TRANSITION METAL DERIVATIVES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1975

LOUIS S. HEGEDUS

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523 (U.S.A.)

CONTENTS

Transition metal derivatives in organic synthesis, Annual Survey covering the year 1974 see J. Organometal. Chem., 103 (1975) 421-474.

TRANSITION METAL DERIVATIVES IN ORGANIC SYNTHESIS

I. GENERAL COMMENTS

This annual survey covers the literature for 1975 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review, but is limited to reports of discrete systems that lead to at least moderate yields of organic compounds, or that allow unique organic transformations, even if low yields are obtained. Catalytic reactions that lead cleanly to a major product and do not involve extreme conditions are also included.

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

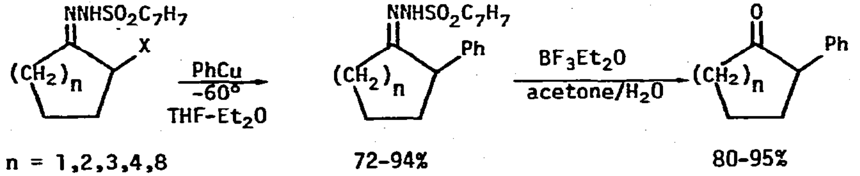
II. CARBON-CARBON BOND FORMING REACTIONS

A. Alkylation

Organocuprates continue to enjoy popularity as alkylating agents for a variety of substrates. They are routinely made *in situ* by treatment of a Cu (I) halide with the desired organolithium reagent. However, it was found that treatment of Cu (I) halide with dimethylsulfide produced Me_2SCuX, a colorless crystalline solid claimed to be the best source of Cu (I) for the preparation of organocuprates [1]. It provides an easy method to purify the Cu (I) halide, and was used to prepare Me_2CuLi and $(vinyl)_2CuLi$

which behaved in the usual fashion. The complex was not soluble in ether itself, but was solubilized by addition of dimethylsulfide to the solution. Fatty acid esters were prepared in 54-80% yields by the treatment of ω iodoesters with long chain alkyl or alkenyl Grignard reagents and methylcopper [2].

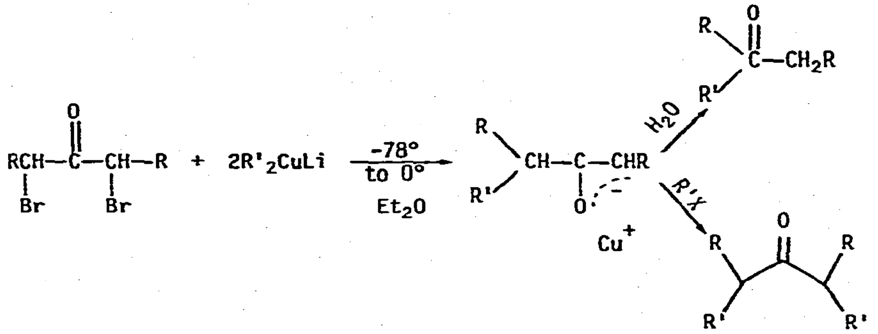
The reactions of α-haloketones with organocopper reagents have been studied by several groups. Very hindered ketones were prepared in low (6-25%) yield by the treatment of hindered α-bromo ketones with isopropyl- and t-butyl copper complexes (R_2CuLi) [3], [4]. These reactions were complicated by simple reduction of the α-halo group. A high yield α-phenylation of α-halo ketones by phenylcopper was effected by using the corresponding α-bromo-p-toluenesulfonylhydrazone, which was converted to the p-toluenesulfonylazocycloalkene and underwent conjugate addition with diphenylcuprate or phenylcopper (eq. 1) [5]. The reaction of o-(dimethylaminomethyl) phenyl copper proceeded under more vigorous conditions (-20°) to produce the corresponding substituted α-phenyl ketone. The reaction also worked well with α-bromo-β-keto ester tosylhydrazones.



(1)

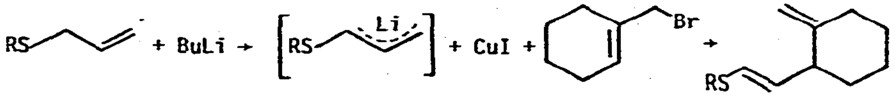
α,α'-dihaloketones reacted with dialkylcuprates to produce copper enolates, which could be reacted with electrophiles to further functionalize the substrate (eq. 2) [6], [7]. This procedure worked well for dimethylation and diethylation (80%) but very poor yields of diisopropropyl and di-t-butylketones were obtained.

Several procedures for the introduction of allylic groups into organic substrates have recently been developed. The anion of allylthioethers reacted with cuprous iodide and allylbromide to produce the corresponding vinylthio-



(2)

ether (eq. 3). This was a general reaction of allylic halides and proceeded with allylic transposition. Carbonyl groups were not compatible with this reaction, and hydrolysis of the sulfide to the aldehyde was not possible. To circumvent this, the sequence described in eq. 4 was developed [8].



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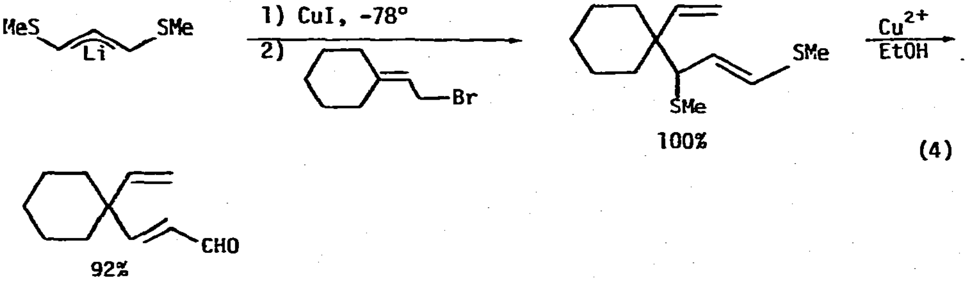
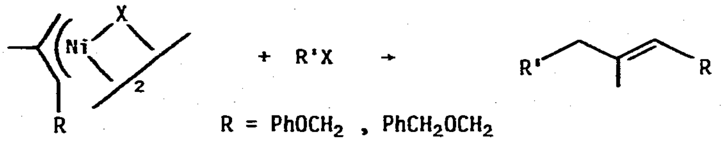


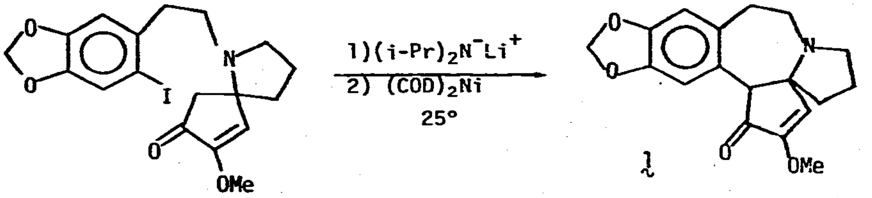
(4)

Allyl ethers reacted with Grignard reagents in the presence of cuprous bromide with Sn2 displacement of the ether in cases in which the allylic position was unsubstituted, and with Sn2' displacement in cases in which the allylic position bore one or two alkyl groups [9]. π-Crotylnickel bromide reacted with alkyl and allylhalides to replace the halogen with the crotyl group [10]. The π-allylnickel halide complexes from 1-bromo-2-methyl-4-phenoxy-2-butene and 4-benzyloxy-1-bromo-2-methyl-2-butene have been prepared and have been reacted with iodobenzene, prenyl bromide and geranyl bromide to produce the corresponding ethers (eq. 5) [11]. It has been proposed that the reaction of π-allylnickel halide complexes with organic halides proceeds via a radical chain reaction [12].



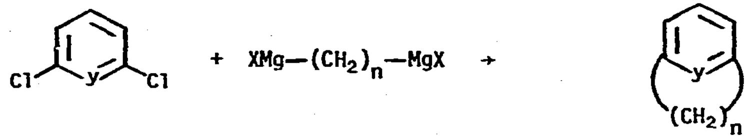
$R = PhOCH_2\ ,\ PhCH_2OCH_2$ (5)

Cephalotaxinone (1) was synthesized in 35% yield by the zero-valent nickel assisted nucleophilic aromatic substitution described in eq. 6. Simple replacement of the iodide by hydrogen (reduction) was a competing process (35%) [13]. The reaction between aryl and vinyl halides and acetylide anions was promoted by stoichiometric amounts of a variety of nickel (0) phosphine complexes, and by catalytic amounts of palladium (0) phosphine complexes [14]. Nucleophilic aromatic substitution of the bromide of ortho-bromobenzoic acids by stabilized carbanions such as diethyl malonate, malononitrile, etc., was best carried out by treatment with NaH and cuprous bromide [15, 16]. This reaction was restricted to o-bromobenzoic acids, but tolerated a wide variety of functional groups in the aromatic ring.. Anions of cyclopentadiene, nitromethane, and DMSO failed to react well under these conditions.



(6)

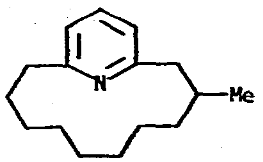
The asymmetric synthesis of (S)(+)-2,2'-dimethyl-1,1'-binaphthyl from the appropriate bromobenzene and aryl Grignard reagent was accomplished using a chiral phosphine-nickel complex catalyst [17]. Alkylation of halopyridines by Grignard reagents was effected by L_2NiCl_2 [18]. A similar system was used to prepare a variety of macrocyclic compounds (eq. 7) including muscopyridine (2) [19].



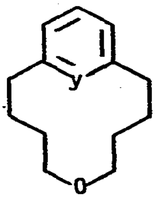
(7)

y = N, n = 6,7,8,9,10,12 10-30%

y = CH, n = 8,9,10,12 10-20%

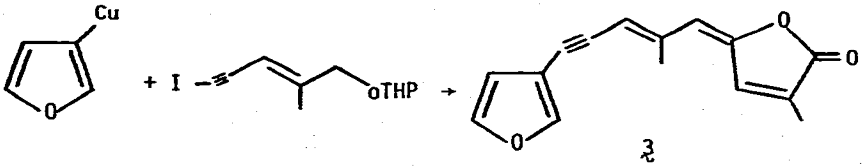


2 (20%)



y = N, CH (20%)

Lithium dimethylcuprate cleanly dialkylated a variety of 1,1-dibromoalkenes [20] although β,β-dibromostyrene suffered extensive monoalkylation followed by dimerization [21]. Vinyl halides were alkylated by Grignard reagents using an iron catalyst [22]. Organocopper reagents of the type YCu (Y = Ph, $BuC\equiv C^-$, $Me_3SiC\equiv C\text{-}CH_2\text{-}$, Br, CN, PhS) cleanly substituted Y for the halide with vinyl halide substrates [23], while vinyl copper complexes were treated with acetylenic halides to produce conjugated eneynes. The insect sex pheremone bombylsol was prepared in this fashion [24]. Similarly, freelingyne (3) was synthesized using the reaction between a copper-furan complex and an acetylenic iodide (eq. 8) [25]. Finally,



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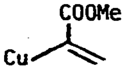
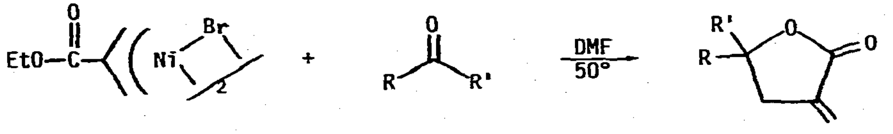
(8)

vinyl halides were alkylated by treatment with L_4Pd followed by RLi with >99% stereospecificity [26] while treatment of monosubstituted alkynes with vinyl, aromatic, or heteroaromatic halides with $L_2Pd(OAc)_2$ as catalyst led to disubstituted alkynes [27].

Acid chlorides were converted to ketones in high yield by reaction with $Rh(PPh_3)_2(CO)R$ (R = Me, n-Bu, Ph, allyl, Et), formed from $RhCl(PPh_3)_2(CO)$ and organolithium reagents. This system tolerated a wide variety of functional groups, and converted chiral acid chlorides to the corresponding ketones without racemization [28]. Palladium (O) complexes catalyzed the reaction of acid halides with dialkylmercury compounds to produce ketones [29]. Trimethylsilyacetylenic ketones were prepared by treating acid halides with $Me_3SiC{\equiv}C^-Cu$ [30].

Although lithium dialkylcuprates normally add 1,4 to conjugated enones, Li^+ (1-hexyne) Cu  $\mathrm{Li^+(1\text{-}hexyne)Cu{-}C(COOMe){=}CH_2}$ reacted exclusively in a 1,2 fashion with conjugated ketones regardless of conditions [31]. Similarly treatment of cyclohexenone with butynyllithium and cuprous iodide resulted in an exclusive 1,2 addition to the carbonyl group [32]. A mixture of methyllithium and lithium dimethylcuprate was used for the selective production of alcohols resulting from axial attack of the corresponding ketones. This reagent gave 94:6 a/e with 4-t-butyl-cyclohexanone while methyllithium alone gave a 79:21 a/e mixture. The reagent also worked well with 2-methylcyclohexanone and 4-α-methyl-trans-2-decalone, but failed with 2-methylcyclopentanone [33].

π-Allylnickel halide complexes reacted with ketones and aldehydes to produce homoallylic alochols in good yield. Use of the π-2-carbethoxyallyl complex produced α-methylene-γ-butyrolactones (eq. 9). The reactions proceeded under mild conditions and tolerated epoxides, nitriles, esters, and acid halides [34]. Lithium dialkylcuprates reacted regio- and stereospecifically with trimethylsilyl epoxides to produce olefins after subjection of the thus-formed β-trimethylsilyl alcohol to elimination conditions. The elimination was *syn* under basic conditions and *anti* under acidic conditions (eq. 10) [35].



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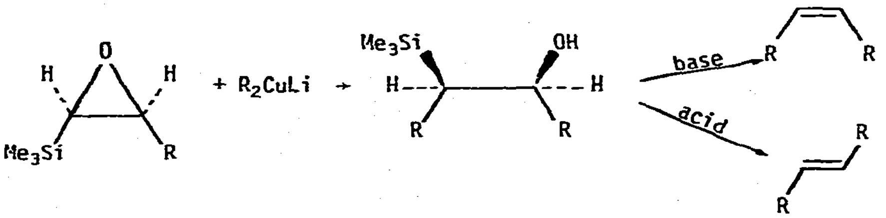
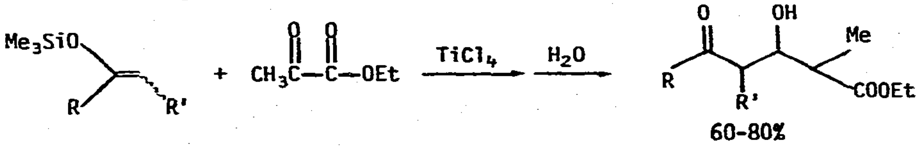


(10)

Titanium tetrachloride promoted the crossed aldol condensation of silyl enol ethers with keto esters (eq. 11) [36] and simple ketones (eq. 12) [37] to produce the corresponding hydroxy carbonyl compounds in moderate to good yield. The crossed condensation of aldehydes with ketones having α-methyl or α-methylene groups was affected by $NaHFe(CO)_4$ (eq. 13). The yields were better with aryl aldehydes than with alkyl aldehydes, and ketones with only the α-methine group were unreactive [38].



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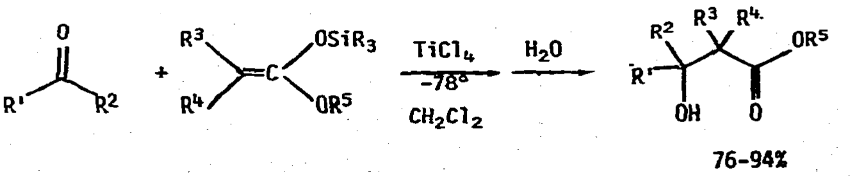
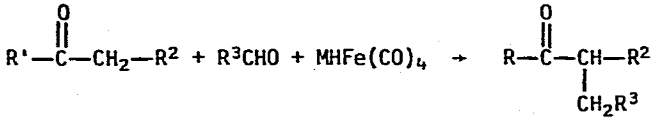


(12)

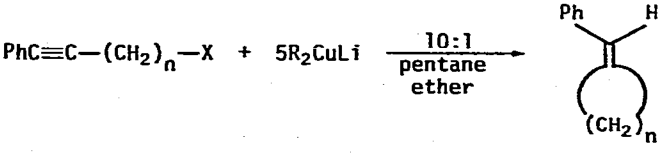


$$R'-C(=O)-CH_2-R^2 + R^3CHO + MHFe(CO)_4 \rightarrow R-C(=O)-CH(R^2)-CH_2R^3$$

(13)

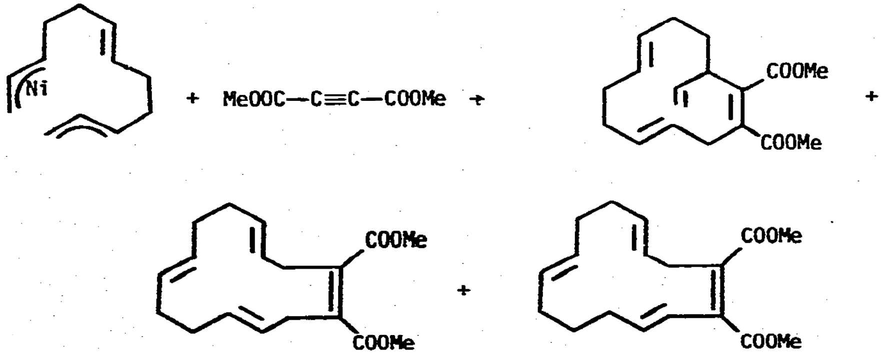
40-80%

Several reports of the alkylation of alkynes by organocuprates have appeared. The *syn* addition of RCu·MgBr to alkynes of the type $HC{\equiv}C{-}(CH_2)_n{-}Z$ (n = 2,3, Z = X, NR_2, OR, SR) was studied. The regioselectivity of the reaction depended on the nature of Z and the solvent. The resulting vinylcopper species were alkylated, carboxylated, and iodinated [39]. Propargyl alcohols were treated under similar conditions to produce 2-substituted allylic alcohols in fair yield [40]. An unusual cyclization of ω haloalkynes by lithium dialkylcuprates has recently been reported (eq. 14) [41]. *Bis*-π-allylnickel reacted with disubstituted alkynes to produce the corresponding *cis*-1,2-diallylolefins in 30-50% yield [42], while the corresponding *bis*-π-allylnickel complex resulting from trimerization of butadiene reacted with dimethyl acetylene dicarboxylate to produce three cyclic addition products (eq. 15) [43]. Finally, $(Et_3P)_2Pt(Cl)(C{\equiv}CPh)$ added to dimethylacetylene dicarboxylate



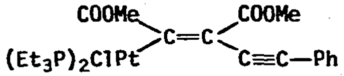
(14)

n = 4 91%
n = 3,5 poor yield
n = 6 no cyclization

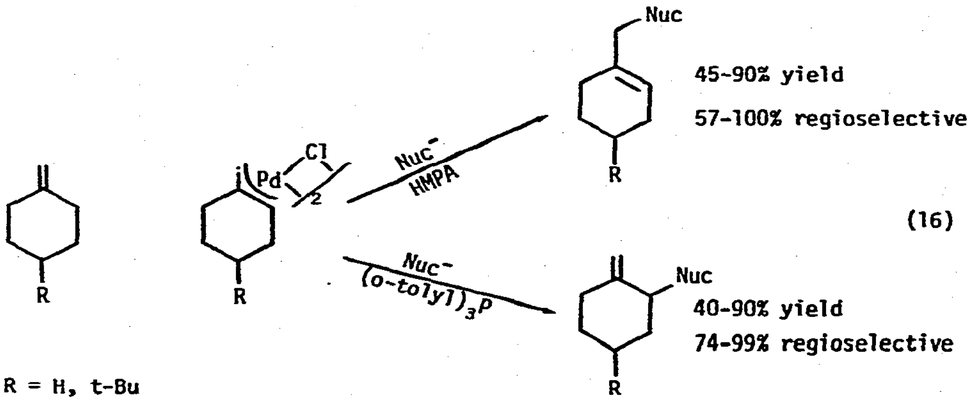


(15)

30-40% overall equal amounts at 0°

to produce  $(Et_3P)_2ClPt(COOMe)C{=}C(COOMe)C{\equiv}C{-}Ph$ which was inert to dry HCl [44].

