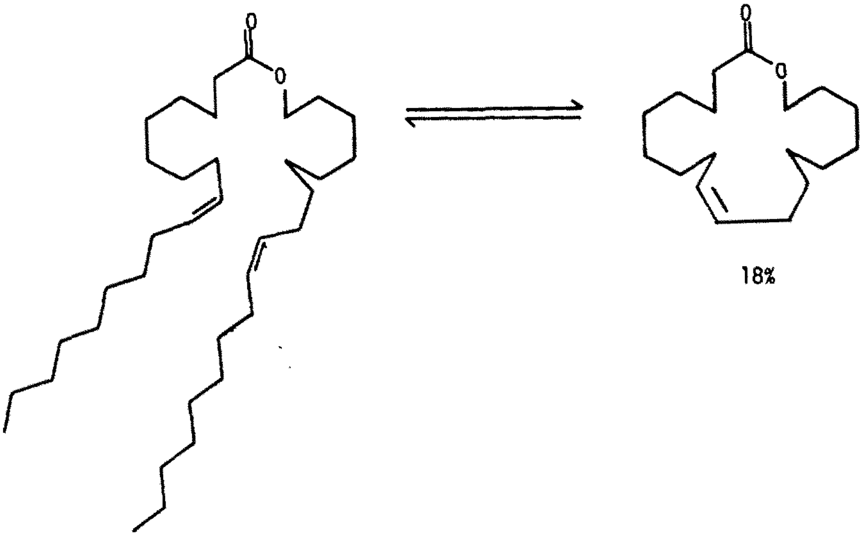
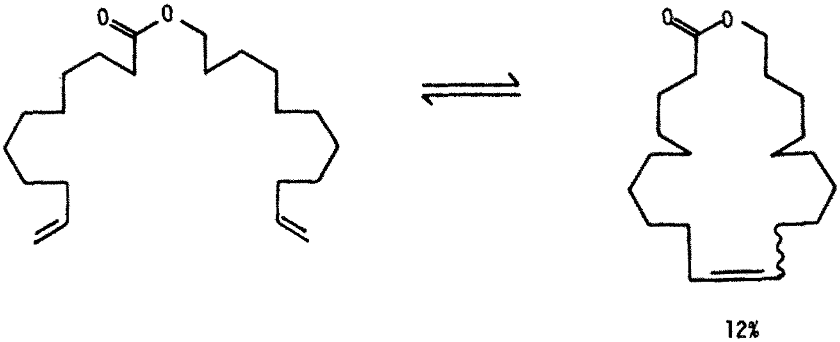


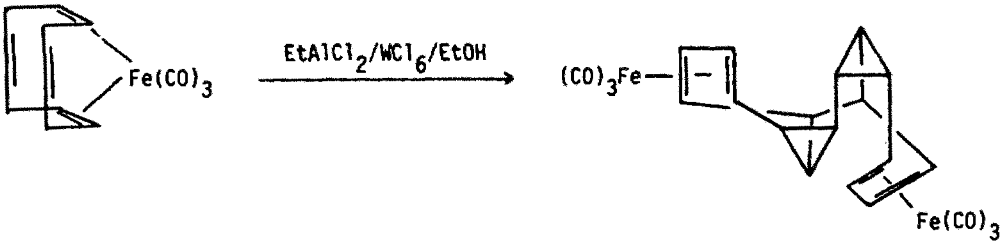


(311)

(312) (312)

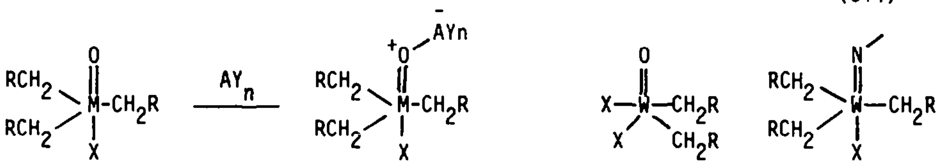


(313)



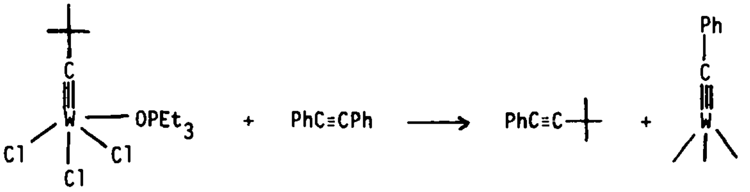
New metathesis catalyst systems continue to be developed and exploited. A variety of tungsten and molybdenum oxo complexes containing alkyl groups were treated with Lewis Acids. Those which released an alkyl ligand in the process were active metathesis catalysts (equation 314) [402]. A tungsten carbyne complex catalyzed the metathesis of alkynes (equation 315) [403]. The role of oxygen in olefin metathesis was studied. It was proposed the olefin epoxidation was an important step in producing the ultimate catalytically active species (equation 316) [404]. The importance of tungsten hydrides in olefin metathesis reactions was studied, and tungsten(II) hydrides were proposed to be involved, but not tungsten IV hydrides [465]. The full details on how nobium and tantalum complexes of the type $M(CHCMe_3)(Pr_3)_2Cl_2$, could be modified to give olefin metathesis catalysts have been published [406]. The stereoselectivity in the cross metathesis of 1-octene, cis- and trans-2-octene over WCl_6/Ph_4Sn, $(PhO)_6W/EtAlCl_2$, or $WCl_6/Et_{3_2}Al$ was claimed to be influenced by 2,4-interactions between the metal and the C^2 alkyl group in the metallacyclobutane intermediate [407]. The use of $W(CO)_6$ and $(arene)W(CO)_3$ complexes in the presence of $RAlCl_2$ and oxygen as metathesis catalysts has been reported [408]. Irradiation of $W(CO)_6$ in CCl_4 produced an active metathesis catalyst [409]. The influence of the molar ratios of olefin to WCl_6, and of acyclic to cyclic olefin ratios on the composition of products in co-metathesis reactions catalyzed by $WCl_6/EtAlCl_2$ has been examined [410]. The tungsten catalyzed $W(NO)_2Cl_2(PPh_3)_2$ was more stereoselective in the metathesis of cis-pentene than were other catalysts which did not contain nitrosyl ligands [411]. Reaction of acetylene and ethylene with $NaBH_4/MoCl_6$ in DMF resulted in formation of disproportionation products [412].

(314)



$AY_n = AlX_3, BX_3, SnCl_4, ZnCl_2, MgBr_2$

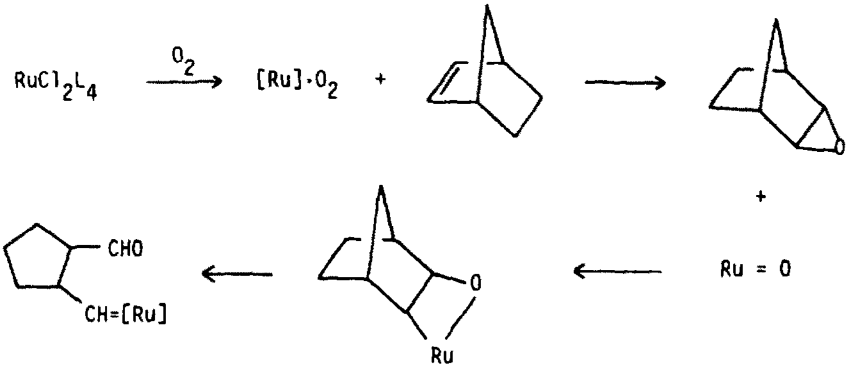
also studied



(315)

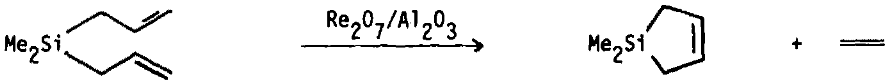
catalyzes metathesis of PhC≡CEt, CyC≡CEt, PhC≡C-tolyl, EtC≡CPr

(316)



Supported catalysts for olefin metathesis were also actively pursued. Unreduced molybdena/alumina catalysts were studied for the metathesis of butenes [413]. The mechanism of the catalyst system was studied using deuterated olefins [414]. The effect of oxide supports on molybdenium oxide-catalyzed metathesis was studied [415], as was the activity of supported tungsten oxides for the metathesis of propene [416]. Reaction of tungsten hexachloride with dry silica gel followed by treatment with tetramethyltin gave a solid catalyst for metathesis of 2-pentene [417]. Functionalized olefins (eg., Cl, I, F, CN) poisoned WO_3/SiO_2 metathesis catalysts [418]. The effects of isobutylamine on the metathesis of olefins catalyzed by WO_3/SiO_2 were studied [419]. The metathesis catalyst Re_2O_7/Al_2O_3 was studied by infrared spectroscopy, and was shown to have two different surface rhenium species, ReO_4^- and $Re_2O_7^-$ [420]. Dialkenyl silanes underwent metathesis and polymerization when exposed to Re_2O_7/Al_2O_3 or $Re_2O_7/Al_2O_3/SnBu_4$ catalysts (equation 317) [421]. The metathesis of propene over unsupported rhenium trioxide was studied [422].

(317)

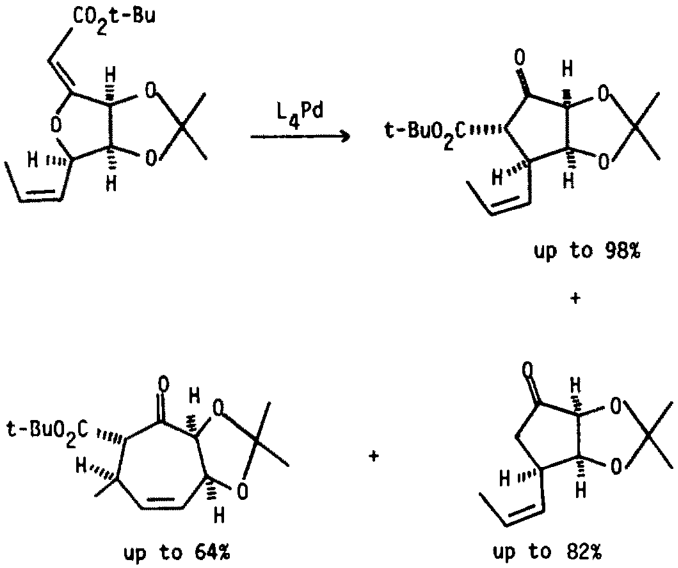


2. Olefin Isomerization

The kinetics of the isomerization of 1-butene and <u>cis</u>-2-butene over rhodium (III) chloride and palladium(II) chloride in chloroform has been studied [423]. A new mechanism for alkene isomerization by palladium(II) compounds has been proposed [424]. The isomerization of 4-methyl-1-pentene by $HCoN_2L_3$ was studied kinetically [425]. Allyl aromatics isomerized under phase transfer conditions using rhodium(I) catalysts [426]. A variety of metal halides ($RhCl_3$, K_3IrCl_6, $PdCl_2$) catalyzed the isomerization of allyl aromatics under phase transfer conditions [427]. Polystyrene-bound <u>bis</u> (cyclopentadienyl)titanium dichloride reacted with Grignard reagents to form active olefin isomerization catalysts [428]. Polymer bound $Cp_2Ti(CO)_2$, $CpTi{\cdot}TiCl_3$ and Cp_2TiCl_2 were prepared and studied as catalysts for the isomerization of allyl benzene to β-methyl styrene [429]. Polystyrene-bound $RuCl_2L_3$ catalyzed the same conversion [430]. This catalyst did not leach from the polymer, and was 2 to 5 times less active than the corresponding homogeneous systems. Allyl protecting groups on sugars were removed by isomerization to the enol ether followed by hydrolysis. The catalyst used was $[Ir(COD)(MePPh_2)_2]^+BF_4^-$, which was preferable to L_3RhCl since competitive reduction of the olefin did not occur [431]. Unsaturated dicarboxylic esters underwent isomerization over $RhCl(PPh_3)_3/SnCl_2$ catalysts [432].

3. Rearrangements of Allylic and Propargylic Oxygen and Nitrogen Compounds

A dissertation entitled "Palladium-Catalyzed 1,3-Oxygen to Carbon Alkyl Shifts in Substituted 2-Alkylidene-5-vinyltetrahydrofurans" has appeared [433]. This process was used to produce either cyclopentanones or cycloheptenones, depending on the catalyst (equation 318) [434][435]. This chemistry was used to synthesize *seco* steroids (equation 319) and prostaglandin E (equation 320) [435][436]. Acyclic vinyl acetals rearranged to conjugated ketones when treated with palladium(II) catalysts (equation 321) [437].



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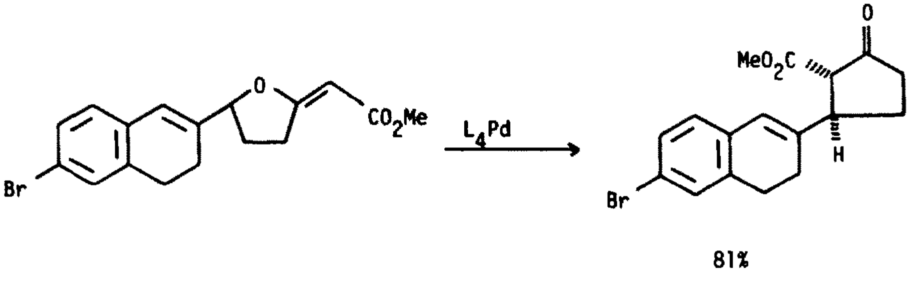
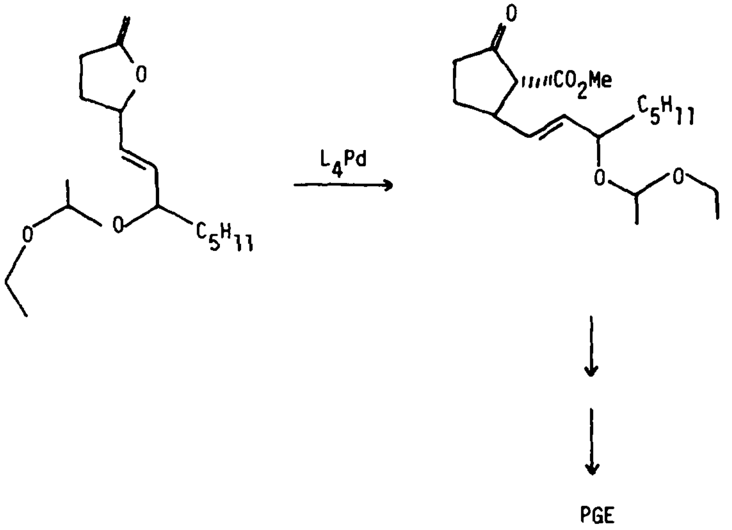
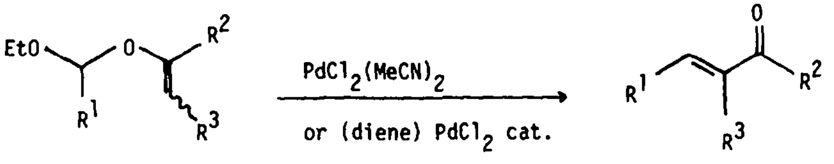




(320)

(321)

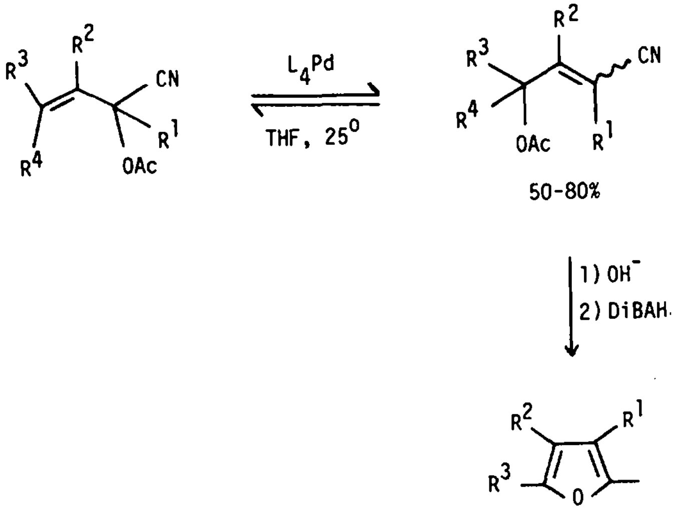


R^1 = Me, Et, n-Pr

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

R^3 = Me, Et

Allylic cyanohydrin acetates rearranged to alkenyl nitriles when treated with palladium(0) catalysts. These were further converted to furans (equation 322) [438]. Chiral allyl acetates underwent a 1,3-acetate rearrangement, stereospecifically, in the presence of palladium(II) catalysts (equations 323 and 324) [439]. Doubly allylic acetates rearranged to $\alpha,\beta,\gamma,\delta$-unsaturated acetates (equations 325-328) [440]. S-Allylthiocarbamates rearranged to N-allylthiocarbamates in the presence of palladium(II) catalysts (equation 329) [441].



(322)

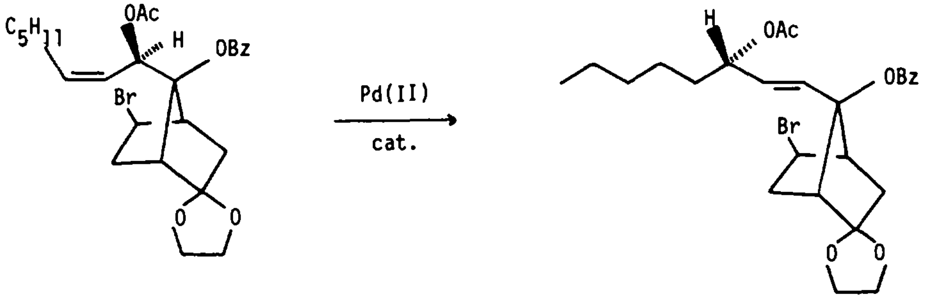
R^1 = H, Me

R^2 = H, Et, n-C_8, PhS$(CH_2)_2$

R^3 = Ph, n-Pr, n-C_6

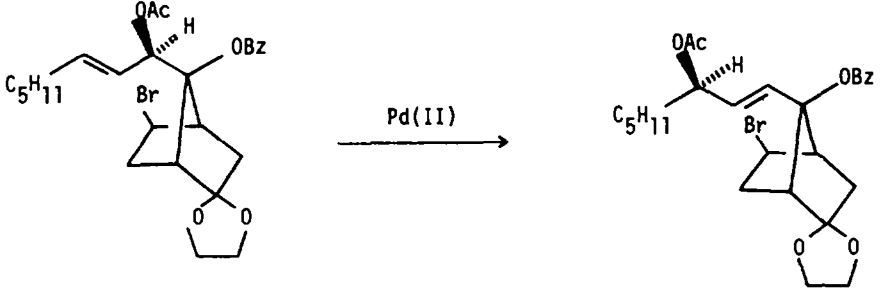
R^4 = H

(323)



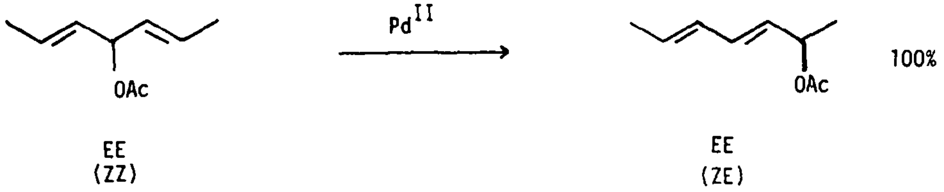
76% yield

(324)



95%

(325)



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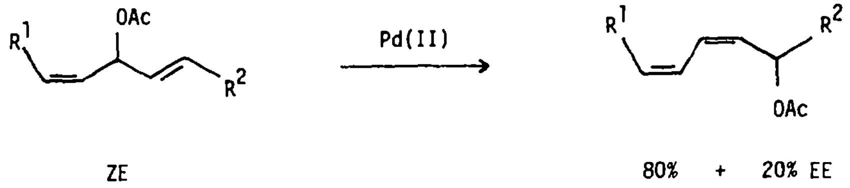
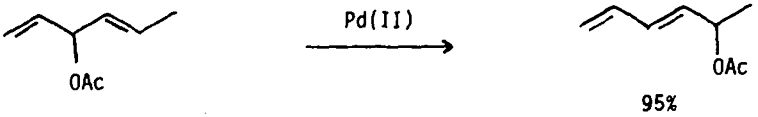


R^1, R^2 = Me, Bu



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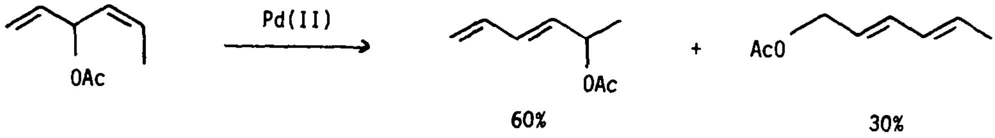

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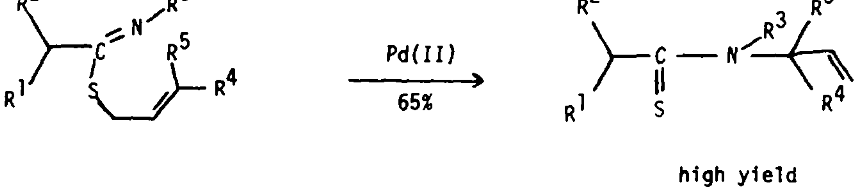
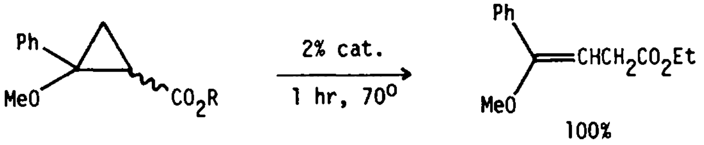


4. Skeletal Rearrangements

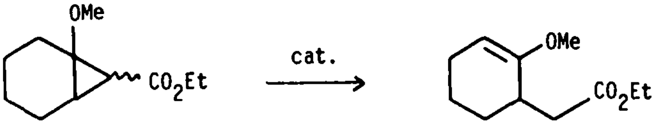
2-Alkoxycyclopropancarboxylic acids rearranged to β,δ-unsaturated esters in the presence of platinum(II), rhodium(I), or ruthenium(II) catalysts (equations 330-

333) [442]. Cyclopropenecarboxylic acid ring opened when treated with iron carbonyl compounds (equation 334) [443]. Metathesis catalysts ring opened cyclopropanes, but did not effect a retro carbene reaction (equation 335) [444]. Molybdenum VI oxide catalysts caused skeletal isomerization of 3,3-dimethyl-1-butene [445].



