TRANSITION METALS IN ORGANIC SYNTHESIS
ANNUAL SURVEY COVERING THE YEAR 1983

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I General Comments

This annual survey covers the literature for 1983 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.

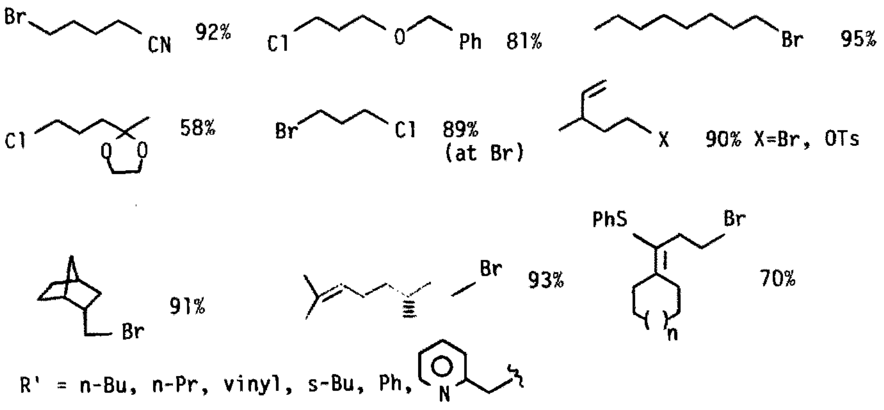
II. Carbon-Carbon Bond-Forming Reactions

A Alkylations

1. Alkylation of Organic Halides, Tosylates, and Acetates

Organocuprates continue to be the reagents of choice for the alkylation of halides, and new reagents and new understanding have continued to evolve. The electrochemical reduction potentials of typical substrates for organocopper reaction (including halides) have been measured in DMF, acetonitrile, and THF [1]. An nmr study of the composition of methylcopper(I) species in solution has also been carried out [2]. The reagent formed by the reaction of two equivalents of organolithium reagent with copper(I) thiocyanate is more efficient in the alkylation of secondary halides than is the typical lithium dialkylcuprate, R_2CuLi [3]. The reagents formed from copper(I) cyanide were efficient in the alkylation of organic bromides, and were more selective than the corresponding dialkylcuprate (equation 1) [4], (equation 2) [5], and (equation 3) [6]. Secondary alcohols were produced from aldehydes by reaction with trimethylsilyl iodide followed by a dialkylcuprate (equation 4) [7]

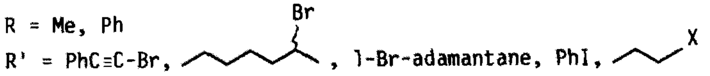
$$RBr + R_2'Cu(CN)Li_2 \longrightarrow RR' \qquad (1)$$

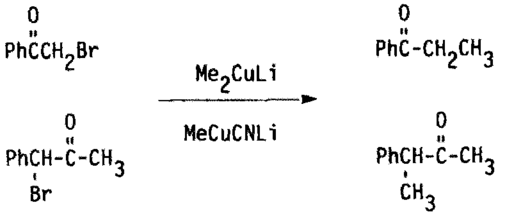


R' = n-Bu, n-Pr, vinyl, s-Bu, Ph,

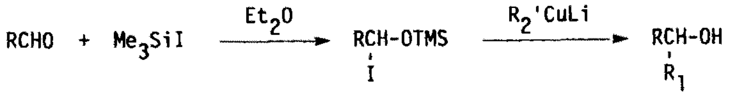
$$RLi + CuCN \longrightarrow [RCuCN]Li \xrightarrow{R'X} R\text{-}R' \qquad (2)$$

R = Me, Ph


R' = PhC≡C-Br, , 1-Br-adamantane, PhI,



$$\begin{matrix} PhCOCH_2Br \\ PhCHBr\text{-}CO\text{-}CH_3 \end{matrix} \xrightarrow[MeCuCNLi]{Me_2CuLi} \begin{matrix} PhCO\text{-}CH_2CH_3 \\ PhCH(CH_3)\text{-}CO\text{-}CH_3 \end{matrix} \qquad (3)$$



$$RCHO + Me_3SiI \xrightarrow{Et_2O} \underset{I}{RCH}\text{-}OTMS \xrightarrow{R_2'CuLi} \underset{R_1}{RCH}\text{-}OH \qquad (4)$$

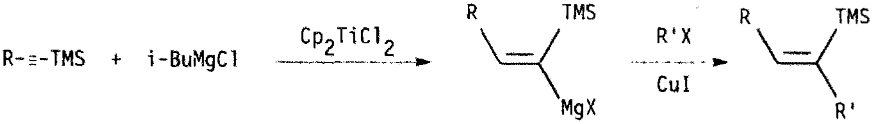
R_2 = Et, n-C_6

R_1 = Bu, Me

48-77%

Alkynes were alkylated with Grignard reagents, then with alkyl halides using titanium and copper catalysts, respectively (equations 5-7) [8]. long chain aldehydes were available from halides and Grignard reagents of protected bromoaldehydes (equation

8) [9]. Allylic bromides of thioenolethers were alkylated by organocuprates (equation 9) [10]. Geminal dihalides were dialkylated by organocopper species (equation 10) [11], (equation 11) [12]. Organocopper chemistry was also useful in the functionalization of β-lactams (equation 12) [13].



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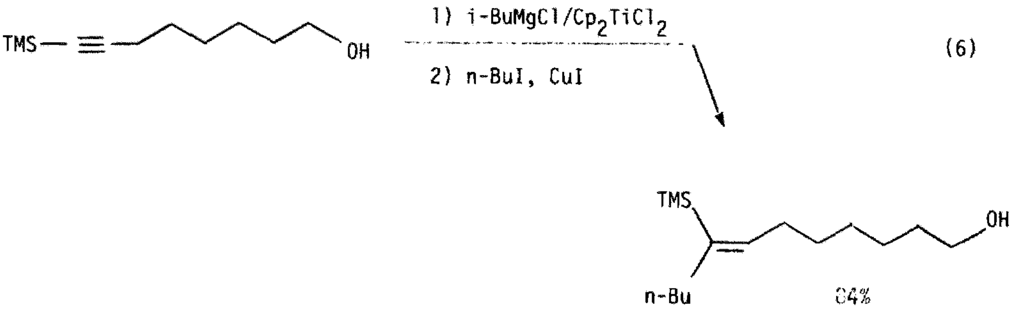

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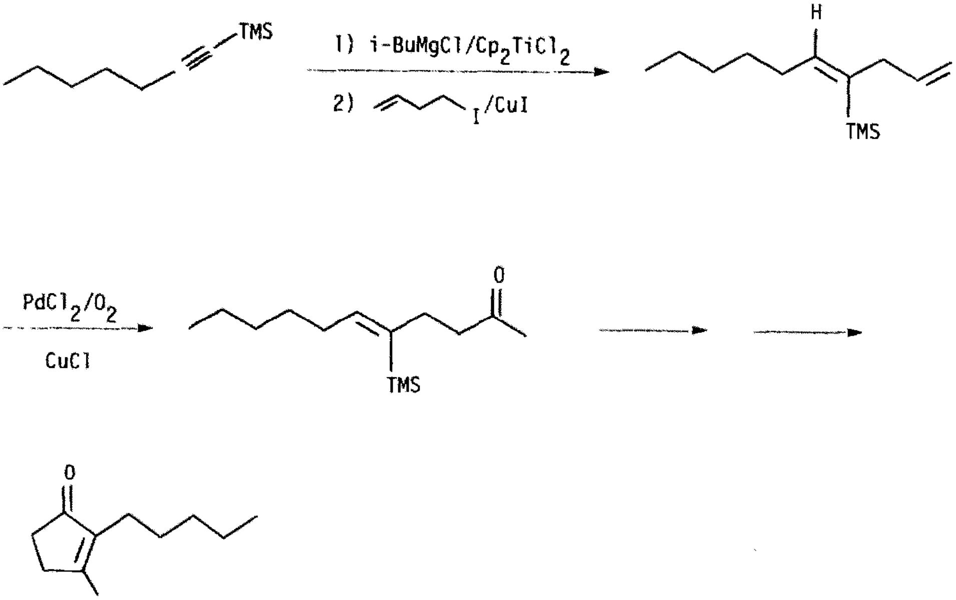
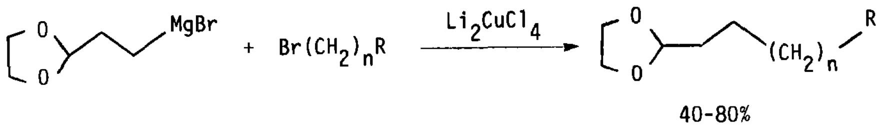
(7)

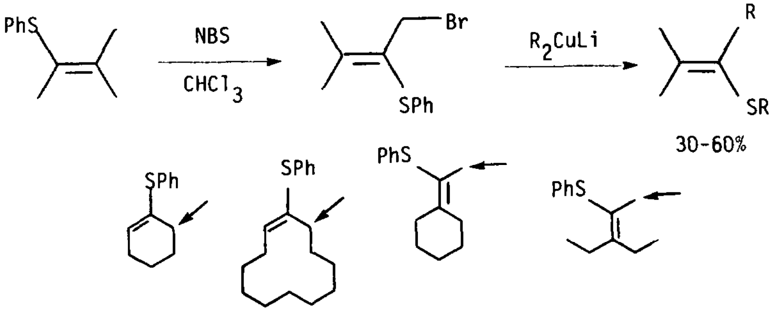




(8)

n = 3, 4, 5, 7

R = Me, OMe, Cl, CN, CO_2Et



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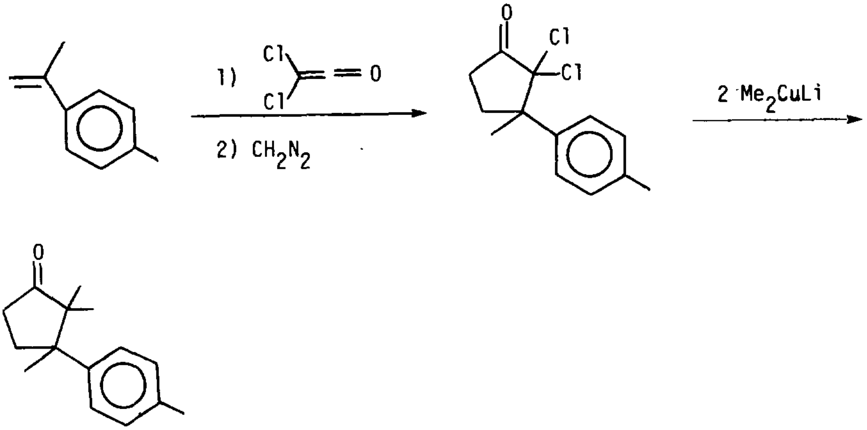

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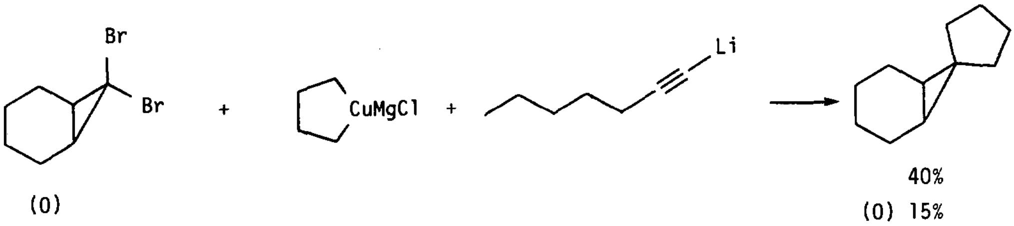
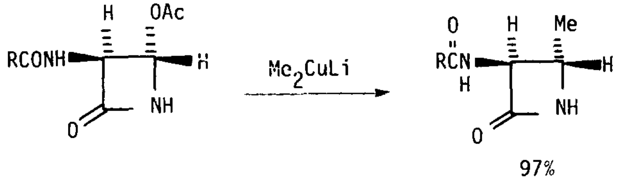
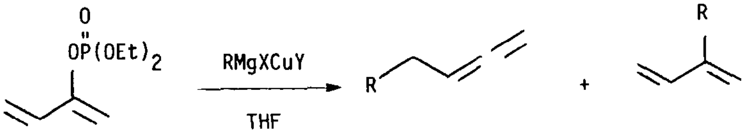


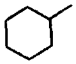


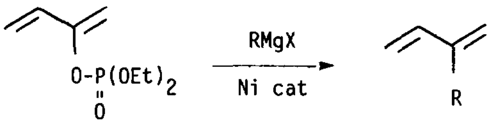
(12)

Enol phosphates were readily alkylated by organocopper species (equation 13) [14], (equation 14) [15], (equation 15) [16].



(13)

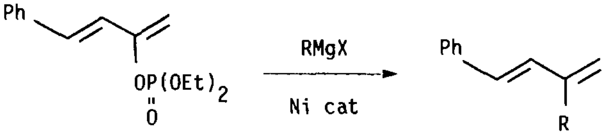
R = $PhCH_2$	72	12%
$n\text{-}C_8$	21	6%
	23	7%



(14)

60-80%; R=Ph, $PhCH_2$, $n\text{-}C_8$, Me

and



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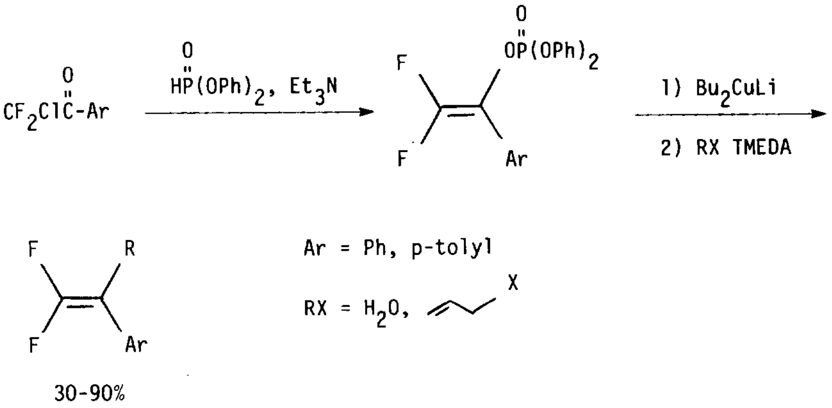
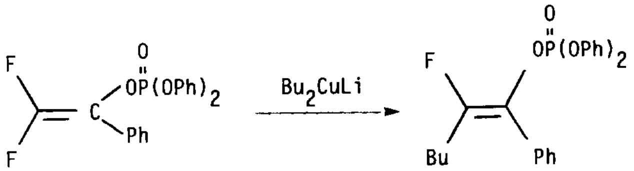


Ar = Ph, p-tolyl

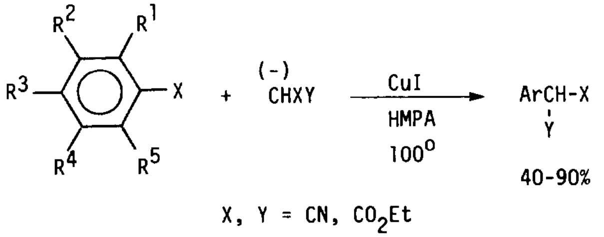
RX = H_2O,

also



In a modification of the well known Hurtley reaction, aryl halides were alkylated by stabilized carbanions in the presence of copper(I) iodide and HMPA (equation 16) [17,18,19].

(16)



X, Y = CN, CO_2Et

R^1 = H, Me

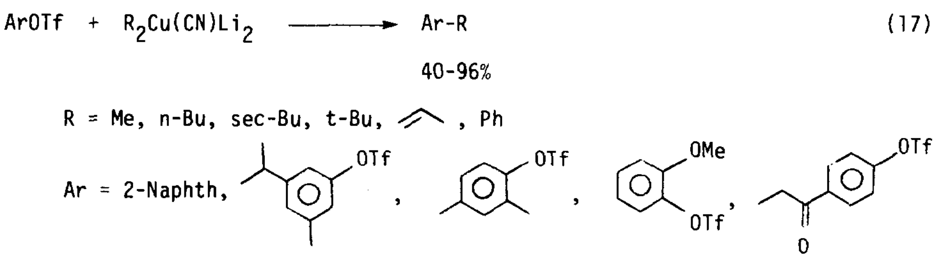
R^2 = H, Me, MeO, CF_3, OCH_2O

R^3 = H, Me, i-Bu, MeO

R^4 = H, Me

R^5 = H, Me

Aryl triflates were alkylated by organocopper species (equation 17) [20], while thiophenols were alkylated in a nickel-catalyzed Grignard reaction (equations 18, 19) [21]. Unsymmetrical biphenyls were available from an Ullmann type coupling of aryl iodides with trinitrobenzene (equation 20) [22].



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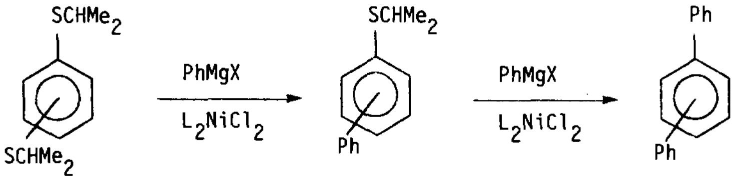

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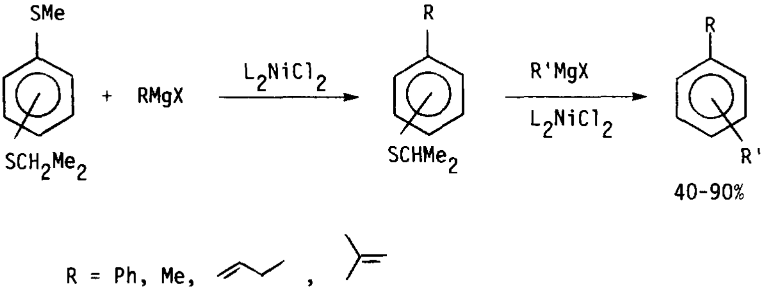
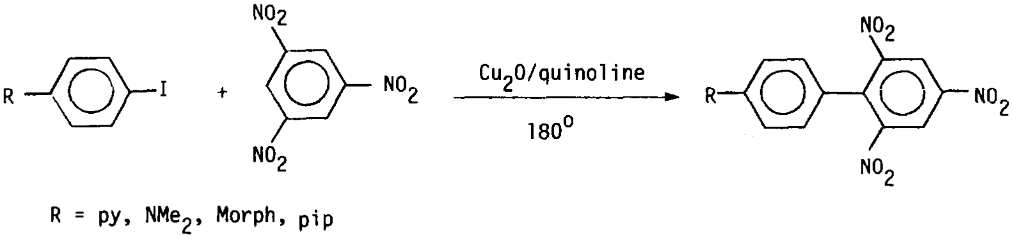


(19)

(20)

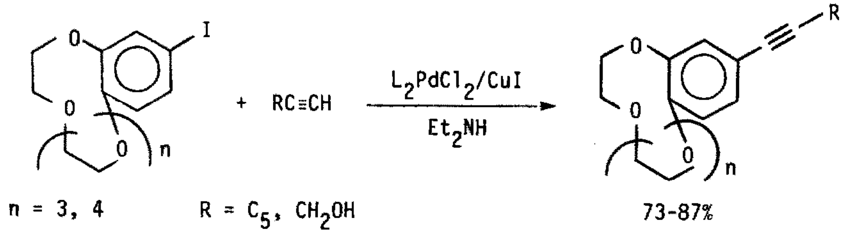


Combined palladium/copper catalysis was used to condense aryl halides with trimethylsilyl acetylenes (equation 21) [23], and other alkynes (equation 22) [24]. Alkynes alkylated acid halides in the presence of a similar catalyst system (equations 23, 24) [25]. Bromoalkynes underwent alkylation by secondary Grignard reagents in the presence of chiral palladium catalysts (equation 25) [26]. Vinyl boranes and bromoalkynes coupled when treated with base and copper(II) acetylacetonate (equation 26) [27].

$$\mathrm{ArX} + \mathrm{TMSC{\equiv}CH} \xrightarrow{L_2PdCl_2/CuI/Et_3N} \mathrm{ArC{\equiv}C\text{-}TMS} \xrightarrow[\mathrm{MeOH}]{\mathrm{KOH}} \mathrm{ArC{\equiv}CH} \qquad (21)$$

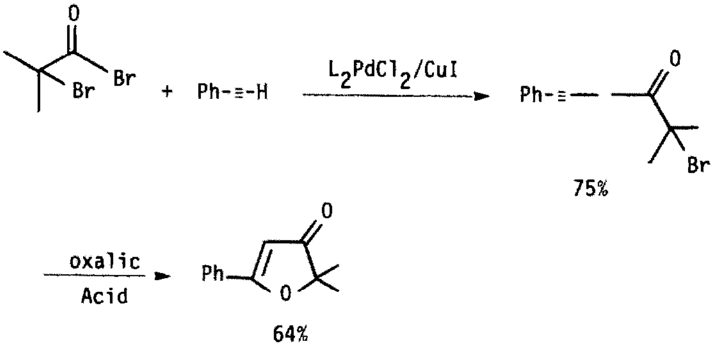
Ar = pyridines, quinolines, isoquinolines,

(22)



$$+ \mathrm{HC{\equiv}CH} \longrightarrow \text{Crown-}{\equiv}\text{-Crown} \quad 98\%$$

(23)



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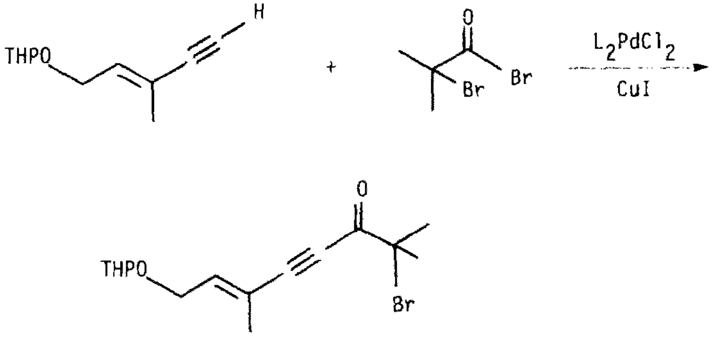

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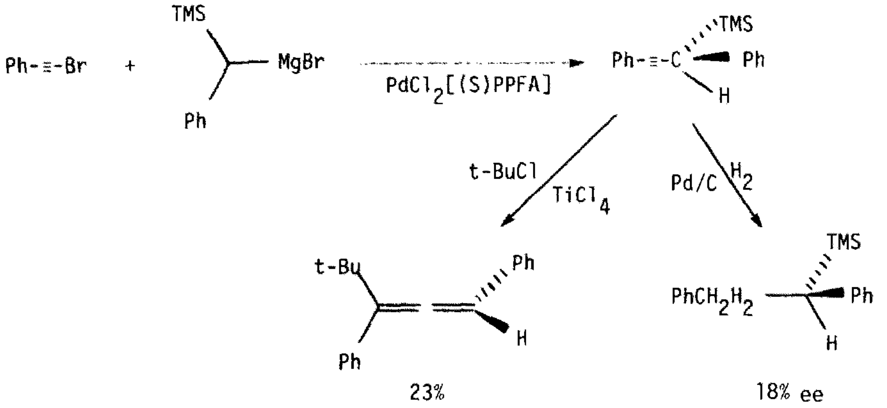
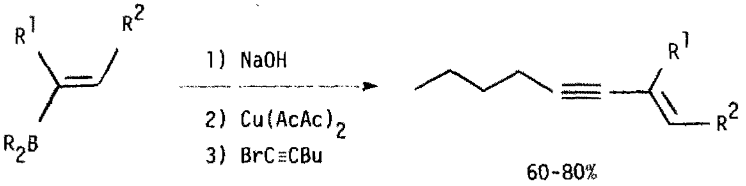


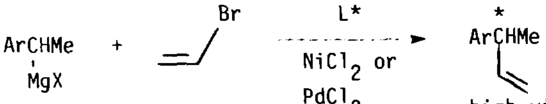


(26)

R^1 = H, Et

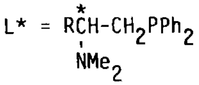
R^2 = Bu, Ph, Et, C_8

Chiral α-aminophosphines were prepared from chiral α-aminoacids, and were used as ligands in the nickel or palladium catalyzed cross coupling of secondary Grignard reagents with vinyl bromide (equation 27). High enantiomeric excesses were observed [28]. A detailed study of similar reaction, the alkylation of bromobenzene with *sec*-butylmagnesium halide in the presence of chiral ligands has also appeared [29]. The chiral ligands (R)-prophos, (R)-cyclophos, (R)-phephos, (S,S)-chiraphos, (R,R)-norphos, and (R,R)-dipamp were used. There was little effect on the enantiomeric excess upon changing the ligand, but the nature of the halide and the solvent were important. With substituted aryl halides, steric effects prevailed. Grignard reagents alkylated halopyrimidines in the presence of nickel catalysts (equations 28 adn 29) [30]. Iron complexes catalyzed the reaction of aryl magnesium halides with vinyl halides (equations 30 and 31) [31]. Vinyl tellurides underwent a similar reaction (equation 32) [32].



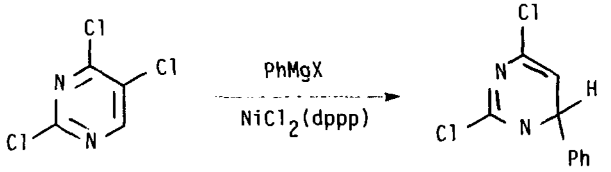
high yield - up to 83% ee

(27)

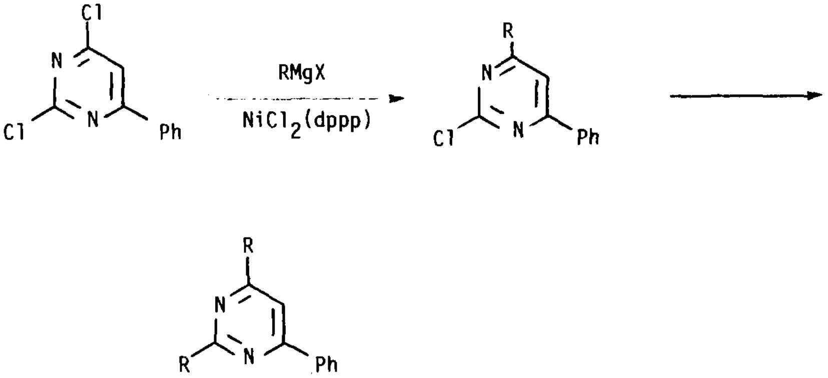


$L^* = R\overset{*}{C}H(NMe_2)\text{-}CH_2PPh_2$

R = Me, i-Bu, $PhCH_2$, i-Pr, s-Bu, Ph, c-C_6, t-Bu



(28)



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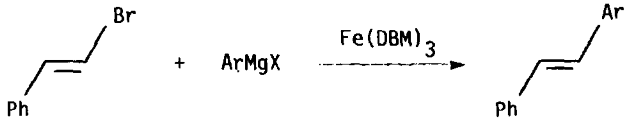


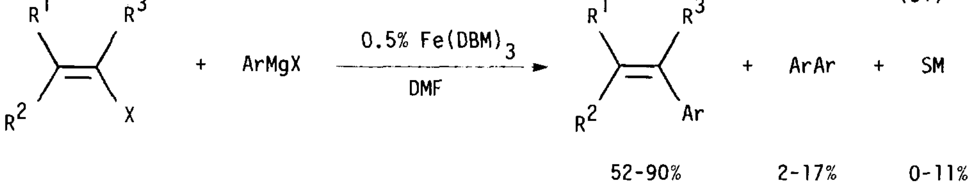
70-80%

(30)

DBM = dibenzoylmethido

Ar = Ph, 1-Naphth, 3-MeOPh, 4-ClPh, o-tolyl

(31)

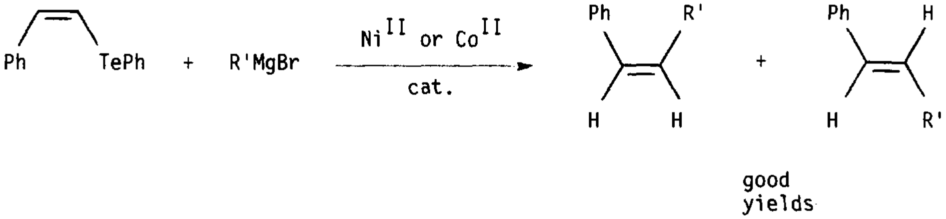


R^1 = Ph, H, Bu

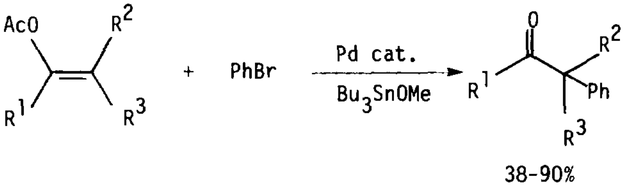
R^2 = Ph, H, Bu

R^3 = H, Ph

(32)



Several routes to the alkylation of halides involve oxidative addition reactions of palladium(0) complexes. Enol acetates were alkylated by aryl halides in the presence of palladium catalysts (equation 33) [33]. Vinyl halides behaved in a similar manner (equation 34) [34]. 2,2'-Diiodobiphenyls cyclized with phenyl acetylene in the presence of a palladium(II)/copper(I) catalyst system (equation 35) [35].

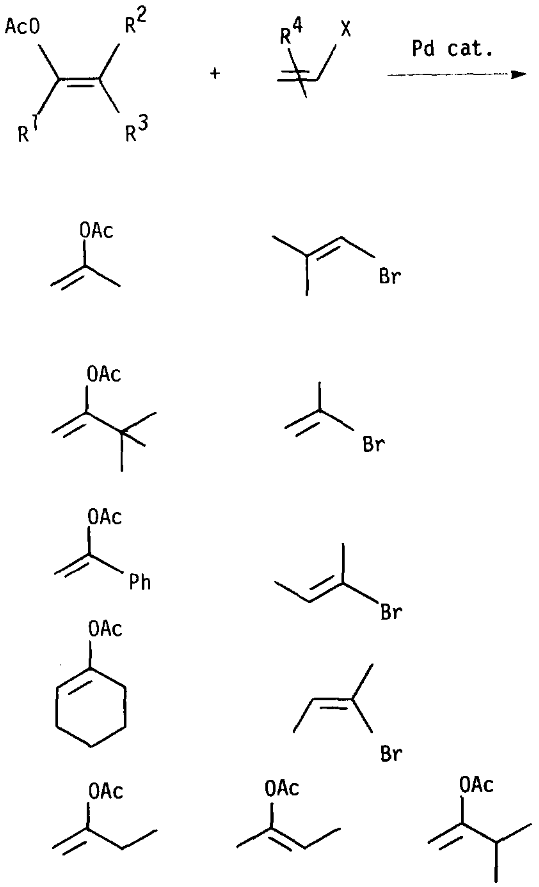


(33)

R^1 = Me, t-Bu, Ph, Et, i-Pr

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

R^3 = H, Me



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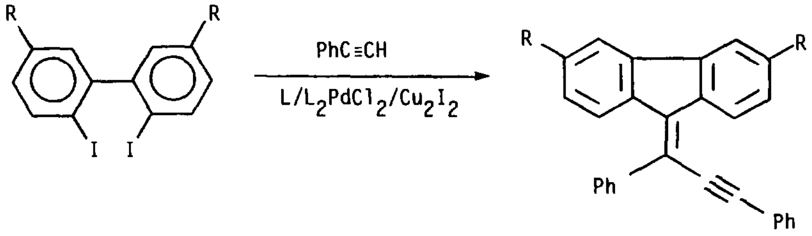
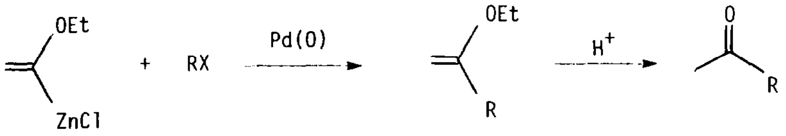


(35)

$R = NO_2$ 62%

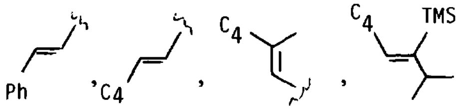
$R = H$ 78%

The cross-coupling reactions of organic halides with organic derivatives of tin, mercury, and copper, catalyzed by palladium (53 references) [36], has been reviewed, as has palladium or nickel-catalyzed cross-coupling involving proximally heterofunctional reagents (56 references) [37]. Aryl and vinyl halides were directly acylated by using palladium catalysts for zinc salts of enol ethers (equations 36 and 37) [38]. Secondary benzyl zinc reagents alkylated vinyl bromide in the presence of chiral palladium catalysts in up to 86% ee (equation 38) [39]. Palladium catalyzed coupling of organozinc reagents and aryl or vinyl halides was a general process (equations 39-41) [40]. Ethyl bromoacetate behaved in a similar manner (equation 42) [41]. Methoxypropadiene was converted to 3-methoxy-1,3-butadiene using a palladium catalyzed organozinc coupling reaction (equation 43) [42].



(36)

R = Ph, o-MePh, p-MePh, m-MePh, m-OMePh, o-H_2NPh, o-NO_2Ph, o-MeO_2CPh



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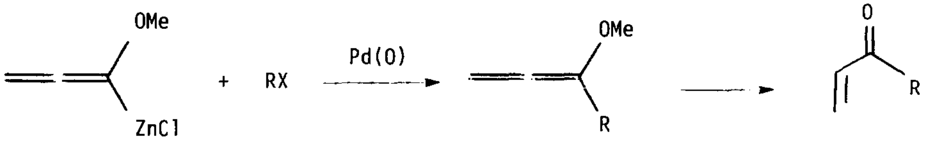

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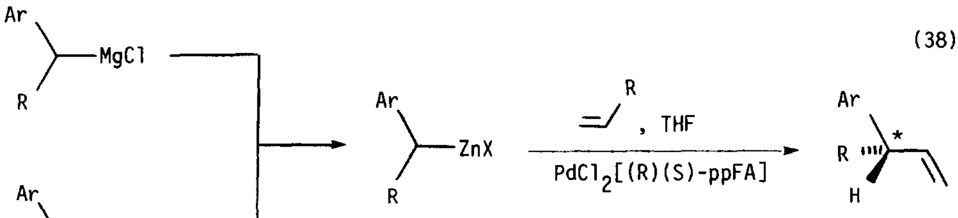
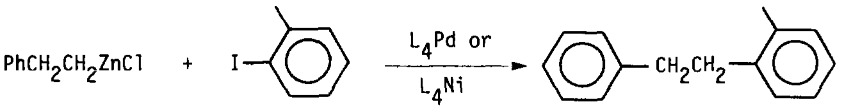


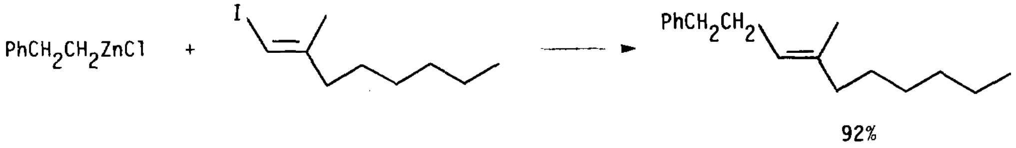
85-86% ee
95% yield



70%

(39)

(40)



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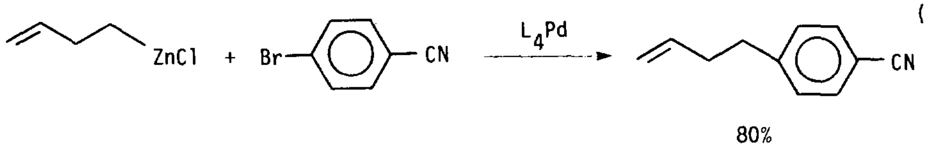
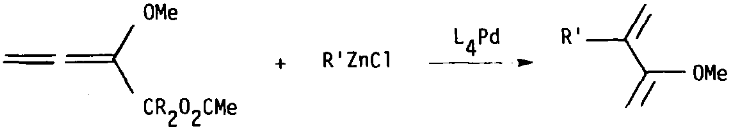


$$\mathrm{ArZnCl} \quad + \quad \mathrm{BrCH_2CO_2Et} \xrightarrow{\mathrm{Ni(acac)_2}} \mathrm{ArCH_2CO_2Et} \qquad (42)$$

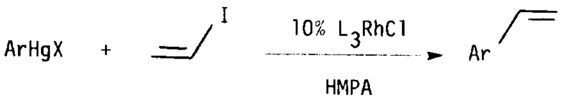
38-60%

Ar = Ph, o-tolyl, o-anisyl, 2-furyl, 2-thienyl, 2-selenienyl



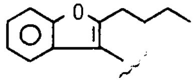
(43)

Rhodium(I) catalyzed the alkylation of vinyl iodide by aryl mercuric halides (equation 44) [43]. Dichloronaphthoquinones were alkylated by alkyl tin reagents in the presence of a palladium(II) catalyst (equation 45) [44]. A variety of highly functionalized molecules were made using palladium catalyzed coupling of allylic halides with unsaturated tin compounds as the key step (equations 46-51) [45]. Vinyl boranes coupled with vinyl halides under the influence of palladium(0) catalysts to form long chain unsaturated alcohols (equations 52-55) [46][47]. Enol ether, thioenol ether and trimethylsilyl organozinc or boron reagents coupled with unsaturated halides in the presence of palladium catalysts (equation 56) [48]. Boron enolates also coupled with allylic halides to give diketones under similar circumstances (equation 57) [49].

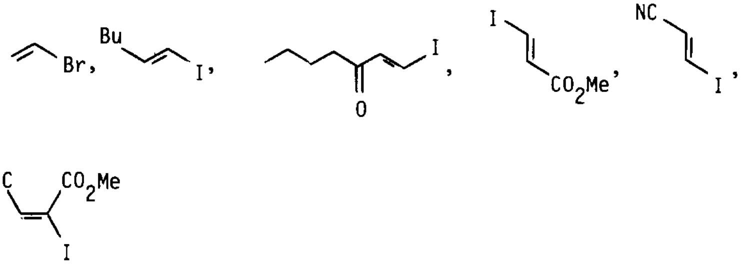


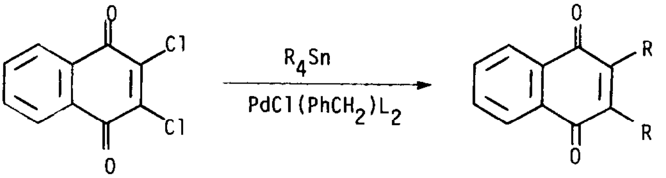
(44)

Ar = Ph, p-MeOPh, m-NO_2Ph,



also:

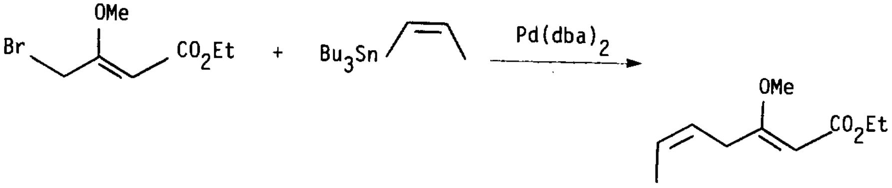




(45)

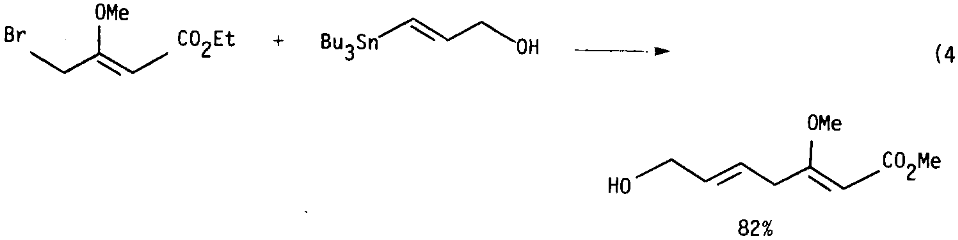
R = Me 88%

R =  65%



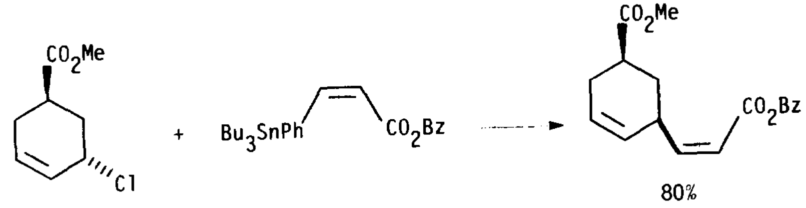
(46)

86%

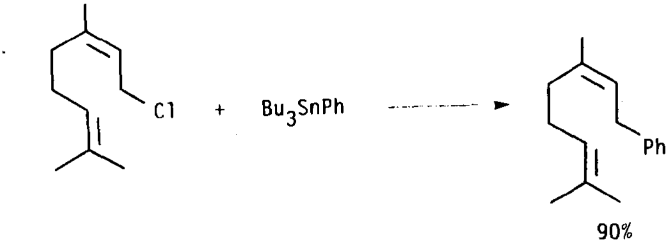


(47)

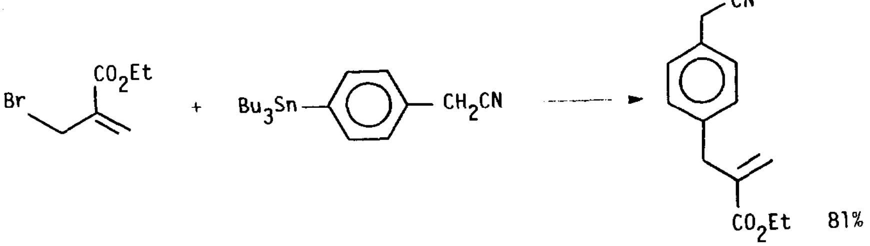
82%


CO2Me
Cl
+
Bu3SnPh
CO2Bz
CO2Me
CO2Bz
80%

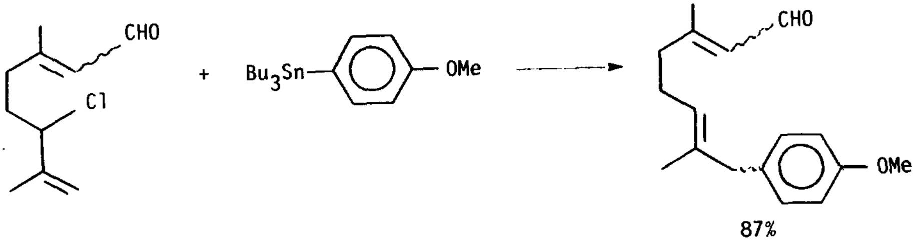
(48)


Cl
+
Bu3SnPh
Ph
90%

(49)

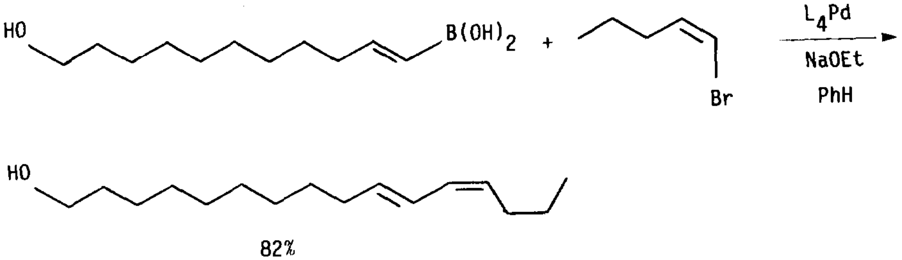

Br
CO2Et
+
Bu3Sn
CH2CN
CN
CO2Et
81%

(50)

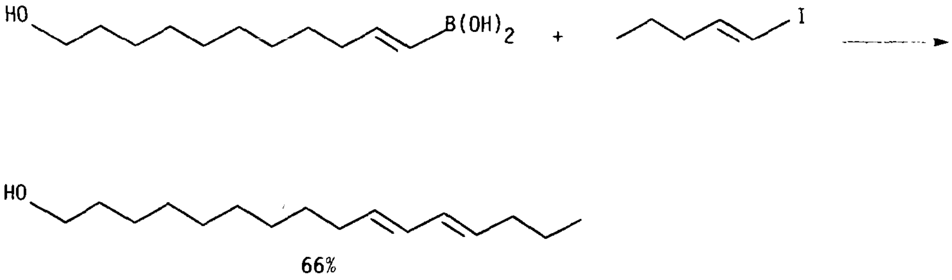

CHO
Cl
+
Bu3Sn
OMe
CHO
OMe
87%

(51)

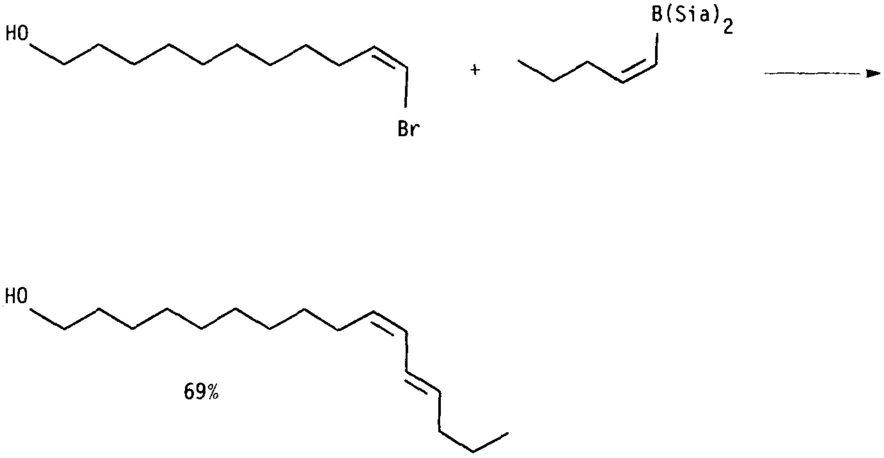
(52)


HO
B(OH)2
+
Br
L4Pd
NaOEt
PhH
HO
82%

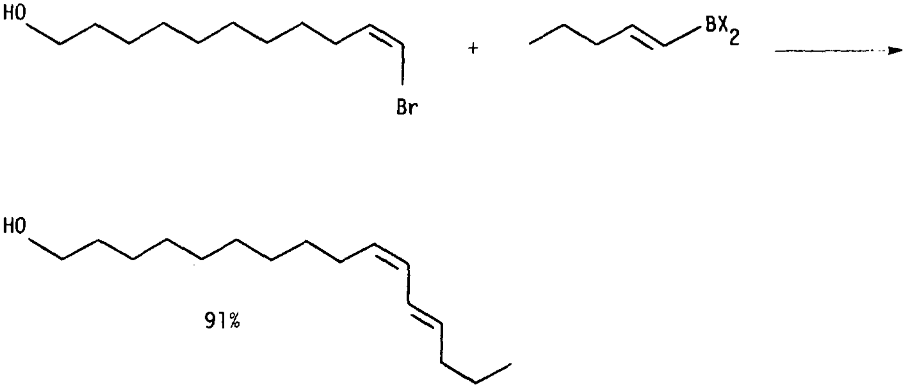
(53)

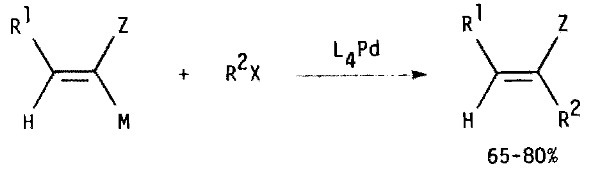


(54)

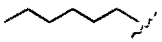


(55)



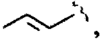


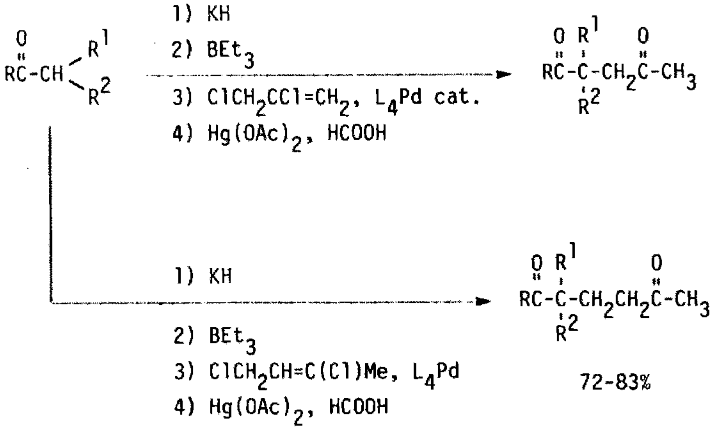
(56)

R^1 = H, 

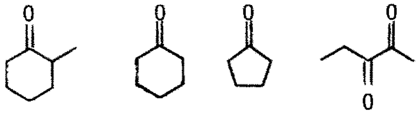
Z = OEt, SEt, $SiMe_3$

M = ZnCl, BR_2, Li

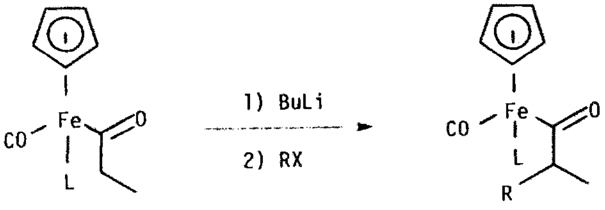
R^2 = n-C_4, , , Ph, p-ClPh



(57)

 used

Iron acyl compounds were α-alkylated by treatment with butyllithium and organic halides (equation 58) [50]. Aryl diazonium salts were alkylated by alkyl tin compounds in the presence of palladium(II) catalysts (equation 59) [51]. β-Dicarbonyl compounds were alkylated by allylic,or benzilic alcohols in the presence of cobalt-(II) chloride (equation 60) [52].

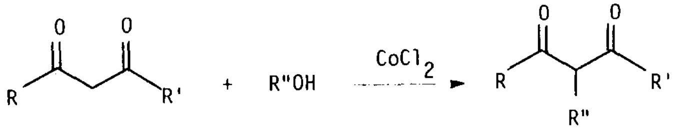


(58)

$$ArN_2^+ \quad + \quad R_3SnR^1 \quad \xrightarrow{Pd^{II}\ cat.} \quad ArR \qquad (59)$$

40-80%

R = Me, Ph, 

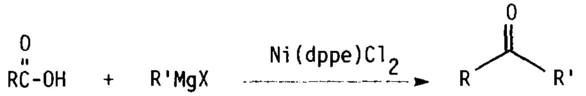


(60)

R" = Ph, $PhCH_2$, Ph_2CH, linalyl

2. Alkylation of Acid Derivatives

Nickel(II) salts catalyzed the reaction of Grignard reagents with carboxylic acids to form ketones (equation 61) [53]. Acid chlorides were converted to ketones by treatment with organozinc reagents and palladium(0) catalysts (equation 62) [54]. Vinyl copper species behaved in a similar manner (equation 63) [55]. Organopalladium species, from ortho-palladation of benzyl amines, reacted with acid halides to give acylated aromatics (equation 64) [56].



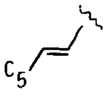
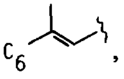
(61)

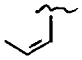
60-75%

R = Ph, m-tol, 2-Naphth, Bu, C_5
R' = n-C_5, n-Bu, Ph

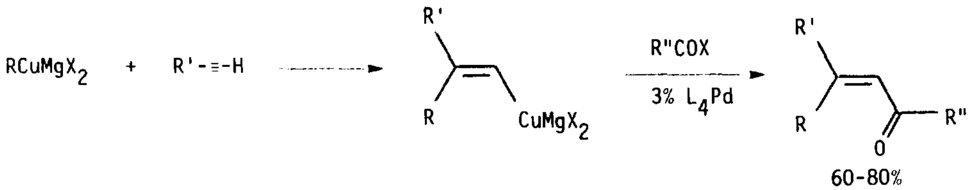
$$R^1ZnX \quad + \quad R^2COCl \quad \xrightarrow[THF]{L_nPd\ cat.} \quad R^1\overset{O}{\overset{\|}{C}}R^2 \qquad (62)$$

60-75%

R^1 = n-Bu, Ph, , , C_5-≡-⌇, p-ClPh, $PhCH_2$, n-C_8, o-tolyl

R^2 = Me, Ph, ═, MeO, 

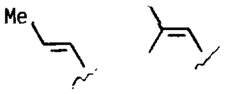
(63)

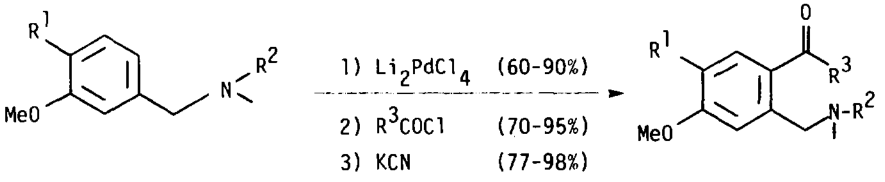


R = n-C_7, n-Bu, i-Pr, Et

R' = Me, H, EtO

R'' = Me, n-Bu, t-Bu, Ph,



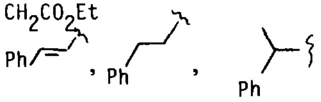


(64)

R^1 = H, OMe

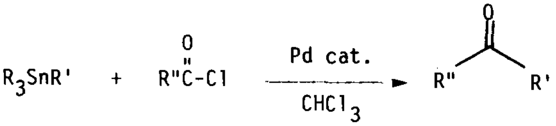
R^2 = Me, CH_2CO_2Et

R^3 = Bz,



, Ph_2CH

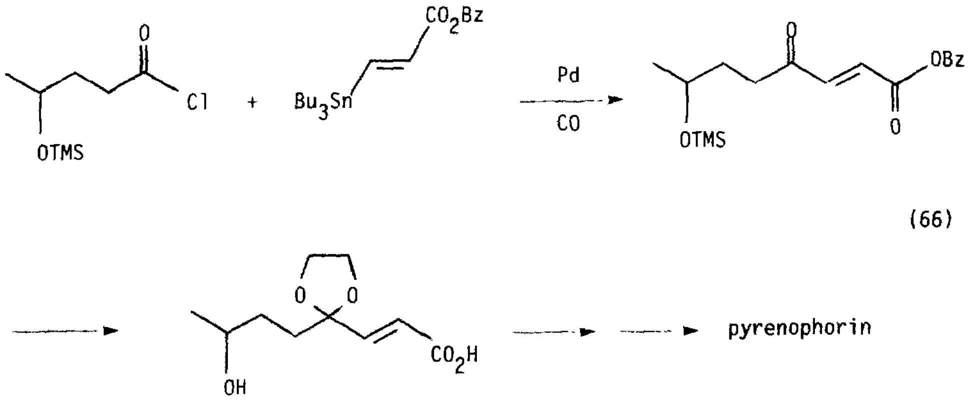
Alkyl tin reagents converted acid halides to ketones in the presence of palladium catalysts (equations 65 and 66) [57], (equation 67) [68]. The mechanism of this process has been studied, and the order of R group transfer from tin is PhC≡C > PrC≡C > PhCH=CH > CH_2=CH > Ph > $PhCH_2$ > CH_3OCH_2 > Me > Bu [59]. α-Diketones could be made using this reaction (equation 68) [60]. Acid derivatives underwent reductive coupling with aldehydes to give diols when treated with titanium(III) chloride (equation 69) [61].



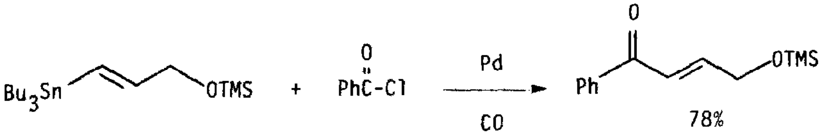
(65)

R' = alkyl, aryl, vinyl, alkyne, $MeOCH_2$

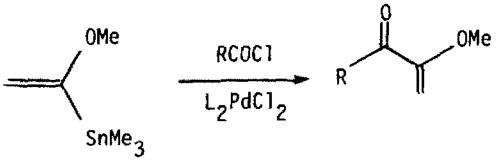
R'' = aryl, alkyl



(66)

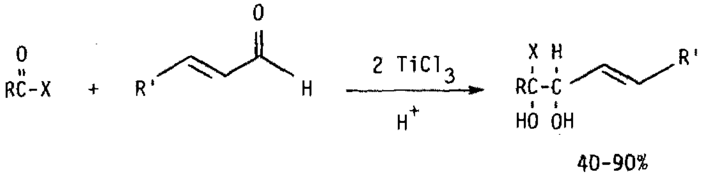


(67)



(68)

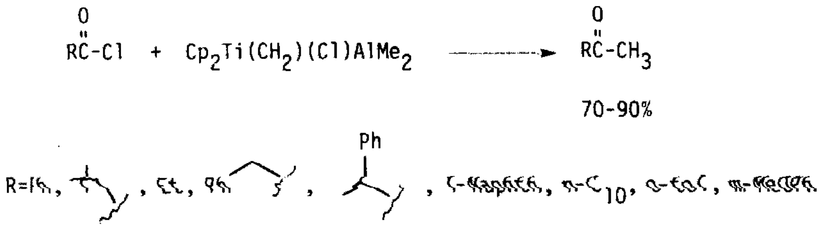
R = Me(44%), n-C_7(82%), c-C_6(86%), t-Bu(79%), $Cl(CH_2)_4$(77%), Ph(73%), 2-furanyl(83%)



(69)

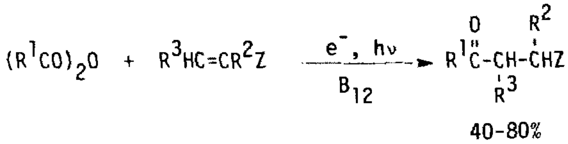
R = Ph, Me
R' = H, Me, Ph
X = CN, CO_2Me, CO_2H, 2 Py, 4 Py

Acid chlorides were converted to methyl ketones by reaction with a titanium methylene complex (equation 70) [62][63]. Acid anhydrides acylated conjugated enones when irradiated in the presence of vitamin B_{12} (equation 71) [64]. Esters were converted to β,γ-unsaturated ketones by reaction with zirconium-diene complexes (equation 72) [65]. Organocuprates converted acid derivatives to ketones (equation 73) [66].



$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}Cl} + \mathrm{Cp_2Ti(CH_2)(Cl)AlMe_2} \longrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}{-}CH_3} \qquad (70)$$

70-90%



$$\mathrm{(R^1CO)_2O} + \mathrm{R^3HC{=}CR^2Z} \xrightarrow[B_{12}]{e^-,\ h\nu} \mathrm{R^1\overset{O}{\overset{\|}{C}}{-}\underset{R^3}{CH}{-}\overset{R^2}{C}HZ} \qquad (71)$$

40-80%

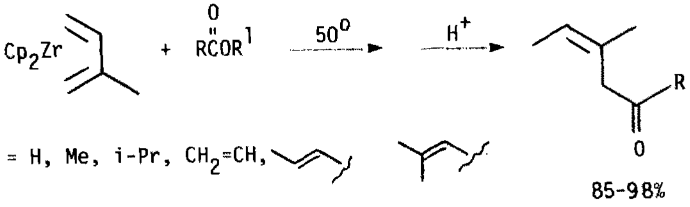
Z = CHO, COR, CO_2R, CN

R^1 = Me, n-C_7, Ph, n-C_6

R^2 = H, Me

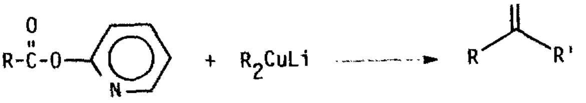
R^3 = H, Me

$-(CH_2)_2-$, $-(CH_2)_3-$



(72)

85-98%



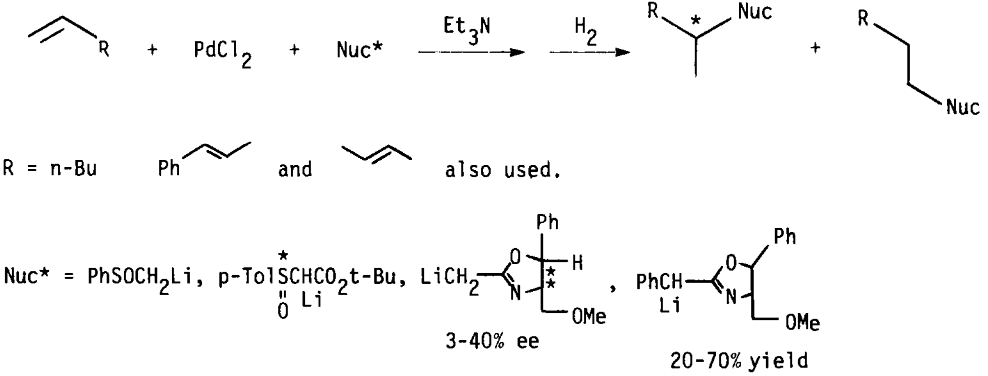
(73)

60-90%

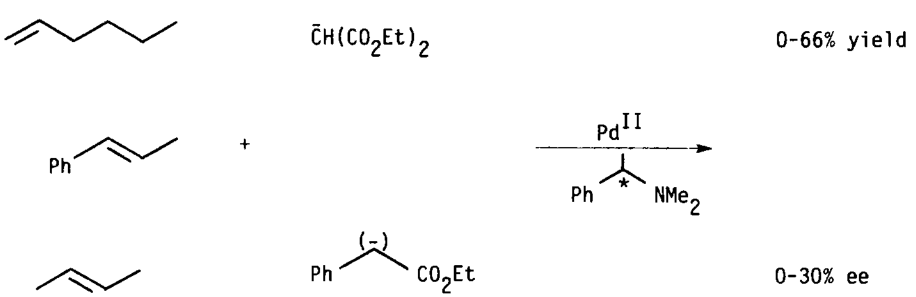
3. Alkylation of Olefins

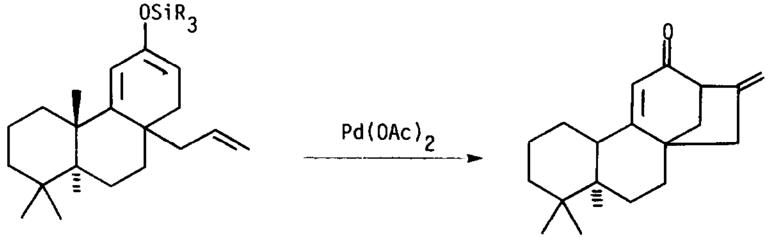
Asymmetric induction was achieved, in modest enantiomeric excess, in the palladium(II) assisted alkylation of olefins by stabilized carbanions (equations 74 and 75) [67], by use of chiral amines as auxilliary ligands. Palladium(II) promoted the cyclization of olefinic trimethylsilyl enol ethers (equation 76) [68], and the cyclization of 1,5-bis(methylene)cyclooctane (equation 77) [69]. 1,5-Hexadienes also cyclized to cyclohexenes when treated with $PdCl_2(RCN)_2$ followed by silica gel (equations 78-81) [70].

(74)



(75)

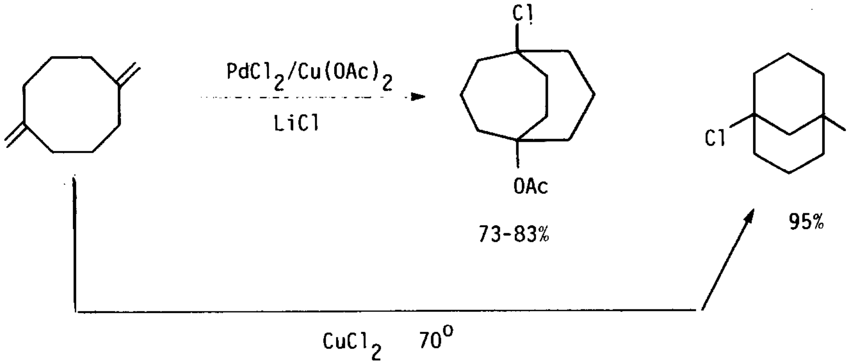




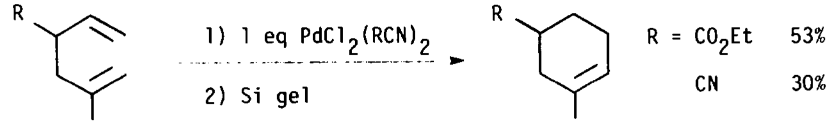
(76)

78%

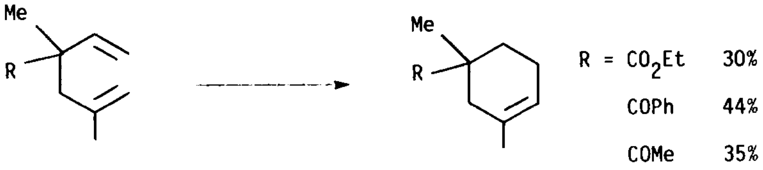
phyllocladene


PdCl2/Cu(OAc)2
LiCl
Cl
OAc
73-83%
Cl
95%
CuCl2 70°

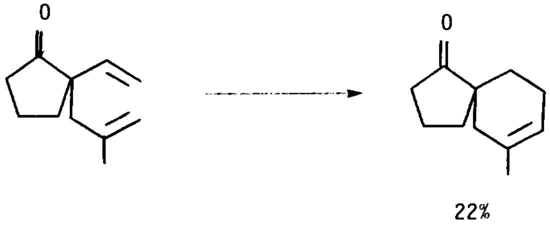
(77)


R
1) 1 eq PdCl2(RCN)2
2) Si gel
R
R = CO2Et 53%
CN 30%

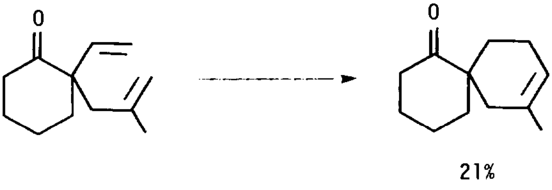
(78)


Me
R
Me
R
R = CO2Et 30%
COPh 44%
COMe 35%

(79)

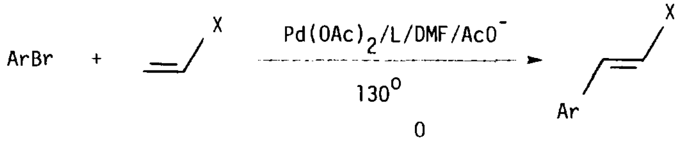

O
O
22%

(80)


O
O
21%

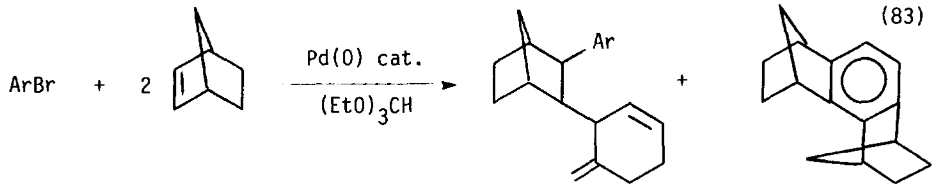
(81)

The "Heck" arylation of olefins continues to be extensively developed. Efficient condition for the arylation of olefins by aryl bromides have been developed, and consist of using palladium(II) acetate, phosphine, and sodium acetate in DMF (equation 82) [71]. Very high catalyst turnovers were observed. Norbornene underwent palladium catalyzed "Heck" arylation with aryl halides, and the intermediate σ-alkylpalladium species inserted another molecule of norbornene (equation 83) [72]. Palladium catalyzed the arylation of α-acetamido acrylic acid by bromoaromatics (equation 84) [73]. Nickel(0) complexes, generated electrochemically, catalyzed similar arylations of olefins (equation 85) [74].

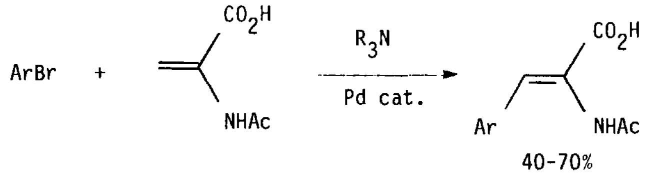


(82)

Ar = Ph, 4-O$_2$NPh, 2, 3, or 4 CN-Ph, 4-$\overset{\text{O}}{\overset{\|}{\text{HC}}}$-Ph

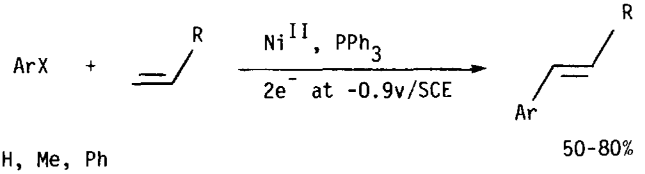


(83)



(84)

Ar = Ph, 4-ClPh, 4-MeOPh, 3,4 (MeO)$_2$Ph, 2-MePh, 4-PhCO$_2$Ph, 1-Naphth, 3,4 (O$_2$CH$_2$)Ph

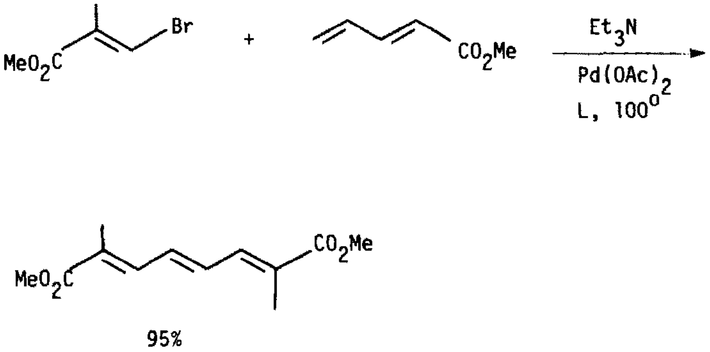


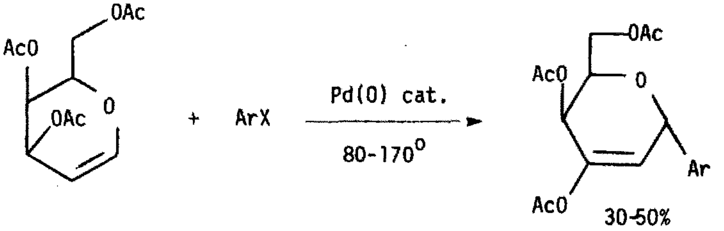
(85)

R = H, Me, Ph
ArX = PhI, PhCl, PhBr, p-HOPhI, p-MeOPhI

Polyenes were prepared by the palladium catalyzed reaction of vinyl bromides with polyunsaturated esters (equation 86) [75]. Glycals were arylated by aryl halides and palladium catalysts (equation 87) [76]. Norbornene was both arylated and carbonylated with a similar catalyst system (equation 88) [77]. Olefins were arylated by acid chlorides and palladium catalysts in a process that involved a decarbonylation along the way (equation 89) [78]. Vinyl silanes were arylated by aryl diazonium salts in the presence of a palladium(0) catalyst (equation 90) [79].