The observation that olefins could readily be converted to π-allyl palladium chloride complexes, and that under appropriate conditions the π-allyl group was subject to nucleophilic attack has produced several very useful functionalization sequences for olefins. The allylic alkylation of π-allylpalladium complexes was highly stereospecific, with alkylation occurring from the face opposite the Pd. Soft nucleophiles that attacked directly at carbon were required [45]. The site of attack could be controlled by adjustment of conditions (eq. 16) [46]. This chemistry was applied to a new isoprenylation sequence (eq. 17) and used to synthesize geranyl geraniol [47]. The π-1-carbethoxyallylpalladium chloride complex reacted with diethylmalonate anion in DMSO to produce a quantitative yield of the substituted acrylate ester regio- and stereoselectively (eq. 18). The anion of ethyl cyanoacetate also reacted well, while cyanide ion failed [48].

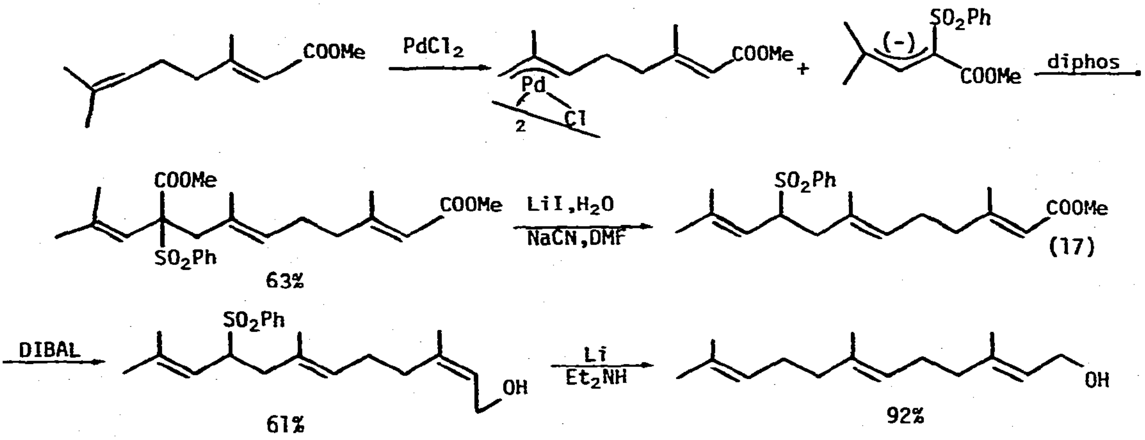


(16)

R = H, t-Bu

Nuc⁻ = $CH(COOMe)_2$, $CH_3SO_2\bar{C}HCOOMe$, $PhS{-}\bar{C}HCOOMe$

Palladium(II) salts were used to cause the condensation of naphthalene with styrene to produce β-styrylnaphthalene (1-β-naphthyl-2-phenylethane) in 40% yield [49]. Similarly palladium acetate was used to promote the



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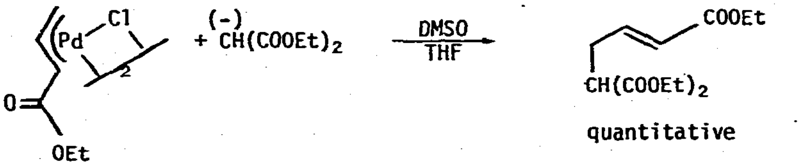
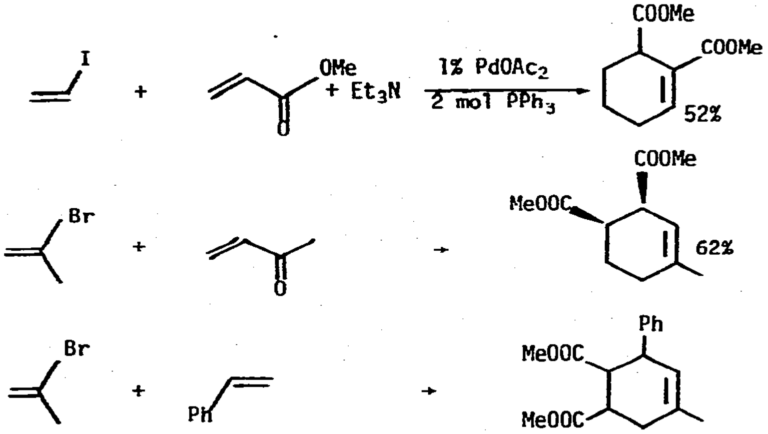


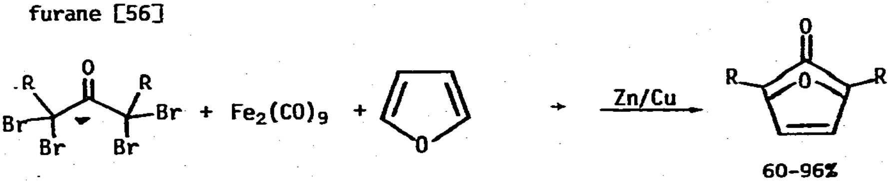
(18)

reaction of benzene with substituted β-methylstyrenes at the methyl group to produce β-benzylstyrenes in 60% yield as a mixture of isomers [50]. Arylthallium compounds reacted with olefins in the presence of lithium chloropalladate to arylate the olefin in 30-60% yields [51]. In a very complex reaction, vinyl halides and conjugated enones reacted in the presence of palladium acetate, a tertiary amine, and triphenylphosphine to produce cyclic systems (eq. 19) [52]. The reaction was thought to proceed via alkylation of the conjugated enone by a vinylpalladium species, with the diene thus formed undergoing a Diels Alder reaction with additional conjugated enone. Disubstituted olefins and electron rich vinyl halides were not very reactive. Vinyl bromides and iodides were of comparable activities. Finally, methyl cobaloxime reacted with benzoquinone in the presence of a palladium(II) catalyst to produce methyl benzoquinone in 70% yield. Very low yields were obtained in the absence of palladium. Methyl cobalamine failed to react [53].



(19)

Several bicyclic systems have been synthesized by the Fe(CO)$_5$ promoted reaction of polyhaloketones with dienes (eq. 20, 21) [54, 55]. In a similar fashion nezukone was prepared from α,α,α'α'tetrabromoacetone and 3-isopropylfurane [56]



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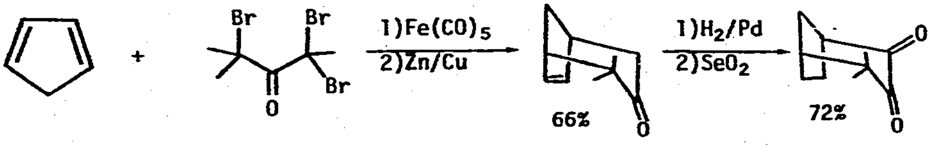
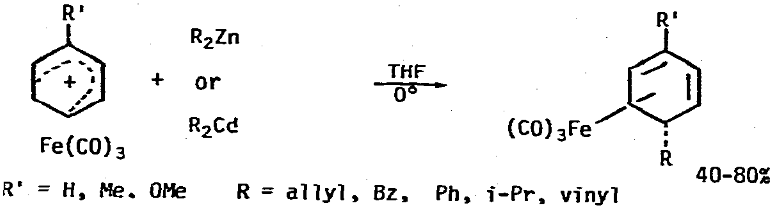


(21)

carbocamphenilone

The cyclohexadienyl group in $[C_6H_7Fe(CO)_3]^+$ was found to be reactive toward nucleophiles, producing substituted 1,3 cyclohexadienyl iron complexes. Dialkylzinc and cadmium reagents (eq. 22) [59] as well as aryl trimethylsilanes (eq. 23) [58] alkylated the cyclohexadienyl group. Trimethyl phosphite also attacked the same group, while Zn/Cu couple lead to reductive coupling (eq. 24) [59]. The allyl group in $[C_4H_7Fe(CO)_3]^+$ underwent a similar alkylation with dialkyl cadmium reagents (eq. 25) [60]. By oxidative removal of the iron, a variety of useful organic compounds would be accessible.



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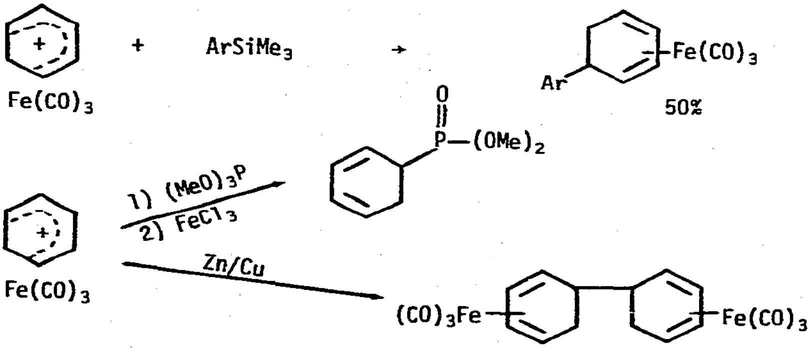

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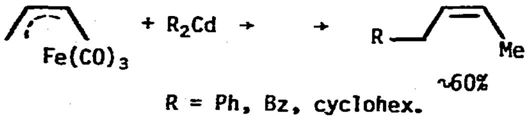
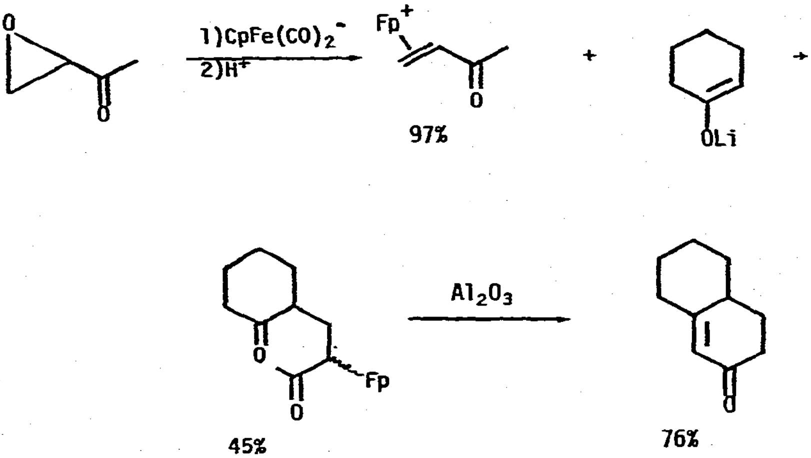


R = Ph, Bz, cyclohex.

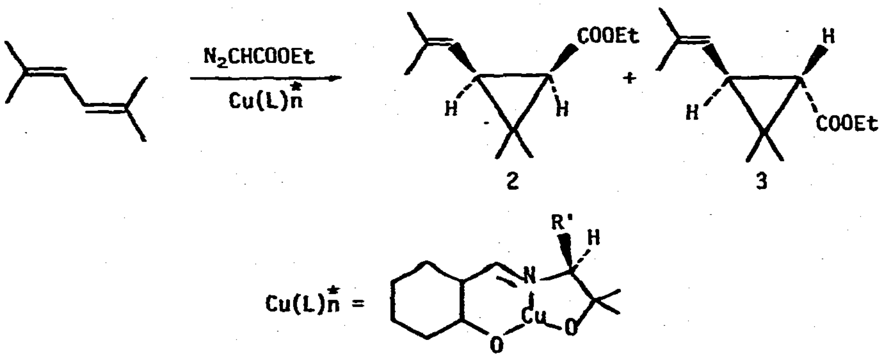
(25)

In an interesting series of reactions the $C_5H_5Fe(CO)_2^+$(= Fp^+) group was used to enhance the reactivity of conjugated enones as Michael acceptors towards simple enolate ions for annelation reactions (eq. 20) [61]. Cyclopentyl and cyclohexylenamines also worked well, as did silylenol ethers. Coordination of the conjugated enone to the iron complex appeared to suppress self condensation.



(26)

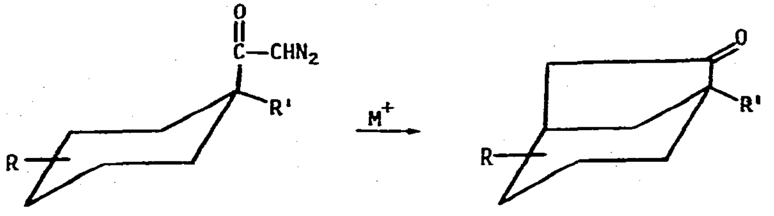
Cyclopropanation of olefins by metal-catalyzed decomposition of diazocompounds has been the subject of several studies. Chrysanthemic acid was synthesized in 50% yield and 65% optical yield by the decomposition of ethyl diazoacetate in the presence of 2,5-dimethylhexa-2,4-diene with a chiral copper catalyst (eq. 27)[62]. This reaction showed a remarkable degree of optical induction. Vinyl cyclopropanes were prepared in low



(27)

yield by the Cu^{2+} catalyzed decomposition of $CH_2{=}CH{-}CHN_2$ in the presence of olefins [63] while norbornene, norbornadiene [64] and conjugated enones [65] were cyclopropanated in excellent yield by palladium acetate catalyzed decomposition of diazomethane. The yield of bicyclic material from diazoketone

4 (eq. 28) was sensitive to both the nature of the ring substituents as well as the metal used to decompose the diazocompound. Cuprous compounds proved to be the best catalysts for this system [66]. Methyl α-chloropropionate reacted with acrylonitrile in the presence of $Bu_3PCuO—tBu$ to produce high yields of the cyano cyclopropanecarboxylic esters [67], while diethyl malonate or ethyl cyanoacetate reacted with olefins in the presence of cupric halides to produce cyclopropane dicarboxylic esters or cyano esters in 30-60% yield [68]. The chromium carbene complex $Cr(CO)_5(C(OMe)Ph)$ reacted with the pyrollidine enamine of isobutyraldehyde to produce 1,1-dimethyl-2-methoxy-2-phenyl-3-pyrrolidinylcyclopropane [69]. This is one of the few instances in which a chromium carbene complex was able to cyclopropanate a double bond. Finally the cyclopropanation of cycloheptatrienone was accomplished in the fashion detailed in eq. 29 [70].



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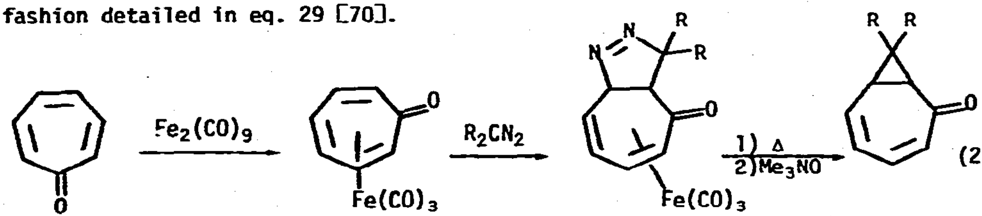
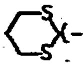
(28)



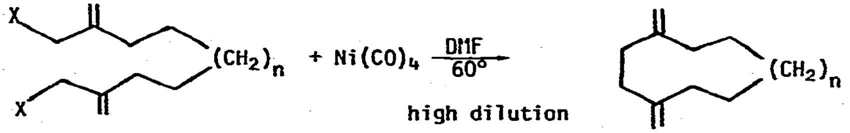
65% 60-90% 90%

(29)

π-Arenechromium tricarbonyl complexes were found to undergo clean nucleophilic aromatic substitution of the benzene ring by a variety of carbanions ($\bar{C}H_2CN$, Me_2CCN, (-), t-Bu^-, Ph^-) to give high yields of the alkylated benzene after removal of the chromium by treatment with iodine.

Grignard reagents and simple enolates failed in this reaction [71]. The enolate chemistry of the π-arene chromium tricarbonyl complexes of acetophenone, phenylacetic ester, ethyl benzene, β-phenylpropionic ester was studied. Alkylation always occurred α to the carbonyl rather than at a benzylic position [72].

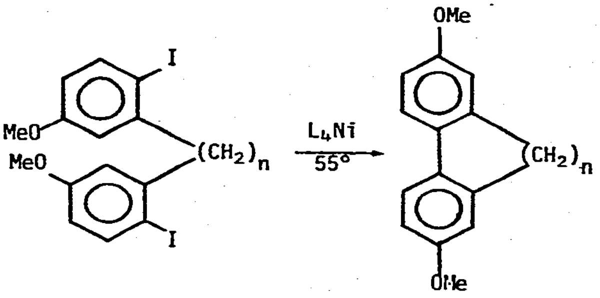
The full experimental details of the synthesis of cembrene, in which a key step was the nickel carbonyl coupling of a <u>bis</u> allylic halide, have been reported [73]. A similar cyclization was used to produce large ring alkanes with exocyclic methylene groups (eq. 30) [74]. Treatment of cuprous iodide with  produced a complex that coupled allylic halides. With unsymmetrical allylic halides, all three possible products were obtained although coupling at the least hindered terminus predominated. This complex was used to convert E,E-farnesyl bromide into squalene in 50% yield [75].