(330)

cat. = $PtCl_2(PhCN)_2$, $[Rh(CO)_2Cl]_2$, $[Ru(CO)_3Cl_2]_2$



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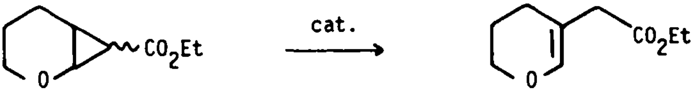

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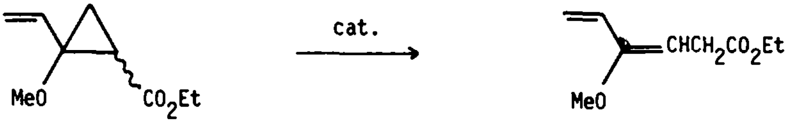

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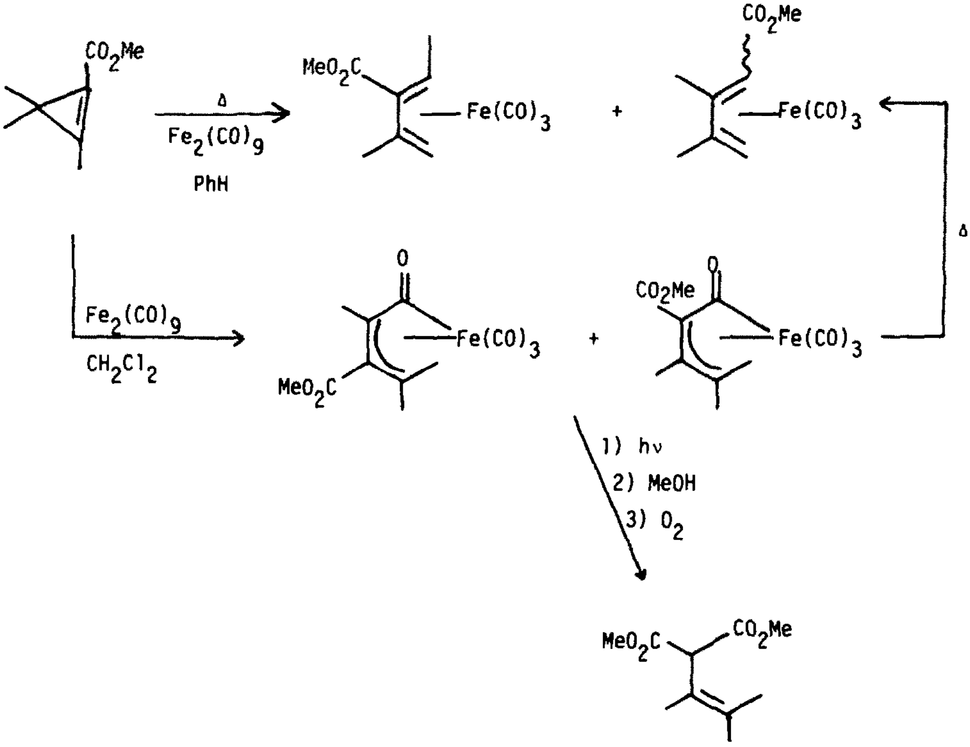
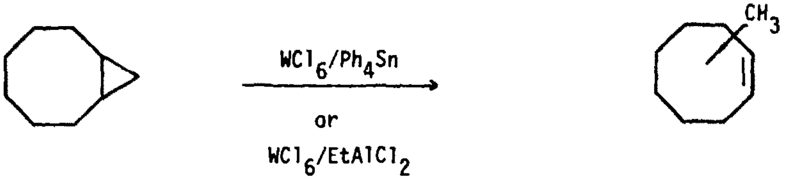
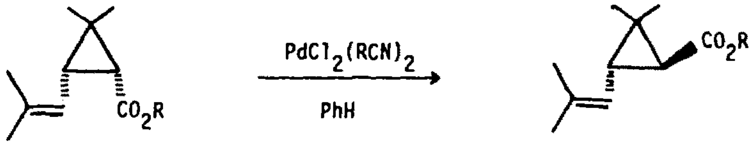




(335)

5. Miscellaneous Rearrangements

Palladium(II) chloride catalyzed a cis-trans isomerization of substituted cyclopropanes (equation 336) [446]. Epiperoxides underwent a palladium(0) catalyzed rearrangement to give a mixture of products (equation 337) [447]. Bicyclic peroxides underwent a similar rearrangement (equations 338-341) [448]. This chemistry was used to prepare prostaglandins (equation 342). Gibberellins underwent a number of palladium catalyzed rearrangements (equation 343) [449].



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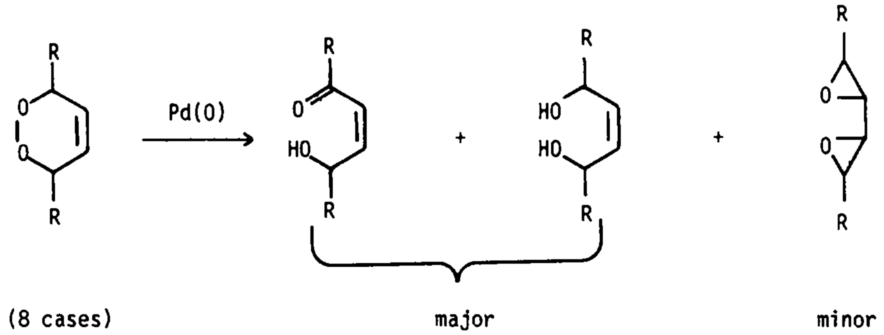

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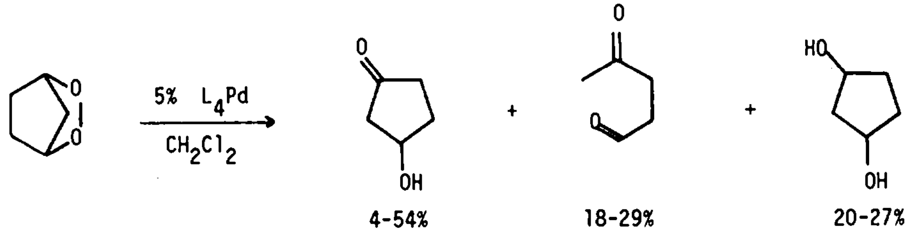

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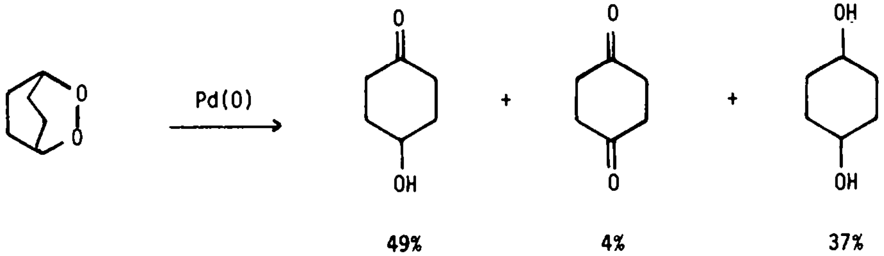

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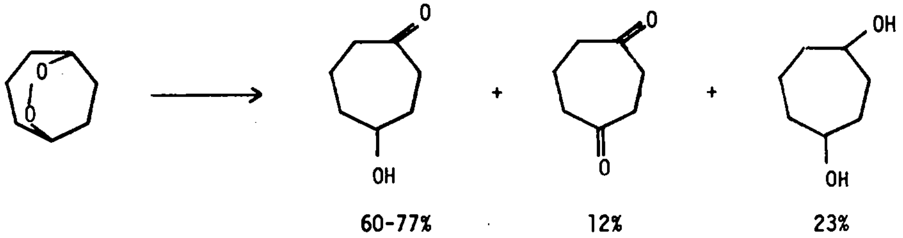

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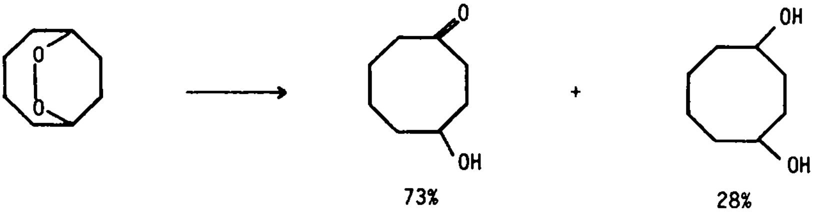

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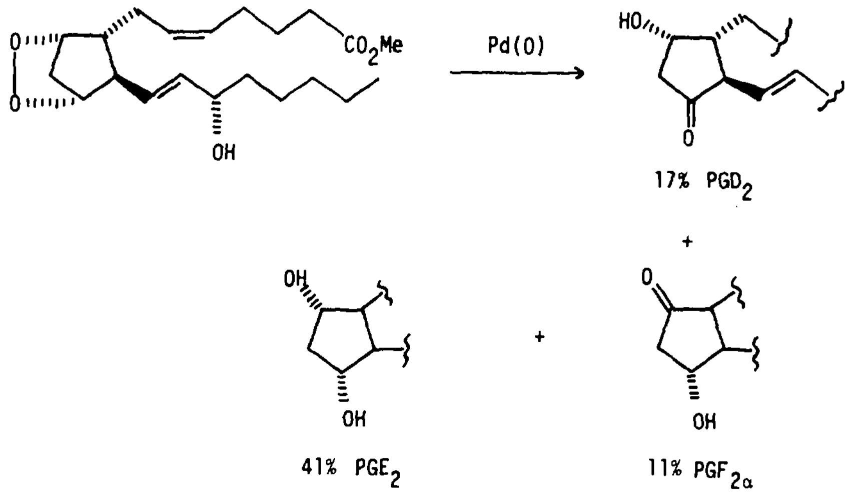

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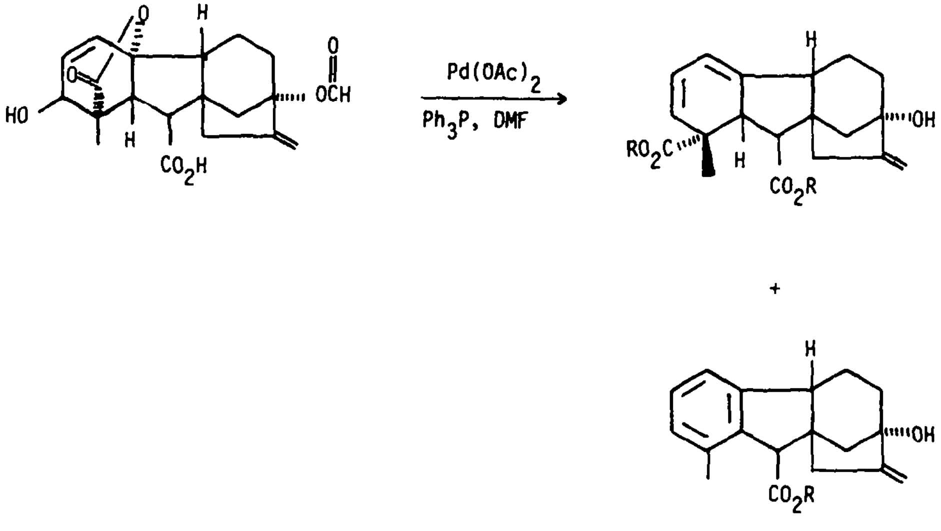
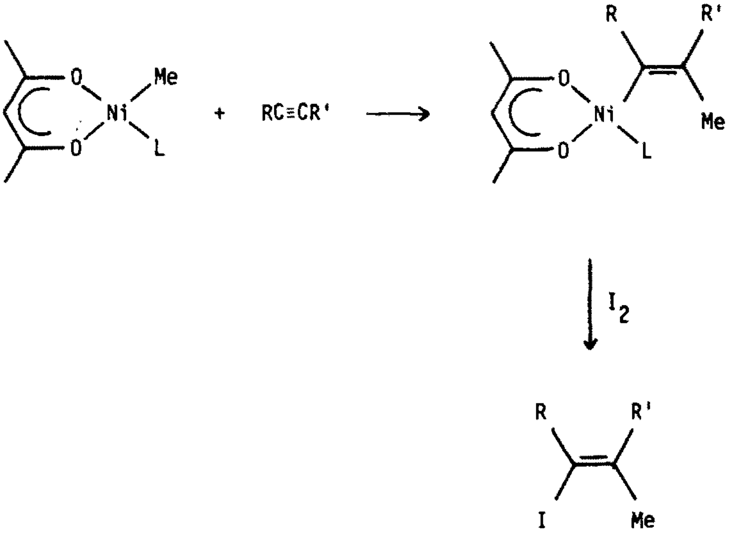


Reaction of $Ph_2PNEtPh$ with bromobenzene in the presence of nickel(II) bromide gave p-$Ph_3P^+C_6H_4NHEtBr^-$ which upon heating in the presence of the same catalyst gave o- and p-$Ph_2PC_6H_4NHEt$ [450]. Platinum on Cab-O-Sil catalyzed the rearrangement of 1,3-dioxacycloalkanes to esters [451]. Reviews entitled "Organometallic compounds: Isomerization: Intramolecular Processes" (137 references) [452], 'The σ,π-Rearrangement: A Key Process in Organometallic Catalysis" (147 references) [453], and "Organometallic 1,2-Shift Type Reactions"(35 references) [454], have appeared.

III. Functional Group Preparations

A. Halides

β-Bromostyrenes were converted to β-chlorostyrenes in high yield by reaction with $(PhO)_3PCuCl$ [455]. Steroidal ketones, cyclohexanone, 5-nonanone, and acetone were α-iodinated by iodine and copper(II) acetate in acetic acid [456]. Alkynes were converted to vinyl iodides by reaction with a nickel(II) methyl complex followed by iodination (equation 344) [457]. Acetylene was hydrochlorinated by HCl in the presence of copper(I) chloride [458]. Toluenes were converted to benzyl bromides by reaction with copper(II)bromide and t-butylhydroperoxide (equation 345) [459]. Acetyl bromide reacted with methyl chloroformate in the presence of nickel(0), palladium(0), or platinum(0) catalysts to give methyl bromide, acetyl chloride and carbon dioxide [460].



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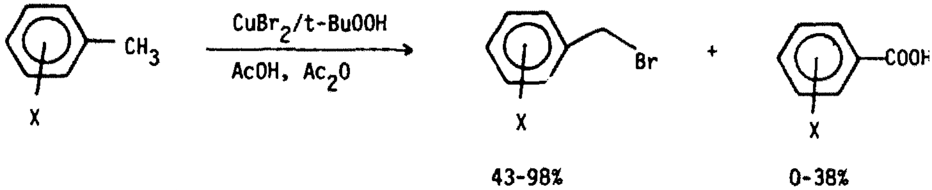
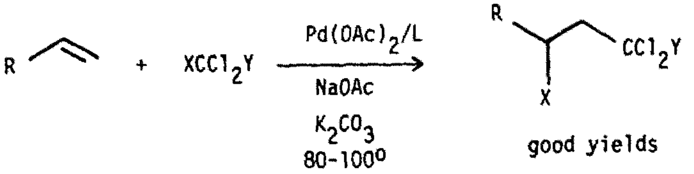


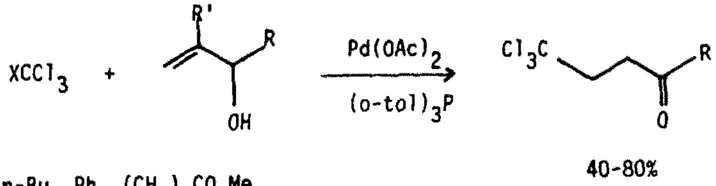
X = 4-Cl, 4-Br, 2-Cl, 2-Br, 3-Br, 4-COOH, H

The mechanism of the addition of carbon tetrachloride to 1-octene catalyzed by hexacarbonyl bis(η-cyclopentadienyl)dimolybdenum started as a redox process but ended up as a radical chain process [461]. Palladium salts catalyzed the addition of polyhalomethanes to olefins (equation 346) [462], and allylic alcohols (equation 347) [463]. Bromotrichloromethane added to styrene in the presence of a chiral rhodium(I) complex to give the addition product with >32% ee (equation 348) [464]. Titanium(IV) chloride ring opened trimethylsilylcyclopropanes (equations 349-351) [465]. Cyclic olefins were converted to acyclic chloroketones by reaction with iron(III) chloride with irradiation (equations 352-354) [466].



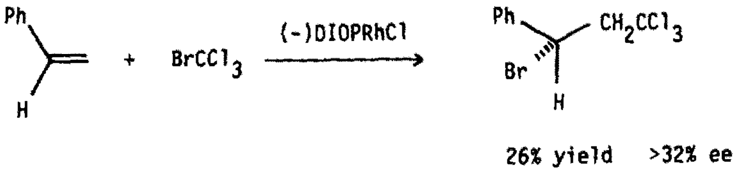
(346)

$R = n\text{-}C_8$, $-(CH_2)_8CO_2Me$,
CH_2OAc, cyclohexyl
X = Cl, Br
Y = Cl, CO_2Me



(347)

R = n-Bu, Ph, $(CH_2)_7CO_2Me$
R' = H, Me



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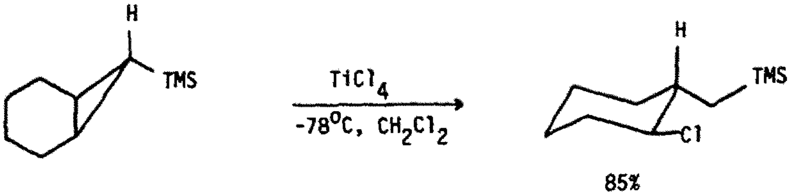

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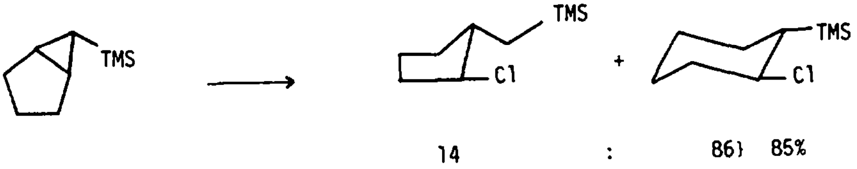

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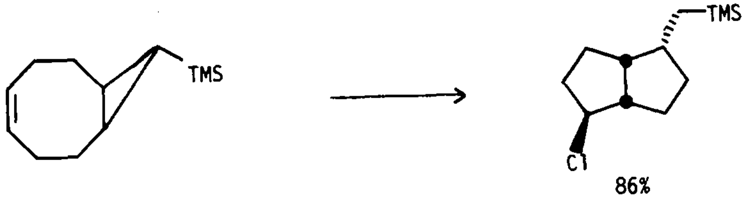

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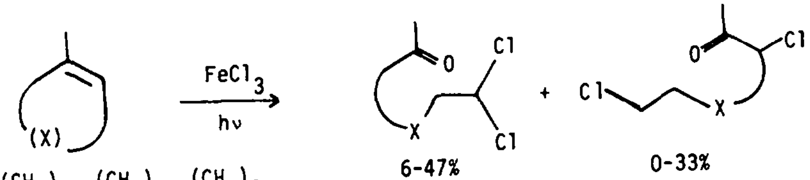
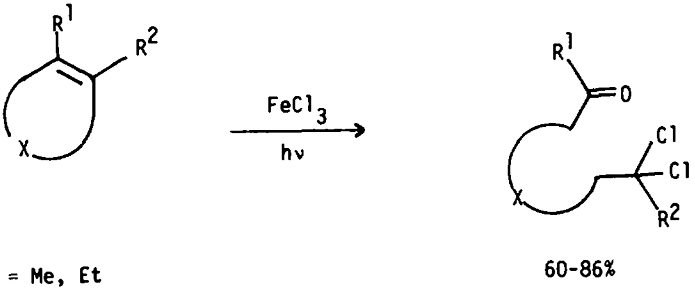


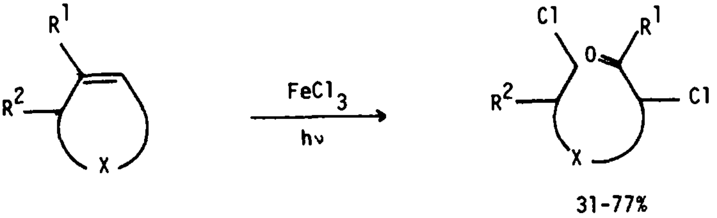
(352)

X = $(CH_2)_3$, $(CH_2)_2$, $(CH_2)_8$



(353)

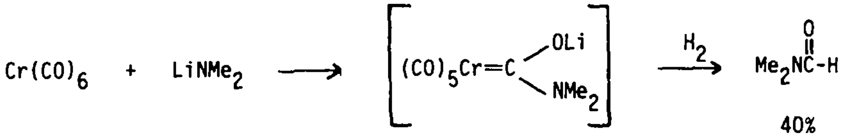
R's = Me, Et



(354)

B. Amides, Nitriles

Reaction of chromium hexacarbonyl with lithium dimethylamide and hydrogen produced a 40% yield of dimethyl formamide in which the carbonyl group came from the chromium carbonyl (equation 355) [467]. Chromium-complexed benzyl alcohols reacted with nitriles in sulfuric acid to give amides (equations 356 and 357). Cobalt complexed propargyl alcohols reacted similarly (equation 358) [468]. A cobalt-amino acid complex provided an alternative to activated esters for polypeptide synthesis (equation 359) [469][470]. A dissertation entitled "The Zinc and Copper Promoted Hydrolysis of Lactams" has appeared [471].