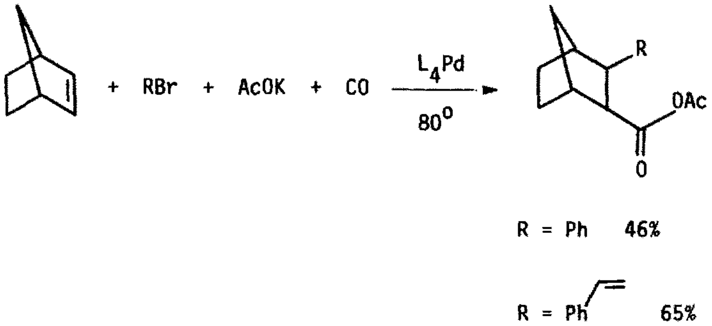
(86)



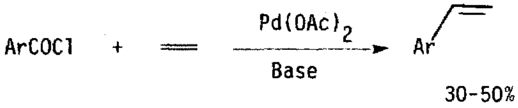


(87)

Ar = Ph, p-MeOPh, 2,4 $(MeO)_2Ph$, 2 MeO-4-NO_2Ph, 2 MeO-4-Ph, OMePh, 2,6 $(MeO)_2Ph$, 2,4 $(MeO)_2Ph$

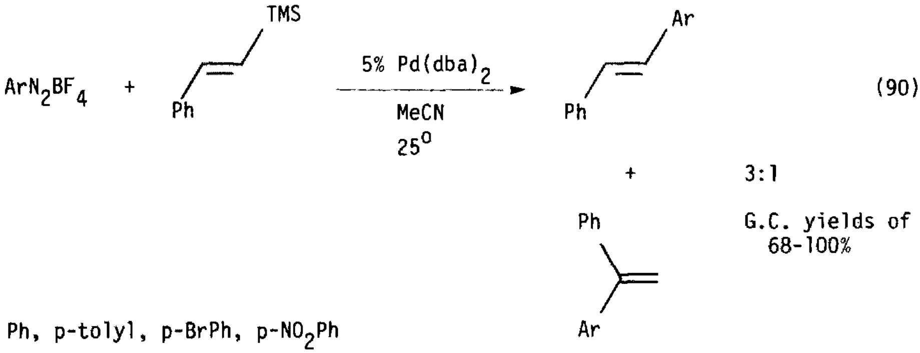


(88)



(89)

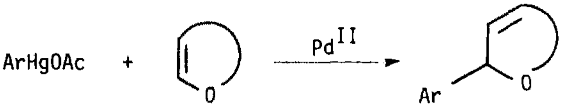
Ar = p-MePh, Ph, NO_2, CHO, MeO, Cl-containing Ar



(90)

Ar = Ph, p-tolyl, p-BrPh, p-NO_2Ph

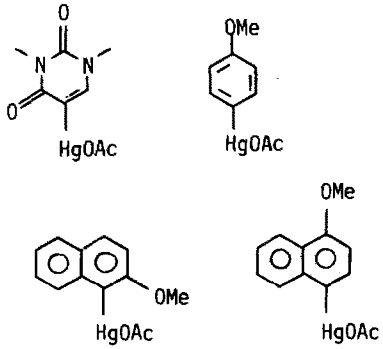
Olefins were also alkylated by transmetallation reactions to palladium. Enol ethers were arylated by a variety of aromatic mercury compounds in this manner (equation 91) [80] (equation 92) [81]. Transmetallation from boron was used to synthesize the sex pheremone of the grapevine moth (equation 93) [82]. Aryl palladium complexes from electrophilic aromatic substitution (equations 94 and 95) [83] and orthopalladation (equation 96) [84] also arylated olefins.



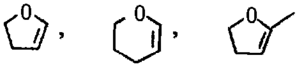
(91)

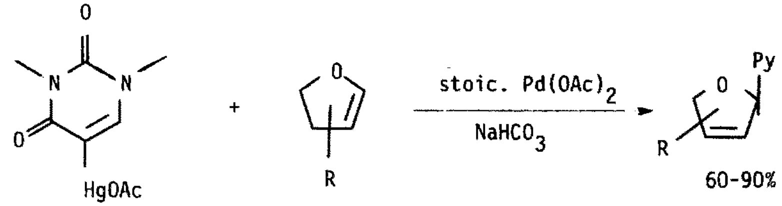
good yields - always this regiochemistry

Ar =



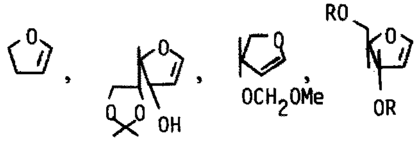
ether =

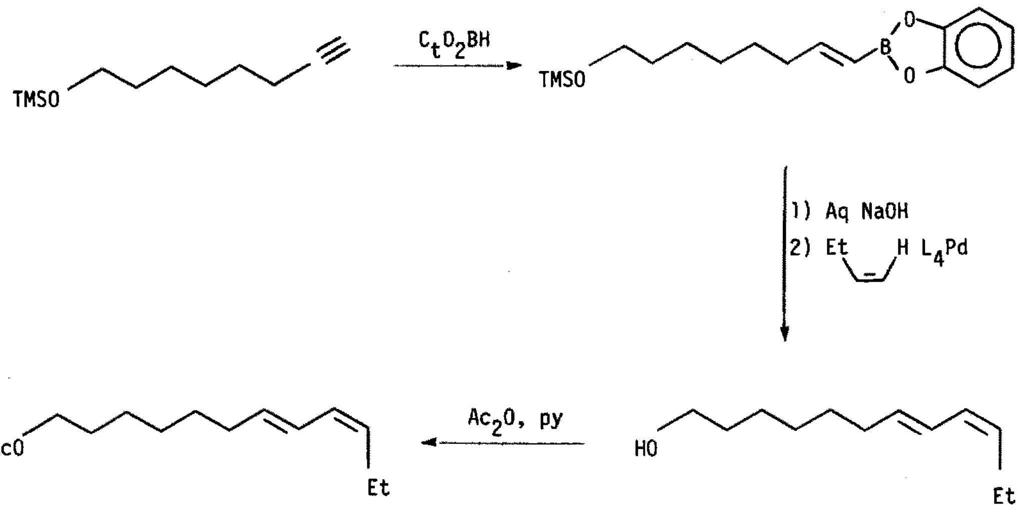


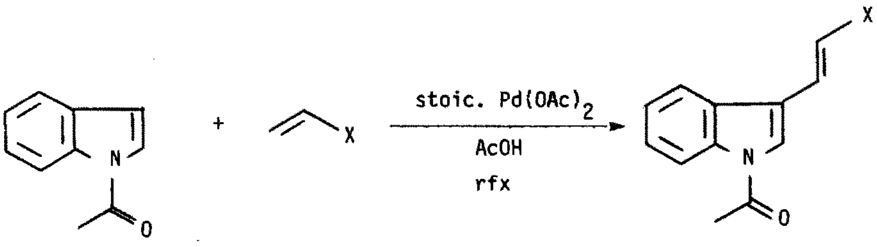


(92)

works with



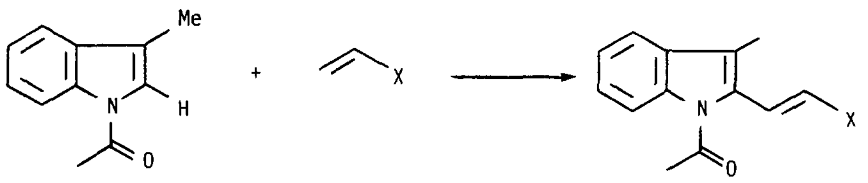




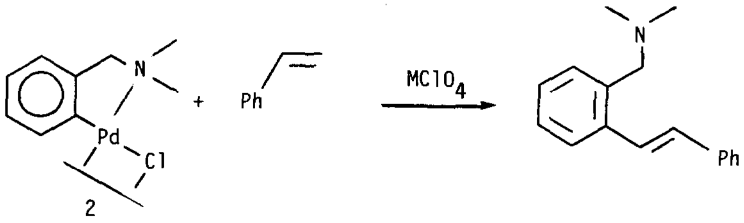
(94)

X = CO_2Me, CN

20-45%

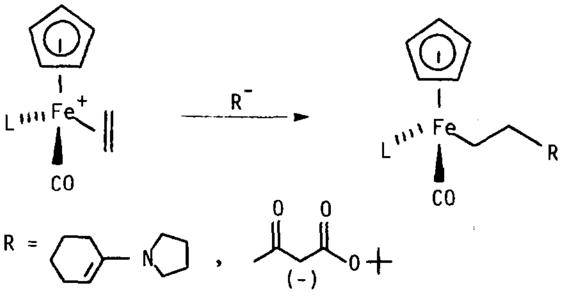


(95)

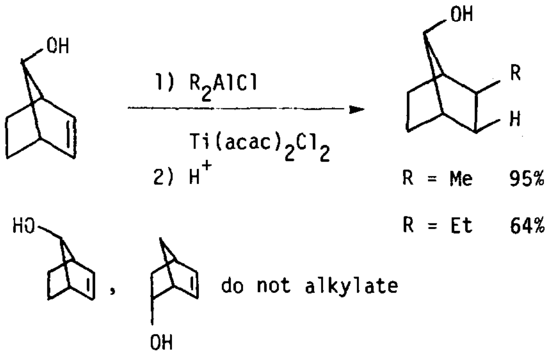


(96)

Prochiral olefins on chiral iron complexes underwent alkylation by stabilized carbanions with asymmetric induction (equation 97) [85]. Titanium(IV) complexes catalyzed the alkylation of norbornene having a 7-hydroxy substituent syn to the olefin (equation 98) [86]. Methylene chloride added to electrophilic olefins when irradiated in the presence of copper(I) chloride (equation 99) [87]. 1,1-Dimethylallene alkylated phenol (probably at oxygen, followed by a Cope rearrangement) in the presence of a platinum(II) catalyst (equation 100) [88]. Iron carbene complexes reacted with olefins to effect carbene transfer (equation 101) [89].

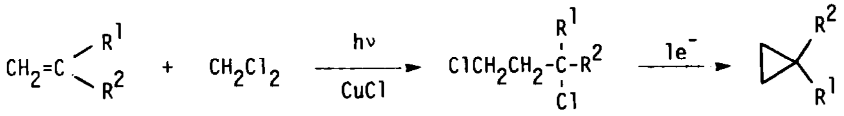


(97)



(98)

(99)



R^1 = H R^2 = CN 72%

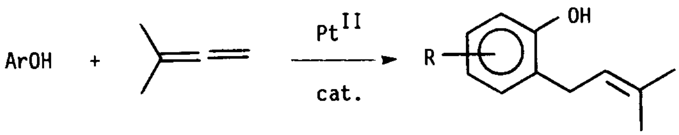
R^1 = H R^2 = CO_2Et 70%

R^1 = H R^2 = COMe 40%

R^1 = Me R^2 = CN 80%

R^1 = Me R^2 = CO_2Et 40%

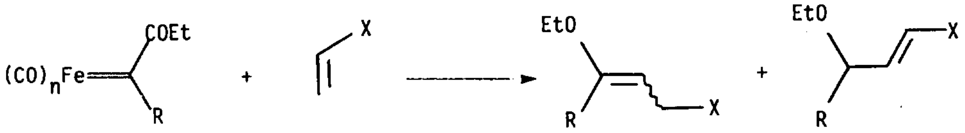
R^1 = CH_2CO_2Et R^2 = CO_2Et 42%



(100)

Ar = Ph, 3-MePh, 3-MeOPh, 4-MePh, 4-MeOPh, 2,6-$(MeO)_2Ph$

(101)



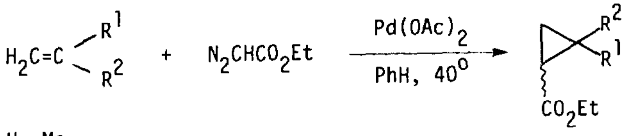
40-60%

R = Ph, n-Bu, t-Bu

X = Ph, OEt, CO_2Me, SPh

4. Decomposition of Diazoalkanes and Other Cyclopropanations

Transition metal catalyzed decompositions of diazo compounds continues to be an active area of research. Cyclopropane carboxylic esters were made by the palladium(II) catalyzed decomposition of ethyl diazoacetate in the presence of olefins (equation 102) [90]. The regioselectivity of this reaction with dienes was studied, and it was found that, with palladium(II) acetate as a catalyst terminal, nonhindered double bonds were most reactive, whereas rhodium(II) acetate was most effective for electron rich olefins (equation 103) [91]. Insertion of carbenes into C-H bonds has been used to make cyclic compounds. With chiral diazoesters, asymmetric induction was observed (equations 104-106) [92]. Insertion into aromatic C-H bonds has also been observed (equation 107) [93] (equation 108) [94]. The copper-catalyzed decomposition of dimethyl diazomalonate in the presence of olefins has been examined, and addition, insertion, and dimerization products were observed [95].

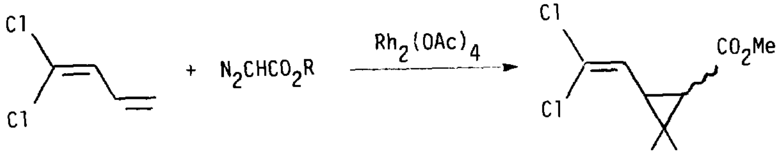


(102)

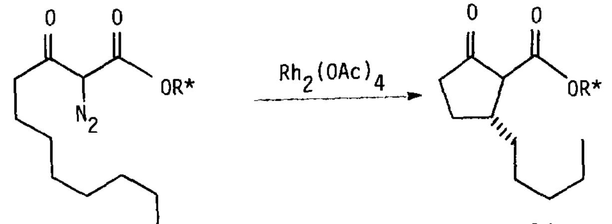
R^1 = H, Me

R^2 = Ph, CO_2Me, COMe

30-76%



(103)

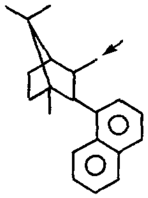


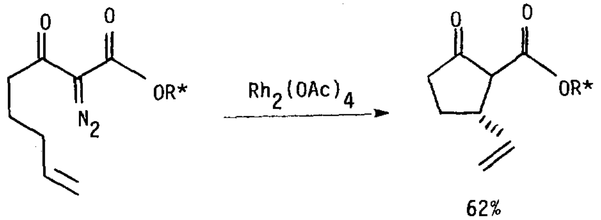
(104)

60% yield

87:13 diastereoselective

R* =

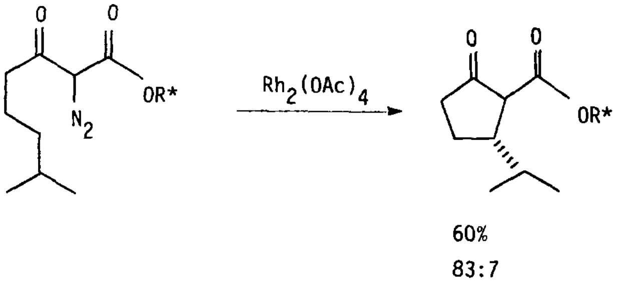




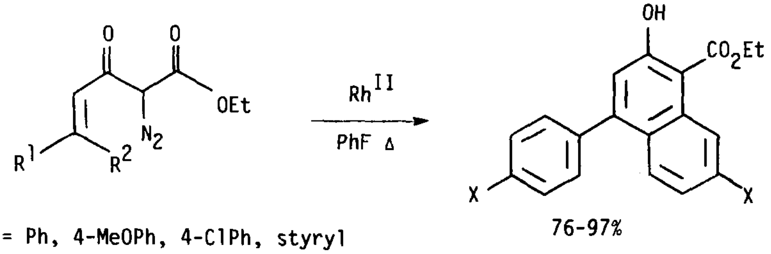
(105)

62%

92:8



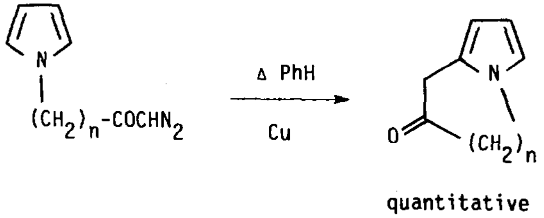
(106)



(107)

R^1 = Ph, 4-MeOPh, 4-ClPh, styryl

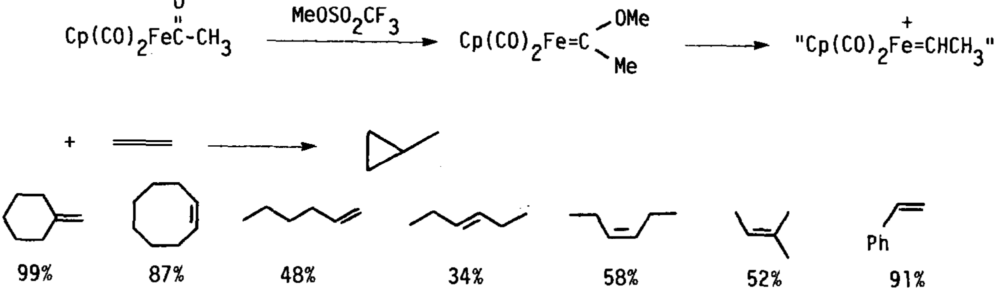
R^2 = Ph, 4-MeOPh, 4-ClPh

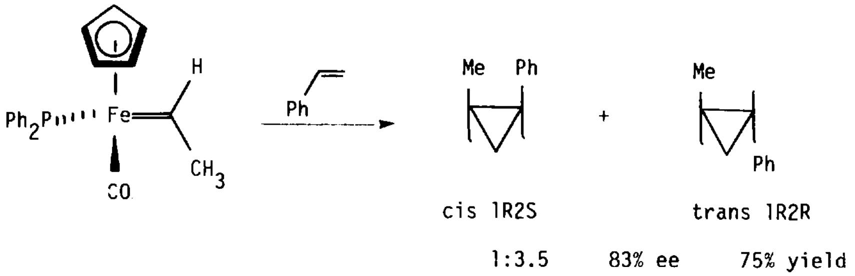


(108)

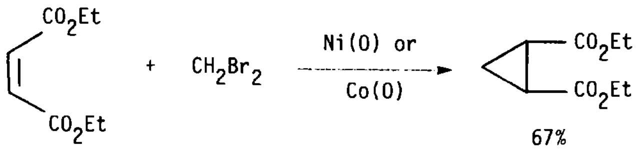
Iron carbene complexes were efficient cyclopropanating reagents (equation 109) [96]. With chiral iron complexes, substantial asymmetric induction was observed (equation 110) [97]. Finally dimethylfumarate and malonate were cyclopropanated by gem dihalides in the presence of nickel(0) or cobalt(0) catalysts (equation 111) [98].

(109)





(110)

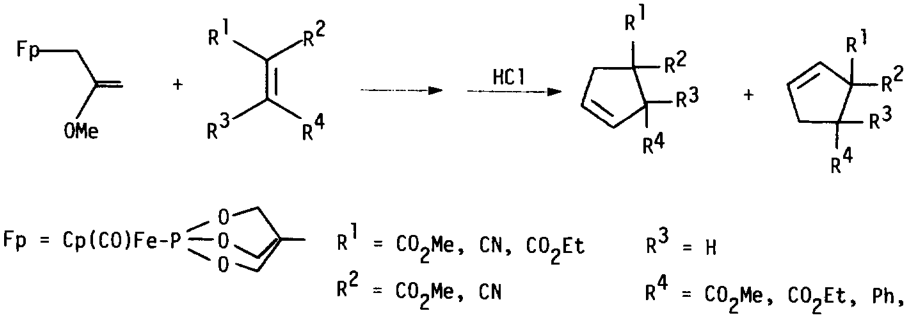


(111)

5. Cycloaddition Reactions

Electron poor olefins reacted with Fp allyl compounds to produce cycloaddition products (equation 112) [99]. Even cationic olefin Fp complexes were sufficiently reactive to cyclize (equation 113 and 114) [100]. The full details of the palladium(0) catalyzed cycloaddition of electron deficient olefins with a trimethylenemethane precursor have been published (equation 115) [101]. The reactive intermediate was claimed to be a $-\!\!<\!\!(\!(^{+}\mathrm{PdL}_2$ species in which all three -CH_2-'s were equivalent, and the cycloaddition was thought to be stepwise [102]. Copper(I) triflate catalyzed a photochemical 2+2 cycloaddition of cyclohexane with cycloheptene (equation 116) [103].

(112)



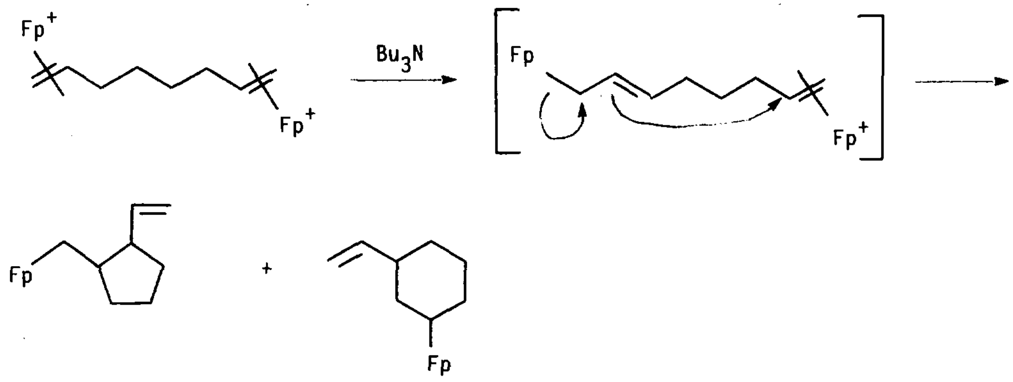
R^1 = CO$_2$Me, CN, CO$_2$Et

R^2 = CO$_2$Me, CN

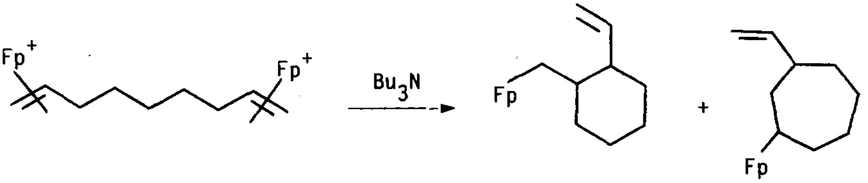
R^3 = H

R^4 = CO$_2$Me, CO$_2$Et, Ph, CH$_2$-dithiolanyl

(113)

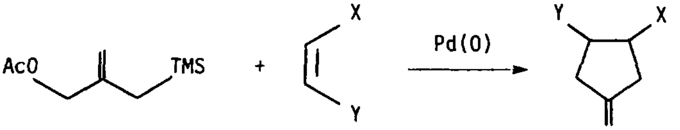


Fp⁺
Fp⁺
Bu₃N
Fp
Fp⁺
Fp
+
Fp



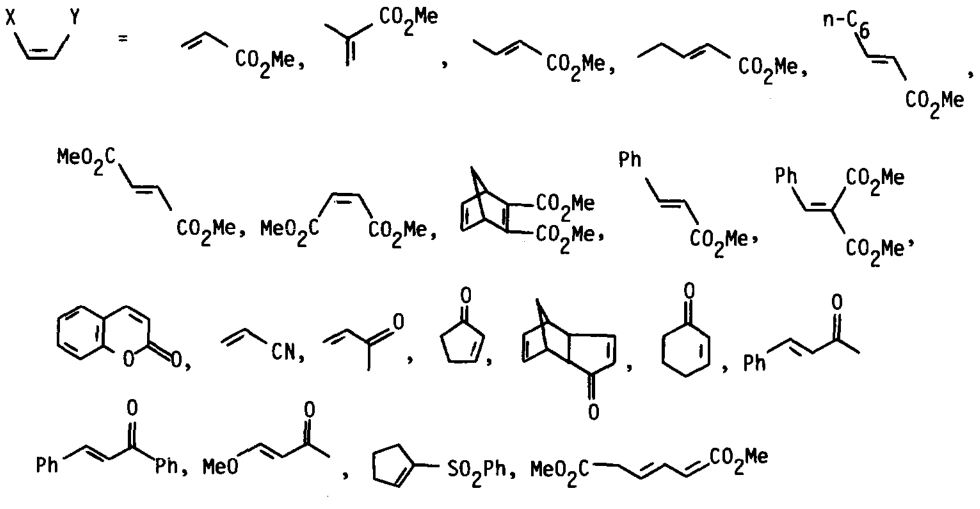
Fp⁺
Fp⁺
Bu₃N
Fp
+
Fp

(114)

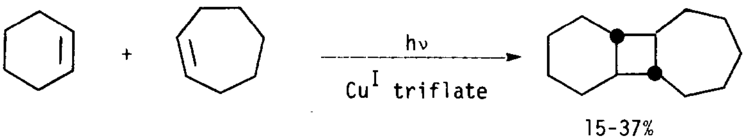


AcO
TMS
+
X
Y
Pd(0)
Y
X

(115)

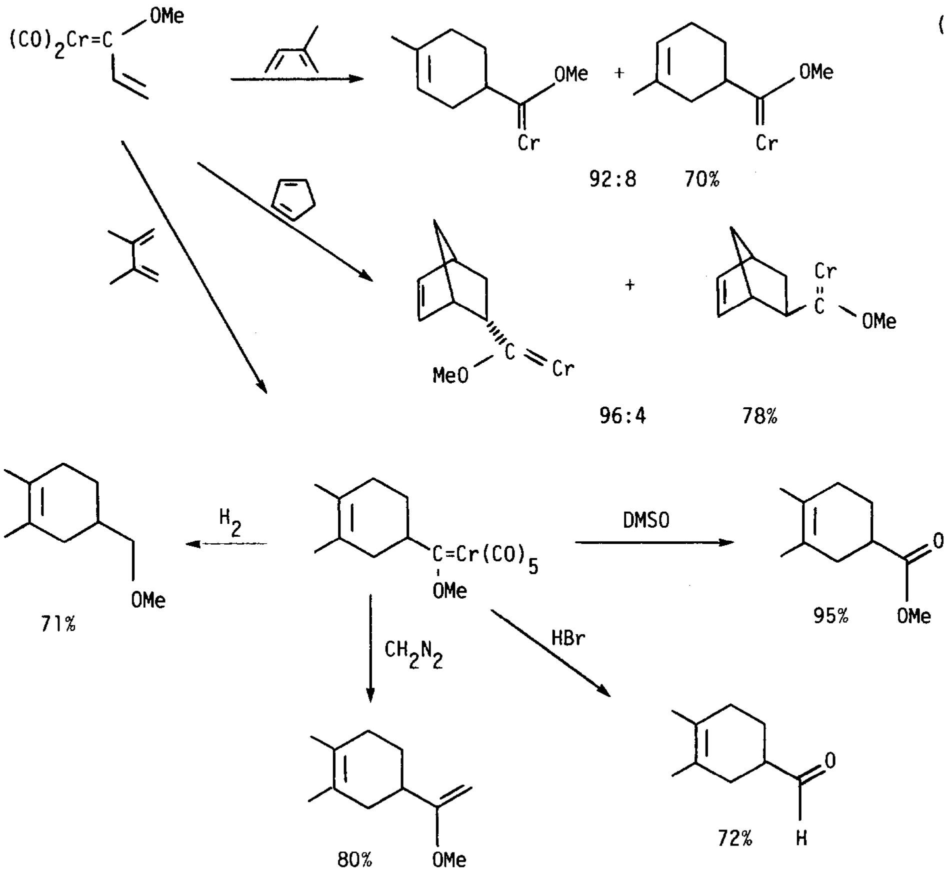


X
Y
=
CO₂Me,
CO₂Me
CO₂Me,
CO₂Me,
n-C₆
CO₂Me
MeO₂C
CO₂Me,
MeO₂C
CO₂Me,
CO₂Me
CO₂Me,
Ph
CO₂Me,
Ph
CO₂Me
CO₂Me,
O
O,
CN,
O
O
O
O
Ph
O
Ph
Ph,
MeO
O
SO₂Ph,
MeO₂C
CO₂Me



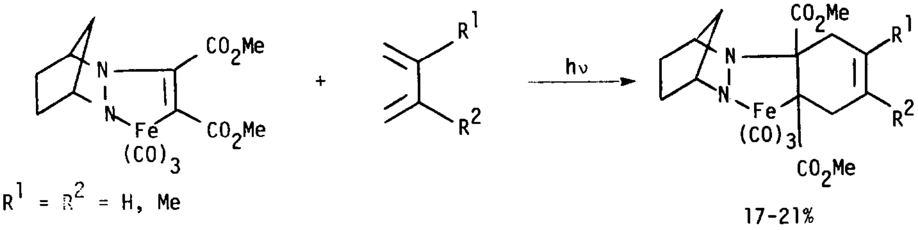
(116)

Diels Alder reactions of metal complexed dienes or dieneophiles is being developed. Unsaturated chromium carbene complexes reacted with dienes to give a variety of functionalized chromium carbene complexes which were converted to useful organic compounds (equation 117) [104]. An organoiron dienophile behaved in a similar manner (equation 118) [105]. An iron complex (η_1) of cyclopentadiene was an efficient diene in cycloaddition reactions (equation 119) [106]. Finally the chromium complex of cyclohexatriene underwent an unusual cycloaddition reaction (equation 120) [107].



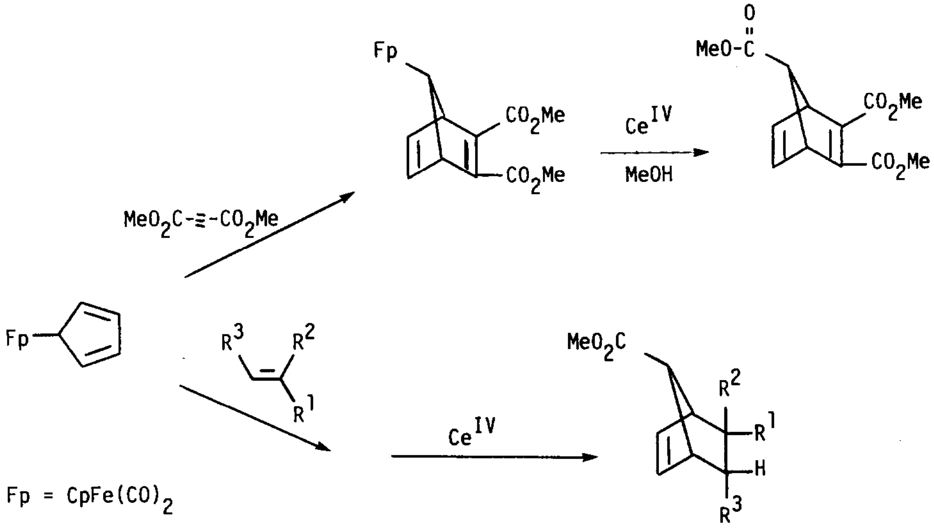
(117)

(118)



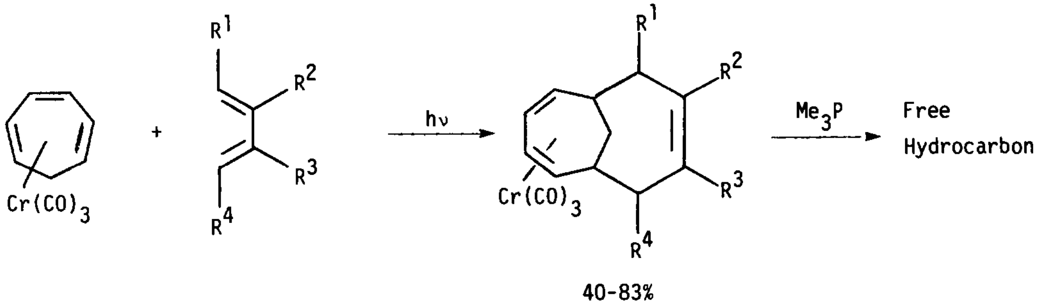
$R^1 = R^2 = H, Me$

(119)



$Fp = CpFe(CO)_2$

(120)



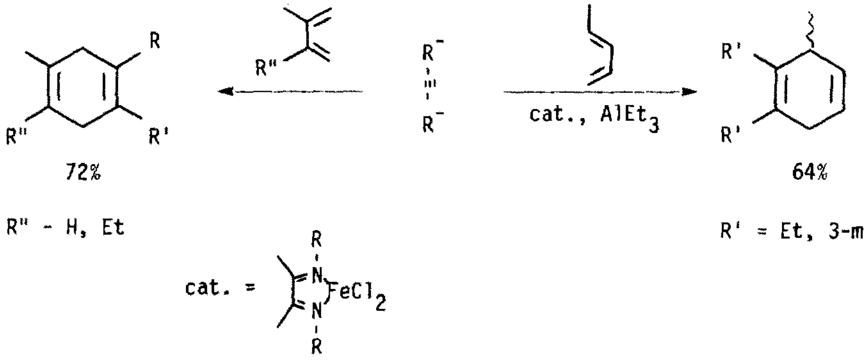
$R^1 = H, Me, CH_2OH$

$R^2 = H, Me$

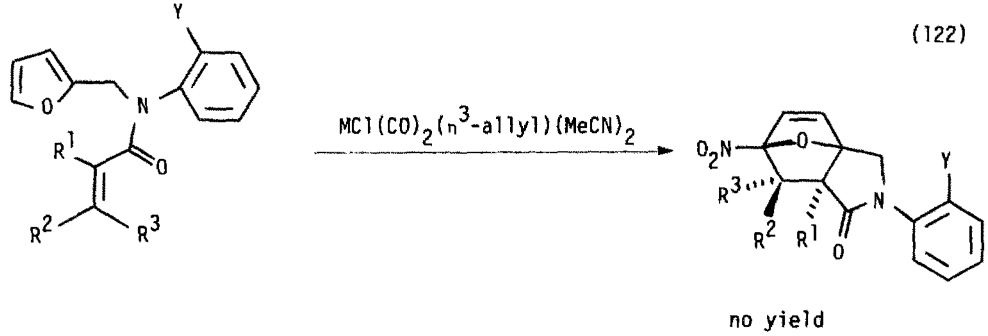
$R^3 = H, Me$

$R^4 = H, Me, CO_2Me$

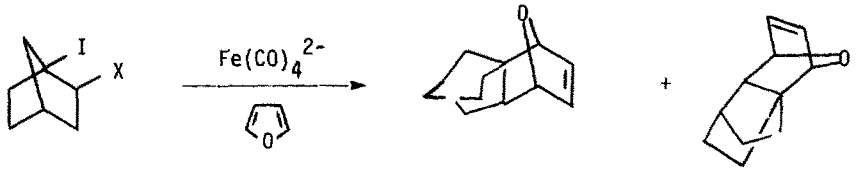
Transition metals were also used to catalyze Diels-Alder reactions. An iron-diazadiene complex catalyzed the reaction between alkynes and dienes (equation 121) [108]. A π-allylmolybdenum complex was claimed to catalyze an intramolecular cyclization with furan (equation 122) [109], while titanium(IV) chloride catalyzed the reaction of quinones with dienes, to give the same products at -78° as obtained thermally at 200°, and opposite that obtained using BF_3 [110]. Finally, bridgehead olefins were generated by the $Fe(CO)_4^{2-}$ assisted elimination of X_2, and the resulting olefins were trapped by furan (equation 123) [111].



(121)



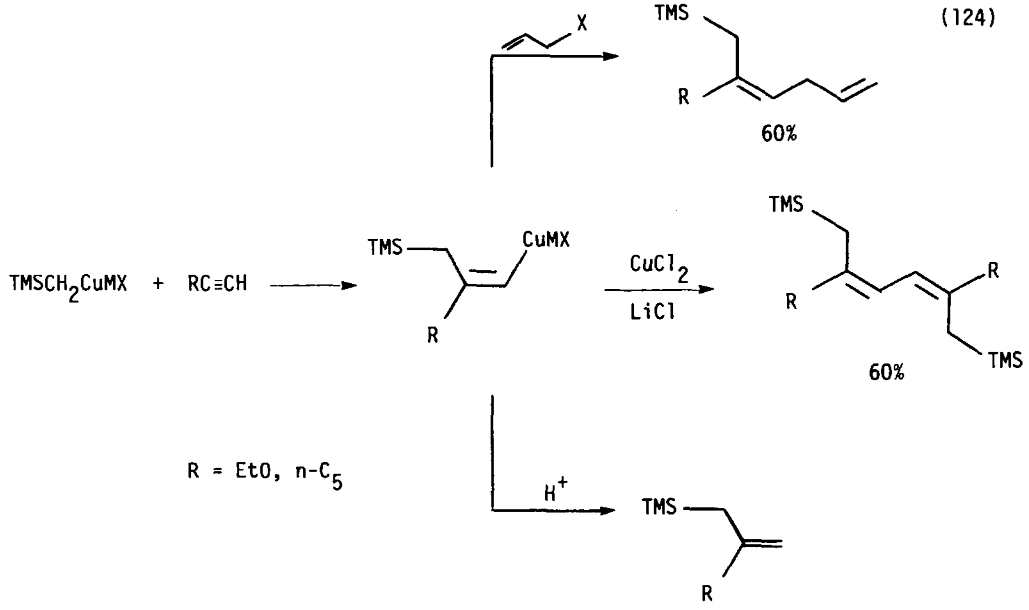
(122)

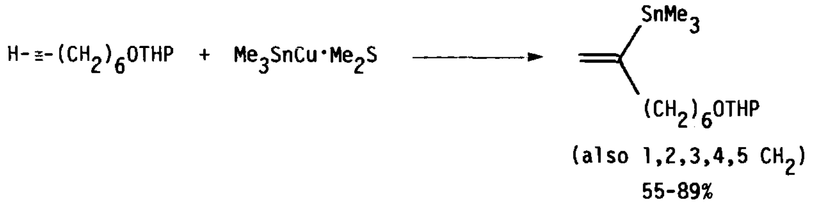


(123)

6. Alkylation of Alkynes

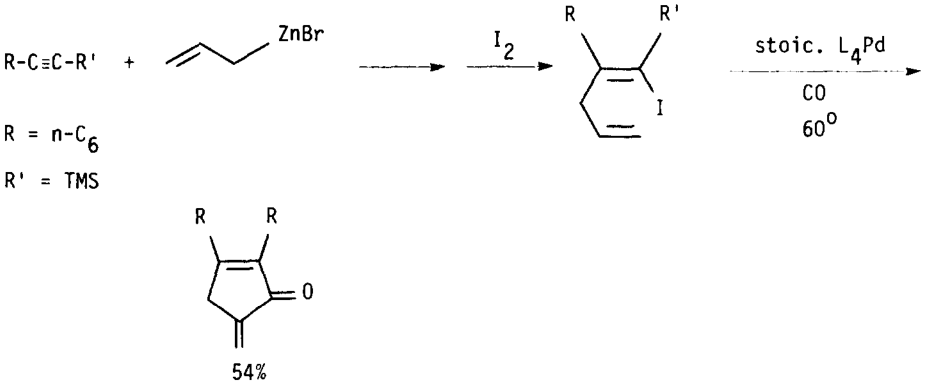
New access to conjugated dienes via carbocupration of alkynes has recently been reviewed (37 references) [112]. Vinyl cuprates were made by the addition of alkyl copper complexes to alkynes. These materials were converted to a number of useful organic compounds (equation 124) [113]. Vinyl tin reagents were prepared by the addition of tin-copper species to alkynes (equation 125) [114]. The zirconium-promoted carbometallation of heterofunctionalized acetylenes was the subject of a dissertation [115]. Vinyl iodides resulted from the addition of allyl zinc bromide to alkynes followed by treatment with iodine (equation 126) [116]. The resulting product was converted to an α-methylene lactone by reaction with carbon monoxide and a palladium(0) catalyst. Zirconium complexes catalyzed the addition of dialkylzinc reagents to alkynes (equation 127) [117]. Allenic iodides and alkynes were coupled by reaction with palladium(0) and copper(I) complexes (equation 128) [118]. Palladium(0) also catalyzed the addition of hexamethylditin to alkynes (equation 129) [119].





(125)

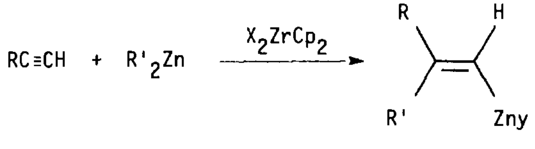
(125)



$R = n\text{-}C_6$

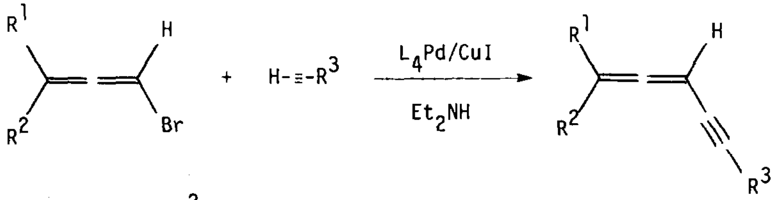
$R' = TMS$

54%



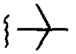
high yield

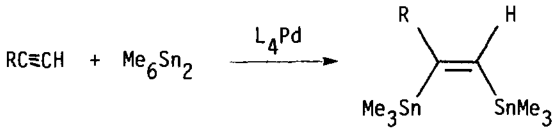
(127)



(128)

$R^1 = Me, n\text{-}Pr \qquad R^2 = H, Me$

$R^3 = Ph$, cyclo C_6, CH_2OH, $n\text{-}C_3COH$,  NEt_2, TMS, $(CH_2)_8OAc$

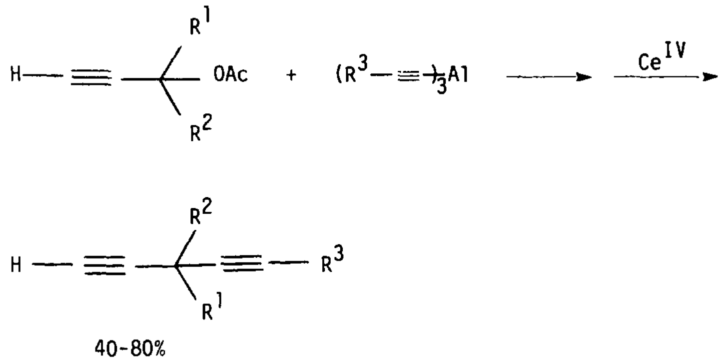


(129)

R = H, 60%; n-Bu, 30%; Ph, 42%; $PhCH_2$, 43%; $MeOCH_2$, 70%

Cobalt complexes of propargyl acetates were alkylated by aluminum acetylides (equation 130) [120], and by thiophene (equation 131) [121]. The latter reaction was used to synthesize intermediates for prostaglandin syntheses. Norbornene and alkynes condensed when treated with palladium catalysts and ammonium formate (equation 132) [122]. Iron(III) chloride coupled trimethylsilyl-stannyl, germanyl acetylenes to produce diynes [123].

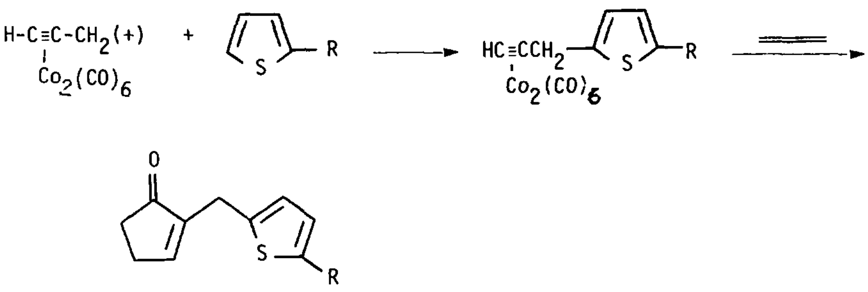
(130)

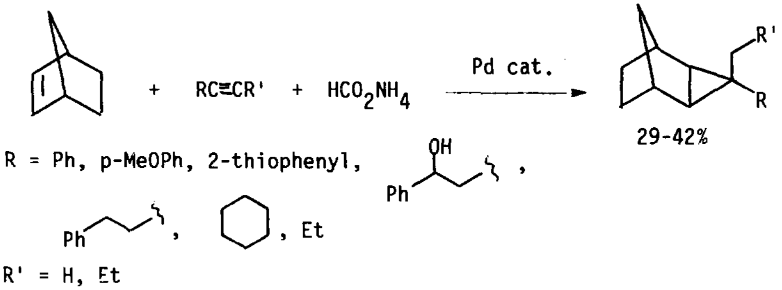


40-80%

R^1 = H, Me R^2 = H, Ph, Me R^3 = n-C_4, n-C_6

(131)





(132)

29-42%

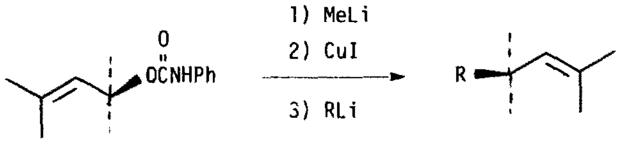
R = Ph, p-MeOPh, 2-thiophenyl, , , , Et

R' = H, Et

7. Alkylation of Allyl and Propargyl Alcohols and Acetates

Allyl carbamates underwent an S_N2' alkylation when treated with organocopper reagents (equation 133) [124]. The regiochemistry of the alkylation of allylic acetates by organocuprates was studied in detail (equations 134-137) [125]. The stereochemistry of this process was shown to be inversion for α-alkylation, whereas γ-alkylation went with "excess antibonding" (?). Allyl silanes were made stereospecifically by the reaction of allylic acetates with silyl cuprates (equations 138 and

139) [127]. S_N2' allylic displacements by organocopper reagents were used in the synthesis of steroids (equations 140 and 141) [128]. Reformatsky reagents alkylated allylic acetates in the presence of copper(II) acetylacetonate (equation 142) [129]. The influence of solvents and substitution patterns on the regiochemistry of the copper catalyzed addition of Grignard reagents to allyl sulfonates was studied [130]. Attack at the less substituted allylic terminus. This chemistry was used to make polyunsaturated alcohols (equation 143) [131].



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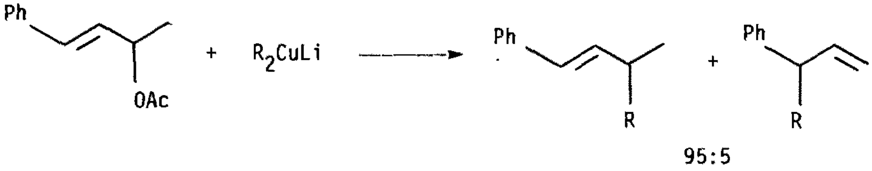

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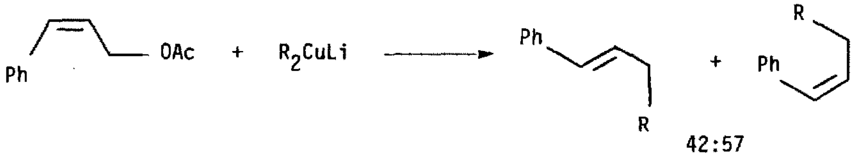

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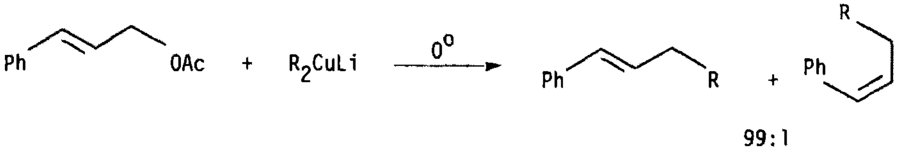

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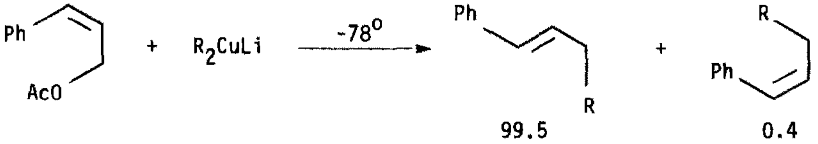
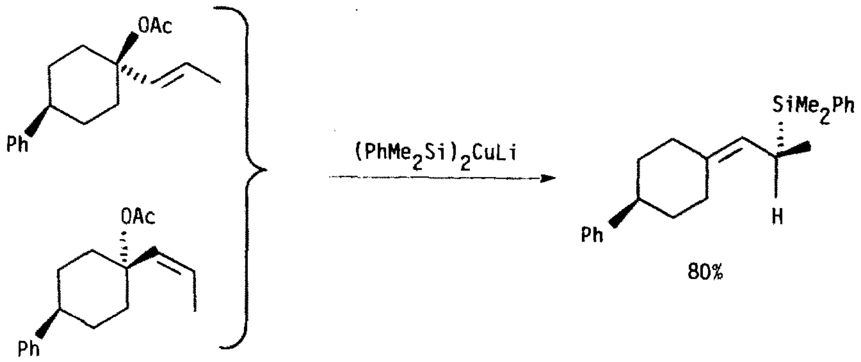
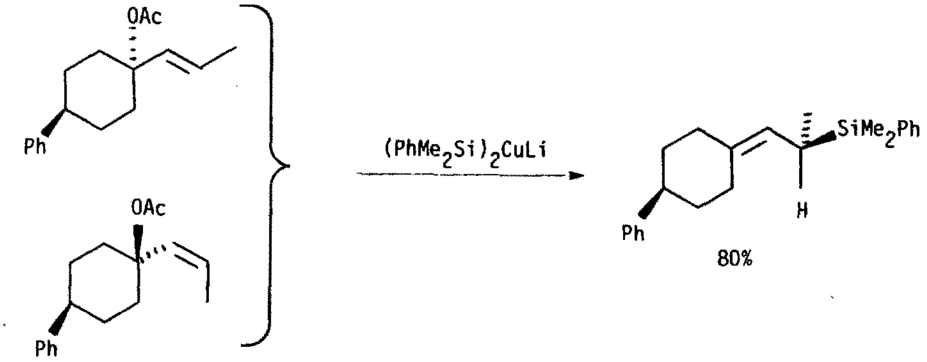


(137)



(138)



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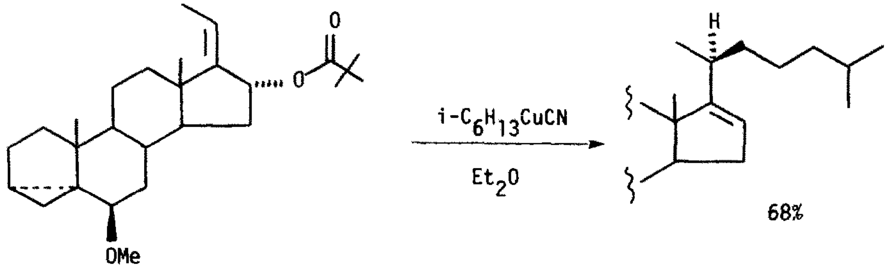

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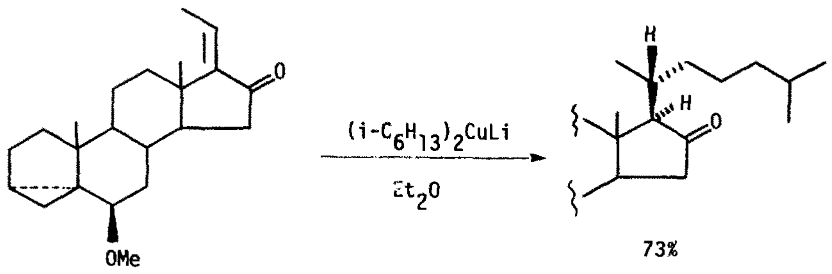

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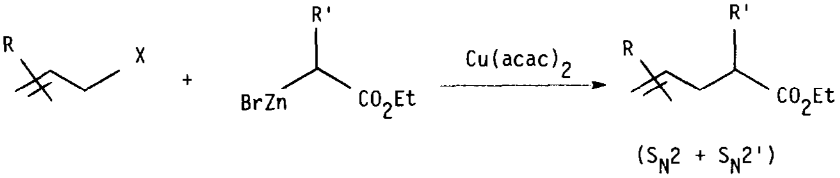
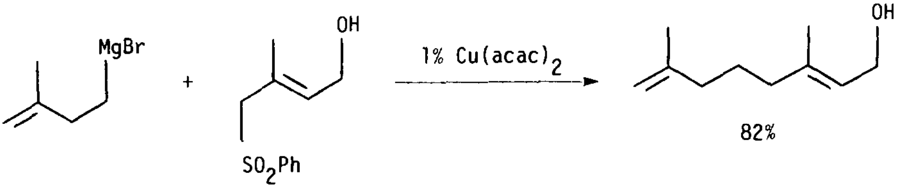
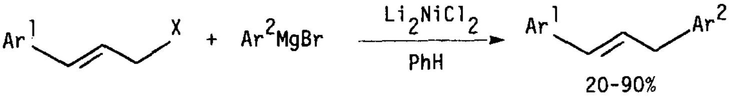


(142)



(143)

Nickel(II) phosphine complexes catalyzed the reaction of aryl Grignard reagents with a wide variety of allylic substrates (equation 144) [132]. With chiral phosphine ligands, allyl phenyl ethers underwent alkylation with substantial asymmetric induction (equation 145) [133]. Nickel(II) phosphine complexes also catalyzed the alkylation of allylic acetates (equations 146 and 147) [134].

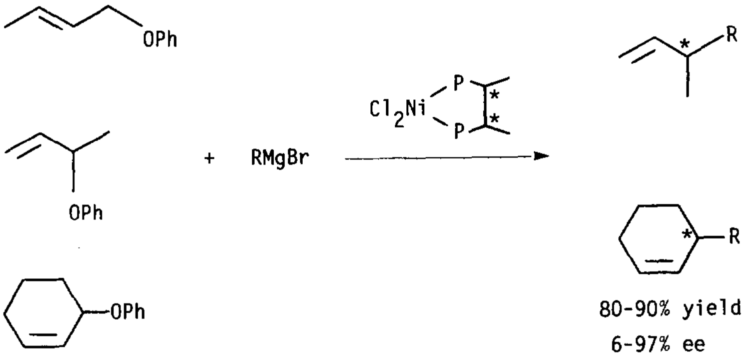


(144)

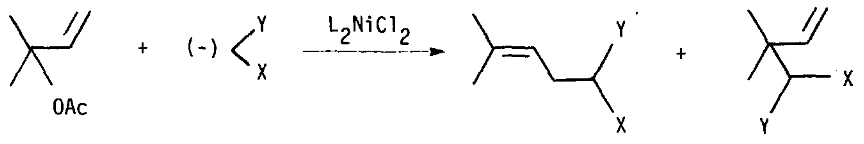
Ar^1 = H, Ph

X = OH, OEt, OMe, SH, SMe, SEt, 1-indolyl

Ar^2 = 4-TMSOPh, 4-MeOPh, 3,4-$(MeO)_2$Ph, 2,4-$(MeO)_2$Ph, 2,3,4-$(MeO)_3$Ph

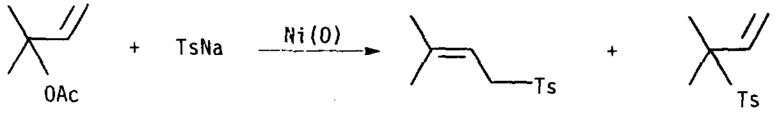


(145)



good yields

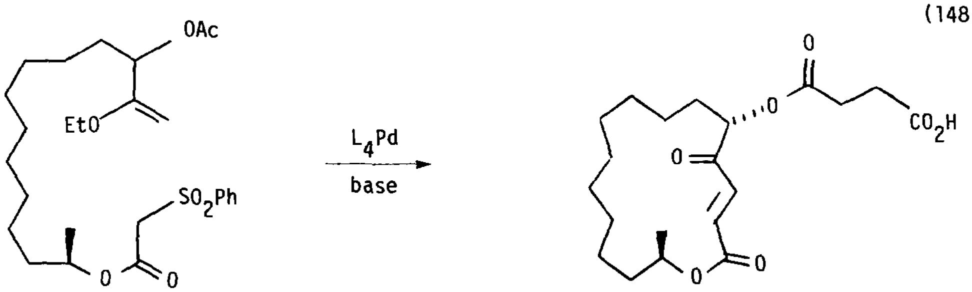
(146)



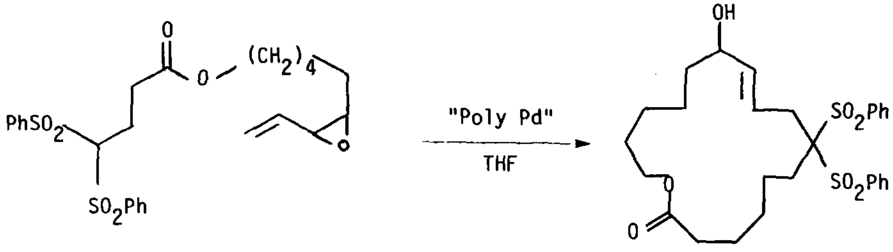
(147)

Macrocycles were synthesized using the palladium catalyzed alkylation of allylic acetates as the key ring-forming step (equation 148) [135], (equations 149 and 150) [136], (equations 151 and 152) [137], (equation 153) [138]. Palladium(0) complexes also catalyzed the reaction of allyl acetates with alkyl tin reagents (equation 154) [139]. Finally, the reaction of allyl acetates with enolates, catalyzed by palladium(0) complexes, was studied in detail. Of all the enolates studied, only zinc and boron enolates were efficient (equation 155) [140].

(148)

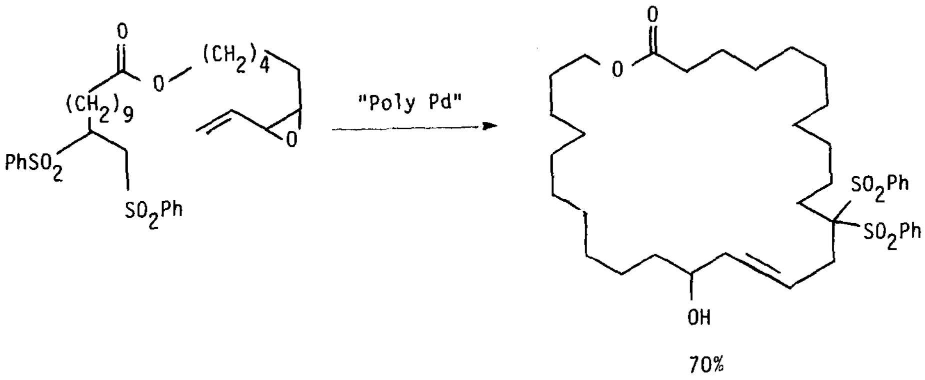


A 26711B 84%

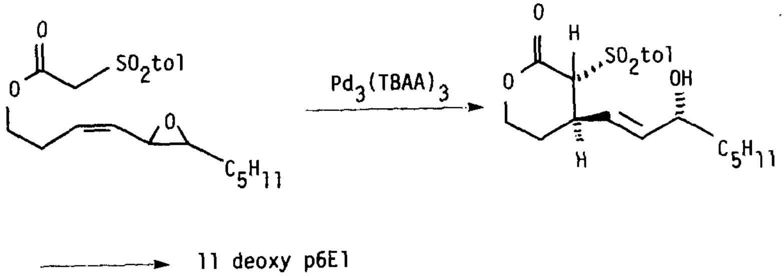


(149)

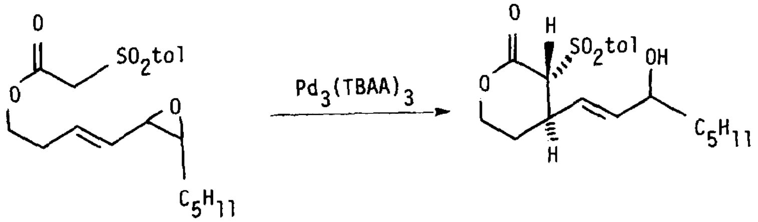
74%



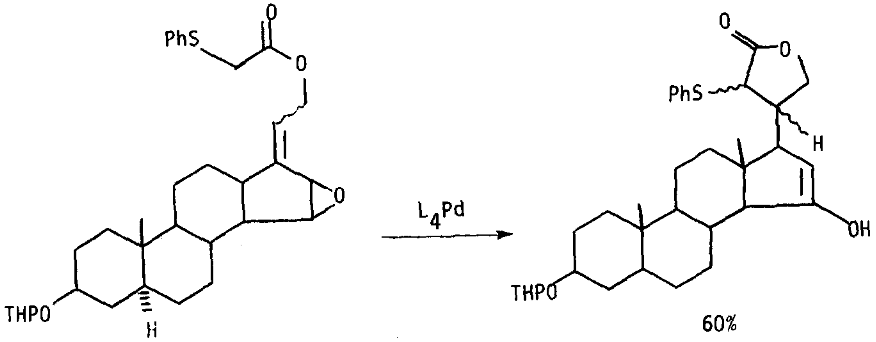
(150)



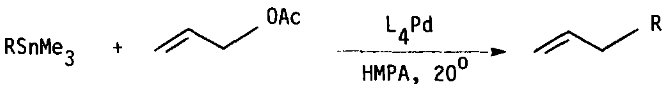
(151)



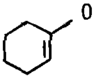
(152)

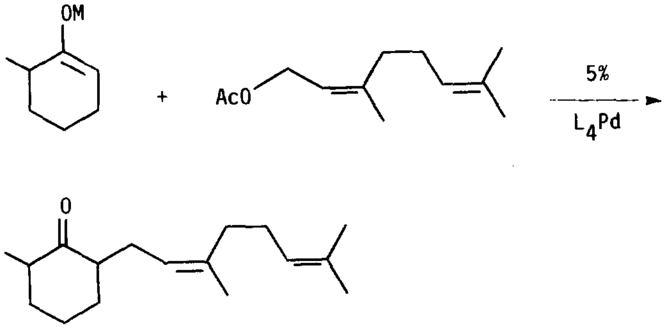


(153)



(154)

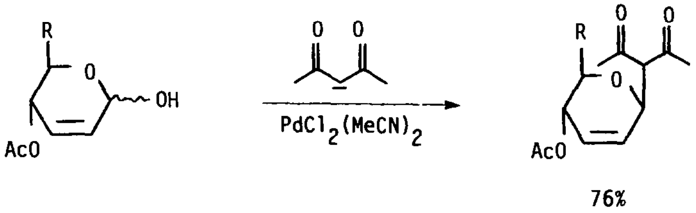
R = *allyl, vinyl, Ar,*  , *$PhCHCO_2Et$*



(155)

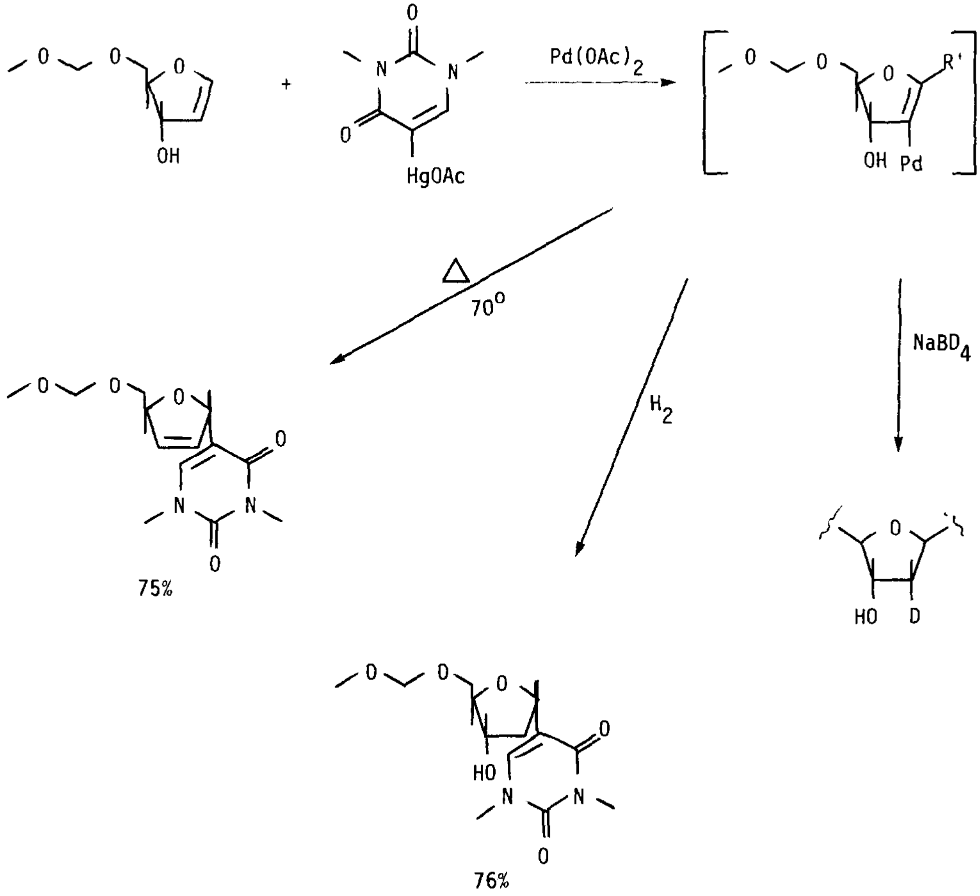
M = K, Li, BEt_3/K, BEt_3/Li, MgCl, Me_2Al, Me_3Al/Li, $AlMe_3/K$, TMS, Bu_3SN, CP_2TiCl

Allylic acetates related to sugars were alkylated by aceto-acetate at the hemiacetal carbon in the presence of palladium(II) catalyst (equation 156) [141]. Elimination of Pd-O was claimed in a palladium-assisted coupling of an aryl mercuric halide with a cyclic allylic alcohol (equation 157) [142].



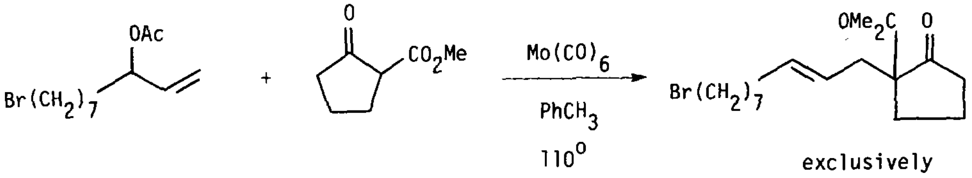
(156)

(157)



Molybdenum complexes also catalyzed the reactions of allylic acetates with carbanions, with regiochemical preferences different from those observed with palladium catalysts (equations 158 and 159) [143]. The regiochemistry strongly depended on the substitution pattern of the allylic acetate (equation 160) [144]. Palladium complexes catalyzed reactions of these same substituted allylic acetates (equations 161-163) [145].

(158)



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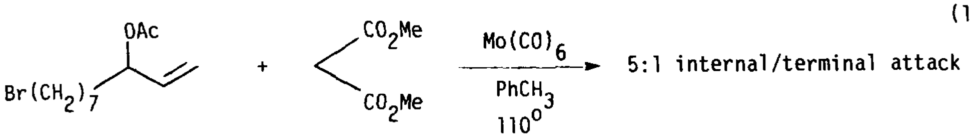
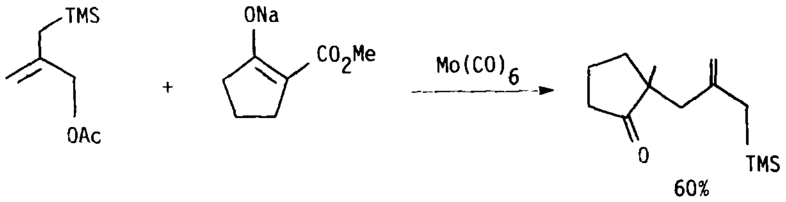
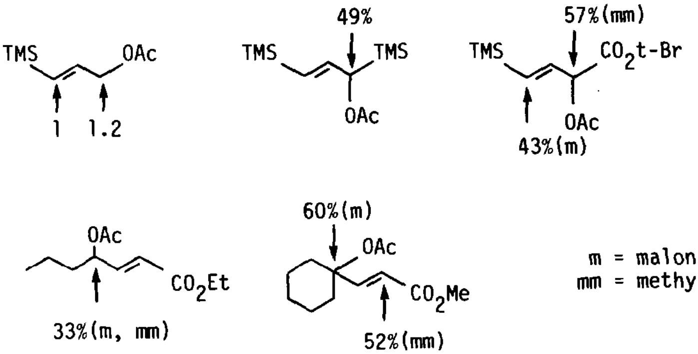


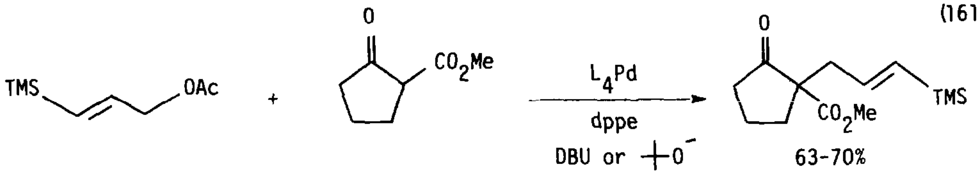


(160)

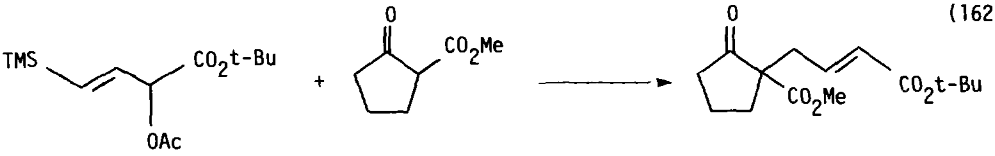


m = malonate
mm = methylmalonate

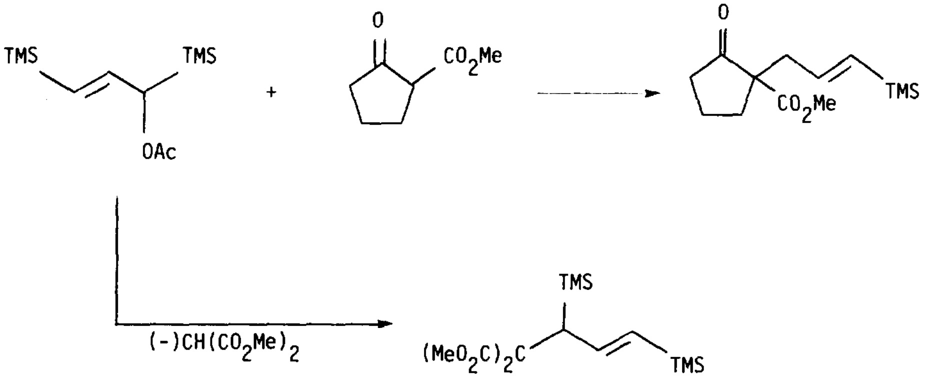
(161)



(162)

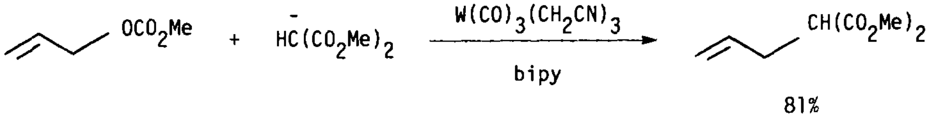


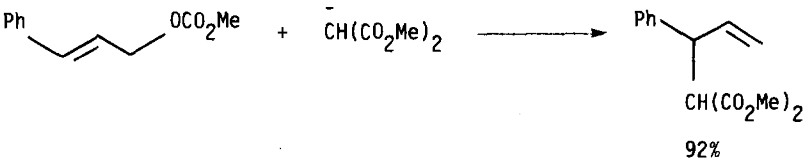
(163)



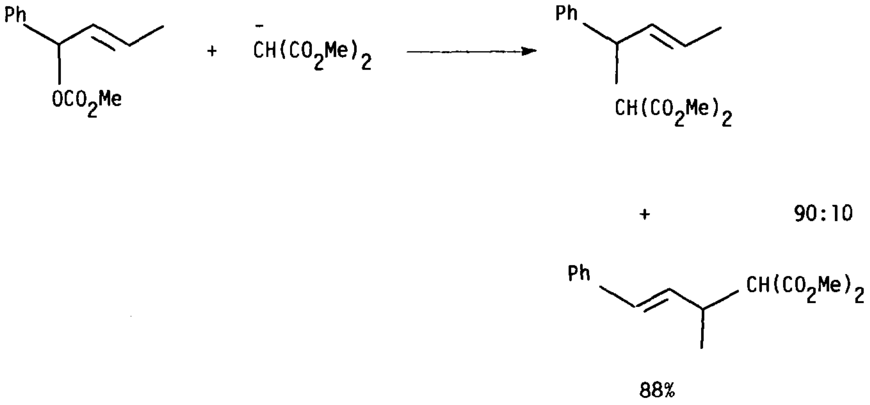
Tungsten compounds also catalyzed allylic alkylation of allyl acetates and carbonates and directed alkylation to the most substituted allyl terminus (equations 164-168) [146]. In a careful study of the stereochemistry of palladium catalyzed allylic alkylation, both the oxidative addition step and the nucleophilic attack step proceeded with inversion (equation 169) [147]. Alkyl nitronates alkylated allyl acetates in the presence of a palladium(0) catalyst [148].