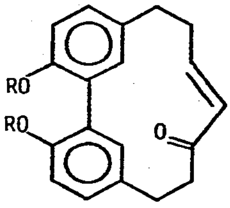


(30)

n = 4	0%
n = 6	37%
n = 8	81%
n =12	40%

Zero valent nickel complexes were used to couple iodoaromatic compounds linked by an alkyl chain (eq. 31) [76] to form biaryls. This route was used to synthesize alnusone (5). Hindered aromatic halides did not couple well. A similar biaryl coupling was promoted by palladium acetate in acetic acid (eq. 32) [77]. A very mild Ullman type coupling of o-iodonitrobenzene

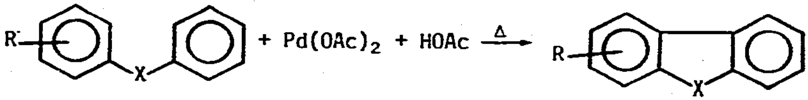




5

(31)

n = 2, 81%; n = 3, 83%; n = 4, 76%; n = 5, 85%; n = 6, 38%; n = 10, 55%



40-70%

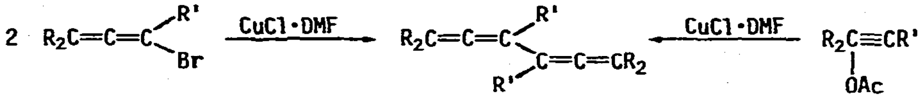
(32)

R = H; X = O, NH, CO, CONH, NMe

X = NH; R = Me, OMe, Cl, Br, NO_2, COOH

to o,o'-dinitrobiphenyl was carried out in aqueous ammonia with $Cu(MeCN)_4^+ClO_4^-$ as the coupling agent. With o-bromonitrobenzene, coupling did not result. Instead the halide was replaced by $^-NH_2$. A variety of other iodoaromatics were unreactive [78]. A very simple and convenient method for the in situ generation of L_4Ni, and subsequent use to couple aromatic and vinyl halides has been developed [79]. In this system L_2NiCl_2 was treated with zinc and triphenylphosphine in DMF to produce the zerovalent nickel complex. The halide was then added and coupling resulted.

Disubstituted acetylenes were converted to tetrasubstituted E,E-1,3-dienes by treatment of the alkyne with BH_2Cl. The resulting vinyl borane was treated with three equivalents of methyl copper, producing the E,E-1,3-diene in 60-100% yield and greater than 99% stereochemical purity [80]. Cuprous chloride DMF was used to couple bromoallenes as well as propargyl acetates to the same bis allene (eq. 33) [81]. Acetylenic thioethers were converted to 1,2,3-cumulated trienes by treatment with dialkylcuprates (eq. 34) [82]. Trimethylsilylenol ethers were coupled to produce 1,4-diketones by Ag_2O in DMSO [83]. Methyl ketones were dimerized by treatment with lithium diisopropylamide followed by cupric chloride to give γ-diketones in 40-90% yields. If two types of enolizable protons were available, mixtures resulted with the less hindered 1,4-diketone predominating. Different methyl ketones could sometimes be cross coupled by using a large excess of one ketone [84].



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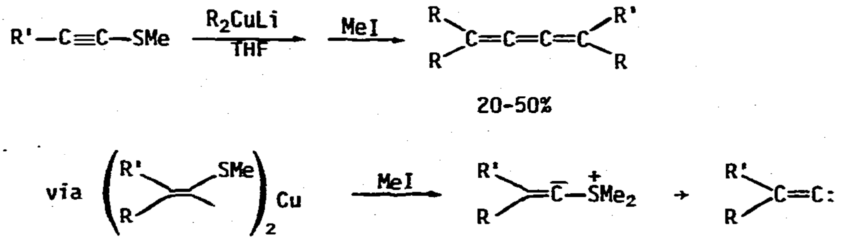
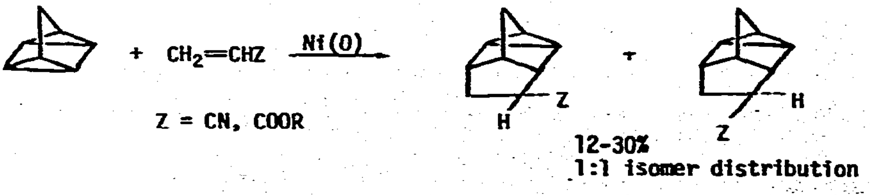


(34)

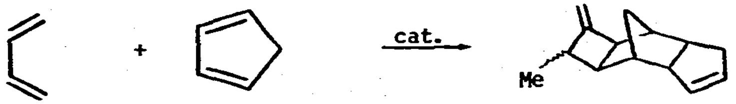
Alcohols were reductively dimerized to hydrocarbons by a titanium reagent prepared by treatment of three equivalents of titanium trichloride with lithium aluminum hydride. The reaction worked well for benzylic and allylic alcohols. It was thought to go via radical intermediates, and allylic alcohols produced a mixture of isomers [85].

Several transition-metal catalyzed condensations and cyclizations of unsaturated substrates have been reported. These are summarized in eq. 35-40.



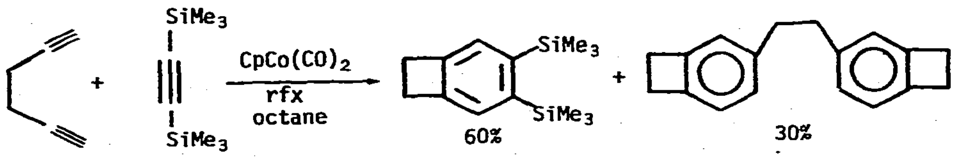
12-30%
1:1 isomer distribution

(35)
[86]

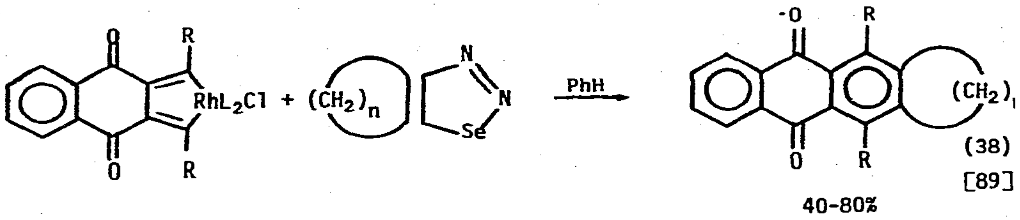


(36)
[87]

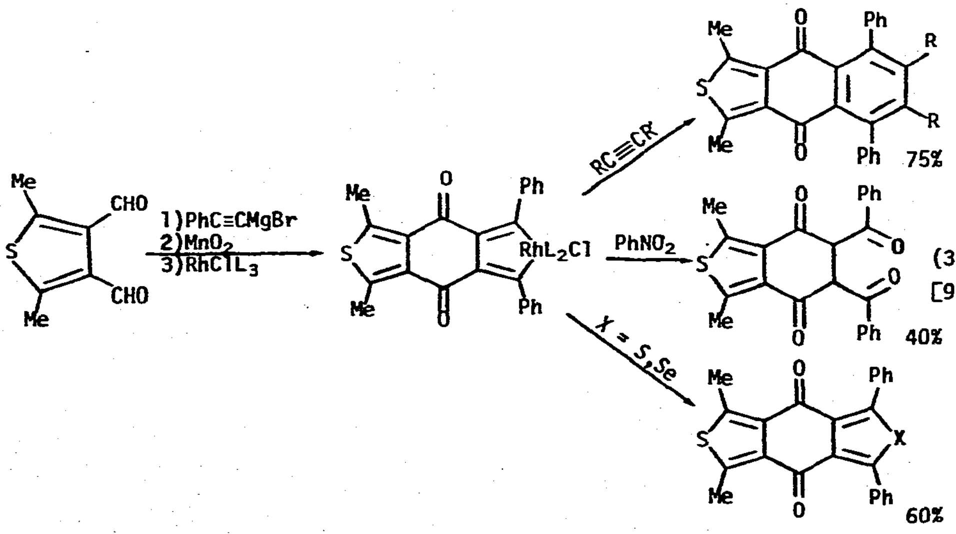
Cat = $[(EtO)_3P]_4Ni \cdot CF_3COOH$
$(\pi\text{-crotyl})Ni[P(OEt)_3]_2^+PF_6^-$
$L_2NiBr_2 + NaBH_4$



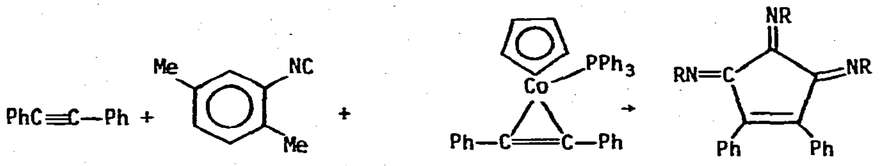
(37)
[88]



(38)
[89]



(39)
[90]

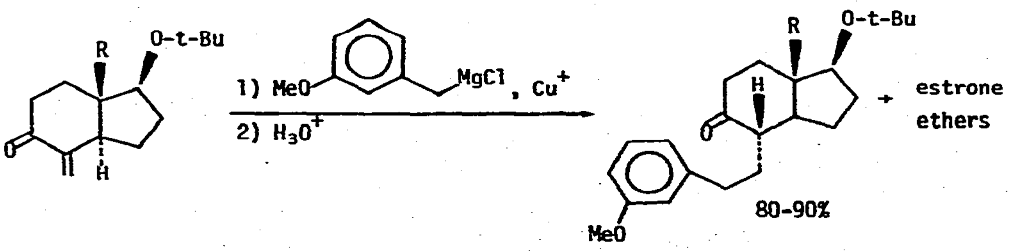


(40)
[91]

Bis (acetylacetone) nickel(II) reacted with benzyl chloride, methyl chloroacetate and chloromethylmethyl ether in DMF to produce the C-3 monoalkylated acetylacetone. No dialkylation or O-alkylation was detected [92]. A method for the specific alkylation of purine bases via their cobaloxime complexes has recently been developed. The purine base was treated with $Bu_3PCo(DMGH)_2Cl$ and silver acetate in 0.1N NaOH to produce the cobalt complex of the purine. Upon treatment with methyl iodide or benzyl chloride the alkylated purine was produced in 40-70% yield. By this method 7-methyladenine, 7-methyl and 7-benzylxanthine, and 7-methyl and 7-benzylhypoxanthine were made [93]. Finally, alkylation and arylation of unsaturated compounds using complexes of transition metals has been reviewed [94].

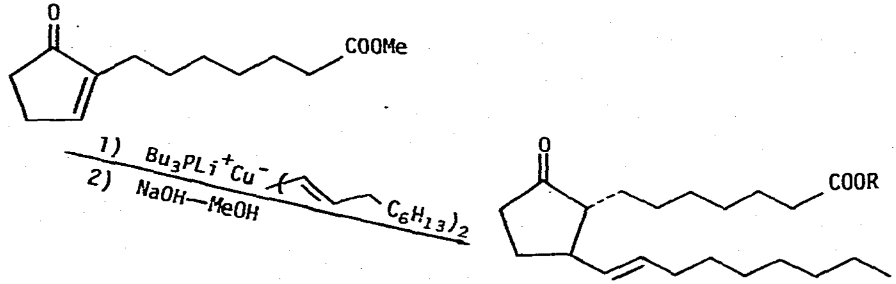
B. Conjugate Addition

Organocuprate complexes continue to be the reagents of choice for 1,4 alkylation of conjugated enones. Copper salts were used to catalyze the 1,4 addition of vinylmagnesium bromide to 16-en-20-oxo- and 19-Nor-4-en-3-oxo-steroids to produce 16α-vinyl-20-oxo- or 19-Nor-5-β-vinyl-3-oxosteroids [95]. Similarly estrone ethers were synthesized using a cuprous salt catalyzed conjugate addition of benzylmagnesium halides to conjugated enones (eq. 41) [96]. Steroids containing conjugated enones have been 1,4-methylated using

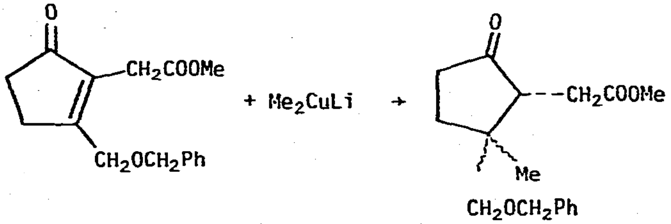


(4

lithium dimethylcuprate [97]. Organocuprates continue to find extensive application in the synthetic approaches to prostaglandins (eq. 42) [98,99] (eq. 43) [100]. Nickel acetylacetonate was used to catalyze the 1,4 addition of trimethyl aluminum to a variety of conjugated ketones. Conjugate addition was favored by β-substitution on the enone. Iron and cobalt complexes worked poorly, leading to messy mixtures [101]. The nickel complex was also used to effect conjugate methylation of 3-oxo-Δ4-steroids [102] and to ring open cyclopropyl ketones in moderate yield [103].



(42)

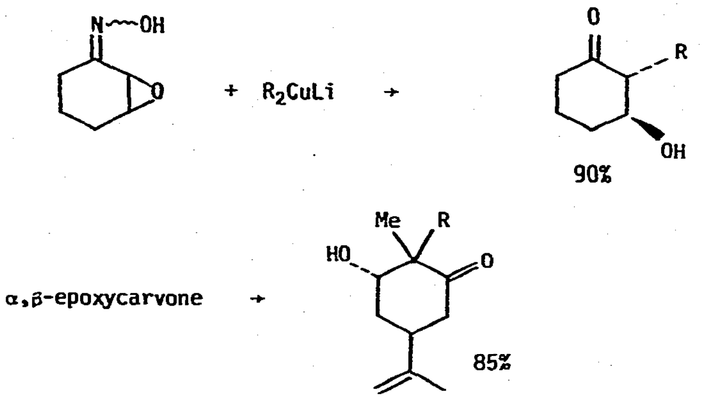


11-deoxy-
12-methyl-
prostaglandi

(43)

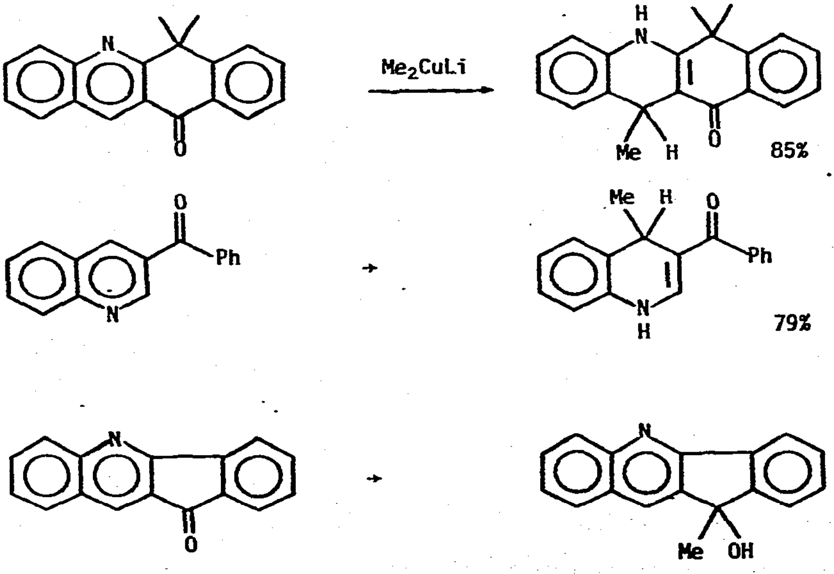
Lithium dialkylcuprates also 1,4 alkylated α,β-unsaturated aryl nitro compounds (β-nitrostyrenes). The yield depended both on the alkyl group added and the substitution on the aromatic ring [104]. A procedure for the α-alkylation of α,β-epoxy ketones by alkylcuprates via the epoxyoxime has been developed (eq. 44) [105].

β-Bromoenones, prepared from the reaction of Ph_3PBr_2 and 1,3-diketones, reacted with one equivalent of $[RCuSPh]^-Li^+$ to cleanly β-alkylate. Excess copper reagent led to conjugate addition as well, resulting in β,β-



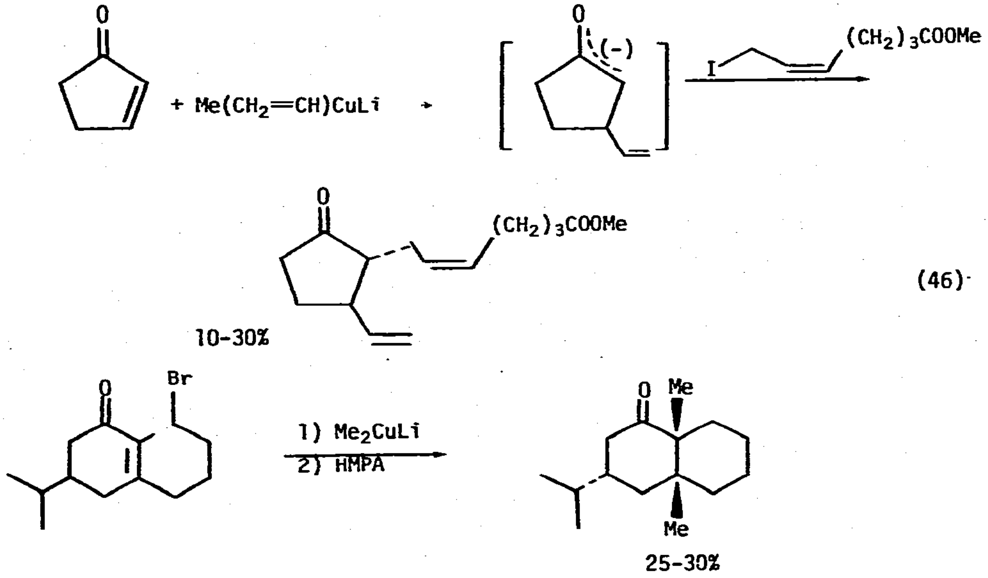
(44)

dialkylation [106]. Lithium dimethylcuprate underwent unusual reactions with ketoquinolines (eq. 45) [107]. The proposed electron transfer mechanism for conjugate addition of dialkyl cuprates was supported by the observation that 4,4-dimethoxycyclohexa-2,5-dien-1-one reacted with lithium dimethylcuprate to produce only p-methoxyphenol, a net reduction [108].