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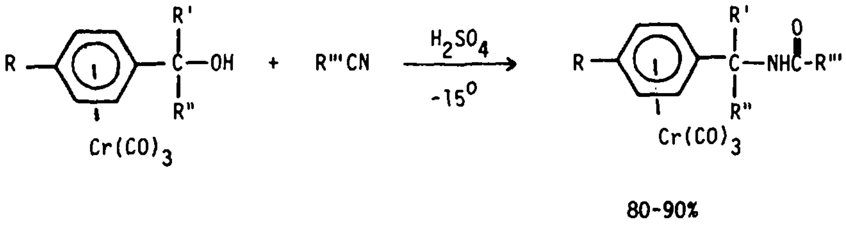
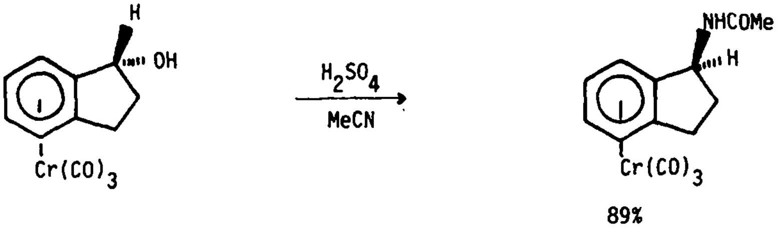
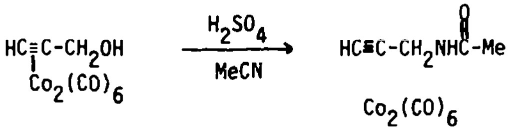


R = Me, MeO, H
R' = H, Me, Ph
R" = H, Me
R''' = Me, Ph



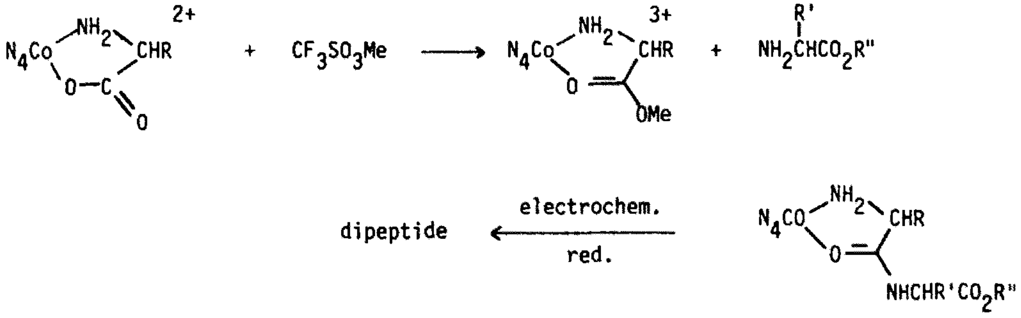
(357)



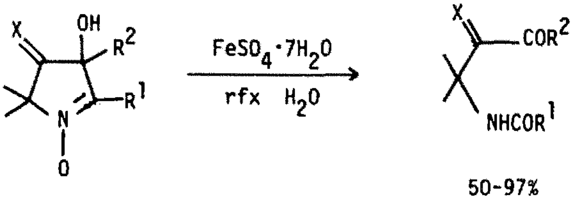
$$\underset{Co_2(CO)_6}{HC{\equiv}C\text{-}CH_2OH} \xrightarrow[MeCN]{H_2SO_4} \underset{Co_2(CO)_6}{HC{\equiv}C\text{-}CH_2NH\overset{O}{\overset{\|}{C}}\text{-}Me}$$

(358)

(359)



The selective hydrolysis of nitriles to amides catalyzed by ClPd(OH)(bipy) was studied in detail [472][473]. Amides were produced by the reaction in equation 360 [474].



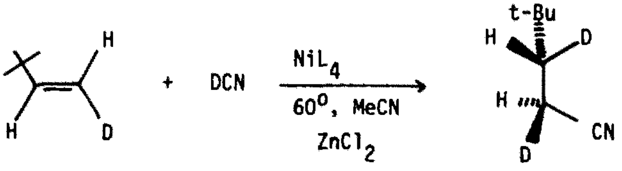
(360)

X = H, H; O

R^1 = t-Bu, Ph

R^2 = Me, Et, Ph

Copper(I) cyanide converted 2-bromo-3-methylphenol into 2-cyano-3-methylphenol in 94% yield [475]. The nickel(0) catalyzed addition of DCN to olefins proceeded with clean cis stereochemistry (equation 361) [476]. Aerogel catalysts comprised of nickel oxide dispersed on aluminum oxide or silicon oxide supports were efficient for the conversion of isobutene and NO into methacrylonitrile [477][478][479].

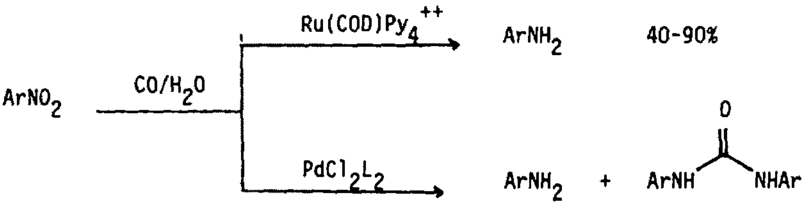


(361)

C. Amines, Alcohols

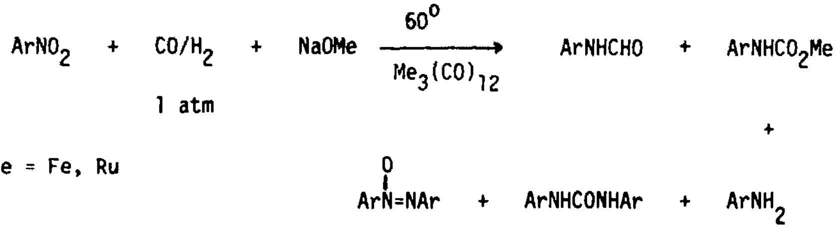
Nitrobenzenes were reduced to anilines by dicobalt octacarbonyl on alumina

[480]. Nitroarenes were reduced to aryl amines by carbon monoxide/water over ruthenium(II) catalysts, while palladium(II) catalysts produced ureas in addition to aryl amines (equation 362) [481]. Nitrobenzene and p-chloronitrobenzene were reduced to the corresponding anilines over $PdCl_2(PhCN)_2$ [482]. Nitroarenes reacted with carbon monoxide/hydrogen mixtures over iron or ruthenium catalysts to give a variety of reduction and reductive acylation products (equation 363) [483]. Aromatic azides were reduced to aryl amines by $(Ph_3P)_2CuBH_4$ [484].



(362)

Ar = PhH, p-MePh, p-OMePh, m-MePh, m-NO_2Ph

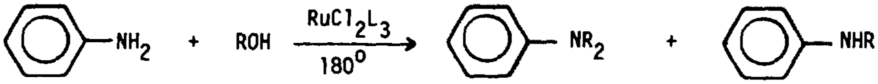


(363)

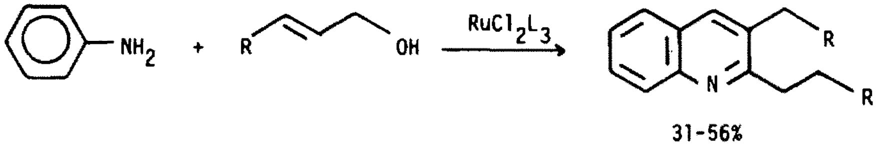
Me = Fe, Ru

Palladium supported on alumina catalyzed the amination of phenols with ammonia [485]. Copper catalyzed the amination of aliphatic alcohols [486]. Aromatic amines were alkyalted by alcohols over ruthenium catalysts at high temperatures (equation 364). Allyl alcohol reacted with aniline to produce quinolines (equation 365) [487]. Aliphatic amines underwent alkylation by alcohols in the presence of iridium and rhodium catalysts (equations 366 and 367) [488]. Primary amines underwent "disproportionation" in the presence of ruthenium catalysts (equation 368) [489].

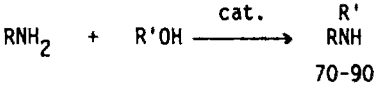
(364)



R = Me, Et, n-Bu



(365)

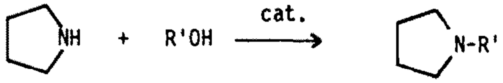


$$\mathrm{RNH_2} + \mathrm{R'OH} \xrightarrow{\text{cat.}} \overset{\mathrm{R'}}{\mathrm{RNH}} \qquad (366)$$

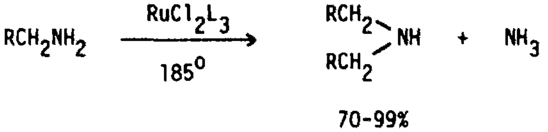
70-90%

R = n-Bu, cyclohex, Ph
R' = Me, Et, Bz, i-Pr

cat = $IrCl_3 \cdot H_2O/PPh_3$, Na_2IrCl_6/PPh_3
$RhCl_3 \cdot 3H_2O/PPh_3$, $RhHL_4$, $IrClL_3$
$RhClL_3$



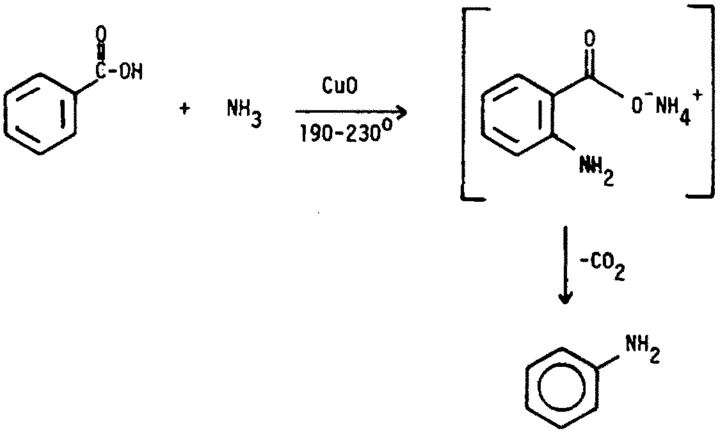
(367)



$$\mathrm{RCH_2NH_2} \xrightarrow[185^{0}]{\mathrm{RuCl_2L_3}} (\mathrm{RCH_2})_2\mathrm{NH} + \mathrm{NH_3} \qquad (368)$$

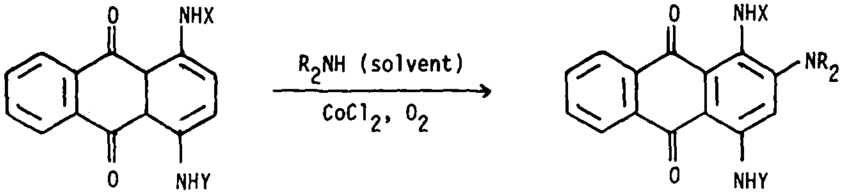
70-99%

Aromatic carboxylic acids reacted with ammonia over copper oxide to produce aryl amines. The amination occurred in the ortho position of the aromatic (equation 369) [490]. Amines aminated anthraquinones in the presence of cobalt(II) catalysts (equation 370) [491], copper(II) catalysts (equation 371) [492], and rhodium(I) catalysts [493][494].



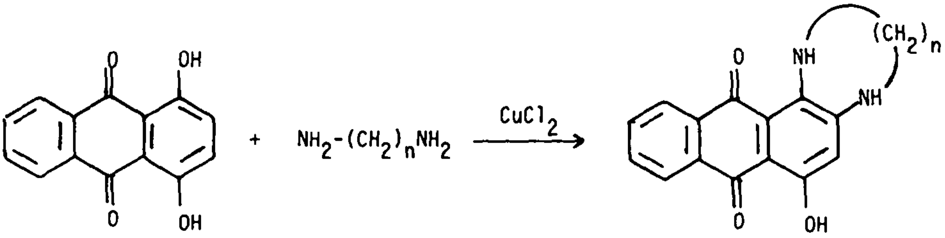
(369)

(370)



40-70%

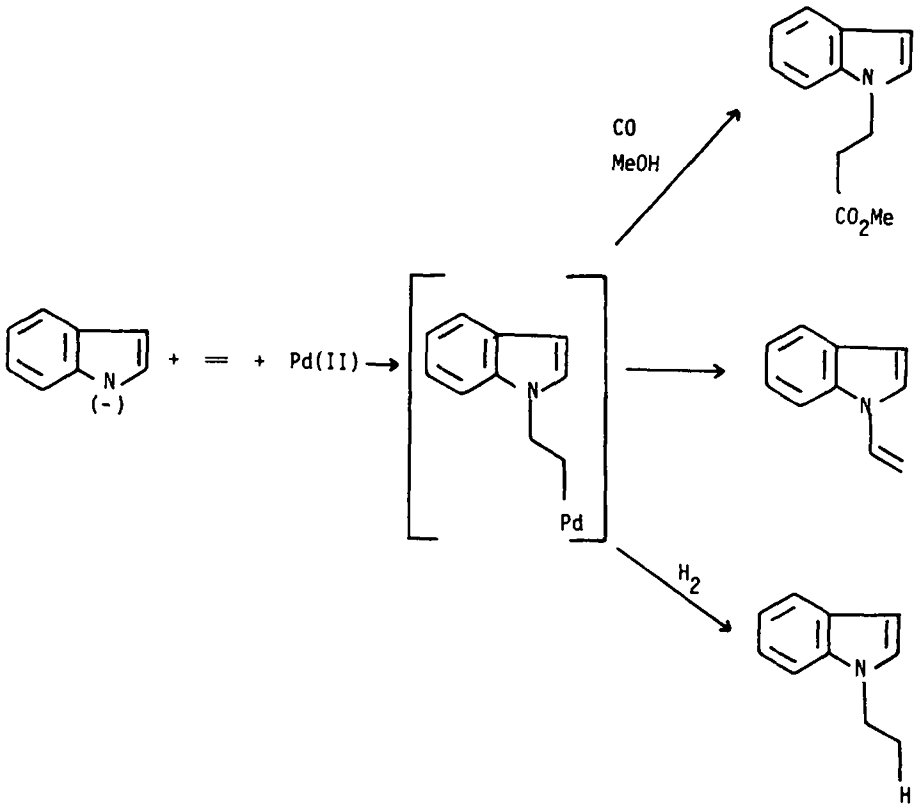
(371)



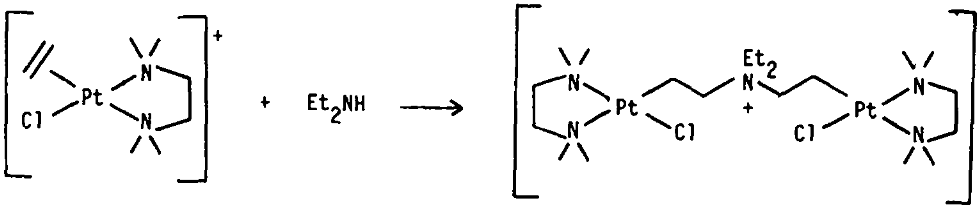
n = 2, 98%
n = 3, 0%

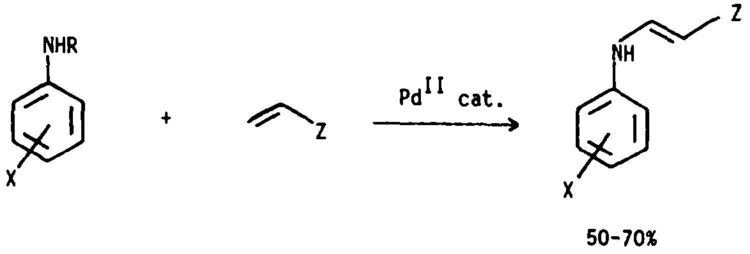
A dissertation entitled "Palladium Assisted Amination of Olefins" has appeared [495]. Indole aminated olefins in the presence of palladium(II) salts. The intermediate σ-alkylpalladium complex was carbonylated (equation 372) [496]. Diethylamine aminated ethylene bound to platinum(II) to produce an ammonium salt (equation 373) [497]. Aromatic amines added to the β-position of conjugated enones in the presence of palladium(II) catalysts (equation 374) [498]. Butadiene was aminated by secondary amines in the presence of nickel(II) complexes of chiral phosphines to give telomers with some optical activity [499]. Allylic acetates were aminated in the presence of catalytic amounts of palladium(II) complexes (equation 375) [500]. The mechanism of amination of π-allyl palladium complexes in the presence of phosphines was claimed to proceed by an S_N2' attack on a σ-allylpalladium complex rather than by nucleophilic attack on a cationic π-allylpalladium species [501].

(372)



(373)

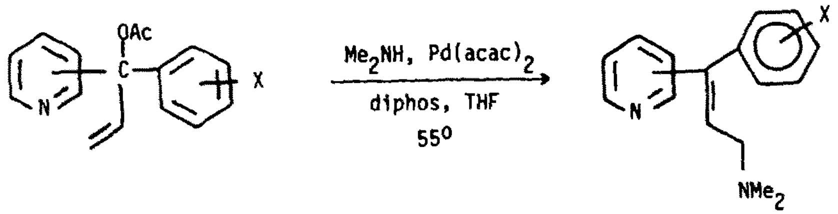




(374)

Z = CO_2Me, COMe, CN

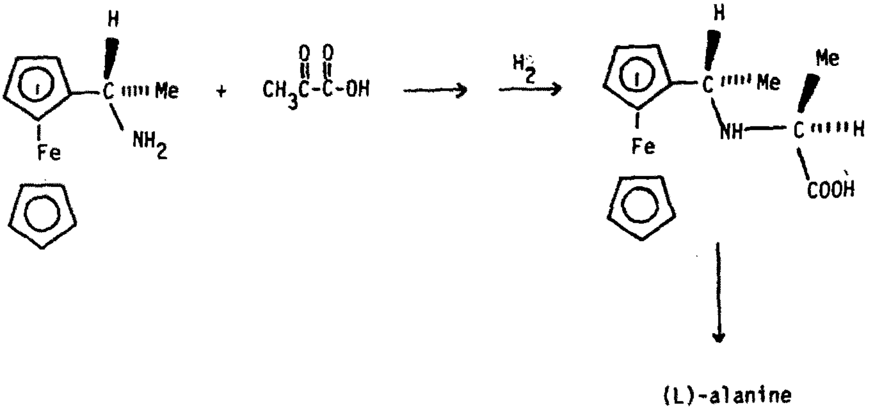
(375)

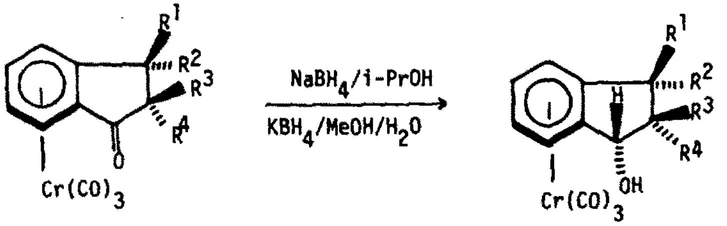


3-Py, 4-Py, 2-Py
X = H, 4-F, 4-Cl, 4-Br, 4-OMe, 2-Br

Rhodium salts catalyzed the aminomethylation of olefins by carbon monoxide, water, and amines [502]. Chiral alanine was synthesized using chiral 1-ferrocenylethylamine (equation 376) [503]. Isocyanates reacted with aldehydes in the presence of $Co_2(CO)_8$, $W(CO)_6$, and $Ni(CO)_2(PPh_3)_2$ to give imines [504]. Chromium complexes of indanone were reduced to complexed indanols exclusively from the face opposite the metal (equation 377) [505].