(164)



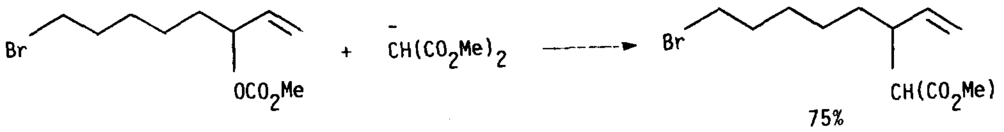


(165)

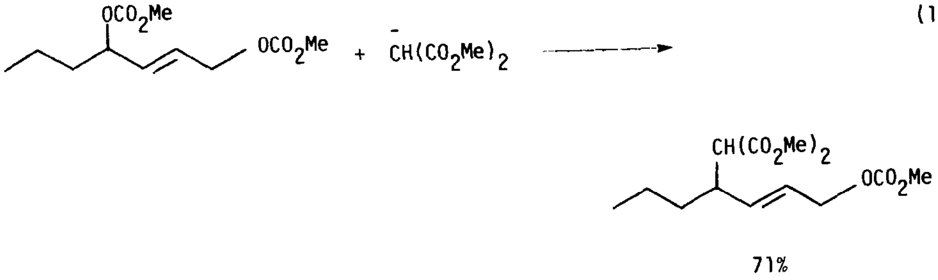


(166)

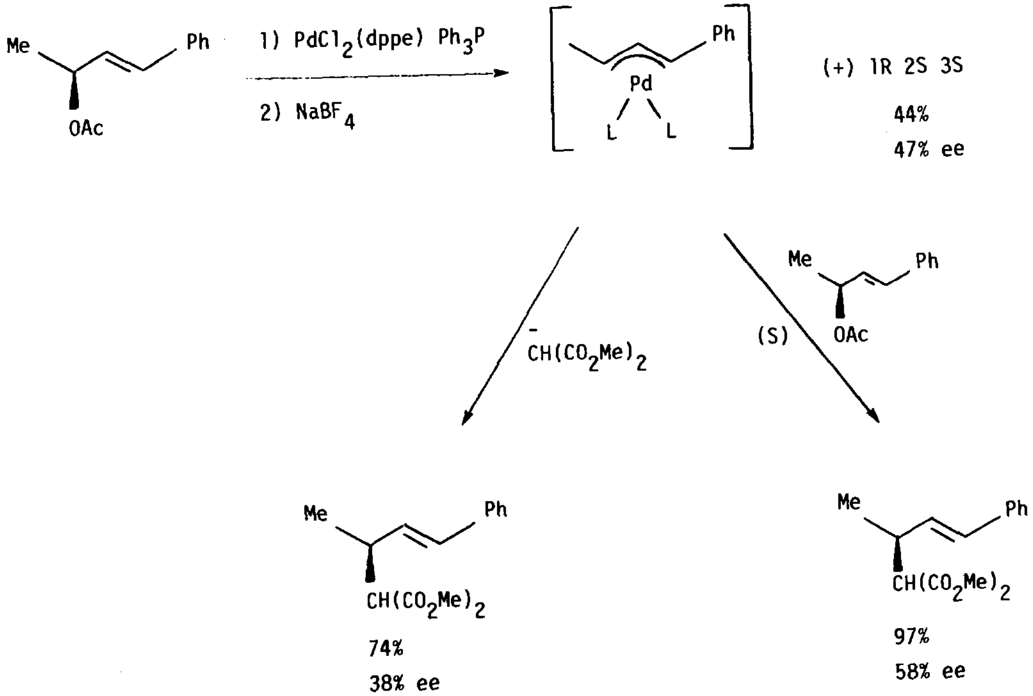
(167)


Br
OCO2Me
+
CH(CO2Me)2
Br
CH(CO2Me)
75%

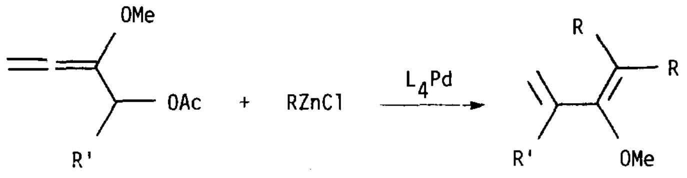
(168)


OCO2Me
OCO2Me
+
CH(CO2Me)2
CH(CO2Me)2
OCO2Me
71%

(169)

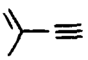

Me
Ph
OAc
1) PdCl2(dppe) Ph3P
2) NaBF4
Ph
Pd
L
L
(+) 1R 2S 3S
44%
47% ee
CH(CO2Me)2
Me
Ph
(S)
OAc
Me
Ph
CH(CO2Me)2
74%
38% ee
Me
Ph
CH(CO2Me)2
97%
58% ee

Allenic acetates were alkylated by organozinc reagents in the presence of palladium catalysts (equation 170) [149], as were propargyl systems (equation 171) [150], (equations 172 and 173) [151]. Palladium catalyzed the reaction of allenic tin reagents with allyl acetates (Equation 174) [152]. Propargyl systems react with tin cuprates to produce allenic tin reagents (equation 175) [153]. "Reactions of Propargylic Substrates with Organocopper Species, Synthetic Aspects" was the title of a dissertation [154].

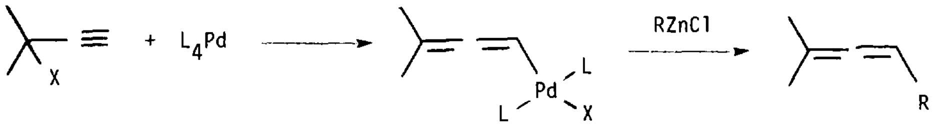


(170)

50-95%

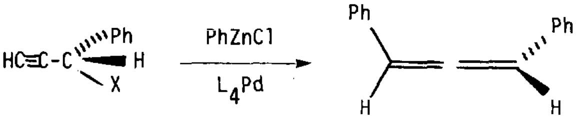
R = CH_2CH-, TMS-≡, Ph, t-BuC≡C≡C, 
R' = H, Me

(171)



isolated

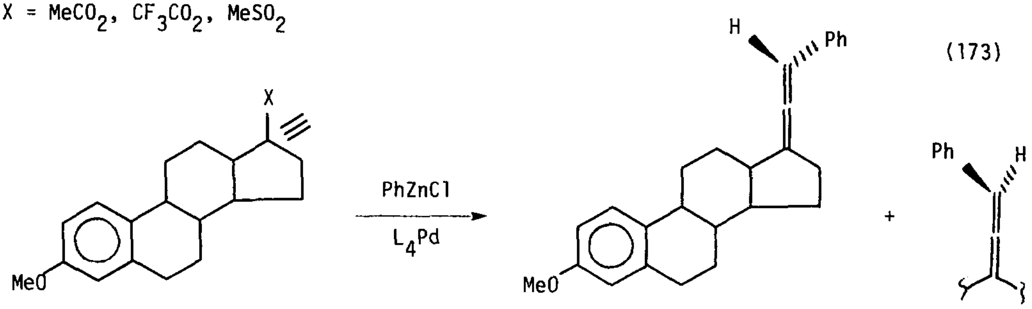
R = Ph, TMS
"quantitative"



(172)

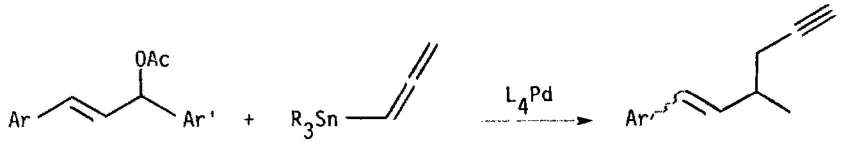
(R)

X = $MeCO_2$, CF_3CO_2, $MeSO_2$



(173)

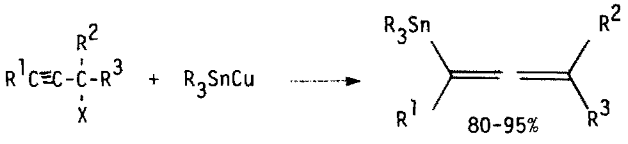
98:2



(174)

Ar = Ph

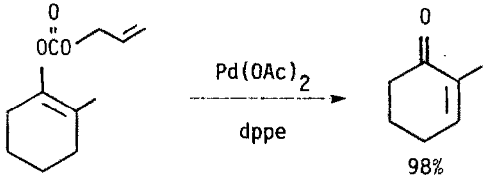
Ar' = 4-FPh, 4-BrPh, 4-MePh



(175)

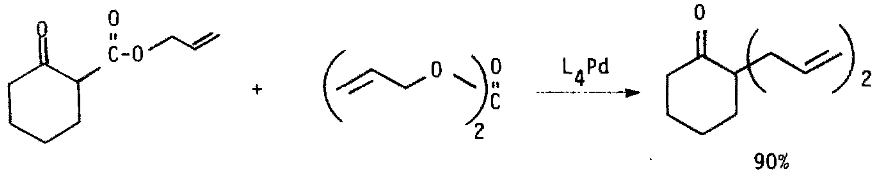
R^1 = H, Me; R^2 = H, Me,$(CH_2)_4$,$(CH_2)_5$; R^3 = H, Me, Ph, Pr, t-Bu

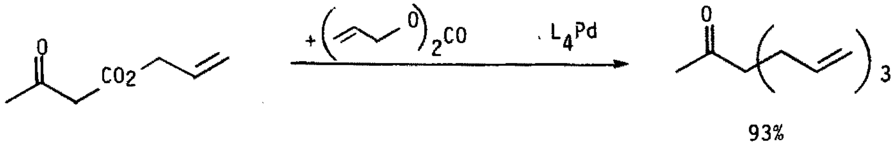
Allylic carbonates underwent a number of palladium catalyzed reactions. Allyl vinyl carbonates underwent a decarboxylation-oxidation process when treated with palladium(II) acetate and a *bis* phosphine (equation 176) [155]. Diallyl carbonates allylated allylic acetates of β-ketoesters (equations 177-180) [156], while methyl allyl carbonate allylated enol acetates (equations 181-185) [157] and trimethylsilylenol ethers (equation 186) [158] (equation 187) [159]. In the presence of tributyltin methoxide, enol acetates were converted to conjugate enones (equation 188) [160].



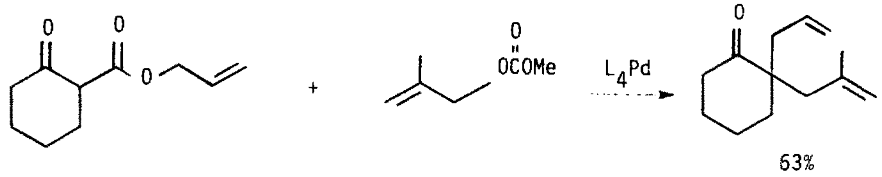
(176)

(177)





(178)



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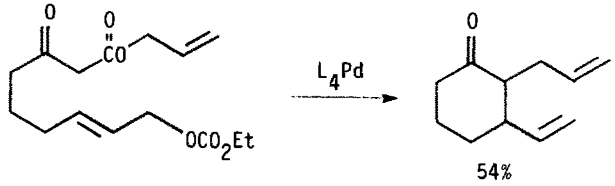
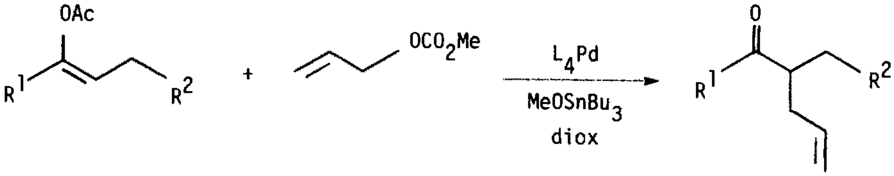


(180)



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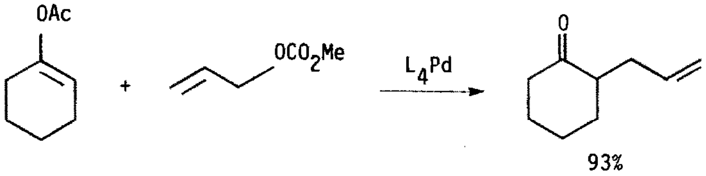
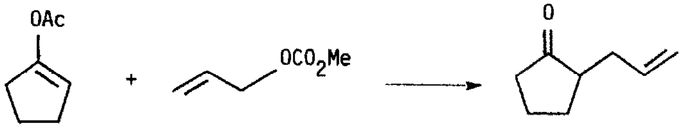
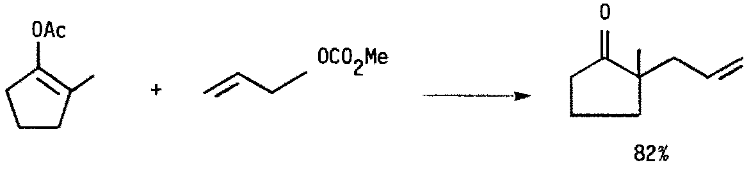


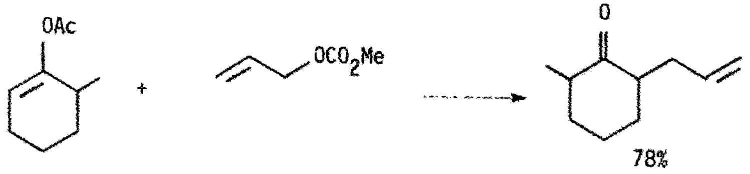
(182)



(183)

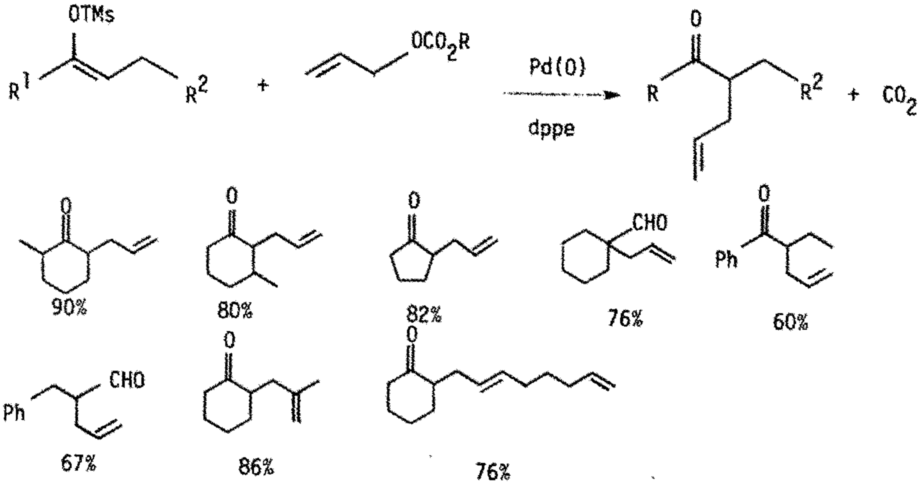


(184)

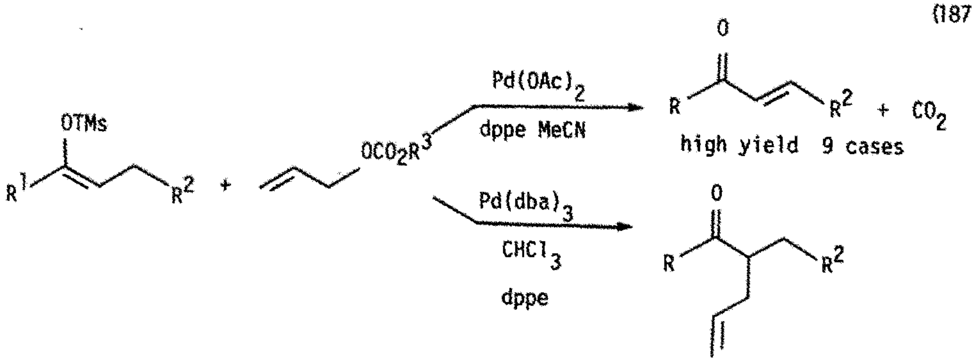


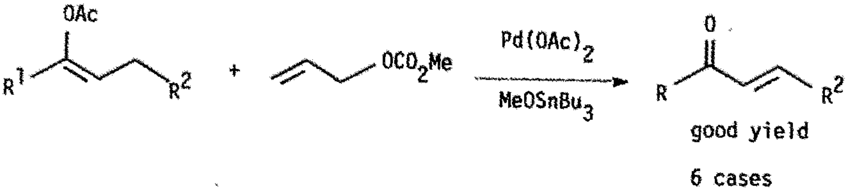
(185)

(186)



(187)

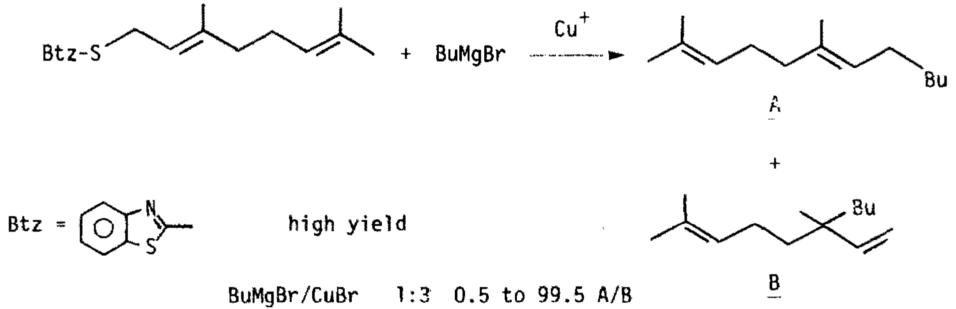




(188)

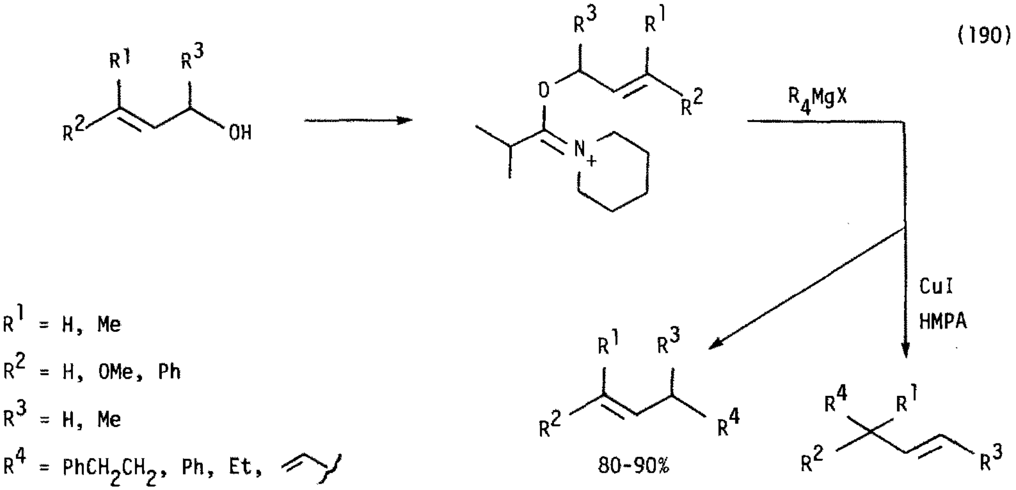
Allylsulfur derivatives underwent alkylation by Grignard reagents in the presence of copper salts (equation 189) [161], as did allyl amidates (equation 190) [162]. Chromium complexes of benzyl acetates reacted with silylenol ethers in the presence of zinc chloride (equations 191 and 192) [163]. Enynes were alkylated by trimethyl aluminum in the presence of titanium(IV) chloride (equation 193) [164].

(189)



BuMgBr/CuBr	1:3	0.5 to 99.5 A/B
	4:1	99:1 A/B

(190)



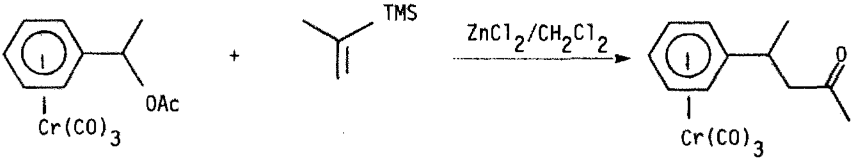
R^1 = H, Me

R^2 = H, OMe, Ph

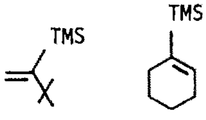
R^3 = H, Me

R^4 = $PhCH_2CH_2$, Ph, Et,

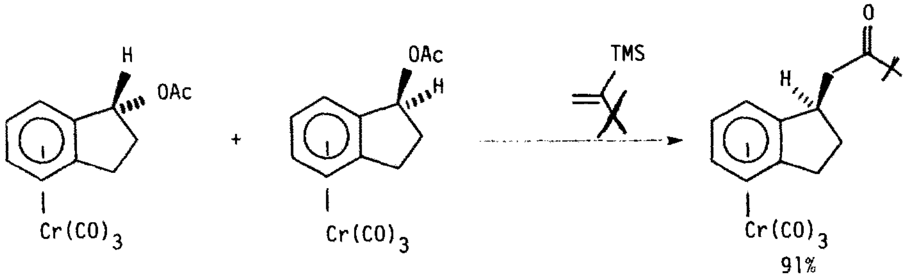
(191)



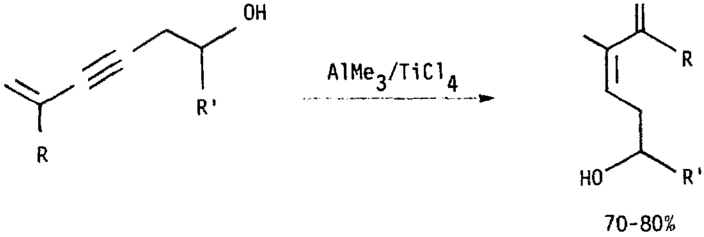
84%



82% 68%



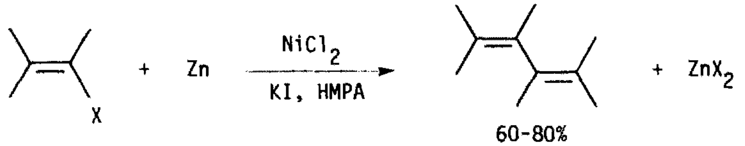
(192)



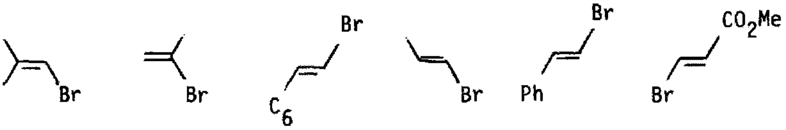
(193)

8. Coupling Reactions

Reductive coupling of halides by low valent transition metal remained a popular pursuit. Vinyl halides were coupled to 1,3-dienes by treatment with nickel(II) chloride and zinc (equation 194) [165]. Aryl halides were coupled to biaryls by nickel powder produced by the reduction of nickel(II) halides with lithium naphthalenide (equation 195) [166]. Similarly reactive nickel powder was produced electrochemically (equations 196 and 197) [167]. Biallyls were produced by the reductive coupling of allylic halides with cobalt(I) complexes (equation 198) [168]. The same reaction with butanoyl chloride as a substrate produced modest yields of a mixture of all possible coupling and deacylation products [169].

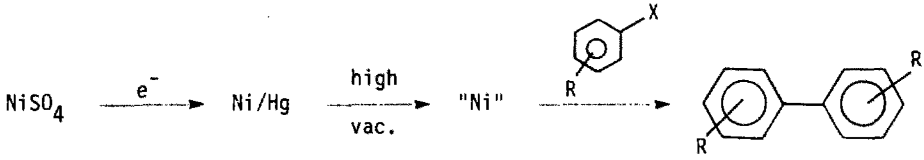


(194)



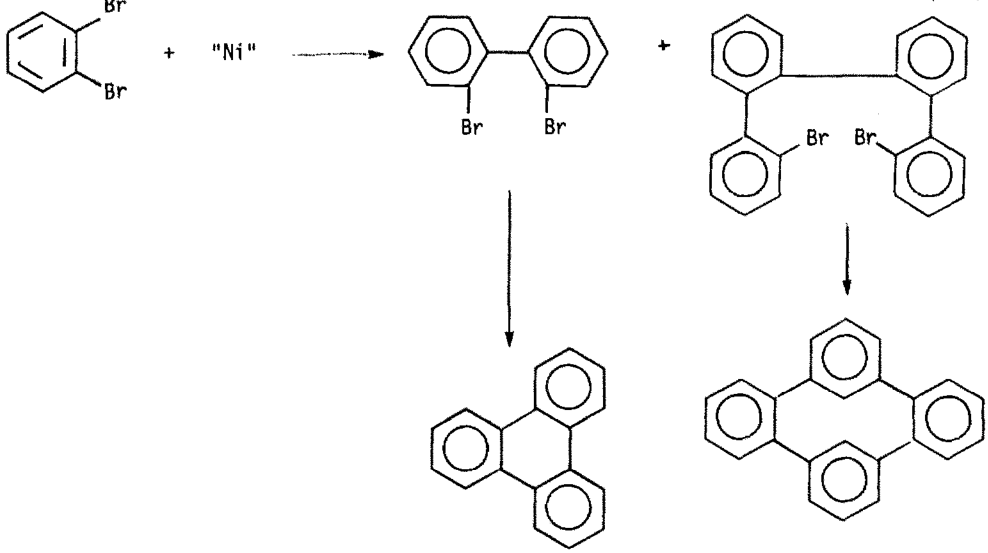
NiX_2 + Li/Naphth $\longrightarrow$ "Ni" $\xrightarrow{ArX}$ Ar-Ar (195)

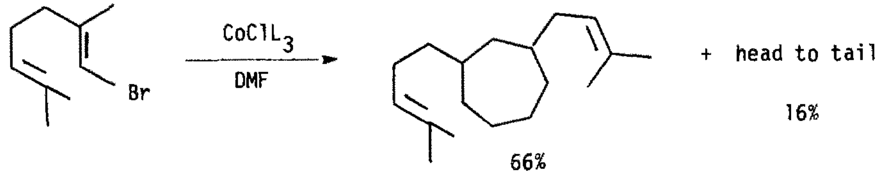
20 cases



(196)

(197)

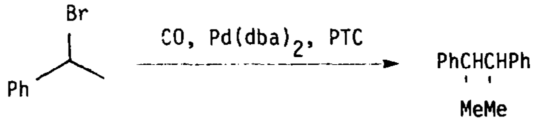




(198)

farnesyl, geranyl, neryl also couple

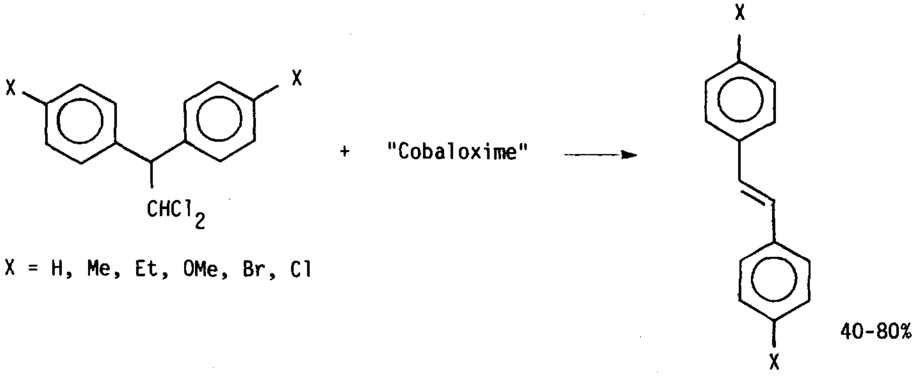
Aryl halides coupled to aryl hydrazones in the presence of palladium(II) chloride to all possible coupling products [170]. α,α-Dichlorotoluene was coupled to dichlorobibenzyl by palladium(0) and hexamethyldisilane [171]. α-Phenethyl bromide dimeriz when treated with palladium dibenzylidene acetone under phase transfer conditions (equation 199) [172]. Diaryl iodonium salts coupled to diaryls when treated with zinc and a palladium catalyst (equation 200) [173]. Dihalides coupled to olefins when treated with cobaloxime (equation 201) [174]. 1,3-Dienes couple to cyclooctadienes when treated with nickel(0) complexes (equation 202) [175].



(199)

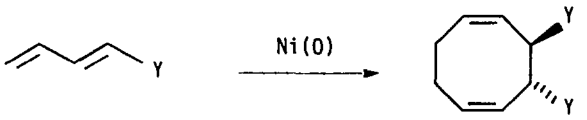
$$2\ [ArIAr]^{+}X^{-} + Zn \xrightarrow[\text{THF}\ 25^{0}]{\text{Pd cat.}} \underset{50\text{-}90\%}{ArAr} + 2\ ArI + ZnX_2 \qquad (200)$$

Ar = Ph, p-MePh, 4 t-BuPh, 4 MeOPh, 4 ClPh, 3 NO_2Ph



(201)

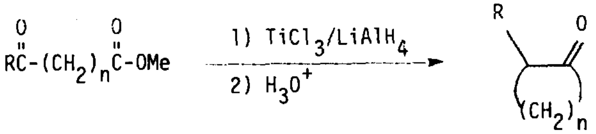
X = H, Me, Et, OMe, Br, Cl



(202)

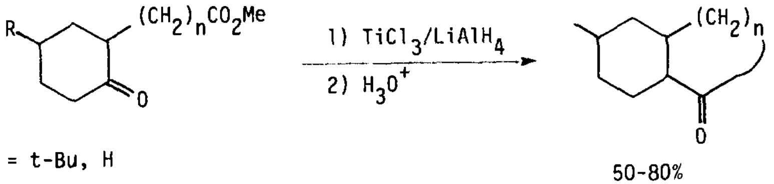
Y = TMS 90%
Y = CO_2Me 70%
Y = OAc NR

The topic "Ti induced dicarbonyl coupling reactions" has been reviewed (29 references) [176]. Ketoester cyclized to cyclic ketones when treated with the reagent resulting from the reaction of titanium(III) chloride with lithium aluminum hydride (equations 203 and 204) [177]. Titanium(III) salts coupled ketones with acetyl pyridines (equation 205) [178]. Cyclobutenes were produced by the titanium(III) chloride zinc-copper couple coupling of diketones (equation 206) [179]. Aldehydes reductively coupled when treated with iron carbonyl anions (equation 207) [180]. Samarium iodide coupled ketones to diols (equation 208) [181]. Aldehydes disproportionated when treated with rhodium(I) hydrides (equation 209) [182].



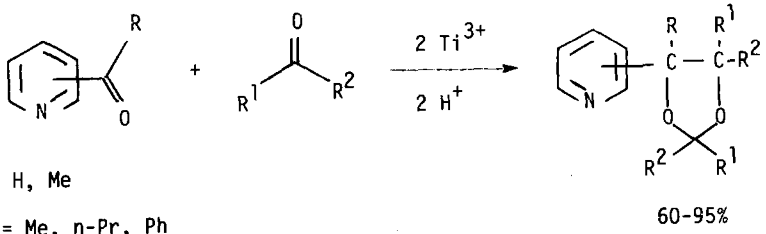
(203)

R = Me n = 8 50%
R = Et n = 9 45%
R = Et n = 10 63%
R = Me n = 11 60%



(204)

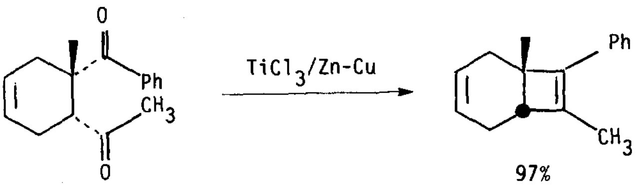
R = t-Bu, H
n = 1, 2, 3, 4, 5, 6, 11



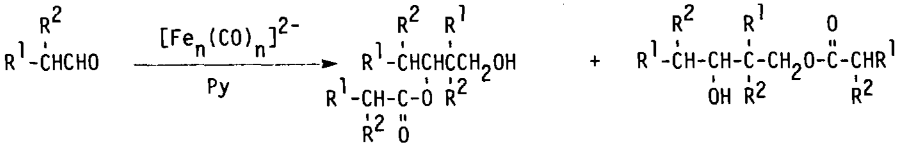
(205)

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

$-(CH_2)_4-$, $-(CH_2)_5-$



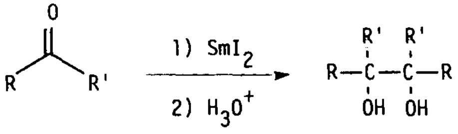
(206)



50-90% (207)

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

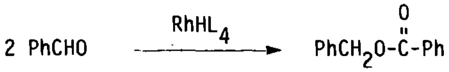
R^2 = H, Me



85-95% (208)

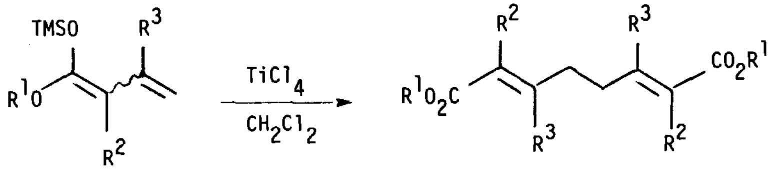
R = H, Me

R' = Ph, p-NO_2Ph, 4-CNPh, 4-HO_2CPh, 4-MeOPh, 4-Me_2NPh, mesityl,  , n-C_6

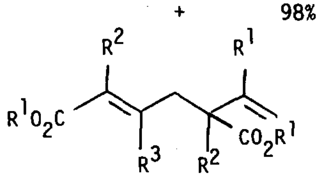


$$2\ PhCHO \xrightarrow{RhHL_4} PhCH_2O\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph \qquad (209)$$

Trimethylsilylenol ethers coupled when treated with titanium(IV) chloride (equation 210) [183]. Cyclopropyl trimethylsilylethers dimerized when treated with copper(II) tetrafluoroborate (equation 211) [184].



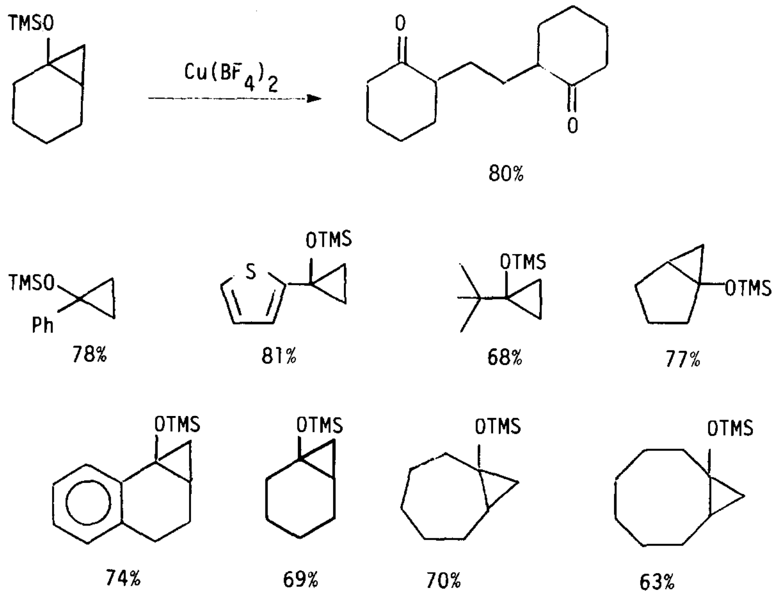
\+ 98% (210)



R^1 = Me

R^2 = Me, H

R^3 = Me, H, TMS, $TMSCH_2$, TMSO

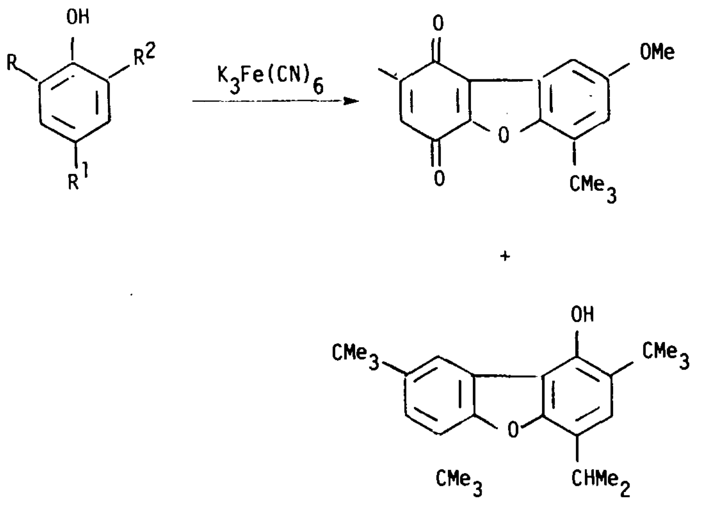


(211)

Arenes coupled to biaryls when treated with thallium trifluoroacetate and catalytic amounts of palladium(II) acetate (equation 212) [185][186]. Thallated aromatics coupled to biaryls when treated with 0.1 equivalent of lithium tetrachloropalladate [187]. Potassium hexacyanoferrate coupled halophenols to dibenzofurans (equation 213) [188]. Copper complexes of poly (amido amines) oxidatively coupled 2,6-dimethylphenol [189], while macromolecular copper catalysts oxidatively coupled 2,6-di-t-butylphenol [190].

$$\text{ArH} \xrightarrow[\text{cat. Pd(OAc)}_2]{\text{Tl(TFa)}_3} \underset{52\text{-}99\%}{\text{Ar-Ar}} \qquad (212)$$

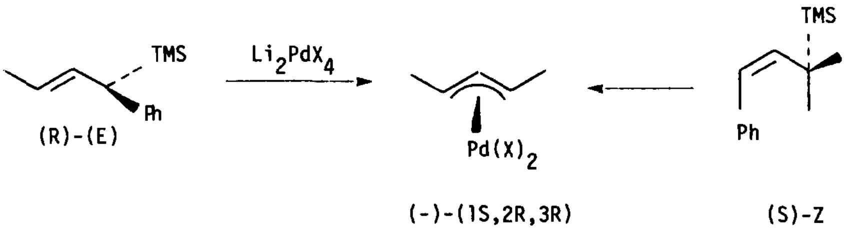
Ar = Ph, 4-MeOPh, EtPh, MePh, FPh, ClPh, BrPh



(213)

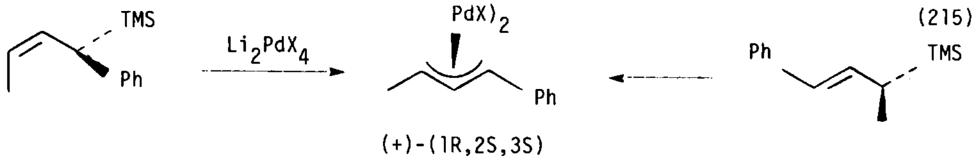
9. Alkylation of π-Allyl Complexes

Catalytic reactions containing π-allylpalladium complexes as intermediates has been reviewed (25 references) [191]. Alkyl trimethyl tin compounds reacted with π-allylpalladium complexes to result in alkylation of the allyl group [192]. Chiral allyl trimethylsilanes were converted to π-allylpalladium complexes with complete transfer of chirality (equations 214 and 215) [193]. Photolysis of π-allylpalladium chloride complexes in the presence of alkyl halides gave low yields of cross coupling (equation 216) [194]. Perillenal was synthesized by the reaction 3-bromomethyl furan with a π-allylnickel halide complex (equation 217) [195]. Chiral π-allyl molybdenum complexes underwent stereospecific attack by enamines (equation 218) [196]. Several new precursors to π-allylcobalt complexes have been developed (equations 219-221) [197].

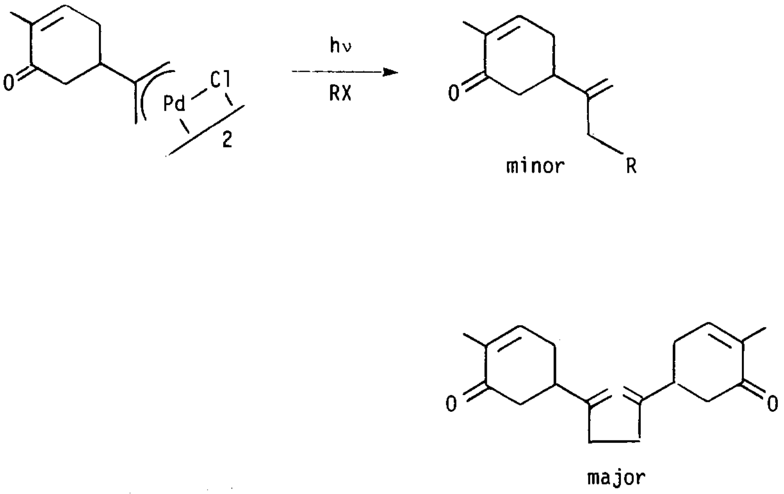


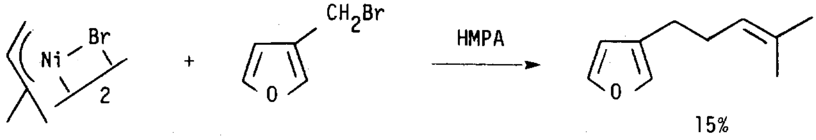
(214)

(215)



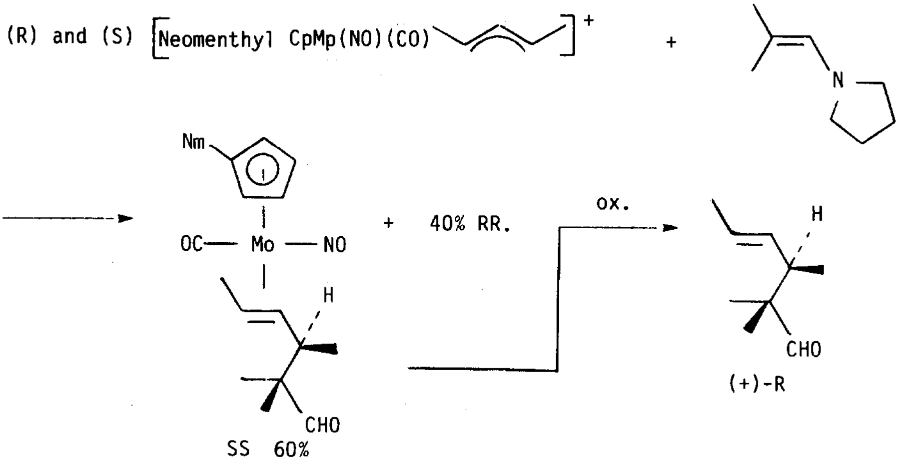
(216)

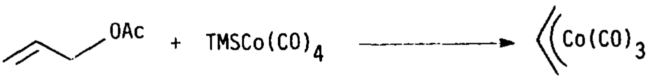




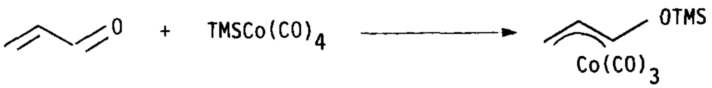
(217)

(218)

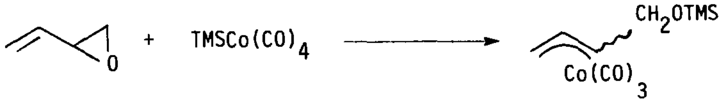




(219)



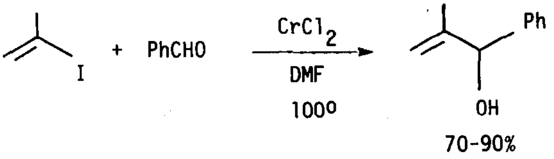
(220)



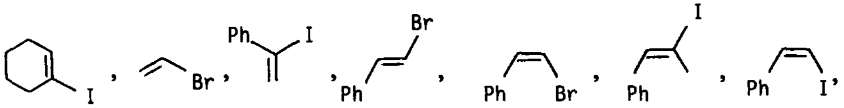
(221)

10. Alkylation of Carbonyl Compounds

Reduction of vinyl halides by chromium(II) in the presence of aldehydes produced allylic alcohols (equation 222). The reaction distinguished between aldehydes and ketones (equation 223) and nitriles (equation 224) [198]. Similar reduction of allylic halides by a chiral chromium(II) complex produced homoallylic alcohols with modest enantiomeric excess (equation 225) [199]. Manganese powder similarly coupled allylic halides to ketones (equation 226) [200]. Samarium(II) iodide coupled halides to aldehydes (equations 227 and 228) and ketones to themselves (equation 229) [201]. Intramolecular reductive coupling of a ketone with as ester was effected by titanium(III) chloride and lithium aluminum hydride (equation 230) [202].

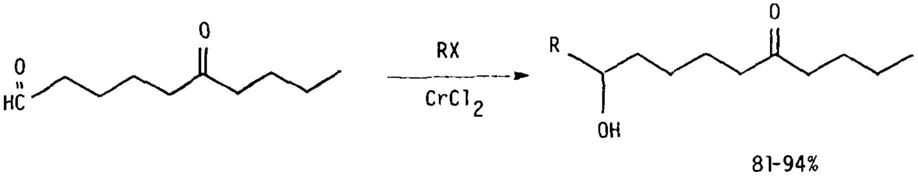


(222)

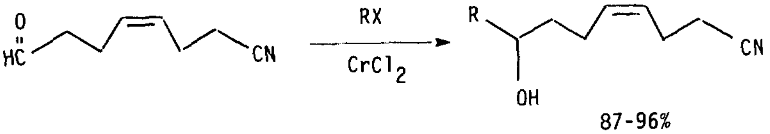


PhI work

PhCHO, n-C_8CHO, Me_2CHCHO work

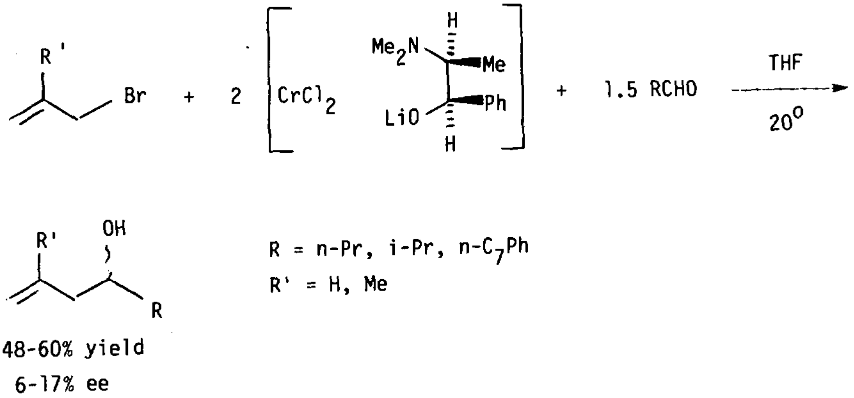


(223)



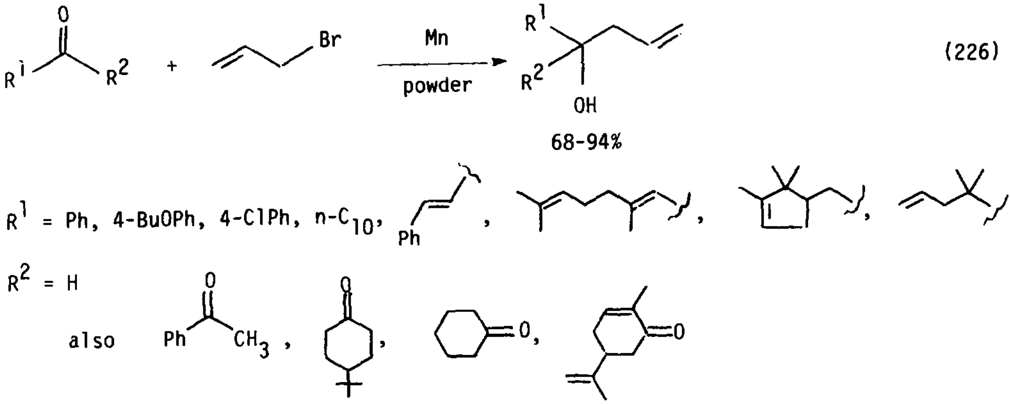
(224)

(225)

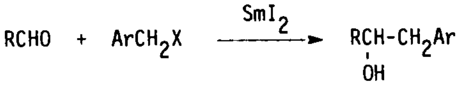


R = n-Pr, i-Pr, n-C_7Ph

R' = H, Me

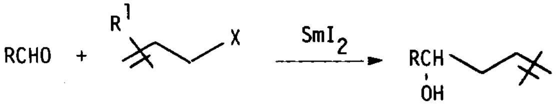


(226)

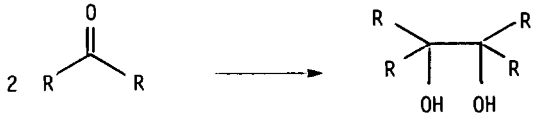


$$\mathrm{RCHO} + \mathrm{ArCH_2X} \xrightarrow{\mathrm{SmI_2}} \underset{\mathrm{OH}}{\mathrm{RCH}}\mathrm{-CH_2Ar}$$

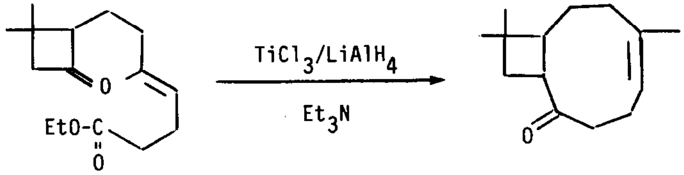
(227)



(228)

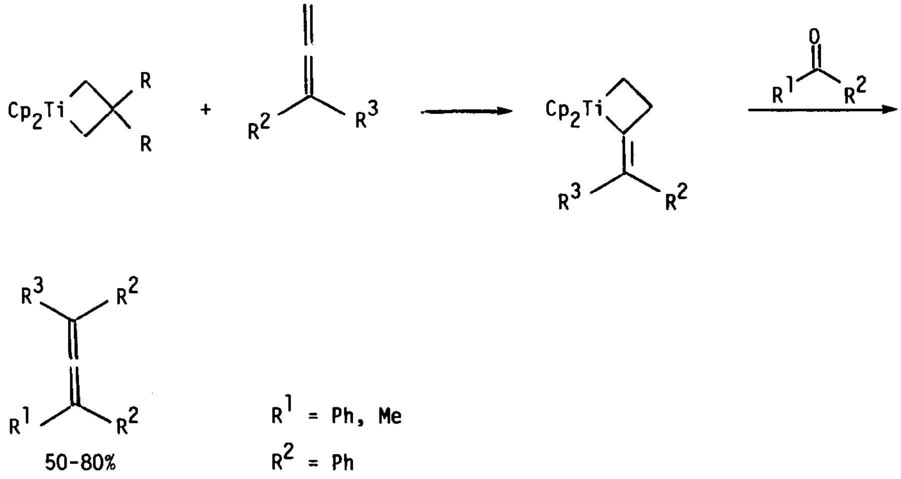


(229)



(230)

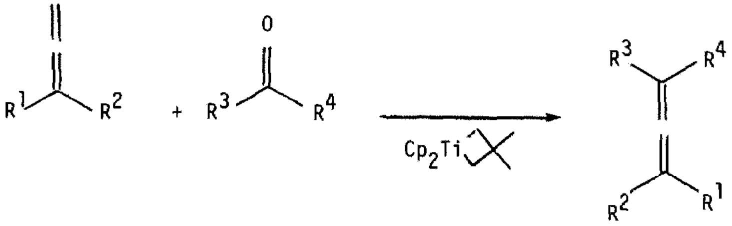
A titanium-based conversion of ketones to allenes has been developed (equations 231 and 232) [203]. A titanium methylene complex behaved similar to a Wittig reagent (equation 233) [204]. Aldehydes were alkylated by π-allyl titanium complexes (equations 234 and 235) [205].



(231)

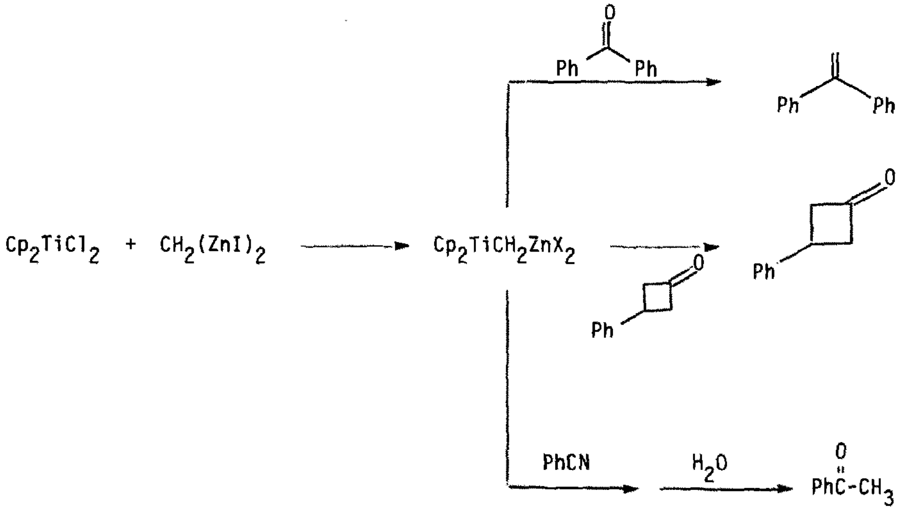
R^1 = Ph, Me

R^2 = Ph



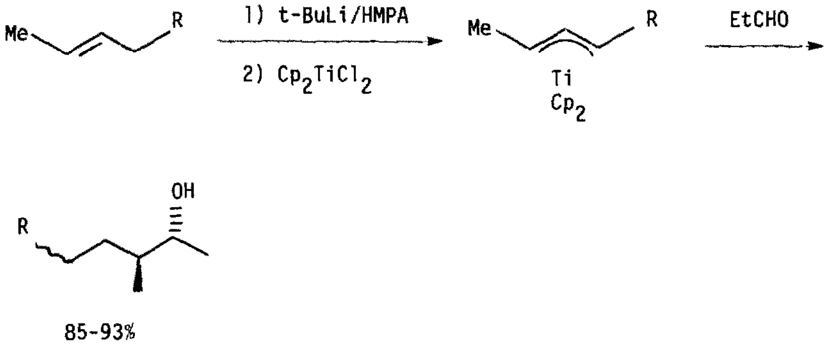
R1
R2
+
R3
R4
O
Cp2Ti
R3
R4
R2
R1

(232)



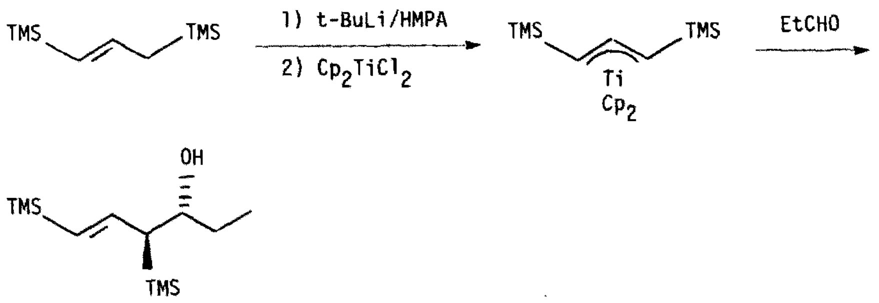
Cp2TiCl2 + CH2(ZnI)2
Cp2TiCH2ZnX2
Ph
Ph
O
Ph
Ph
Ph
O
Ph
O
PhCN
H2O
PhC(O)-CH3

(233)



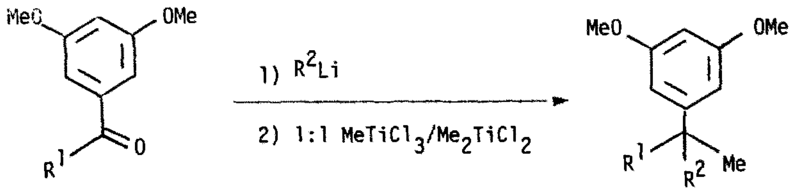
Me
R
1) t-BuLi/HMPA
2) Cp2TiCl2
Me
R
Ti
Cp2
EtCHO
R
OH
85-93%

(234)



(235)

Ketones were converted to tertiary alkyl groups by sequential treatment with an organolithium reagent, followed by an organotitanium reagent (equation 236) [206]. Alkyltitanium trichlorides alkylated β-alkoxy aldehydes with a high degree of stereoselectivity (equations 237 and 238) [207]. The stereochemistry could be reversed by changing the ligands on titanium (equations 239 and 240) [208]. Other titanium reagents also were reactive toward oxy ketones (equation 241) [209]. 1,3-Dienes were produced in the reaction of aldehydes with a titanium containing vinyl phosphine (equation 242) [210].

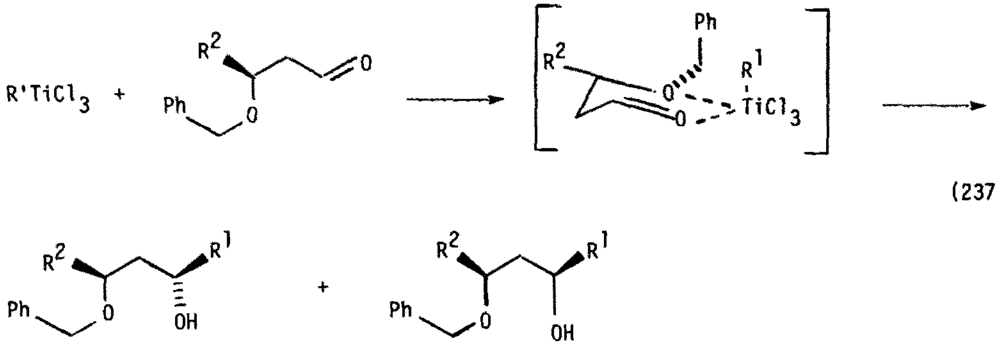


(236)

R^1 = Me, n-Bu, n-C_6

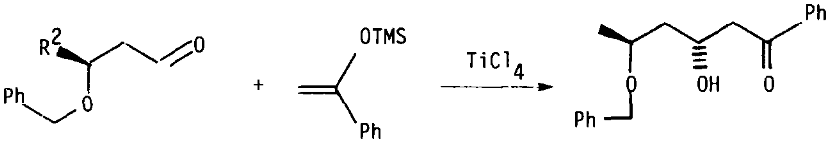
R^2 = Et, n-Bu, n-C_6, Me

70-90%



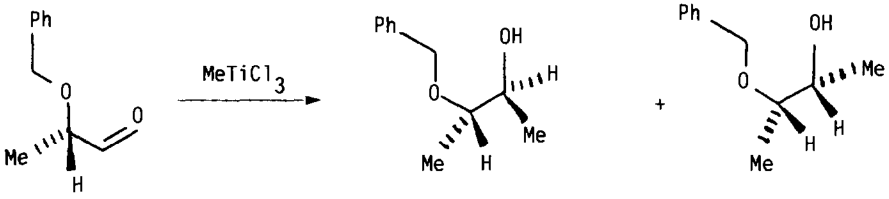
(237)

90:10 $R^1 = R^2 = Me$



(238)

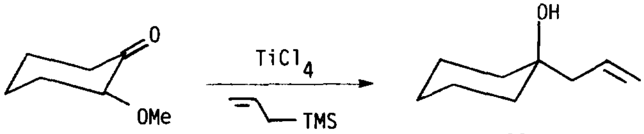
92:8 (other isomer)



(239)

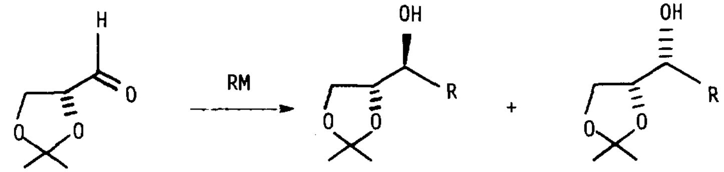
$\xrightarrow{\text{MeTi(O-i-Pr)}_3}$

92:8
8:92



(240)

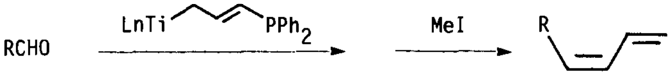
>99%



(241)

R = Ph, Me, n-Bu, allyl
M = Li, MgBr, Zn, Ti(O-i-Pr)$_3$

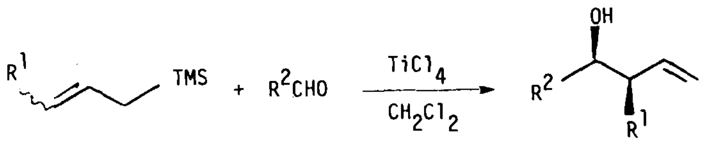
91;9 with Ti



(242)

76-89%
5:95 E:Z

Allyl silanes condensed with aldehydes in the presence of titanium(IV) chloride to give high erythro ratios of homoallylic alcohols (equation 243) [211]. With silylenol ethers, high threo ratios were observed (equation 244) [212]. Alkynes were converted to conjugated enones by reaction with ortho esters in the presence of titanium (IV) chloride (equation 245) [213].

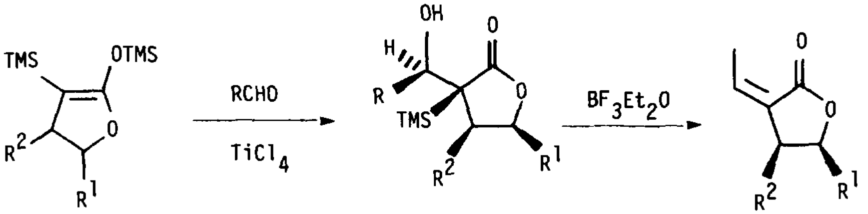


(243)

R^1 = Me, Ph

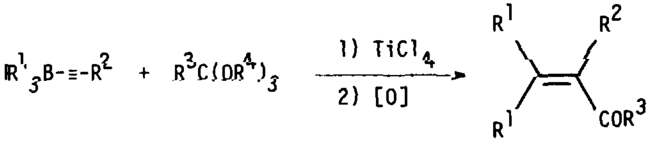
R^2 = t-Bu, i-Pr, Et, Me

91% erythro



(244)

82-98% yield
100% threo



(245)

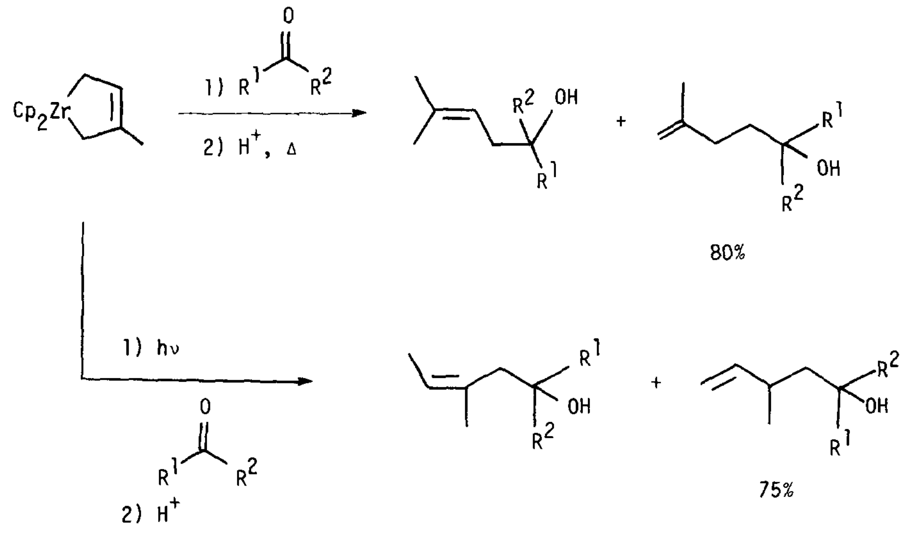
R^1 = n-Pr, n-Bu, i-Bu, n-C_6

R^2 = Ph, n-Bu

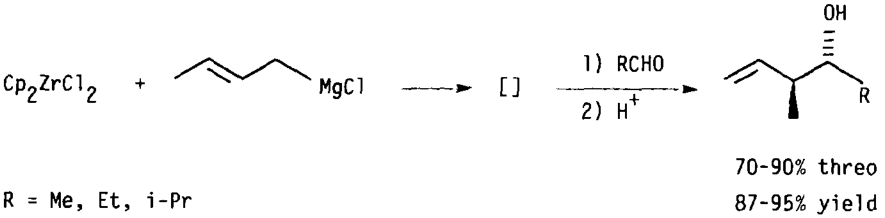
R^3 = H, Me

40-100%

Zirconocycles combined with ketones to give homoallylic alcohols (equation 246) [214][215]. High threo selectivity was noted in the reaction of allylzirconium with aldehydes (equation 247) [216].

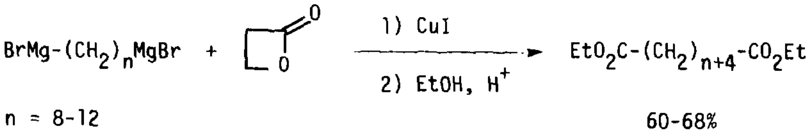


(246)

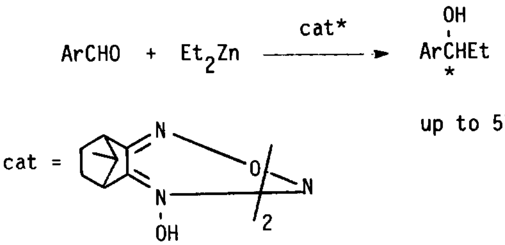


(247)

Diesters were produced from β-lactones and *bis*-Grignard reagents (equation 248) [217]. Aldehydes were alkylated by dialkylzinc reagents in the presence of a chiral ligand in the presence of a chiral cobalt or palladium catalyst (equation 249) [218]. Palladium(II) complexes catalyzed the reaction of aldehydes with allylic alcohols to give dienes (equation 250) [219]. Nickel and palladium phosphine complexes catalyzed the reaction of main group organometallics with diketene to give 3-substituted-3-butenoic acids [220]. Chromium complexes of ethyl benzene underwent condensation with ketones at the benzylic position (equation 251) [221].



(248)

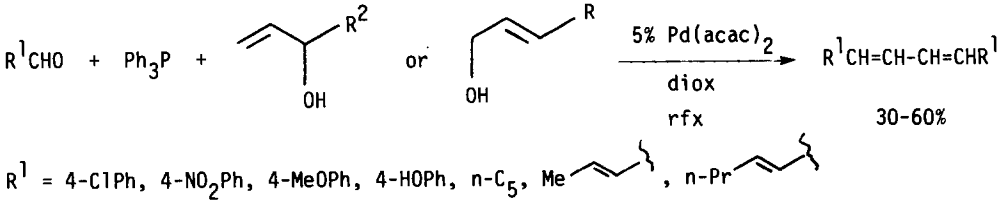


(249)

up to 57% ee

M = Co, Pd

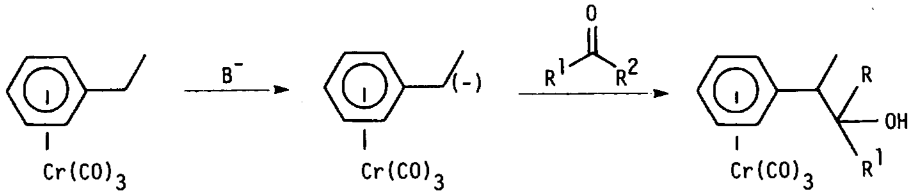
(250)



R^1 = 4-ClPh, 4-NO$_2$Ph, 4-MeOPh, 4-HOPh, n-C$_5$, Me, n-Pr

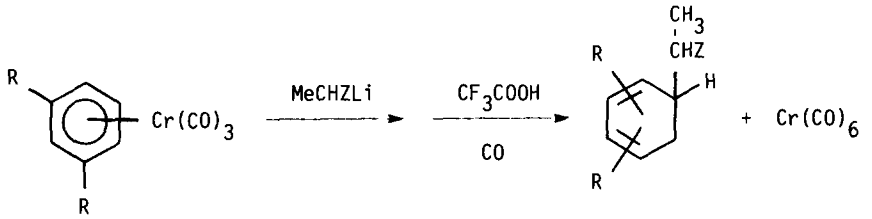
R^2 = n-C$_5$, Me

(251)



11. Aromatic Substitution

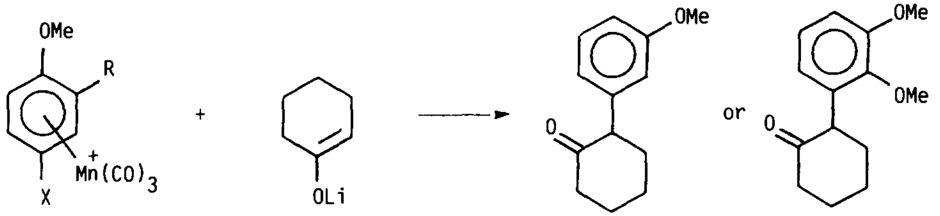
The application of arene-metal complexes in organic synthesis has been reviewed (27 references) [222]. A study of the regioselectivity of nucleophilic attack on π-arene chromium tricarbonyl complexes correlated with frontier orbitals using low energy arene-centered MO's on the complex, but was also sensitive to steric effects [223]. Cleavage of addition products from alkylation of π-arene chromium complexes with trifluoroacetic acid and carbon monoxide freed the cyclohexadiene ligand and regenerated chromium hexacarbonyl (equation 252) [224]. Cationic π-arene manganese complexes also underwent alkylation by enolate anions (equation 253) [225], as did aromatic phosphabenzene derivatives (equation 254) [226].