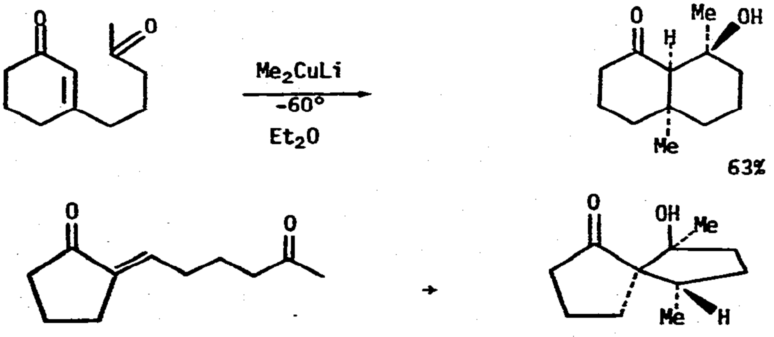
(45)

Several groups have reported on the reactions of copper enolates, generated by 1,4 addition of dialkylcuprates to conjugated enones, with electrophiles such as RI, Me_3SiX, and RCHO. Alkylation of a copper enolate with an allylic iodide was used to synthesize a deoxyprostaglandin E_2 model, while d,l-valerane was prepared by an intramolecular alkylation (eq. 46) [109]. Copper enolates generated in this manner were also acylated with acid halides [110] and aldehydes [111]. An extremely interesting intramolecular

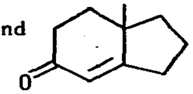


(46)

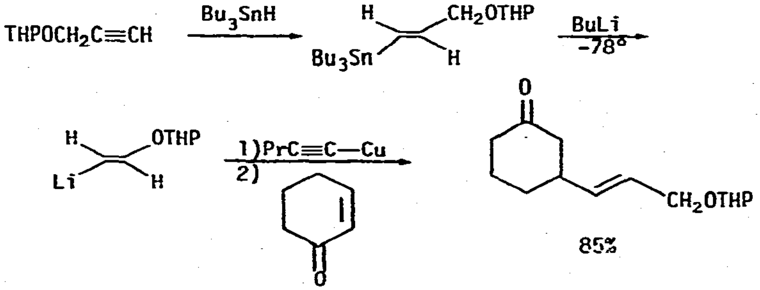
alkylation with a keto side chain has also been carried out (eq. 47) [112].



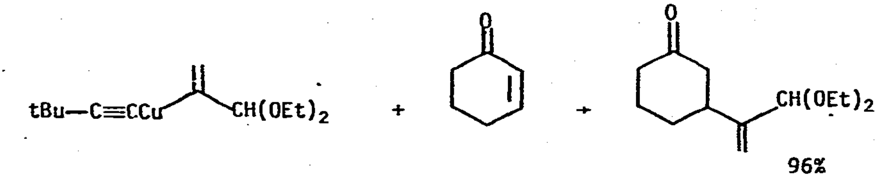
(47)

Several functionalized diorganocuprates have been developed to allow the introduction of functional groups. Substituted cyclohexenones were treated with 1-methoxyvinyllithium and $CuI \cdot Me_2S$ to produce 3-acetylcyclohexanones after hydrolysis. This reagent reacted well with benzyl bromide, but secondary alkyl halides were unreactive [112]. Similarly 1-ethoxyvinyl cuprate was studied [113]. This reagent added 1,2 to cyclopentene aldehyde, and failed to react with 2,3,6-trimethylcyclohex-2-ene-1-one, 1-bromooctane, and 

A vinyl cuprate from a masked allylic alcohol has been developed (eq. 48) [114] as has one from a blocked acrylaldehyde (eq. 49) [115].

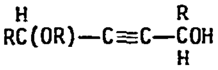


(48)

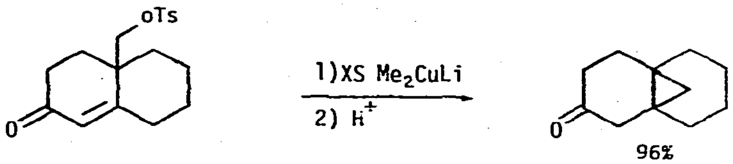


(49)

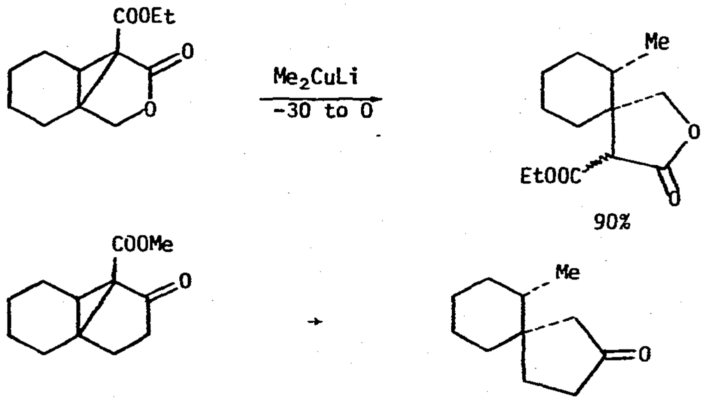
Polymeric organocopper reagents were found to react with conjugated enones in a highly stereoselective fashion and in high yield to alkylate at the β position with E stereochemistry. This reaction was used in the synthesis of Juvenile Hormone analogs [116]. Alkynyl sulfones reacted with "$RCu \cdot 2CuBr$" in a similar fashion to give vinyl sulfones [117]. Propargyl alcohols reacted with alkyl, phenyl, and allyl Grignards in the presence of cuprous iodide to produce allylic alcohols alkylated at the internal carbon of the olefin [118].

Compounds of the type  $\overset{H}{RC}(OR)\text{—}C\equiv C\text{—}\overset{R}{\underset{H}{C}}OH$ reacted with the same reagent to to produce allenes by alkylation of the OH side of the alkyne with displacement of OR [119]. Similarly the acetal of acrylaldehyde (acrolein) reacted with Grignard reagents and cuprous bromide to produce the enol ether $RCH_2CH{=}CHOEt$ via an apparent S_N2' reaction [120].

Excess lithium dimethylcuprate reacted with the decalenone in eq. 50 to produce the bridgehead cyclopropyl compound. The reaction was claimed to proceed by a $2e^-$ transfer to the conjugated enone followed by electrophilic attack at the β-carbon of the copper complexed dianion [121].

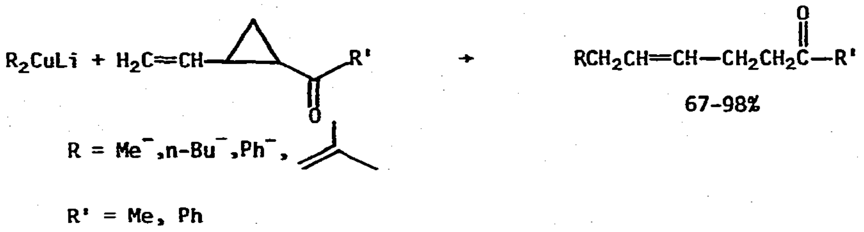


(50)



(51)

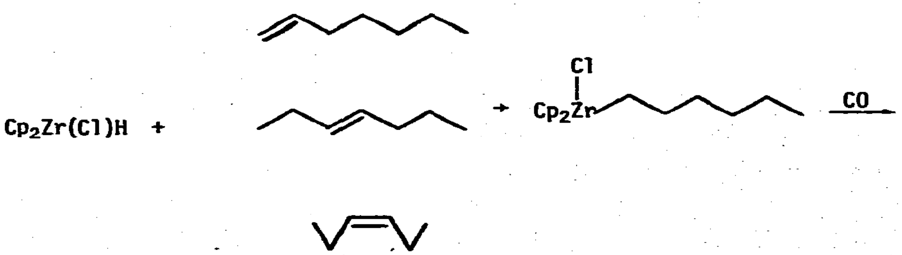
In contrast the cyclopropylmalonates in eq. 51 reacted to produce spirolactones [122]. The γ,δ-unsaturated-α,β-cyclopropyl ketones reacted with lithium dialkylcuprates at the δ position to produce γ,δ-unsaturated ketones (eq. 52) [123]. Butadiene reacted with RCuMgBr to alkylate at a terminal carbon and produce the allylcopper species which was then alkylated at the 4 position by allyl bromide and chloromethylbenzyl ether, and carboxylated at the 2 position [124]. A similar 1,4 addition of a variety of allyl Grignards to isoprene was catalyzed by titanium (IV). This procedure was used to synthesize lanceol, damascone, and lavandurol [125].

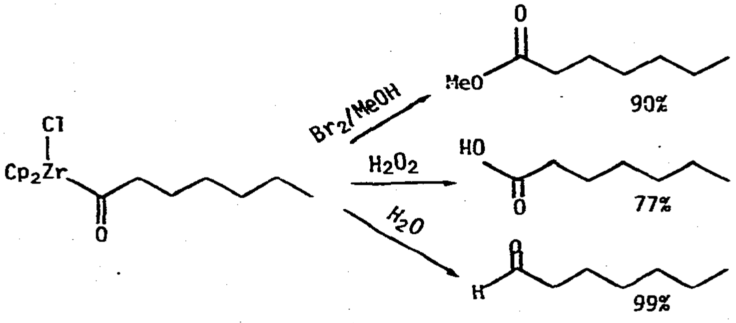


(52)

C. Acylation

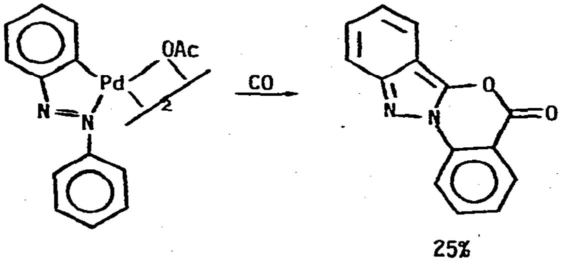
1-Pentene was converted to n-hexanal in 95% yield under oxo conditions (H_2/CO) with $PtH(SnCl_3)(CO)(PPh_3)_2$ as a catalyst. The use of a mixture of stannous chloride and $PtH(Cl)(PPh_3)_2$ gave similar results [126]. Hydrozirconium complexes which were converted in high yield to the corresponding acyl complex by treatment with carbon monoxide. These acyl complexes could be converted to aldehydes, acids or esters in good yield (eq. 53) [127]. Phenyl, benzyl, and phenacyl halides were acylated to esters with 50-90% conversion by treatment with CO (200 psi) a base such as triethyl amine or sodium acetate, an alcohol, and $PdCl_2(PPh_3)_2$ as a catalyst [128]. Similar results were obtained with $Pd(CO)(PPh_3)_3$ and $Pd_3(CO)_3(PPh_3)_3$ [129]. Palladium acetate was used to prepare ortho-palladated complexes of azobenzenes, Schiffs bases, benzaldazines, acetophenone dimethylhydrazones and tertiary benzyl amines.





(53)

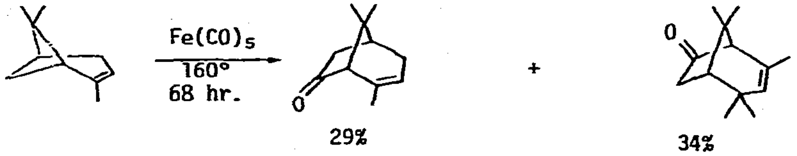
Treatment of these with carbon monoxide produced a variety of unusual heterocycles (eq. 54) [130].



(54)

Ethyl ketones were prepared by treatment of a variety of primary halides with $Fe(CO)_4^{=}$ and one atmosphere of ethylene, replacing the halide by the C_2H_5CO group. Ethylene was the only olefin that worked [131]. Enamines reacted with iodobenzene and nickel carbonyl in benzene or DMF to introduce the benzoyl group at the enamine carbon, producing 1,3 diketones upon hydrolysis of the enamine [132]. Vinyl mercuric halides were carbonylated to α,β-unsaturated esters by treatment with carbon monoxide (1 atm) and lithium chloropalladate in alcohol solvent. The reaction proceeded in high yield and could be made catalytic in palladium [133]. Transition metal catalysts continued to be used to carbonylate strained ring compounds as in eq. 55 [134] and eq. 56 [135]. Finally, a review entitled "Technische

Reactionen von CO mit Metallcarbonylen als Katalysatoren" has appeared [136].



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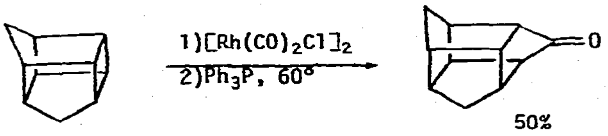
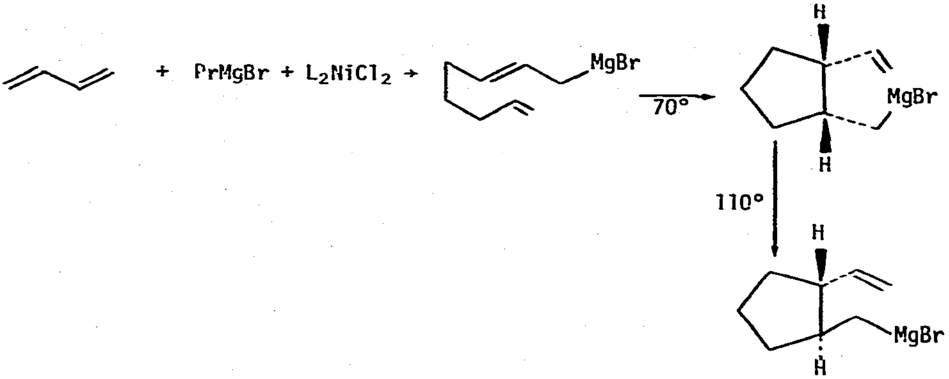


(56)

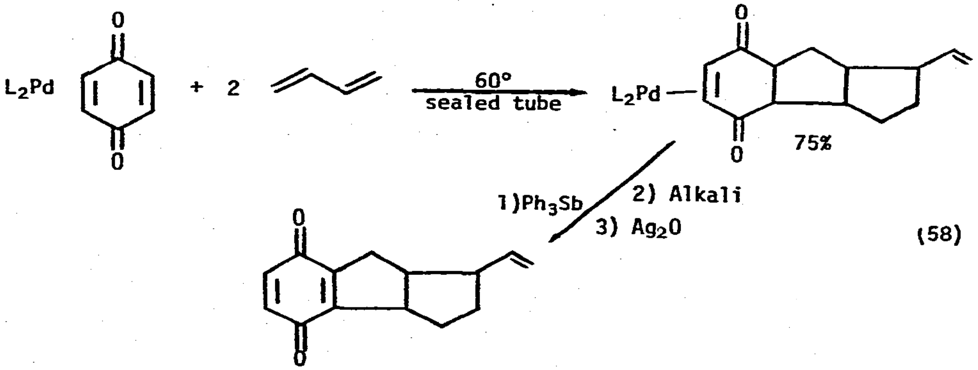
D. Oligomerization

Catalytic systems for butadiene polymerization continued to be intensively studied. The dimerization of butadiene to 2,4,6-octatriene was catalyzed by $(Ph_3P)_3P$ at 110° at 9Kg/cm^2 pressure in a carbon dioxide atmosphere. Without CO_2 the dimerization proceeded very slowly [137]. A mixture of tetra-benzyltitanium and aluminum trichloride catalyzed the room temperature atmospheric pressure conversion of butadiene to 1,4-*cis* or 1,4-*trans*-polybutadiene [138]. The complex $NiBr_2(PPh_3)_2$ was attached to a polystyrene polymer *via* polymer-bound triphenylphosphine groups. Treatment of this solid supported catalyst with sodium borohydride produced a catalyst which converted butadiene to 1,3,6-octatriene in greater than 99% yield [139]. The same polymer-bound phosphine when treated with nickel carbonyl produced polymer-bound $Ni(CO)_2(PPh_3)_2$. Treatment of this catalyst with butadiene and trioctylphosphite at 115° in benzene produced 1,5-cyclooctadiene in 92% yield. When run under an atmosphere of carbon monoxide, vinylcyclohex-3-ene resulted in 98% yield [140]. In a similar fashion polymer-bound $Rh(H)(CO)(PPh_3)_2$ was used to hydroformylate olefins, and $Ru(Cl_2)(CO)_2(PPh_3)$ was used to reduce olefins [141]. Finally, a mixed polymer-supported catalyst system containing both $Ni(CO)_2(PPh_3)_2$ and $RhCl(PPh_3)_3$ was used to perform a sequential cyclooligomerization of butadiene followed by reduction to cycloalkanes, in a one-pot procedure [142]. Treatment of butadiene with n-propylmagnesium bromide and $Ni(Cl)_2(PPh_3)_2$ produced 2,7-octadienylmagnesium bromide which, upon warming, ring closed to a cyclopentane which isomerized upon further heating (eq. 57) [143]. Metal arenes, produced from metal vapors and arenes, were used as catalysts for butadiene polymerization [144].

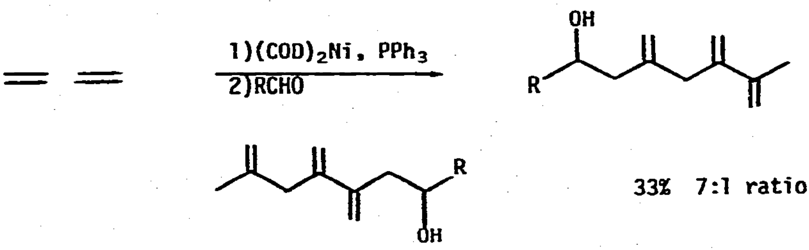


(57)

Several new cooligomerizations of butadiene with unsaturated species have been developed. Treatment of butadiene with bis-triphenylphosphine palladium (benzoquinone) produced polycyclic material (eq. 58). The reaction worked with naphthoquinone, acetylbenzoquinone, and carbomethoxybenzoquinone



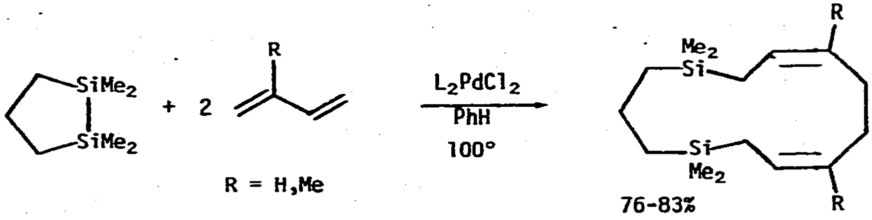
(58)



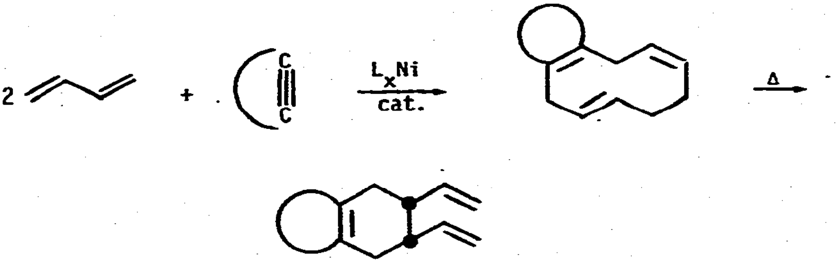
(59)

33% 7:1 ratio

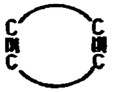
[145]. Allene reacted with bis (cyclooctadiene) nickel, triphenylphosphine and an aldehyde to produce a mixture of triene alcohols (eq. 59) [146]. Both butadiene and isoprene reacted with five-membered cyclic disilanes and Pd(PPh$_3$)$_2$Cl$_2$ catalyst at 100° to give a thirteen-membered cyclic disilane (eq. 60). Larger ring disilanes and linear disilanes were not useful in this reaction [147]. Butadiene co-condensed with cyclic alkynes (eq. 61) [148] and norbornene (eq. 62) [149] to produce unusual cyclic materials.