(376)





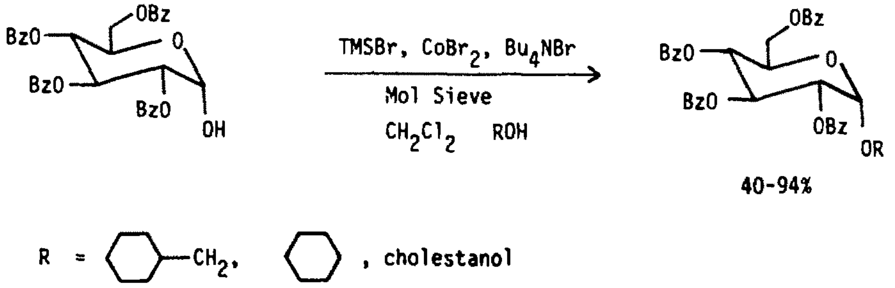
(377)

R^1 = Me, Et, i-Pr: $R^2=R^3=R^4=H$
R^2 = Me, Et, i-Pr; $R^1=R^3=R^4=H$
R^3 = Me, Et, i-Pr, t-Bu; $R^1=R^2=R^4=H$
R^4 = Me, Et, i-Pr, t-Bu; $R^1=R^2=R^3=H$

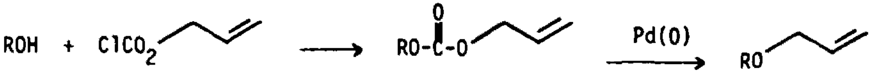
D. Ethers, Esters, Acids

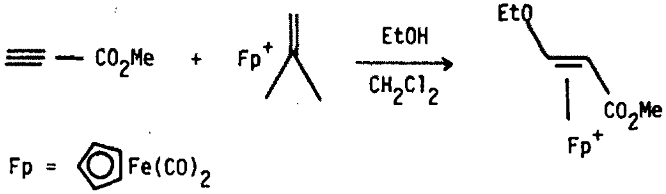
Diphenylethers were synthesized by the reaction of copper(I) phenoxide with aryl halides [506]. A Hammett σ,ρ study of the reaction of phenoxides with cationic iron-chlorobenzene complexes has been carried out [507]. A one-stage α-glycosidation of alcohols involving the use of cobalt(II) bromide as a promoter has been developed (equation 378) [508]. Palladium(0) complexes converted allyl esters into allyl ethers (equation 379) [509]. Enol ethers were prepared by the iron-assisted alkoxylation of alkynes (equations 380 and 381) [510]. Copper(II) perchlorate oxidatively cleaved cyclopropanes to ethers under irradiation (equation 382) [511]. Thioketones were converted to a variety of compounds by hydrozirconation followed by further reaction (equation 383) [512].

(378)

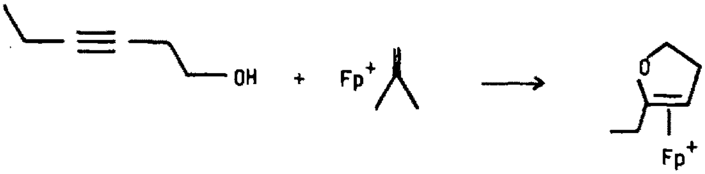


(379)



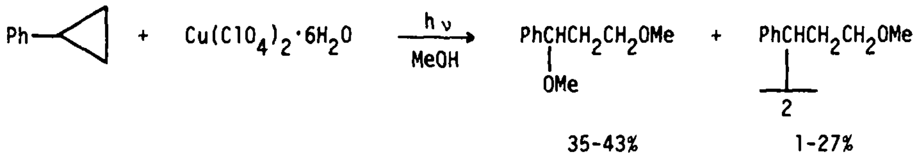


(380)

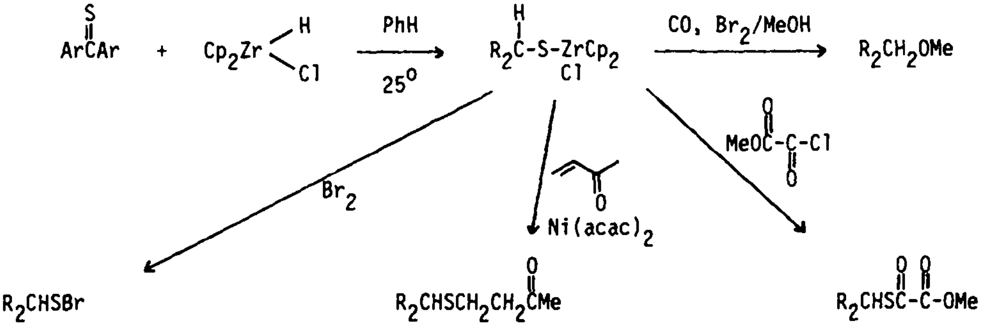


(381)

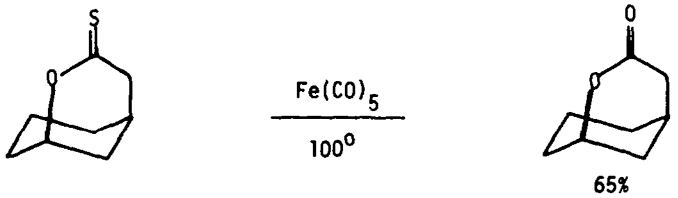
(382)



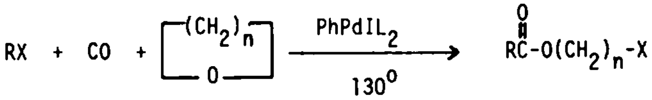
(383)



Thioesters were converted to esters by treatment with iron pentacarbonyl (equation 384) [513]. Propylene carbonate was prepared from propylene and carbon dioxide in the presence of transition metal oxidants [514]. Organic halides reacted with THF in the presence of carbon monoxide and palladium(II) salts to give δ-chloroesters (equation 385) [515]. Alcohols were oxidized and then condensed to esters by reaction with $Ru_3(CO)_{12}$ in the presence of a hydrogen acceptor (equation 386) [516]. The mechanism of the acetoxylation of arenes by acetic acid in the presence of palladium(II) catalysts has been studied [517]. Copper oxide oxidized alcohols to esters at temperatures in excess of 170° (equation 387) [518]. Phenols were converted to diaryl carbonates by oxidative carbonylation in the presence of palladium(II) and manganese(II) salts (equation 388) [519]. A methylene-bridged iron species was converted to esters by reaction with alcohols (equation 389) [520].

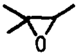
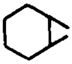


(384)

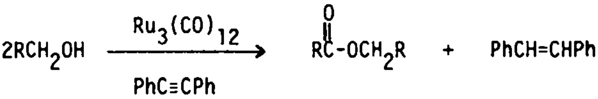


$$RX + CO + \text{(CH}_2\text{)}_n\text{O} \xrightarrow[130^\circ]{PhPdIL_2} RC(=O)\text{-}O(CH_2)_n\text{-}X$$

(385)

n = 2,4  , O also react

R = $PhCH_2$, Ph, p-anisyl, Ph , Ph , $PhCOCH_2$

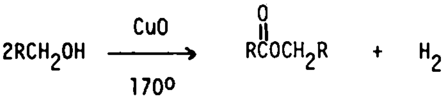


$$2RCH_2OH \xrightarrow[PhC{\equiv}CPh]{Ru_3(CO)_{12}} RC(=O)\text{-}OCH_2R + PhCH{=}CHPh$$

(386)

70-80%

R = Ph, n-Bu

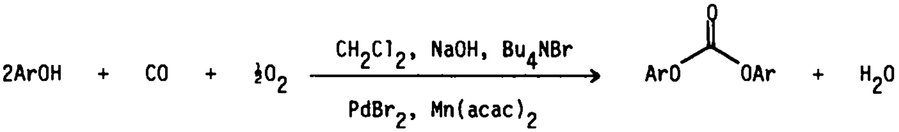


$$2RCH_2OH \xrightarrow[170^\circ]{CuO} RC(=O)OCH_2R + H_2$$

(387)

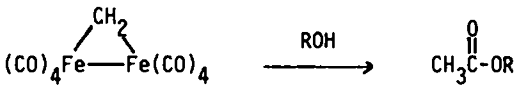
R = C_6 or longer (diols ⟶ polyesters)

(388)



$$2ArOH + CO + \tfrac{1}{2}O_2 \xrightarrow[PdBr_2,\ Mn(acac)_2]{CH_2Cl_2,\ NaOH,\ Bu_4NBr} ArOC(=O)OAr + H_2O$$

up to 61%



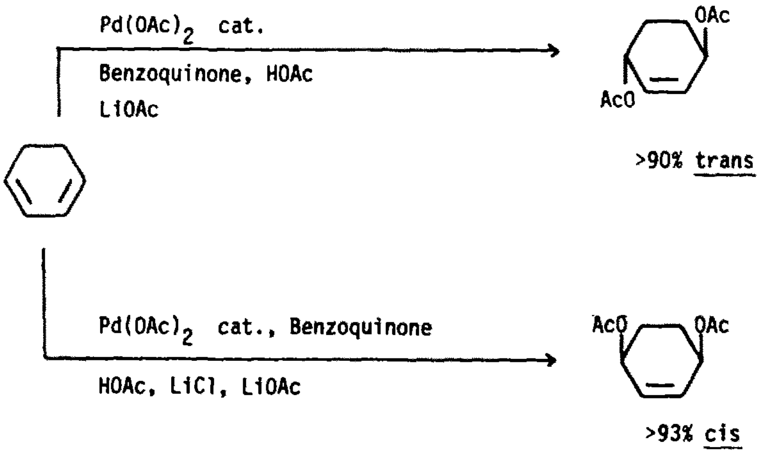
$$(CO)_4Fe(\mu\text{-}CH_2)Fe(CO)_4 \xrightarrow{ROH} CH_3C(=O)\text{-}OR$$

(389)

R = Me, Et

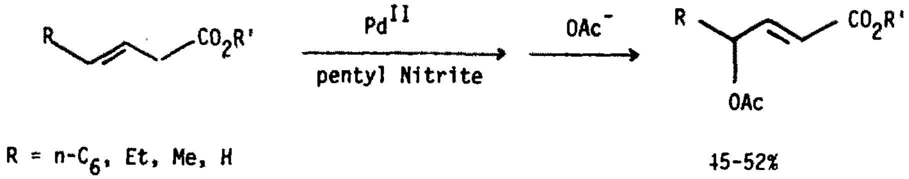
Oxidative acetoxylation of propene was effected by a palladium/potassium acetate/amorphous aluminosilicate catalyst [521]. The nature of the active center of this catalyst was studied [522]. Palladium(0) clusters catalyzed the oxidative acetoxylation of ethylene [523]. The mechanism of this process was also studied [524], as was the stability of alumina-supported palladium catalysts for the synthesis of vinyl acetate from ethylene [525].

Palladium(0) complexes catalyzed the oxidative acetoxylation of toluene to benzyl acetate [526]. Olefins were converted to allyl acetates by reaction with cobalt(III) acetate in acetic acid [527]. Cyclohexa-1,3-diene was converted to either *cis* or *trans* 1,4-acetoxycyclohex-2-ene by palladium-catalyzed acetoxylation (equation 390) [528]. β,γ-Unsaturated esters were acetoxylated in the γ-position by palladium(II) salts under oxidizing conditions (equations 391 and 392) [529]. Allyl sulfones were acetoxylated by conversion to π-allylpalladium complexes (equation 393) [530].

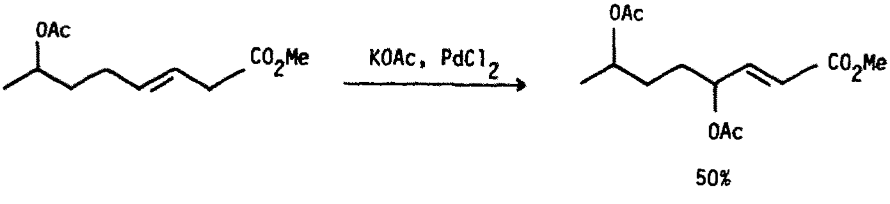


(390)

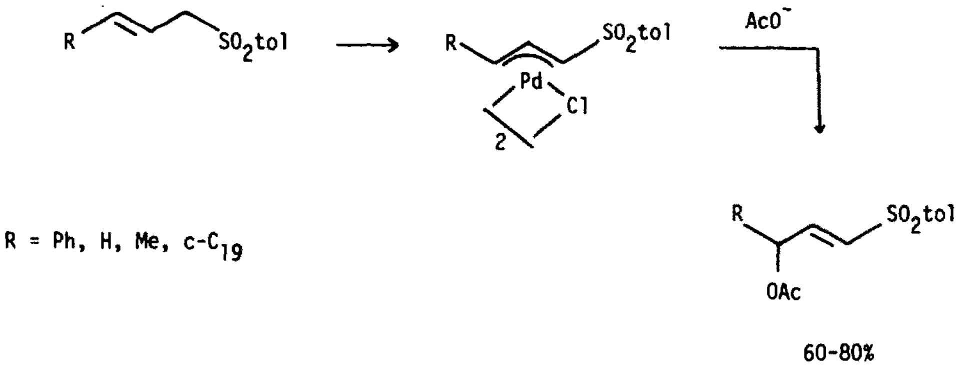
(391)



(392)



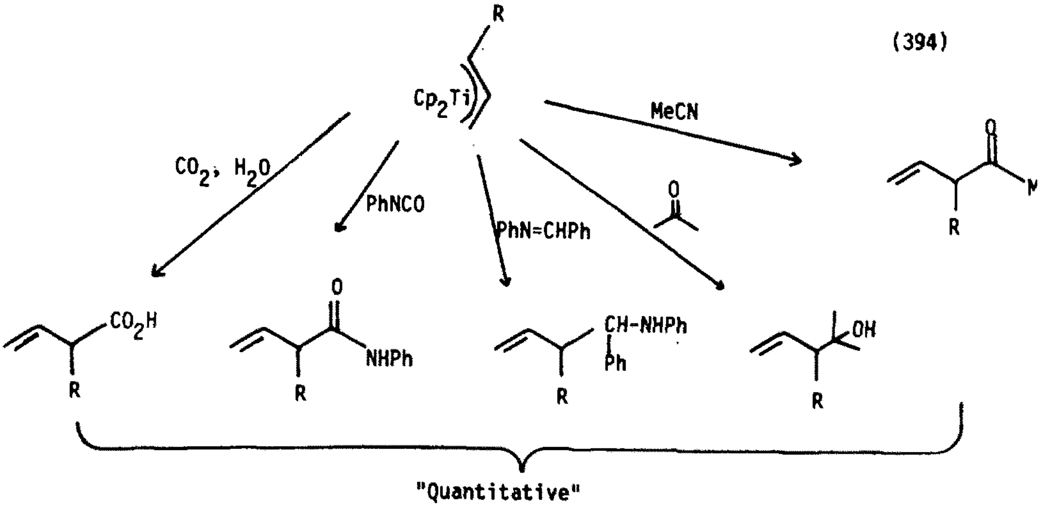
(393)

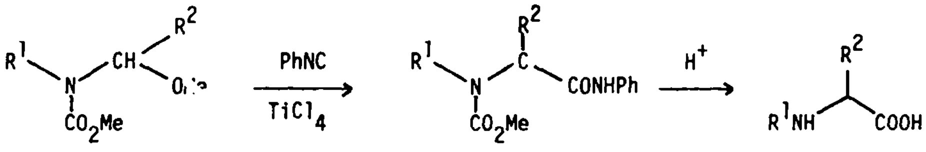


R = Ph, H, Me, c-C_{19}

π-Allyltitanium complexes were converted to carboxylic acid derivatives (equation 394) [531]. α-Aminoacids were synthesized by titanium(IV) assisted reactions of isonitriles (equation 395) [532]. Acids or diacids were produced from the molybdenum(VI) oxidative cleavage of trimethylsilylenol ethers (equations 396-398) [533]. The synthesis of carboxylic acids by copper(I) or silver carbonyl catalysts has been reviewed (27 references) [534]. Acid hydrazides were converted to carboxylic acids, esters, and amides by reaction with copper(II) compounds [535]. Anhydrides of aromatic carboxylic acids were prepared from aryl diazonium salts and carboxylates in the presence of palladium(II) salts (equation 399) [536], and from α-diketones and platinum-oxygen complexes (equation 400) [537].

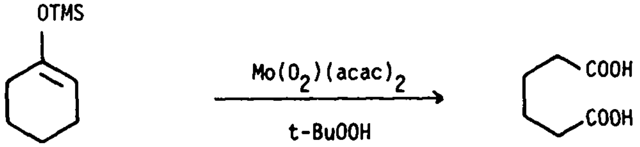
(394)



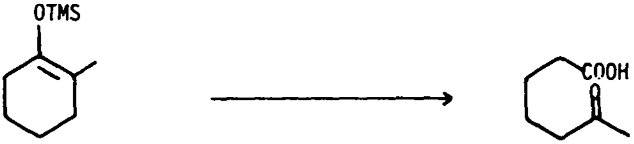


34-82%

(395)



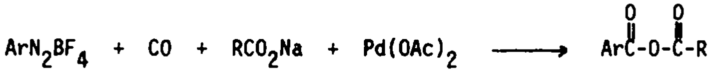
(396)



80-90%

(397)

(398)

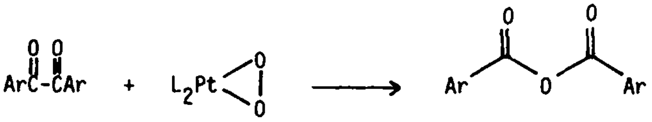


$$\mathrm{ArN_2BF_4 + CO + RCO_2Na + Pd(OAc)_2 \longrightarrow Ar\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R}$$

45-86%

(399)

Ar = Ph, 3-MePh, 4-MePh, 2-OMePh, 4-BrPh, 4-IPh, 4-NO_2Ph, 1-naphth
R = H, Et, Me, t-Bu, Ph



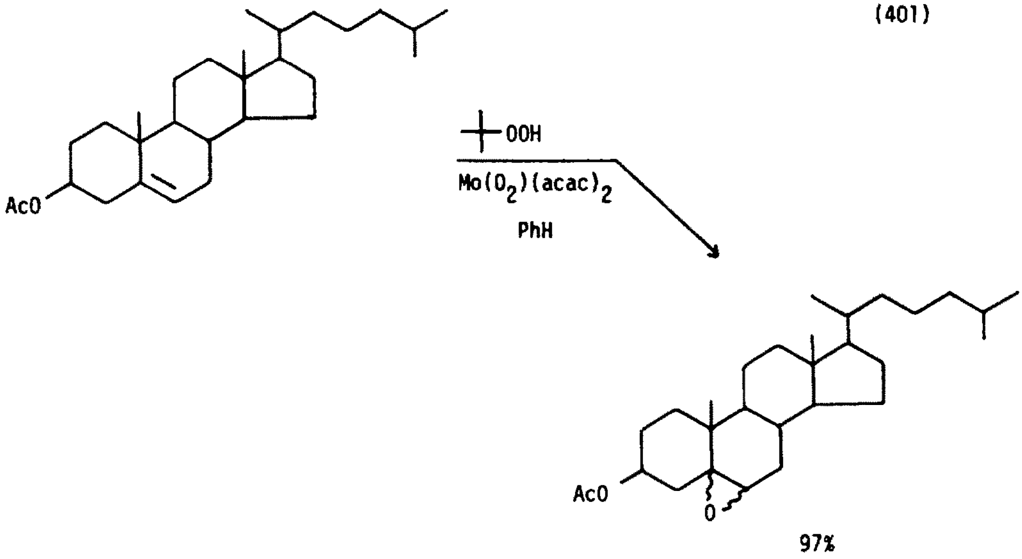
14-50%

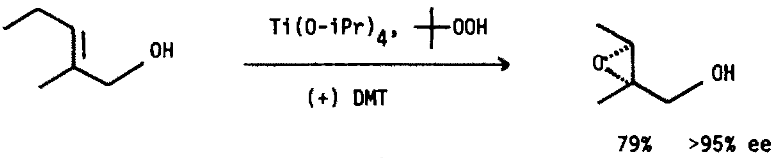
(400)

E. Heterocycles

A review entitled "New Synthetic Methods of Heterocyclic Compounds Using Organometallic Complexes" (33 references) has appeared [538]. The catalytic epoxidation of olefins with organic hydroperoxides has been reviewed (197 references) [539] as has synthetic and mechanistic aspects of metal catalyzed epoxidations with hydroperoxides (49 references) [540]. The reactivity of olefins and hydroperoxides in the hydroperoxide epoxidation with vanadyl acetylacetonate catalysts has been studied [541][542]. The epoxidation of monoterpenes with t-butylhydroperoxides and metal catalysts was studied [543], as was the use of polymer-supported vanadium(IV) catalysts for similar reactions [544]. Cholesteryl acetate was epoxidized by t-butylhydroperoxide in the presence of a molybdenum catalyst (equation 401) [545]. A leukotriene precursor (equation 402) a methamycin intermediate (equation 403) and a disparalure intermediate (equation 404) were synthesized using titanium-(+) dimethyl tartrate catalysts for key epoxidation steps [546]. The stereochemistry of the epoxidation of homoallylic alcohols using vanadium(V)-t-butylhydroperoxide was predicted by considering the transition state having the least steric interactions (equation 405) [547]. Racemic 2^{0} allylic alcohols resolved by consuming one enantiomer in a chiral epoxidation reaction (equation 406) [548].