(252)

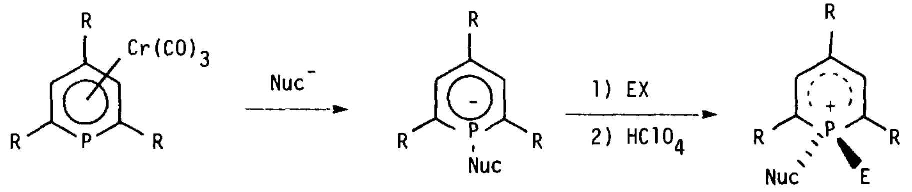
Z = CN, CO$_2$t-Bu
R = H, i-Pr

(253)



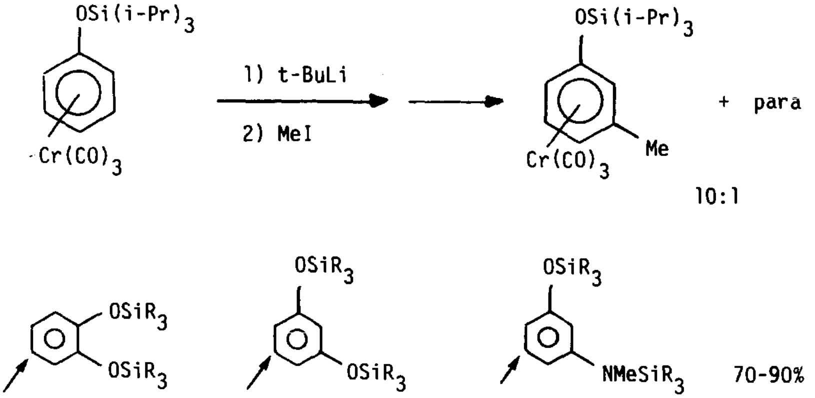
X = H, Br
R = OMe, H

(254)

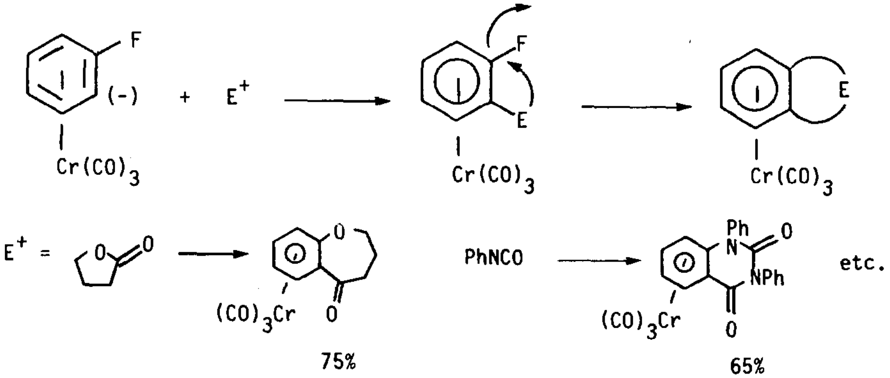


R = Ph, t-Bu
Nuc = Me, Et, Ph, MeO
E = Me, Et, CD$_3$, H

Lithiation of the arene ring in arene chromium tricarbonyl complexes has also been extensively developed and applied to synthesis. Electronic effects directed the site of lithiation/electrophilic attack (equation 255) [227]. A variety of heterocyclic systems were prepared from the lithiated fluorobenzene chromium complex (equation 256) [228]. Lithiation was also directed by ring substituents (equation 257) [229]. This process was used to prepare a number of fused bicyclic systems (equations 258-260) [230], (equations 261 and 262) [231]. Chromium complexed benzocyclohexanones underwent combined-metal directed cyclizations, alkylation, and lithiation to produce complex organic molecules (equation 265) [232], (equation 266) [233]. Frenolicin was synthesized using this type of chemistry (equation 267) [234]. (See reference 234a for dissertation).

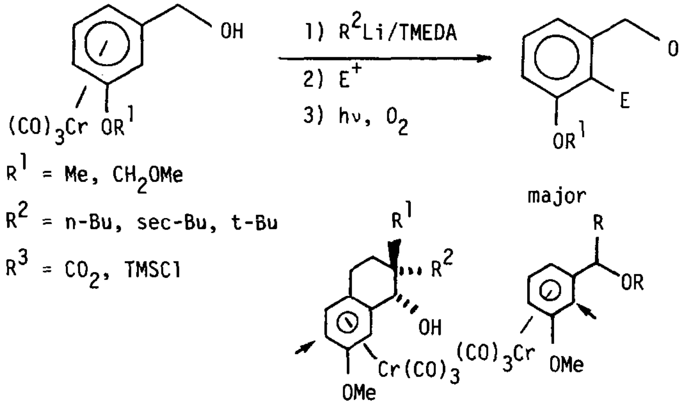


(255)

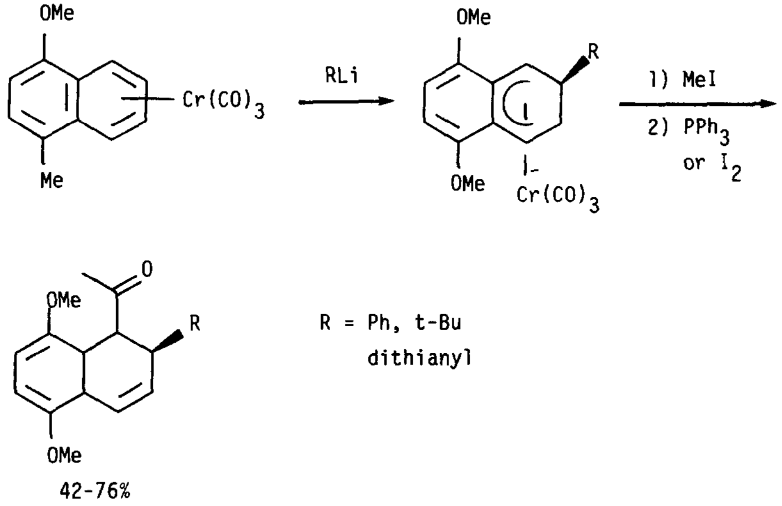


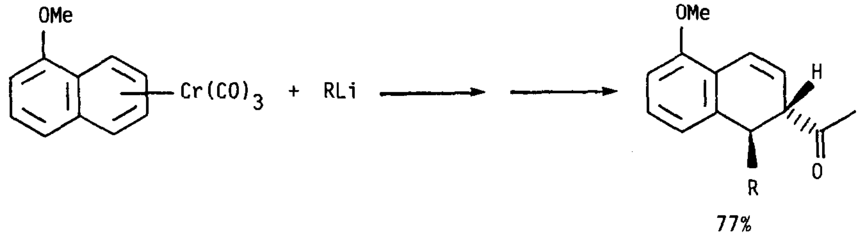
(256)

(257)

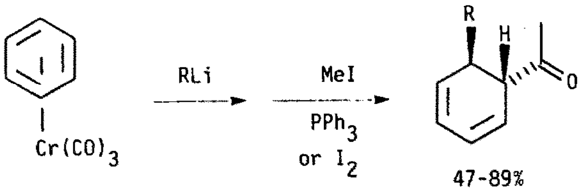

OH
(CO)$_3$Cr OR^1
R^1 = Me, CH$_2$OMe
R^2 = n-Bu, sec-Bu, t-Bu
R^3 = CO$_2$, TMSCl
1) R^{2}Li/TMEDA
2) E$^+$
3) hν, O$_2$
OH
E
OR^1
+
OH
E
OR^1
major
minor
R^1
R^2
OH
Cr(CO)$_3$
OMe
R
OR
(CO)$_3$Cr
OMe

(258)

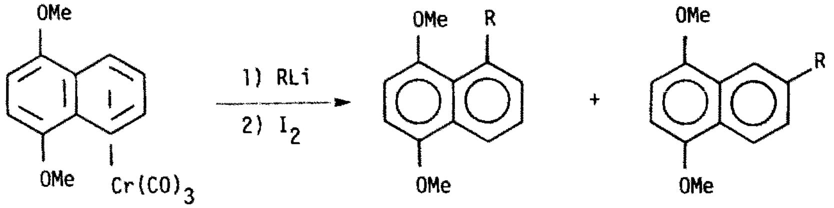

OMe
Cr(CO)$_3$
Me
RLi
OMe
R
OMe
Cr(CO)$_3$
1) MeI
2) PPh$_3$
or I$_2$
O
OMe
R
OMe
R = Ph, t-Bu
dithianyl
42-76%


OMe
Cr(CO)$_3$
+
RLi
OMe
H
O
R
77%

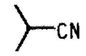
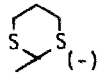
(259)



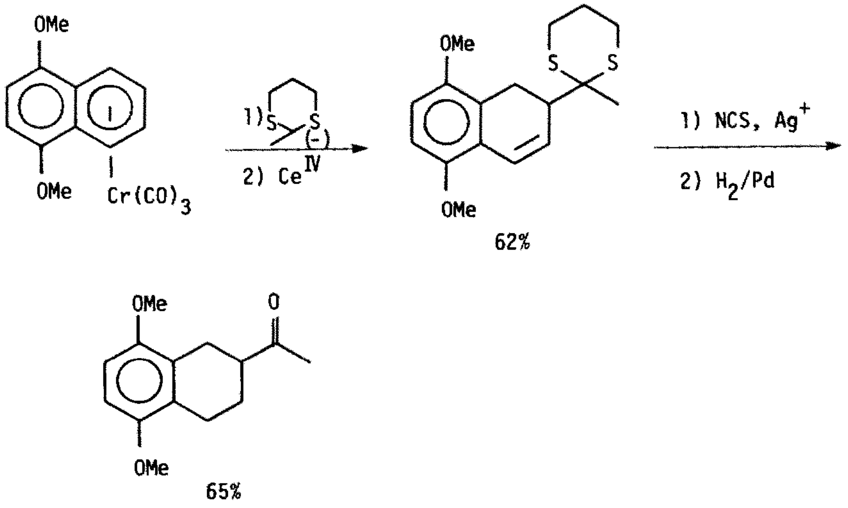
(260)



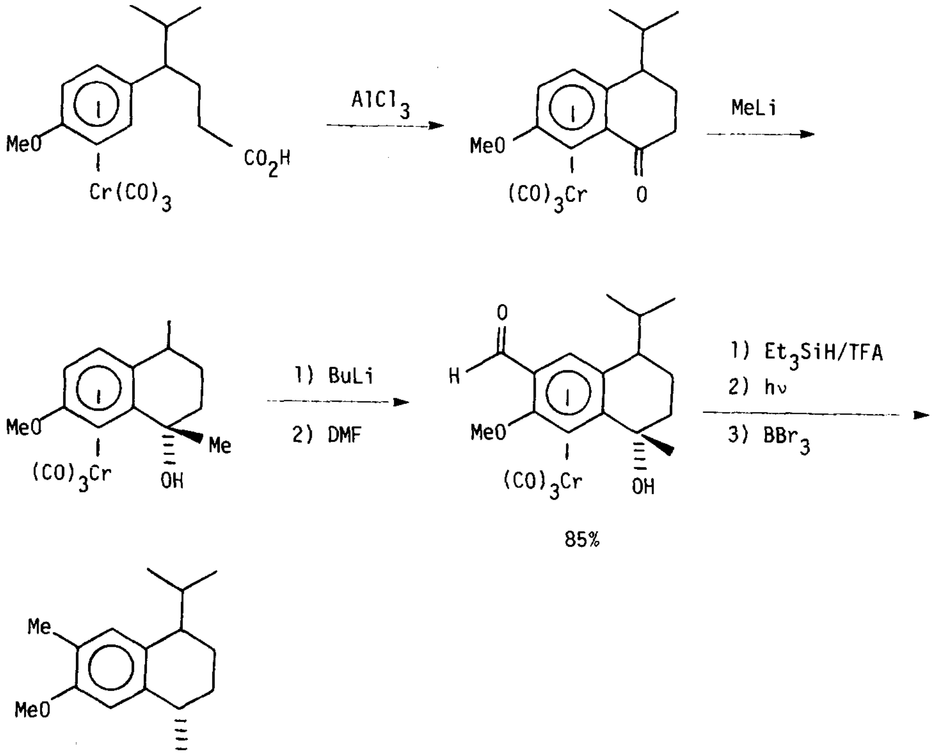
(261)

R = CH_2CN	50°	75	25	34%
	-20°	100	0	72%
	-40°	27	73	84%
	0	97	3	72%
CH_2CO_2t-Bu	0	98	2	84%
	0	0	100	71%

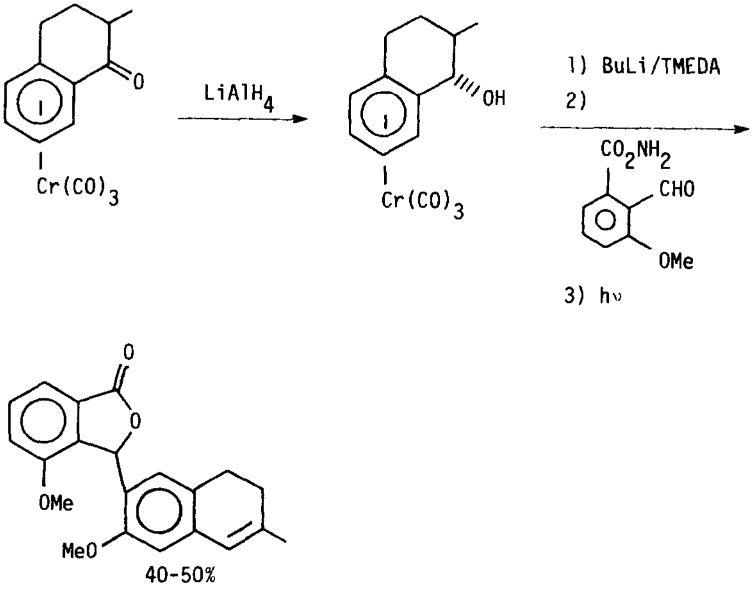
(262)



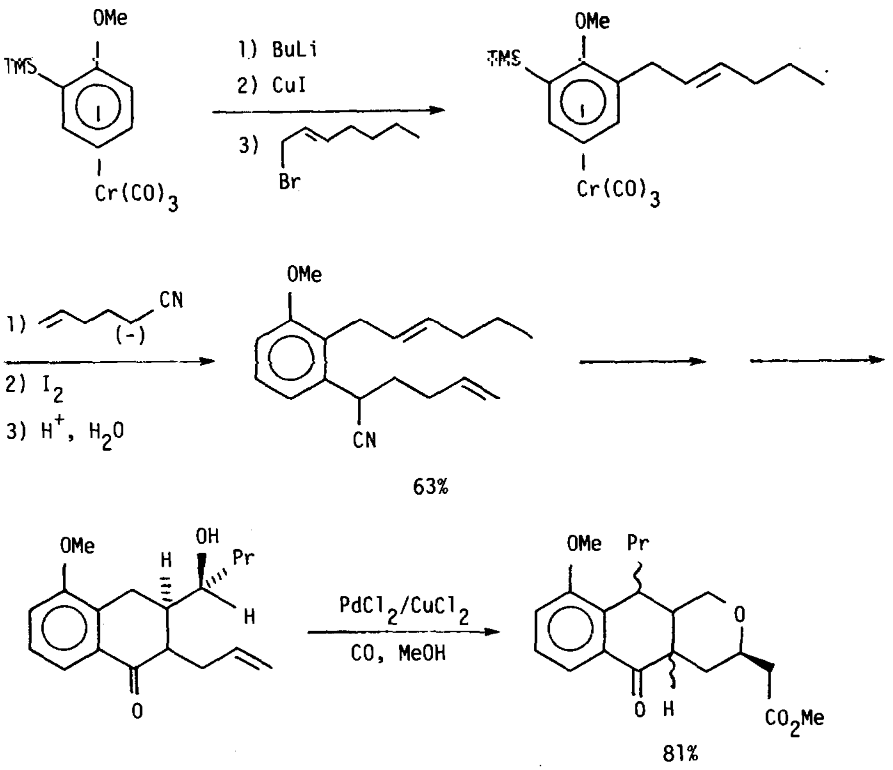
(263)


MeO
Cr(CO)$_3$
CO$_2$H
AlCl$_3$
MeO
(CO)$_3$Cr
O
MeLi
MeO
(CO)$_3$Cr
OH
Me
1) BuLi
2) DMF
O
H
MeO
(CO)$_3$Cr
OH
85%
1) Et$_3$SiH/TFA
2) hν
3) BBr$_3$
Me
MeO

(264)

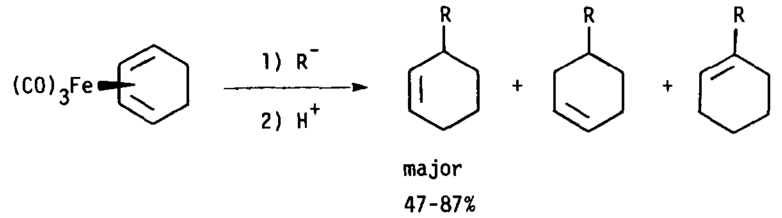

O
Cr(CO)$_3$
LiAlH$_4$
OH
Cr(CO)$_3$
1) BuLi/TMEDA
2)
CO$_2$NH$_2$
CHO
OMe
3) hν
O
O
OMe
MeO
40-50%

(265)

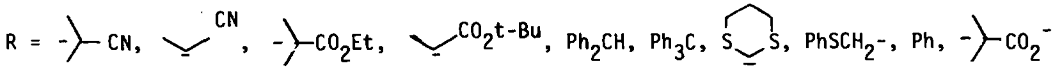


12. Alkylation of Diene and Dienyl Compounds

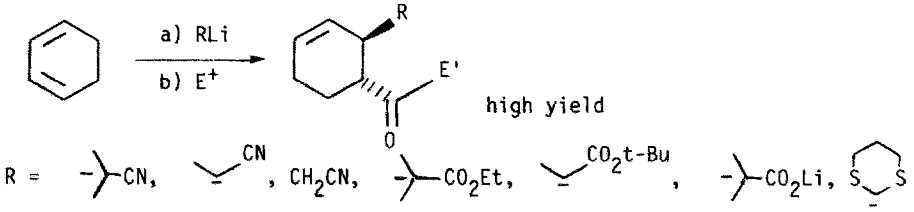
The chemistry of novel transition metal-diene complexes and their application to organic synthesis has been reviewed (21 references) [235]. Cyclohexadiene iron tricarbonyl complexes underwent ring alkylation when treated with carbanions (equation 266) [236]. When the intermediate from this process was treated with an electrophile, carbonyl insertion occurred (equation 267) [237]. Iron pentacarbonyl was used to convert cyclohexenyl alcohols to arenes (equation 268) [238]. Optically active hemicaronaldehydes were synthesized from chiral butadiene iron tricarbonyl complexes (equation 269) [239].



(266)

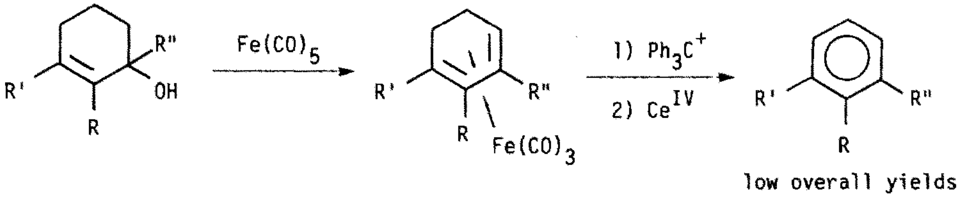


(267)



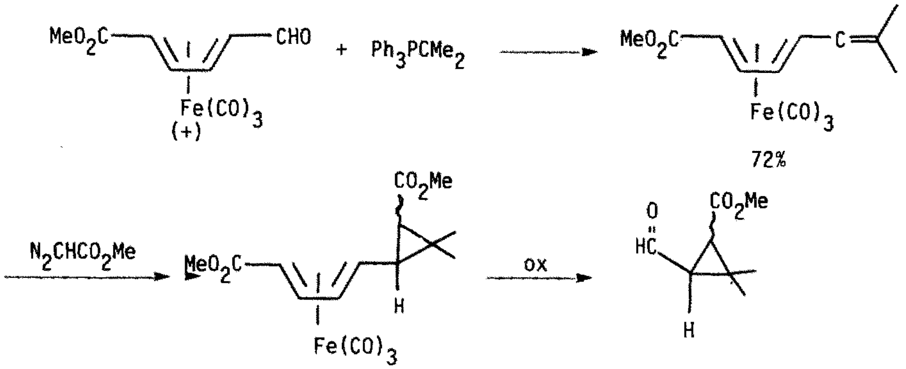
E' = H, Me, OH, OEt

(268)

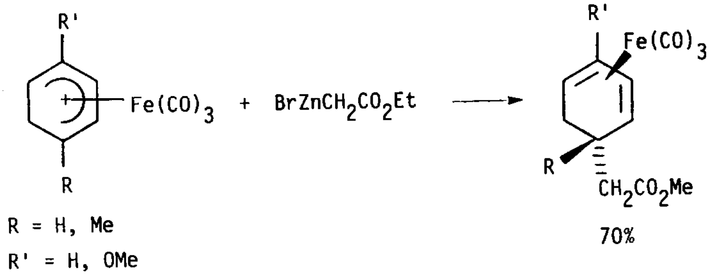


R = H, n-Bu
R' = H, Me
R" = Me, n-Bu, H

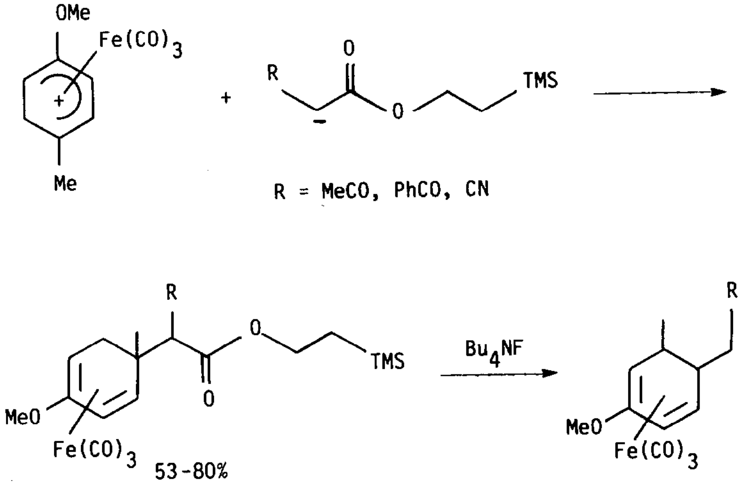
(269)



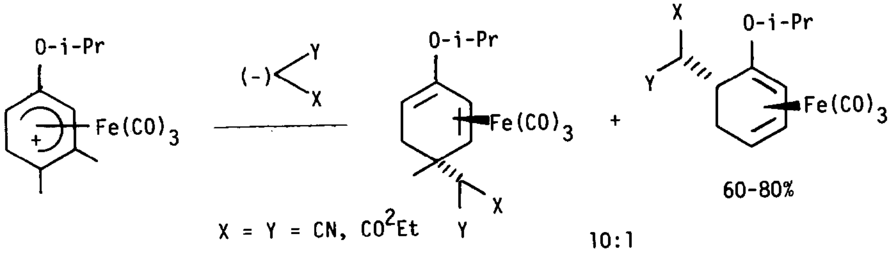
Dienyliron complexes were alkylated by Reformatsky reagents (equation 270) [240] and by stabilized enolates (equation 271) [241]. A detailed study of the regiochemistry of alkylation of substituted dienyliron complexes by stabilized carbanions has been carried out (equation 272) [242]. One of these complexes was used as a precursor to ± limnaspermine (equation 273) [243]. Two separate groups have resolved chiral iron dienyl complexes by attacking them with chiral nucleophiles, separating the diastereoisomers, then regenerating the complex (equation 274) [244][245].



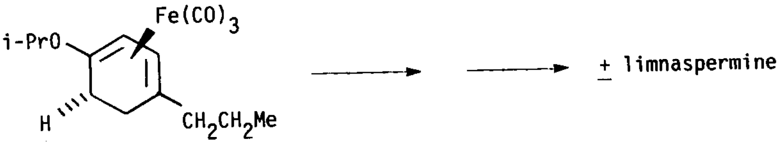
(270)



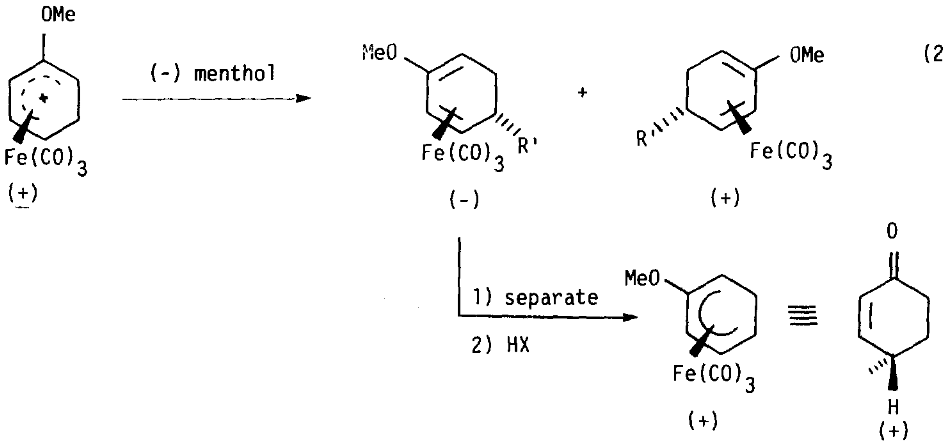
(271)



(272)



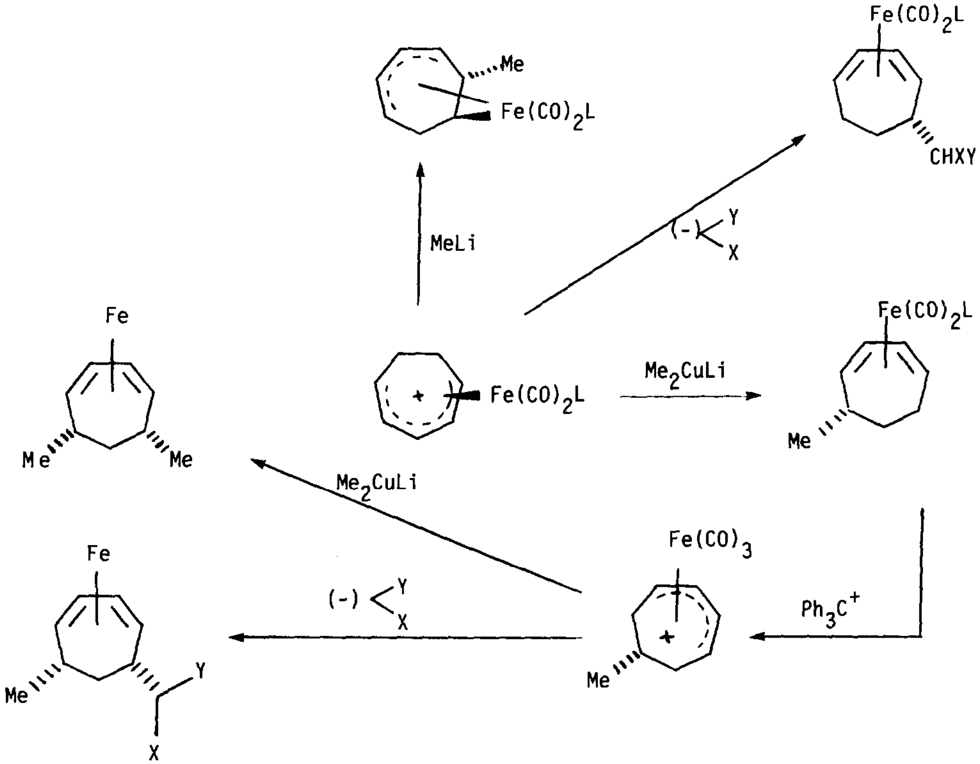
(273)

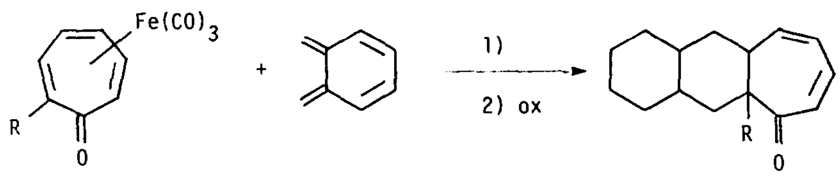


(274)

Cycloheptadienyliron complexes also were alkylated by carbanions (equation 275) [246]. Tropanoneiron complexes were used to permit the synthesis of otherwise unobtainable [4 + 2] adducts (equation 276) [247].

(275)



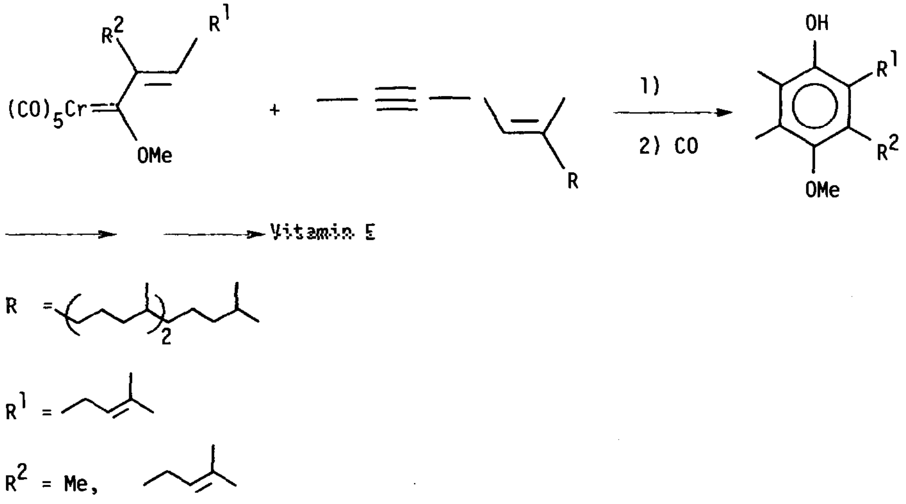


(276)

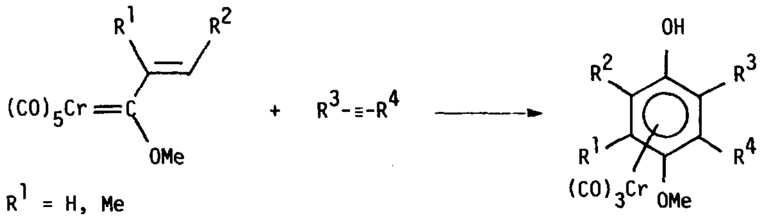
R = H 40-15%

13. Alkylation + Cyclization Processes of Metal Carbene Complexes

Quinone synthesis with organometallic reagents has been reviewed (34 references) [248]. Vitamin E analogs have been synthesized from alkynes and α,β-unsaturated chromium carbene complexes (equation 277) [249], as have other phenolics (equation 278) [250], and 2-allylnaphthoquinones (equation 279) [251]. In contrast, tungsten carbene complexes reacted with alkynes under photolytic conditions to produce stable alkyne complexes which decomposed to indenes (equation 280) [252]. The diphenylcarbene tungsten complex decomposed to diphenylketene under relatively mild conditions (equation 281) [253].



(277)



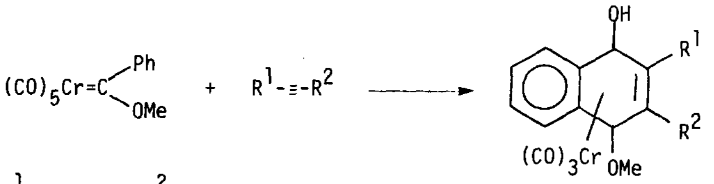
(278)

R^1 = H, Me

R^2 = H, Me, Ph

R^3 = Me, n-Pr, Ph

R^4 = Me, n-Pr, Ph, H

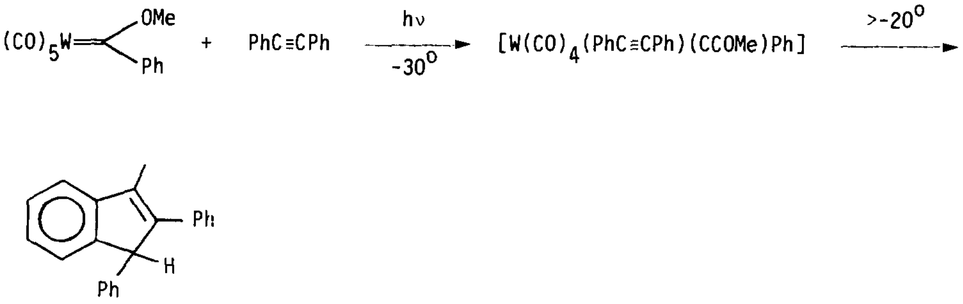


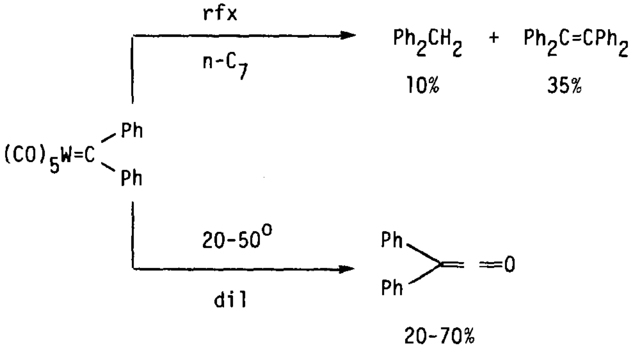
(279)

R^1 = alkyl; R^2 = H, -regiospecific for 2-alkyl

R^1 = R^2 = alkyl, aryl - no regioselectivity

(280)

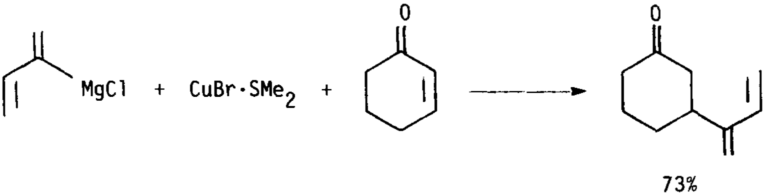




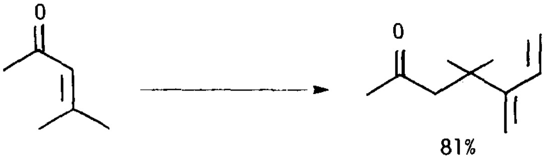
(281)

B. Conjugate Addition

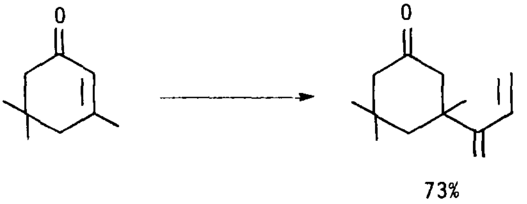
Dienyl Grignard reagents added 1,4 to conjugated enones in the presence of copper catalysts (equations 282-285) [254]. Mixed cuprates alkylated γ-pyrones in a similar manner (equation 286) [255]. Cyanocuprates were very efficient in the 1,4-alkylation of conjugated esters which lacked α-substitution (equation 287) [256]. Copper salts also catalyzed conjugate alkylation of carbohydrate-containing α,β-unsaturated esters (equation 288) [257]. As usual, conjugate alkylation by organocopper reactions was used in the synthesis of prostaglandins (equation 289) [258]. Vinyl cuprates containing remote halogen substitution, added 1,4- to conjugated enones (equation 290) [259]. Cyclization to the halide was then carried out. The reagent "$MeCuBF_3$" added 1,4- to chiral unsaturated esters to give a high degree of asymmetric induction (equation 291) [260]. Much poorer enantiomeric excess was observed when chiral copper reagents were used (equations 292) [261]. Even remote chirality in the conjugated enones resulted in reasonable enantiomeric excess (equations 293 and 294) [262]. γ-Acetoxy-α,β-unsaturated nitro compounds were converted to cyclopropyl oximes by dimethyl copper reagents (equation 295) [263]. Organocopper reagents added 1,6- to dienoic amides, while Grignard reagents added 1,4 (equations 296) [264]. β-Iodo-α,β-cyclohexenones were converted to seven membered ring systems by vinylcyclopropyl cuprates (equation 297) [265]. β-Thio-α,β-unsaturated enones underwent conjugate alkylation by organocuprates with loss of sulfide to regenerate the enone (equation 298) [266].



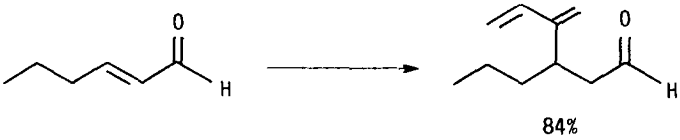
(282)



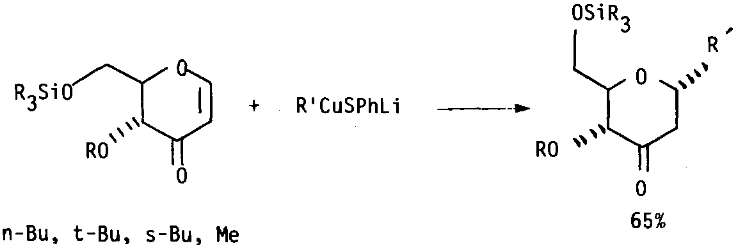
(283)



(284)

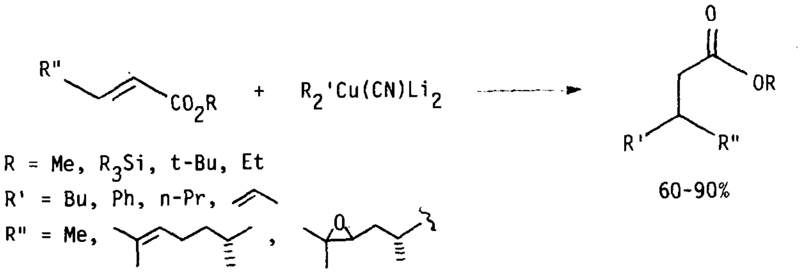


(285)

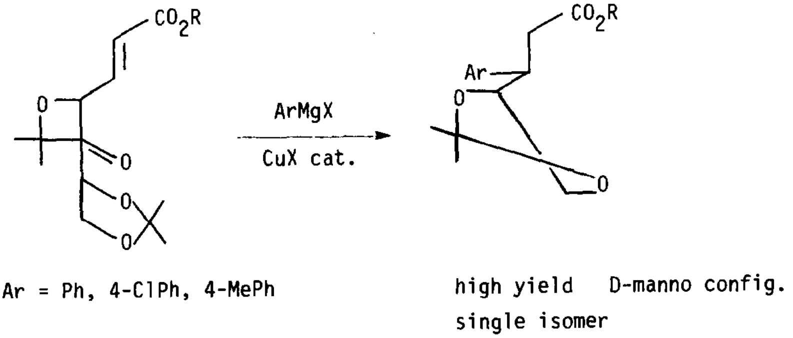


(286)

R' = n-Bu, t-Bu, s-Bu, Me



(287)



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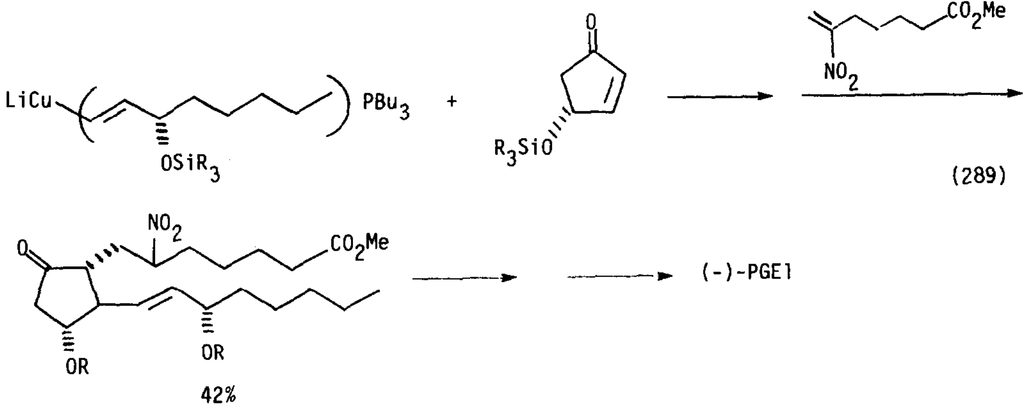

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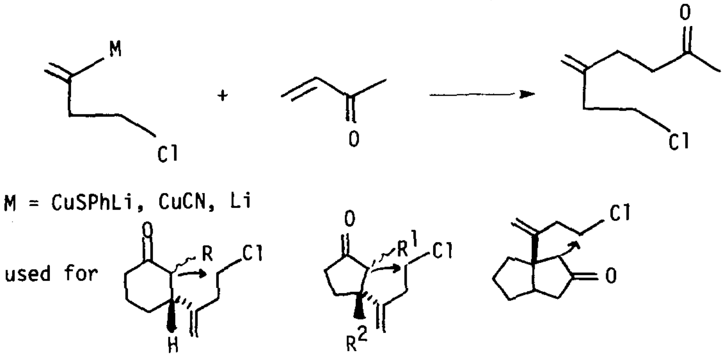

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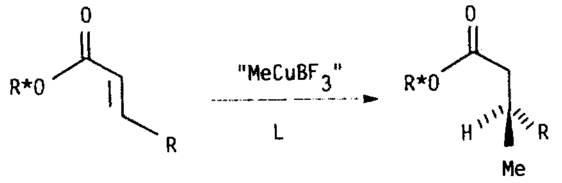
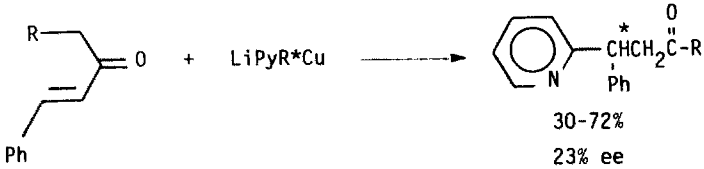


(291)

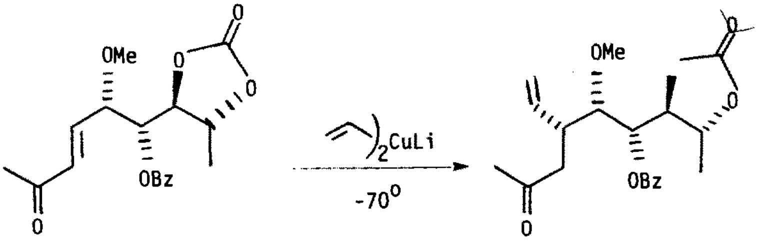
R = n-Bu, Et, C_{18}
L = CN, PBu_3
R* = camphor

78-98% ee
76-90% yield



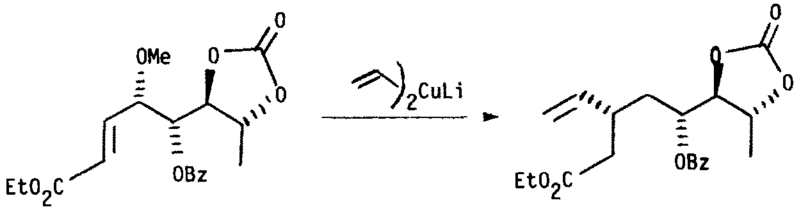
(292)

30-72%
23% ee



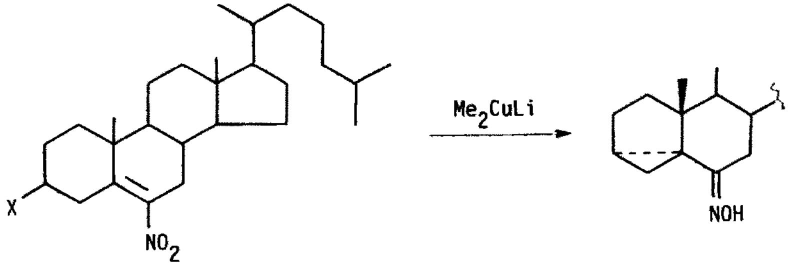
(293)

86%
>10:1 diastereoselective



(294)

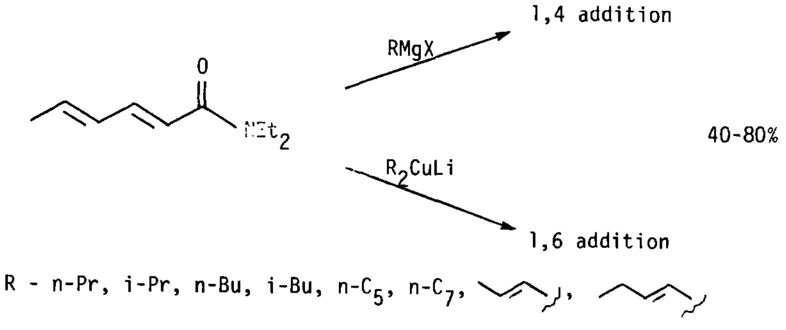
62%



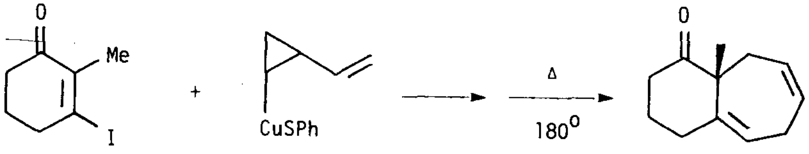
(295)

(via SET)

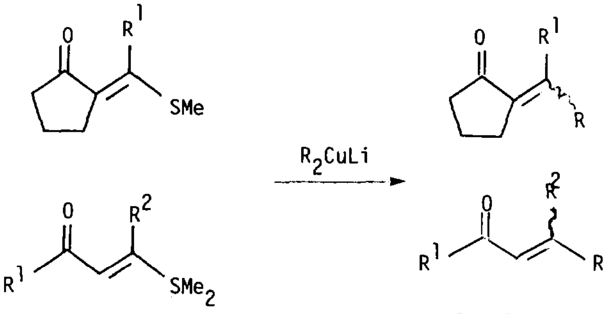
X = OAc, OTs



(296)



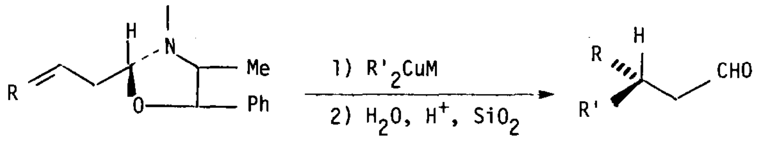
(297)



(298)

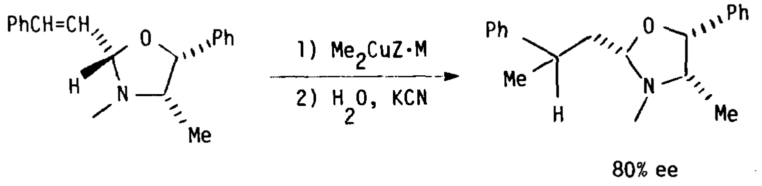
Et$_2$O - inversion of S. C.
THF - retention of S. C.

Organocopper species added 1,4 to unsaturated chiral aminals to give chiral aldehydes after hydrolysis (equation 299) [267], (equation 300) [268], (equation 301) [269]. Organocuprates also added 1,4 to 3-(1-imidazolyl)-2-alken-1-ones [270].

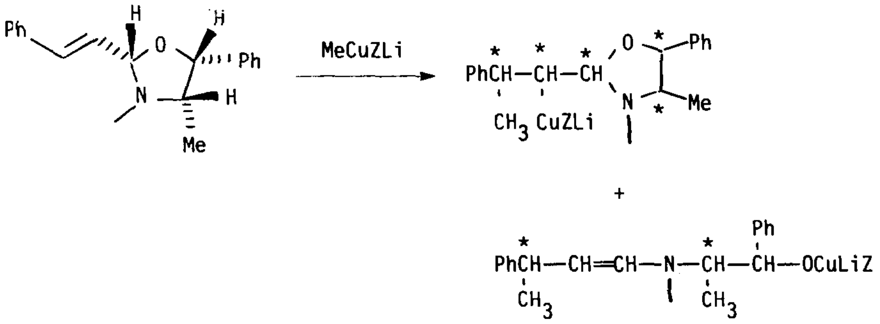


(299)

30-70% yield
25-51% ee



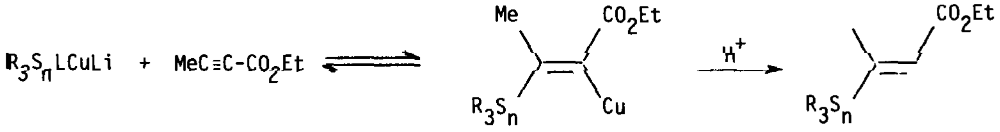
(300)



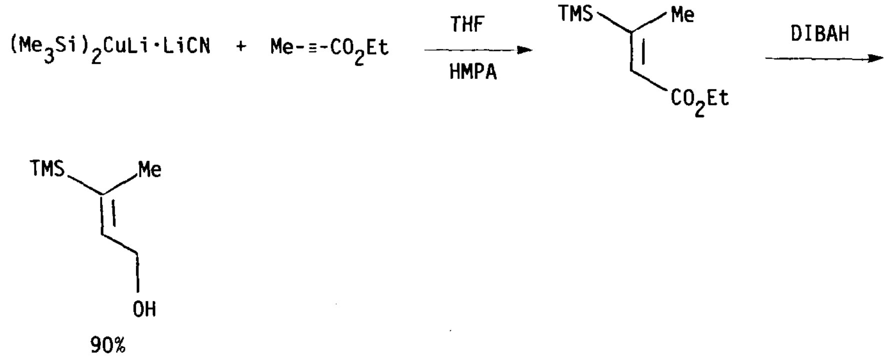
(301)

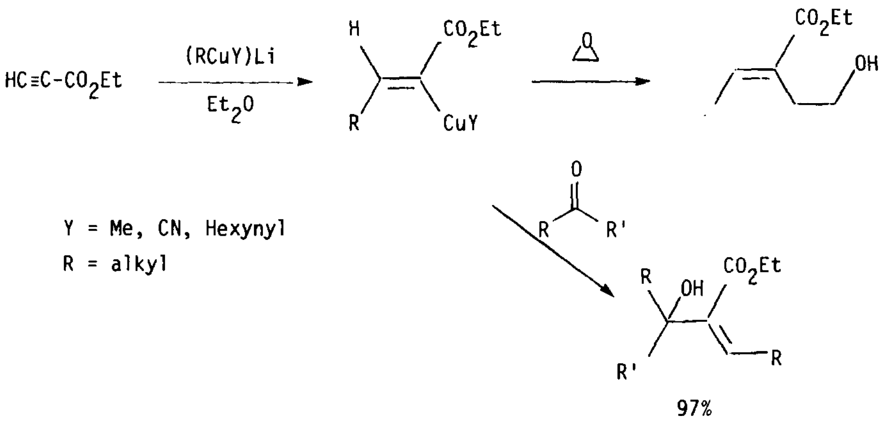
Conjugated ynones also underwent conjugate addition with organocuprate reagents (equation 302) [271], (equation 303) [272], (equation 304) [273].

(302)



(303)

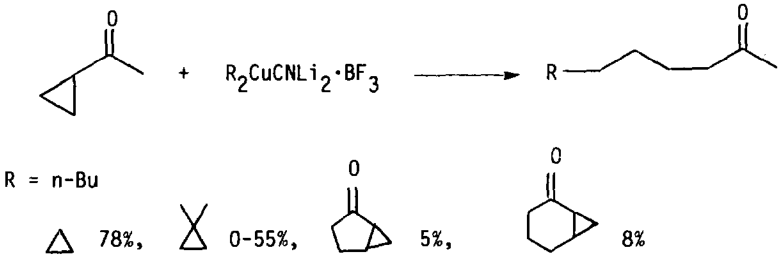




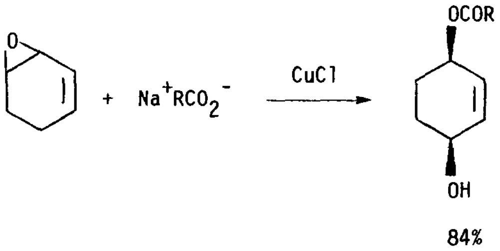
Y = Me, CN, Hexynyl
R = alkyl

(304)

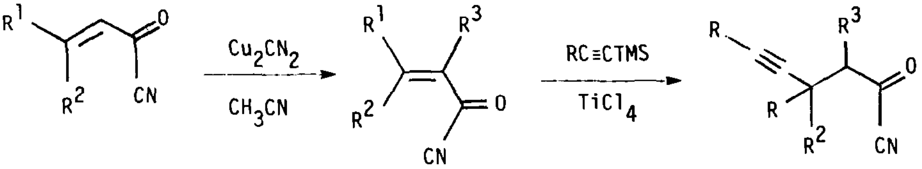
Cyclopropyl ketones underwent 1,4-addition with organocuprates (equation 305) [274]. Cyclohexadiene monoxide gave a 1,4-adduct when treated with carboxylate salts in the presence of copper(I) chloride (equation 306) [275]. Trimethylsilylacetylenes added 1,4 to α,β-unsaturated and cyanides in the presence of titanium(IV) chloride (equation 307) [276]. Copper also catalyzed the cyclopropanation shown in equation 308 [277].



(305)



(306)



(307)

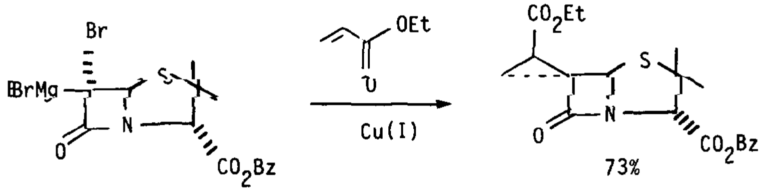
30-80%

R = Me, Bu

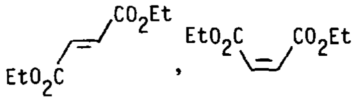
R^1 = H, Me, Ph

R^2 = H, Me

R^3 = H, Me

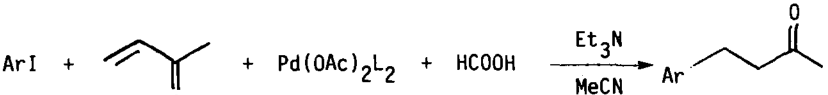


(308)



also work.

Palladium catalysis of conjugate addition of arylmercury and aryl halide compounds to α,β-enones has been reviewed (15 references) [278]. Aryl iodides added in a 1,4 fashion to conjugated enones in the presence of palladium(II) acetate and formic acid (equation 309) [279]. Ferrocene was orthopalladated, then added 1,4- to conjugated enones (equation 310) [280]. Organomercury compounds added 1,4- to conjugated enones in the presence of palladium(II) chloride under phase transfer conditions (equation 311) [281].

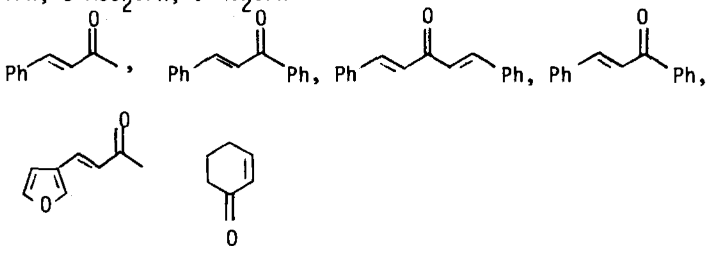


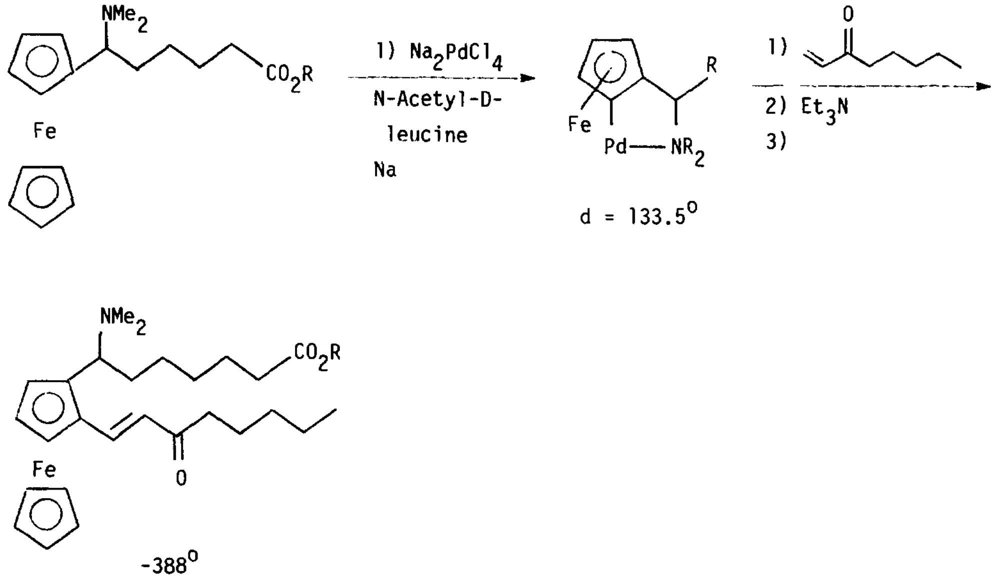
(309)

20-60%

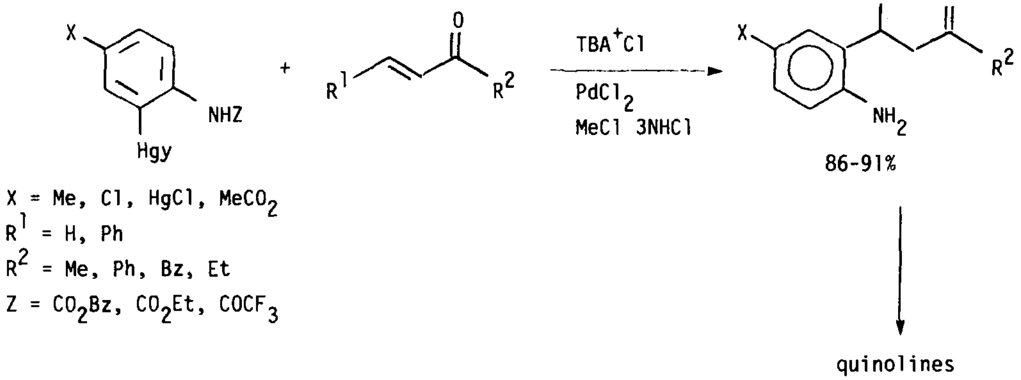
Ar = Ph, 4-tol, 4-MeOPh, 4-HOPh, 4-H_2NPh, 4-HOCH_2Ph, o, m, p, MeCONHPh, 4-ClPh, 3-MeO_2CPh, 3-HO_2CPh

enone =





(311)

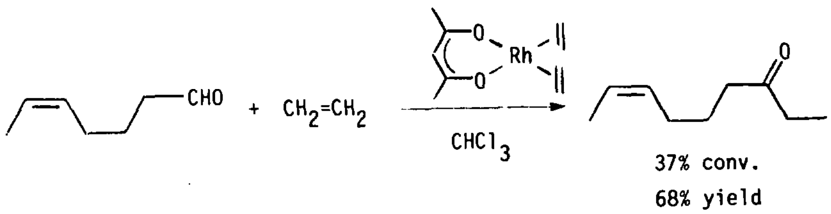


X = Me, Cl, HgCl, MeCO$_2$
R^1 = H, Ph
R^2 = Me, Ph, Bz, Et
Z = CO$_2$Bz, CO$_2$Et, COCF$_3$

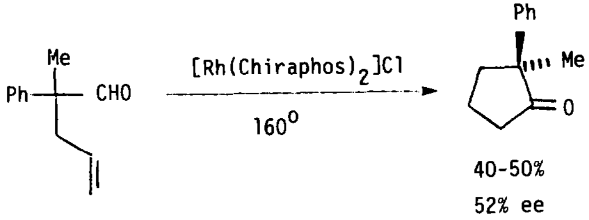
C. Acylation Reactions (Excluding Hydroformylation)

1. Carbonylation of Alkenes and Alkynes

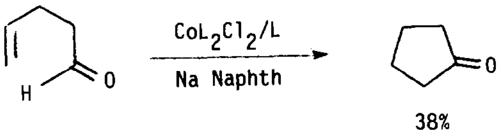
4-Heptenal was converted to 7-nonene-3-one by reaction with ethylene in the presence of excess rhodium catalyst (equation 312) [282]. Unsaturated aldehydes cyclized to give cyclopentenones with modest enantiomeric excess in the presence of a chiral rhodium(I) catalyst (equation 313) [283]. Cobalt(O) complexes catalyzed a similar cyclization (equation 314) [284]. Butadiene iron tricarbonyl complexes reacted with organolithium reagents to produce cyclopentanones or open chain unsaturated aldehydes (equation 315) [285]. 1,4-Pentadienes cyclized to cyclopentanones when treated with cobalt octacarbonyl and carbon monoxide (equation 316) [286].



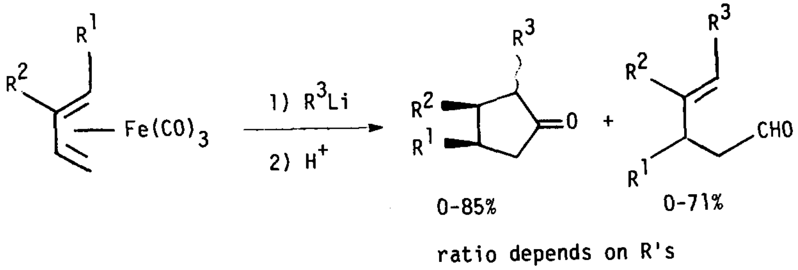
(312)



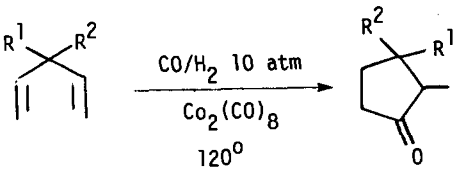
(313)



(314)



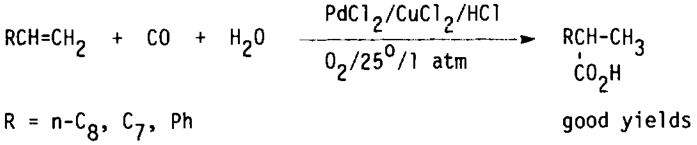
(315)



(316)

$R^1 = R^2 = Me$	39%
$R^1, R^2 = (CH_2)_4$	76%
$R^1, R^2 = (CH_2)_5$	81%

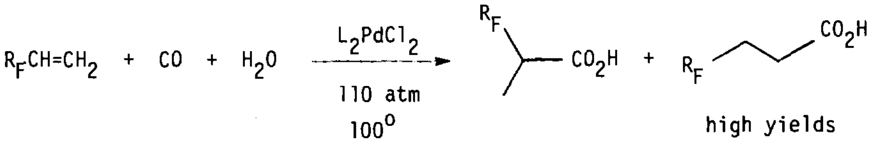
Olefins were hydroacylated by treatment with carbon monoxide and water in the presence of a palladium(II)/copper(II) catalyst system (equation 317) [287]. Fluoroalkyl olefins underwent a similar reaction (equation 318) [288]. Acrylonitrile was hydroesterified by carbon monoxide and methanol in the presence of a base-promoted cobalt catalyst (equation 319) [289]. Palladium catalyzed hydrocarboxylation of olefins in the presence of steroidal phosphines gave optically active products with modest stereoselectivity [290]. Anchored palladium catalysts were compared with their homogeneous counterparts in the alkoxycarbonylation of olefins [291]. Styrene was asymmetrically carbomethoxylated in the presence of a palladium catalyst [292]. β-Chloroacrylic acid was the product from the reaction of ethylene with carbon monoxide in the presence of a palladium catalyst [293].



$$RCH{=}CH_2 + CO + H_2O \xrightarrow[O_2/25^{o}/1\ atm]{PdCl_2/CuCl_2/HCl} \underset{CO_2H}{RCH\text{-}CH_3} \qquad (317)$$

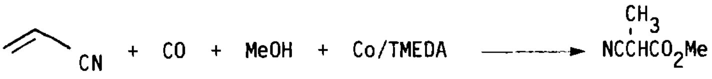
R = n-C_8, C_7, Ph
cyclo C_{12}

good yields



$R_FCH{=}CH_2$ + CO + H_2O $\xrightarrow[110\ atm,\ 100^{o}]{L_2PdCl_2}$ (318)

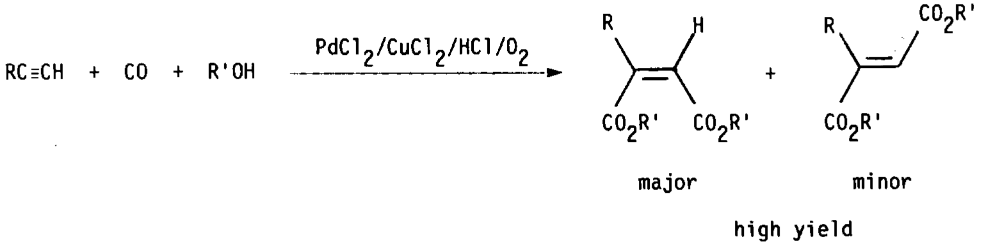
R_F = CF_3, C_6F_6

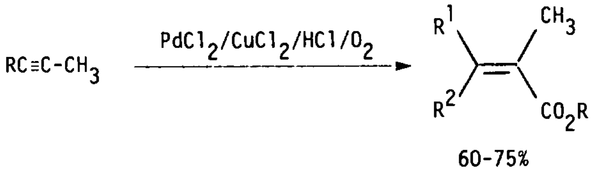


$$+ CO + MeOH + Co/TMEDA \longrightarrow NC\overset{CH_3}{C}HCO_2Me \qquad (319)$$

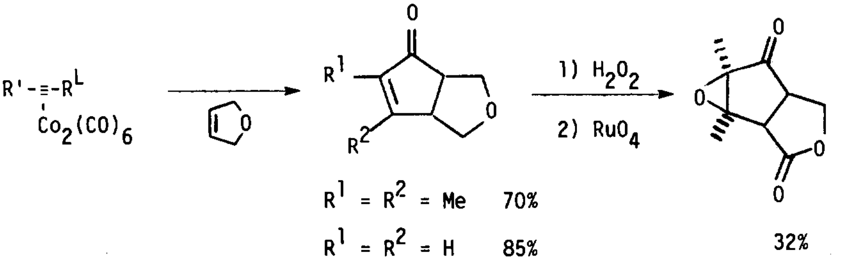
Terminal alkynes were converted to fumarates and maleates, while internal alkynes were converted to acrylates by carbonylation in the presence of palladium catalysts (equations 320 and 321) [294]. Cobalt alkyne complexes were converted to bicyclic keto esters by reaction with dihydrofuran (equation 322) [295]. Rhodium(I) catalyzed the conversion of alkynes to butenolides (equations 323 and 324) [296]. Eneynes cyclized to bicyclic ketones when treated with dicobalt octacarbonyl (equations 325 and 326) [297]. Acetylene was converted to acetylenic amides when treated with bis-diethylamine nickel(II) bromide and carbon monoxide (equation 327) [298].

(320)





(321)

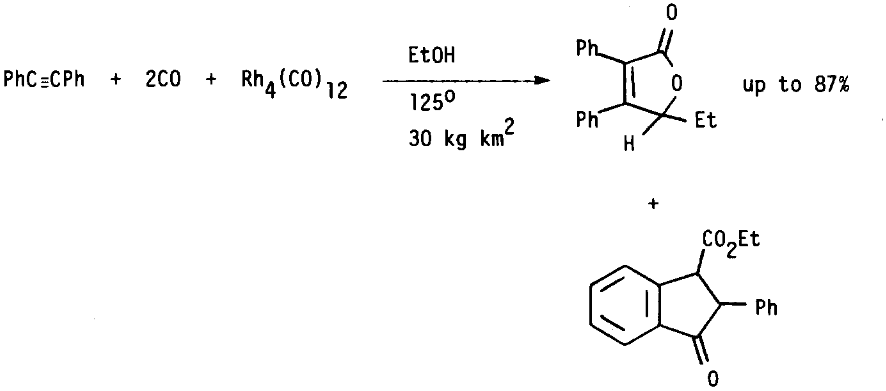


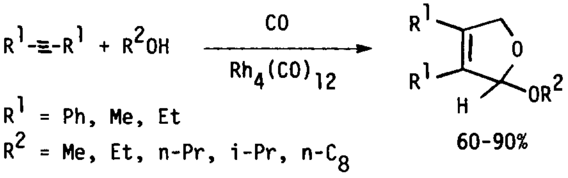
$R^1 = R^2 = Me$ 70%

$R^1 = R^2 = H$ 85%

(322)

(323)

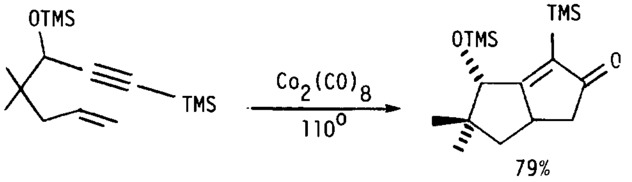




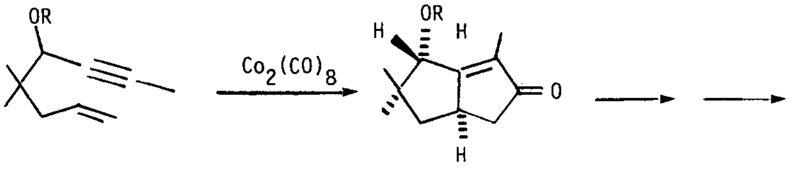
R^1 = Ph, Me, Et

R^2 = Me, Et, n-Pr, i-Pr, n-C_8

(324)



(325)



(326)

d,l coriolin

precursor

$$(Et_2NH)_2NiBr_2 + HC{\equiv}CH + CO \longrightarrow HC{\equiv}C\text{-}\overset{O}{\overset{\|}{C}}NEt_2 + Et_2N\overset{O}{\overset{\|}{C}}\text{-}{\equiv}\text{-}\overset{O}{\overset{\|}{C}}NEt_2 \quad (327)$$

Diphenylacetylene cyclized to tetracyclone when treated with TMSCN and nickel(bis) cyclooctadiene [299]. The rate of carbonylation of acetylene with $[PdLBr]_2CO$ was faster than with $PdBr_2$ [300].