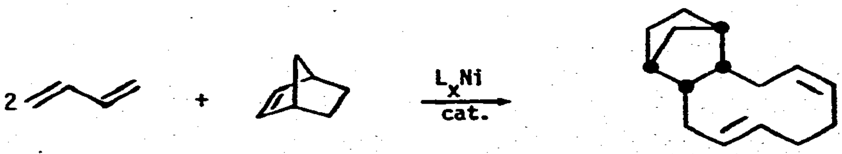


(60)



(61)

 and HC≡CC≡CH were also studied.

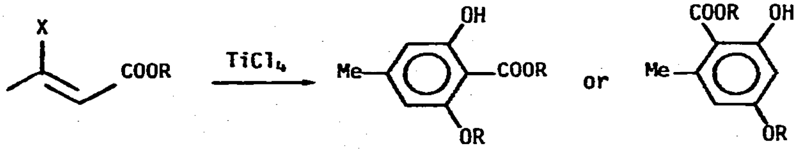


(62)

92%

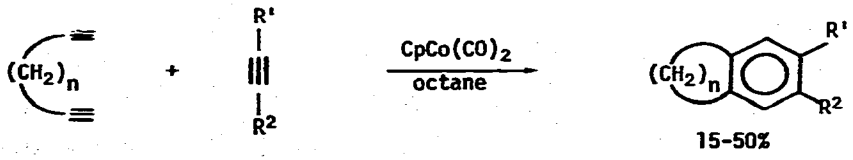
A variety of L's were studied.

Rhodium trichloride supported on silica gel was used as a catalyst for ethylene dimerization. This material was 10^4 more reactive than homogeneous $RhCl_3$, more reactive than rhodium on Y-Zeolite, and its activity was enhanced by HCl [150]. An active catalyst for ethylene polymerization was prepared by treating a Cp_2TiCl_2—Me_2AlCl mixture with 0.2 equivalents of water. The system was inactive in the absence of water [151]. The selective dimerization of ethylene was also catalyzed by $CoCl(PPh_3)_3$ and $BF_3 \cdot Et_2O$ in o-chlorotoluene as solvent [152]. A catalyst for the dimerization of propene to linear hexenes was prepared from ethylaluminum chloride, trialkylphosphine, and <u>bis</u> (acetylacetonato) palladium (II) [153]. The codimerization of styrene with α-olefins was catalyzed by $Ni(Ar)(Br)(PPh_3)_2$ [154]. Titanium tetrachloride was used to cyclotrimerize acrylic esters to orsellinic acids (eq. 63) [155]. Alkynes were codimerized with α,ω-bis acetylenes to produce aromatic systems (eq. 64) [156]. Acetylene and allyl chloride reacted to produce 1-chloro-1,3,6-heptatriene, resulting from two moles of acetylene and one of allyl chloride, with a palladium acetate-lithium chloride catalyst [157]. Ruthenium (0) catalysts were used to promote the reaction of ethyl iodide and ethylene to produce mixtures of butyl iodide, hexyl iodide, octyl iodide, decyl iodide and dodoecyl iodide. The product distribution depended on the catalyst and reaction conditions used [158].



(63)

X = OMe, OEt, O-i-Pr, O-<u>n</u>-Bu, O-i-Bu



(64)

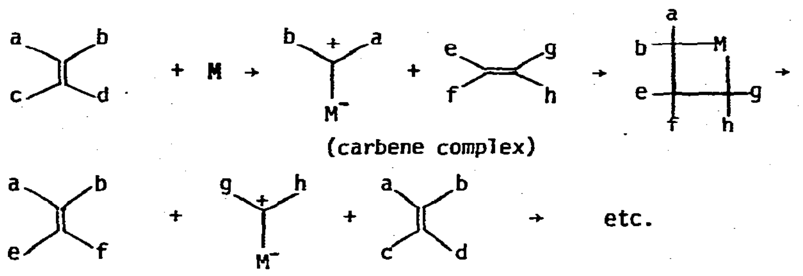
n = 3,4

R's = COOMe, Ph, H, Me_3Si, n-C_6H_{13}-

E. Rearrangements

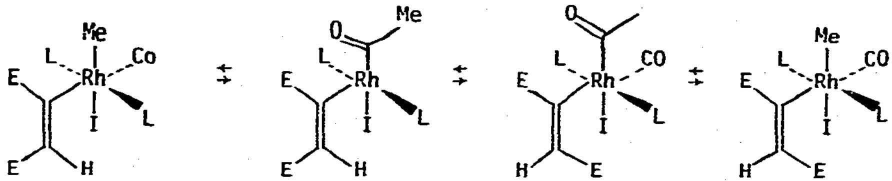
A rapid growth of interest in the olefin metathesis reaction, as evidenced by the large number of papers and reviews on this subject, took place. Many new catalyst systems for this reaction were developed. A 1:3 mixture of $W(CO)_5(CH_3CN)$ and ethylaluminum chloride catalytically converted 2-pentene to 2-butene and 3-hexene [159]. A molybdenum catalyst prepared from $MoN_2(PPh_3)_2 \cdot PhMe$ or $Mo(CO)(PPh_3)_2$ and aluminum trichloride was also an effective catalyst for olefin metathesis [160]. An 8:1 mixture ethylaluminum chloride and chlororhenium pentacarbonyl also was a catalyst for metathesis of terminal as well as internal olefins. The reactions with this catalyst proceeded in high conversion and yield, and the catalyst was stable and could be used for several days. Simple irradiation of tungsten hexacarbonyl in carbon tetrachloride produced an efficient catalyst for the metathesis of cis-2-heptene, 2-pentene, 4-nonene, and 4-methylpent-2-ene [162]. An extensive study of the metathesis of 1-hexene and of cyclooctene has been reported [163]. The best catalyst appeared to be WCl_6, $\cdot EtOH/EtAlCl_2$. The reaction of 1-vinylcyclohex-2-ene and ethylene to give 1-(2-butenyl) cyclohexene and 1-methylenecyclohex-2-ene was catalyzed by a mixture of $NiCl_2(Bu_3P)_2$, Et_3Al and Et_2AlBr [164]. The conversion of 3-phenyl-1-propenes to 1,4-diphenyl-2-butenes via a metathesis reaction was catalyzed by a mixture of $Mo(NO)_2Cl_2(PPh_3)_2$, chlorobenzene, and ethylaluminum chloride. The aromatic ring could carry Me, t-Bu, Cl and F as substituents, but OMe substituents stopped the reaction [165]. A catalyst of moderate activity for the metathesis of 2-pentene was prepared by treating polystyrene-bound $Mo(PPh_3)(CO)_5$ with ethylaluminum chloride and oxygen [166]. The mechanism displayed in eq. 65 has been advanced for olefin metathesis [167]. Two reviews on the subject of olefin metathesis have appeared [168,169].

It was found that the loss of stereochemistry observed in nickel-catalyzed coupling of vinyl Grignard reagents is due to nickel salts catalyzing the cis-trans isomerization of 1-alkenyl Grignard reagents [170]. The rhodium complex



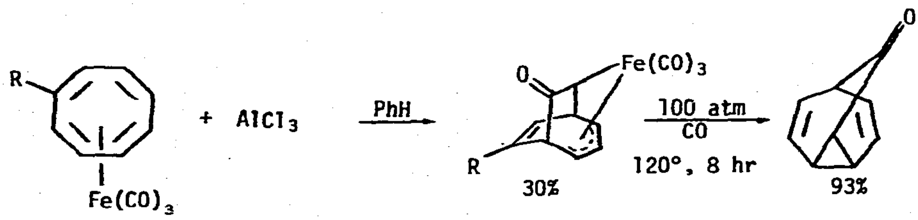
(65)

$[RhCl(PF_3)_2]_2$ catalyzed the isomerization of 1-decene to a 1:3 mixture of cis- and trans-2-decene [171]. The rate of cis-trans isomerization in vinylrhodium (III) complexes increased as the electron donating ability of the phosphine ligands (L) on the complex increased (eq. 66) [172]. The cyclooctatetraene complex of iron reacted with aluminum chloride followed by carbon monoxide to produce the unsaturated polycyclic ketone in eq. 67 [173]. The preparative aspects of silver ion-catalyzed rearrangements of polycyclic systems have been reviewed [174], as has transition metal catalysis of pericyclic reactions [175], and metal induced valence isomerization of bullvalene and related compounds [176].

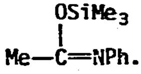


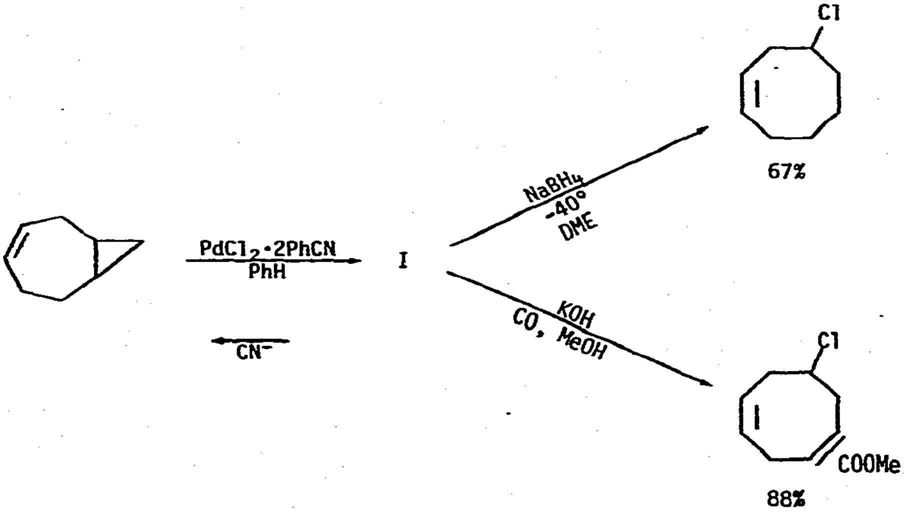
(66)

E = COOEt



(67)

Allyl phenylethers were cleanly rearranged to o-allylphenols by a mixture of titanium tetrachloride and  $Me{-}\overset{OSiMe_3}{\overset{|}{C}}{=}NPh$. The reaction proceeded in high yield at 25° [177]. Palladium chloride ring opened the fused cyclopropane system in eq. 68 to give a complex which was converted to a variety of substituted cyclooctenes [178]. A useful ring expansion based on a cuprous ion assisted migration has been developed (eq. 69) [179]. Finally, rhodium (I) catalysis in olefin photoreactions has been examined [180].



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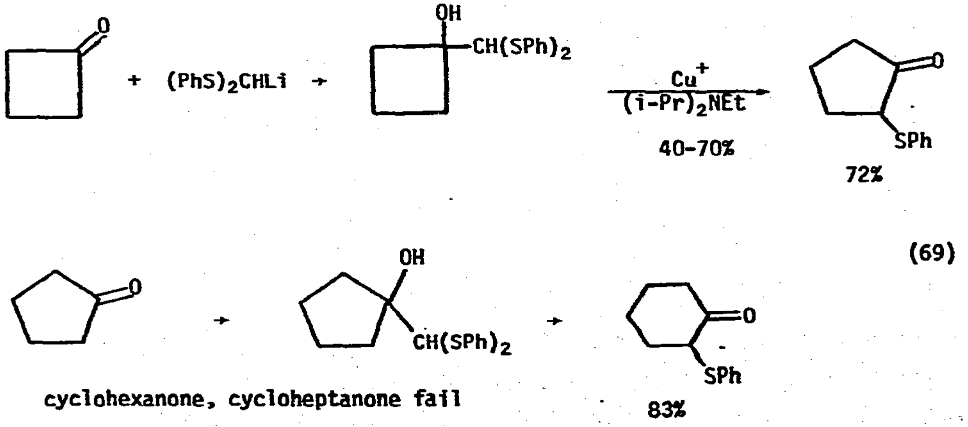
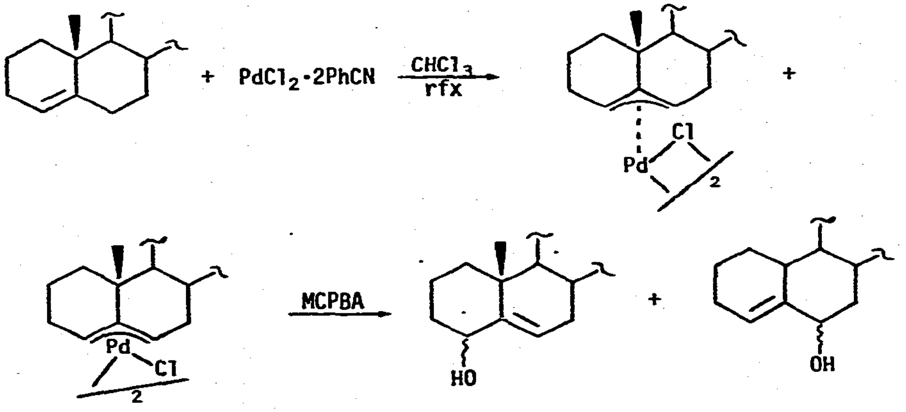


(69)

III. OXIDATION

Two new chromium reagents for the oxidation of alcohols to aldehydes or ketones have been developed. Treatment of a mixture of two equivalents of t-butanol and three equivalents of pyridine with methylene chloride followed by one equivalent of chromyl chloride produced $(t\text{-}BuO)_2Cr(O)_2$. This reagent was superior to Collins' reagent ($CrO_3\cdot$pyridine) in several respects. Only 1.1 eq. was required for complete oxidation. The reagent worked well with 1-decanol, citronellol, geraniol, benzyl alcohol, cinnamyl alcohol and pinocarveol, although allylic alcohol oxidations were accompanied by cis-trans isomerization [181]. Treatment of chromium trioxide in 6M HCl with pyridine led to $Py\cdot CrO_3Cl$. Only 1.5 equivalents of this reagent was required to oxidize primary or secondary alcohols to aldehydes or ketones in good yield. The reagent was slightly acidic, but could be buffered with sodium acetate so that acid labile THP protecting groups survived [182]. The ruthenium complex $Ru(O_2CCF_3)_2(CO)(PPh)_3$ catalyzed the oxidation of alcohols to aldehydes or ketones in boiling trifluoroacetic acid. Tertiary alcohols were inert [183]. Aromatic aldehydes and benzyl alcohols were oxidized to the corresponding carboxylic acids in 70-90% yield by sodium hypochlorite in aqueous sodium hydroxide with $NiCl_2\cdot 6H_2O$ or $CoCl_2\cdot 6H_2O$ as a catalyst [184]. Nickel peroxide oxidations of organic compounds have been reviewed [185].

A new osmium reagent for the oxamination of olefins has been developed. Treatment of osmium tetroxide with t-butylamine or 1-adamantyl amine produced $Os(O)_3(=NR)$ which reacted with olefins to produce α-amino alcohols in 30-90% yield. The reaction involved a cis addition, with the C—N bond formed exclusively at the least substituted carbon. Monosubstituted olefins reacted faster than di- or trisubstituted olefins [186]. Treatment of terminal olefins with palladium chloride and a secondary amine, followed by oxidation of the resulting complex with lead tetraacetate produced α-aminoacetates in 70-84% yield. In this case, the C—N bond formed at the most substituted carbon [187]. Cyclohexene-3-hydroperoxide was converted to *cis*-2,3-epoxycyclohexanol by VO(AcAc)$_2$ catalyst in benzene at 40° [188]. 3,7-Dimethylocta-1,6-diene was oxidized to 3,7-dimethyloct-6-ene-2-one in 80% yield by oxygen using a catalyst composed of rhodium trichloride trihydrate and ferric chloride. In other cases some isomerization of the unoxidized double bond was noted [189]. Oxidation of the π-allylpalladium complex of steroidal olefins with *meta*chloroperbenzoic acid was a regio- and stereoselective reaction which produced moderate to high yields of the allylic alcohol in which the -OH appeared on the same face as had the Pd in the starting complex (eq. 70) [190]. Titanium tetrachloride catalyzed oxidation of a steroidal diene by triplet oxygen in a dark reaction (eq. 71) [191]. The oxidation of olefins in the presence of transition-metal complexes, including the uses of group VIII metals to produce α,β-unsaturated alcohols and ketones, Mo compounds to produce epoxides, and V compounds to produce epoxy alcohols has been reviewed [192]. The mechanisms of olefin oxidation by MnO_4^-, RuO_4, OsO_4, SeO_2 and H_2CrO_4 have also been reviewed [193].