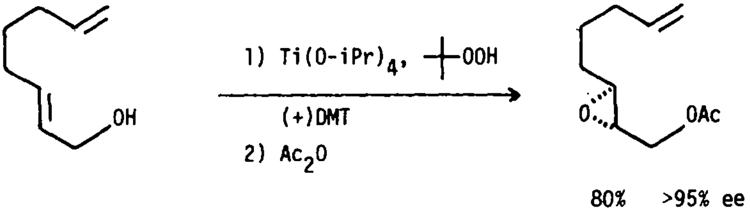
(401)



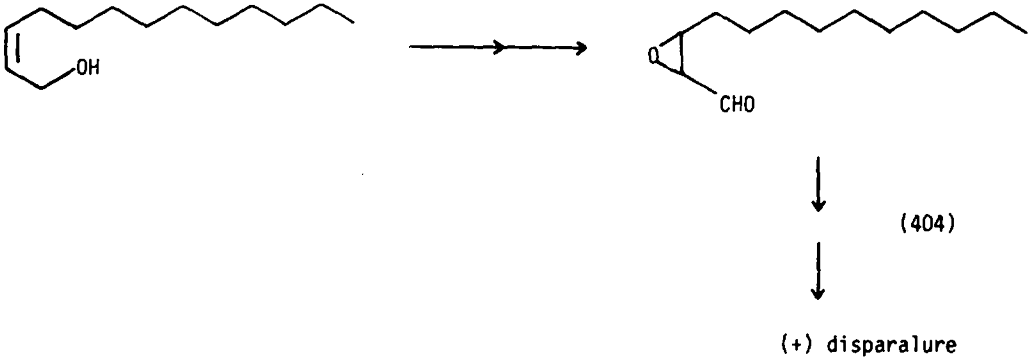


(402)

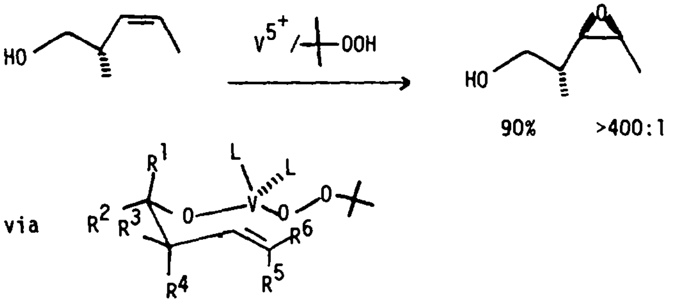
(DMT = dimethyl tartrate)



(403)

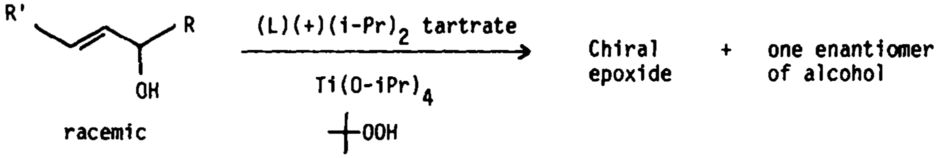


(404)

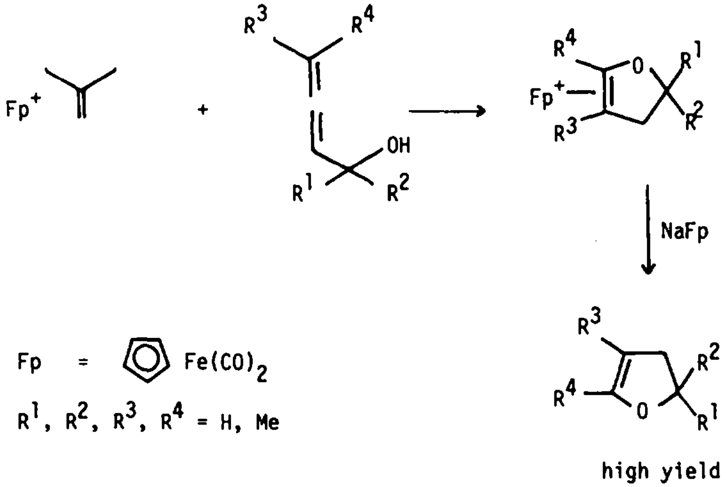


(405)

(406)



Allenyl allyl alcohols cyclized to dihydrofurans when treated with cationic iron-olefin complexes (equation 407) [549]. Furans were formed from the titanium(IV) chloride induced condensation of trimethyl silylenol ethers with α-functionalized ketones (equation 408) [550]. Ortho-allylphenols cyclized to chiral dihydrobenzofurans in the presence of chiral π-allylpalladium catalysts (equation 409) [551]. Oxidation of hindered phenols produced benzofurans (equation 410) [552]. Diolefins were oxidatively cyclized to oxygen heterocycles by reaction with PhSeCN in the presence of copper(II) chloride (equations 411-413) [553]. Cyclohexane-1,2-dione reacted with diols to give aromatic cyclic diethers in the presence of palladium(II) salts (equation 414) [554]. Carpanone formed in an oxidative dimerization with a number of metal catalysts (equation 415) [555]. Diazoacetoacetates reacted with aldehydes in the presence of copper(II) salts to give acetals (equation 416) [556].



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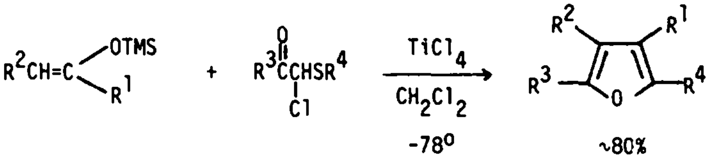
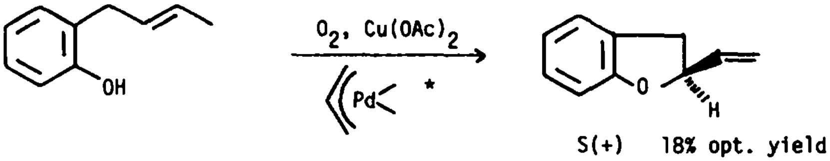
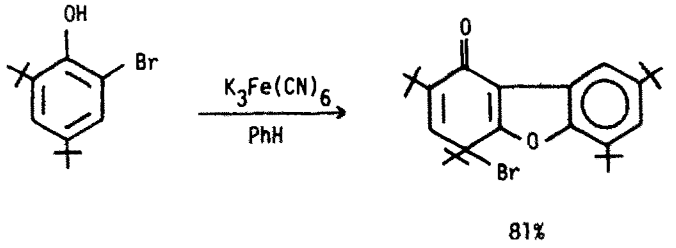


(408)

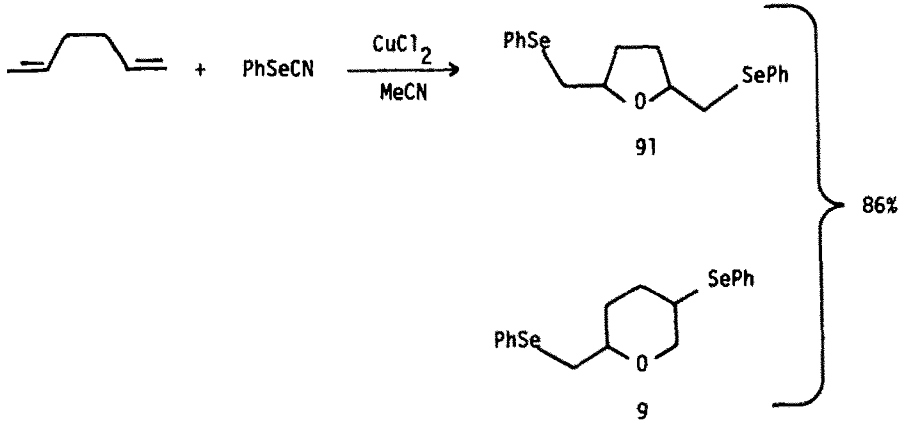


(409)

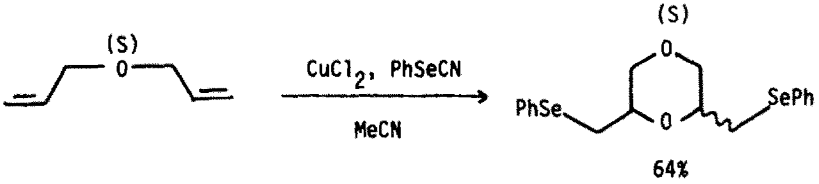


(410)

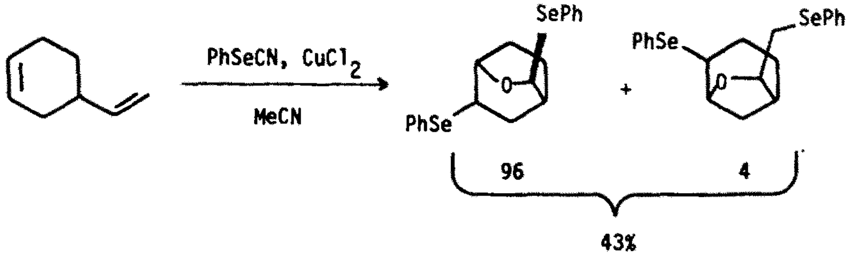
(411)



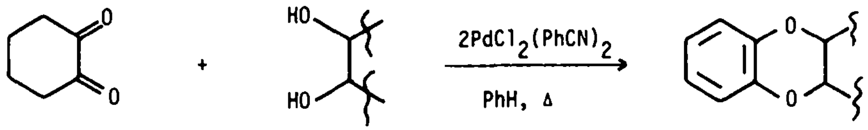
(412)



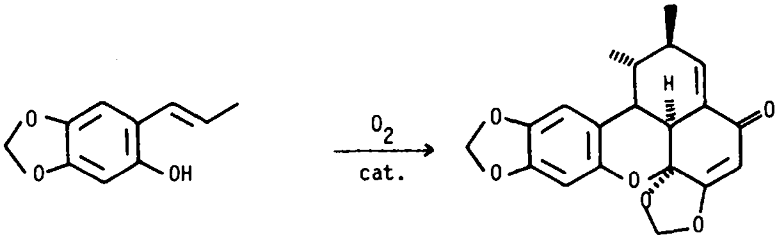
(413)



(414)



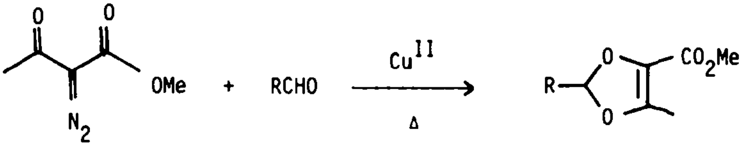
50-65%



(415)

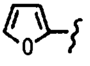
cat =		
	Co(II) Salpr	96%
	Co(II) Salen	94%
	Fe(II) Salen	78%
	Mn(II) Salen	80%

$PdCl_2$/NaOAc	46%
O_2, hν, TPP	29%
BPO	40%
AIBN	10%

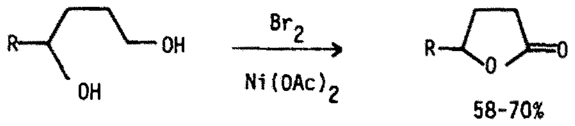


(416)

76-83%

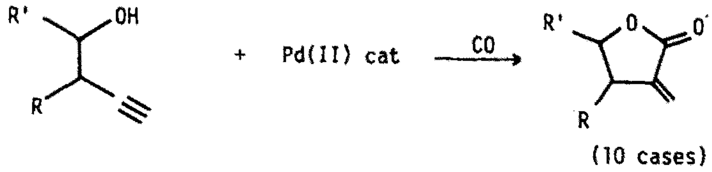
R = n-Pr, i-Pr, , Ph, 

Lactones resulted from the oxidation of 1,4-diols with bromine in the presence of nickel(II) acetate (equation 417) [557]. The full details of the palladium-catalyzed cyclization of homopropargyl alcohols to α-methylene lactones (equation 418) have appeared [558]. A dissertation entitled "Nickel-Promoted Synthesis of Sesquiterpene α-Methylene Lactones" has appeared [559]. Butenolides (5-alkyl-2(5H)-furanones) were formed in the rhodium catalyzed reaction of alkynes, carbon monoxide and olefins (equation 419) and alcohols (equation 420) [560][561]. γ,δ-Unsaturated allyl esters cyclized to lactones, when treated with palladium(0) complexes (equation 421) [562]. The cyclization of o-allyl benzoic acids to isocoumarins using palladium(II) catalysts was again reported [563]. More complex lactones were also prepared by organometallic routes (equation 422) [564] (equation 423) [565].



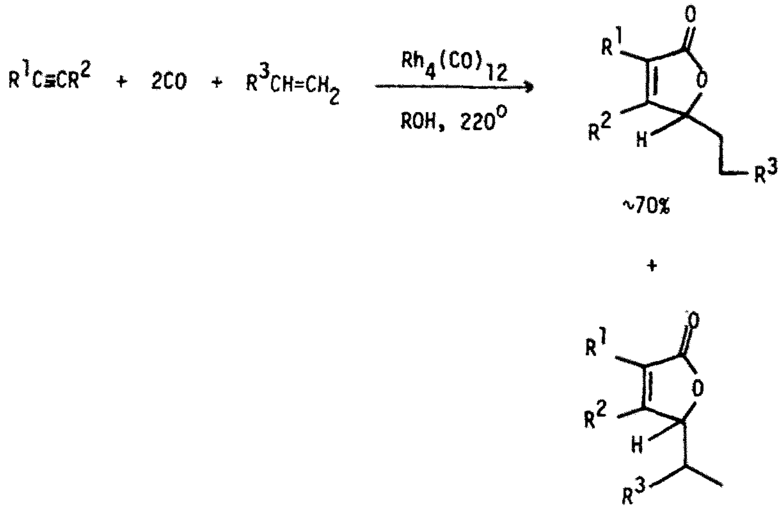
(417)

R = Ph, n-Bu, n-hex

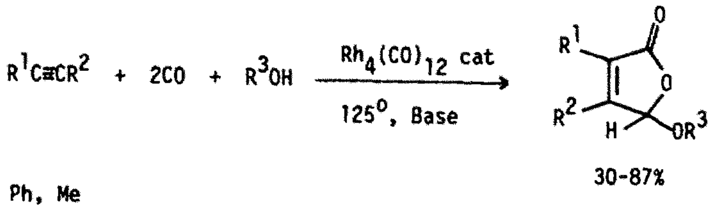


(418)

cat = $PdCl_2/SnCl_2/PR_3$



(419)

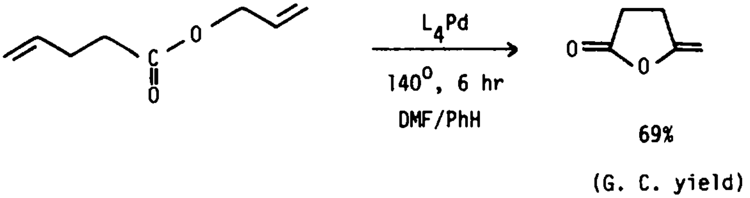


(420)

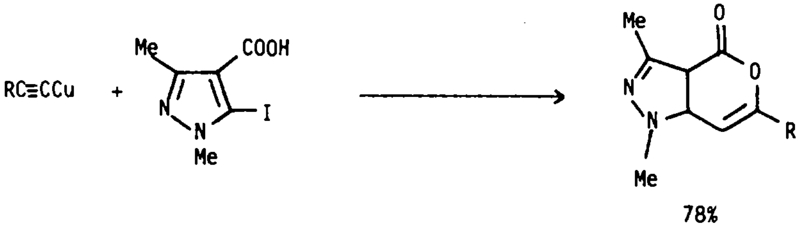
R^1 = Ph, Me

R^2 = Ph, Me

R^3 = Me, Et, i-Pr, n-C_8

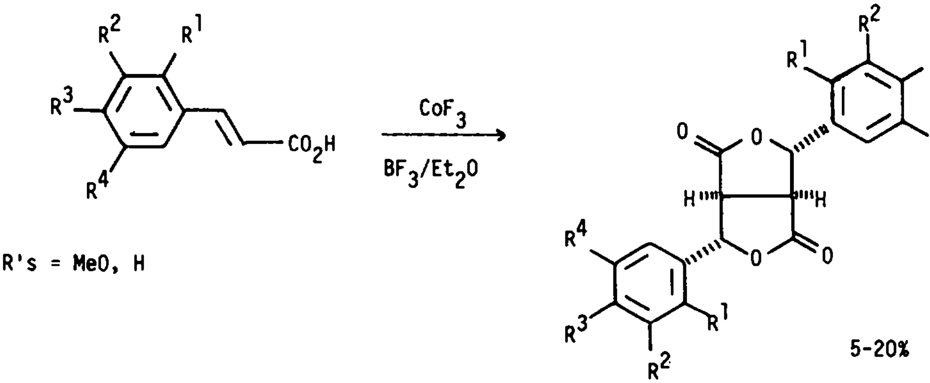


(421)



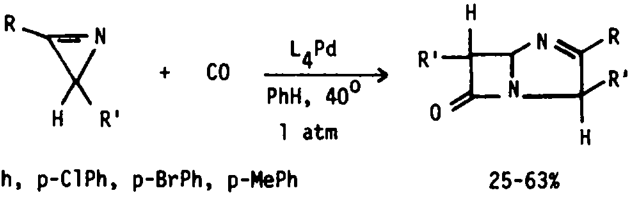
(422)

(423)



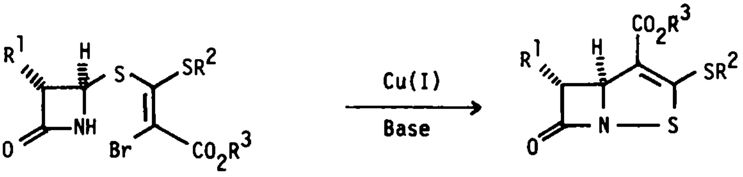
R's = MeO, H

β-Lactams were made as in equations 424 [566] and 425 [567].



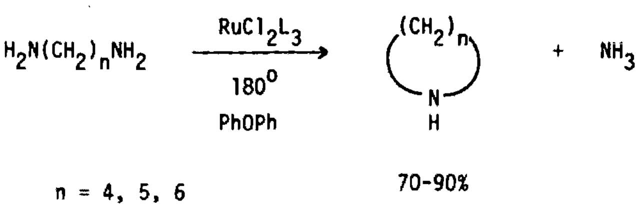
(424)

R = Ph, p-ClPh, p-BrPh, p-MePh
R' = H, Me



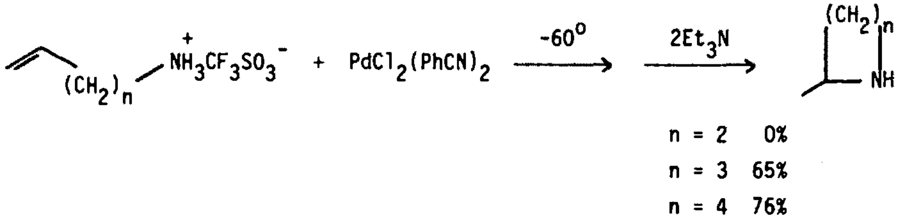
(425)

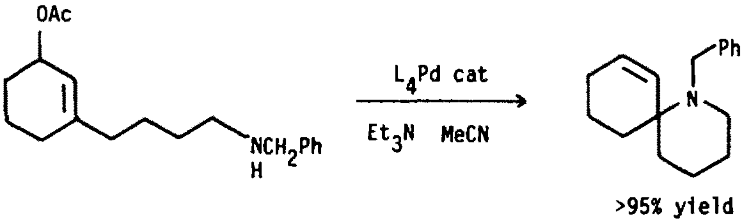
α,ω-Diamines cyclized to cyclic monoamines when treated with $RuCl_2L_3$ catalysts at high temperatures (180°) (equation 426) [568]. ω-Olefinic amines cyclized to nitrogen heterocycles when their trifluoromethane sulfonate salts were neutralized in the presence of palladium(II) chloride (equation 427) [569]. Spiro fused heterocyclic amines were synthesized by the palladium(0) catalyzed amination of suitably constituted allylic acetates (equation 428) [570].