2. Carbonylation of Halides

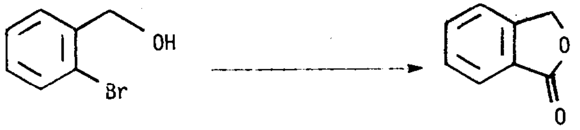
Aryl halides were converted to carboxylic acids under phase transfer conditions with cobalt carbonyl as catalyst (equation 328). Intramolecular versions (equations 329 and 330) also worked [301]. Cobalt carbonyl attached to a cationic exchange resin also catalyzed the conversion of organic halides to acids or esters [302]. Benzyl halides were converted to phenylacetic esters by cobalt carbonyl in the presence of base and alumina (equation 331) [303]. Iron pentacarbonyl in aqueous hydroxide catalyzed the same reaction (equation 332) [304].

$$ArX \xrightarrow[Bu_4NBr\ 65^{\circ},\ h\nu]{Co_2(CO)_8,\ PhH/5\underline{N}NaOH/CO} \underset{>90\%}{ArCO_2Na} \quad (328)$$

ArX = PhBr, PhI, 4-MePhBr, 2-MePhBr, 4-MeOPhBr, 2-MeOPhBr, 1-Br Napth
2-Br Napth

(329)

high yield



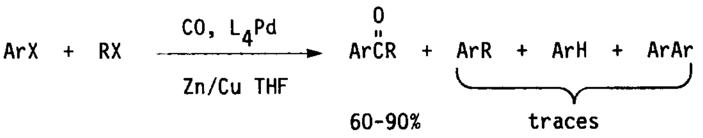
(330)

$$\mathrm{PhCH_2X + CO + ROH + base/Al_2O_3 \xrightarrow[Co_2(CO)_8]{Co(CO)_4^-} \underset{70\%}{PhCH_2CO_2R}} \qquad (331)$$

$$\mathrm{ArCH_2X \xrightarrow[aq\ NaOH,\ (Bu_4N)_2SO_4]{Fe(CO)_5\ cat.\ CO} ArCH_2CO_2H} \qquad (332)$$

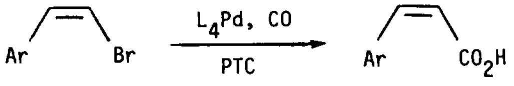
Ar = Ph, 3-MePh, 2-MePh, 3-CNPh, 4-BrPH, β-napth, 3-MeOPh

Palladium(0) catalyzed the reductive cross coupling of aryl halides with alkyl halides to give aryl alkyl ketones (equation 333) [305]. Styryl bromides were converted to cinnamic acids by reaction with carbon monoxide under phase transfer conditions with a palladium catalyst (equation 334) [306]. Dihalides underwent reductive coupling or carbonylation, depending on conditions (equation 335) [307]. Halides were converted to aldehydes by reaction with tributyltin hydride, carbon monoxide, and a palladium(0) catalyst (equation 336) [308]. Diaryliodonium salts were also carbonylated using a palladium catalyst (equation 337) [309].



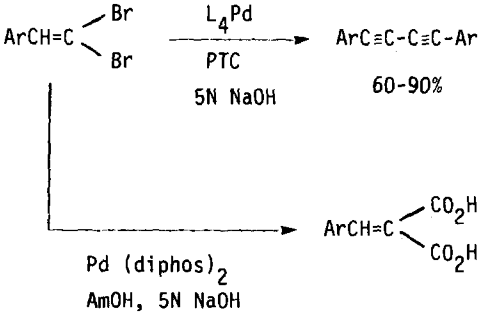
$$\mathrm{ArX + RX \xrightarrow[Zn/Cu\ THF]{CO,\ L_4Pd} \underset{60\text{-}90\%}{Ar\overset{O}{\overset{\|}{C}}R} + \underbrace{ArR + ArH + ArAr}_{traces}} \qquad (333)$$

Ar = Ph, p-MeOPh, p-tolyl, [4-BrPh, 2-MeO$_2$CPh, -failed]
R = Me, n-Pr, i-Pr, n-C$_8$, cyclohex



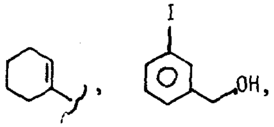
(334)

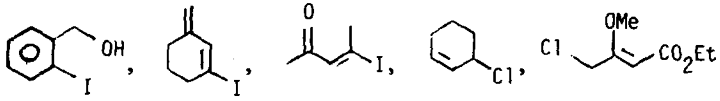
Ar = Ph, p-ClPh, m-BrPh, p-MePh, p-CF$_3$Ph, o-MePh, p-OMePh

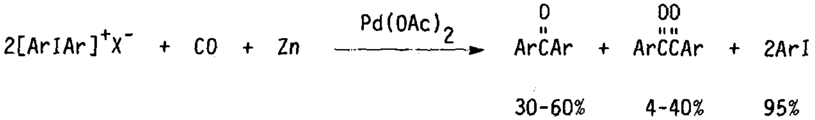

(335)

$$RX + CO + Bu_3SnH \xrightarrow[50^0]{Pd(0)} RCHO \qquad (336)$$

R = Ph, 4-MePh, 2-MePh, 4-BrPh, 4-MeOPh, 4-NO_2Ph, $PhCH_2$,





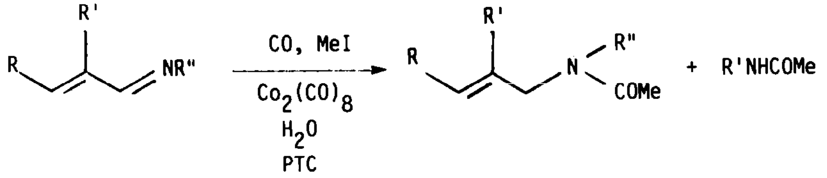


$$2[ArIAr]^+X^- + CO + Zn \xrightarrow{Pd(OAc)_2} \underset{30\text{-}60\%}{Ar\overset{O}{\overset{\|}{C}}Ar} + \underset{4\text{-}40\%}{Ar\overset{OO}{\overset{\|\|}{CC}}Ar} + \underset{95\%}{2ArI} \qquad (337)$$

Ar = Ph, 4-MePh, 4-t-BuPh, 4-ClPh, 4-BrPh

3. Carbonylation of Nitrogen Compounds

Conjugated imines were converted to allyl acetamides by reaction with cobalt carbonyl (equation 338) [310]. Trimethylsilyl amines were carboxylated by reaction with carbon dioxide in the presence of a ruthenium catalyst (equations 339-341) [311]. Amines were carbonylated by nickel catalysts (equation 342) [312]. Organic halides reacted with the complex resulting from treatment of N-methylbenzyl amine with butyllithium, carbon monoxide, and copper(I) iodide to give acetanilides [313]. Nitrobenzene was converted to phenyl carbamates by reaction with carbon monoxide in alcohol in the presence of a palladium-zeolite catalyst [314].

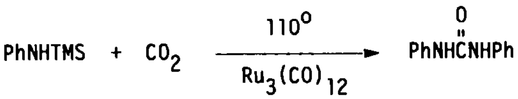


(338)

from 1:1 to 65:35

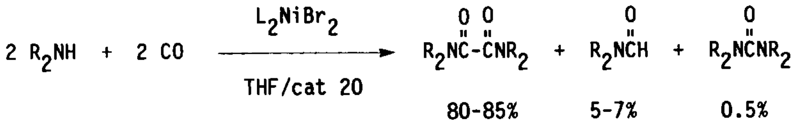
R = aryl Me, H

$$\text{PhNHTMS} \xrightarrow[\substack{Ru_3(CO)_{12} \\ 100^{\circ}}]{CO_2} \text{PhNHCO}_2\text{TMS} \qquad (339)$$



$$\text{PhNHTMS} + CO_2 \xrightarrow[Ru_3(CO)_{12}]{110^{\circ}} \text{PhNH}\overset{O}{\overset{\|}{C}}\text{NHPh} \qquad (340)$$

$$(\text{TMS})_2\text{NH} + CO_2 \xrightarrow{Ru_3(CO)_{12}} \text{TMSNHCO}_2\text{TMS} \qquad (341)$$

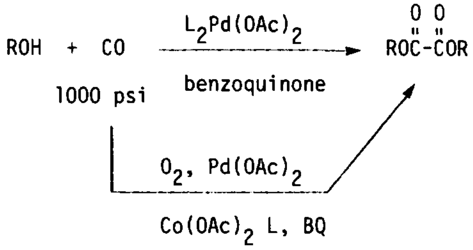


$$2\ R_2NH + 2\ CO \xrightarrow[\text{THF/cat 20}]{L_2NiBr_2} \underset{80\text{-}85\%}{R_2N\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}NR_2} + \underset{5\text{-}7\%}{R_2N\overset{O}{\overset{\|}{C}}H} + \underset{0.5\%}{R_2N\overset{O}{\overset{\|}{C}}NR_2} \qquad (342)$$

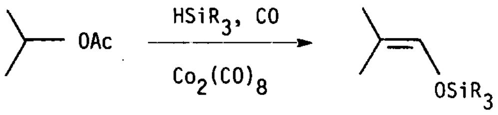
R = Et, $-(CH_2)_4-$ $\qquad$ RNH_2 also works

4. Carbonylation of Oxygen Compounds

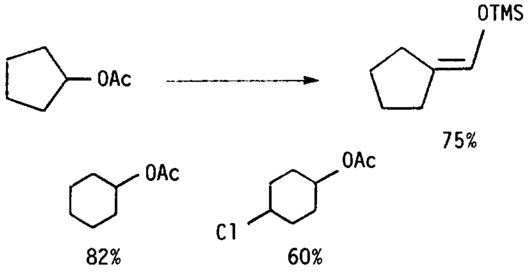
Alcohols were converted to carbonates by reaction with palladium catalysts and carbon monoxide (equation 343) [315]. The catalytic hydrocarbonylation of alcohols has been reviewed (50 references) [316]. Acetates were converted to trimethyl silyl enol ethers by reaction with carbon monoxide, trimethyl silane, and cobalt carbonyl (equations 344-346) [317].



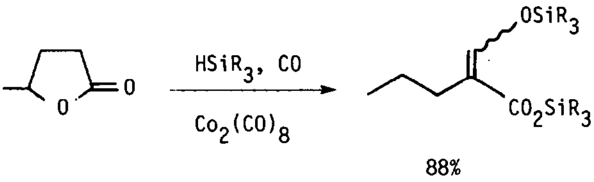
(343)



(344)



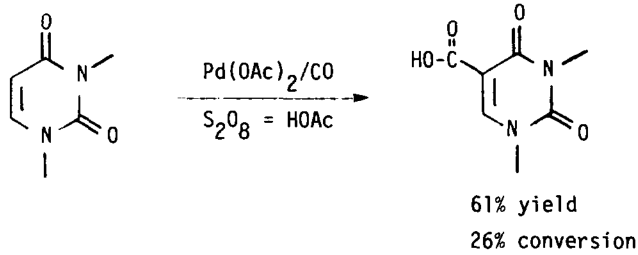
(345)



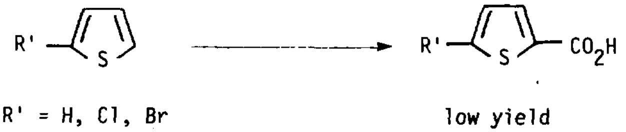
(346)

5. Miscellaneous Carbonylations

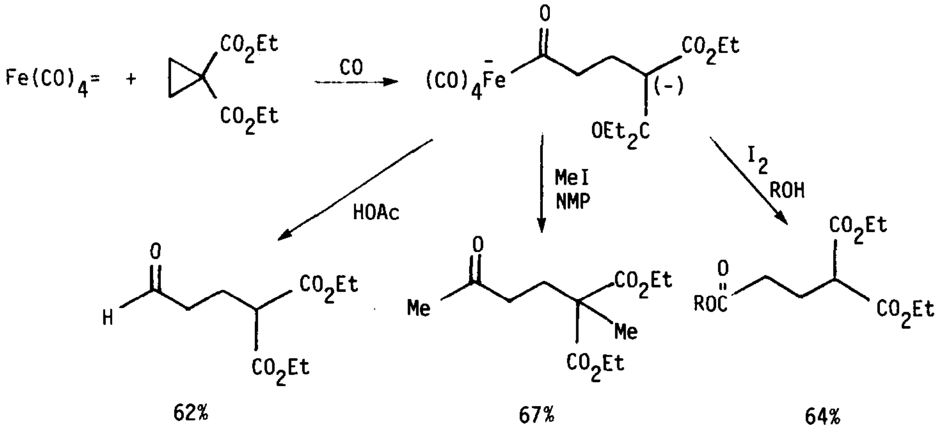
Heteroaromatic compounds were carbonylated by carbon monoxide in the presence of a palladium catalyst (equations 347 and 348) [318]. Cyclopropane dicarboxylic esters were ring opened and carbonylated by anionic iron carbonyl compounds (equation 349) [319]. Aromatic hydrocarbons were converted to benzoic acids using a palladium catalyst (equation 350) [320]. The kinetics and mechanism of ethyl formate formation from (ethoxycarbonyl) cobalt tetracarbonyl and hydrogen were studied [321].



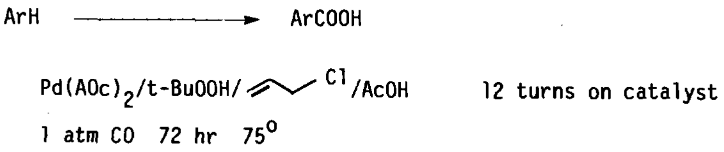
(347)



(348)



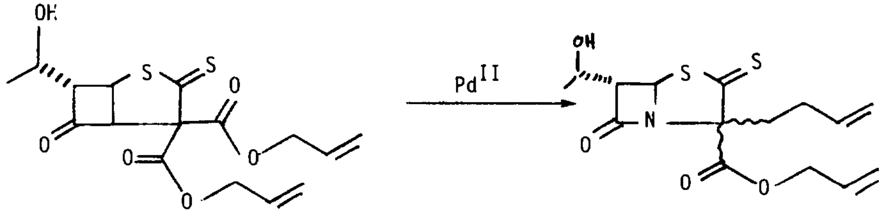
(349)



(350)

6. Decarbonylation Reactions

Decarbonylation of aliphatic α,β-unsaturated aldehydes by a Wilkinson complex has been studied [322]. Allyl acetates were decarboxylated by treatment with palladium(II) salts (equation 351) [323].

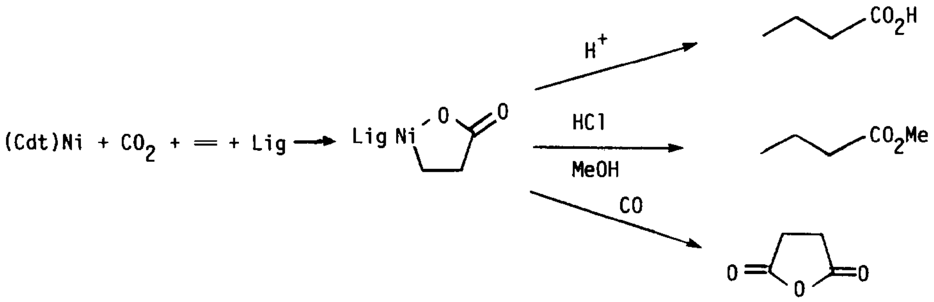


(351)

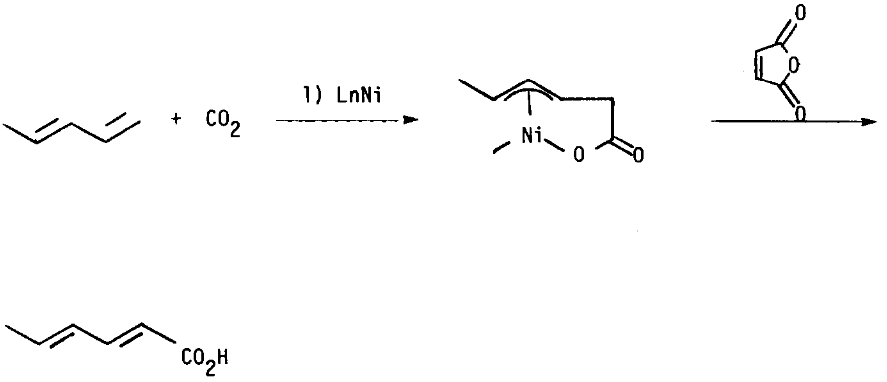
7. Reactions of Carbon Dioxide

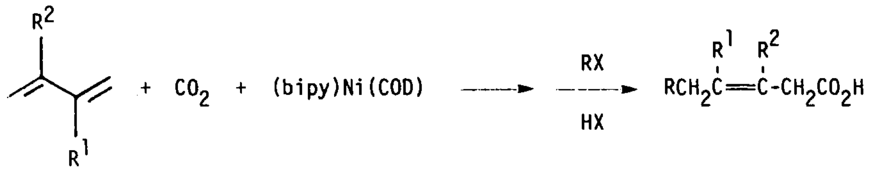
Carbon dioxide and ethylene combined in the presence of a nickel(0) catalyst (equation 352) [324]. Dienes were carboxylated by reaction with carbon dioxide and a nickel(0) catalyst (equation 353) [325], (equation 354) [326][327]. Carbon dioxide coupled with dicyclohexyl carbodiimide in the presence of a nickel(0) catalyst (equation 355) [328]. Methylene cyclopropanes combined with carbon dioxide in the presence of palladium(0) complexes to give furanones [329].

(352)



(353)





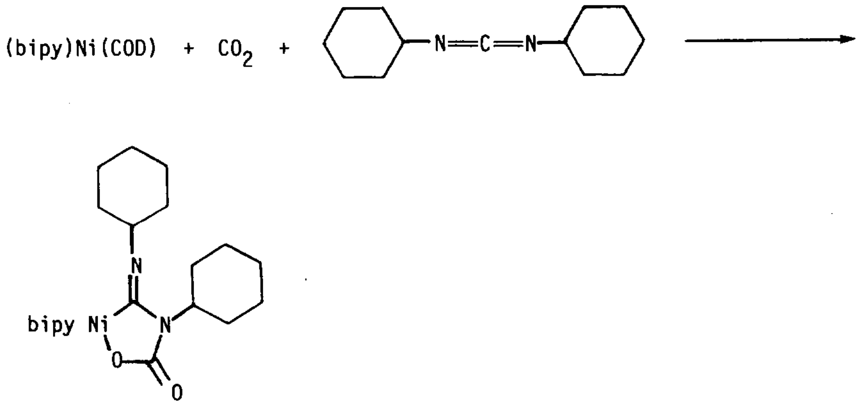
(354)

R^1 = Me, H

R^2 = Me, H

R = Me, Bz

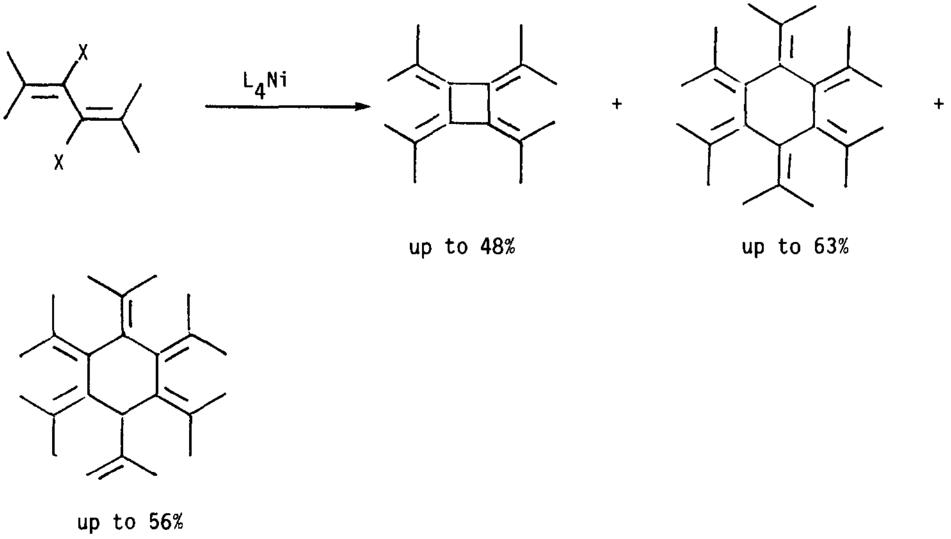
(355)

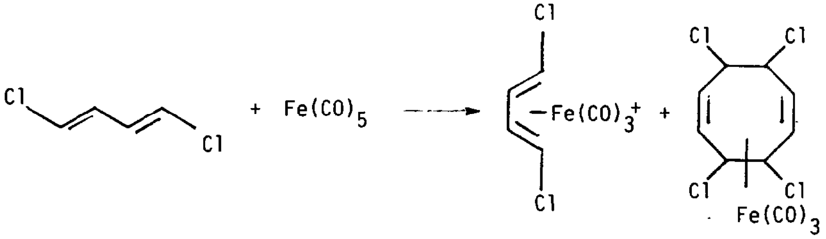


D. Oligomerizations

The dimerization of ethylene by nickel carbonyl/triphenylphosphine catalysts on alumina was studied [330], as was the use of nickel complexes of poly(2-methyl-5-vinylpyridine)/diethylaluminum chloride as a catalyst for propene dimerization [331]. Propylene was also dimerized in the homogeneous phase by the use of $Co(acac)_3/HAlEt_2/L/COD$ catalysts [332]. Dimerization and oligomerization of butene was effected by an alkylnickel catalyst [333]. Cationic π-allylpalladium complexes dimerized ethylene and styrene, and the π-allyl complex, $[allyl\ Pd\ (MeNO_2)_2]BF_4$, was recovered unchanged [334]. Dimethyl phthalate was stereospecifically dimerized to tetramethyl-3,4,3',4' biphenyltetracarboxylate by a phenanthroline containing palladium catalyst [335]. The cationic nickel π-allyl complex $(Me\underline{CHCHCH_2}NiL_2)^+$ was a catalyst precursor for the formation of linear and cyclic butadiene dimers [336]. 2,3-Dihalobutadiene cyclo dimerized or trimerized in the presence of nickel(0) catalysts (equation 356) [337]. 1,4-Dichlorobutadiene cyclodimerized when treated with iron pentacarbonyl (equation 357) [338].

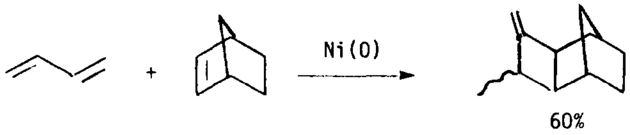
(356)



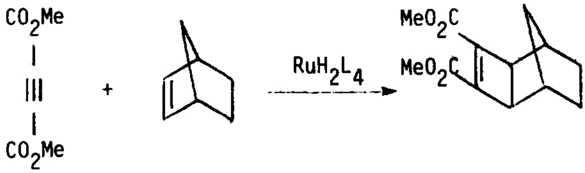


(357)

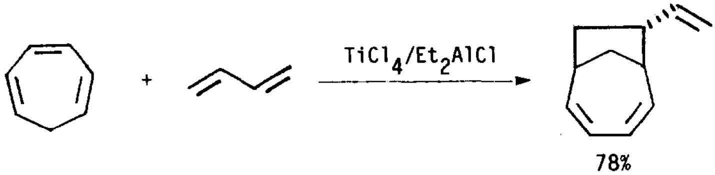
Nickel(0) complexes catalyzed the codimerization of butadiene with norbornene (equation 358) while ruthenium complexes catalyzed the codimerization of dimethylacetylene dicarboxylate with norbornene (equation 359) [339]; and cobalt catalyzed the codimerization of nobornadiene with tetracyclo $[4.3.0.0.^{2,4}0^{3,7}]$ non-8-ene [340]. Low valent titanium catalyzed the codimerization of cycloheptatriene with butadiene (equation 360), norbornene (equation 361), and alkynes (equation 362) [341]. Acetylene combined with (cyclooctadiene) (cyclooctatriene) ruthenium to produce a bicyclic dimer (equation 363) [342]. Butadiene and methyl acrylate codimerized when treated with a cationic π allyl palladium catalyst (equation 364) [343]. Butadiene was dimerized and carbonylated when treated with palladium(II) acetate, trialkyl phosphine and maleic anhydride [344].



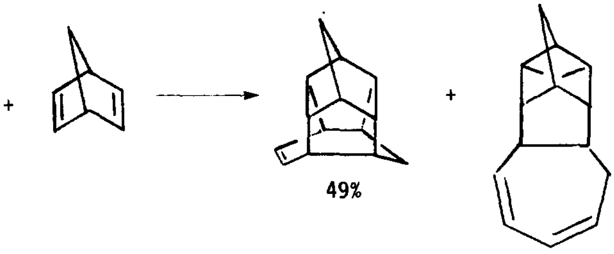
(358)



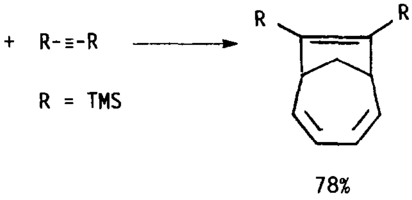
(359)



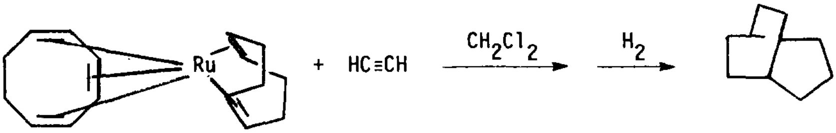
(360)



(361)

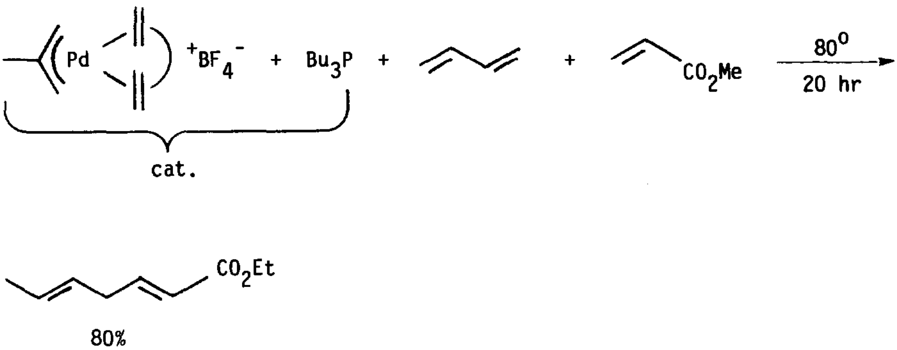


(362)



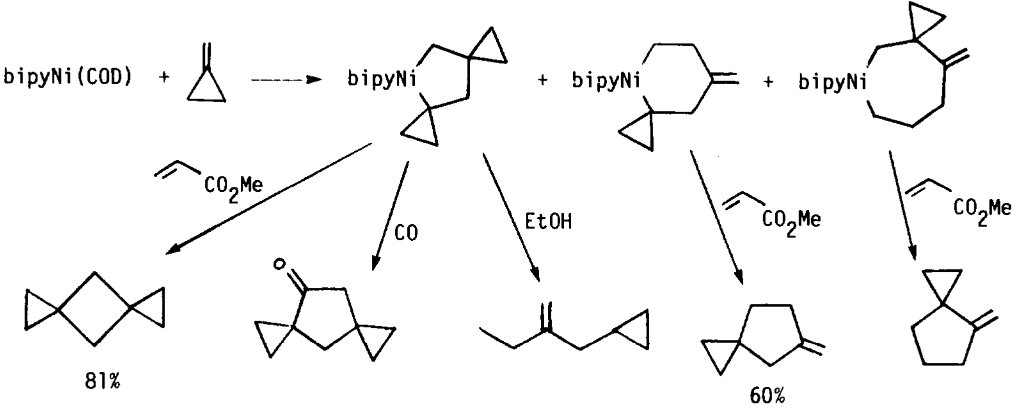
(363)

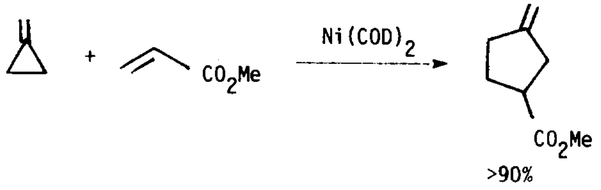
(364)



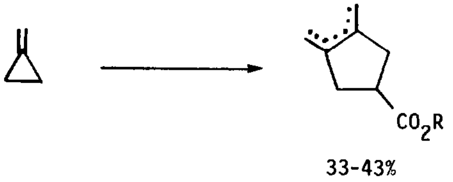
Nickel(0) complexes catalyzed the cyclodimerization of vinylcyclopropane as well as the cooligomerization (equation 365) [345]. The same complexes catalyzed the codimerization of this substrate with methyl acrylate (equations 366-369) [346], and methyl pentadienoate (equation 370) [347]. With chiral acrylates modest diastereoselectivity was observed (equation 371) [348]. More complex products resulted from the diene analog of methylene cyclopropane (equation 372) [349]. Methyl acrylate dimerized to trans dimethylhex-2-enedioate with a cationic palladium catalyst (equation 373) [350].

(365)





(366)



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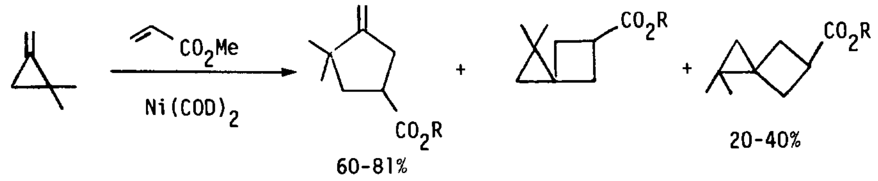

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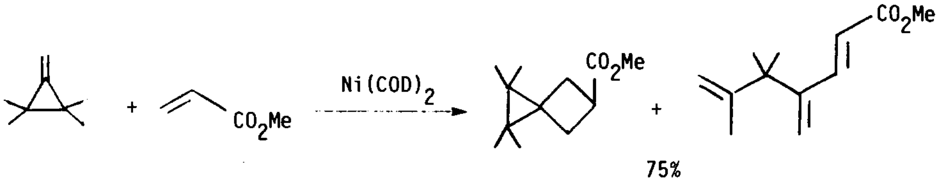

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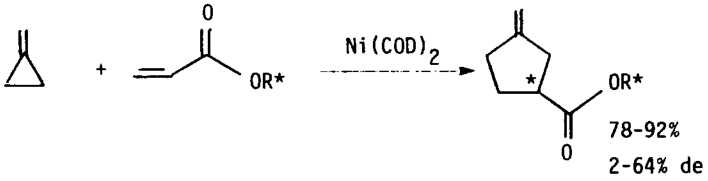
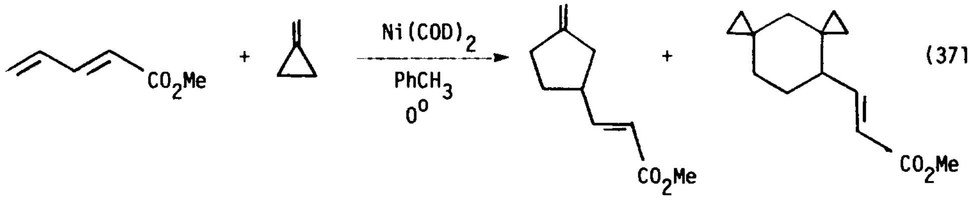


(370)



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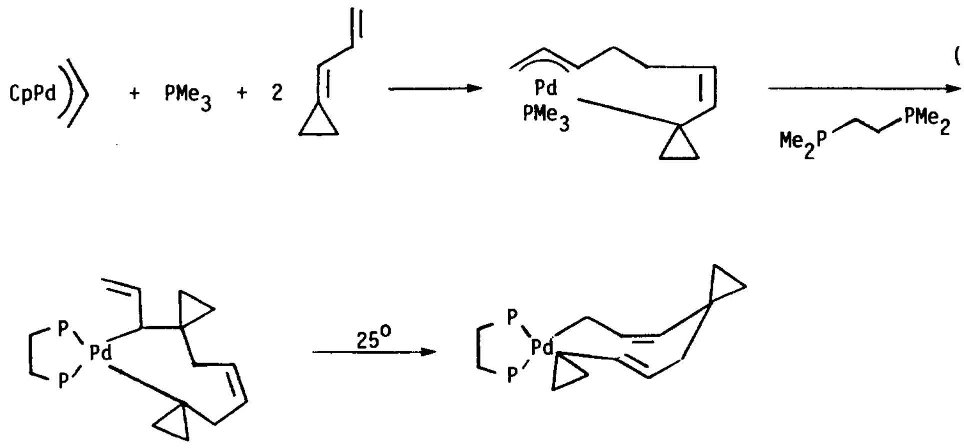
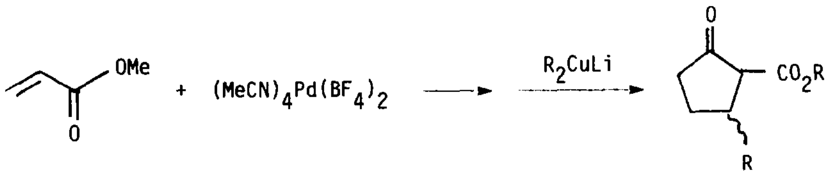
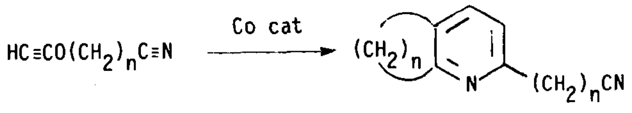


(372)



(373)

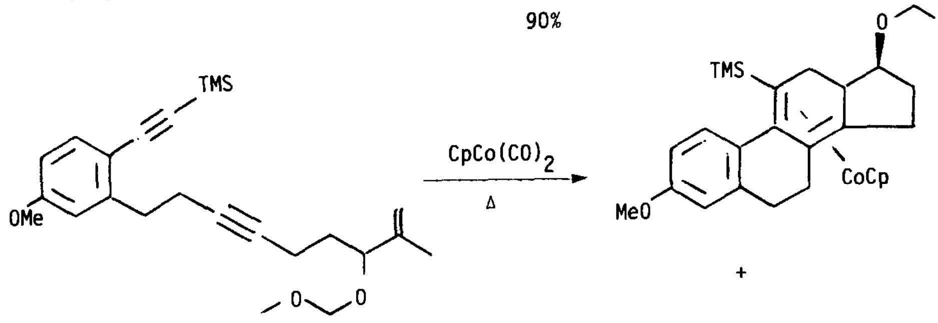
Cobalt mediated cyclizations of α,ω-enzynes was the topic of a dissertation [351]. α,ω-Cyanoacetylenes cyclized to pyridines when treated with low valent cobalt catalysts (equation 374) [352]. The steroid nucleus was synthesized by a cobalt catalyzed enzne cyclization (equation 375) [353]. Dihydroisoindoles were prepared from a nickel-catalyzed cyclocodimerization of propargyl amines with alkynes (equation 376) [354], (equation 377) [355]. Manganese(III)acetate/copper(II) acetate dimerized butadiene and acetone (equation 378) [356].



(374)

n = 4, 5, 6, 8

90%

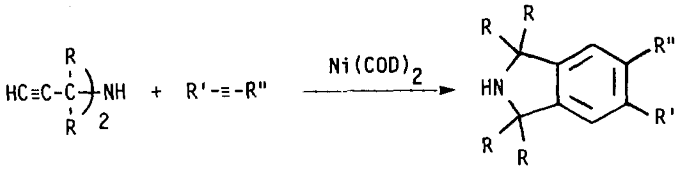


72%

+

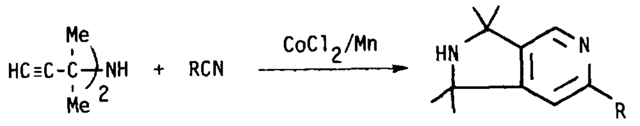
(375)

20% 17α



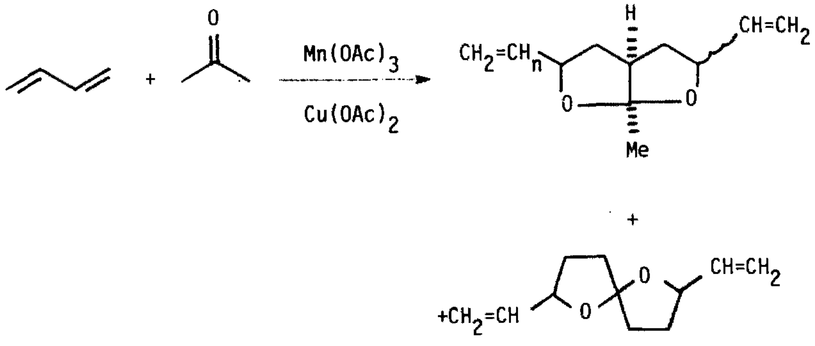
(376)

20-82%



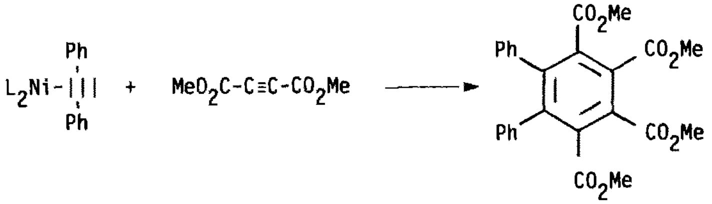
(377)

R = Me, Pr, Ph, PhCH$_2$, NCCH$_2$CH$_2$



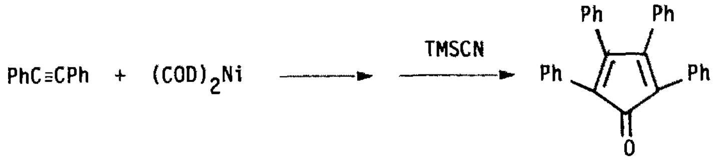
(378)

Dispersed nickel on silica catalyzed the cyclotrimerization of acetylene [357]. Nickel(0) tolan complexes co cyclotrimerized with dimethylacetylene dicarboxylate (equation 379). Tetracyclone was also made under different conditions (equation 380) [358]. Palladium(II) complexes of sulfoxides catalyzed the cyclotrimerization of tolan (equations 381) [359]. The cobalt(I) catalyst $CpCo(C_2H_4)_2$ cyclotrimerized a number of alkynes (equation 382) [360]. Tantalum(V) and Niobium(V) halides cyclotrimerized 1-pentyne, while tungsten(VI) and molybdenum(V) halides led to linear polymers [361]. Butadiene cyclotrimerized to 1,5,9-cyclododecatriene when treated with a titanium(IV) alkoxide/triethyl dialuminum trichloride catalyst [362][363].



(no yield)

(379)



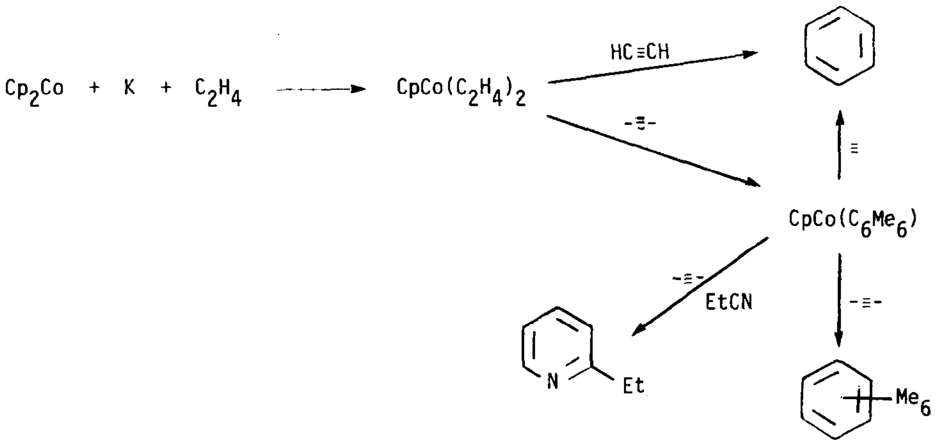
50%

(380)

L = 4-MeOPhSOCH$_3$

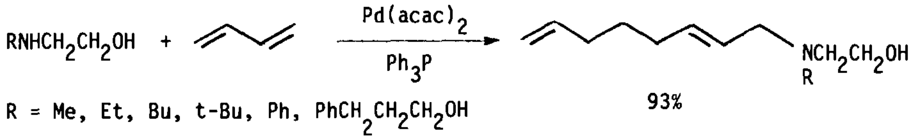
4 turn on catalyst

(381)

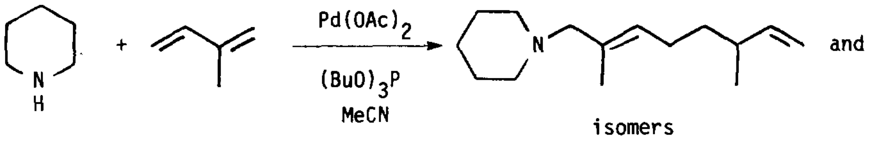


(382)

Palladium catalyzed telomerization of isoprene with diethylamine led to the tail-to-tail terpene amine in the absence of acids, while carbon dioxide favored the head-to-tail and tail-to-head isomers, and $BF_3 \cdot Et_2O$/tricyclohexylphosphine favored the head-to-head isomer [364][365]. Aminoalcohols reacted with butadiene in the presence of palladium(II) acetylacetonate and triphenylphosphine to give telomerization products (equation 383) [366]. Piperidine telomerized with isoprene in the presence of a palladium(II) catalyst (equation 384) [367]. Allene and allylamine were telomerized by a similar catalyst system (equation 385) [368]. Palladium(0) and nickel(0) complexes telomerized vinylcyclopropane, butadiene, and secondary amines (equation 386) [369].

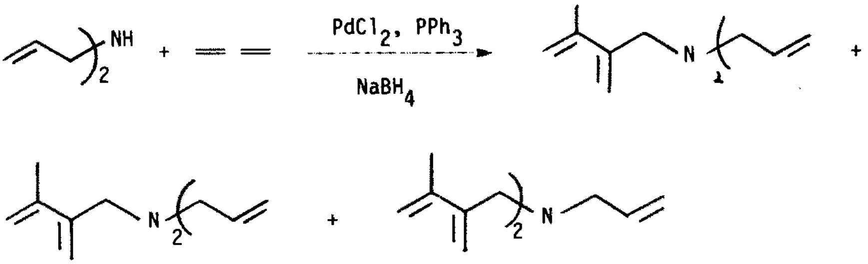


(383)



(384)

(385)



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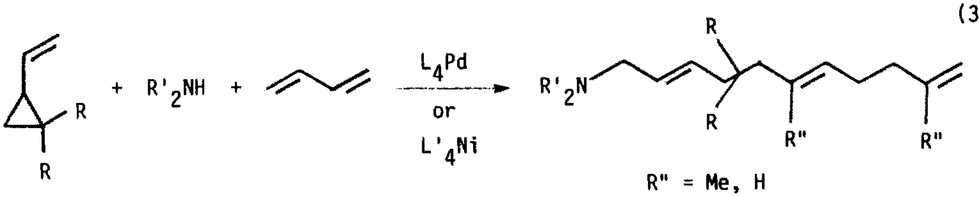
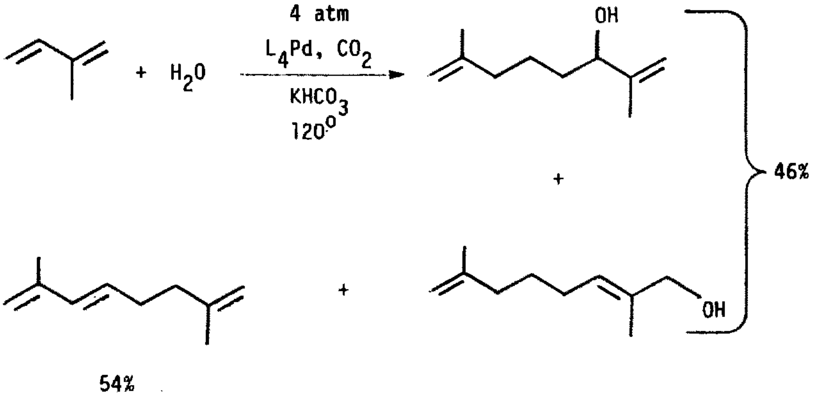
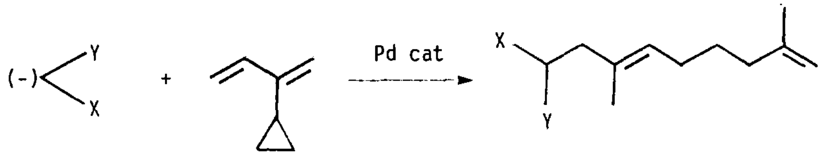


R" = Me, H

Palladium(II) complexes telomerized butadiene, isoprene, and piperylene in the presence of water to give polyunsaturated alcohols [370]. Isoprene underwent a similar process using a palladium(0) catalyst (equation 387) [371]. Palladium catalysts also telomerized 2-cyclopropyl-1,3-butadiene with activated methylene compounds (equation 388) [372]. Ester sulfones behaved similarly [373]. In the presence of carbon dioxide, butadiene telomerization incorporated carbon dioxide to produce esters and lactones (equation 389) [374].

(387)

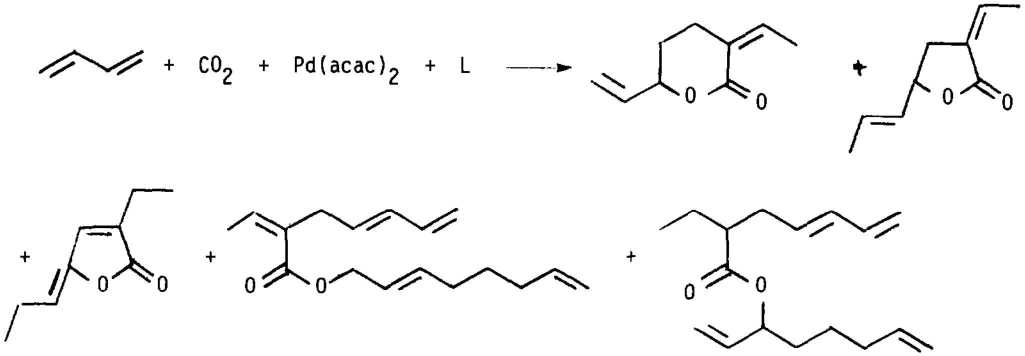




(388)

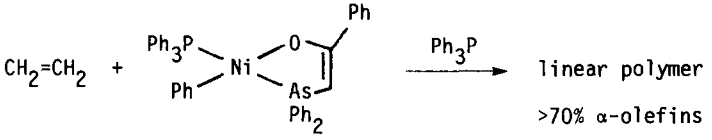
X, Y = CO_2Me, $PhSO_2$, COMe, NO_2

(389)

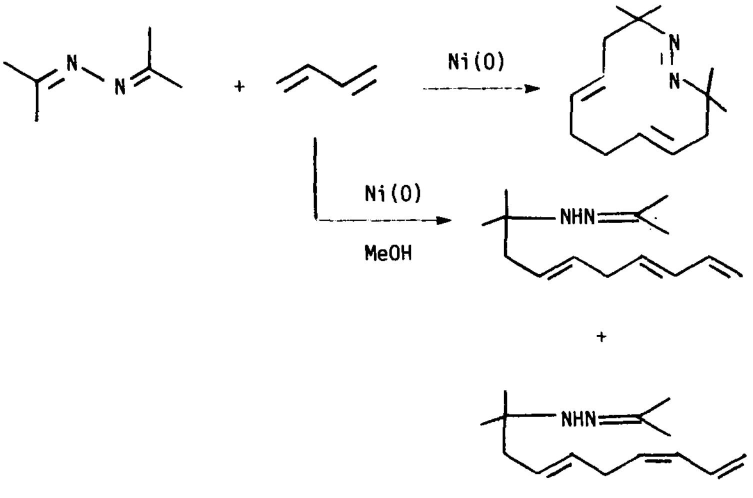


The study of organometallic polymerization catalysts was the topic of a dissertation [375]. Polyethylene of molecular weights of C_{40}-C_{200} was made using a tantalum carbene catalyst (equation 39) [376]. Niobium(IV)halides and tantalum(V) halides converted trimethylsilylpropyne to a high polymer having a molecular weight of $\approx 10^6$ [377]. Ethylene was polymerized by a nickel arsine catalyst (equation 391) [378]. Heteroolefins and butadiene cooligomerized in the presence of a nickel(0) catalyst (equation 392) [379].

$$\mathrm{Ta(CHCMe_3)(H)L_3I_2} + {=} \xrightarrow[\mathrm{PhCH_3}]{0^{\circ}} \text{Living polymer} \xrightarrow{\mathrm{HCl}} \underset{C_{40}\text{-}C_{200}}{\text{polyethylene}} \quad (390)$$



(391)



(392)

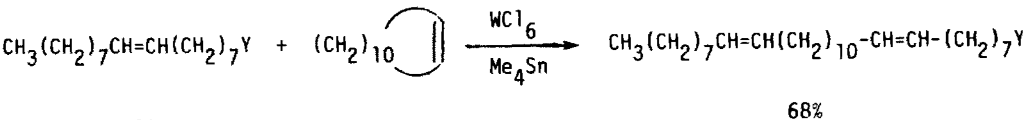
E. Rearrangements

1. Metathesis

Metathesis of functionalized olefins has been reviewed (46 references) [380]. Metathesis of propene on metal oxide supported catalysts (Group VIB metal oxides on alumina) was studied [381]. An olefin metathesis catalyst was formed by electrolytic reduction of tungsten(VI) chloride with an aluminum electrode in methylene chloride solvent [382]. Isobutylene was metathesized by a samarium oxide-tungsten-alumina catalyst [383]. A discussion of alternative mechanisms for the olefin metathesis reaction has been published [384]. Several new metathesis reactions were studied with a number of substrates and catalysts [385]. The stereochemistry of the cross metathesis of 1-butene and 2-butene over rhenium oxide-alumina oxide was studied [386]. The relation between oxygen chemisorption and olefin disproportionation activity of tungsten oxide/silica catalysts was examined [387]. The kinetics of the first alkylation step in the metathesis catalyst system tungsten(VI) chloride-tetramethyltin was second order with an activation energy of 26 kJ/mol [388]. The catalyst system arene tungsten tricarbonyl, alkyl aluminum dichloride, oxygen was studied by infrared and proton nmr spectroscopy [389].

Long chain aliphatic esters were prepared by the metathesis of cyclododecene and olefinic esters (equation 393) [390]. Dinitriles were prepared by the metathesis of unsaturated nitriles (equation 394) [391]. A molybdenum carbene converted ketones to methylene compounds (equation 395) [392], while tungsten diphenylcarbene complexes metathesized with enol ethers (equation 396) [393]. Racemic 1-methylnorbornene polymerized to all cis syndiotactic all head-to-tail product when treated with rhenium(V) chloride (equation 397) [394].

(393)

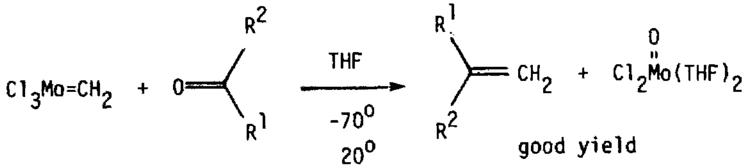


$Y = CO_2Me, OAc$

$$CH_2{=}CH(CH_2)_nCN \underset{Me_4Sn}{\overset{Re_2O_7\text{-}Al_2O_3}{\rightleftarrows}} CH_2CH_2 + NC(CH_2)_nC{=}C\text{-}(CH_2)_nC{\equiv}N \qquad (394)$$

80-91%

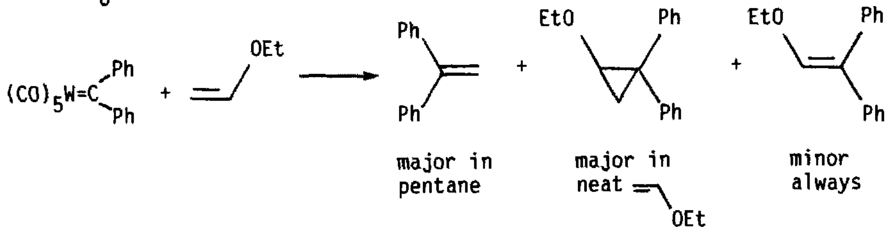
$n = 2\text{-}5$



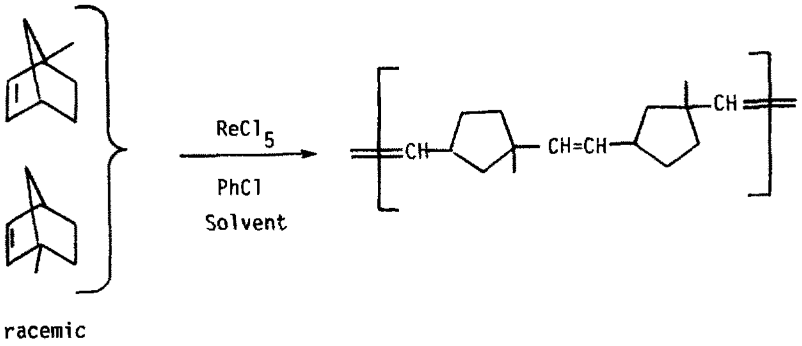
(395)

$R^1 = H, Me$

$R^2 = n\text{-}C_6, Ph, 4\text{-}MeOPh$



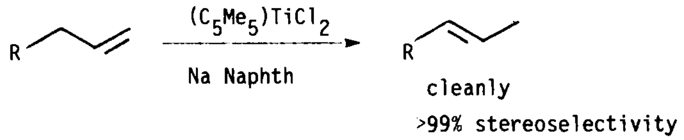
(396)



(397)

2. Olefin Isomerization

Alumina-supported osmium clusters catalyzed the isomerization of 1-hexene [395]. Bromocarbonyl hydridotris(triphenylphosphine)osmium(II) was also an efficient olefin isomerization catalyst [396], while silica supported triosmium clusters were catalysts for butene isomerization [397]. Terminal olefins isomerized to 2-olefins when treated with reduced titanium species (equation 398) [398]. Allyl benzene rearranged to β-methyl styrene under the influence of cobalt hydride catalysts (equation 399) [399]. ω-Olefinic amines rearranged to enamines when treated with iron carbonyl under photolysis (equation 400) [400]. The photo catalyzed isomerization of safrole and eugenol by iron carbonyl was studied [401].



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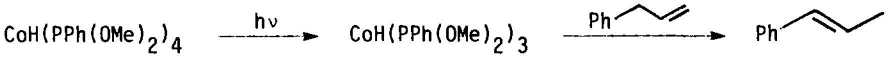
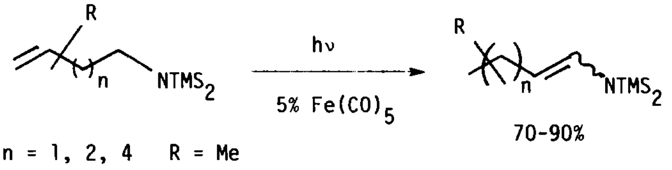


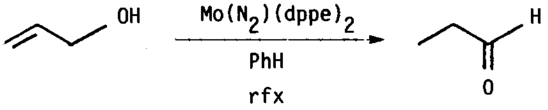
(399)



(400)

3. Rearrangements of Allylic and Propargylic Oxygen and Nitrogen Compounds

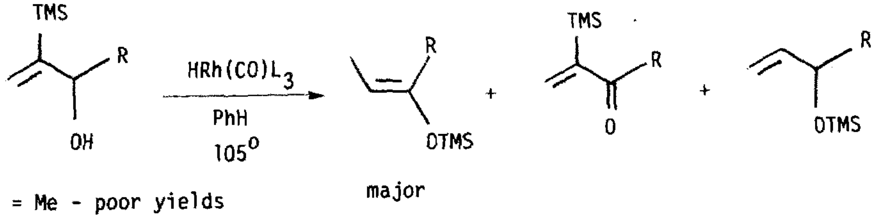
Allylic alcohols rearranged to aldehydes (equation 401) or ketones (equation 402) and allyl amines to enamines (equation 403) when treated with a molybdenum nitrogen complex [402][403]. Vinyl silanes bearing allylic OH groups rearranged to trimethylsilylenol ethers when treated with a rhodium(I) hydride catalyst (equation 404) [404]. Palladium(0) complexes catalyzed allylic O to S rearrangement (equation 405) [405], and allylic S to N rearrangements (equation 406) [406]. Allylic acetate rearrangement also occurred with this catalyst (equation 407) [407]. Allyl vinyl carbonates rearranged with loss of carbon dioxide when treated with palladium(0) catalysts (equation 408) [408].



(401)

(402)

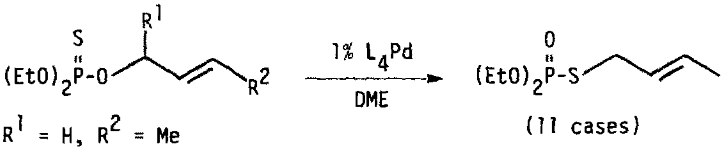
(403)



(404)

R = Me - poor yields

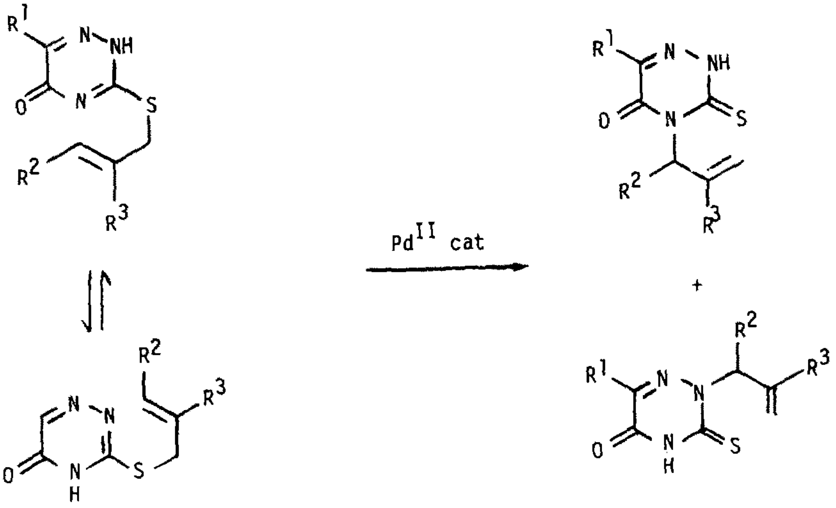
$n\text{-}C_5$, C_7, C_{10}, Ph, 3-hept, cyclohex - 80-100%



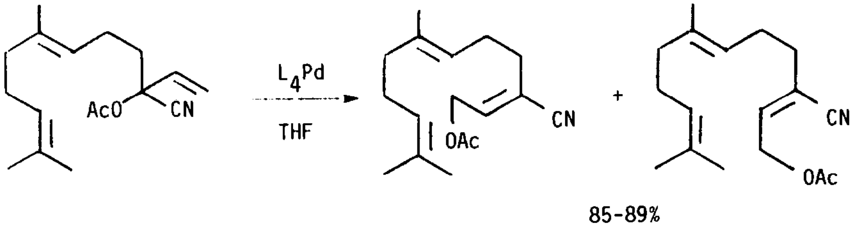
(405)

R^1 = H, R^2 = Me

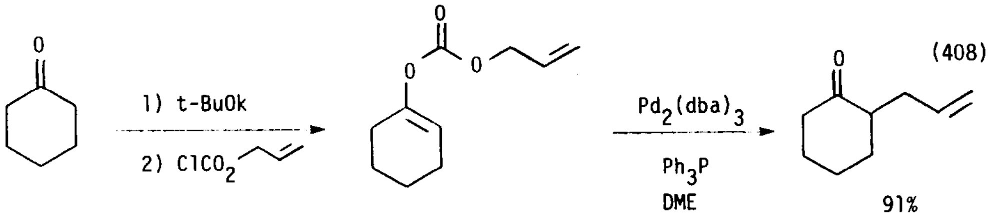
R^1 = Me, R^2 = H



(406)



(407)



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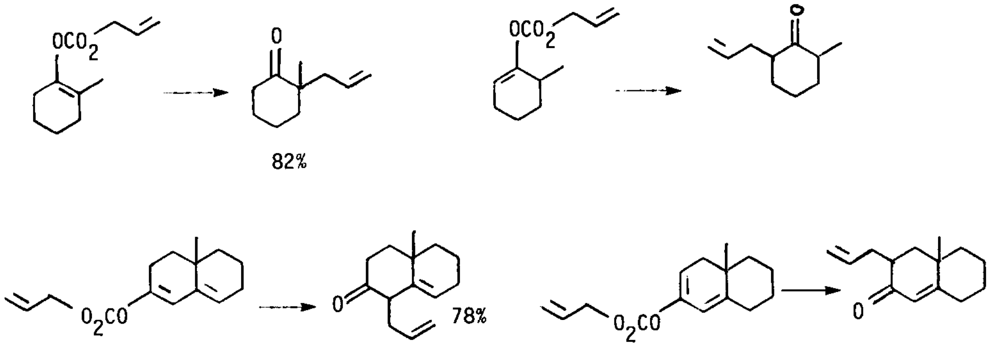
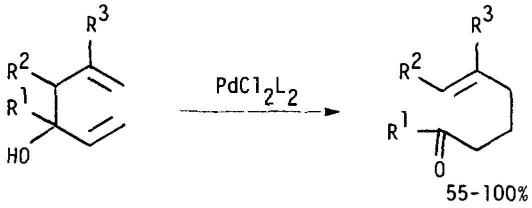
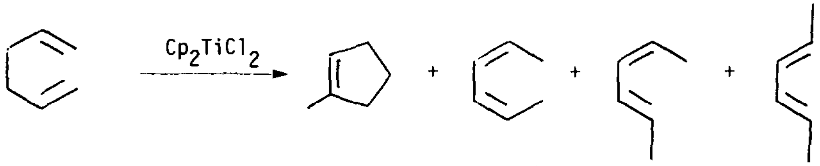


4. Skeletal Rearrangements

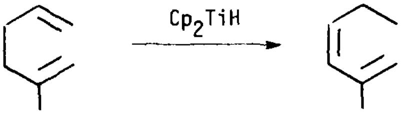
The mechanism of C_5 and C_6-dehydrocyclization and skeletal isomerization of hydrocarbons on metal-containing catalysts has been reviewed (170 references) [409], as has platinacyclobutane chemistry, skeletal isomerization, α-elimination, and ring expansion reactions (22 references) [410]. Oxycope rearrangements were catalyzed by palladium(II) complexes (equation 409) [411]. 1,5-Hexadienes underwent several different rearrangements when treated with cyclopentadienyl titanium catalysts (equations 410-413) [412]. Divinylcyclobutane rearranged to 4-vinylcyclohexene over nickel catalysts (equation 414) [413]. Norcarenes isomerized over rhodium or platinum catalysts (equation 417) [414]. Iron carbonyl promoted a photochemical isomerization to give cyclobutane fused to cyclooctatetraene (equation 416) [415]. Nickel chloride catalyzed the skeletal rearrangement of dienyl alcohols containing thioenol ethers (equations 417 and 418) [416]. Chromium carbonyl promoted 1,5-sigmatropic rearrangements in hexaethylidenecyclohexane (equation 419) [417].



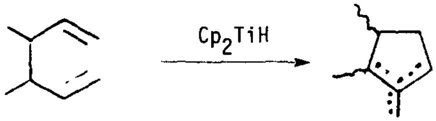
(409)



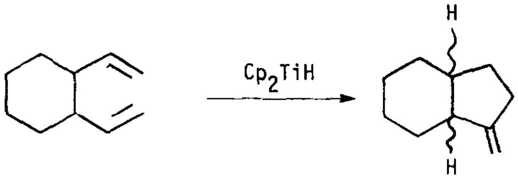
(410)



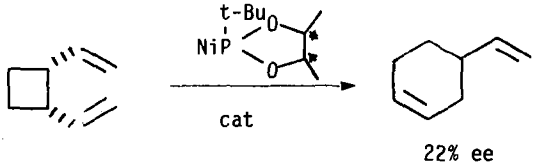
(411)



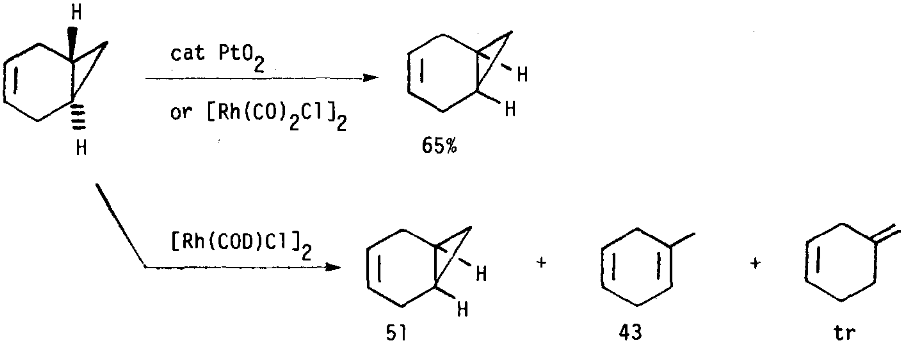
(412)



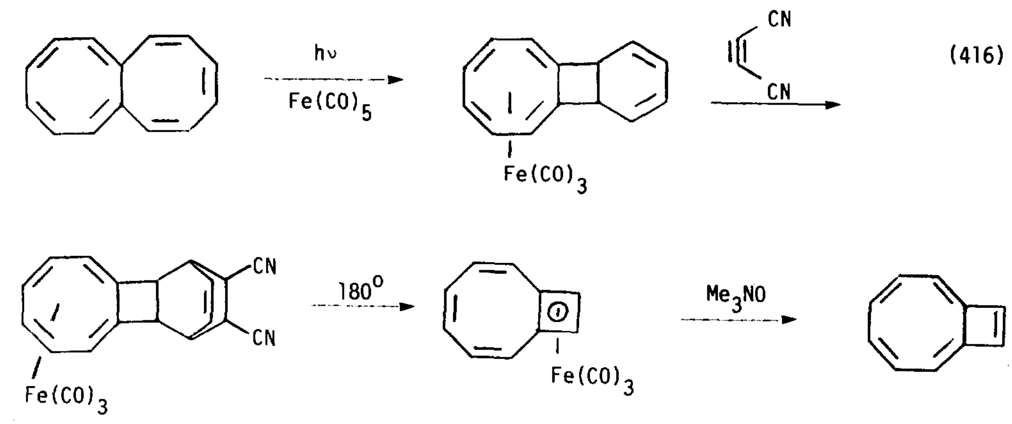
(413)



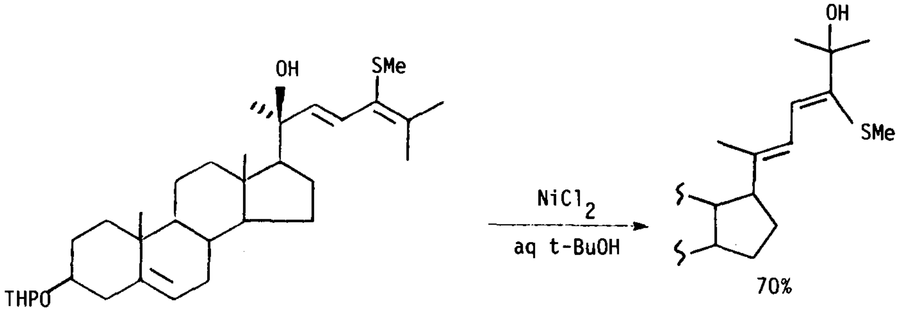
(414)



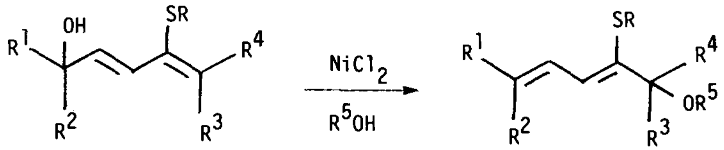
(415)



(416)

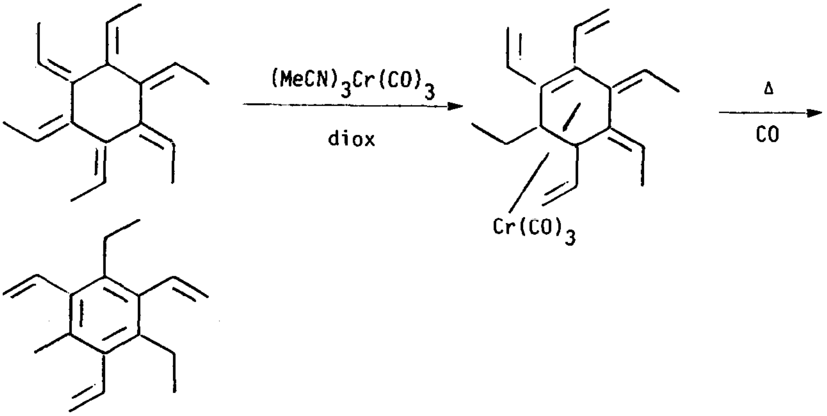


(417)



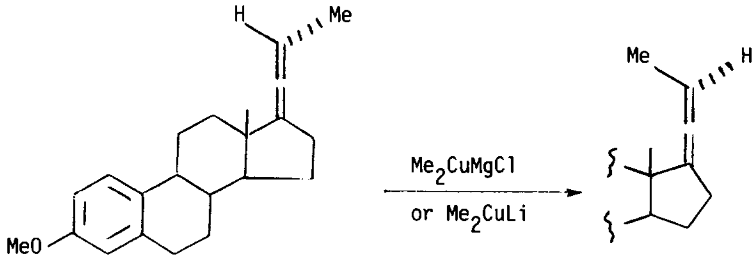
(418)

(419)



5. Miscellaneous Rearrangements

Catalytic rearrangements of epoxide compounds has been reviewed (117 references) [418]. Allenes were epimerized by organocopper reagents, ostensibly by an electron transfer process (equations 420 and 421) [419]. The redistribution reactions of methylsiloxanes catalyzed by transition metal complexes has been examined [420].



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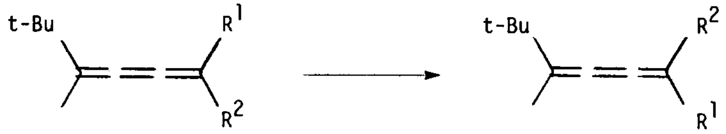
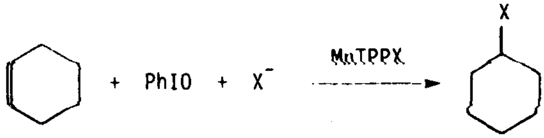


(421)

III. Functional Group Preparations

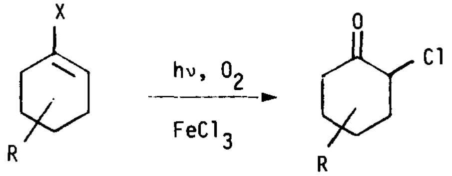
A. Halides

Cyclohexane was converted to cyclohexyl halides or azides by reaction with iodosyl benzene in the presence of manganese-porphyrin compounds (equation 422) [421]. Thioenolethers (equation 423) and vinyl silanes (equation 424) were converted to α-haloketones by irradiation in the presence of oxygen and iron(III) chloride [422]. Similar conditions ring opened cyclic olefins to chloroketones (equations 425-427) [423]. Vinyl halides were haloalkylated by organic halides when irradiated in the presence of copper(I) halides and phosphines (equation 428) [424]. Exocyclic 1,5-dienes were halogenated and cyclized by reaction with copper(I) chloride and palladium(II) chloride (equation 429) . Cyclic ethers combined with acid chlorides in the presence of platinum(II) catalysts to give ω-chloroesters (equation 430) [426]. Cyclohexene oxide was converted to 1,2-dibromocyclohexane by a molybdenum complex (equation 431) [427]. Epoxy sugars were converted to chlorohydrins by palladium(II) chloride (equations 432 and 433) [428]. Acetylene was converted to 1-chloro-1,3-butadiene by reaction with several different metals (equation 434) [429].