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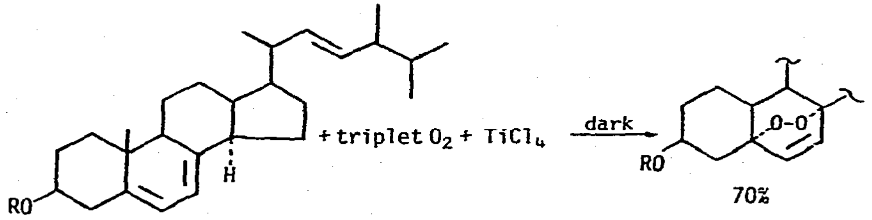
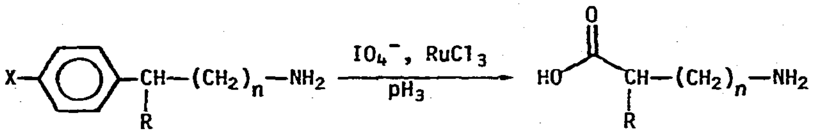


(71)

N-Acetylpyrroles were oxidized to the corresponding N-acetylpyrrolidines by ruthenium tetroxide. The oxidation also worked with piperidines [194]. Cycloalkanes were oxidized by sodium hypochlorite with a ruthenium tetroxide catalyst to produce a mixture of the cyclic ketone and the open chain diacid by ring cleavage. Cyclopentane was converted to cyclopentanone (18%) and $HOOC—(CH_2)_3—COOH$ (63%), cyclohexane to cyclohexanone (26%) and $HOOC(CH_2)_4COOH$ (58%), cycloheptane to cycloheptanone (68%) and $HOOC—(CH_2)_5—COOH$ (20%) and cyclooctane to cyclooctanone (55%) and $HOOC(CH_2)_6COOH$ (23%) [195]. Cyclohexanone was cleaved to adipic acid by oxygen and carbon monoxide using $Rh_6(CO)_{16}$ as a catalyst [196]. Ruthenium trichloride was used to catalyze the periodate cleavage of amino-aromatic compounds to amino acids (eq. 72) [197]. The



(72)

X = R = H, n = o 66% glycine

X = H, R = Me, n = o 10% alanine

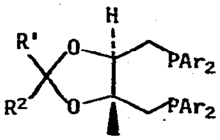
X = OMe, R = Me, n = o 50% alanine

Tyrosine → Aspartic acid 60%

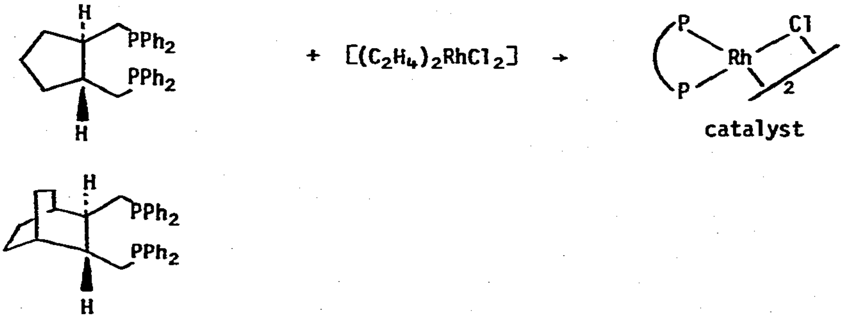
cleavage of α-hydroxyketones to carboxylic acids by oxygen was catalyzed by cuprous chloride in pyridine [198]. The oxidation of organic compounds by hydroperoxides catalyzed by metals has been reviewed [199].

IV. REDUCTION

The use of transition metals coordinated to chiral ligands as hydrogenation catalysts to induce chirality in the reduced substrate reached a high degree of development this year. The complex Rh[(+)diop]Cl was used to catalyze the H_2 reduction of enamides to α-amino acids in 90-100% yield and 45-85% enantiomeric excess. The same catalyst was used for the hydrosilation of imines [200]. A variety of other chiral phosphine ligands of the (+)diop type were prepared and studied for use in catalysts for the production of chiral α-amino acids. The results are summarized in eq. 73 [201]. A similar catalyst in which the phosphorous center was chiral gave even higher optical induction in the reduction process (eq. 74) [202]. Use of $[Ru_2X_4\ (+)\text{-}(diop)_3]$ as catalyst for reduction of similar substrates produced only 60% optical yields [203]. Use of the chiral ligand from [1S, 2S]-cyclohexanediol and Ph_2PCl with

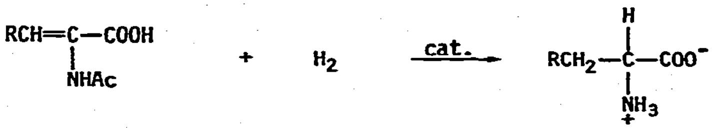


(diop)



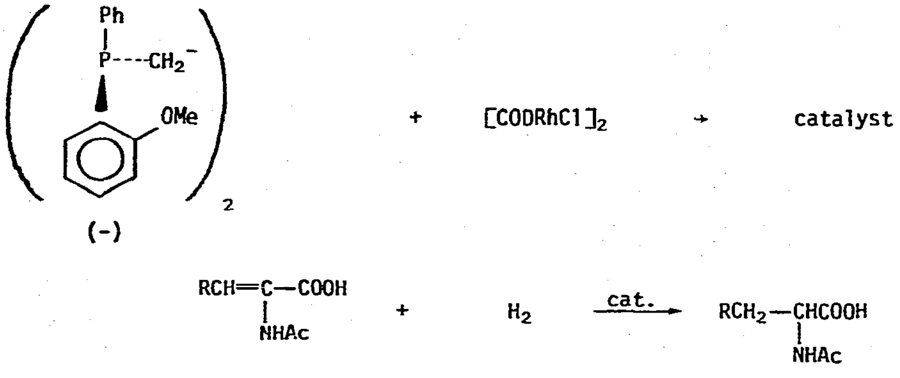
catalyst

(73)



$$\mathrm{RCH{=}\underset{\displaystyle NHAc}{C}{-}COOH} + H_2 \xrightarrow{\text{cat.}} \mathrm{RCH_2{-}\overset{\displaystyle H}{\underset{\displaystyle \overset{+}{N}H_3}{C}}{-}COO^-}$$

100% yield
88% optical yield



(74)

$$\mathrm{RCH{=}C(NHAc){-}COOH} + \mathrm{H_2} \xrightarrow{\text{cat.}} \mathrm{RCH_2{-}CH(NHAc)COOH}$$

L amino acid
89-95% ee

[CODRhCl]$_2$ produced a catalyst that reduced enamides to N-acyl amino acids with about 80% optical yield. However olefins were reduced with low (15-30%) optical yields, and hydroformylation reactions proceeded in only 0.4 to 2.6% optical yield [204]. Rhodium-chiral phosphine catalysts gave similarly poor optical yields in the reduction of ketones and imines [205], as did ruthenium catalysts [206].

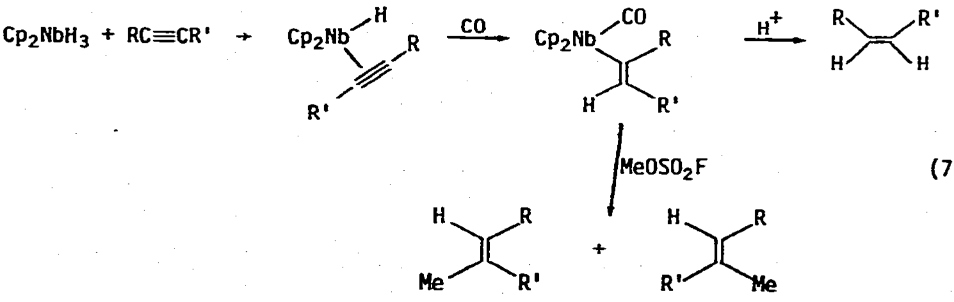
The use of solid-phase supported hydrogenation catalysts has been the subjec of considerable study. The catalytic hydrogenation of 1-hexene by rhodium (II) complexes in the intracrystal space of a swelling layer lattice silicate was found to proceed at 1/7 the rate of homogeneous rhodium (II) [207]. The selective hydrogenation of olefins and ketones over a polymer-bound catalyst prepared from polystyrene-bound phosphine and (norbornadiene) Rh (acetylacetonate) has been reported [208]. Polymer-bound bis (cyclopentadienyl) titanium dichloride was prepared. It did not reduce molecular nitrogen, but was 20-150 times as active a catalyst for the reduction of olefins as was free complex [209]. Functionalized soluble polystyrenes containing phosphine groups were coordinated to a variety of rhodium (I) complexes as well as PdCl$_2$ and PtCl$_2$, and the catalytic activity of these systems was studied. The catalysts could be separated by membrane filtration or precipitation and could be reused [210]. Rhodium trichloride was attached to a styrene-divinylbenzene copolymer containing iminoacetate groups, and was used to catalyze the reduction of olefins. It was selective for olefins not reacting with carbonyls or aromatics. Sterically-hindered olefins reduced much more slowly than unhindered ones [211].

The rate of hydrogenation of cyclohexene with $RhCl(PPh_3)_3$ as catalyst was studied with added Lewis acids such as BF_3, $AlCl_3$, $AlBr_3$, and $Al(i\text{-}Bu)_3$. Triisobutylaluminum increased the rate significantly by forming a rhodium hydride species, while the other additives had little effect [212]. Under ultraviolet irradiation the rate of homogeneous catalytic reduction of cyclooctene with $RhCl(PPh_3)_3$ increased by 2.5. After one hour irradiation, reduction continued in the dark at the same rate [213]. 1-Octene was isomerized to a 1:1 mixture of cis and trans 2-octene by exposure to H_2 and a variety of π-allylcobalt-$(PF_3)_2PPh_3$ complexes. Hydrogen was required, added triphenylphosphine retarded the rate, and no reduction was observed [214].

An improved preparation of $RuCl_2[(p\text{-}OMePh)_3P]_3$ has been reported to give material sixteen times more reactive for the reduction of 1,4-androstadiene-3,17-dione and 4-androsten-3,17-dione [215]. The complex $[(cyclooctene)_2RhCl]_2$ was found to be an effective homogeneous hydrogenation catalyst for unsaturated carboxylic acids in the presence of excess Cl^- or diethylsulfide. The results with this rhodium (I) catalyst paralleled the results using rhodium (III) complexes [216]. Chiral rhodium complexes were used to catalyze the hydrosilation of β-methylbenzalacetones or chalcones. After hydrolysis the saturated ketones were obtained in 72-94% yield and 1-15% optical yield [217]. Polymer bound (1% crosslinked polystyrene) (arene) $Cr(CO)_3$ was used as a catalyst to reduce α,β,γ,δ-unsaturated esters to cis-β,γ-unsaturated esters, using 500 psi H_2 at 160° [218]. Basic polysaccharide resins (Sephadex, Cellulose) were used to support $PdCl_4^=$ for use as catalysts to reduce conjugated aldehydes to saturated aldehydes. The selectivity of various supports was studied and compared to results with free catalyst [219]. Treatment of cuprous bromide with either $LiAlH(OMe)_3$ or $NaAlH_2$(O)$_2$produced a complex that efficiently reduced conjugated enones to saturated ketones at -20° in high yield. The reduction appears to involve electron transfer, the Li salt works best on cyclic systems, and neither reduce methyl-3-phenylpropionate well [220].

The mechanism and kinetics of the hydrogen transfer catalyzed reduction of conjugated enones to saturated ketones by $RuCl_2(PPh_3)_3$ were studied. Primary alcohols were found to be the best source of hydrogen, the reduction was exclusively cis, and most other unsaturated substrates were inert [221]. Transfer hydrogenation using $RhCl(PPh_3)_3$ as a catalyst was also studied in detail [222]. Hydrogen transfer from organic compounds catalyzed by transition metal complexes has been reviewed [224].

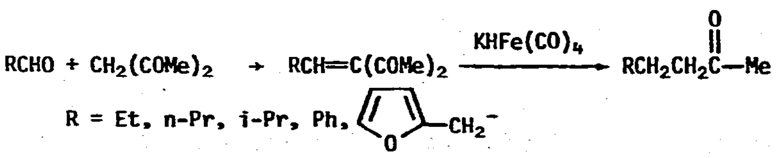
1-Alkynes were reduced in a cis reduction to 1-alkenes by hydrogen with either $[(COD)Rh(L)Py]^+PF_6^-$ or $CODRh(O_2CPh)L$ as catalyst. Ketones, internal alkynes, and nitriles were not reduced [225]. Internal alkynes were reduced, or reductively methylated by bis-(cyclopentadienyl)niobium trihydride (eq. 75) [226]. Heterogeneous catalytic hydrogenation of allenes over supported palladium has been reported [227] as has the competitive hydrogenation of allenes and acetylenes with homogeneous and heterogeneous catalysts [228].



(75)

Benzene was reduced to cyclohexane at room temperature and subatmospheric pressures of hydrogen using π-allylcobalt $[P(OMe)_3]_3$ as a catalyst. This catalyst reduced benzene 3-4 times faster than it did cyclohexene [229]. Hexadeutero-benzene was reduced to all cis cyclohexane-d^6 by this catalyst [230]. The reduction of the aromatic ring of quinolines, isoquinolines, and other pyridines while maintaining the heteroaromatic ring was best effected by the use of platinum oxide in trifluoroacetic acid. Quinoline was reduced to 5,6,7,8-tetrahydroquinoline in 84% yield by this method [231]. α and β naphthols were completely reduced to hydroxydecalines by hydrogen with rhodium on carbon catalysts. Tetralones were reduced to decalols and decalones [232].

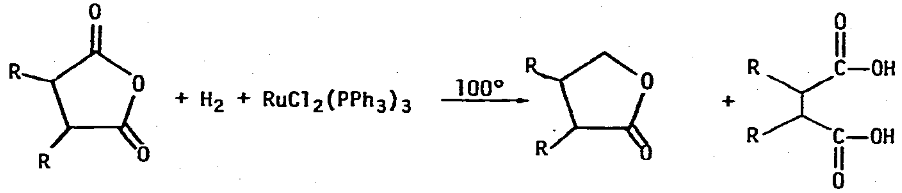
Wilkinson's complex ($RhCl(PPh_3)_3$) was used to catalyze the hydrosilation of ketones, to produce alcohols in 98% yield after hydrolysis of the silyl ether. Conjugated ketones underwent 1,4 reduction via silylenol ethers which themselves were of some synthetic interest [233]. Dicobalt octacarbonyl with trialkylphosphines produced catalysts for the homogeneous hydrogenation of ketones at 200°, and 150-250 atm of hydrogen. Carbon monoxide retarded the reaction while tertiary amines had no effect [234]. The 1,2-reduction of conjugated aldehydes to allylic alcohols was catalyzed by $RhCl_3 \cdot 3H_2O$ or $Rh_2(CO)_4Cl_2$ in benzene-tertiary amine solvent under 80kg/cm^3 H_2/CO pressure [235]. Ethyl acylcarbonates (RCO_2COOEt, R = Ph, nonyl, octyl) were reduced to aldehydes in 40-80% yields by $Na_2Fe(CO)_4$[236]. Methyl alkyl ketones were prepared by condensing acetylacetone with a variety of aldehydes and reducing the condensation product with $KHFe(CO)_4$ (eq. 76) [237]. The same reducing agent cleanly reduced enamines to amines in high yield and was an efficient reagent for the reductive amination of some aldehydes and ketones [238]. Glyoxylic acid was reductively aminated to the α-amino acid in 40-80% yield



$$RCHO + CH_2(COMe)_2 \rightarrow RCH{=}C(COMe)_2 \xrightarrow{KHFe(CO)_4} RCH_2CH_2\overset{\overset{O}{\|}}{C}{-}Me \qquad (76)$$

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

by $HFe(CO)_4^-$ in 1N ethanolic KOH under a carbon monoxide atmosphere [239]. Acid anhydrides were reduced to the ester or lactone by 150 psi hydrogen at at 100° using $RuCl_2(PPh_3)_3$ as a catalyst in 50% yield. The remainder of the product was the free acid of the anhydride (eq. 77) [240].



(77)

Treatment of titanium trichloride with magnesium in THF produced a black "titanium" which was effective for the reduction of organic halides to the corresponding hydrocarbon. The order of reactivity of the halides was I>Br>Cl>F. Aliphatic, cycloaliphatic, aromatic and benzylic halides were cleanly reduced in 80-100% yields [241]. Similar treatment of Cp_2TiCl_2 with magnesium produced a black "titanium" which also reduced organic halides, including α-bromoketones and α-bromoesters to the corresponding hydrocarbon in high yield [242]. The reduction of nitroalkanes to aliphatic amines was carried out by hydrogenation using $RuCl_2(PPh_3)_3$ as a catalyst [243]. The same catalyst selectively reduced only one of the two nitro groups in meta dinitroaromatics [244]. Palladium on carbon was used to catalyze the transfer hydrogenation of nitroaromatics to aminoaromatics. The hydrogen source was cyclohexene. Esters and amides were not reduced by this system, but halides were [245]. Polystyrene bound nickel catalysts prepared by treating polymer-bound triphenylphosphine with nickel chloride and sodium borohydride reduced nitrobenzene to azobenzene oxide in 85% yield. The free catalyst produced aniline (40%) and azobenzene (40%) [246]. A variety of aromatic amine oxides including picoline N-oxide and purine N-oxides were reduced to the amine in high yield by titanium trichloride/water in methanol [247].

Aziridines were ring opened to amines in which the nitrogen was on the most substituted position using hydrogen and a Raney nickel catalyst [248]. A clean reduction of the azide group to the amino group was carried out using the Lindlar catalyst [5% Pd on $CaCO_3$]. A large amount (30-40% based on substrate) of catalyst was required, but the reduction went in high yield, and tolerated sensitive functional groups such as olefins, carbonyls, benzyl esters and benzyl ethers [249].

Thioketones and thioamides were desulfurized in 40-80% yield by refluxing with $HFe(CO)_4^-$ in DME for 8-12 hr. Both hydrogens were shown to come from the iron reagent [250]. Phenylmercuric halides were reduced to the free aromatic compound, and metallic mercury by hydrogen with a rhodium catalyst. The reaction was shown to proceed _via_ a rhodium (III) complex [251]. Finally platinum oxide was used to catalyze the H—D exchange (from D_2O) of nucleosides and nucleotides. Pyrimidines exchanged 5 and 6H, while purines exchanged 2 and 8H [252].

V. FUNCTIONAL GROUP PREPARATIONS

A. Halides

Halogen exchange between _gem_ dihalides and monohalides was catalyzed by a variety of transition metal complexes (eq. 78) [253]. Alkyl halides

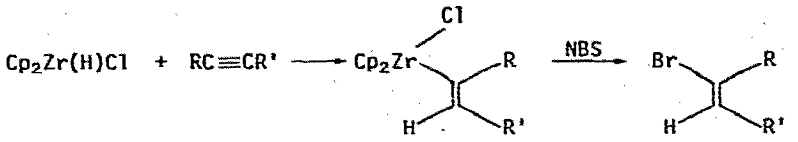
$$R'X' + R^2R^3CX_2^2 \xrightleftharpoons[100^\circ]{\text{metal}} R'X^2 + R^2R^3CX'X^2 \qquad >90\%\ \text{exchange} \qquad (78)$$

$R'X' = MeI, MeCH_2I, i\text{-}PrI, BzBr, EtBr$

$R^2R^3CX_2^2 = CH_2Cl_2, CH_2Br_2, PhCHBr_2$

$\text{Metal} = IrCl(CO)(PPh_3)_2, RhCl(CO)(PPh_3)_2, RhCl(PPh_3)_3$

were converted to alkyl chlorides by treatment with $MoCl_5$ in methylene chloride. Primary halides worked poorly, but secondary and tertiary iodides, bromides, and fluorides were cleanly converted to chlorides [254]. Disubstituted alkenes were converted to α,β-dichloroalkanes, and disubstituted acetylenes were converted to α,β-dichloroalkenes by $MoCl_5$ in dichloromethane at -78°. Terminal, tri- and tetrasubstituted olefins, and terminal acetylenes produced only low yields [255]. Substituted phenyl ketones reacted with MoF_6 to replace the carbonyl oxygen with two fluorines. The reaction tolerated F, Cl, Br, CN, NO_2, COOR, $CONR_2$, $P(O)R_2$ functionality on the ring but not OH, NH, OR, NR_2 or C=C [256]. Alkynes were converted to vinyl halides by treatment with $Cp_2Zr(H)Cl$ followed by N-bromosuccinimide cleavage of the vinyl zirconium (eq. 79) [257].