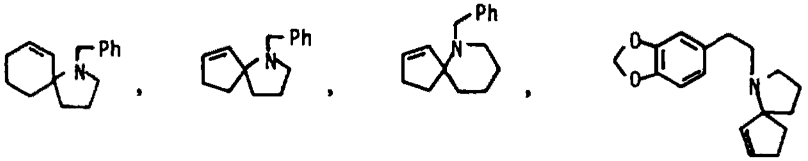
(426)

(427)



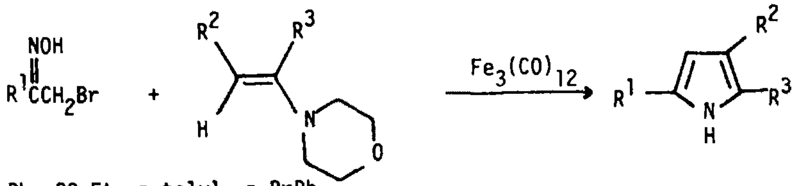


(428)



also made

Enamines reacted with α-halooximes with the presence of $Fe_3(CO)_{12}$ to produce pyrroles (equation 429) [571]. Palladium(II) salts catalyzed the cyclization of acetylenic aminoalcohols to pyrroles (equation 430) [572]. Dienes were converted to pyrroles by allylic acetoxylation followed by reaction of the resulting π-allylpalladium complex with amines in the presence of silver and copper salts (equation 431) [573].



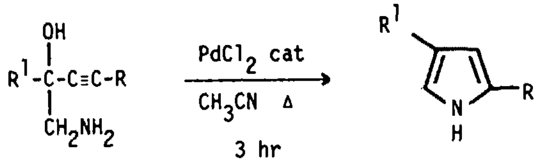
(429)

49-72%

R^1 = Ph, CO_2Et, p-tolyl, p-BrPh

R^2 = Me

R^3 = Et $-(CH_2)_4-$, $-(CH_2)_3-$



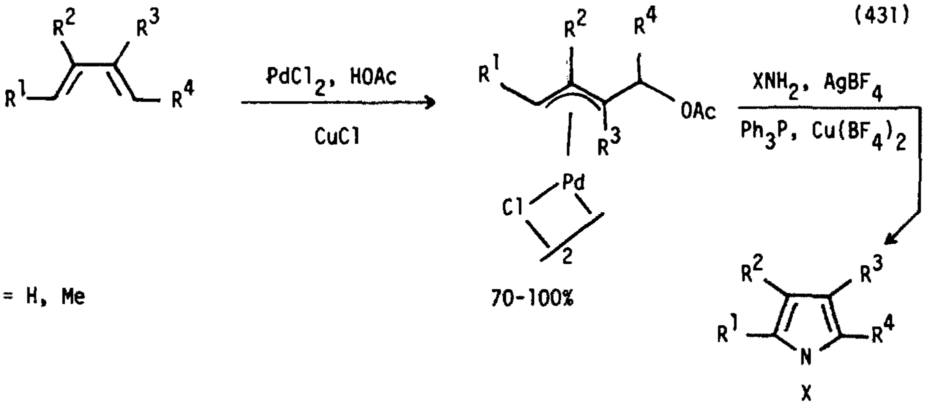
(430)

84-100%

R = n-C_6, Ph

R^1 = Et, t-Bu

(431)

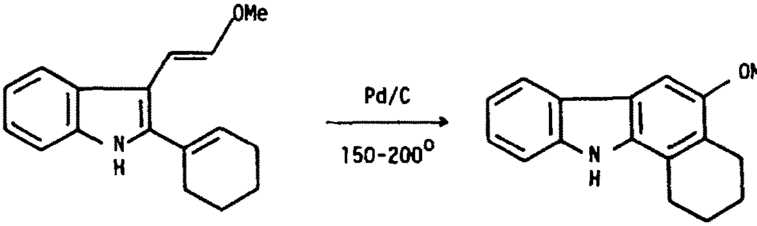


R's = H, Me

70-100%

12-45%

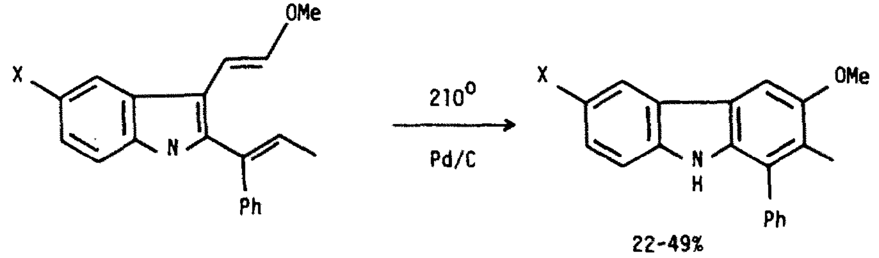
More complex pyrrole-containing heterocyclic systems (equations 432 and 433) [575], (equation 434) [576], and others (equation 435) [577] have also been made. "Approaches to Mitomycin C using Palladium-Mediated Ring Closures" was the title of a dissertation [574].



(432)

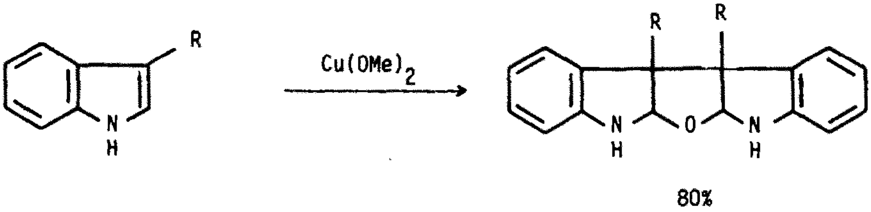
16-23%

(433)

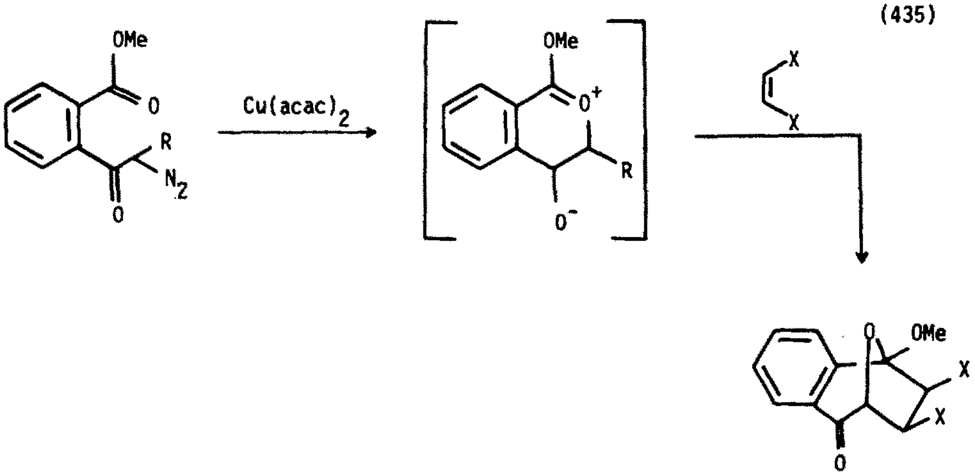


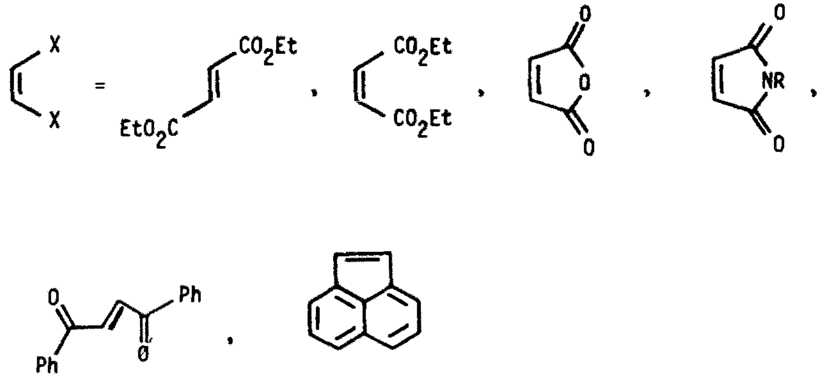
X = H, Cl

(434)

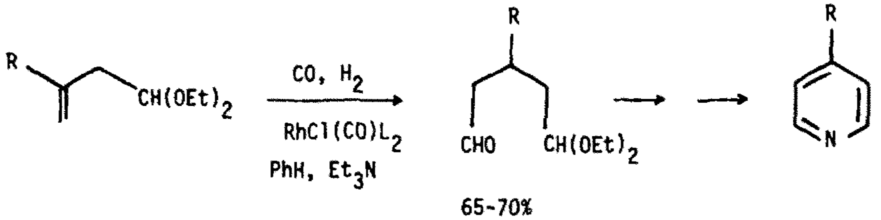


(435)





Unsaturated acetals were converted to pyridines as in equation 436 [578]. Tolan reacted with a nickel-carbodiimide complex to give the pyridine ring system (equation 437) [579]. Alkylpyridines were synthesized from ethylene and ammonia over mixed palladium/copper catalysts [580]. Nitrobenzene reacted with alcohols at high temperatures (180°) over $RuCl_2L_3$ to produce quinolines in modest yield (equation 438) [581]. Anilines reacted with aldehydes over a rhodium(I) catalyst to give similar compounds (equation 439) [582]. Phthalocyanine complexes of cobalt condensed o-nitroaldehydes with ketones to produced quinolines (equations 440 and 441) [583]. Acridines were formed in a palladium(II) catalyzed condensation of allylated enaminones (equation 442) [584]. Azepines were produced from 1-aminohexatrienyl systems using $PdCl_2(PhCN)_2$ as the catalyst [585].



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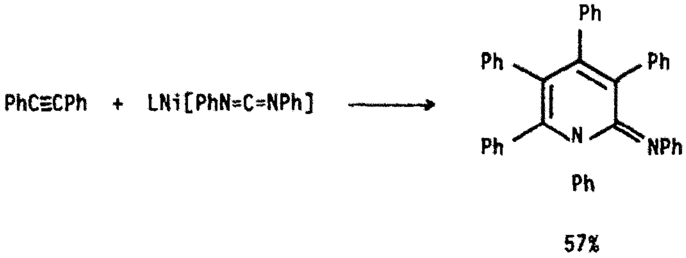
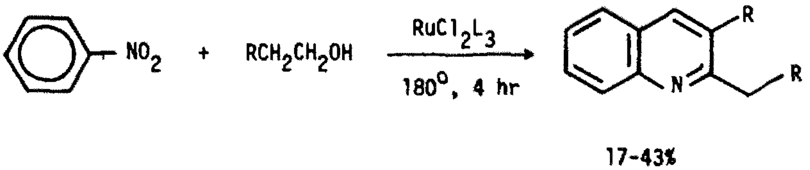
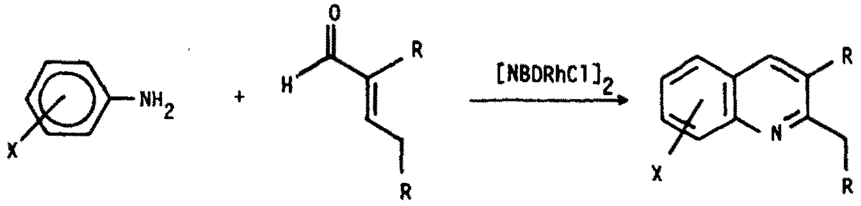


(437)



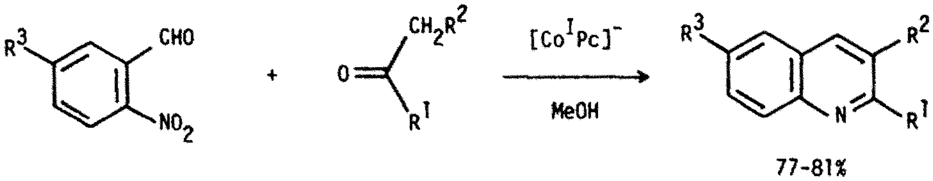
(438)

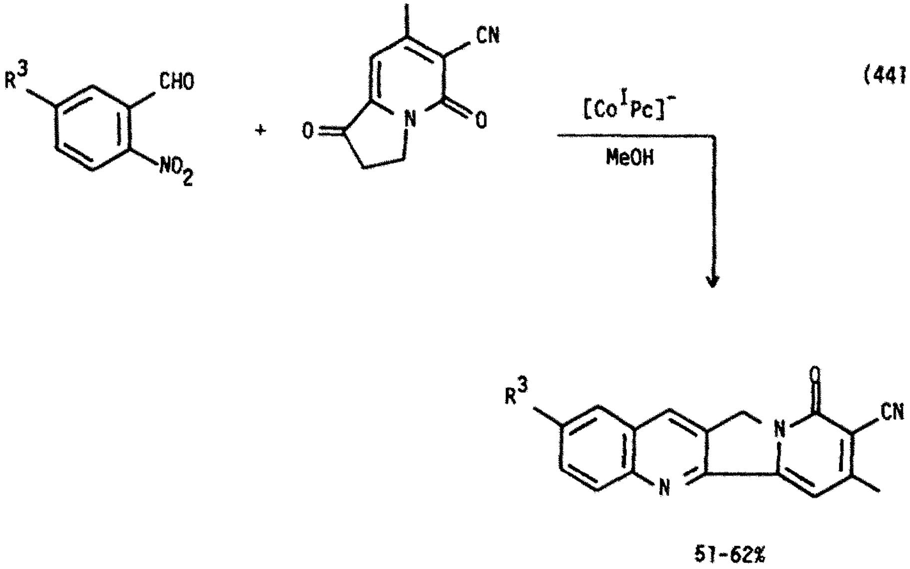


(439)

R = H, Me, Et, n-Pr
X = OMe, Me, Cl

(440)





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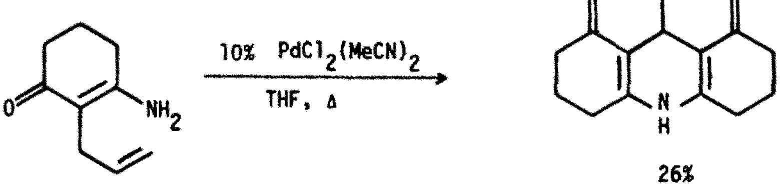
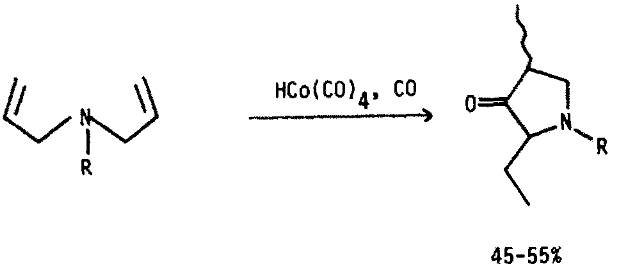
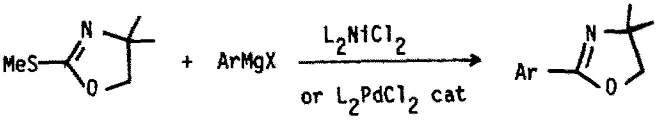


(442)

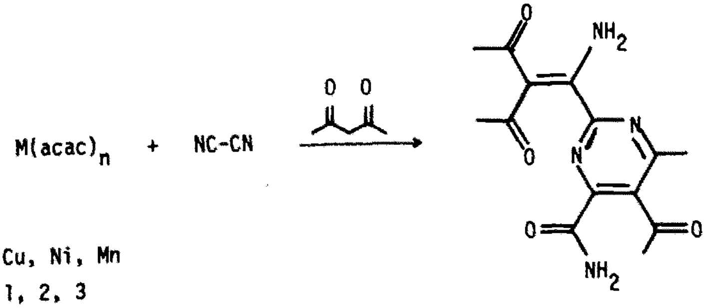
Heterocyclic systems containing two heteroatoms have also been prepared using organometallic reagents (equation 443) [586]; (equation 444) [587]; (equation 445) [588]; and (equation 446) [589].



(443)



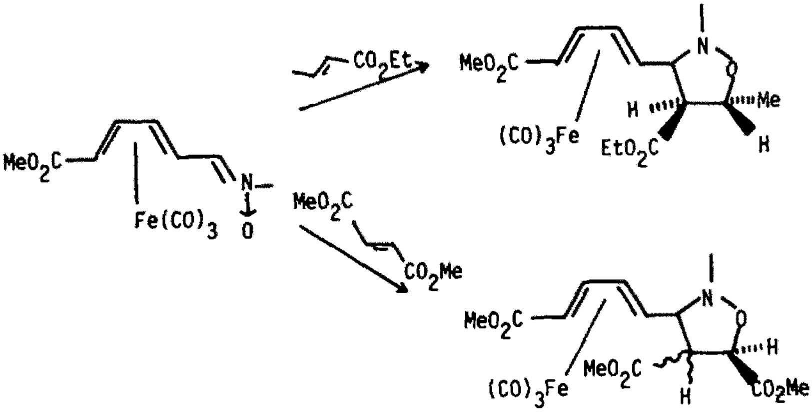
(444)



(445)

M = Cu, Ni, Mn

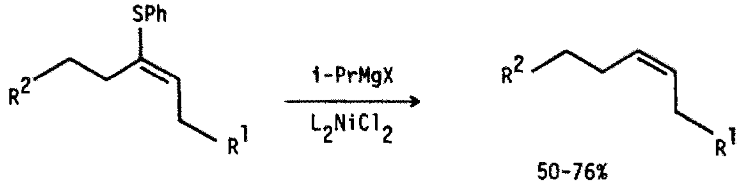
n = 1, 2, 3



(446)

F. Alkenes

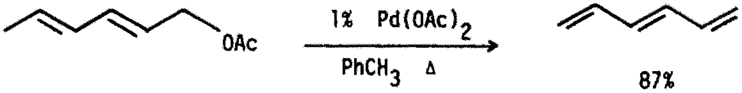
Epoxides were deoxygenated to cis-trans mixtures of olefins by $V(acac)_2$, $V(dpm)_2$, $V(tfa)_2$, $Mo(acac)_2$, $Mo(dpm)_2$ [590] and by WCl_6/BuLi [591]. Thioenol ethers were desulfurized by treatment with isopropylmagnesium halides and a nickel(II) catalyst (equation 447) [592]. Rhodium(II) acetate catalyzed the decomposition of alkyl α-diazoesters to cis-α,β-unsaturated esters [593]. Allylic acetates were converted to olefins by reaction with palladium(II) salts (equations 448 and 449) [594] (equations 450-452) [595]. Steroidal enones were converted to dienones via their π-allylpalladium complexes [596]. 1,2,4,6-Tetraenes were prepared from 4,6-dien-2-yn-1-ol sulfonates by reaction with organocopper compounds [597].