(422)

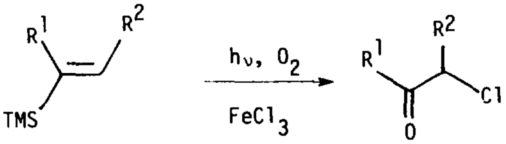
X =	N_3	Cl	F	OAc	CN	Br	I	NCO
	55%	8%	0	0	0	55%	25%	7%



(423)

X = St-Bu, SPh, SEt 40-80%

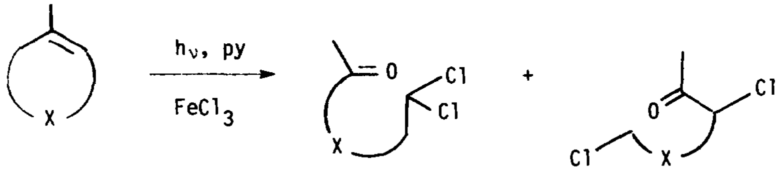
R = H, 2-Me, 3-Me, 4-Me, 5-Me, 6-Me



(424)

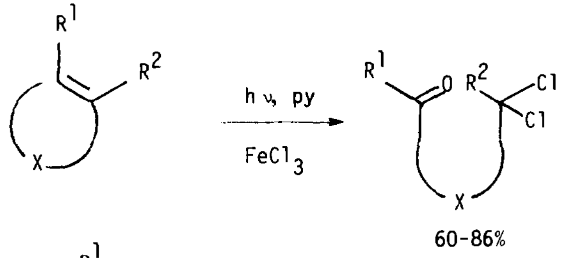
$R^1 = C_6$, $R^2 = H$ 47%

$R^1 = n\text{-Pr}$, $R^2 = Et$ 67%

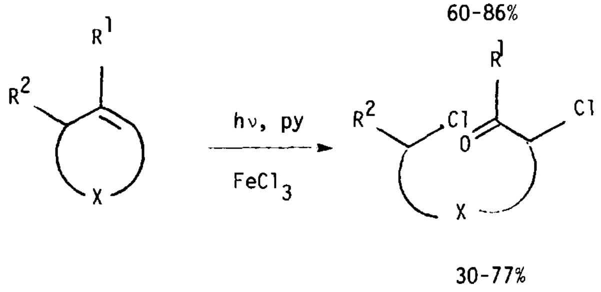


(425)

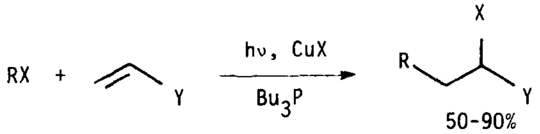
X =		
CH_2	45%	8%
$(CH_2)_2$	47%	7%
CH_2CH-i-Pr	26%	12%
$(CH_2)_3$	6%	0
$(CH_2)_8$	35%	33%



(426)



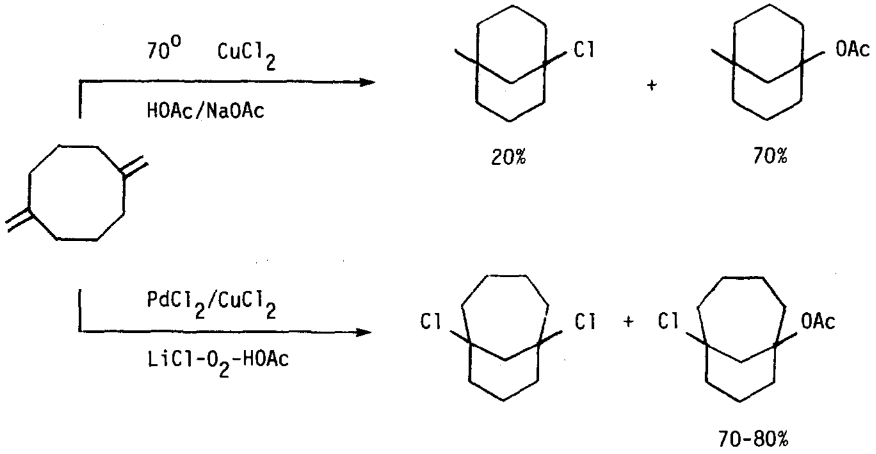
(427)

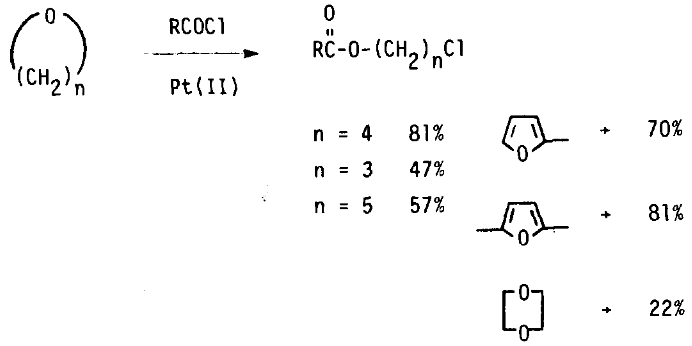


(428)

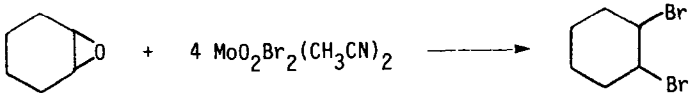
R = n-Bu, c-C_6, t-Bu, Br$(CH_2)_3$-Br, Br$(CH_2)_2CO_2Et$
X = Br, Cl
Y - CN, CO_2Et

(429)



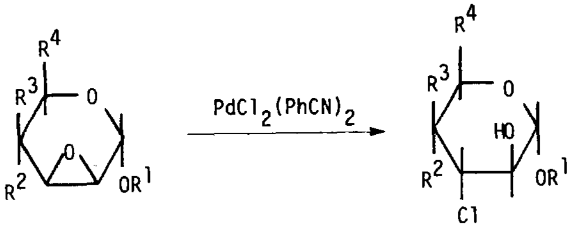


(430)



70%

(431)



40-50%

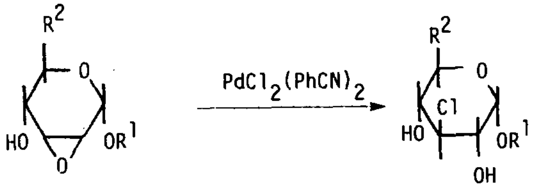
(432)

R^1 = $PhCH_2$, Me

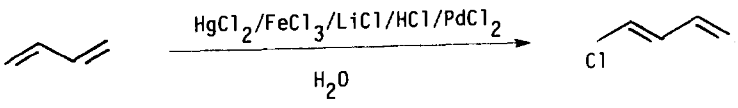
R^4 = H, CH_2OH

R^2 = OH, H

R^3 = OH, H



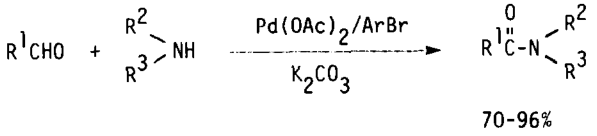
(433)



(434)

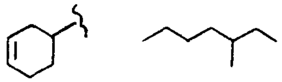
B. Amides, nitriles, nitrocompounds

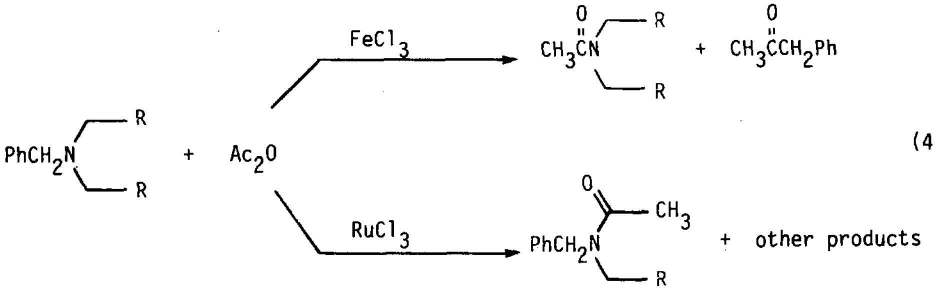
Aldehydes and secondary amines were oxidatively transformed to amides by palladium(II) acetate (equation 435) [430]. Iron(III) chloride oxidized secondary amines to amides, while ruthenium(III) chloride gave an isomer (equation 436) [431]. Imines and isocyanates condensed to give urea in the presence of nickel(0) catalysts (equation 437) [432]. Copper(II) acetate catlayzed the hydrolysis of α-helocyanoimines to amides (equation 438) [433]. Primary amides were alkylated to secondary amides by alcohols in the presence of a ruthenium catalyst (equation 438) [434]. Propargyl amines were converted to citraconic acid diamides by cobalt carbonyl (equation 439) [435].



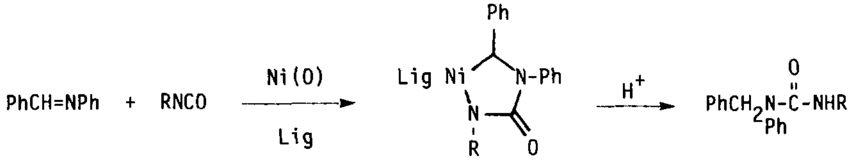
(435)

R^1 = Ph, 4-CNPh, 4-MeOPh, n-C_7, $PhCH_2CH_2$, PhCH=CH



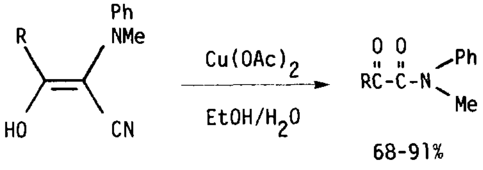


(436)



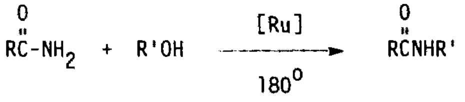
(437)

R = Me, Ph, 4-MePh
n-Bu, t-Bu, c-C_6



(438)

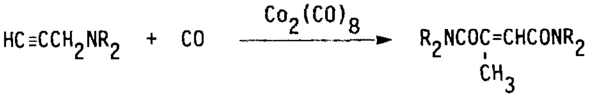
R = Ph, 4-MePh, 4-MeOPh, 4-ClPh



$$\overset{O}{\overset{\|}{RC}}\text{-}NH_2 + R'OH \xrightarrow[180^0]{[Ru]} \overset{O}{\overset{\|}{RC}}NHR' \qquad (439)$$

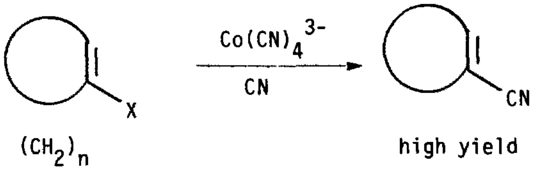
R = Me, Ph, n-Bu, 4-ClPh
R' = Me, Et, n-Bu, C_8

9-58% conversion
30-100% selectivity



$$HC{\equiv}CCH_2NR_2 + CO \xrightarrow{Co_2(CO)_8} R_2NCO\underset{CH_3}{\underset{|}{C}}{=}CHCONR_2 \qquad (440)$$

Vinyl halides were converted to vinyl cyanides by reaction with cobalt(I) cyanide (equation 441) [436]. A similar reagent converted aryl halides into aryl cyanides (equation 442) [437]. Oximes were dehydrated to nitriles by copper(II) acetate (equation 443) [438]. Cobalt(II) cyanides converted alkynes to saturated and unsaturated nitriles under a hydrogen atmosphere (equation 444) [439]. Tetracyano nickelate did the same to diynes (equation 445) [440]. The kinetics and mechanism of copper-catalyzed hydrocyanation of olefins has been studied [441].



high yield

(441)

n = 3, 4, 5, 6

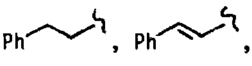
$$ArX + CoCl_2 + KCN + KOH \longrightarrow ArCN + ArH \qquad (442)$$

Ar = 4-H_2NPh, 4-MeOPh,
α-Napt, β-Napt

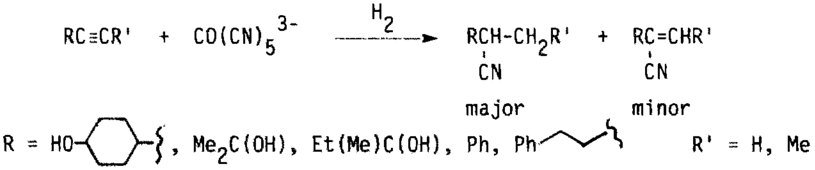
0-84% 0-55%

$$RCH{=}NOH \xrightarrow[CH_3CN]{Cu(OAc)_2} RCN \qquad (443)$$

85-98%

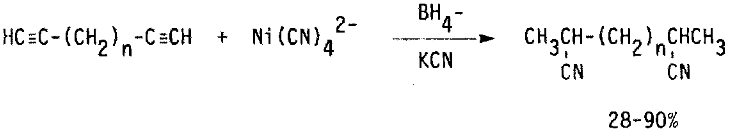


R = n-C_7, n-C_9, Ph, Ph, 4-MePh, 4-MeOPh, 3-NO_2Ph



$$RC\equiv CR' + CO(CN)_5^{3-} \xrightarrow{H_2} \underset{\text{major}}{\underset{CN}{RCH}\text{-}CH_2R'} + \underset{\text{minor}}{\underset{CN}{RC}=CHR'} \qquad (444)$$

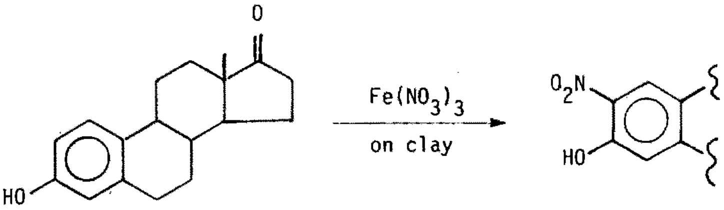
$R =$ HO–, $Me_2C(OH)$, $Et(Me)C(OH)$, Ph, Ph $R' = H, Me$



$$HC\equiv C\text{-}(CH_2)_n\text{-}C\equiv CH + Ni(CN)_4^{2-} \xrightarrow[KCN]{BH_4^-} \underset{CN}{CH_3CH}\text{-}(CH_2)_n\underset{CN}{CH}CH_3 \qquad (445)$$

28-90%

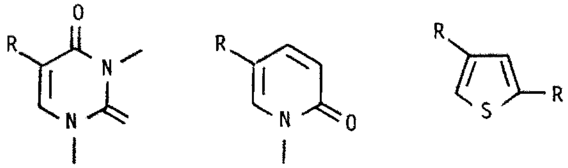
Iron(III) nitrate on clay nitrated phenolic steroids (equation 446) [442]. Sodium nitrate and palladium(II) acetate nitrated a number of heteroaromatic compounds (equation 447) [443].



(446)

$$\text{Het Ar} + NaNO_2 + Pd(OAc)_2 \longrightarrow O_2N\text{-Het Ar} \qquad (447)$$

Het Ar =



C. Amines, Alcohols

Aryl bromides were converted to anilines by reaction with tributyltin amines in the presence of a palladium catalyst (equation 448) [444]. The mechanism of the copper catalyzed amination of bromoanthroquinones was studied (equation 449) [445]. Copper metal catalyzed the amination of aryl bromides (equation 450) [446].

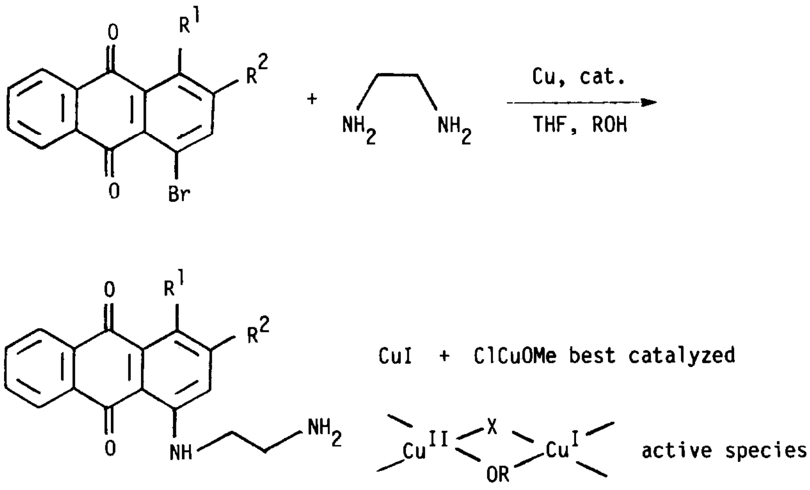
$$Bu_3SnNEt_2 + ArBr \xrightarrow[PhCH_3 \quad 100^0]{L_2PdCl_2} ArNEt_2 + Bu_3SnBr \qquad (448)$$

ArCl, ArI don't react

Ar = Ph, 4-MePh, ∿80%

Ar = 2-MeOPh, 2-MePh, 4-MeOPh, 4-ClPh, 4-BrPh, 4-MeCOPh, 4-NO_2Ph, 4-Me_2NPh } 20-45%

(449)

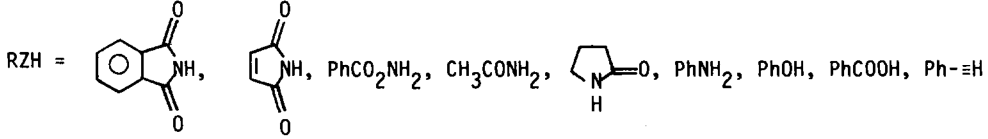


CuI + ClCuOMe best catalyzed

active species

$$RZH + ArX \xrightarrow[150\text{-}270^0]{Cu} RZAr \qquad (450)$$

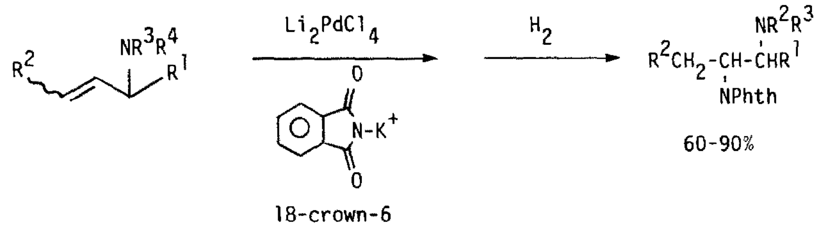
moderate to good yields



RZH = NH, NH, $PhCO_2NH_2$, CH_3CONH_2, =O, $PhNH_2$, PhOH, PhCOOH, Ph-≡H

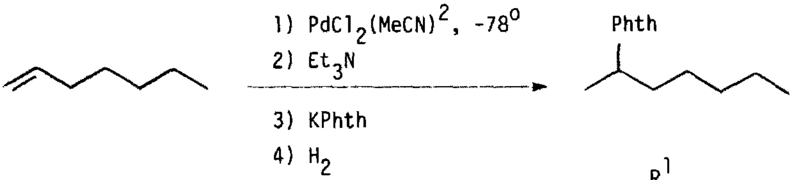
ArX = PhI, PhBn, PhCl, 4-MePhBr, 4-FPhBr, 4-MeOPhBr

The amination of alkenes has been reviewed (189 references) [447]. Palladium promoted addition of nucleophiles to allylic amines and isolated olefins was the topic of a dissertation [448]. This work has also appeared in the primary literature (equations 451 and 452) [449]. Olefins were converted to diamines by reaction with a cobalt nitrosyl species (equation 453) [450]. This work was also the subject of a dissertation [451]. Olefins were aminated by reaction with metal amides (equation 454) [452].

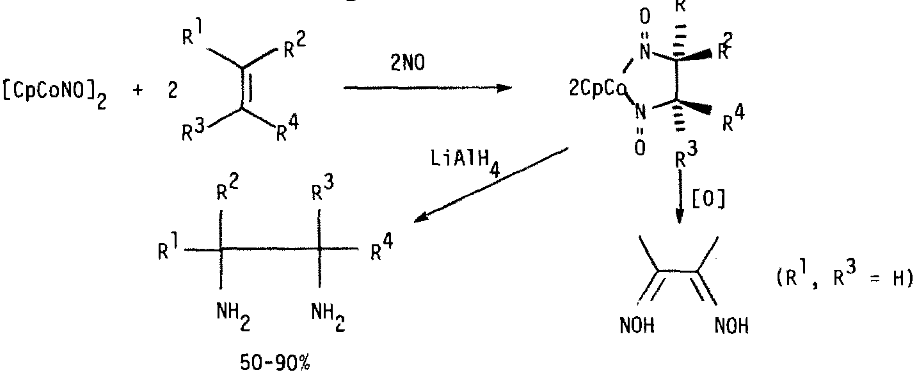


(451)

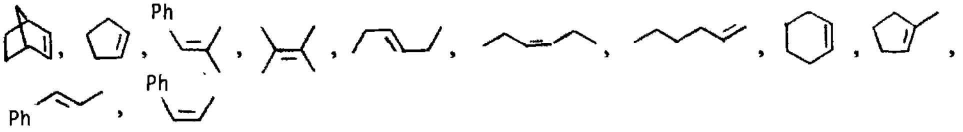
R^1 = H R^1, R^4 = $(CH_2)_3$ R^1 = Ph, Me -- reaction fails
R^2 = H R^3, R^4 = $(CH_2)_4$ or CH_3NSO_2Ph
R^3 = Me
R^4 = Bz, n-Bu

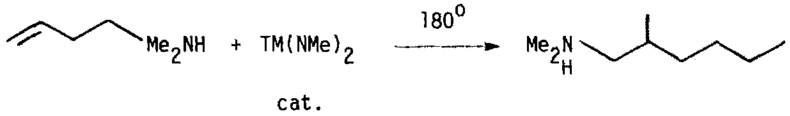


(452)



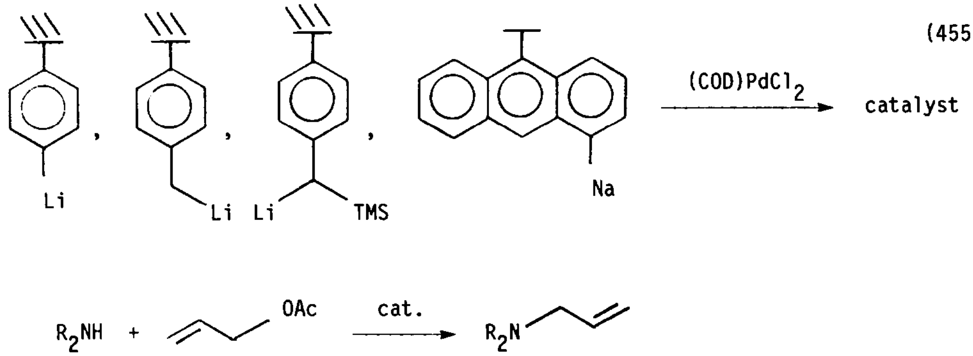
(453)



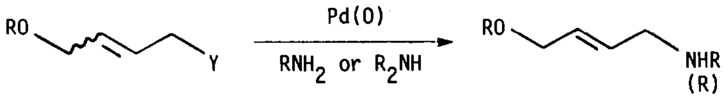


(454)

Polymer supported palladium species catalyzed the allylic amination of allyl acetates (equation 455). The catalyst, characterized by ESCA and electron microscopy was mainly palladium crystallites of about 25A [453]. This same process was catalyzed by 1% palladium on carbon with added triphenylphosphine to activate it [454]. Oxygen-containing allylic acetates were catalytically aminated in a stereo- and regioselective manner in the presence of Palladium(0) catalysts (equation 456-458) [455]. Amination of π-allyl palladium complexes occured trans to the palladium, while carbonylation was a cis process (equation 459) [456]. Diallylamines were deallylated by methane sulfonic acid and palladium on carbon (equation 460) [457].

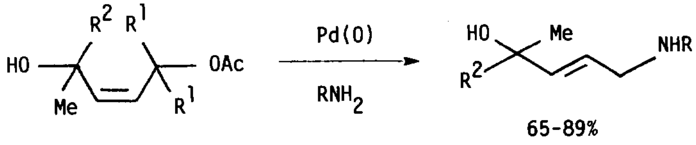


(455)



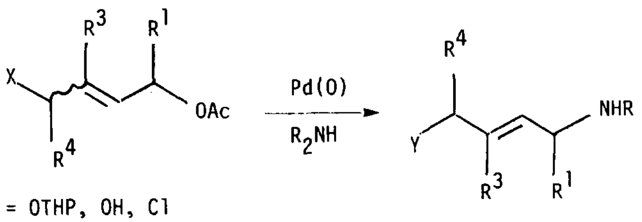
(456)

R = H, OAc
Y = OAc, $OPO(OEt)_2$, Cl



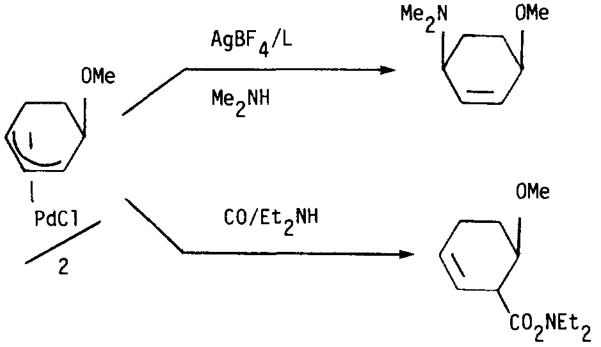
(457)

R^1 = H, Me
R^2 = C_9

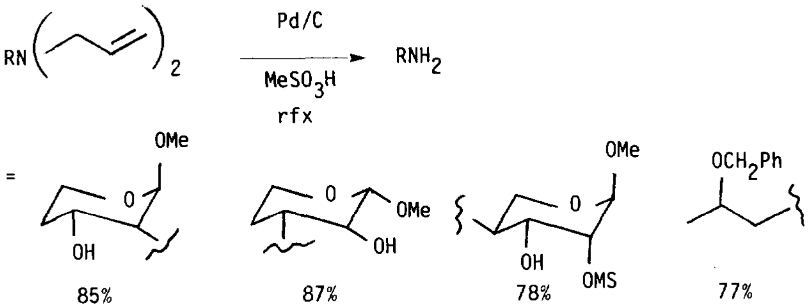


Y = OTHP, OH, Cl

(458)



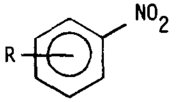
(459)



(460)

Nitrobenzene was reduced to aniline by hydrogenation over silica supported poly(vinylpyrrolidone)-palladium complexes [458], palladium/silica alumina phosphate catalysts with cyclohexene as the hydrogen source [459], palladium supported catalysts (study of influence of metal dispersion) [460], platinum-rhodium on poly(hexamethylenesuccinimide) and -sebacamide [461], $Fe_3(CO)_{11}^-$ on alumina [462], and $HFe(CO)_4^-$ on benzylammonium ion exchange resins [463]. Cobaloxime catalyzed the reduction of nitrobenzene by hydrogen in the olefins [464]. The rhodium cluster $Rh_6(CO)_{16}$ was an effective catalyst for nitrobenzene reduction with carbon monoxide/water and amine ligands [465]. Aryl nitro compounds were reduced under similar conditions using platinum(II), tin(IV) catalysts (equation 461) [466]. Iridium(I) complexes with chelating diamine ligands catalyzed the reduction of nitrobenzene by isopropanol [467]. Reduced titanium speciesreduced nitroaromatics in the presence of a large variety of other functional groups (equation 462) [468]. Aryl imines were reduced to amines by

$[Fe_4S_4(SR)_4]^{3-}$ under acidic conditions [469]. Alkyl azides were reduced to amines by ammonium formate in the presence of palladium on carbon in methanol [470].



$$+ \ 3CO \ + \ H_2O \xrightarrow[Et_3N,\ 80^0]{PtCl_2L_2/SnCl_4} \underset{95\text{-}100\%}{ArNH_2} \ + \ CO_2 \qquad (461)$$

Ar = Ph, 4-MePh, 4-ClPh, 3-OMePh

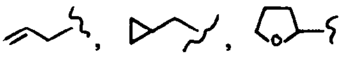
$$ArNO_2 \ + \ TiCl_4/Mg/Hg \xrightarrow[t\text{-}BuOH]{THF} \underset{87\text{-}95\%}{ArNH_2} \qquad (462)$$

tolerates OH, Cl, CO_2Et, CN, CO_2

reduces aliphatic nitro → NH_2

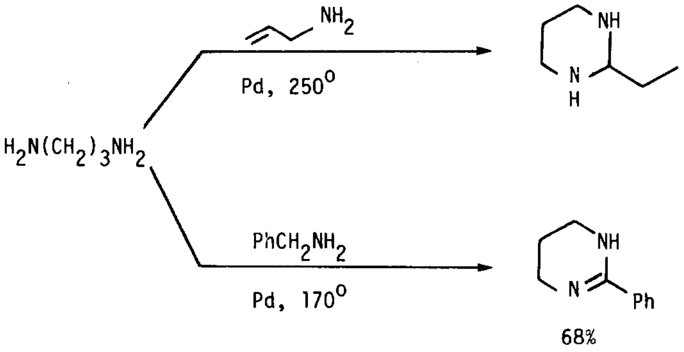
Amines scrambled alkyl groups when heated in the presence of palladium (equations 463 and 464) [471]. Ruthenium catalysts effected amine dehydrogenation and condensation (equation 465) [472]. Platinum on titanium dioxide also catalyzed the conversion of primary amines to secondary amines (equations 466-469) [473]. Secondary amines disproportionated to primary amines in the presence of reduced rhodium-platinum catalysts supported on alumina [474]. Tertiary amines were dealkylated to secondary amides by acid anhydrides in the presence of iron(II) chloride or rhodium(III) chloride [475]

$$R^1R^2CHNHR^3 \ + \ R^4R^5NH \xrightarrow[80\text{-}200^0]{Pd} R^1R^2CHNR^4R^5 \ + \ R^3NH \qquad (463)$$

R^1 = Bz, Me, Et, Bu, $(CH_2)_4$, $(CH_2)_5$, 

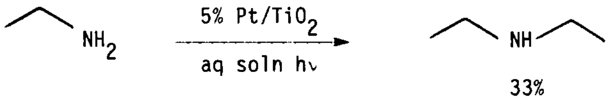
R^2 = Me, H, Ph

R^3 = n-C_6, Ph, H_2NCH_2, 



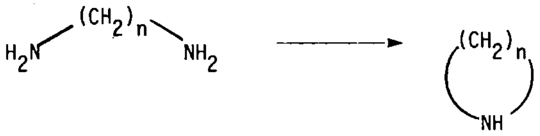
(464)

$$RCH_2NH_2 \xrightarrow{RuCl_3 \cdot L} (RCH_2)_2NH \tag{465}$$



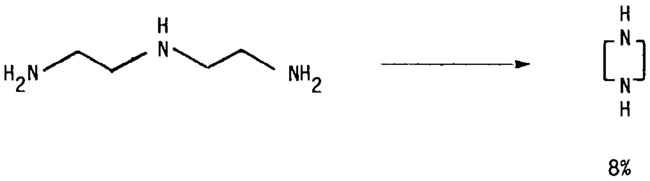
(466)

(467)



n = 5 33%
n = 6 20%
n = 4 67%

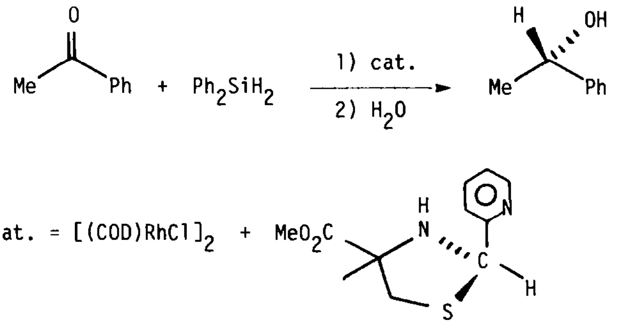
(468)



(469)

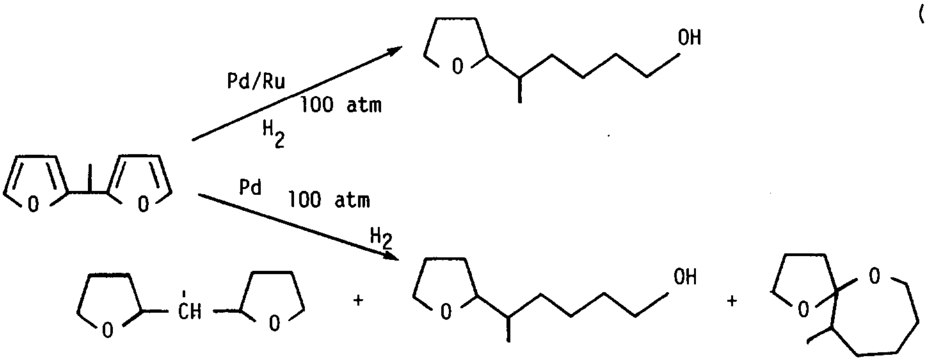
Aryl ketones were reduced to chiral secondary alcohols in up to 86% ee by diphenylsilane in the presence of a chiral rhodium catalyst (equation 470) [476].

Aldehydes and ketones were reduced to alcohols in tertiary amine solvents by hydrogen and $HFe(CO)_4^-$ [477]. α,β-Unsaturated ketones were reduced by alcohols using $HRh(PPh_3)_4$ as a transfer hydrogenation catalysts [478]. Difuryl ethane was hydrogenalyzed over palladium catalysts (equation 471) [479].

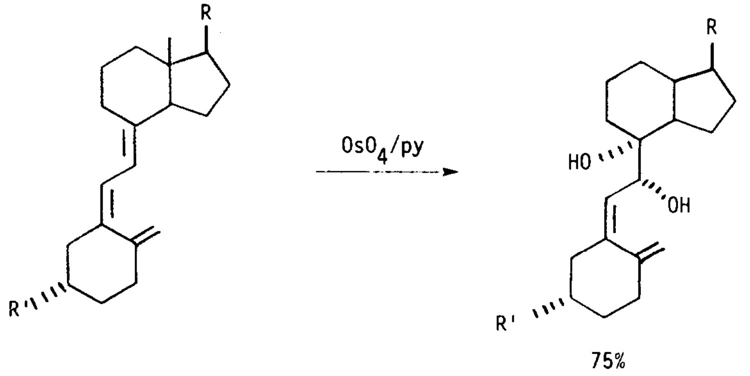


(470)

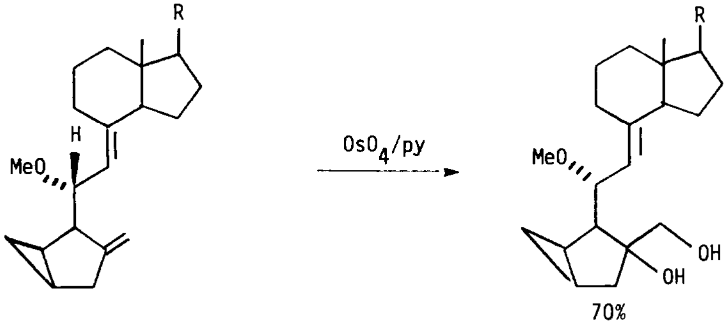
(471)



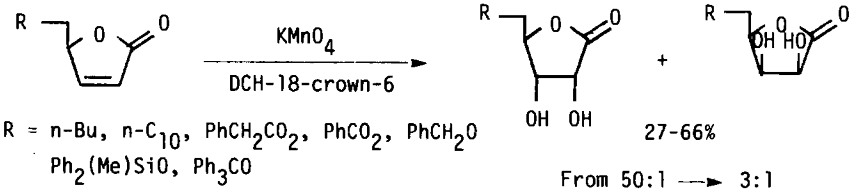
The stereochemistry of cis hydroxylation of allylic alcohols was examined, and it was stated "The relative stereochemistry between the pre-existing OH or OR group and the adjacent newly introduced OH group of the major product in all cases is erythro" [480]. Forty two examples of the above formalism were provided [480a]. The site of osmium tetroxide oxidation of polyenes depended on substrate structure (equations 472 and 473) [481]. Potassium permanganate cis hydroxylated butenolides. The stereochemistry depended on the substitution pattern of the substrate (equation 474) [482]. An organic synthesis procedure for the hydroxamination of E-stilbene by N-chloro-N-argentocarbamates in the presence of osmium tetroxide has appeared [483]. Indoles were oxidized by $MoO_5 \cdot HMPA$ (equations 475-477) [484]. Iron carbonyls were used to protect poly dienes from hydroboration (equation 478) [485].



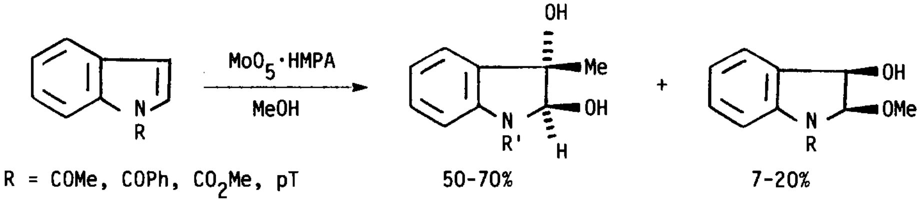
(472)



(473)



(474)



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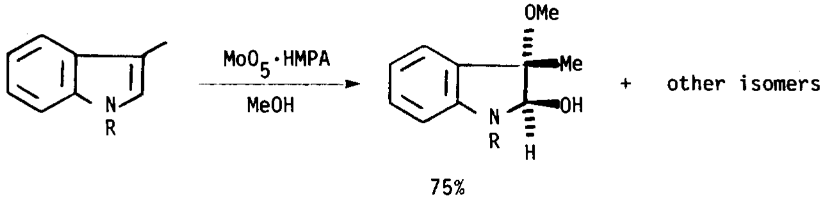

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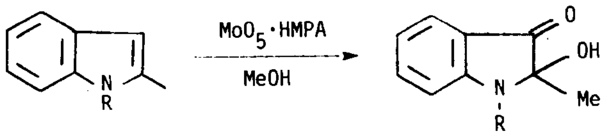
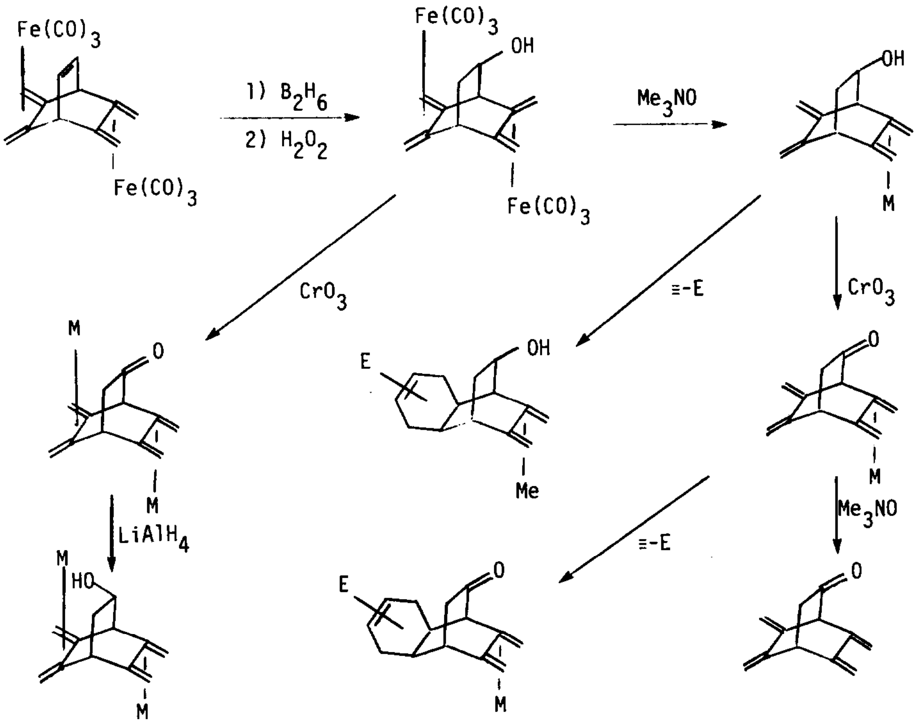
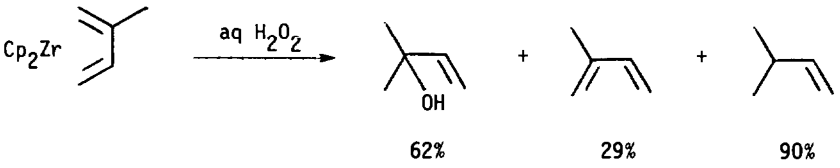


(477)

(478)



Zirconium diene complexes were oxidized to allylic alcohols (equations 479-481) [486], as were π-allylpalladium complexes (equation 482) [487]. Benzene was converted to phenol by hydrogen peroxide and iron(III) in the presence of 1,2-naphthoquinone-4-sulfonate [488]. Epoxides were opened to alcohols by alkyl cuprates (equation 483) [489]. Allyl alcohol was converted to 1,4-butane diol by carbonmonoxide and a $Rh_6(CO)_{16}$ catalyst (equation 484) [490].



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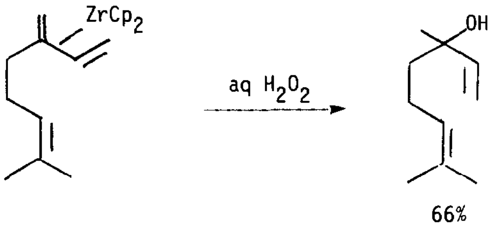

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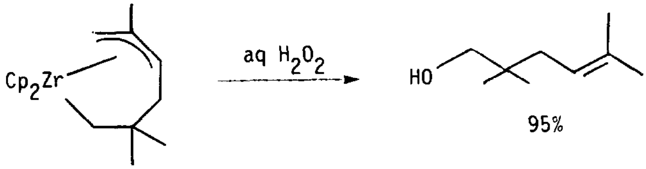

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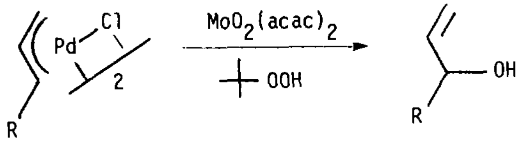
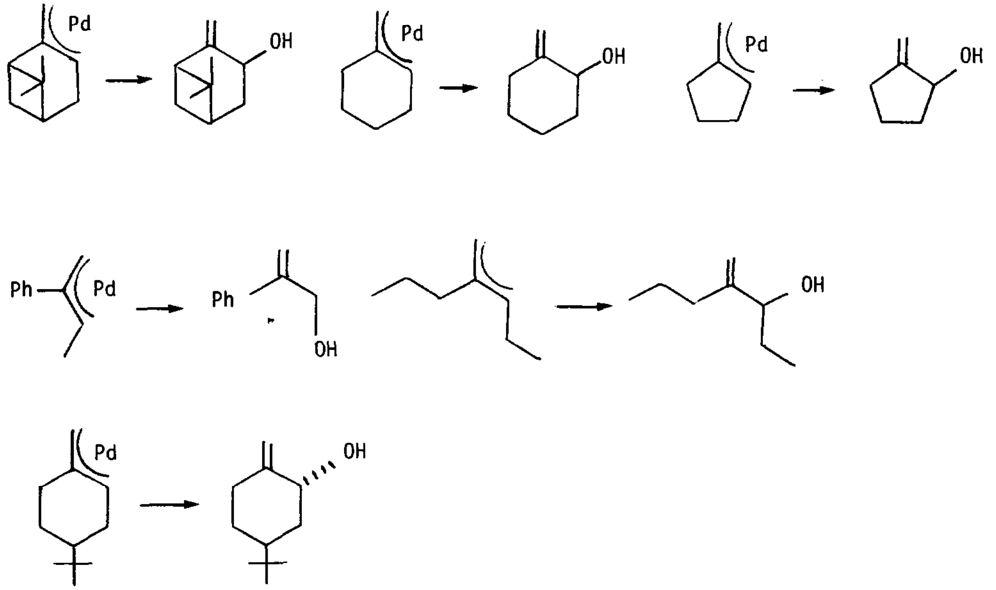
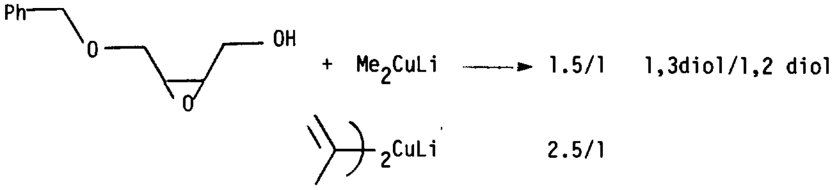


(482)

50-60% conversion

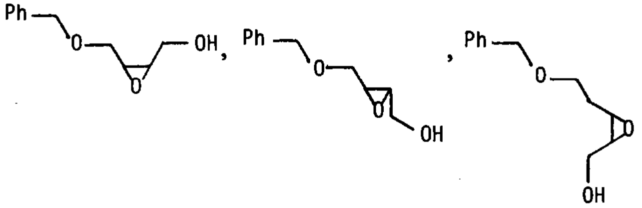
90% yields - always most substituted position



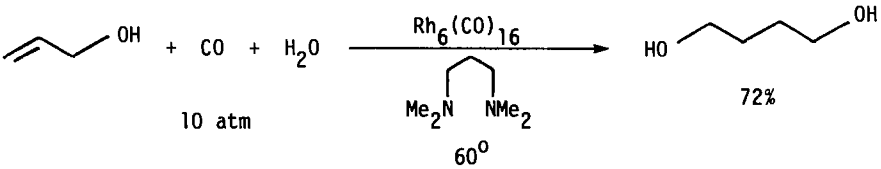


(483)

RMgX/Cu cat. with



all gave 1,3 diol as major product



(484)

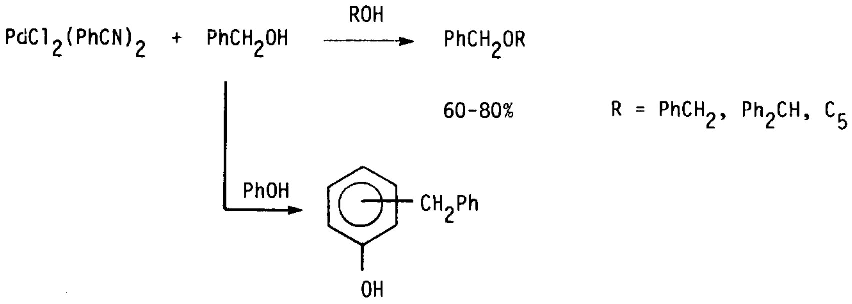
D. Ethers, Esters, Acids

Phenols and aryl halides combined in the presence of copper acetylides to produce diaryl ethers (equation 485) [491]. Palladium(II) chloride condensed benzyl alcohol with alcohols to ethers (equations 486 and 487) [492]. Benzyl halides and acid chlorides were coupled to benzyl ethers by reduced nickel species (equation 488) [493]. Furans were ring opened to silylethers by trialkylsilanes and cobalt carbonyl (equations 489-491) [494]. Enol ethers reacted with iron carbene complexes to produce new enol ethers (equation 492) [495]. Steroidal tosylhydrazones were oxidized to ethers by copper(II) chloride (equation 493) [496]. Photolysis of methanol solutions of sugars in the presence of titanium(IV) led to ethers (equation 494) [497], (equation 495) [498].

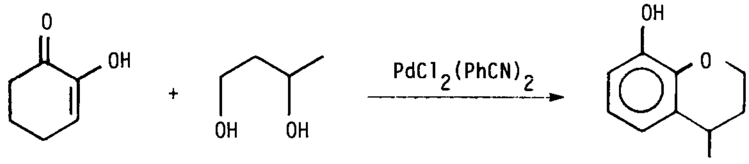
$$\mathrm{ArOH} + \mathrm{Ar'X} \xrightarrow[\text{py, rfx}]{\text{Cu-}\equiv\text{-Ph}} \underset{40\text{-}70\%}{\mathrm{ArOAr'}} \qquad (485)$$

Ar = Ph, α, Naph, 2-MeOPh, 4-NO_2Ph, 2-BrPh, 2,7-di OH Naph

Ar' = Ph, 3-MePh, 4-MeOPh

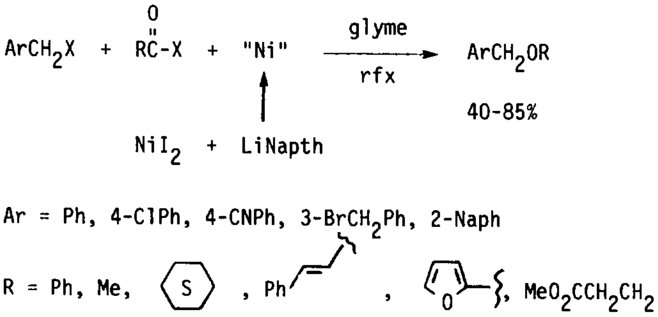


(486)



(no yield)

(487)



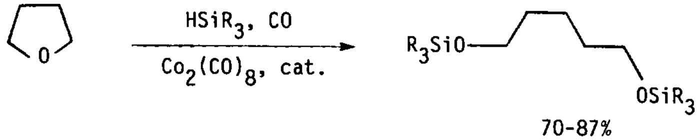
$$ArCH_2X + \overset{O}{\overset{\|}{RC}}\text{-}X + \text{"Ni"} \xrightarrow[\text{rfx}]{\text{glyme}} ArCH_2OR$$

40-85%

NiI_2 + LiNapth

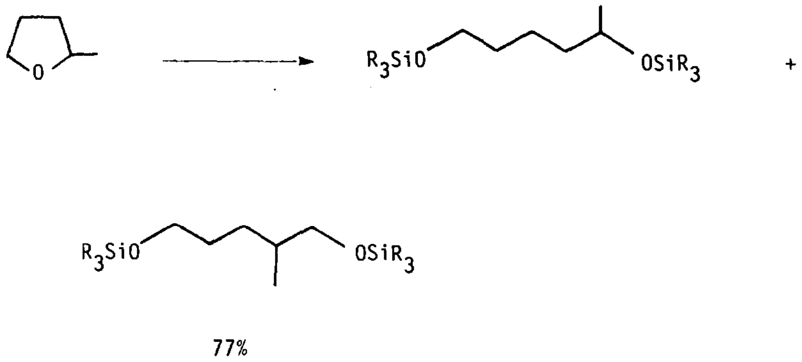
(488)

Ar = Ph, 4-ClPh, 4-CNPh, 3-$BrCH_2Ph$, 2-Naph

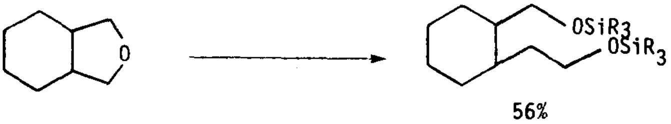


70-87%

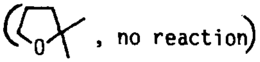
(489)

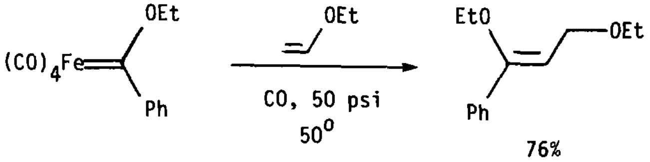


(490)

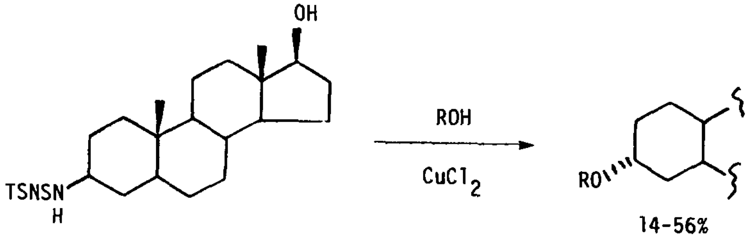


(491)

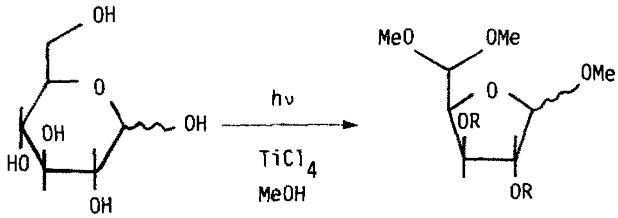




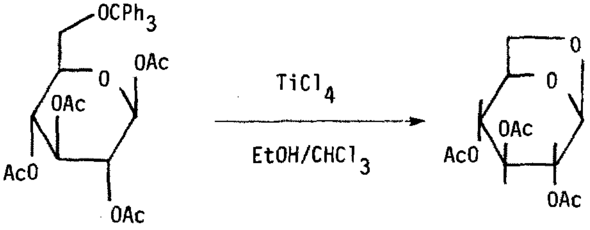
(492)



(493)



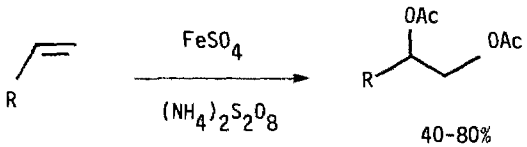
(494)



76%

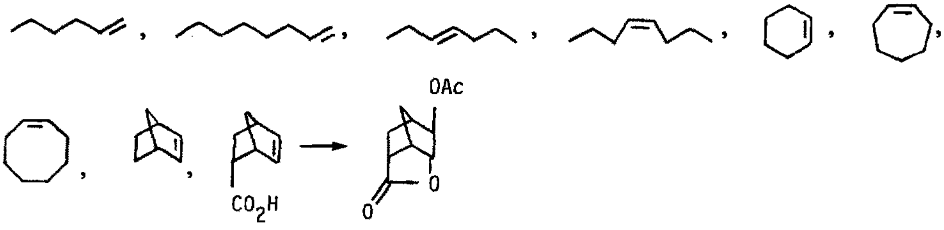
(495)

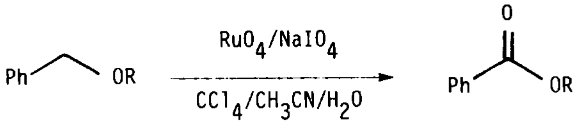
Olefins were converted to diacetates by iron(II) sulfate and peroxodisulfate (equation 496) [499]. Propylene was oxidized to allyl acetate benzoyl peroxide and palladium black [500]. Benzyl ethers were oxidized to benzoate esters by ruthenium tetraoxide/sodium periodate (equation 497) [501]. Other systems were dibenzylated by this catalyst (equations 498 and 499) [502]. Aldehydes were converted to acetal diacetates by treatment with acetic anhydride and iron(III) (equation 500) [503]. Formate esters were converted to propionates by reaction with ethylene and a ruthenium catalyst (equation 501) [504]. Acetylenes were converted to enol esters by treatment carboxylic acids and $Ru_3(CO)_{12}$ (equation 502) [505]. Allyl epoxides were opened to allyl acetates by copper(I) chloride (equation 503) [506]. Acetals were oxidized to ω-hydroxy esters by t-butylhydroperoxide and a palladium(II) catalyst (equation 504) [507]. Wilkinson's compound, L_3RhCl, was used to deprotect allylesters of amino acids [508].



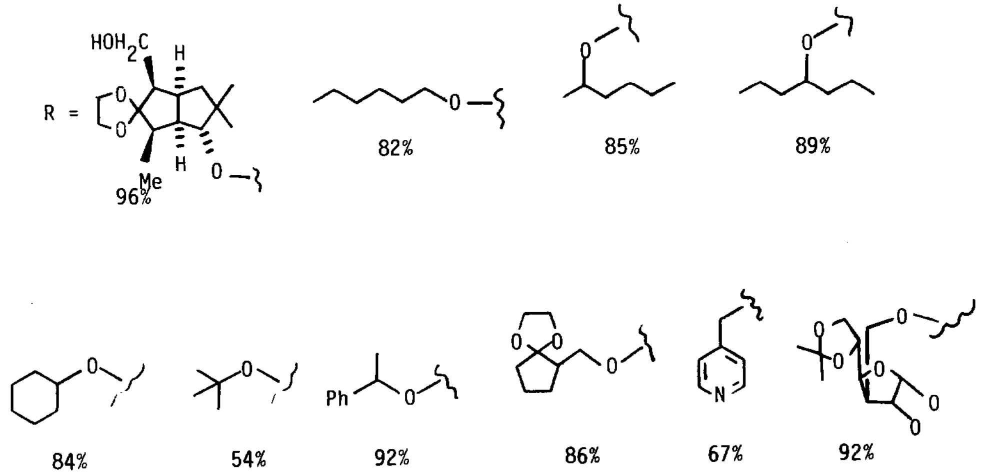
40-80%

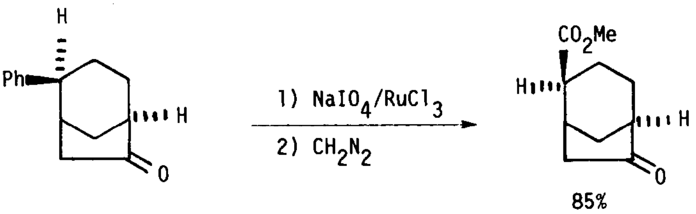
(496)



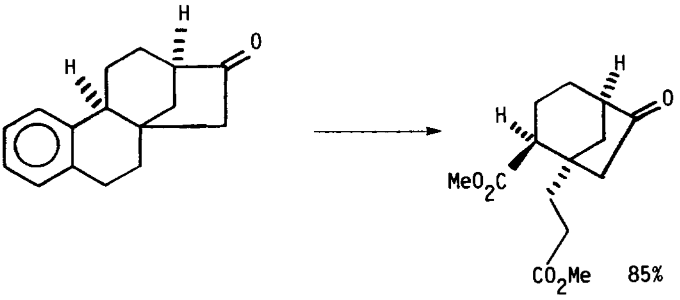

Ph
OR
$RuO_4/NaIO_4$
$CCl_4/CH_3CN/H_2O$
O
Ph
OR

(497)

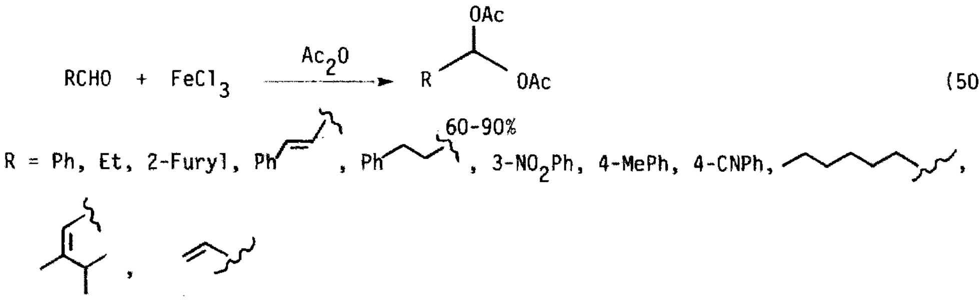

R =
HOH_2C
H
O
O
H
Me
O
96%
O
82%
O
85%
O
89%
O
84%
O
54%
Ph
O
92%
O
O
O
86%
N
67%
O
O
O
O
O
O
92%


H
Ph
H
O
1) $NaIO_4/RuCl_3$
2) CH_2N_2
CO_2Me
H
H
O
85%

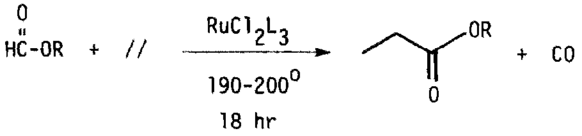
(498)


H
H
O
H
O
H
MeO_2C
CO_2Me
85%

(499)

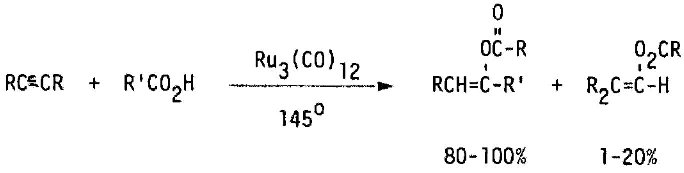


(500)



$$HC(=O)-OR + // \xrightarrow[190-200^\circ,\ 18\ hr]{RuCl_2L_3}$$

(501)



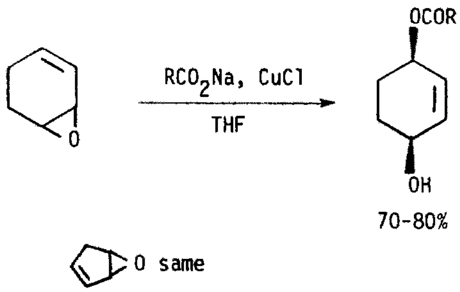
$$RC\equiv CR + R'CO_2H \xrightarrow[145^\circ]{Ru_3(CO)_{12}} RCH=C(OC(=O)-R)-R' + R_2C=C(O_2CR)-H$$

80-100% 1-20%

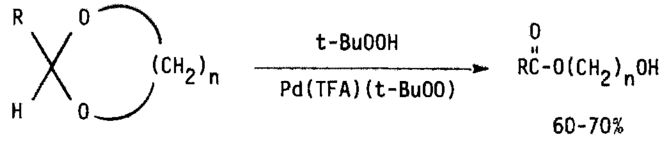
(502)

R = Ph, n-Pr, CO_2Me

R' = Me, t-Bu, Ph, 4-FPh, 4-MePh



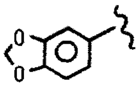
(503)



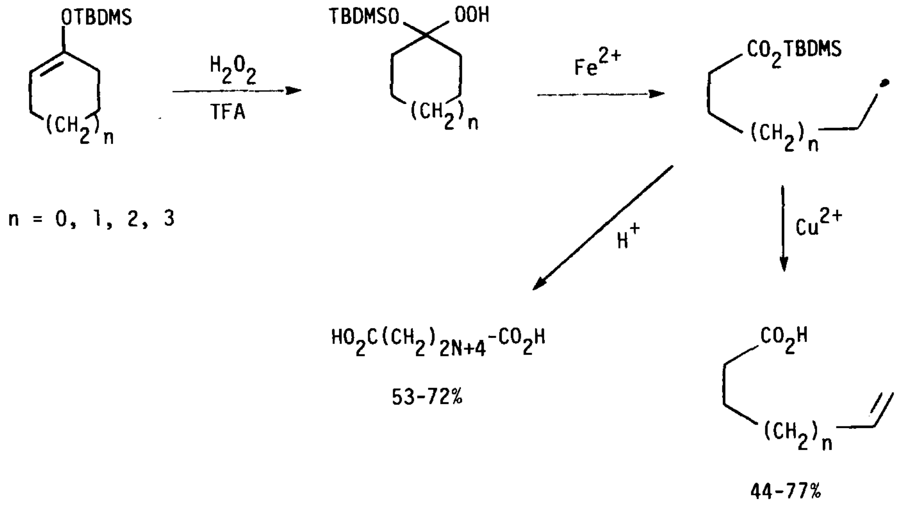
$$\xrightarrow[Pd(TFA)(t\text{-}BuOO)]{t\text{-}BuOOH} RC(=O)-O(CH_2)_nOH$$

(504)

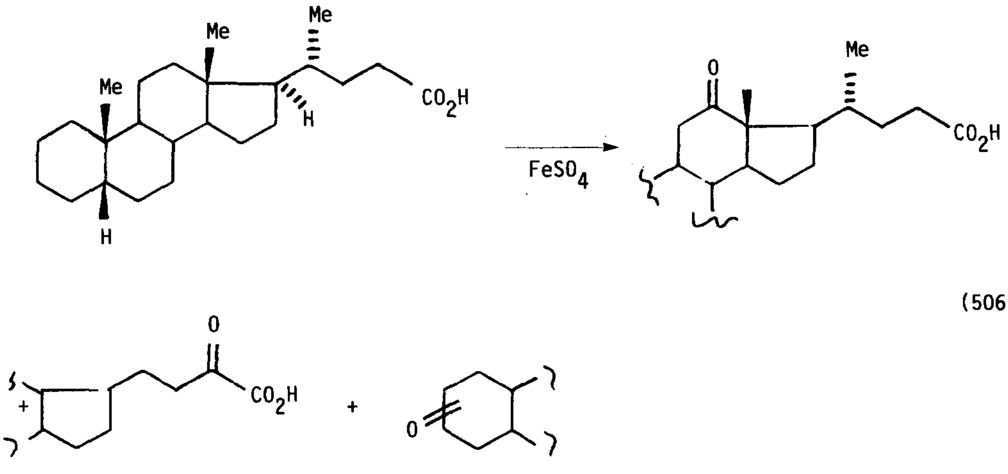
n = 2, 3, 4

R = Ph,  , 2-$MePhCH_2$, t-$BuC(=O)CH_2$-, 

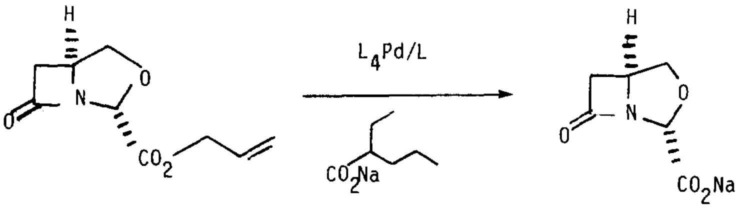
Cyclic silylenol ethers were oxidized to acids by iron(II) chloride and copper (II) chloride (equation 505) [509]. Cholanic acid was oxidized by iron(II) sulfate (equation 506) [510]. Molybdenum/titanium oxides catalyzed the oxidation of butadiene to maleic acid [511]. Allyl esters of penams were cleaved to the corresponding carboxylate by palladium(0) catalysts (equation 507) [512].



(505)



(506)

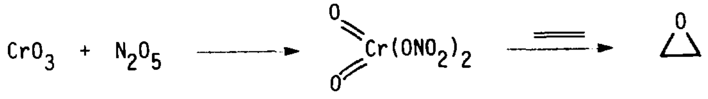


(507)

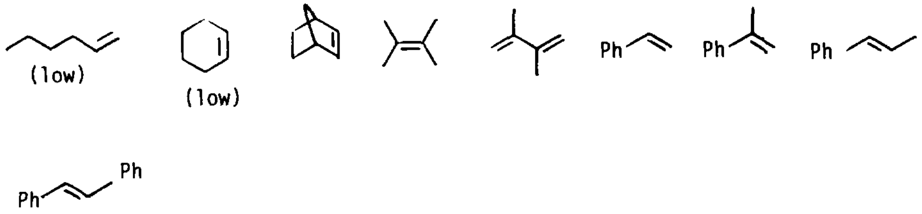
E. Heterocycles

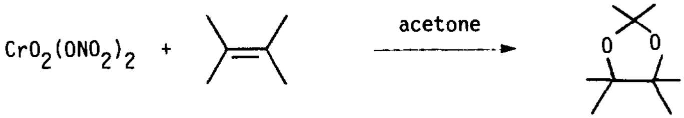
π-Complexes of heterocycles-preparation, reactivity and use in organic syntheses has been reviewed (115 references) [513], as has transition metal catalyzed selective oxidation (63 references) [514]. The effects of the acetylacetonates of vanadium, molybdenum, chromium and cobalt on the autoxidation of methyl oleate were studied [515]. Mechanistic studies of the catalytic oxidation of olefins by trityl hydroperoxide and a molybdenum(VI) catalyst were carried out [516]. The catalytic activity of molybdenum naphthenate in epoxidation of cyclohexene and styrene was probed [517]. Propylene oxide and 1,2-propandiol accelerate the epoxidation of propylene by diperoxomolybdenum(VI) complexes by forming active epoxidizing agents [518]. Electrophilic olefin epoxidation by molybdenum(VI) peroxospecies has been studied [519], as has the catalytic activity of molybdenum(V) bis-(diphenylphosphine)ethane in epoxidation reactions [520]. Aqueous hydrogen peroxide epoxidized olefins in the presence of molybdenum acetylacetonate bis-(tri-n-butyl)tin oxide [521]. Activated molybdenum oxide epoxidized olefins [522]. Cyclohexene was epoxidized by ethyl benzene hydroperoxide in the presence of vanadium catalysts [523], and propylene was epoxidized by α-phenethyl hydroperoxide in the presence of molybdenum naphthenate [524]. Organic hydroperoxides epoxidized styrene in the presence of several transition metals, of which molybdenum was the most efficient [525].

Chromium trioxide reacted with dinitrogen pentoxide to form an efficient epoxidizing agent (equation 508 and 509) [526]. A chromium oxosalen complex behaved in a similar manner (equation 510) [527]. Vanadium peroxospecies epoxidized, then cleaved olefins (equation 511), oxygenated benzene (equation 512), and oxidized cyclohexane (equation 513) [528]. Tungstate catalyzed the epoxidation of olefins by hydrogen peroxide under phase transfer conditions (equation 514) [529], or under normal conditions (equation 515) [530]. A manganese porphyrin complex catalyzed the epoxidation of terpenes (equations 516 and 517) [531]. Iron-porphyrin complexes catalyzed the epoxidation of olefins by iodosylbenzene (equation 518) [532]. With chiral porphyrins, asymmetric induction was observed (equation 519) [533].