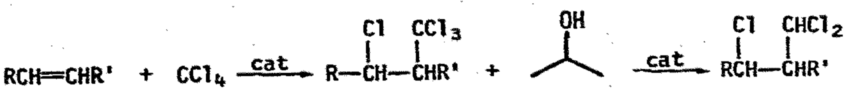
(79)

75-100%

R = H, Me

R' = Et, n-Bu, t-Bu, n-Pr, i-Pr

Treatment of carbon tetrachloride with black "titanium", produced from titanium tetrachloride and lithium aluminum hydride, effected a dichlorocyclopropanation of a variety of alkenes in good yield. The reagent was thought to be a source of "dichlorocarbene" [258]. Treatment of alkenes with carbon tetrachloride and $RuCl_2(PPh_3)_3$ as a catalyst in isopropanol produced excellent yields of polychlorinated product (eq. 80) [259]. The second step proceeded by transfer hydrogenolysis. Treatment of cyclohexanone with cupric chloride in acetic acid produced the polychlorinated hydroxy ketone (eq. 81) [260]. Cycloheptanone reacted in a similar fashion.



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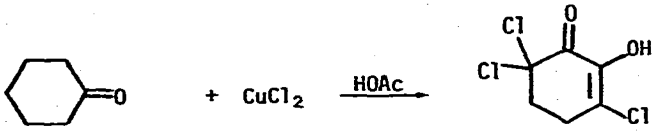
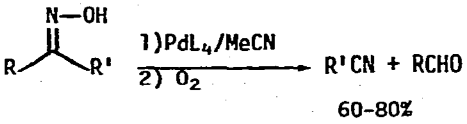


(81)

B. Amides, Nitriles

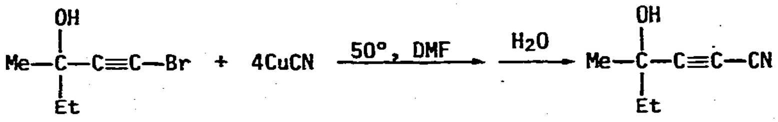
Treatment of oximes with $Pd(PPh_3)_4$ in acetonitrile, followed by oxygen produced nitriles in 60-80% yield (eq. 82) [261]. Cuprous cyanide converted bromoacetylenes to cyanoacetylenes in good yield (eq. 83) [262]. Isocyanates were converted to carbamates by $Zr(OR)_4$ [263]. Diarylureas were produced in 40-80% yield by treatment of an aryl amine and an aryl nitrocompound with carbon monoxide in xylene in the presence of a tertiary amine and a PdX_2L_2 catalyst. When the aryl amine and the aryl nitrocompound were different, a mixture of all possible products was obtained [264].



(82)

R' = Ph, p-NO_2Ph, p-OMePh

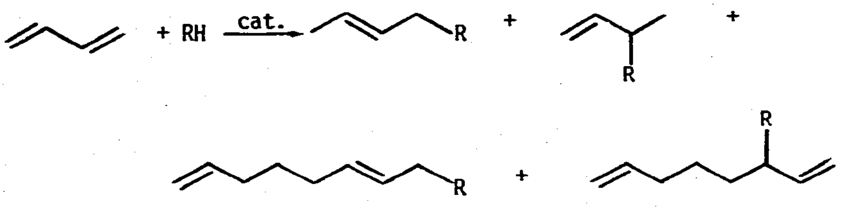
R = COPh, CH_2Ph, p-NO_2PhCO, p-OMePhCO



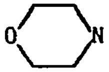
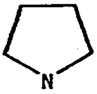
$$Me-\underset{Et}{\overset{OH}{C}}-C\equiv C-Br + 4CuCN \xrightarrow{50°,\ DMF} \xrightarrow{H_2O} Me-\underset{Et}{\overset{OH}{C}}-C\equiv C-CN \qquad (83)$$

C. Amines, Alcohols

π-Allylpalladium chloride complexes reacted with secondary amines in the presence of excess phosphine to produce allylamines in good yield. Amination occurred at the less substituted terminus of unsymmetrical π-allyl complexes [265] A complete study of the reaction of butadiene with amines in the presence of transition metal catalysts has been reported, and is summarized in eq. 84 [266]. The product distribution as a function of amine and catalyst was reported. α-Hydroxyketones were converted to α hydroxyamines by reduction of the ketone

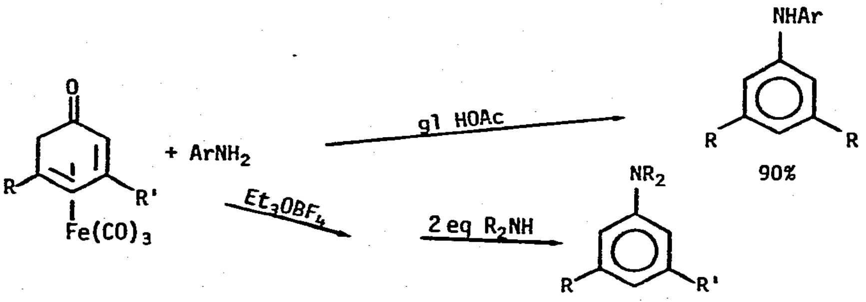


(84)

R =  ,  , Pr_2N, Et_2N, PhNH, PhCHCOMe, $CH(COOEt)_2$

cat = $IrCl_3$, $RhCl_3$, $NiCl_2$ / Ph_3P / $NaBH_4$, $CoCl_2$ / Ph_3P / $NaBH_4$, $Al(i\text{-}PrO)_3$

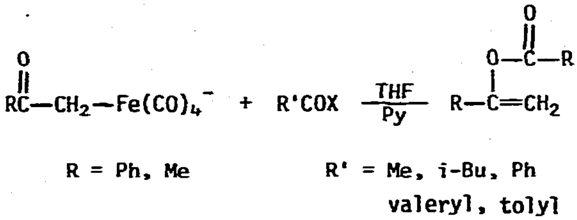
oxime with hydrogen using 5% Rh on Alumina catalyst [267]. Iodobenzenes were converted to the corresponding phenylhydrazines in 40-50% yield by treatment with $(Me_3Si)_2N{-}N(SiMe_3)Cu$ followed by hydrolysis [268]. Cyclohexadienone complexes of iron were aminated by weakly basic amines such as aniline (eq. 85) [269]. Olefins were converted to terminal alcohols by hydrozirconation with $Cp_2Zr(H)Cl$ followed by oxidation of the primary alkyzirconium complex with H_2O_2 or t-butylhydroperoxide [270].



(85)

D. Ethers, Esters, Acids

Enol esters were prepared in 71-97% yield by the treatment of α-ketoalkyl iron carbonylates with acid halides (eq. 86) [271]. Vinyl bromides were converted to vinyl acetates by cuprous acetate in refluxing acetonitrile. A variety of unusual compounds were prepared in this fashion (eq. 87) [272]. Palladium acetate introduced an acetate in an allylic position of nonconjugated dienes (eq. 88) [273]. Several bis benzylisoquinolines containing a diphenylether link were synthesized in good (53%) yield by coupling of a phenol to an aromatic halide by $(C_6F_5Cu)_4$ (eq. 89). The best previous yield for this coupling was 2% [274]. The iodide in o-iodoazobenzene was replaced by CN, OMe, OEt, O-i-Pr,

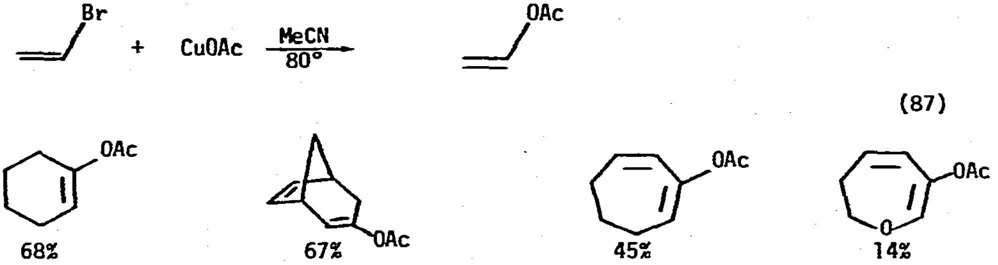


$$RC(=O)-CH_2-Fe(CO)_4^- + R'COX \xrightarrow[Py]{THF} R-C(O-C(=O)-R')=CH_2$$

R = Ph, Me

R' = Me, i-Bu, Ph valeryl, tolyl

(86)



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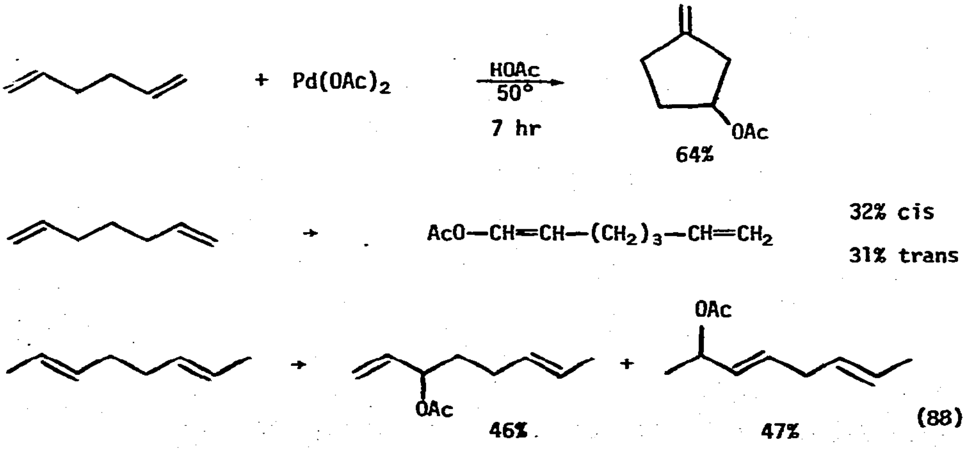

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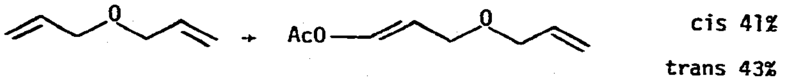
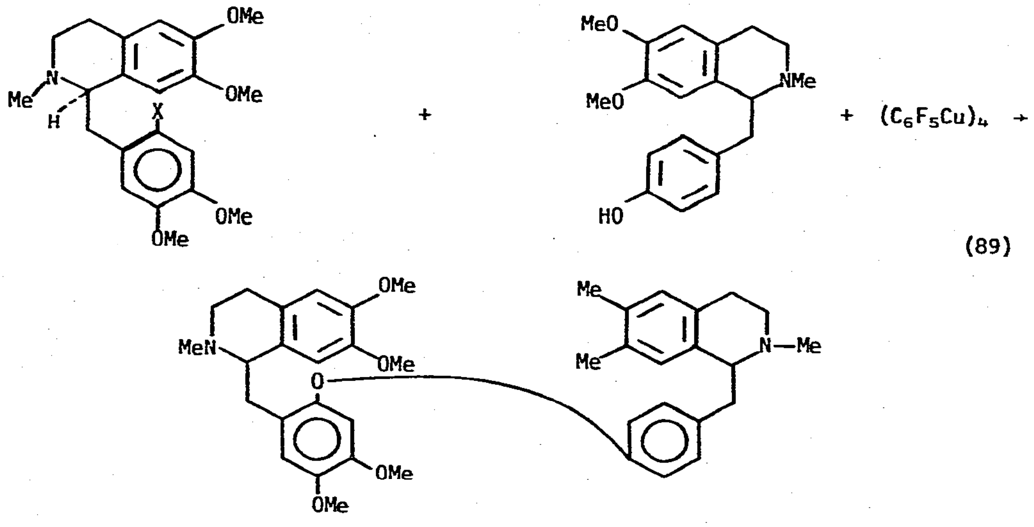




(89)

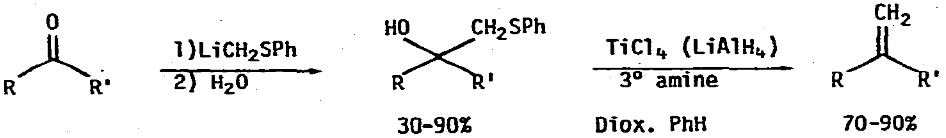
53%

O-t-Bu, and OH by treatment with the corresponding cuprous salt. The reaction went in 60-90% yield [275].

Organocopper complexes of the type RCu·MgX were converted to carboxylic acids by treatment with carbon dioxide in ether-HMPA [276]. Alcohols were carboxylated to formate esters by treatment with hydrogen and carbon dioxide using either Pd(diphos)$_2$ 3° amine, or HCo (diphos)$_2$ as a catalyst [277]. Acid hydrazides were oxidized to the free carboxylic acid by oxygen and copper salts [278]. 2-Methylbut-1-ene was carboxylated to 2,2-dimethylbutanoic acid in 70-90% yield by $CO_2 \cdot BF_3$ and cuprous salts in the presence of H_3PO_4 [279]. The use of manganic acetate to initiate the free radical addition of acid anhydrides to olefins was reported. Fatty acids were produced from α-olefins in this manner [280].

E. Olefins, Ketones

Bromohydrins were cleanly converted to the corresponding olefin by treatment with "titanium" prepared by the reaction of titanium trichloride and lithium aluminum hydride. The reaction went in high yield, the reagent was nonacidic, but the elimination was nonstereospecific. In this fashion, cycloheptene, indene, and cholesterol were prepared in 80-96% yield from the corresponding bromohydrin [281]. Keto groups were converted to methylene groups, as in a Wittig reaction, by treatment of the ketone with $LiCH_2SPh$ to produce the β-hydroxythioether, which upon treatment with titanium tetrachloride and lithium aluminum hydride in the presence of a tertiary amine produced the alkene (eq. 90) [282]. Epoxides were converted to olefins in fair yield with loss of stereochemistry by the titanium trichloride-lithium aluminum hydride reagent [283]. Epoxides were converted stereospecifically to either cis or trans olefins, depending on reaction conditions, using cyclopentadiene iron dicarbonyl anion (eq. 91). The reaction worked best with diaryl and dialkyl epoxides. α,β-epoxycarbonyls gave poorer stereospecificity [284]. Cuprous



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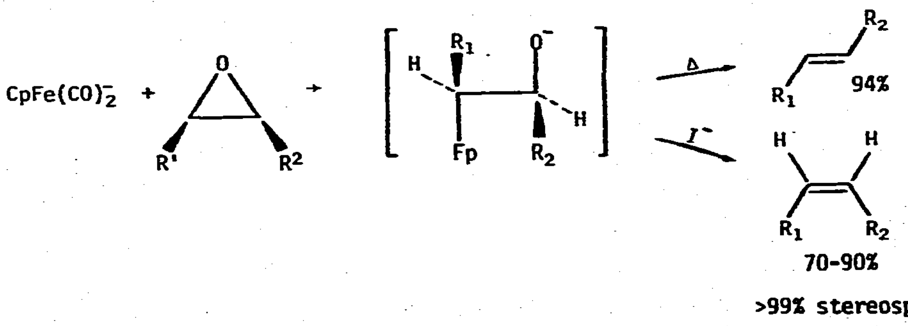
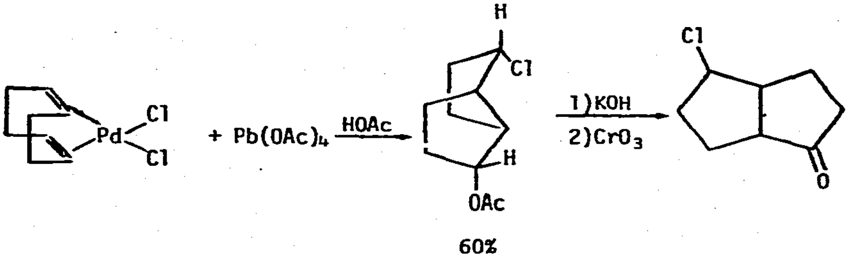


(91)

ion desulfurized gem-bis (thiophenyl) alkanes to vinylsulfides in 85-94% yield [285]. Treatment of α-bromoketones with Pd(PPh_3)$_4$ in benzene produced α,β-unsaturated ketones. With 2-bromotetralones high yields of naphthols were obtained, while other substrates reacted in 35-55% yield [286].

Commercially available 20% aqueous titanium trichloride in DME converted 2,4-dinitrophenylhydrazones to the corresponding ketones in greater than 95% yield. The reaction worked with a variety of saturated and unsaturated ketones including cholestanone and testosterone, and appears to be the method of choice for this conversion [287]. Nitriles were converted to ketones by treatment with trimethylaluminum and a nickel acetylacetonate catalyst [288]. Styrene was converted to phenylbenzyl ketone by treatment with palladium chloride in DME [289]. Oxidation of cyclooctadiene palladium dichloride with lead tetraacetate, followed by sequential treatment with potassium hydroxide and chromium trioxide produced a bicyclic chloroketone (eq. 92) [290].

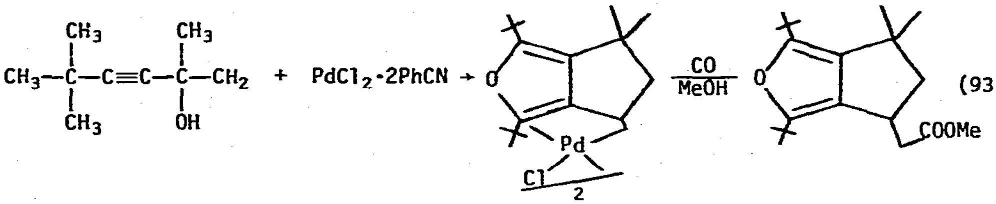


(92)

F. Heterocycles

Several new syntheses of furans have been developed. Treatment of o-allylphenols with palladium chloride and base produced 2-substituted benzofurans in 20-50% yield via an intramolecular oxypalladation. The reaction of o-allylnaphthols worked as well. The system could be made catalytic using oxygen and cupric chloride under Wacker process conditions [291]. Treatment of 1-phenyl-2-hydroxynaphthoquinone with palladium on carbon at 250° produced a low (10%) yield of the benzofuran fused to the naphthoquinone [292].

Palladium chloride converted the propargyl alcohol in eq. 93 to the di-t-butylfuran via a palladium alkyl complex intermediate [293]. Dihydrofurans were produced from the reaction of allylic alcohols with carbon monoxide and hydrogen using a rhodium catalyst (eq. 94) [294]. Hydroxybenzofurans were formed by the reaction of 3-acetylfurans with β-diesters in the presence of titanium tetrachloride (eq. 95) [295]. Irradiation of conjugated ketones in the presence of titanium tetrachloride produced dihydrofurans in some instances (eq. 96) [296]. Treatment of cyclohexane-1,3-diones with 1,2-diols using $RuCl_2(PPh_3)_2$ as a catalyst produced tetrahydrofurans (eq. 97) [297].