(447)

R^1 = Ph, n-Pr, Me, n-Bu

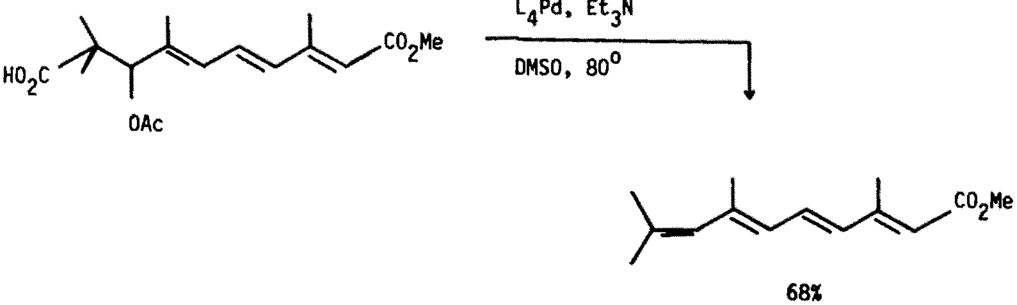
R^2 = $(MeO)_2CH$, $THPOCH_2$



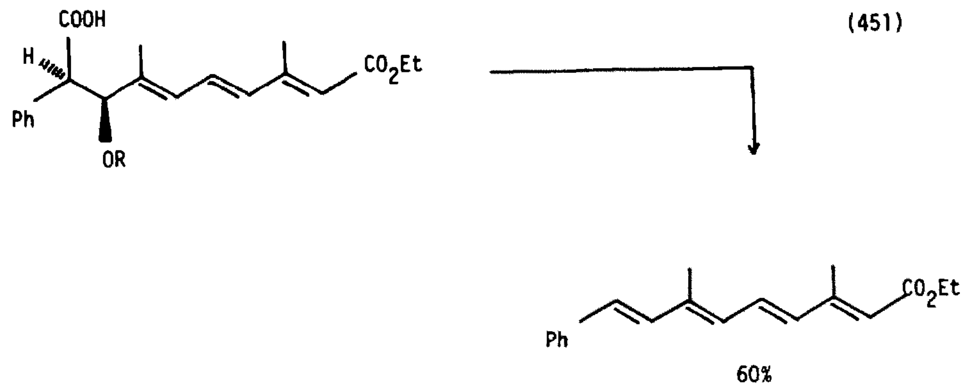
(448)

(449)

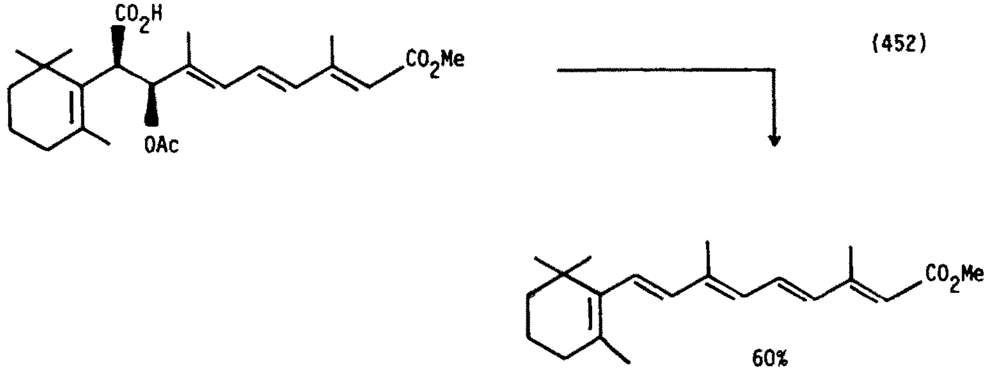
(450)



(451)



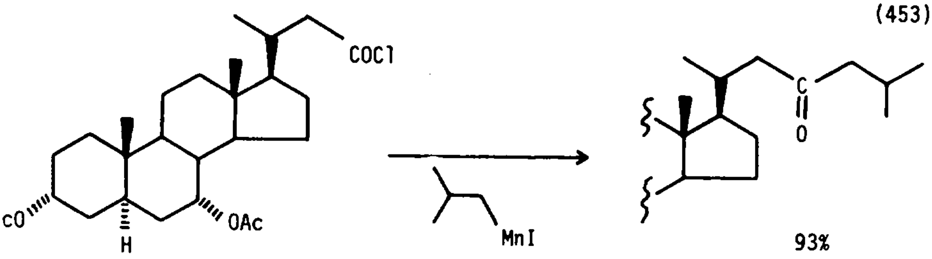
(452)



G. Ketones and Aldehydes

Copper(II) sulfate assisted the hydrolysis of hydrazones, oximes and semicarbazones to carbonyl compounds [598]. The oxidation of olefins to ketones in a "Wacker" type oxidation was catalyzed by $PdCl(NO_2)(MeCN)_2$. The nitro group was claimed to be the source of the carbonyl oxygen [599]. Alcohols were oxidized to carbonyl compounds by carbon tetrachloride and palladium(II) salts [600]. Steroidal acid chlorides were alkylated to ketones by organomanganese compounds (equation 453) [601]. Allyl ethers were oxidized to unsaturated aldehydes by oxygen and palladium(II) chloride [602]. Acid chlorides were reduced to aldehydes by reaction with tri-n-butyltin hydride in the presence of palladium(0) catalysts [603]. Twenty six cases were reported. Carboxylic acids were converted to aldehydes by reaction with isobutylmagnesium chloride with a Cp_2TiCl_2 catalyst [604]. Secondary nitro compounds were converted to ketones by oxidation with molybdenum oxo compounds (equation 454) [605]. 1,5-Hexadiene was oxidatively cleaved to acetone by $PdCl_2/CuCl_2/CuCl/H_2O$ mixtures [606]. Steroidal π-allylpalladium complexes were oxidized to α,β-unsaturated carbonyl compounds by MCPBA (equation 455) [607] and by chromic oxide (equations 456-459) [608].

(453)



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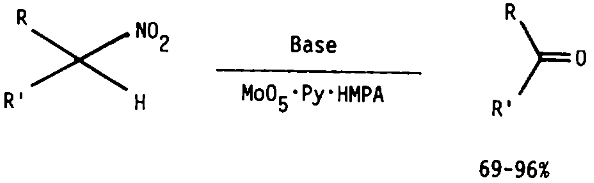

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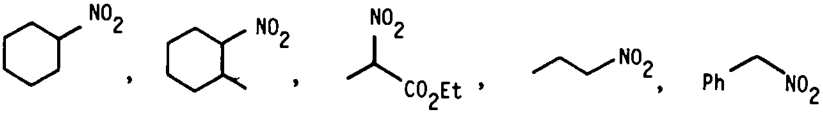

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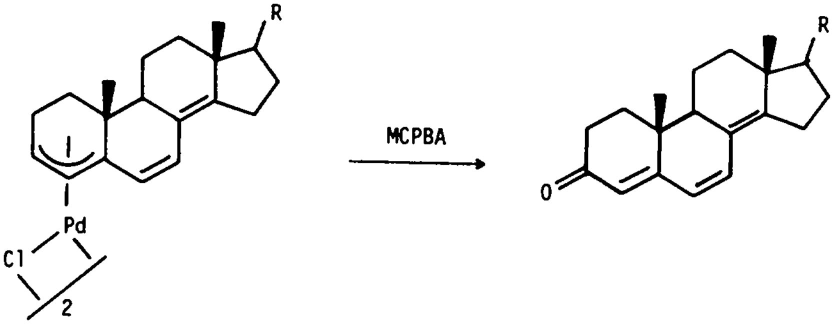

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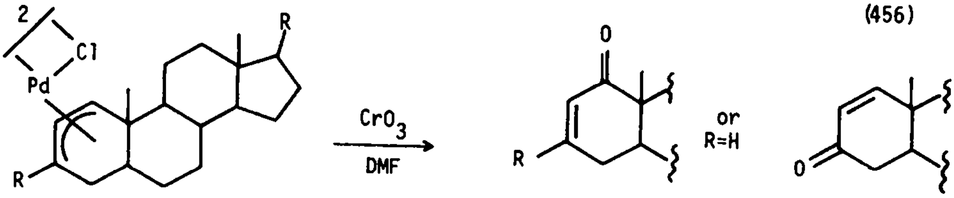

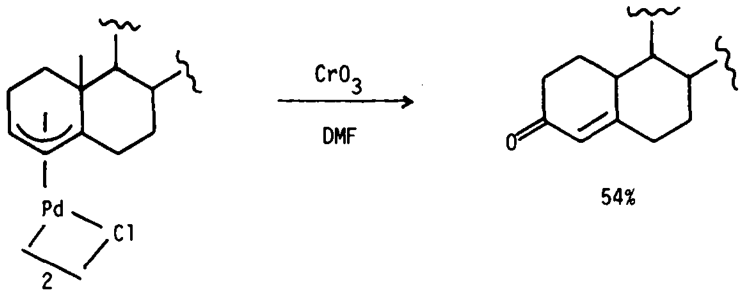

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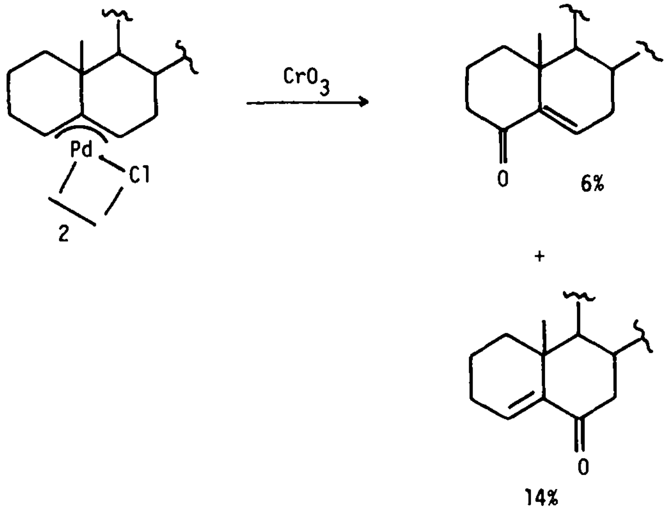

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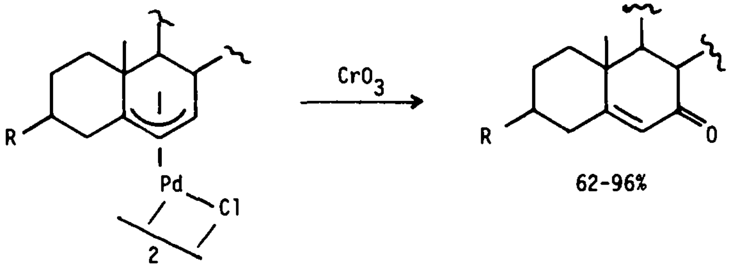
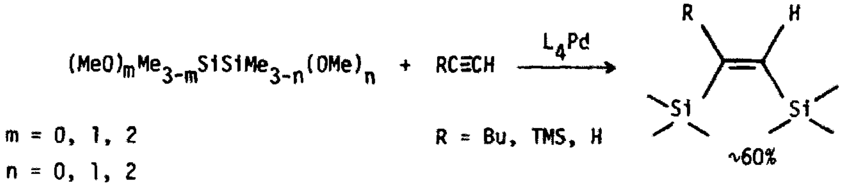


(459)

H. Organosilanes

Reaction of Wilkinson's compound with oxygen, followed by irradiation produced L_2RhCl, a very active hydrosilation catalyst [609]. Hydrosilylation of olefins over $NiCl_2(Bu_3P)_2$ [610], H_2PtCl_6 and chlorides of Al, Ge, Ce, Nd, Nb, and Ta [611], and silica supported rhodium catalysts [612] has been developed. Terminal alkynes were converted into mixtures of cis and trans terminal vinyl silanes by reaction with

Et_3SiH in the presence of rhodium(I) catalysts [613]. Alkenes and ketones were hydrosilylated using rhodium(II) catalysts [614]. Alkynes were converted into bis-1,2-vinylsilanes using palladium(0) catalysts (equation 460) [615]. Allenes were converted to allyl silanes by hydrosilylation with $X_nSi_2Me_{6-n}$ in the presence of palladium(0) catalysts [616]. α-Olefins reacted with Et_3SiH in the presence of rhodium(II) complexes to give mixtures of allyl and vinylsilanes [617]. Butadiene was hydrosilylated by irradiation in the presence of iron pentacarbonyl (equation 461) [618]. Butadiene and trimethylvinyl silane telomerized over reduced nickel catalysts (equation 462) [619]. Styrene, cyclopentadiene, and 1,3-cyclohexadiene were hydrosilylated over palladium catalysts having chiral phosphine ligands. Up to 34% optical yields were obtained [620]. Chiral phosphinites were used as ligands in the rhodium(I) catalyzed hydrosilylation of aryl ketones [621]. The β-position of conjugated enones was protected by the introduction of a trialkyl silyl group using copper chemistry (equation 463) [622]. The cuprate of Me_2PhSi- was used to prepare a number of silicon-containing vinyl copper reagents (equation 464) [623].



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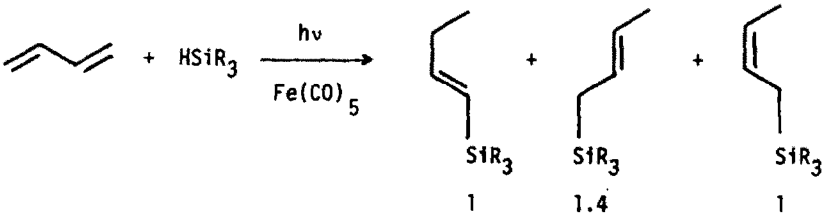

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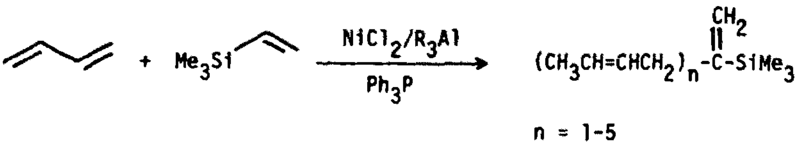

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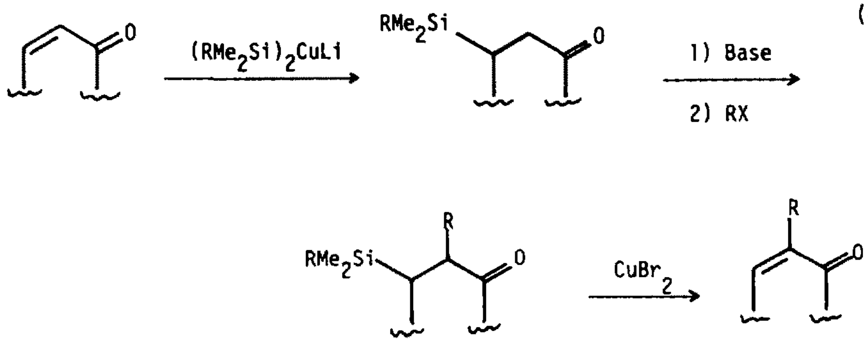

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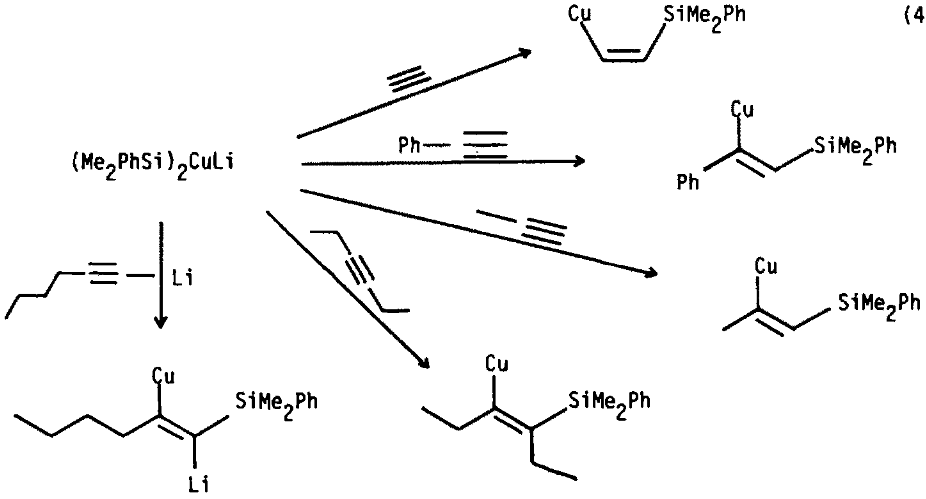
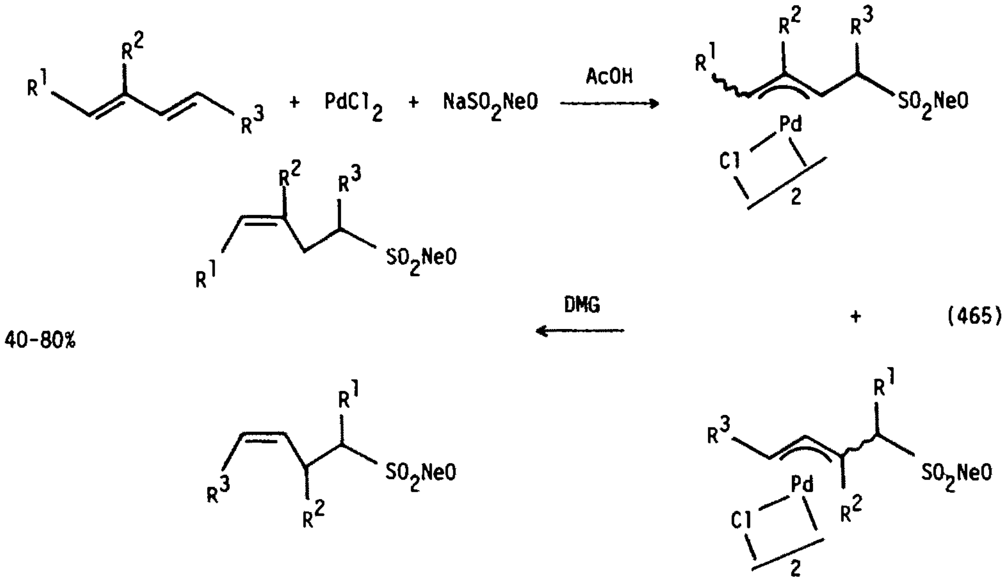


I. Miscellaneous

"Cyclometallated Compounds of Palladium(II), Rhodium(III), and Iridium(III)" is the title of a recent dissertation [624]. 1-Azo-naphthalenes o-palladated at the β-position [625]. The o-palladation products of a number of N,N-dimethylbenzylamines were again reacted with styrenes to produce insertion products [626]. Both 2-aryl-4,4-dimethyl-2-oxazolines [627] and arylhydrazones [628] underwent facile o-palladation. 1,3-Dienes were converted to sulfones by the palladium(II) assisted reaction with sulfinates (equation 465) [629]. Allylic acetates reacted in a similar manner in the presence of palladium(0) catalysts (equation 466) [630]. Thiophenols were converted to diarylsulfides (14 cases) by reaction with aryl bromides in the presence of nickel(II) catalysts at 200° [631]. Aryl and vinyl halides reacted with thiols under phase transfer conditions in the presence of nickel(II) catalysts to give the corresponding sulfides (equation 467) [632]. Alkynes reacted with PhSeCN in the presence of copper catalysts (equation 468) [633]. Diarylselenides were prepared by the copper(I) promoted alkylation of arylselenides (equation 469) [634].



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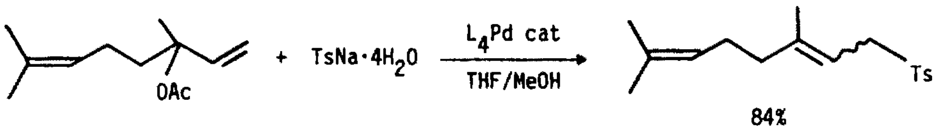

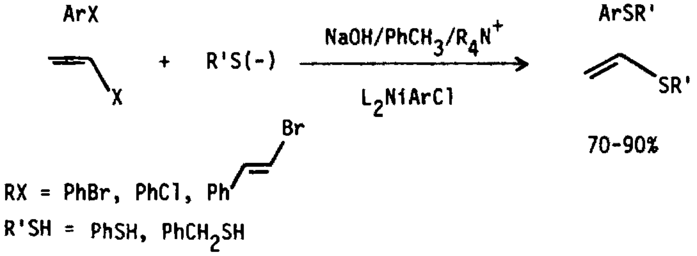

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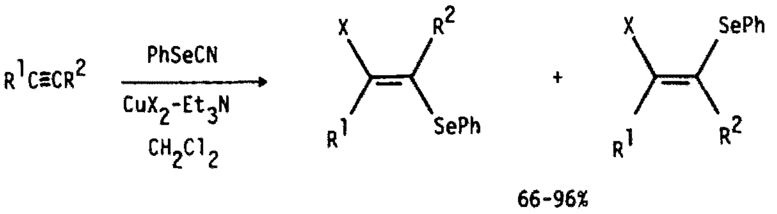
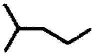
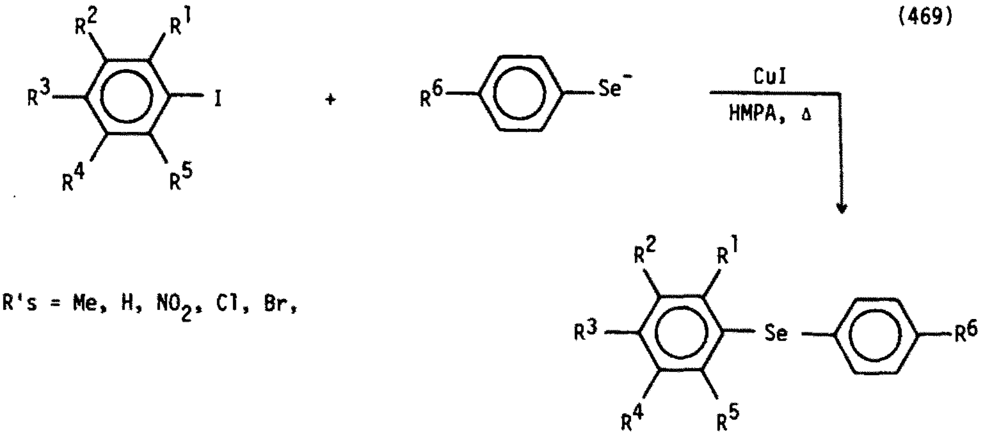


(468)

R^1 = Et, n-Pr, H

R^2 = n-C_6, n-Pr, n-Bu, n-C_8, 

X = Cl, Br

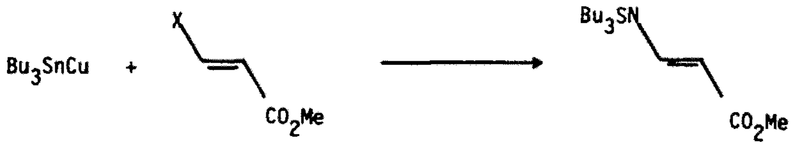


(469)

R's = Me, H, NO_2, Cl, Br,

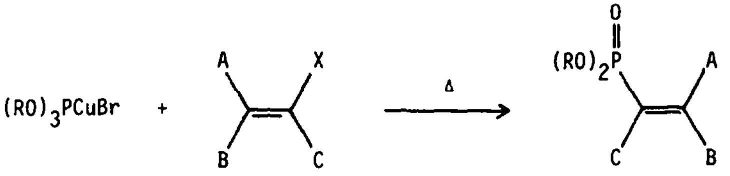
Vinyl tin compounds were prepared by the reaction of Bu_3SnCu with vinyl halides (equation 470) [635]. Aryl halides reacted with R_3SnSnR_3 in the presence of palladium(0) catalysts to produce R_3SnAr compounds in fair to high yield [636][637]. Allyl halides reacted similarly. Olefins reacted with diisobutylaluminum chloride in the presence of Cp_2ZrCl_2 to produce dialkylaluminum chlorides in which the alkyl groups had come from the olefin [638].