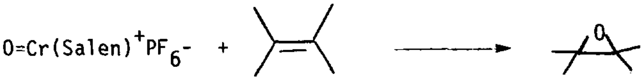


(508)

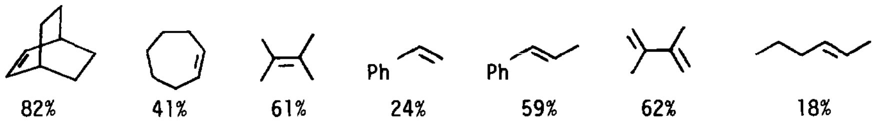




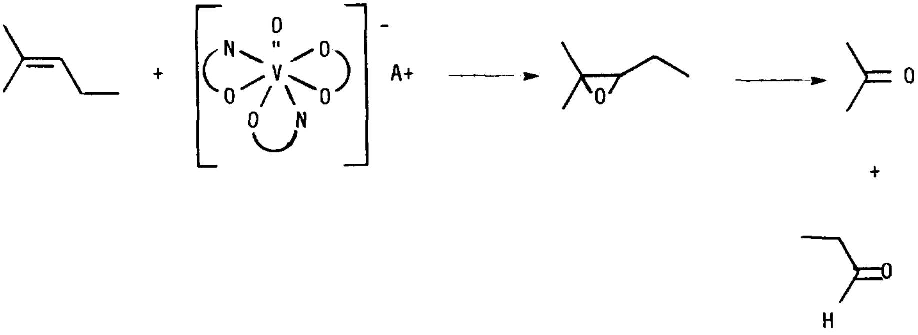
(509)



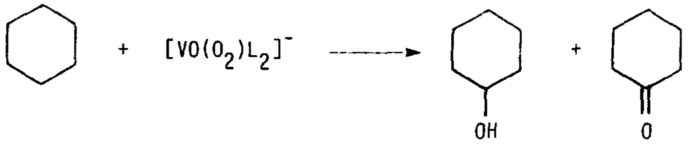
(510)



(511)

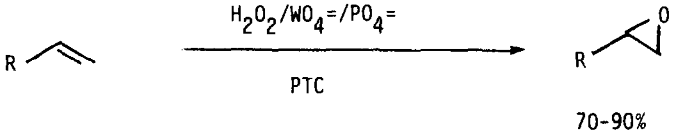


$$ArH \quad + \quad [VO(O_2)L_2] \longrightarrow ArOH \qquad (512)$$



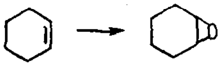
(513)

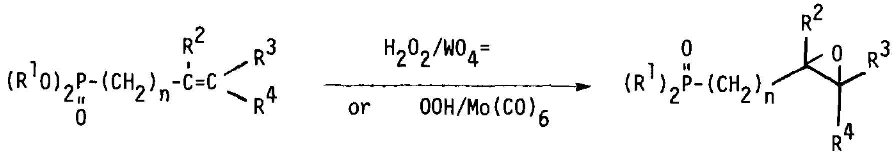
low yields



(514)

R = C_6, C_8, CH_2Cl, Ph

also 



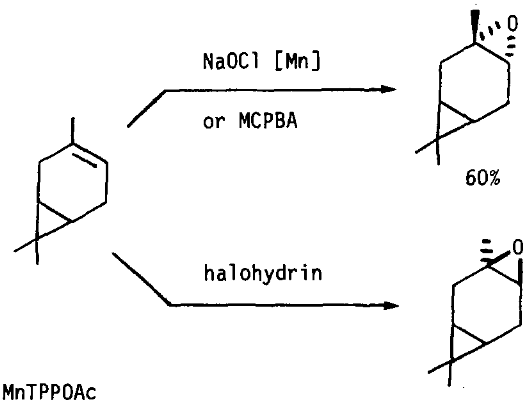
(515)

R^1 = Et, Me, i-Pr, n-Bu n = 0, 1

R^2 = H, Me

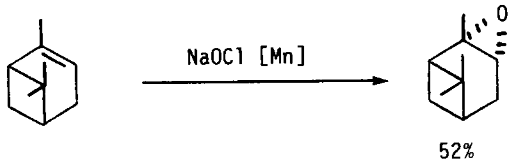
R^3 = H

R^4 = H, Me

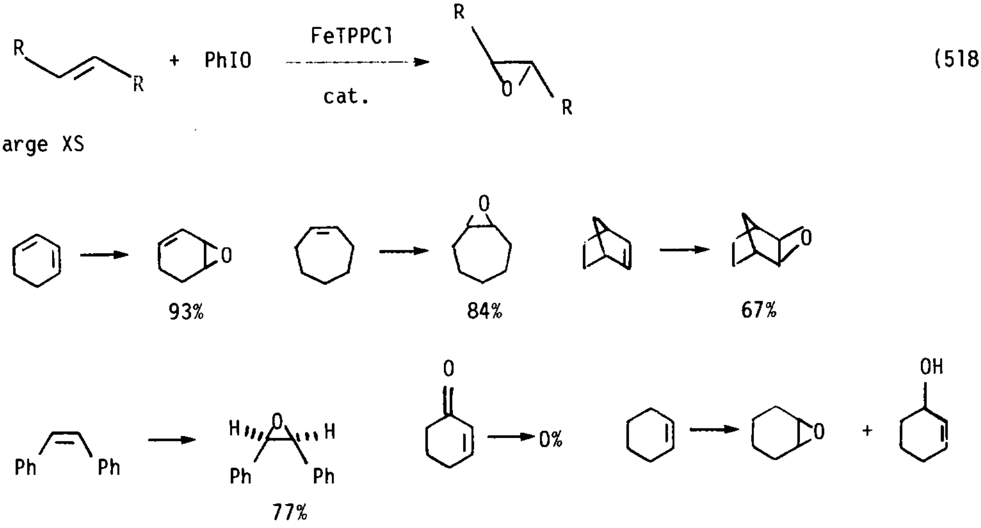


(516)

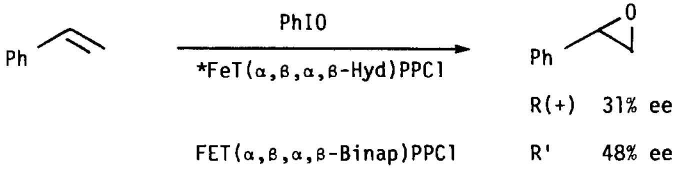
[Mn] = MnTPPOAc



(517)

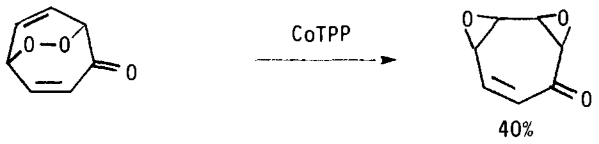


(518)

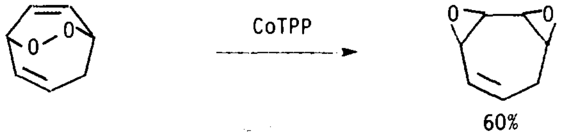


(519)

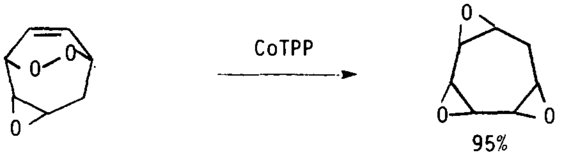
Olefinic peroxides rearrange to epoxides when treated with cobalt tetraphenylporphyrin (equations 520-523) [534]. Silylated allyl alcohols were epoxidized by t-butylhydroperoxide silyl ether in the presence of a vanadium catalyst with stereochemistry intermediate between t-butylhydroperoxide/vanadium and MCPBA (equation 524) [535]. Titanium catalyzed epoxidation was used in the synthesis of leukotriene (equation 525) [536], whereas vanadium catalysts were used in the synthesis of elemenone (equation 526) [537]. Polymer bound molybdenum and vanadium complexes catalyzed the epoxidation of allylic alcohols (equation 527) [538]. Selective epoxidations of olefins, allylic alcohols, and homoallylic alcohols with t-butylhydroperoxide and molybdenum, vanadium, and titanum catalysts. Application to asymmetric synthesis of (+)-disparalure and (-)-γ-amino-β-(R) hydroxybutyric acid was the topic of a dissertation [539]. Epoxidation of 3-methyl-2-buten-1-ol with arene hydroperoxide catalyzed by Mo(O_2)(acac)$_2$ in the presence of L-N-methylprolinol gave epoxy alcohols with 50% optical purity at low conversion. The optical purity fell as conversion increased [540]. Olefins were converted to aziridines by a manganese imine complex (equation 528) [541].



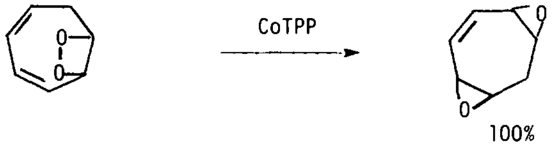
(520)



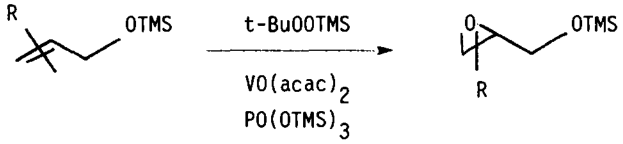
(521)



(522)

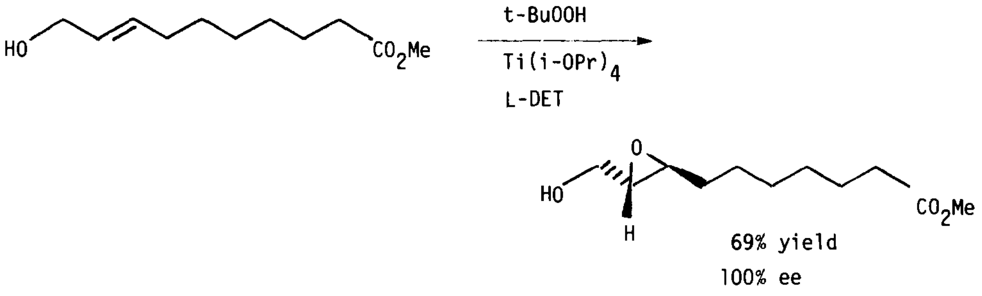


(523)

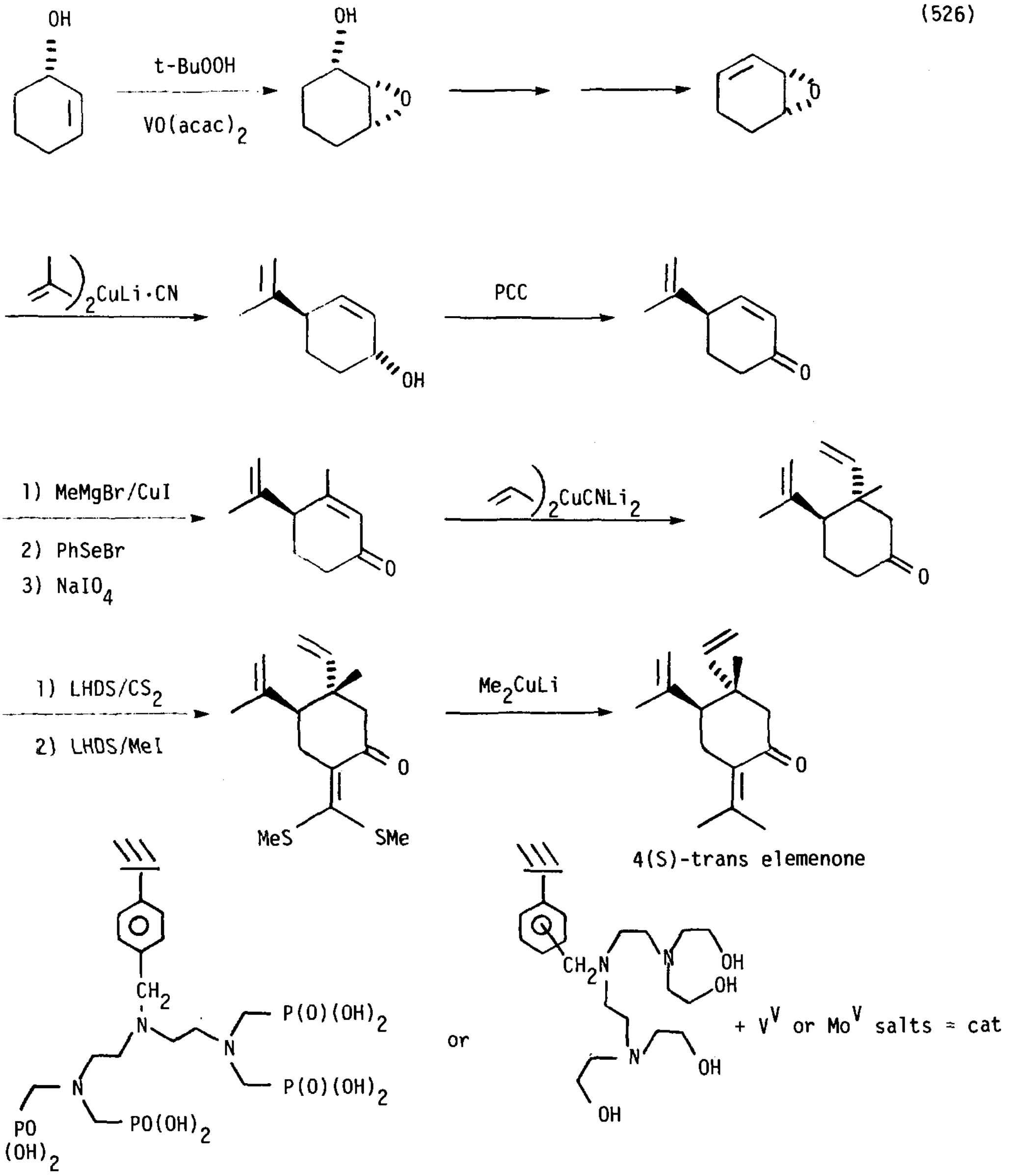


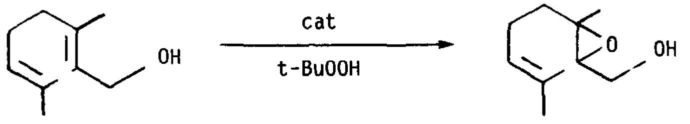
(524)

(525)



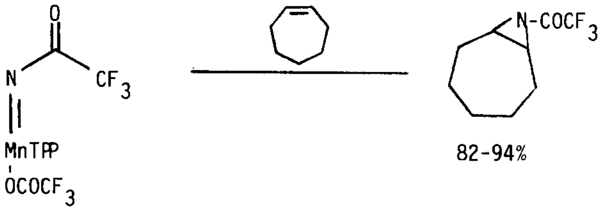
(526)





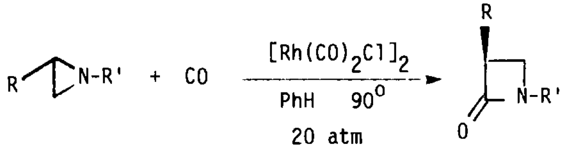
(527)

100% conversion
98% selectivity



(528)

Several new β-lactam synthese have appeared. Aziridines were converted to β-lactams by carbonmonoxide in the presence of a rhodium(I) catalyst (equation 529) [542]. Iron(0) species converted diene monoepoxides into β-lactams (equation 530) [543]. Unsaturated esters were converted into bicyclic β-lactams using iron olefin complex chemistry (equation 531) [544].

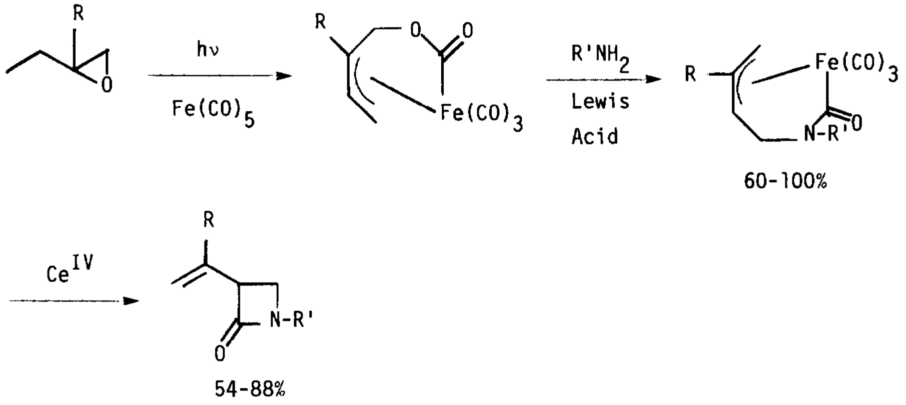


(529)

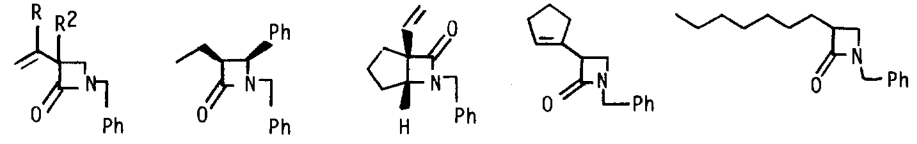
R = Ph, H-PhPh, 4-BrPh

R' = t-Bu, 1-adamantyl

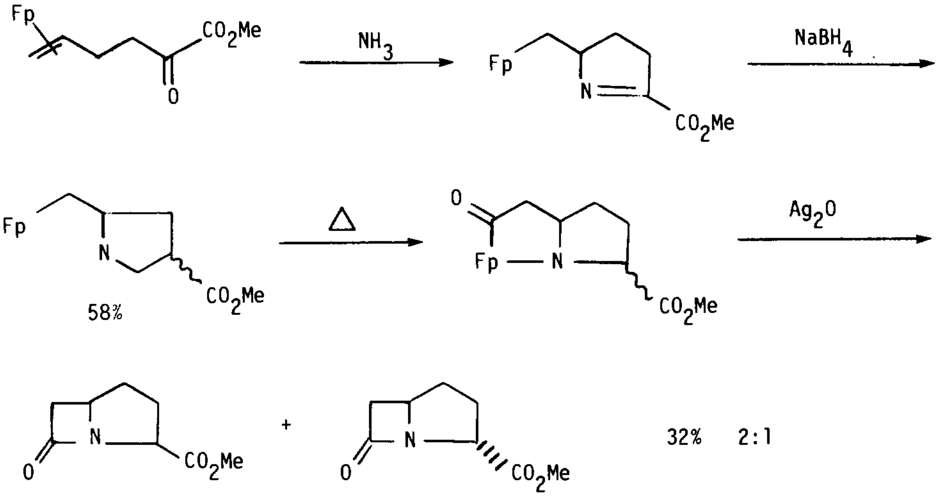
(530)



made

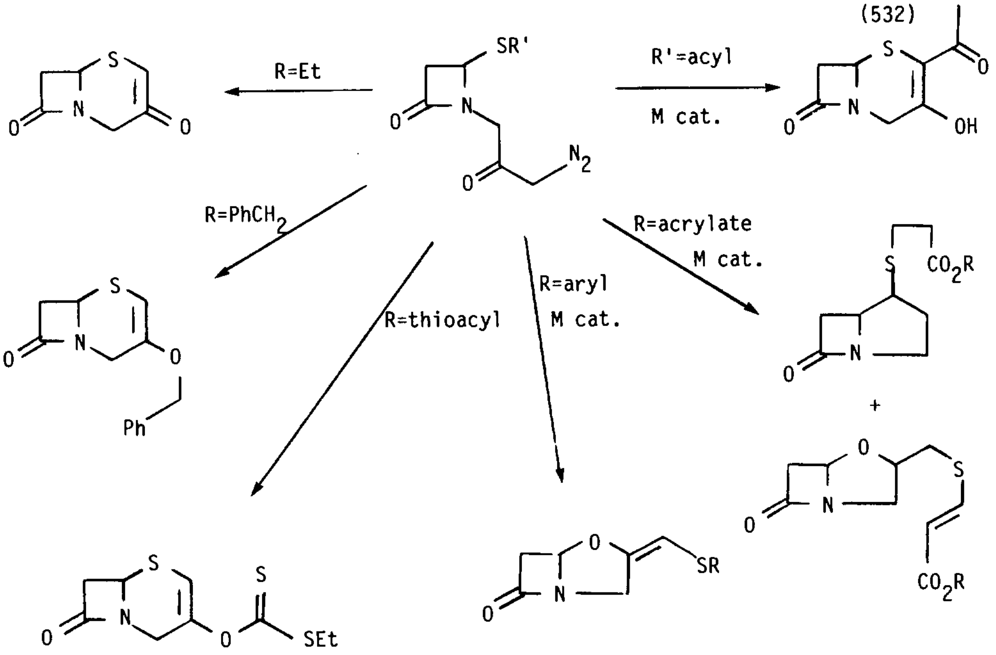


(531)

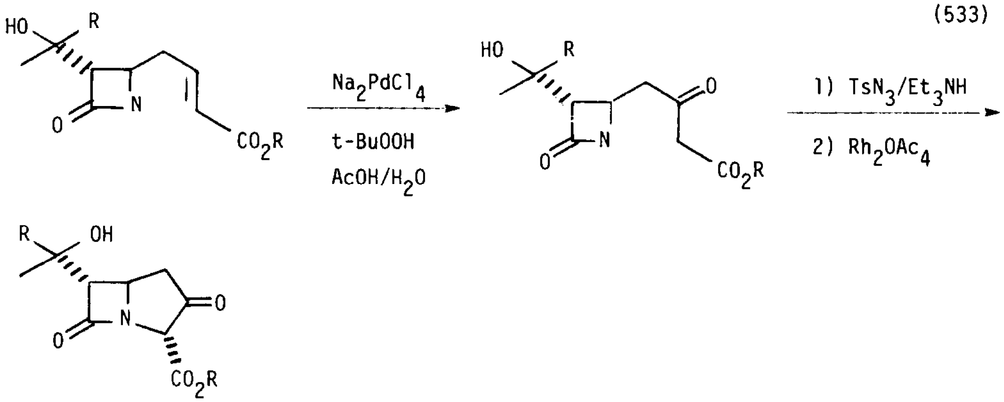


Metal-catalyzed decomposition of azocompound was used to generate a variety of bicyclic β-lactams (equation 532) [545], (equation 533) [546], (equation 534) [547], (equation 535) [548]. Copper promoted intramolecular aromatic substitution also was used to produce fused bicyclic β-lactams (equation 536) [549]. On the other hand, attempts to use $Fe(CO)_4^=$ chemistry to elaborate β-lactams resulted in lactam cleavage instead (equation 537) [550].

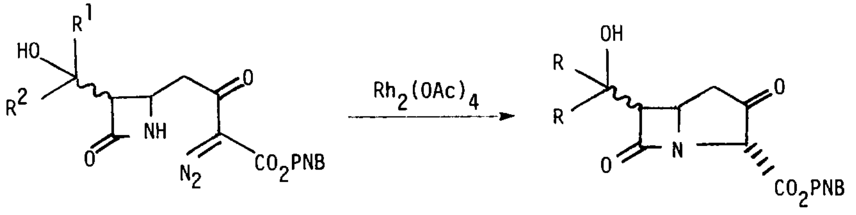
(532)



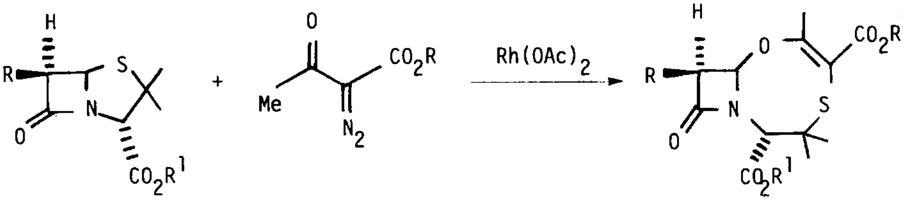
(533)



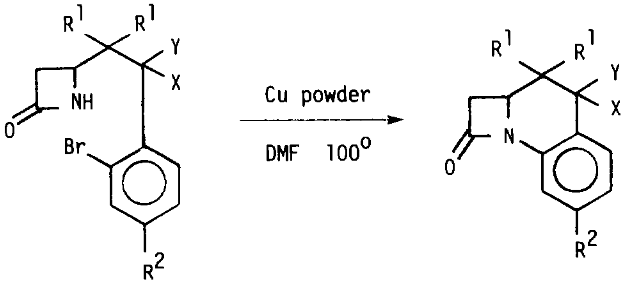
No yield reported



(534)



(535)



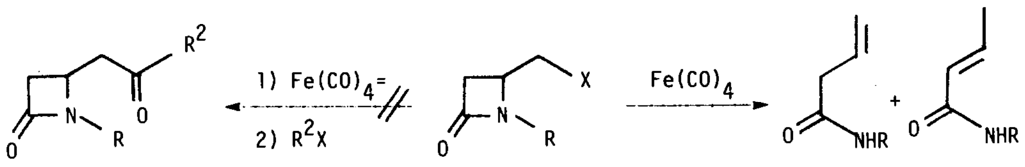
(536)

R^1 = CO_2Et R^2, X, Y = H 36% R^1=R^2=CO_2Et X=Y=H 48%

R^1 = CO_2Bz R^2 = H X, Y = O 23% R^1=R^2=H X, Y = O 93%

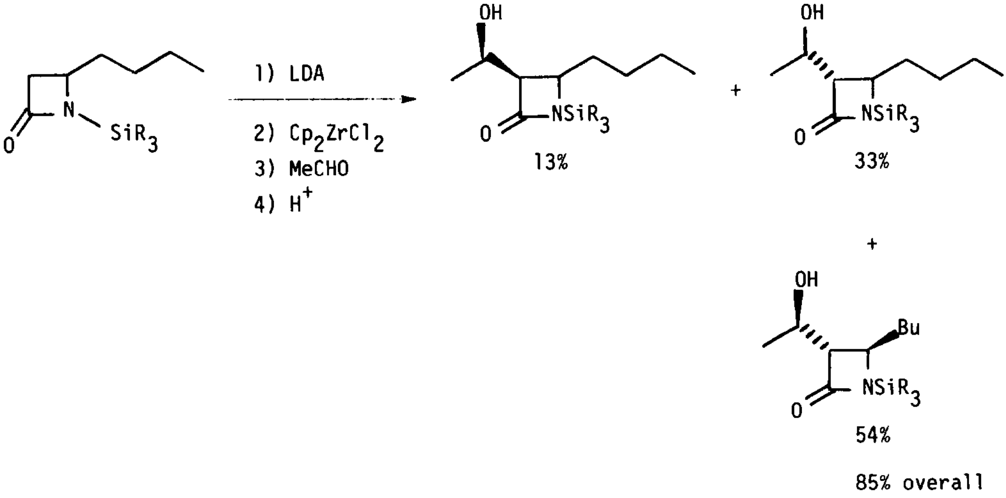
R^1 = H R^2 = CO_2Me X, Y = O 27%

(537)

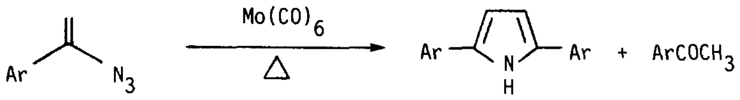


β-Lactams were functionalized α- to the carbonyl using zirconium chemistry (equation 538) [551]. A variety of ferrocene derivatives of β-lactams were made and tested for biological activity [552]. β-Lactams were hydrogenized to chiral oligopeptides [553].

(538)

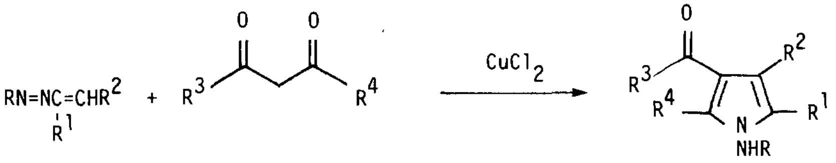


Vinyl azides cyclized to pyrroles when treated with molybdenum carbonyl (equation 539) [554]. Copper(II) chloride catalyzed the reaction between β-dicarbonyl compounds with arylazoalkanes (equation 590) [555]. Phenylazirenes were converted to indoles by reaction with palladium(0) complexes (equation 541) [556]. Alkynes and diarydiazene cyclized to form indoles in the presence of cobalt(I) complexes (equation 542) [557]. Nitroenamines cyclized to indoles when treated with titanium(III) chloride (equation 543) [558], while iron in acetic acid cyclized ortho nitro-β-nitrostyrenes to indoles (equation 544) [559]. Orthoallyl acrylanilides were again shown to cyclize to pyrroloindoles when treated with palladium(II) salts (equations 545 and 546) [560]. Ortho iodoanilines reacted with dienes in the presence of palladium(0) catalysts to form indoles (equation 547) [561].



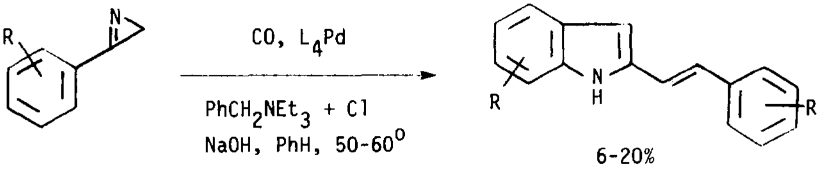
(539)

Ar = Ph, 64%; 4-MePh, 54%; 4-BrPh, 57%



(540)

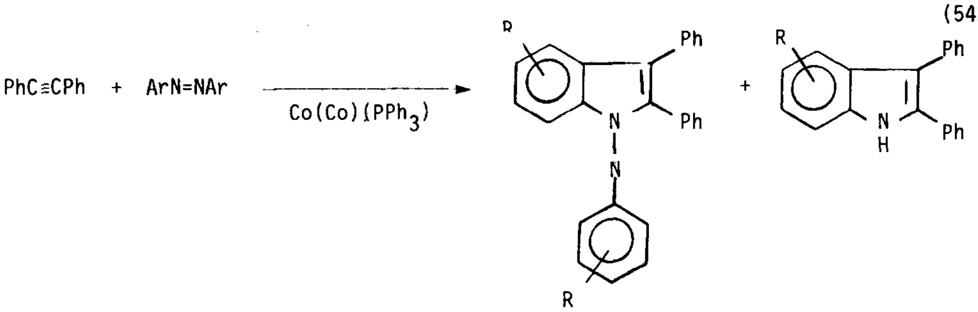
R = Ph, 4-NO_2Ph; R^1 = Ph, Bz; R^2 = Ph, $(CH_2)_4$; R^3 = Me, OMe, OEt; R^4 = Ph, $(CH_2)_3$



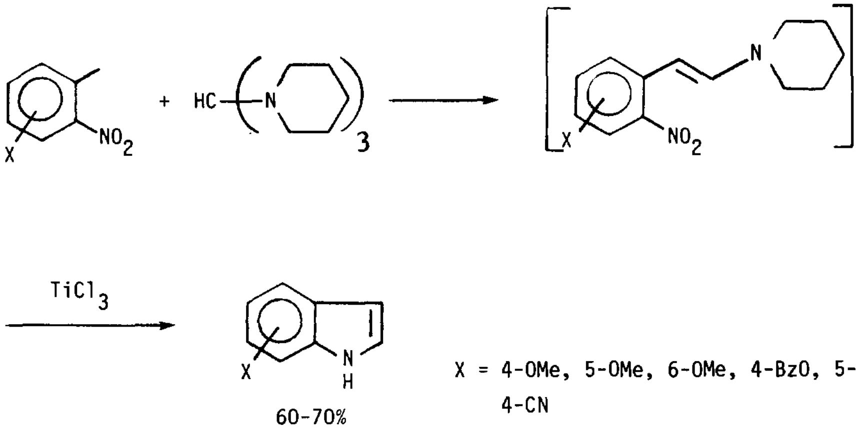
(541)

R = H, 4-Me, 4-OMe, 2,4-diOMe

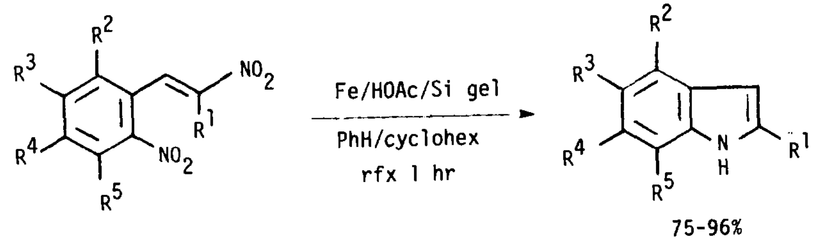
(542)



(543)



X = 4-OMe, 5-OMe, 6-OMe, 4-BzO, 5-BzO, 4-Cl, 4-CN



(544)

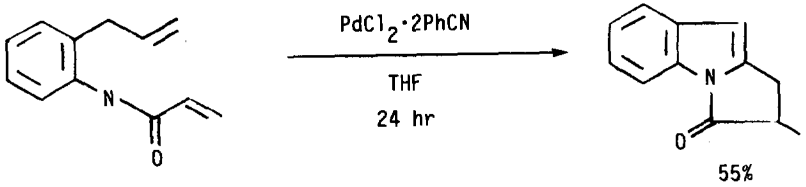
R^1 = H, Me

R^2 = Me, H

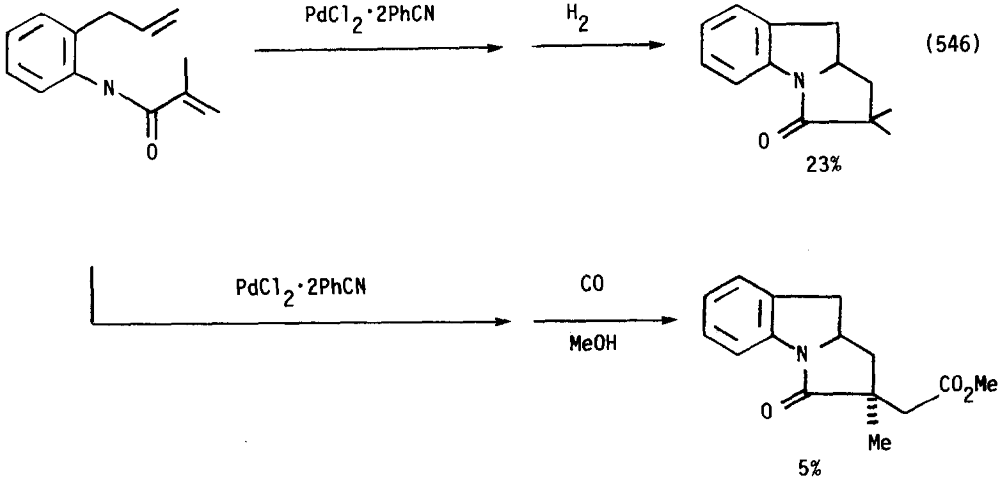
R^3 = OMe, OBz

R^4 = OMe, OBz

R^5 = H, Me, OMe, OBz

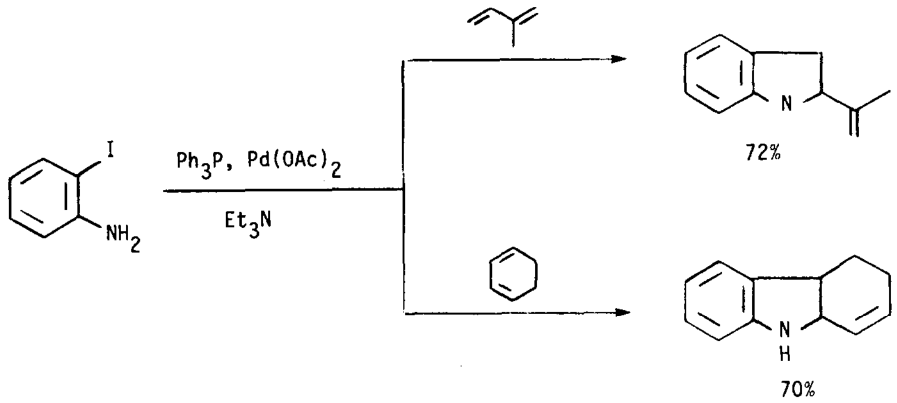


(545)

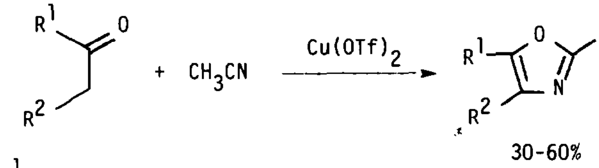


(546)

(547)



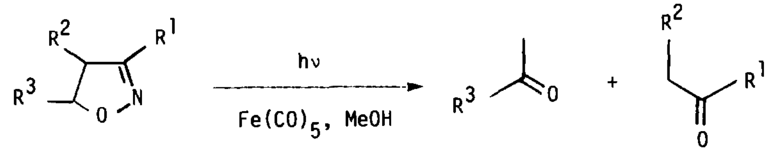
Copper triflate promoted the reaction of ketones with nitriles to give oxazoles (equation 548) [562]. Iron carbonyl promoted heterocyclic ring openings (equation 549) [563]. A variety of unsaturated lactams and lactones were synthesized by the palladium(0) catalyzed cyclization of amino- or hydroxy vinyl iodides (equation 550) [564]. Aromatic aldehyde diimines underwent a cyclocarbonylation when treated with carbon monoxide and cobalt carbonyl (equations 551 and 552) [565].



(548)

R^1 = Me, n-Pr, Ph

R^2 = Me, Et, i-Pr, n-Bu, Ph

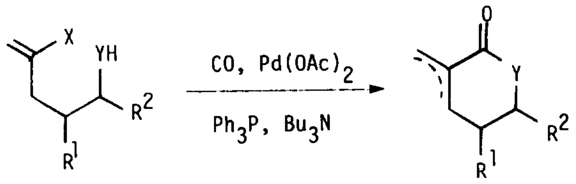


(549)

R^1 = Ph, Me, mesityl

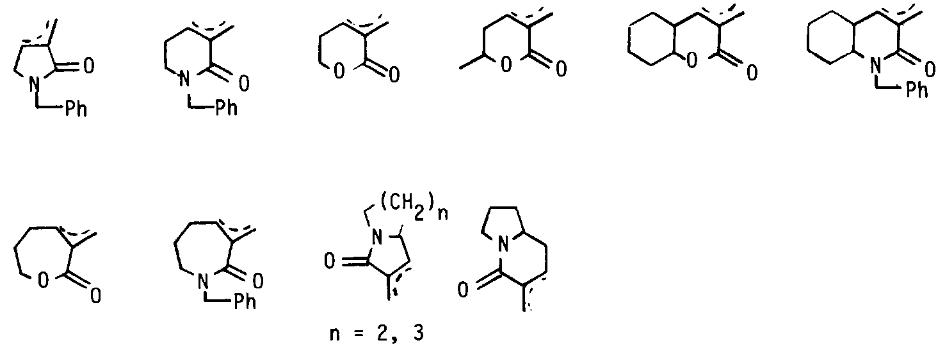
R^2 = H, Ph

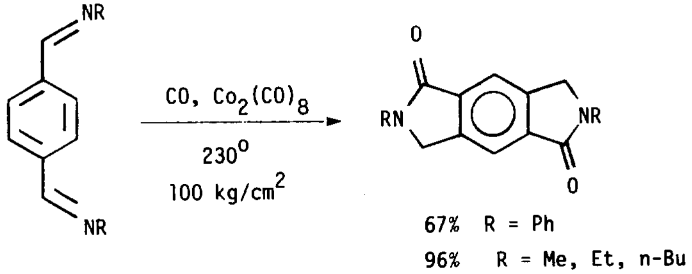
R^3 = Ph, n-C_6, H



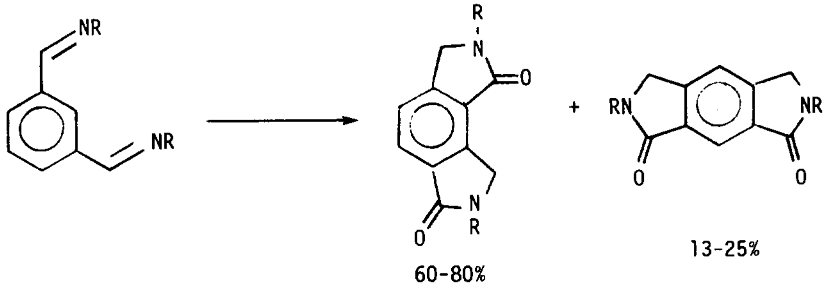
(550)

made



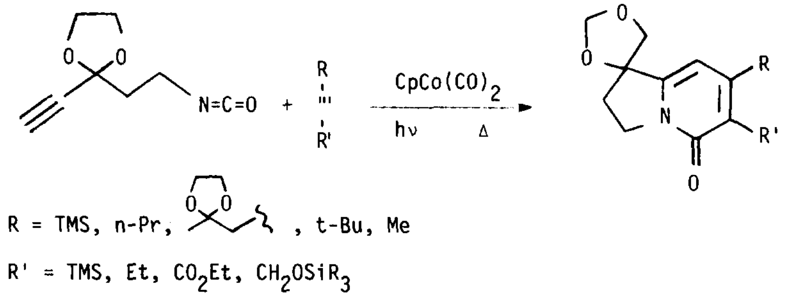


(551)

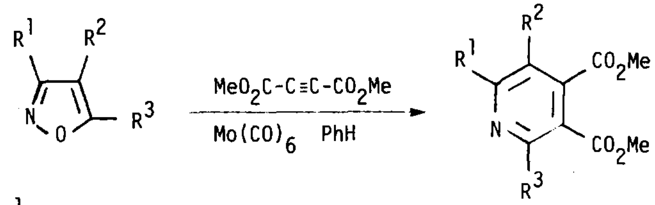


(552)

Acetylenic isocyanates cyclized to pyridones when treated with alkynes and $CpCo(CO)_2$ as a catalyst (equation 553) [566]. Pyridines were also made from alkynes and smaller heterocycles (equation 554) [567]. Alkynes and isocyanates formed pyrimidines or pyridones with nickel(0) TMEDA catalysts (equations 555 and 556) [568].



(553)



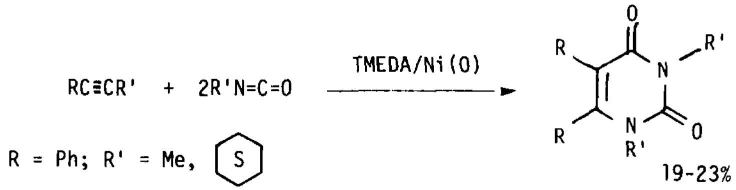
12-28%

(554)

R^1 = Ph, Me

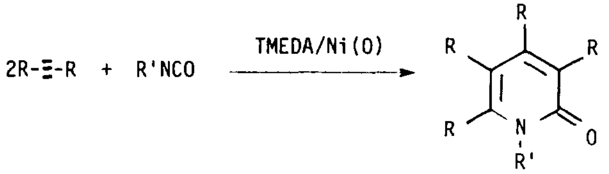
R^2 = H, Ph

R^3 = Ph, H, Me



19-23%

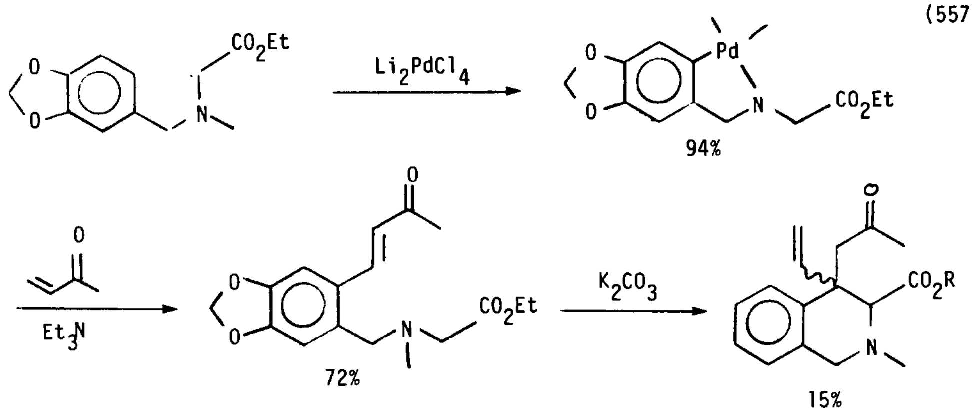
(555)



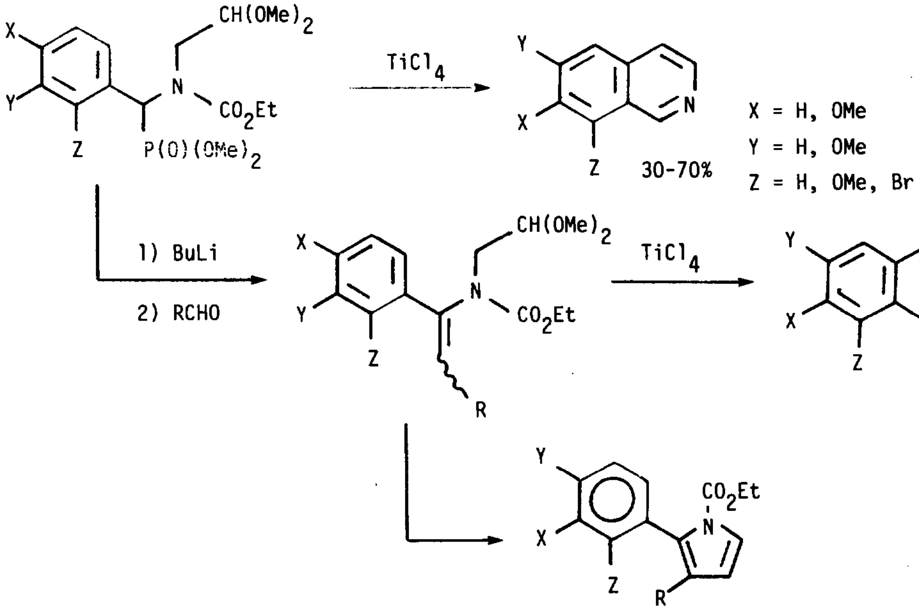
(556)

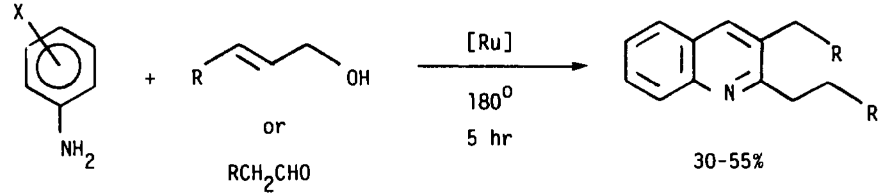
Isoquinolines were prepared by an ortho-palladation/insertion process with substituted benzylamines (equation 557) [569]. Titanium(IV) chloride also produced isoquinolines from related starting materials (equation 558) [570]. Aniline and allyl alcohols combined to form quinolines under ruthenium catalysis (equation 559) [571]. direct aromatic palladation followed by olefin insertion also produced quinolines (equation 560) [572]. A cobalt-catalyzed protoberberine synthesis has appeared (equation 561) [573]/

(557)



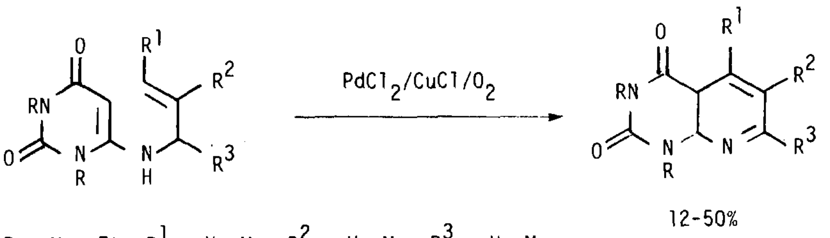
(558)





(559)

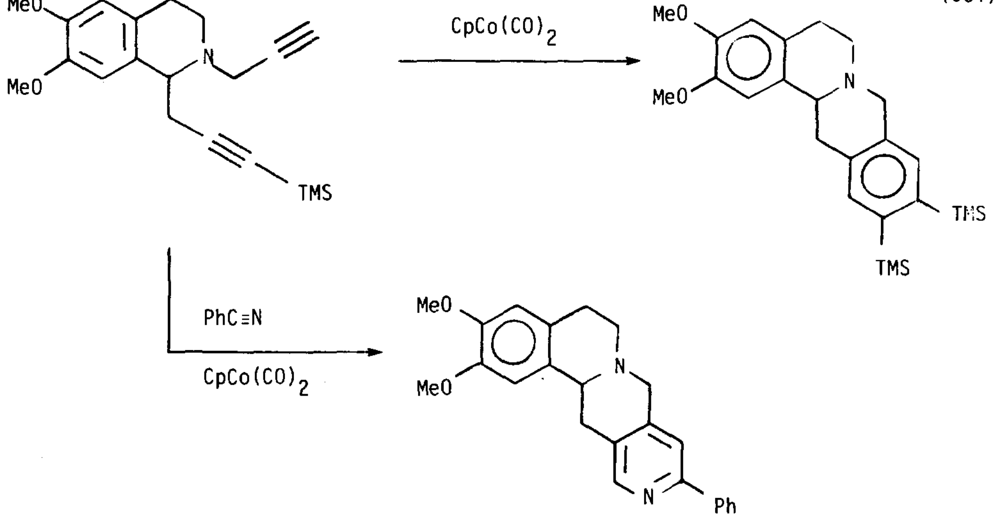
R = Me, H; X = 4-MeO, 4-Me, 4-Cl, 2-MeO, 2-Me, 2-Cl



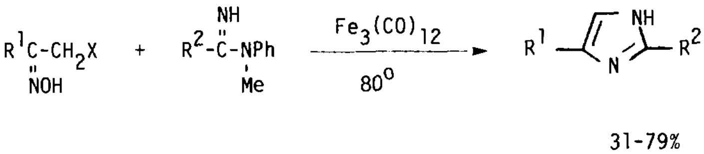
(560)

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

(561)



Imidazoles were produced from α halooximes and imines in the presence of $Fe_3(CO)_{12}$ (equation 562) [574]. Tungsten dinitrogen compounds were reduced, then reacted with cyanoolefins to produce nitrogen heterocycles (equation 563) [575]. 2,6-bis-Trifluoromethylpyridine and 4,5-bis-trifluoromethyl imidazole were prepared by treating the corresponding dicarboxylic acids with molybdenum(VI) fluoride at 200° for 40 hr [576]. Iron and copper salts catalyzed the reaction of benzylamine with carbon tetrachloride to form 1-benzyl-2,4,5-triphenylimidazoline [577].

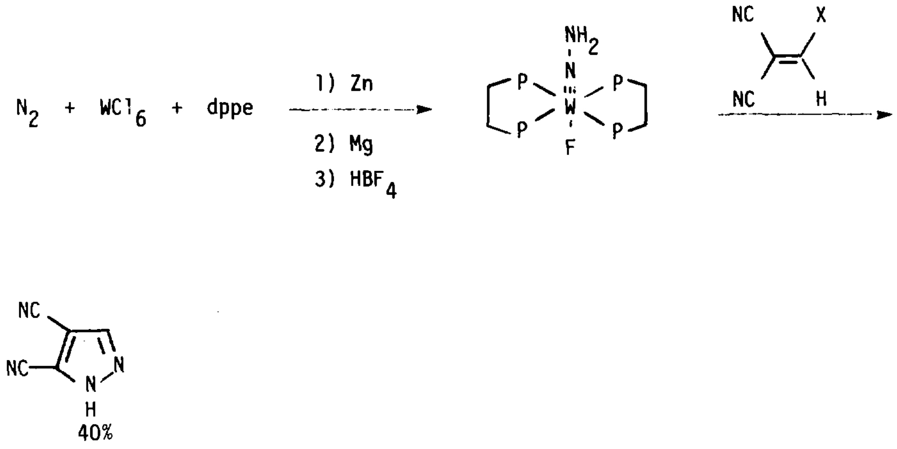


(562)

R^1 = Ph, Me, EtO_2C, 4-MePh, 4-BrPh

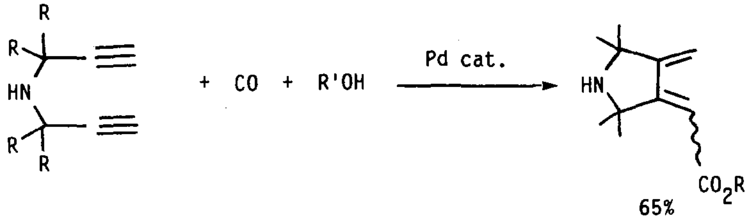
R^2 = Ph

R^3 = Ph, 3-MePh

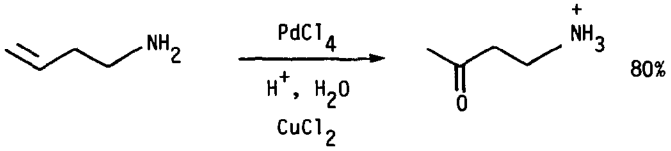


(563)

Palladium-catalyzed synthesis of heterocycles (13 references) [578], and the role of palladium catalyst in the synthesis of N-heterocycles (82 references) [579] have been the subjects of reviews. Palladium catalyzed the cyclization of bis-propargyl amines to divinylpyrroles (equation 564) [580]. Olefinic amines underwent a palladium catalyzed oxidation followed by cyclization to give cyclic imines or aminoketones (equations 565-570) [581]. ω-Olefinic bromides were cyclized and aminated by secondary amines in the presence of palladium(0) catalysts (equations 571-573) [582]. Spiro fused bicyclic amines resulted from palladium catalyzed intramolecular amination of allyl acetates (equation 574) [583], (equation 575) [584].

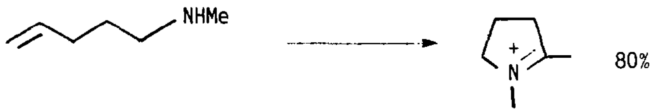


(564)

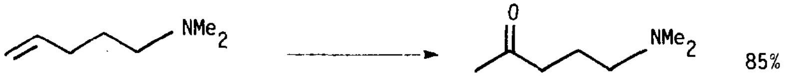


(565)

(566)

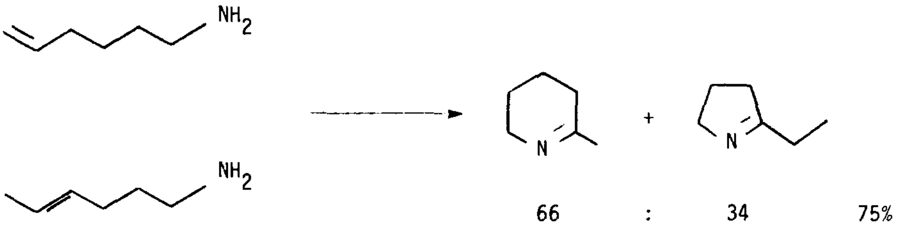


(567)



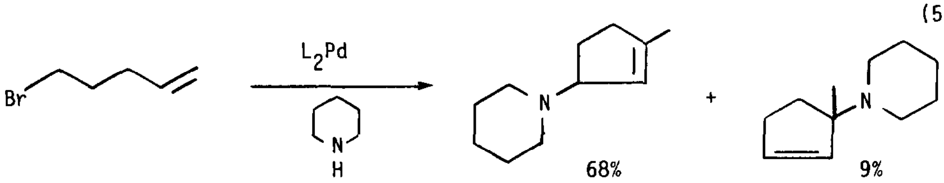
(568)

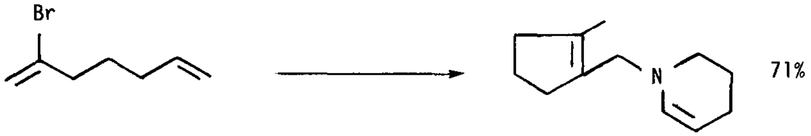
(569)



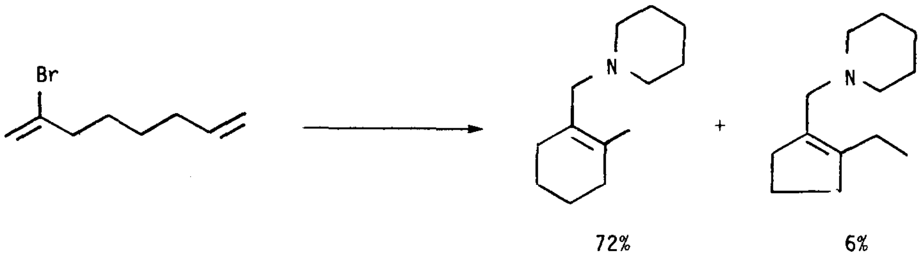
(570)

(571)

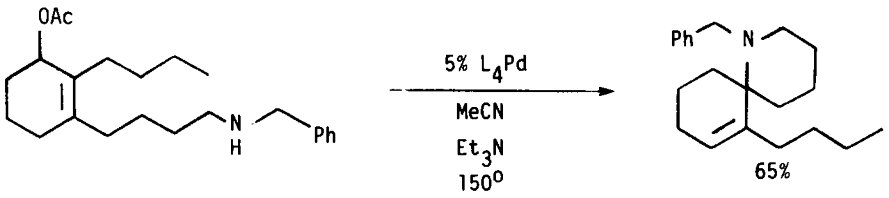




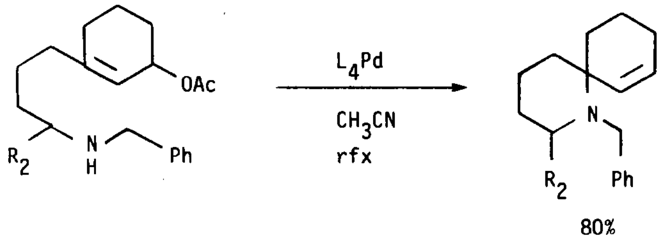
(572)



(573)

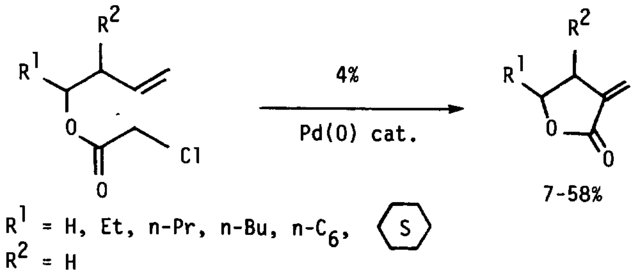


(574)

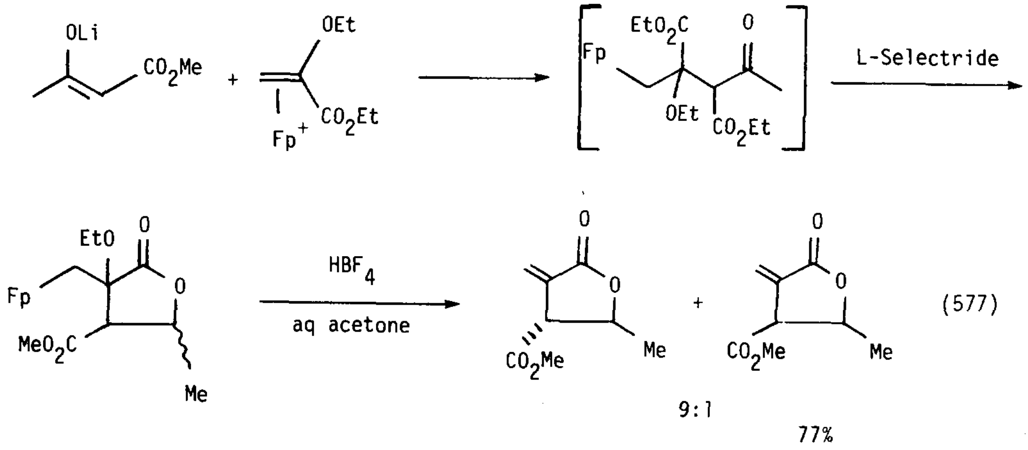


(575)

The scope of the catalytic α-methylene lactone synthesis (Pd) was the topic of a dissertation [585]. Chlorocarbonates having α-olefins cyclized to α-methylene lactones when treated with palladium(0) complexes (equation 576) [586]. These same heterocycles were also available from β-diketones and Fp-α-keto ester enol ethers (equation 577) [587]. Copper(I) chloride cyclized olefinic trichloroesters to lactones (equations 578 and 579) [588]. Alkynes combined with carbon monoxide and methyl iodide to give butenolides (equation 580) [589]. Acetylenic esters underwent 1,4-addition with organocuprates, followed by oxidation by osmium tetroxide to form α,β-dihydroxylactones (equation 581) [590]. Iron(II) complexes oxidized 3,5-di-tert-butylcatechol to a furanone (equation 582) [591]. α,ω-Diols were oxidatively cyclized to lactones in the presence of nickel(II) salts (equations 583 and 584) [592], or by ruthenium complexes (equations 585 and 586) [593]. A bicyclic β-lactam was oxidized to a lactone by osmium tetroxide (equation 587) [594]. Palladium acetate cleaved a cyclic enol ether to a γ-pyrone (equation 588) [595]. Furans were oxidized to furanones by t-butylhydroperoxide and a vanadium catalyst (equation 589) [596], or by $Ru_3(CO)_{12}$ in the presence of carbon monoxide (equation 590) [597].



(576)



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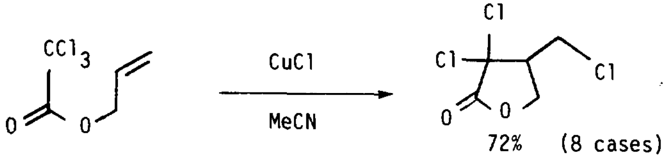
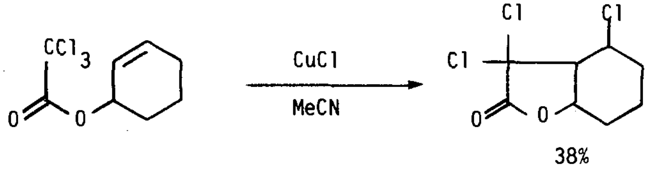
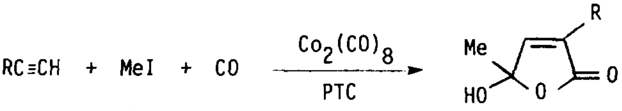


(578)

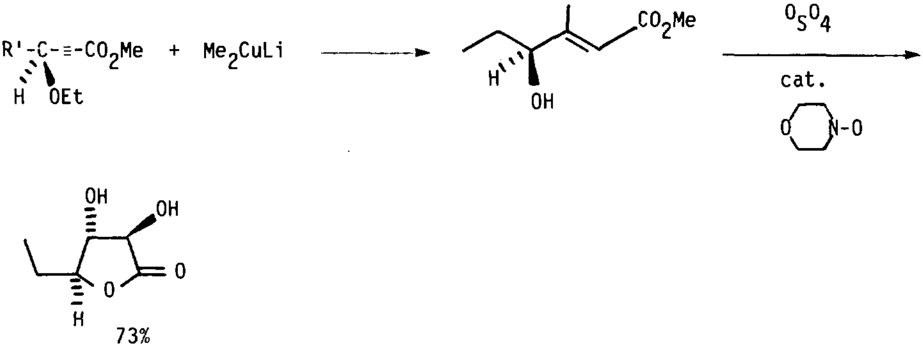


(579)

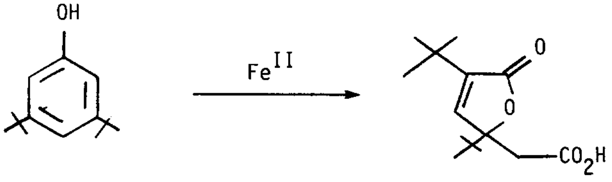


(580)

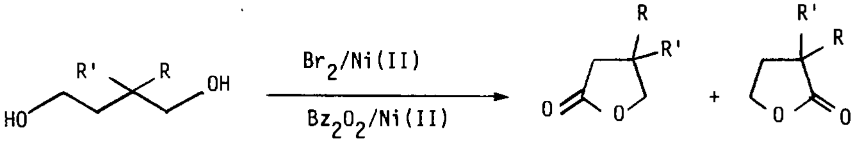
(no yields reported)



(581)

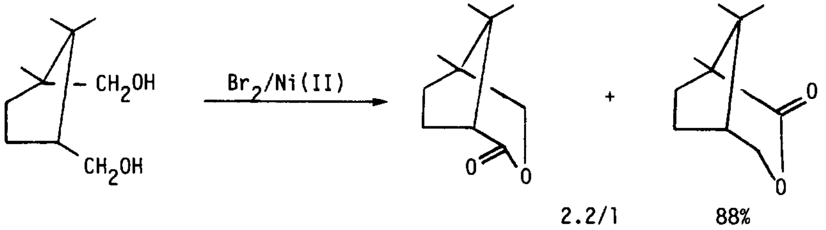


(582)

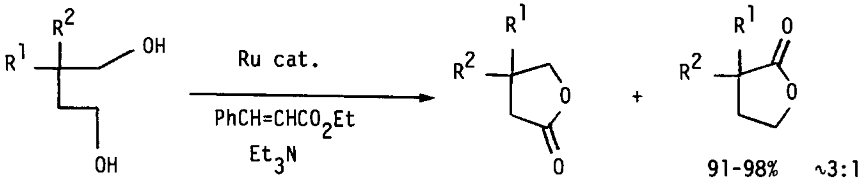


(583)

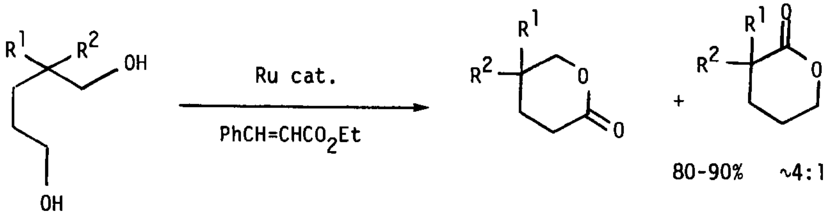
R = R' = Ph	99:1	99%
R = Et, R' = Me	0.45:1 to 49:1	49%
R = R' = Me	0.83:1 to 24:1	58%



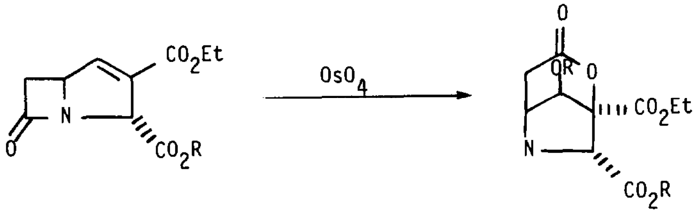
(584)



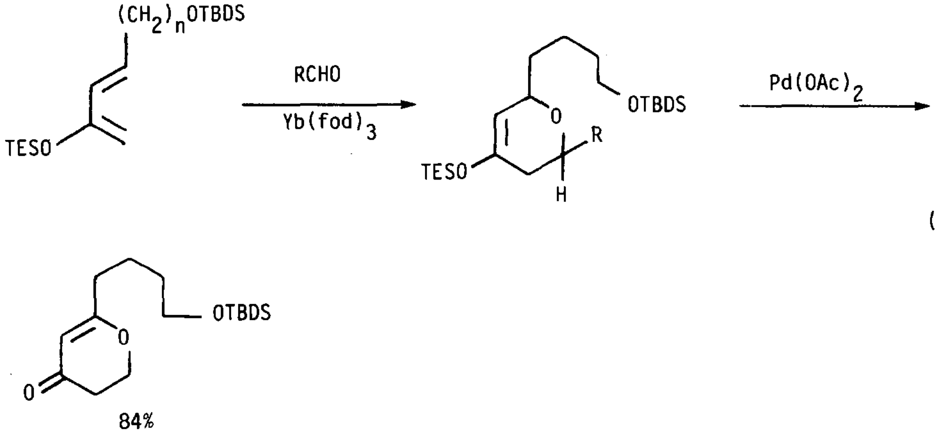
(585)



(586)



(587)



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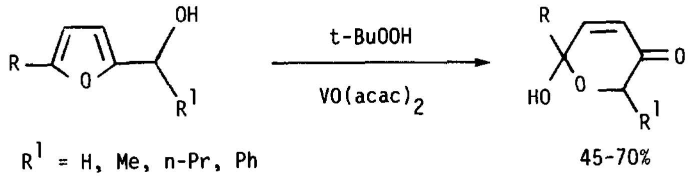
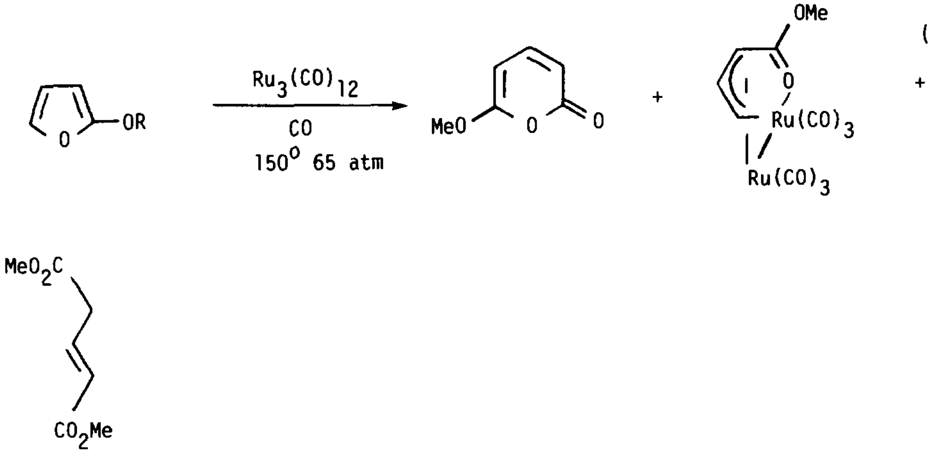


(589)

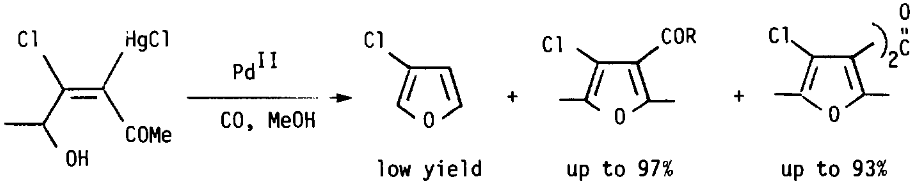
R^1 = H, Me, n-Pr, Ph

R^2 = Me



(590)

Chloromercuration of propargyl alcohols followed by reaction with carbon monoxide and palladium(II) give chlorofurans (equation 591) [598]. Palladium complexes also catalyzed the cyclization of o-bromo-diphenyl ethers to benzofurans (equation 592) [599]. Substituted phenols were oxidatively coupled by $Fe(CN)_6^{3-}$ to benzofurans if the substituents were large (equation 593) [600]. Bromo-bis-propargyl ethers were converted to furans by cobaloxime complexes (equation 594) [601].



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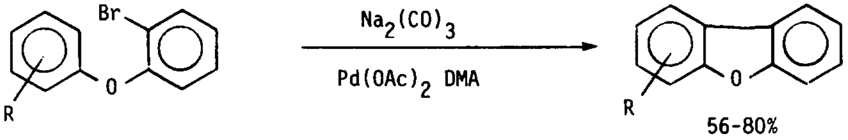
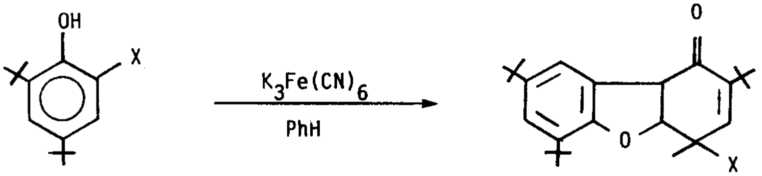
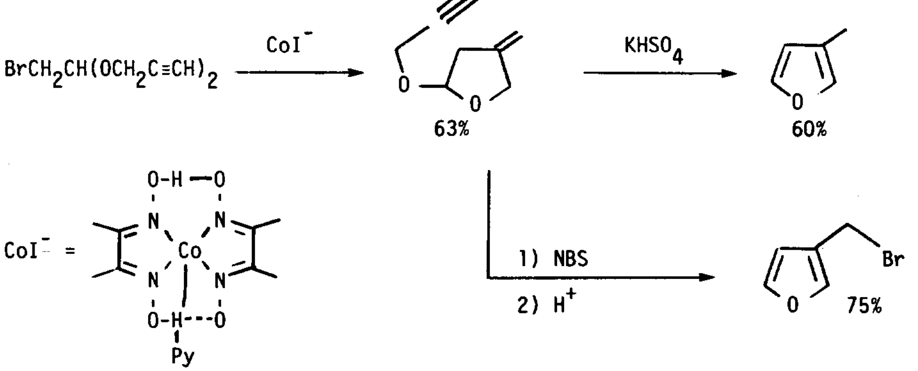


(592)

R = 4-NO_2, 3-NO_2, 2-NO_2, 2-CN, H, 2-CH_2OH, 1,3-diMe, 2-COOH

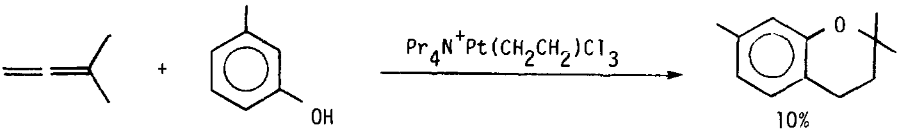


(593)



(594)

Platinum catalyzed the reaction of 1,1-dimethyl allene with phenol to give chromans (equation 595) [602]. Bromine-containing allyl ethers cyclized to oxygen heterocycles when treated with palladium(II) catalysts and secondary amines (equations 596-600) [603]. ω-Haloketones cyclized to oxygen heterocycles when treated with alkyl tin reagents and palladium(II) catalysts (equation 601) [604]. Allyl acetates containing OH - bearing side chains cyclized to oxygen heterocycles when treated with palladium catalysts (equations 602 and 603) [605]. Secondary hydroxylamines combined with ethyl acrylate in the presence of palladium black to give bicyclic heterocycles (equation 604) [606]. Arene chromium complexes having fluorine on the ring and alcoholic side chains cyclized when treated with base (equation 605) [607]. Amines and enamines were oxidized to dihydrofurans by a number of metal(II) acetates (equqtion 606) [608]. Other oxygen heterocycles were prepared as in equation 607 [609] and equation 608 [610].