(470)



X = Cl, I, TsO, PhS

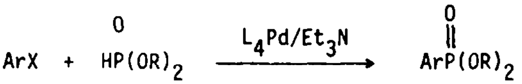
Vinylphosphonates were prepared by the reaction of vinyl halides with copper(I)-phosphite complexes (equation 471) [639][640]. Aryl halides reacted with $HP(O)(OR)_2$ in the presence of palladium(0) catalysts (equation 472)[641].



(471)

good yield

A = H, Ph
B = Ph, H, Me, Et
C = H, Ph



$$ArX + HP(O)(OR)_2 \xrightarrow{L_4Pd/Et_3N} ArP(O)(OR)_2 \qquad (472)$$

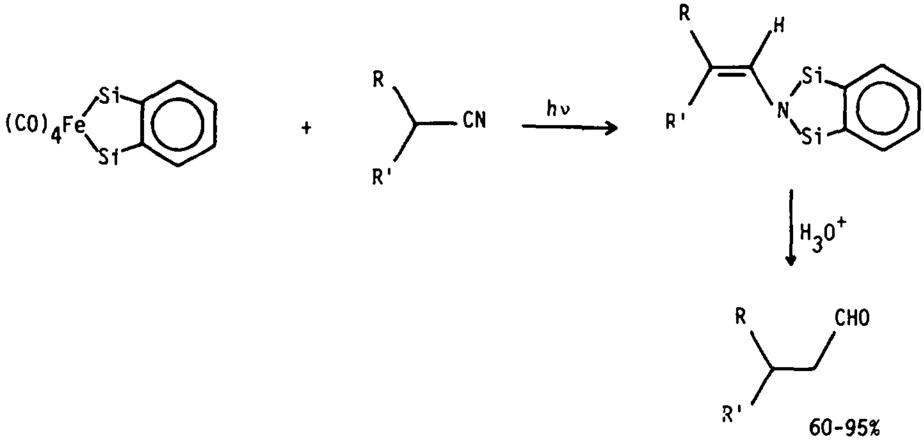
70-90%

Ar = Ph, p-MePh, o-MePh, p-ClPh, p-OMePh, p-NO_2Ph, p-CNPh, p-BrPh
3-pyridyl, 1-naphth

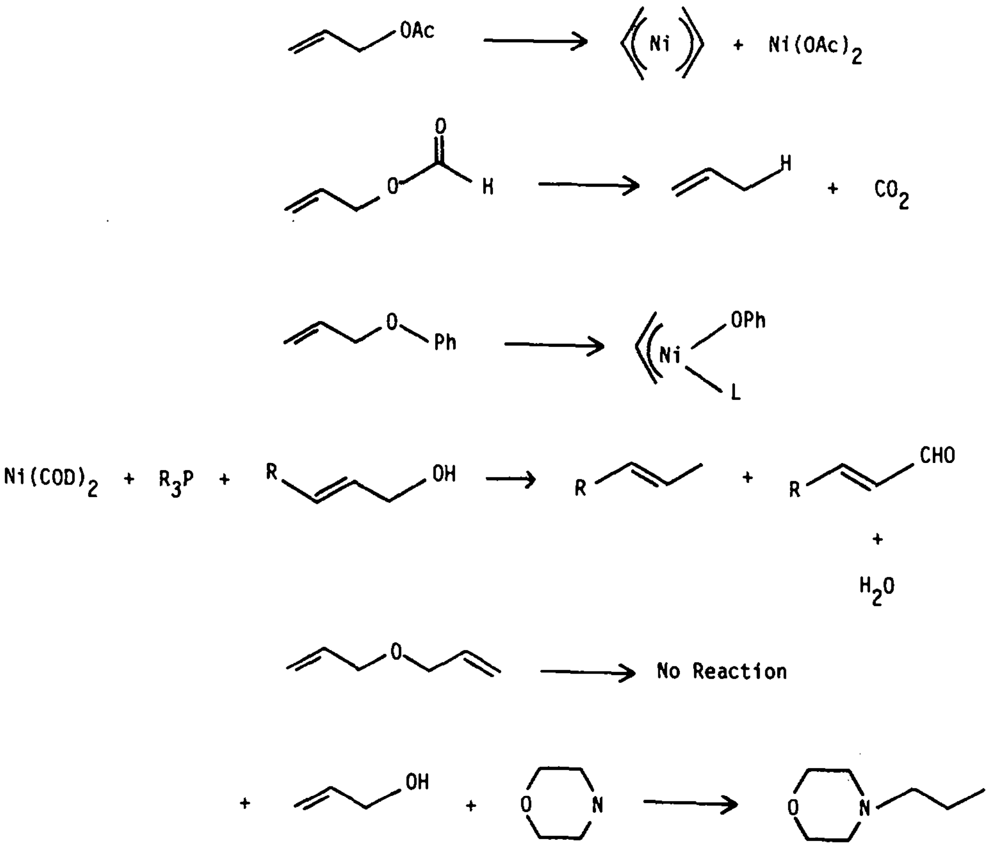
Ketones were deoxygenated to the corresponding hydrocarbons (products corresponding to a Clemmenson reduction) in high yield by reaction with hydrogen over a nickel/alumina catalyst at 190° in a flow system [642]. Diaryl- and triaryl carbinola were reduced to diaryl- and triarylmethanes by treatment with benzoyl chloride and iron pentacarbonyl [643]. Arene-1,4-endoxides were deoxygenated to arenes in high yield by reaction with n-butyllithium in the presence of $FeCl_3$, WCl_6, or $TiCl_3$ [644]. Azoxyaromatics were deoxygenated to azoaromatics, and amine oxides to amines by reaction with alumina supported $Mo(CO)_6$ or $Fe_3(CO)_{12}$ [645]. Nitrosobenzene was converted to PhN=NPh by reaction with $Ru(CO)_3L_2$ in refluxing ethanol [646]. Aromatic sulfur compounds were desulfurized by nickel(0) complexes [647].

Nitriles were converted to disilylenamines by reaction with an iron-silicon species (equation 473) [648]. These were unreactive toward organolithium reagents, lithium aluminum hydride, or acid chlorides, but hydrolyzed readily to the aldehyde. Palladium(II) chloride cleaved allylphenyl ethers [649]. Mixtures of bis(cyclooctadiene)nickel and tertiary phosphines reacted with a variety of allylic substrates (equation 474) [650]. Polypeptides were synthesized by palladium-catalyzed hydrogenalysis of β-lactams (equation 475) [651].

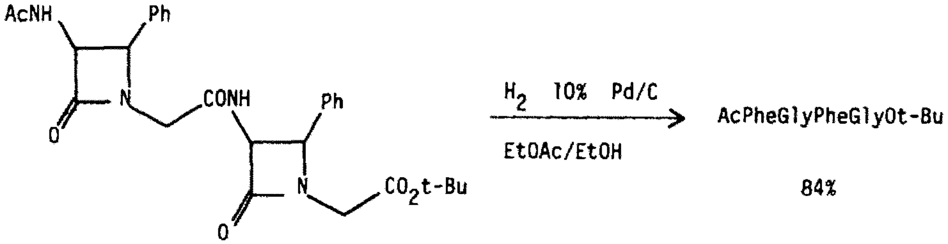
(473)


(CO)4Fe
Si
Si
+
R
R'
CN
hν
R
H
R'
N
Si
Si
H3O+
R
CHO
R'
60-95%

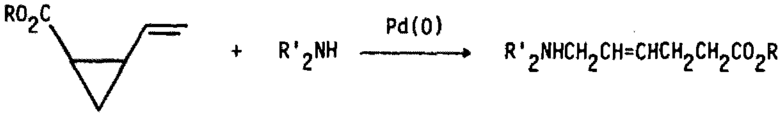
(474)


OAc
Ni
+ Ni(OAc)2
O
O
H
H
+ CO2
O
Ph
OPh
Ni
L
Ni(COD)2 + R3P +
R
OH
R
+
R
CHO
+
H2O
O
No Reaction
+
OH
+
O
N
O
N

(475)



Copper(I) chloride converted acyl- and tosylhydrazines into amides [652]. Oxygen oxidatively cleaved indoles in the presence of CuCl-pyridine complexes [653]. β-Bisabolene was synthesized by the carboxymethylation of (+)-limonene with manganese (III) acetate [655]. Unsaturated cyclopropanes (equation 476) and lactones (equation 477) reacted with amines in the presence of nickel(0) or palladium(0) catalysts to result in ring opening [656]. Copper(II) thiocyanate converted ketones to α-thiocyano ketones [657]. Carbon disulfide reacted with triethyl phosphine in the presence of iron(II) tetrafluoroborate to give $[Et_3PCH_2S_2CH_2PEt_2][BF_4]_2$ [658].



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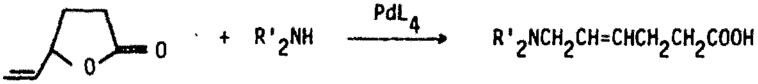
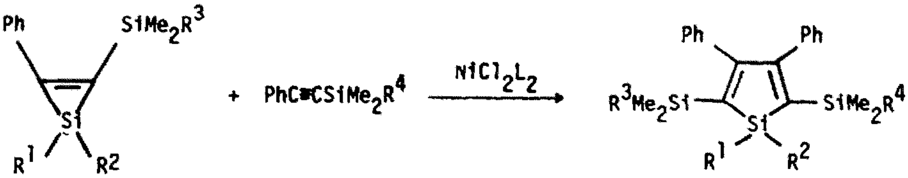
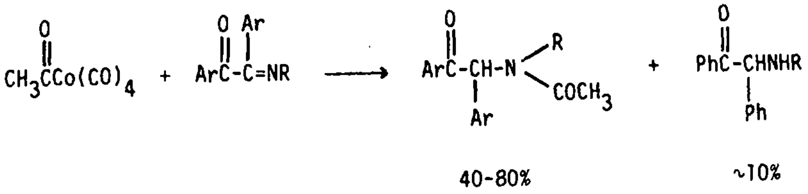


(477)

A number of unclassified reactions are summarized in equations 478 [659], 479 [660], 480 [661], 481 [662], 482 [663], and 483 [664].

(478)





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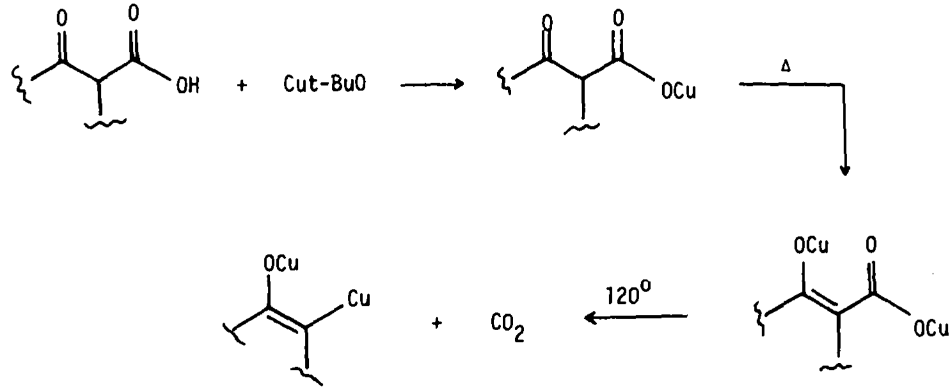

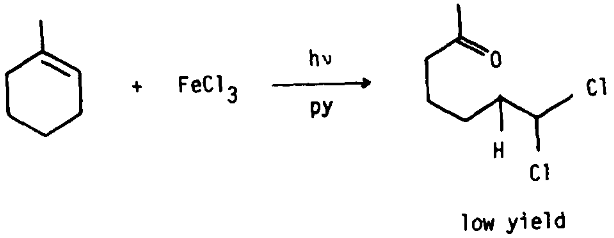

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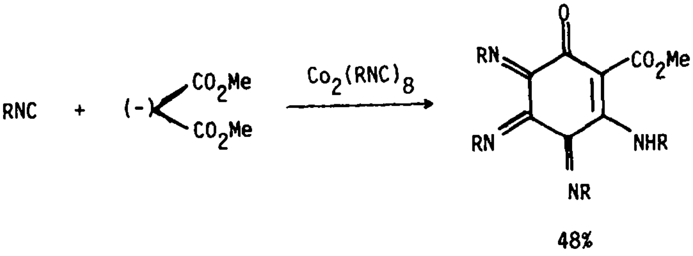

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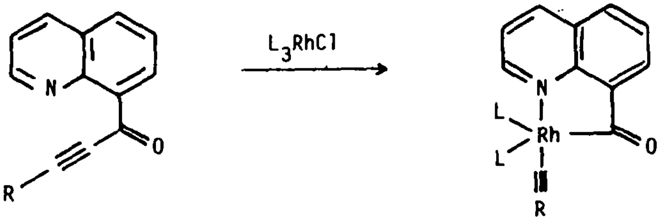

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IV. Reviews

The following reviews have appeared:

Organic reactions of selected π-complexes -- Annual Survey, 1979. (284 references) [665]

Transition metals in organic synthesis -- Annual Survey, 1979. (809 references) [666]

Transition metals in organic synthesis. (no references) [667]

New applications of organometallic reagents in the synthesis of natural products. (Dissertation) [668]

Organometallics in synthesis. Part II. Main group elements. (217 references) [669]

Organometallics in synthesis. Part I. The transition elements. (60 references) [670]

Organometallic compounds. Reactions of coordinated ligands. (61 references) [671]

Organic synthesis using transition-metal complex: Palladium-catalyzed reactions. (32 references) [672]

Organic synthesis using transition-metal complex: Reactions utilizing nucleophilicity of metal complex. (43 references) [673]

Overview on the highly selective organic syntheses -- transition metal catalyzed asymmetric reactions (68 references) [674]

Progress in organic synthesis using organocopper. (18 references) [675]

Copper salts in catalytic reactions of organic compounds. (343 references) [676]

Applications of organocopper reagents in syntheses. (30 references) [677]

Commercial applications of reactions catalyzed by soluble complexes of cobalt and rhodium. (12 references) [678]

Homogeneous catalysis in technology. (no references) [679]

Homogeneous catalysis. (no references) [680]

The organometal complex-catalyzed reactions in petroleum chemistry. (60 references) [681]

Homogeneous or heterogeneous catalysis? (29 references) [682]

Homogeneous catalysis in organic syntheses. I. (21 references) [683]

Homogeneous catalysis in organic synthesis. II. (17 references) [684]

Organometallic compounds. (236 references) [685]

Organometallics -- metal complexes. [686]

Transition metal hydrides as intermediates in organometallic reactions. [687]

Organometallics -- σ-bonded alkyls and aryls. [688]

Ligand Free Platinum Compounds. (63 references) [689]

Carbon-carbon bond forming reactions of allyl complexes of nickel, palladium, and iron. (25 references) [690]

Organic syntheses using metals; palladium is a favorite. (8 references) [691]

Tilden lecture. η^5-Cyclopentadienyl and η^6-arene as protecting ligands towards platinum metal complexes. (207 references) [692]

Organic synthesis using palladium. [693]

Catalytic properties of palladium complexes fixed on nitrogen- and sulfur-containing silica gels in isomerization and hydrogenolysis. [694]

Palladium-carbon catalysts. (14 references) [695]

Nickel and palladium complexes in the synthesis of macrocyclic compounds. (18 references) [696]

Transformation reaction of functional groups using palladium compounds. (217 references) [697]

β-Aminoacyl, π-olefin, and π-allylpalladium chemistry. (Dissertation) [698]

Palladium-assisted ring closures. (Dissertation) [699]

Synthesis via organopalladium intermediates. (Dissertation) [700]

$HCo(CO)_4$, The quintessential catalyst. (54 references) [701]

Phase-transfer catalysis in organometallic chemistry. (78 references) [702]

Triiron dodecacarbonyl in organic synthesis (44 references) [703].

The chemistry of organoiron-alkyl vinyl ether and acetylene complexes. (Dissertation) [704]

Reactions of transition metal π-complexed cations with selected nucleophiles. (Dissertation) [705]

Synthetic applications of the chemistry of dicarbonyl cyclopentadienyliron complexes. [706]

The chemistry of organoiron-alkyl vinyl ether and acetylene complexes. (Dissertation) [707]

Aspects of homogeneous carbon monoxide fixation. Selective conversion of carbonyl ligands on tricarbonyl (η^5-cyclopentadienyl)iron(+) to C_2 organic compounds. (88 references) [708]

Chiral metal atoms in optically active organotransition metal compounds. (194 references) [709]

Asymmetric catalysis using rhodium-phosphine complexes. (18 references) [710]

Catalytic asymmetric synthesis. (no references) [711]

Asymmetric syntheses by catalysts composed of optically active transition metal complexes. (19 references) [712]

Asymmetric synthesis by transition-metal catalysts. (65 references) [713]

Asymmetric catalysis -- progress and problems. (40 references) [714]

Application of asymmetric catalyst in the synthesis of chrysanthemic acid. (26 references) [715]

Immobilized transition metal carbonyls and related catalysts. (308 references) [716]

Supported rhodium-phosphine catalysts. Effects of the polymer support and ancillary chiral centers. (Dissertation) [717]

A study of the methylcyclopropane hydrogenolysis reaction over supported palladium catalysts. (Dissertation) [718]

Organic syntheses with the titanocomplex. (11 references) [719]

Zirconium reagents in organic synthesis. [720]

The reactivity and syntheses of mono and bis(permethylcyclopentadienyl)zirconium hydrides. (Dissertation) [721]

The insertion of olefins into metal carbon bonds. (35 references) [722]

Organometallic compounds. Insertion reactions. (21 references) [723]

Oxidative addition and reductive elimination of carbon-hydrogen bonds for alkyl, olefin, and hydride derivatives of group IV metallocenes. (5 references) [725].

Oxidative addition and insertion reaction of organometallic complexes. (95 references) [725]

Organometallic compounds. Oxidative addition and reductive elimination. (27 references) [726]

Synthesis and reactivity of iron carbene complexes. [727]

Chemistry of metal-metal multiple bonds in group VI complexes. (16 references) [728]

Studies on the reactivity of carbyne complexes of tungsten and molybdenum. [729]

Stereochemistry of organic reactions using transition-metal complexes. (66 references) [730]

Transition-metal templates for selectivity in organic synthesis. (34 references) [731]

Regiochemical control elements. (5 references) [732]

Selectivity in organic synthesis. (24 references) [733]

Carbon dioxide activation using metal complexes. (16 references) [734]

Novel synthetic reactions using carbon monoxide. (5 references) [735]

Carbon-carbon bond formation. I. Carbonylation. (30 references) [736]

Activation of carbon monoxide and acetylenes by cobalt carbonyls. (42 references) [737]

Experimental optimization of organic syntheses. Homogeneous transition metal catalysis using statistical methods. [738]

Property- and concentration control in metal-catalyzed organic syntheses. (14 references) [739]

Organometallic complex compounds. Part 7. Ligand concentration control in the organometallic system P-ligand/carbon monoxide/bis(μ-methyl-1,3-dimethyl-η^3-allylnickel). [740]

The reactivity of some simple hydrocarbon ligands attached to transition metals. [741]

The activation of inert carbon-oxygen and carbon-hydrogen bonds by reaction with metal atoms. (Dissertation) [742]

Hydroacylation and related reactions based on carbon-hydrogen bond activation. (19 references) [743]

Chlorotris(triphenylphosphine)rhodium(I): its chemical and catalytic reactions. (650 references) [744]

Studies on the reactions of tris(triphenylphosphine)chlororhodium(I) with aroyl chlorides and phenylacetyl chlorides. (Dissertation) [745]

Studies of organodimetallic reagents. Synthesis of reserpine. (Dissertation) [746]

Some organometallic chemistry of iminium salts. (Dissertation) [747]

Heteropolyacids as the catalysts in organic syntheses. (69 references) [748]

Activation of alkynes by transition metal elements. [749]

Catalysis of diolefin reactions by η^3-allyl metal complexes. (111 references) [750]

Controlled release applications of organometals. (25 references) [751]

Transmetallization. (265 references) [752]

The cleavage of three-membered ring compounds by transition metal organometallic complexes. (77 references) [753]

Interactions of metal centers with the 1,4-diaza-1,3-butadiene (α-diimine) ligand. Versatile coordination chemistry and applications in organic synthesis. (69 references) [754]

A Comprehensive Mechanism for the Fischer-Tropsch synthesis. [755]

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