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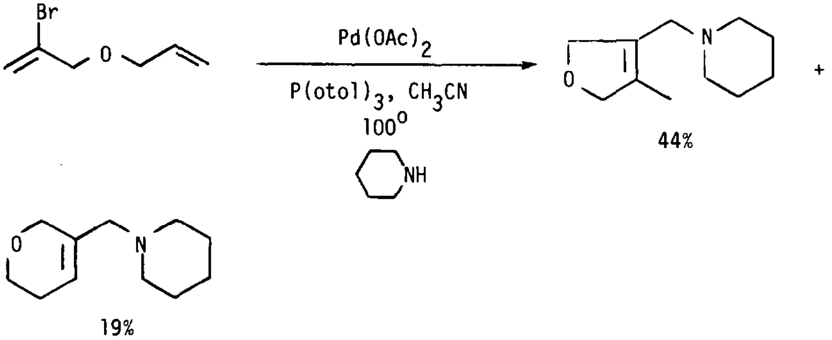


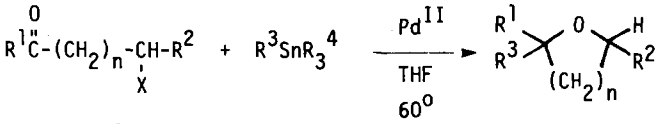
(596)

(597)

(598)

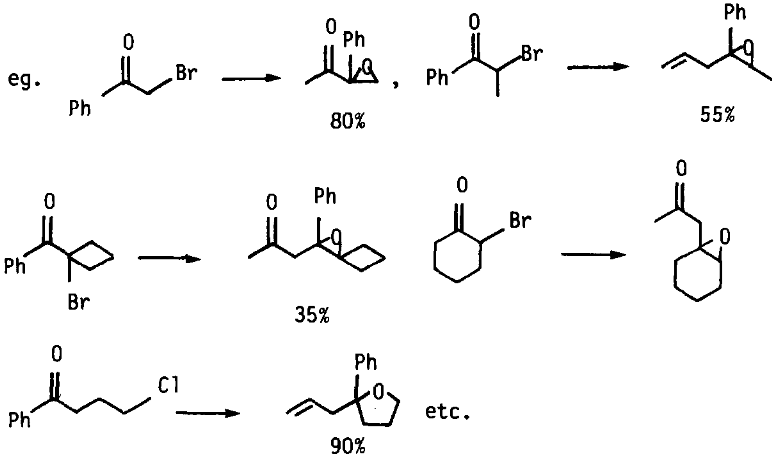
(599)

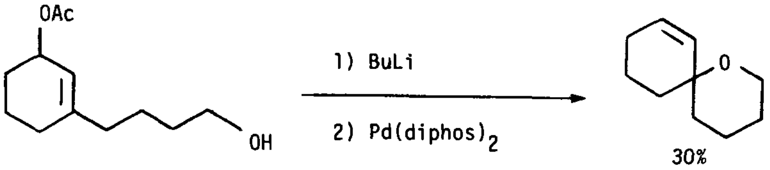
(600)



(601)

n = 0, 1, 2; R^3 = $CH_2CH=CH_2$, CH_2COMe
X = Cl, Br; R^4 = n-Bu





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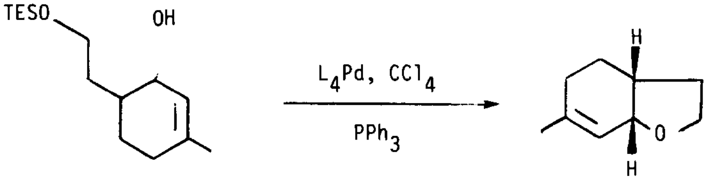
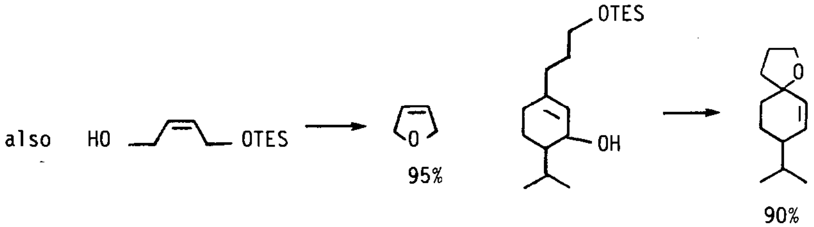
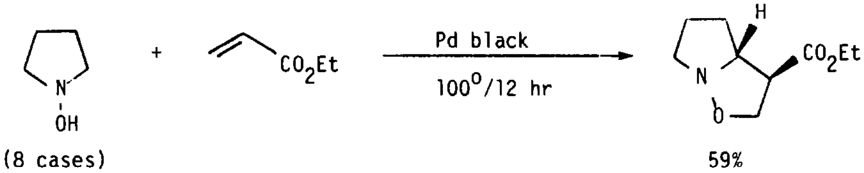


(603)





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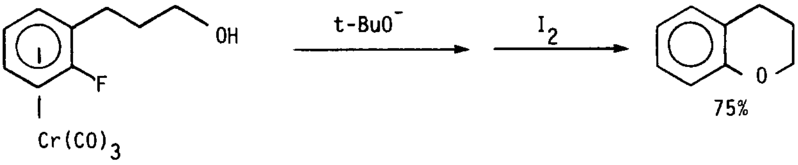

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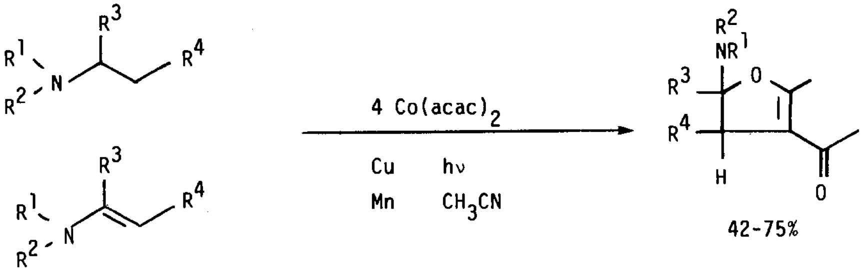
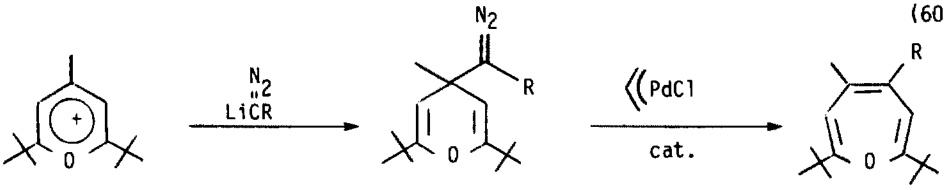


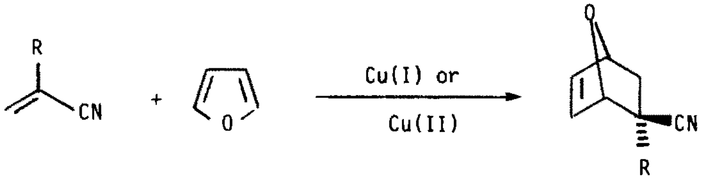
(606)

R^1 = n-Pr, n-Bu; R^2 = n-Pr, n-Bu

R^3 = H; R^4 = Me, Et

(607)

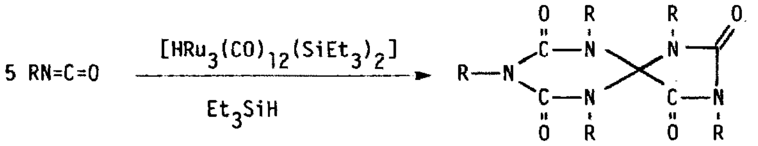




(608)

R = OAc, Cl

Transition metals were also used to make a number of more complex heterocycles (equation 609) [611], (equation 610) [612], (equation 611) [613], and (equation 612) [614].

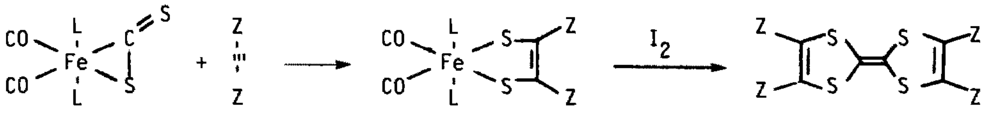


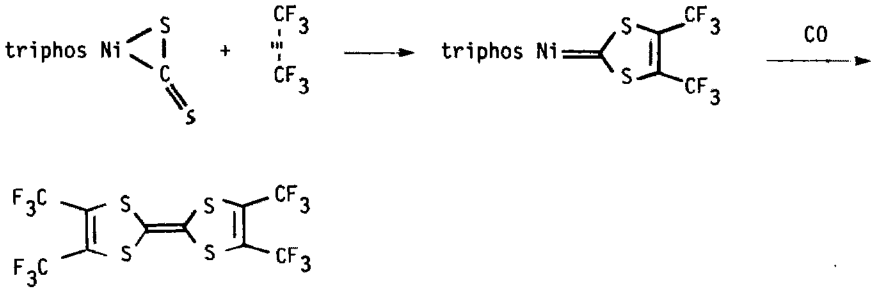
(609)

R = Me, Et, n-Pr

(no yield)

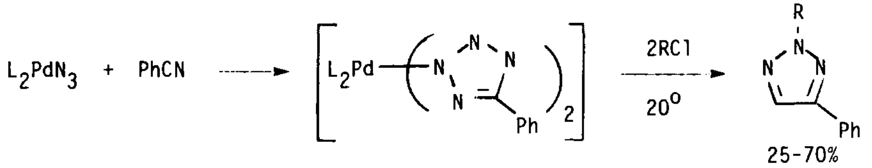
(610)





(611)

62%

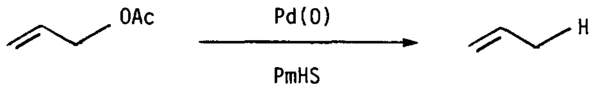


(612)

R = Ph_3C, COMe, COPh

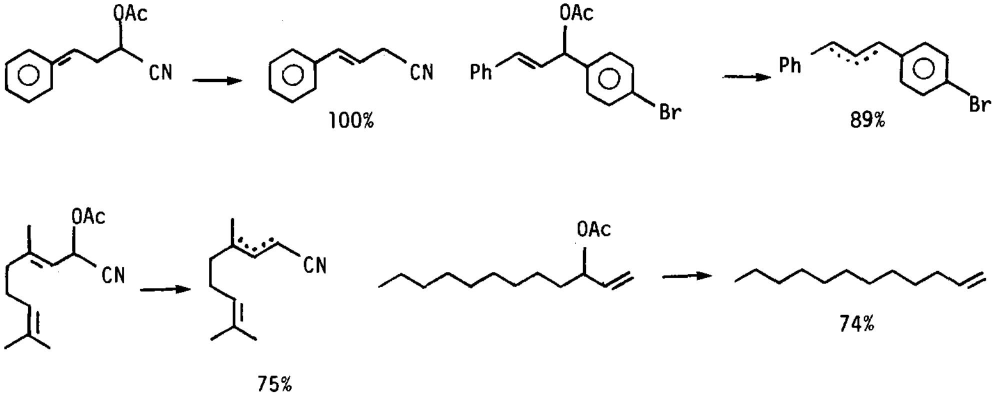
F. Alkenes, Alkanes

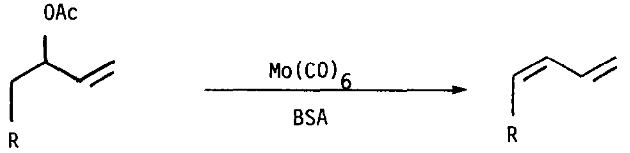
Allyl acetates were reduced to alkenes by palladium(0) catalysts and polymethylhydrosiloxane (equation 613) [615]. In contrast, molybendum carbonyl and O,N-bis(trimethylsilyl)acetamide caused an elimination of allyl acetates to 1,3-dienes (equations 614 and 615) [616], as did palladium(0) catalysts in THF (equation 616) [617].



(613)

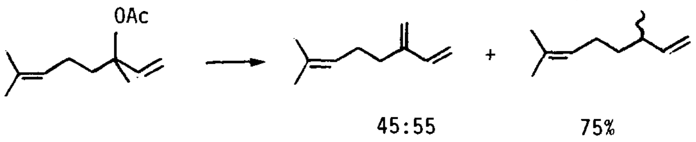
pmHS = polymethylhydrosiloxane

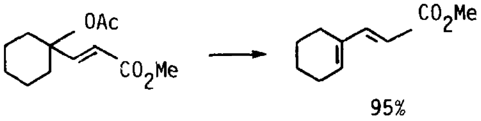


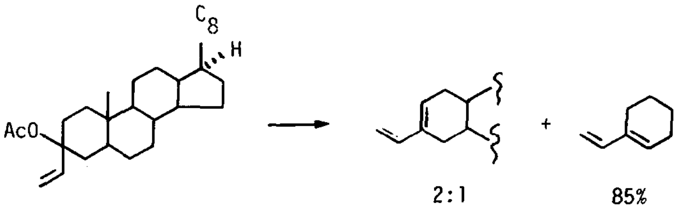


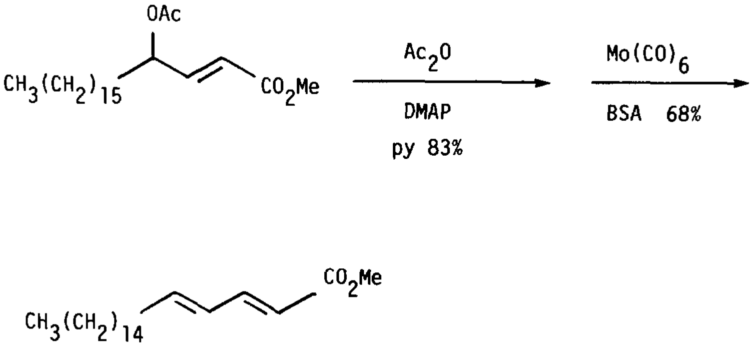
(614)

BSA = O,N-bis(trimethylsilyl)acetamide

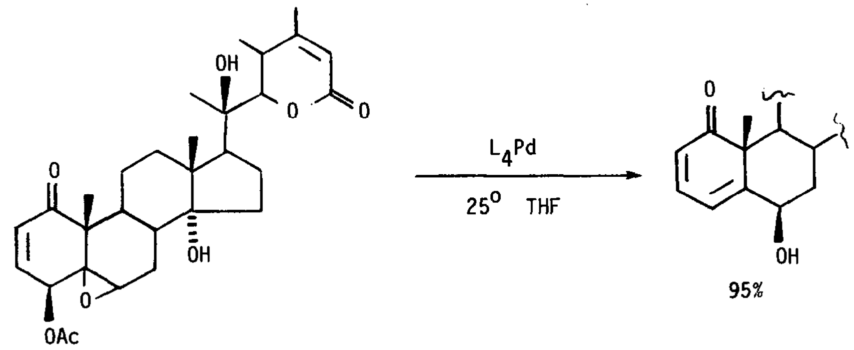








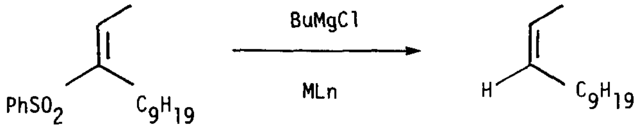
(615)



(616)

(4 cases)

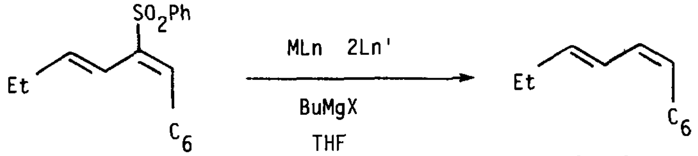
Reduction of trichloromethyl compounds by hydrogen donors induced by transition metal carbonyls, their complexes or their salts has been reviewed [618]. Vinyl- and dienylsulfones were reduced to the corresponding olefin (equation 617) or diene (equation 618) by butylmagnesium chloride in the presence of nickel or palladium salts [619][620].



48-64%

(617)

MLn = Ni(acac)$_2$, NiCl$_2$, NiL$_2$Cl$_2$ + dppe, Bu$_3$P, i-Pr$_3$Ph, DABCO, Et$_3$N



15-61%

(618)

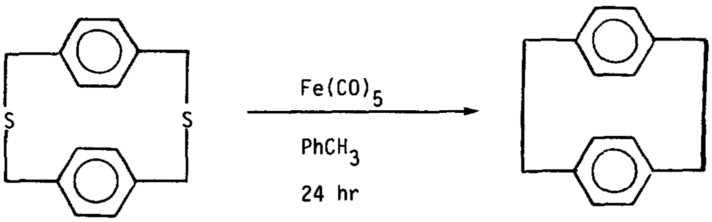
Iron complexes were efficient in the desulfurization of organosulfur compounds such as thiols (equation 619) [621], thioethers (equation 620) [622], and thioketones (equations 621 and 622) [623].

$$R^1R^2R^3CSH \xrightarrow[\substack{\text{5N NaOH, PhH} \\ BuN^+}]{Fe_3(CO)_{12}} \underset{60\text{-}80\%}{R^1R^2R^3CH} \qquad (619)$$

R^1 = 4-MePh, 2-MePh, 2,4-Cl$_2$Ph, Ph

R^2 = H, Ph, 4-MeOPh, 4-MePh

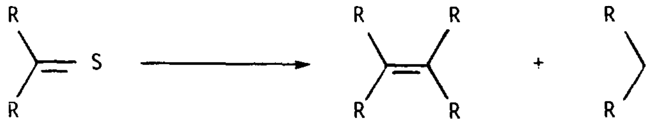
R^3 = H, Ph



62%

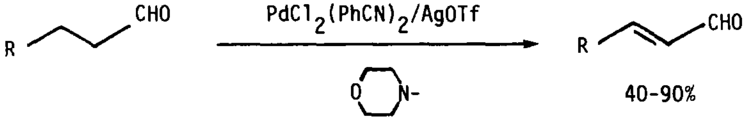
(620)

$$\mathrm{RSH}\ \xrightarrow[\mathrm{FeCl_3,\ THF/PhH}]{\mathrm{NaEt_3BH/Al_2O_3}}\ \mathrm{RH} + \mathrm{RR} \qquad (621)$$



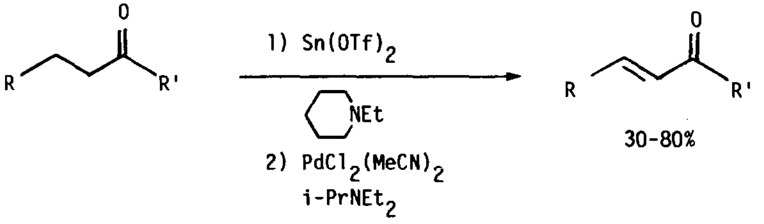
(622)

Aldehydes (equations 623) and ketones (equation 624) were oxidized to α,β-unsaturated carbonyl compounds by treatment with two equivalents of palladium(II) and four equivalents of silver or tin reagents [624]. Copper(II) bromide was also an efficient reagent for the oxidation of ketones to conjugated enones (equation 625) [625]. Allylic amines underwent a Hoffmann type elimination to produce dienes (equation 626) [626]. Reduced titanium species effected the elimination of HCl from α-halosulfoxides as well as reduction of the sulfoxide (equation 627) [627], while copper(II) chloride/oxygen/pyridine converted α-dihydrazones into alkynes (equation 628) [628].



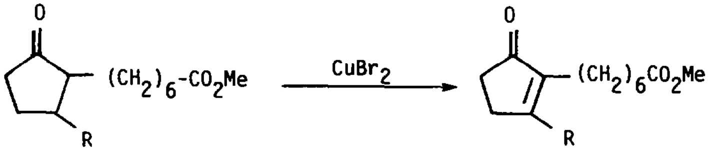
(623)

R = Ph, C_8, $CH_3CO(CH_2)_6$, $EtO_2C(CH_2)_7$, $CH_3CH(Cl)(CH_2)_6$



(624)

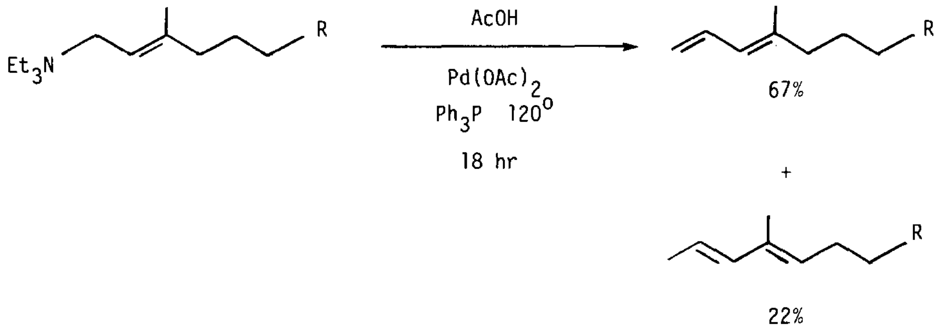
R = n-Pr, Ph , n-C_5, i-Pr
R' = Ph, i-Pr, n-C_5



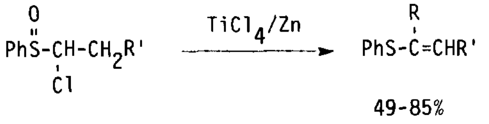
(625)

R = H 66%
R = CHO 38%

(626)



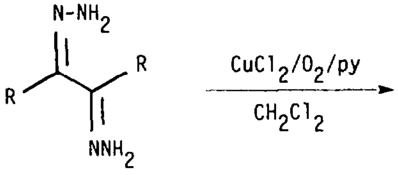
(627)



$$\mathrm{PhS(=O)\text{-}CH(Cl)\text{-}CH_2R'} \xrightarrow{\mathrm{TiCl_4/Zn}} \mathrm{PhS\text{-}C(R){=}CHR'}$$

49-85%

(628)

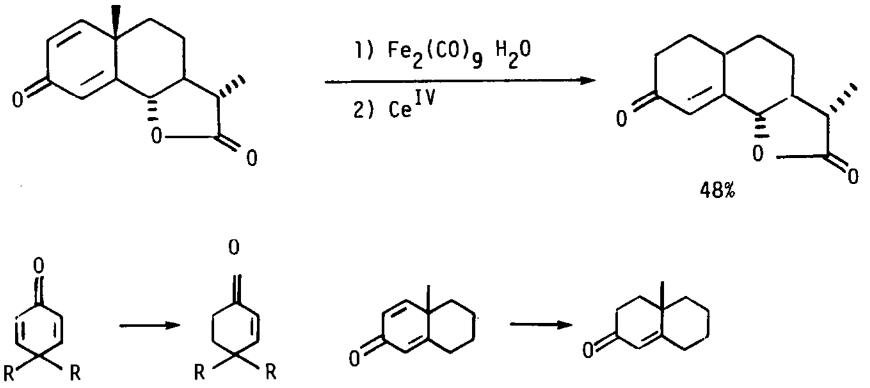


R-≡-R

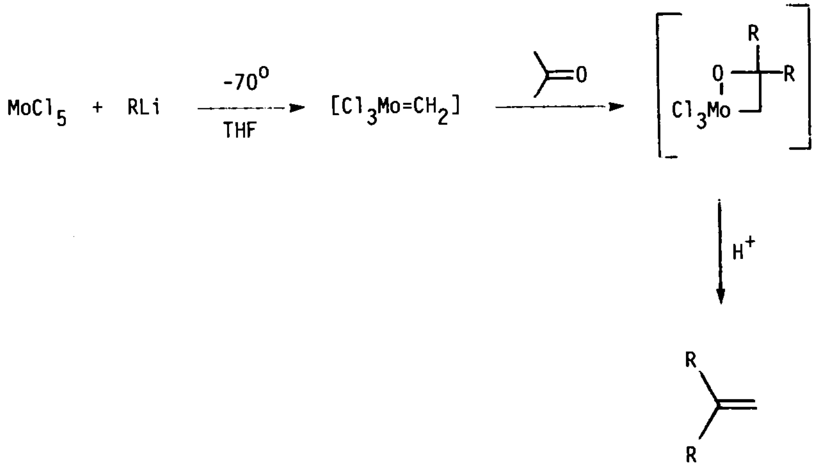
R = Ph 97%

R = n-C_5 88%

Investigation of the hydrogenolysis of linear hydrocarbons and the synthesis and chemistry of diiron diphenylphosphido complexes was the topic of a dissertation [629]. Dienones were converted to enones by treatment with diiron eneacarbonyl and water, followed by cerium(IV) (equation 629) [630]. A detailed study of the reduction of alkenes to alkanes by primary Grignard reagents and titanium(IV) chloride has appeared [631]. Primary alcohols and alkyl iodides were reduced to alkanes by sodium iodide in the presence of perchloric and platinum(II) [632]. A substituted cyclopentadienyliron dicarbonyl spcies was used as an olefin protecting group [633]. Iron could be removed from diene complexes by oxidation with alkaline hydrogen peroxide [634]. Ketones were converted to olefins by reaction with high valent molybdenum-carbene complexes (equation 630) [635].



(629)

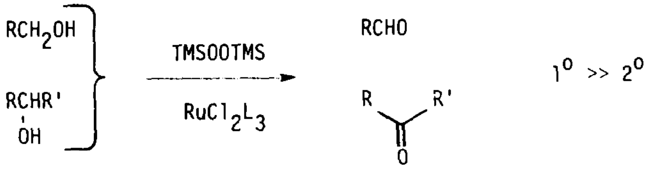


(630)

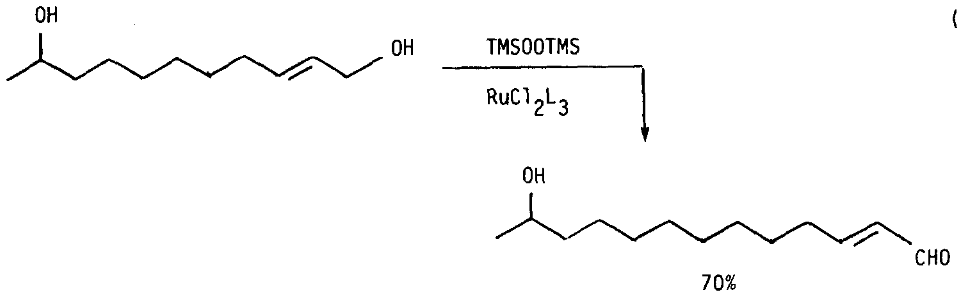
G. Ketones, Aldehydes

Several new methods for the oxidation of alcohols to aldehydes or ketones using transition metals have appeared. Cobalt nitrite and nitrate complexes catalyzed the oxidation of benzyl alcohol by nitrosyl tetrafluoroborate (equation 631) [636]. Ruthenium(II) catalyzed the oxidation of alcohols by bis-trimethylsilylperoxide (equation 632). This reagent could discriminate between primary and secondary alcohols (equations 633 and 634) [637]. Palladium(0) catalyzed the oxidation of alcohols by aryl halides (equation 635) [638]. Vanadium(IV) catalyzed the oxidation of secondary alcohols to ketones (equation 636). Primary alcohols did not react (equation 637) [639].

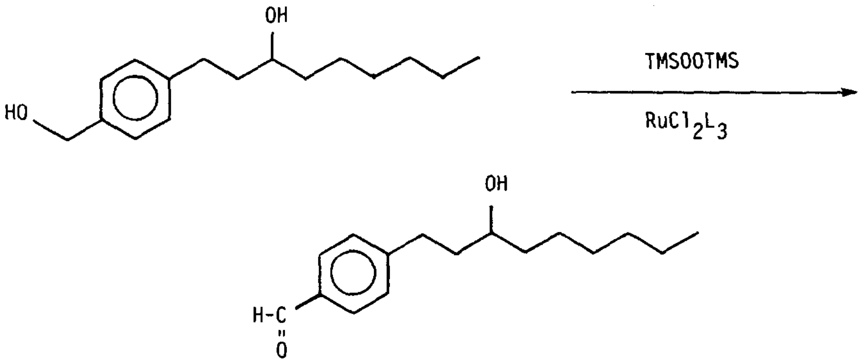
$$NOBF_4 + PhCH_2OH \xrightarrow[CpCo(S_2CNR_2)NO_2]{CpCo(S_2CNR_2)NO_3 \text{ or}} PhCHO \qquad (631)$$



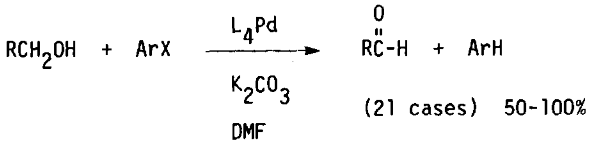
(632)



(633)



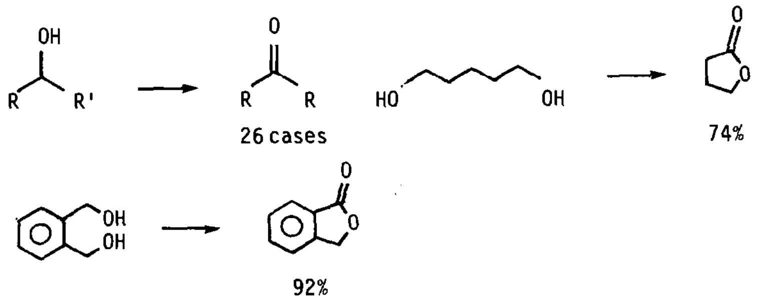
(634)

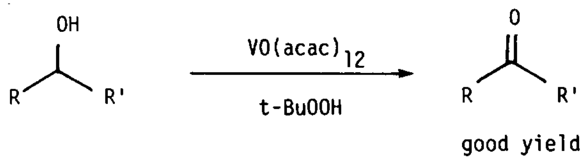


$$RCH_2OH + ArX \xrightarrow[K_2CO_3,\ DMF]{L_4Pd} R\overset{O}{\overset{\|}{C}}-H + ArH$$

(21 cases) 50-100%

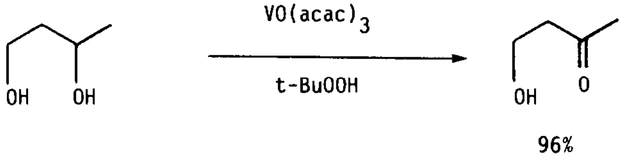
(635)





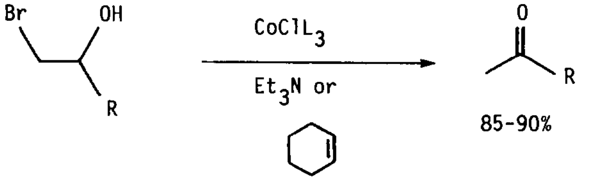
(636)

R = C_6, C_8, Ph; R' = CH_3,Et, $(CH_2)_5$, $(CH_2)_7$, $(CH_2)_4$



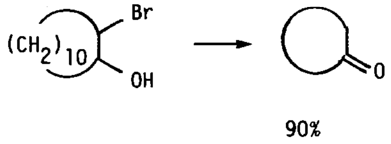
(637)

Bromohydrins were converted to ketones by cobalt(I) compounds and cyclohexene or triethylamine (equation 638) [640]. Geminal cyclopropyldibromides were carbonylated by nickel carbonyl in the presence of alcohols or amines (equation 639) [641]. Anthracenes were oxidized to anthraquinones by t-butylhydroperoxide in the presence of a rhodium(I) catalyst (equation 640) [642]. Phenols were oxidized to quinones by hydrogen peroxide and transition metals (equation 641) [643]. Cyclohexenones were oxidized to ene diones by t-butylhydroperoxide and transition metal catalysts (equations 642 and 643) [644].



(638)

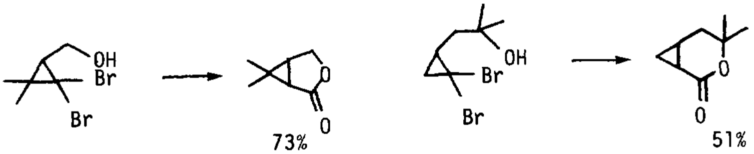
R = $(CH_2)_6CO_2Me$,

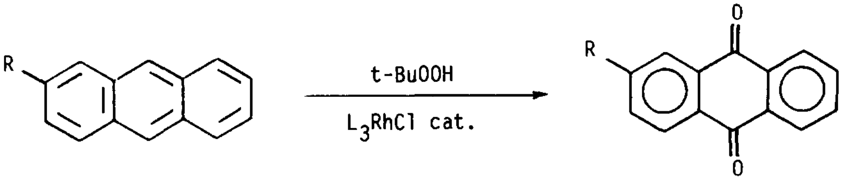


(639)

R^1 = Ph, Me; R^2 = H, CO_2Me, CN

40-78% Q = O, NH, NR

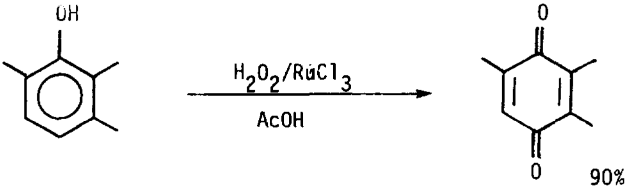




(640)

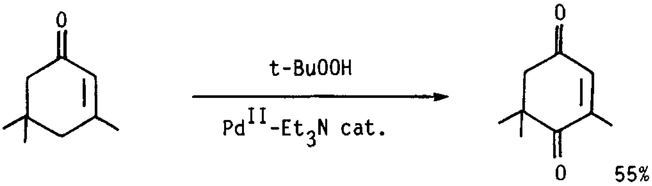
R = H, Me, Cl, OMe, OCOMe, NO_2, CN

30-90%

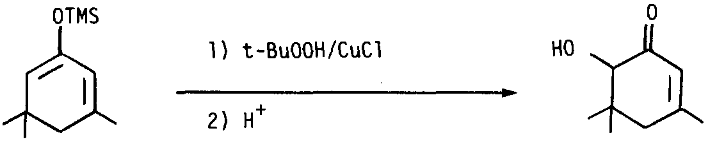


(641)

Fe, Cu, Zn, Co, Ni, Pd, Sn, Al, Ce, V, Mo, La, W less efficient.

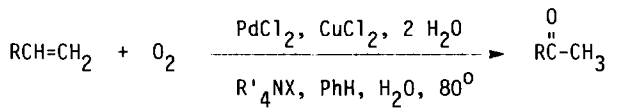


(642)



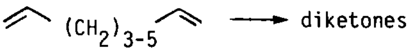
(643)

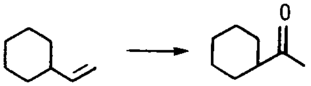
Terminal olefins were oxidized to ketones by Wacker type chemistry (palladium/copper catalysts) under phase transfer conditions (equation 644). The yield depended on the quaternary salt used, and the reaction required a large lipophilic phase transfer catalyst [645]. The mechanism of the oxidation of olefins with participation of nitrochloropalladium complexes has been reviewed (18 references) [646]. Conjugated enones reacted with chiral 2,4-pentanediol in the presence of palladium(II) chloride/copper(I) chloride to give β-ketoacetals (equations 645 and 646) [647]. Terminal monoolefins were oxidized to methyl ketones by rhodium or ruthenium salts, in modest yield, under phase transfer conditions [648]. Cationic rhodium(I) complexes containing the hemilabile ligand $Ph_2PCH_2CH_2SR$ catalyzed the air oxidation of terminal olefins to ketones, primary alcohols to acetals, and secondary alcohols to ketones [649]. Cyclooctadiene was converted to cyclooctanedione by oxygen and a rhodium-oxygen complex catalyst (equation 647) [650]. Wilkinson's compound, $RhCl(PPh_3)_3$ catalyzed the oxidative cleavage of olefins to ketones by molecular oxygen [651]. π-Allylpalladium complexes were oxidized to conjugated enones by oxygen under photolysis (equation 648) [652].

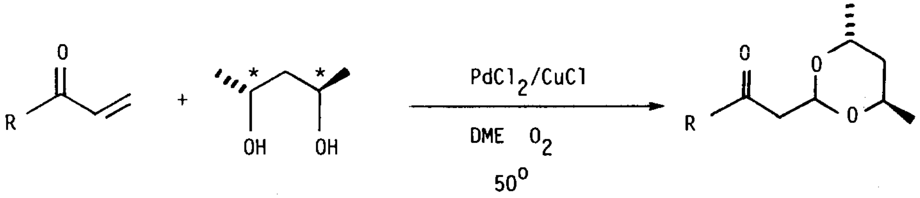


$$RCH{=}CH_2 + O_2 \xrightarrow[R'_4NX,\ PhH,\ H_2O,\ 80^0]{PdCl_2,\ CuCl_2,\ 2\ H_2O} R\overset{O}{\overset{\|}{C}}{-}CH_3 \qquad (644)$$

R = C_8, C_{10}, C_3, C_2; PTC = $C_{14}NMe_3^+$, $C_{12}NMe_3^+$

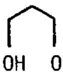




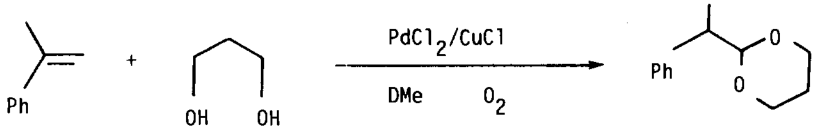


(645)

R = Ph, 86%; Me, 57%;
t-Bu, 63%

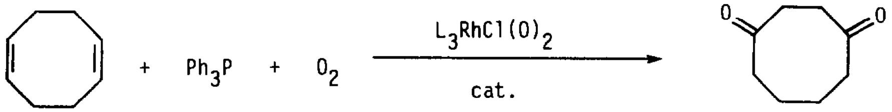


also works.

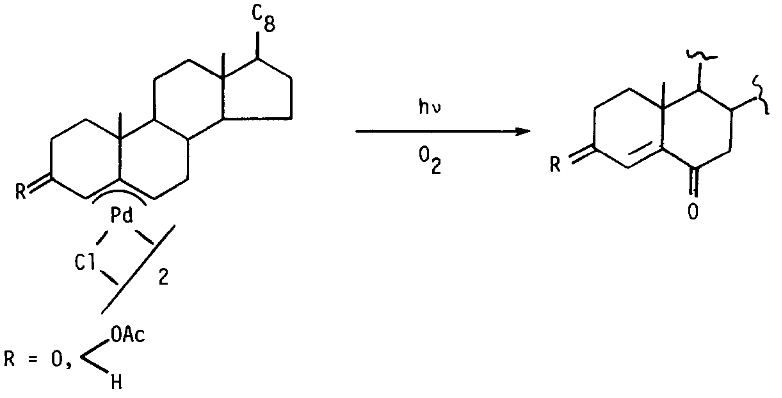


(646)

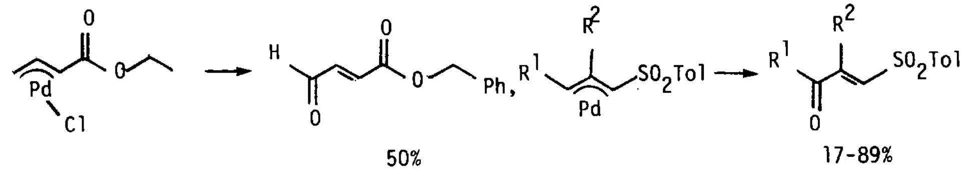
84%



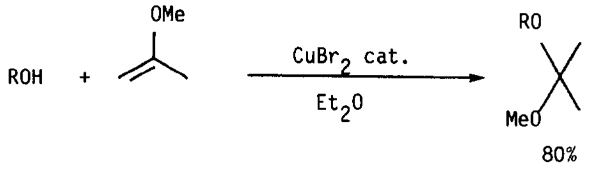
(647)



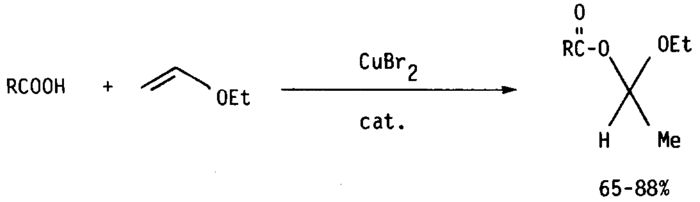
(648)



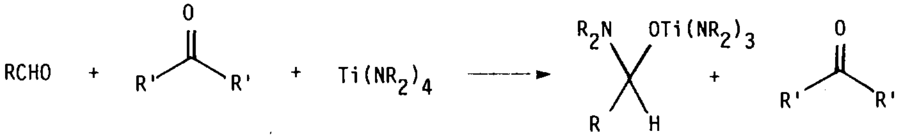
Enol ethers were converted to ketals or acetals by reaction with alcohols (equation 649) or carboxylic acids (equation 650) in the presence of copper(II) bromide [653]. Titanium(IV) amide complexes protected aldehydes in the presence of ketones (equation 651) [654]. Cyclic hemi acetals were converted to dithioacetals by reaction with titanium(IV) chloride and ethane dithiol (equation 652) [655][655a]. Titanium(IV) chloride was a very mild catalyst for the conversion of ketals or acetals to carbonyl compounds, in ether solvent [656]. Palladium(II) complexes catalyzed the selective deprotection of bis-trimethylsilylenol ethers by tri-n-butyltin fluoride (equation 653). The least hindered site was hydrolyzed [657]. Acid chlorides were converted to aldehydes by polymer bound bis-triphenylphosphine copper borohydride [658]. Nickel(II) acetylacetonate was a catalyst for the Friedel Crafts acylation of electron rich aryl compounds with acid chlorides [659].



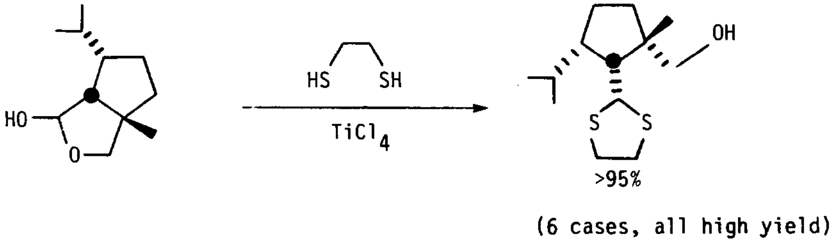
(649)



(650)

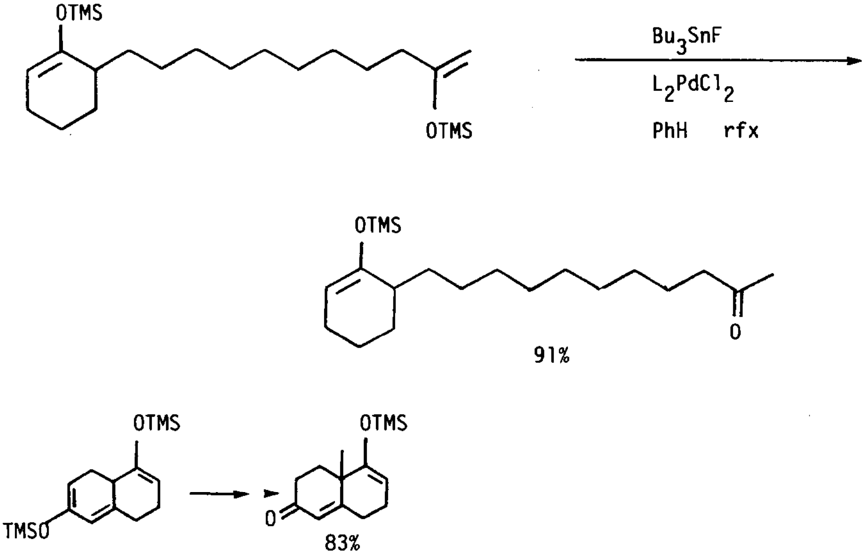


(651)



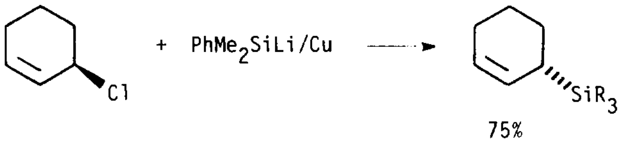
(652)

(653)

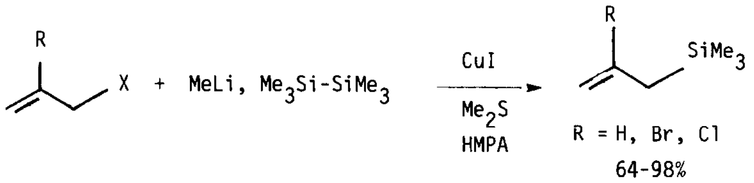


H. Organosilanes

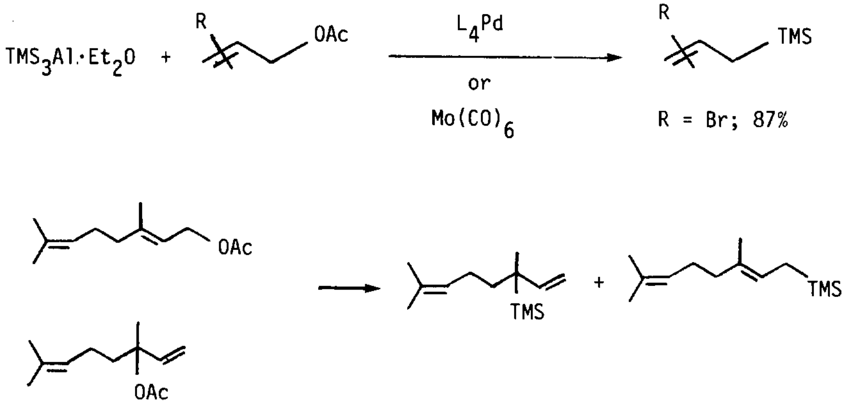
Allyl chlorides were converted to allyl silanes by reaction with trimethylsilyl copper reagents (equation 654) [660] (equation 655) [661]. Allyl acetates were converted allylsilanes by trimethylsilyl aluminum reagents with palladium or molybdenum catalysts (equation 656) [662]. α,β-Unsaturated esters were converted to β-silyl conjugated esters by reaction with trialkylsilanes and cobalt carbonyl catalysts (equation 657) [663]. Dienes were converted to allylsilanes by palladium catalyzed hydrosilation. With chiral catalysts, most asymmetric induction was observed (equation 658) [664]. Sonication of trialkylsilanes and olefins in the presence of platinum on carbon resulted in a low temperature (30^0) hydrosilation (equation 659) [665]. Alkynes were converted to vinyl silanes by reaction with silyllithium reagents in the presence of metal catalysts (equation 660) [666]. Titanium and vanadium complexes catalyzed the reaction of trimethylsilylazide with epoxides (equation 661) [667].



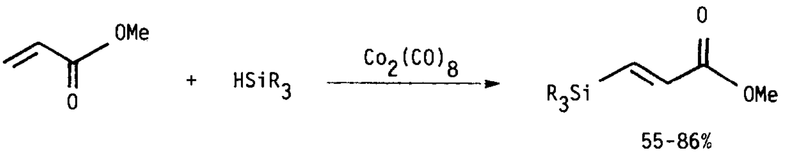
(654)



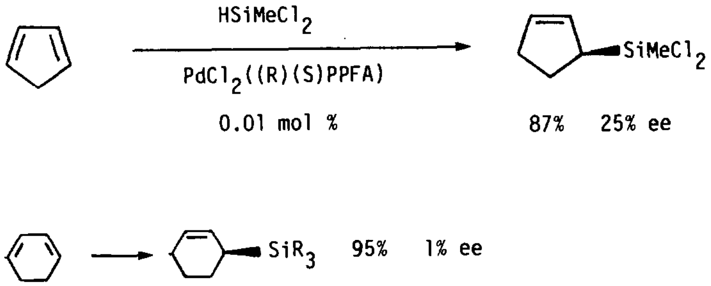
(655)



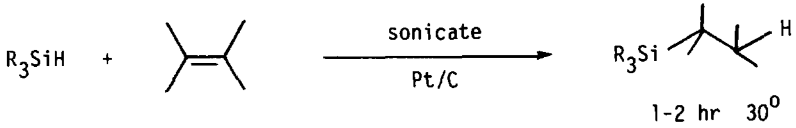
(656)



(657)

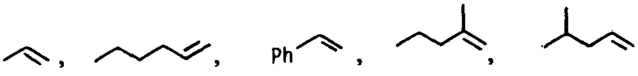


(658)

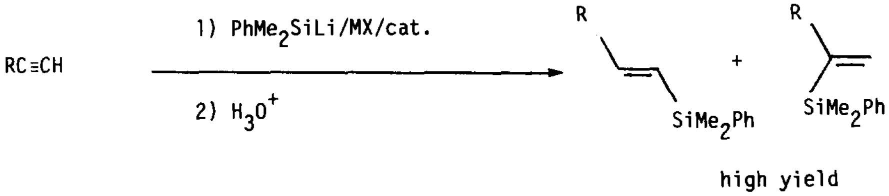


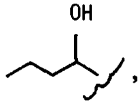
(659)

R$_3$ = Cl$_3$, Cl$_2$Me, (OEt)$_3$, Et$_3$

olefin = 

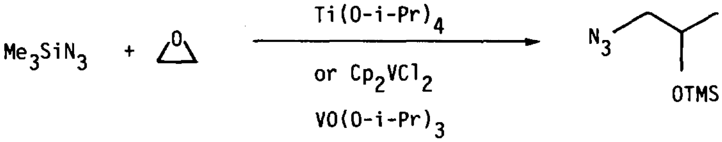
(660)



R = n-C$_{10}$,  , PhCH$_2$OCH$_2$CH$_2$

MX = MeMg, Et$_2$AlCl, ZuBr

cat. = L$_2$PtCl$_2$, CuI, PdCl$_2$L$_2$, RhClL$_3$

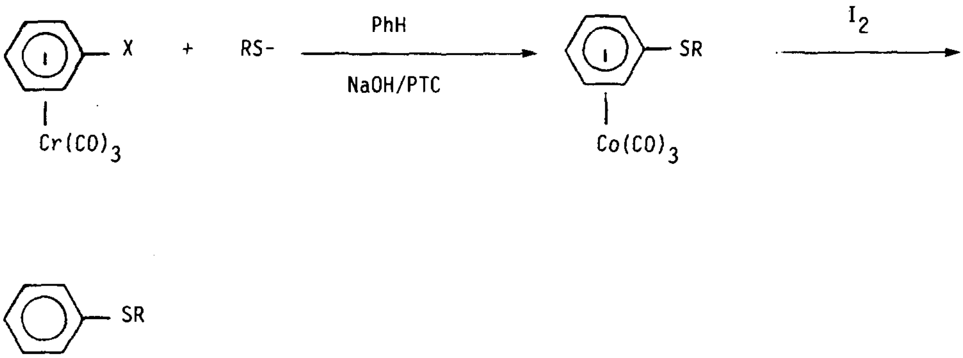


(661)

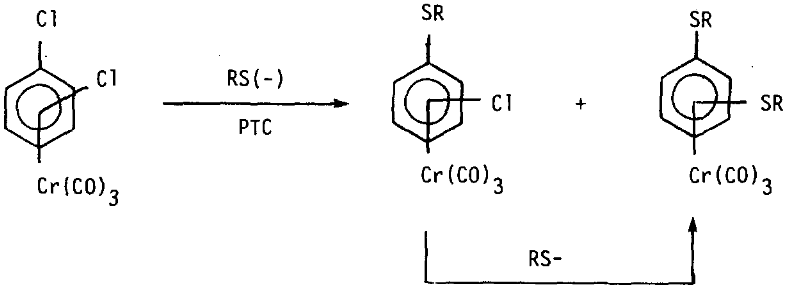
I. Miscellaneous

Thiophenols were prepared by the reaction thio anions with halobenzene chromium complexes (equation 662) [668], (equation 663) [669], (equation 664) [670]. *Allenic sulfides were prepared from propargyl sulfonates by reaction with thiophenol* copper complexes (equation 665) [671]. Sodium sulfinates attacked dienes in the presence of palladium(II) chloride (equation 666) [672]. Ruthenium(I) complexes catalyzed the reaction of arenesulfonyl chlorides with olefins (equation 667) [673]. α-Halosulfoxides were converted to sulfoxides by cobalt carbonyl on alumina (equation 668) [674]. Other sulfur and phosphorous compounds were also prepared using transition metal catalysts (equation 669) [675], (equation 670) [676], (equation 671) [677], (equation 672) [678].

(662)



X = F, Cl; R = Me, n-Bu, t-Bu

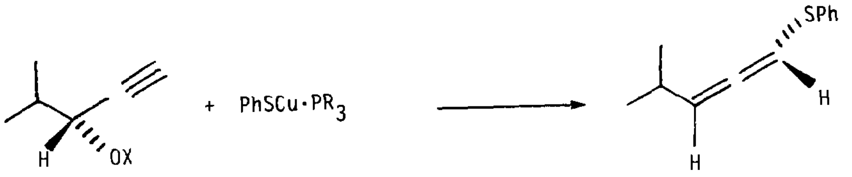


(663)

$$\mathrm{ArI} + \mathrm{Ph}\overset{O}{\overset{\|}{C}}\mathrm{-SCu} \longrightarrow \mathrm{ArS}\overset{O}{\overset{\|}{C}}\mathrm{-Ph} \qquad (664)$$

71-94%

5 cases

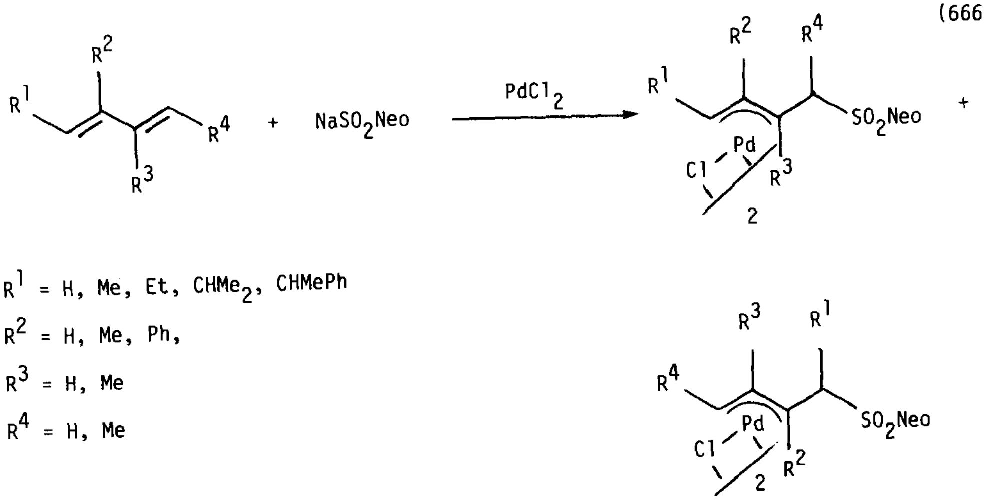


(665)

X = SO_2Me, SO_2CF_3

66% racemic X = SO_2Me
inversion X = SO_2CF_3

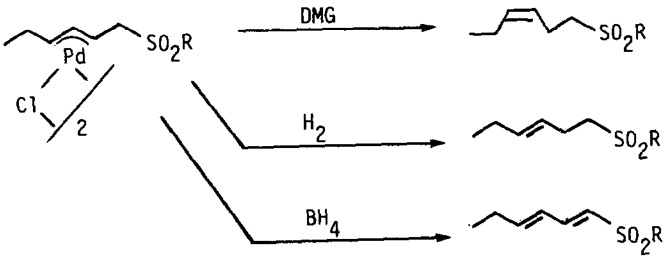
(666)

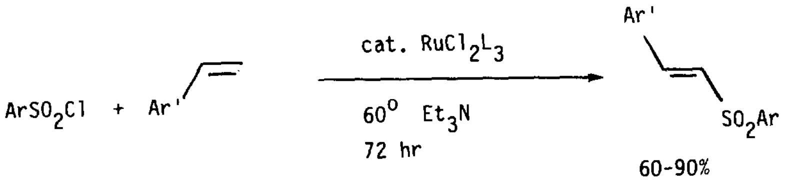


R^1 = H, Me, Et, $CHMe_2$, CHMePh
R^2 = H, Me, Ph,
R^3 = H, Me
R^4 = H, Me

16 cases

NOTE:

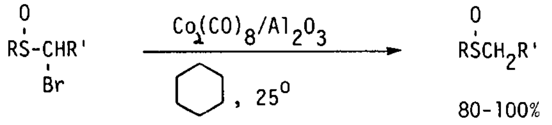




(667)

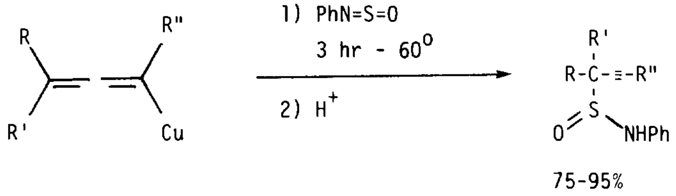
60-90%

Ar = 4-MeOPh, 4-MePh, Ph, 4-ClPh, 3-NO_2Ph
Ar' = H, HClPh, 4-MePh, 4-NO_2Ph

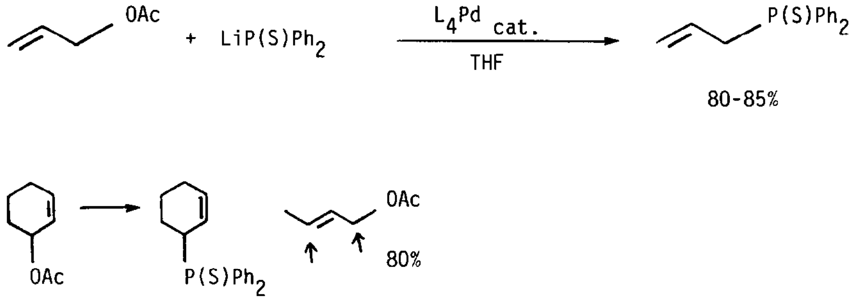


(668)

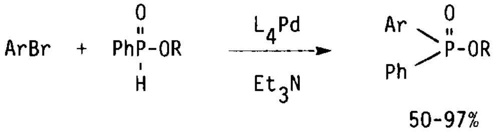
R = Ph, 4-ClPh, $PhCH_2$, 4-MePh, β-naphth



(669)

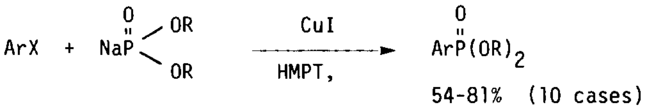


(670)



(671)

Ar = Ph, 4-MePh, 2-MePh, 4-ClPh, 4-MeOPh, 4-PhPh, $4\text{-}NO_2Ph$, $4\text{-}CH_3COPh$, $4\text{-}CH_3\overset{O}{\overset{\|}{C}}NHPh$,
4-CNPh, β-naph, 2-thiophenyl
R = Et, n-Bu



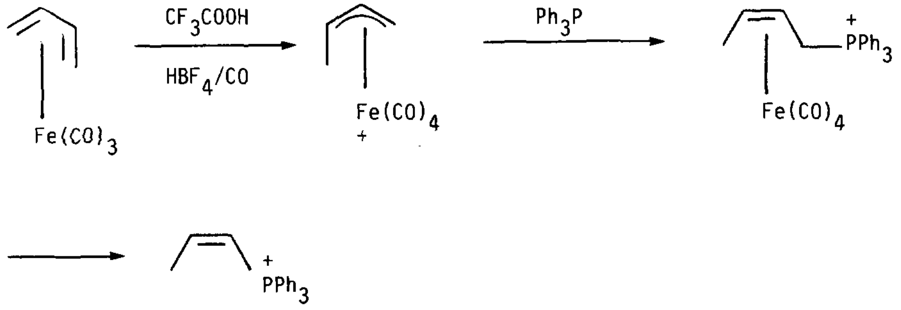
(672)

R = Ph, Et; Ar = Me, NH_2, OMe; X = Br, I

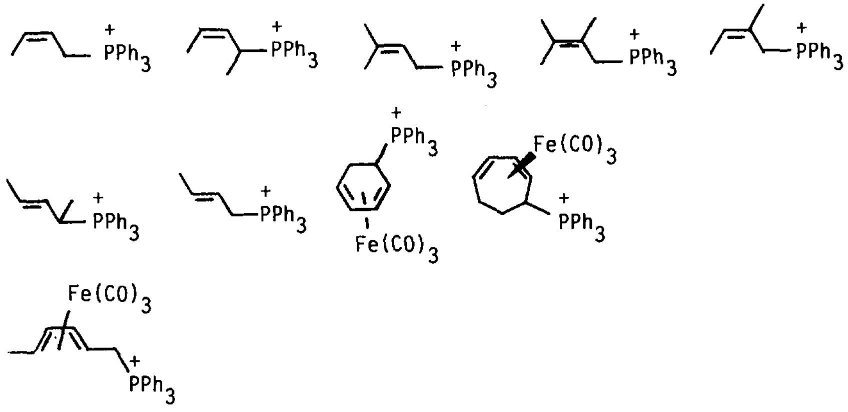
Thiols were oxidized to disulfides by iron(III) nitrate on bentonite in 40-97% yield [679], by t-butylhydroperoxide or hydrogen peroxide in the presence of vanadium and molybdenum catalysts [680], by bipy copper(II) permanganate [681], and by hydrogen peroxide in the presence of tungsten catalysts [682].

Allylphosphonium salts were made by the nucleophilic attack of phosphines on π-allyliron complexes (equation 673) [683]. These were homologated into polyene iron complexes by Wittig chemistry (equation 674) [684]. Diastereoisomeric prostaglandin precursors were separated by making cobalt-acetylene complex (equation 675) [685]. The stereochemistry of a tetraene was confirmed by making and characterizing an iron complex of it (equation 676) [686].

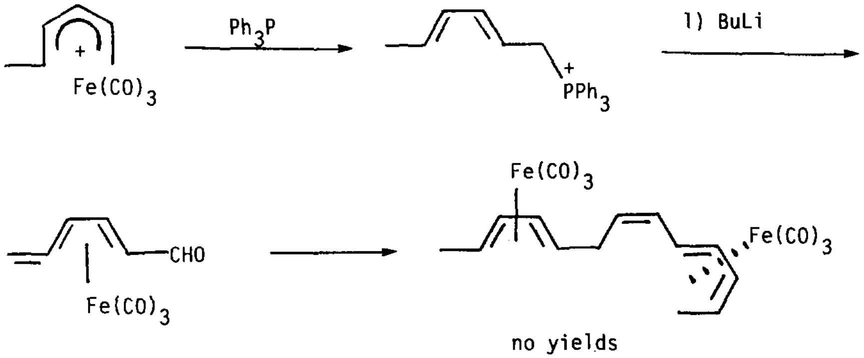
(673)



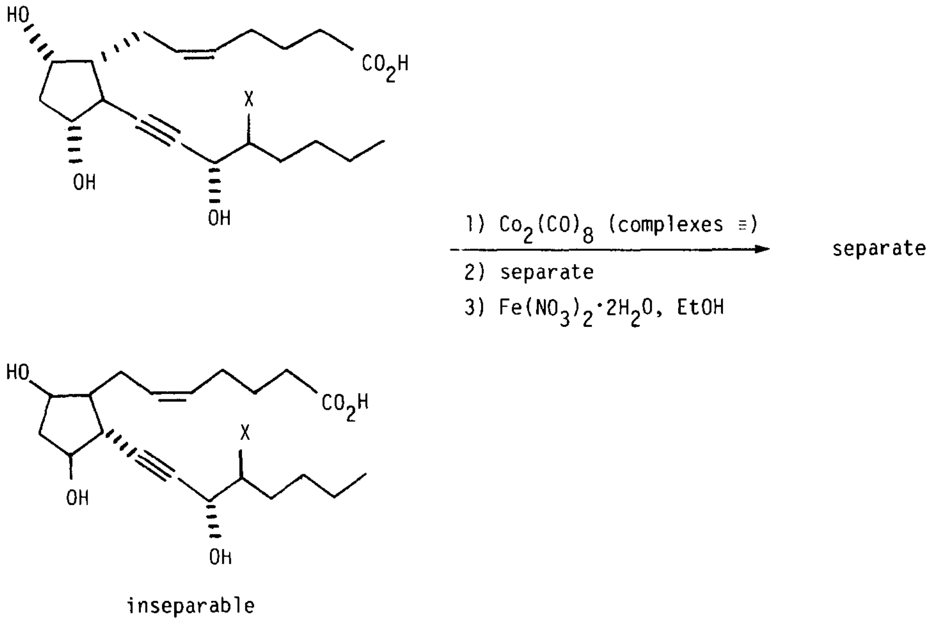
made



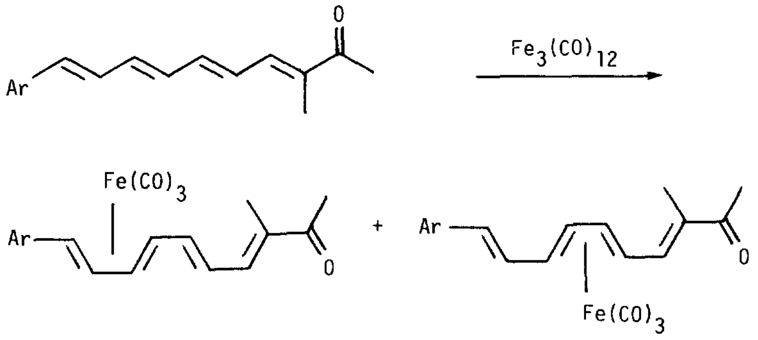
(674)



(675)

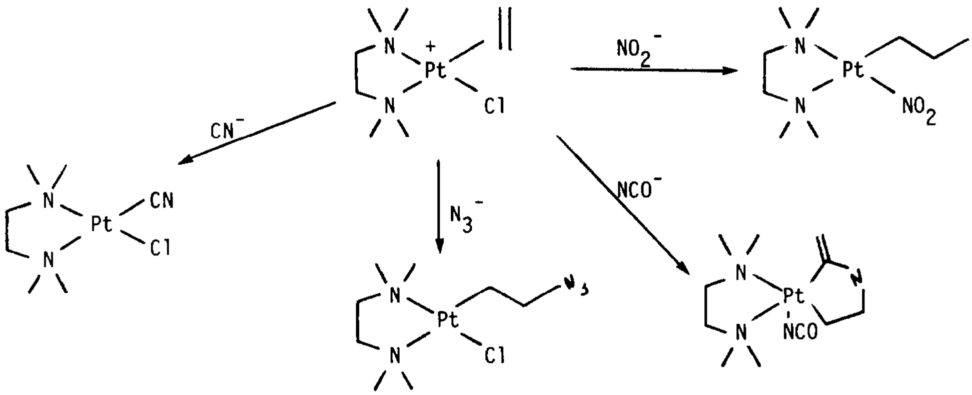


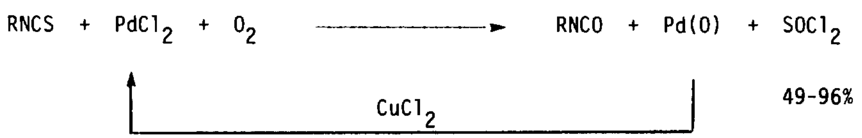
(676)



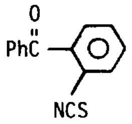
Palladium(II) bromide catalyzed the adiditon of B_5H_9 to olefins to give 1- and 2-substituted alkenylpentaboranes [687]. Cationic platinum olefin complexes were converted to a number of substituted σ-alkyl complexes by reaction with nucleophiles (equation 677) [688]. Isothiocyanates were converted to isocyanates by oxygen in the presence of a palladium(II) catalyst (eqaution 678) [689]. Organocopper chemistry was used to convert nitro compounds to oximes (equation 679) [690].

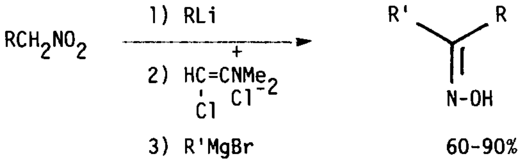
(677)





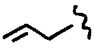
$$\mathrm{RNCS} + \mathrm{PdCl_2} + \mathrm{O_2} \longrightarrow \mathrm{RNCO} + \mathrm{Pd(0)} + \mathrm{SOCl_2} \qquad (678)$$

R = Me, Et, n-Pr, i-Pr, Ph, PhCH$_2$, 



(679)

R = Me, Et, n-C$_5$m 

R' = Me, n-Bu, n-C$_8$, Ph,  , Ph, , 

IV. Reviews

The following reviews has appeared.

Transition metals in organic synthesis - carbon-carbon bond forming reactions and functional group preparations. (755 references) [691]

Transition metals in organic synthesis: hydroformylation, reduction and oxidation. Annual survey covering the year 1981. (245 references) [692]

Organotransition metal chemistry for organic synthesis. (37 references) [693]

Transition metal mediated formation of carbon-carbon bonds. (Dissertation) [694]

Catalysts in organic synthesis. (3 references) [695]

Organometallics in synthesis. (270 references) [696]

Group VIII transition metals in organic synthesis. (127 references) [697]

The challenge of the synthesis of natural substances by homogeneous catalysis. (32 references) [698]

Transition metals in organic synthesis. Principles of transition metal chemistry. (115 references) [699]

Organic reactions of selected π-complexes. Annual survey 1982. (333 references) [700]

Plenary lectures (18 of them) of 2nd International Symposium on Organometallic Chemsitry Directed Toward Organic Synthesis. [701]

Advances in organic synthesis promoted by transition metal complexes. (97 references) [702]

Transition metal nitrosyls in organic synthesis and in pollution control. (143 references) [703]

New methods for stereo- and regiocontrol in organic synthesis via organometallic compounds. (15 references) [704]

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