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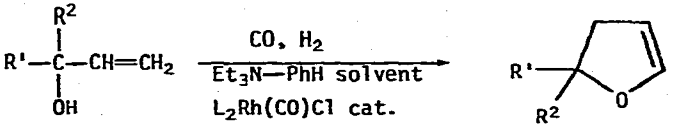

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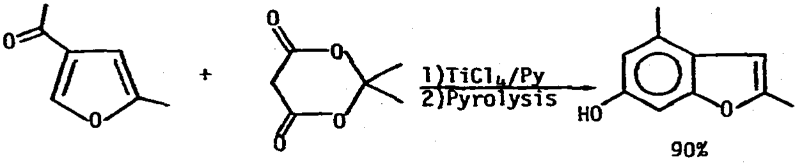

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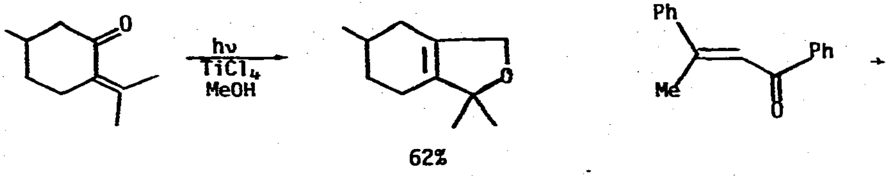

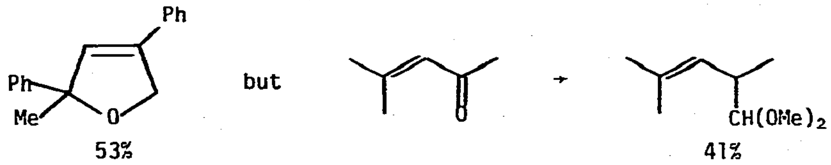

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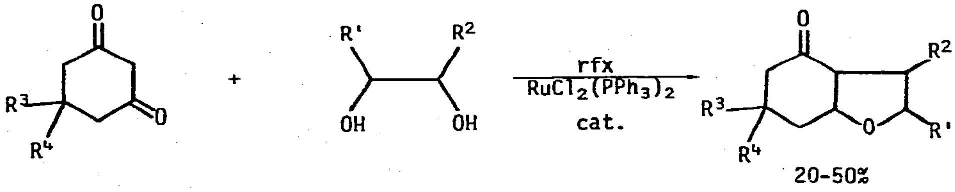


(97)

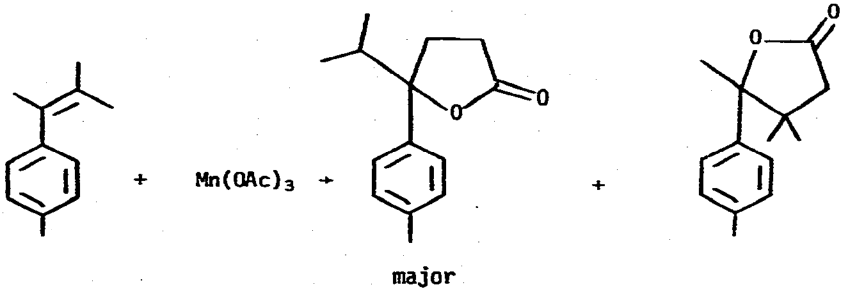
R' = H

R^2 = H, Me

R^3 = H, Me

R^4 = H, Me, t-Bu

Manganic acetate converted trimethylstyrene to a mixture of γ butyrolactones (eq. 98) [298]. Methylmethacrylate reacted with diethyl dibromomalonate in the presence of $Fe(CO)_5$ to produce a substituted γ-butyrolactone (eq. 99) [299]. α-Methylene-γ-butyrolactones were produced from 4-hydroxyacetylenes by treatment with carbon monoxide in acetone, with palladium chloride and thiourea as a catalyst (eq. 100) [300]. Diols were oxidized and closed to lactones by treatment with silver carbonate on Celite in 75-95% yields.



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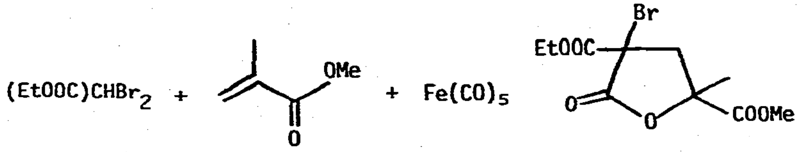

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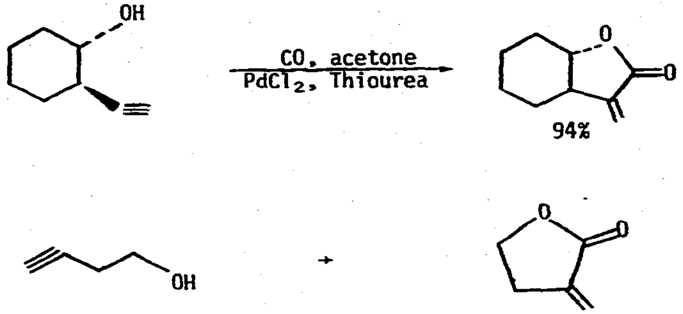
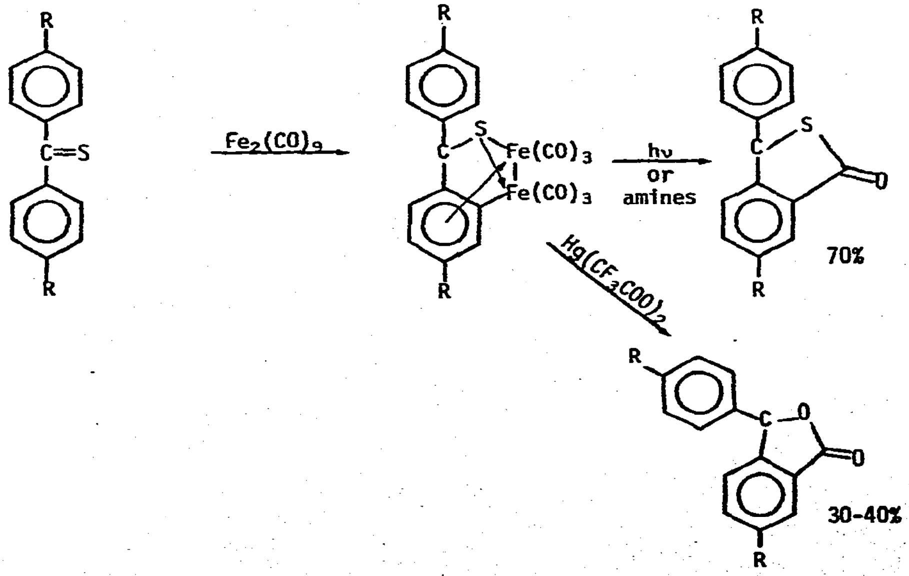


(100)

Many complex diols, including steroidal systems were studied [301]. Diarylthioketones were converted to lactones and thiolactones by treatment with $Fe_2(CO)_9$ and decomposition of the intermediate iron complex (eq. 101) [302]. A general preparation of 4,5-dihydro-2-H-pyran-2-ones from 4-hydroxy-α,β-acetylenic acids or the corresponding trimethylsilyl derivative utilized conjugate alkylation by lithium dialkylcuprates as a key step (eq. 102) [303]. Lithium tetrachloropalladate cyclized α,β,γ,δ-carboxylic acids to α-pyrones



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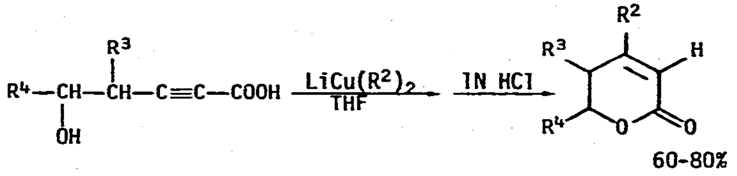

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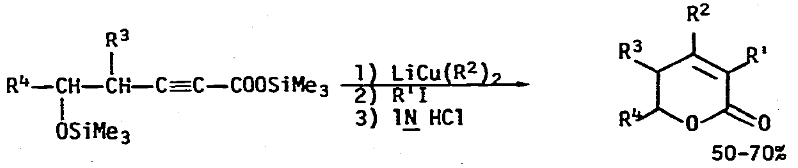
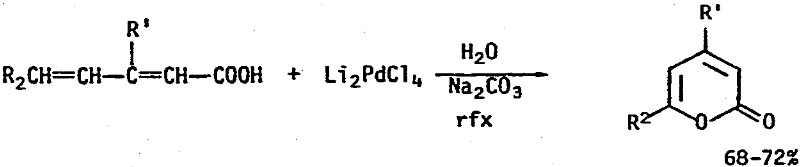


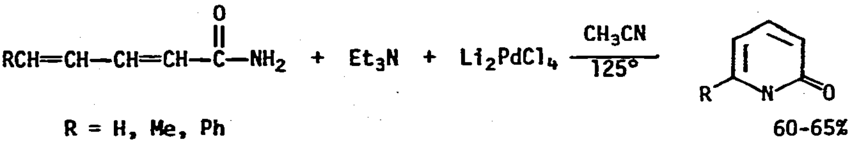
(102)

in good yield (eq. 103) [304]. The corresponding amide produced the pyridone (eq. 104) [305]. The reductive amination of glutaraldehyde using primary amines and $HFe(CO)_4^-$ produced a variety of N-alkylpiperidines in 51-90% yield [306]. Cupric trifluoroacetate was used to catalyze the reaction of nitriles with ethyl diazoacetate to produce substituted oxazoles in moderate yield [307].



(103)

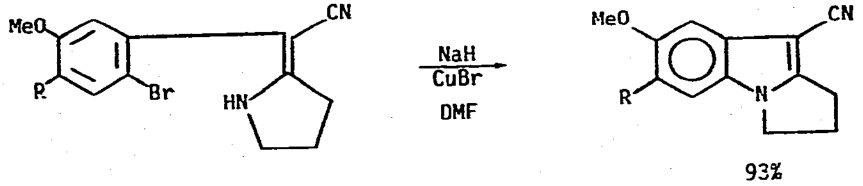
R', R^2 = H, Me, Ph



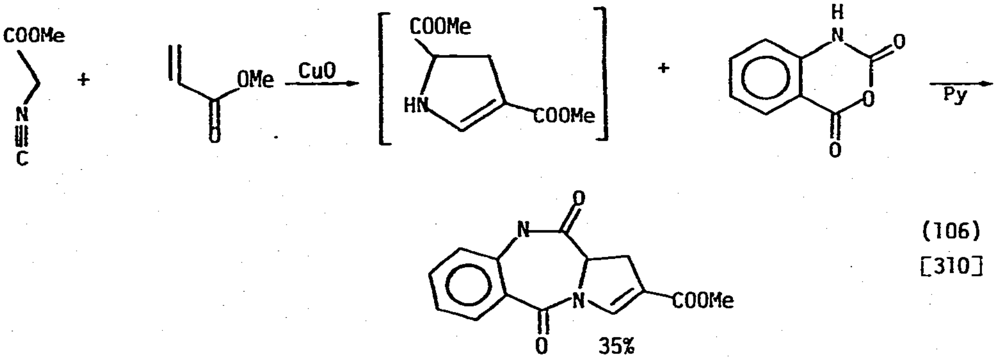
(104)

R = H, Me, Ph

A variety of complex heterocyclic ring systems have been synthesized utilizing transition metal complexes in key steps. These are summarized in eq. 105-115. The synthesis of cyclic compounds via copper isonitrile complexes has been reviewed [308].



(105)
[309]



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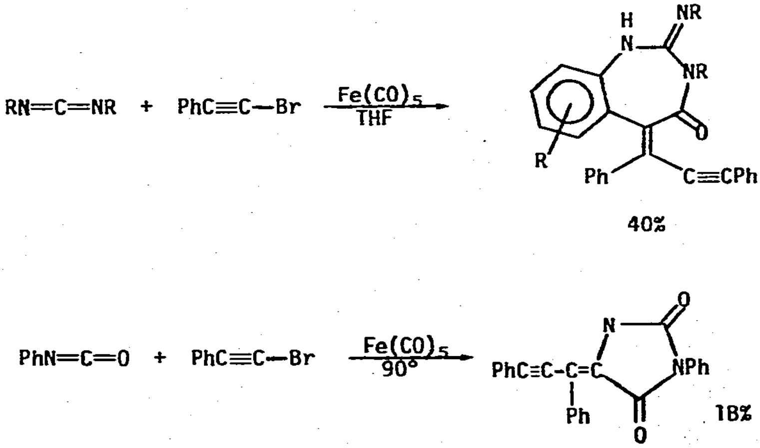
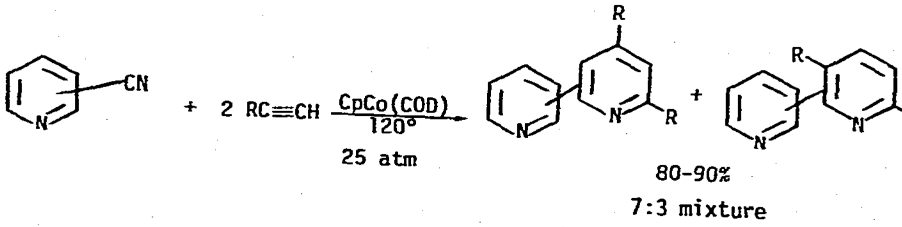
[310]



(107)
[311]



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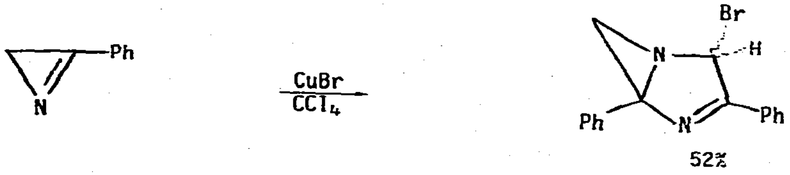
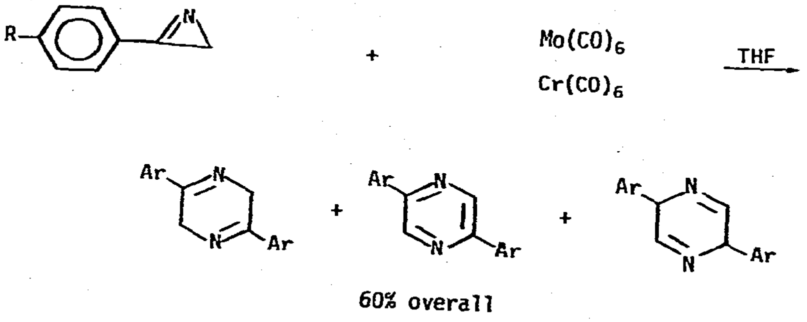
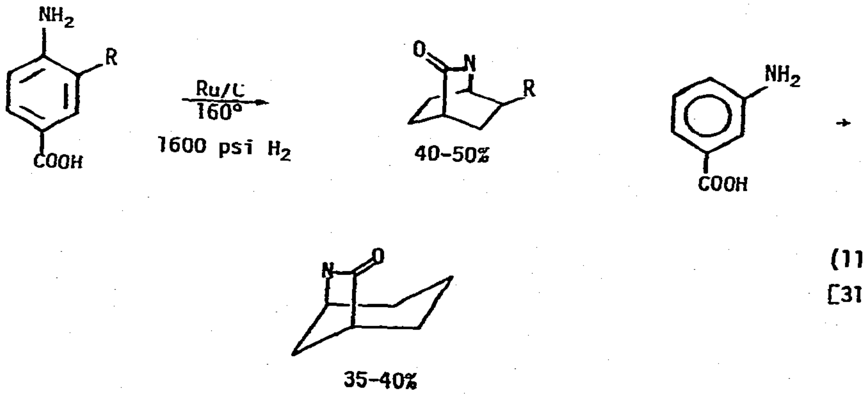
[312]



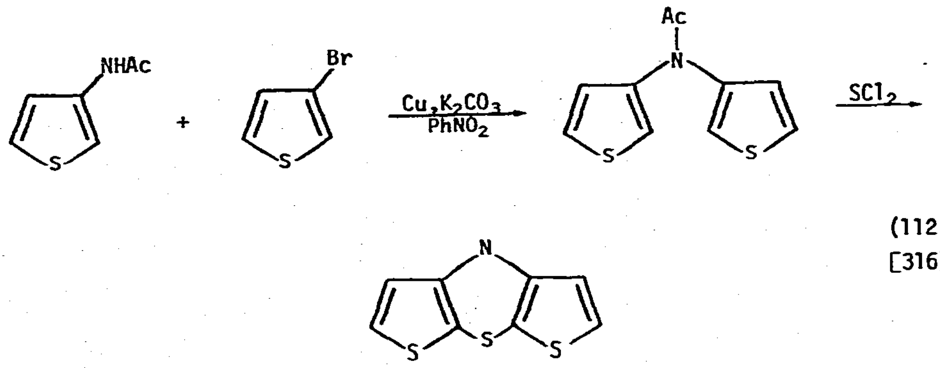
(109)
[313]



(110)
[314]



(111)
[315]



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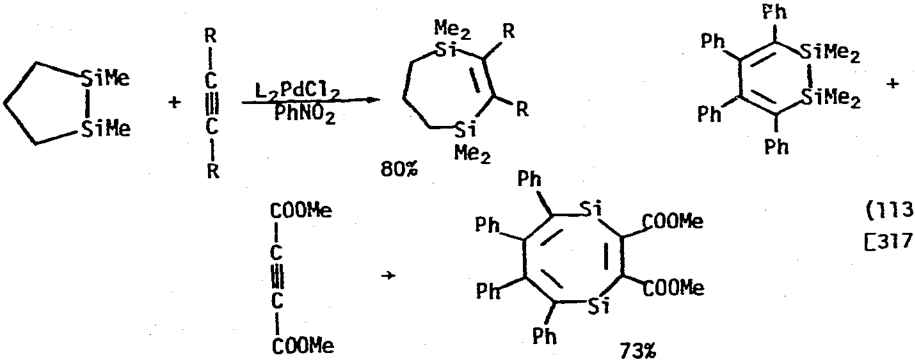
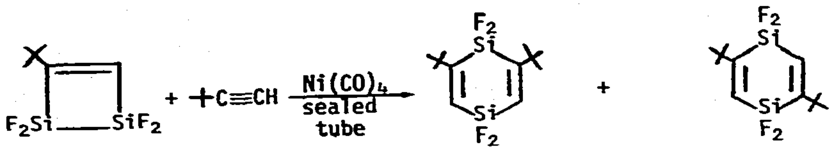
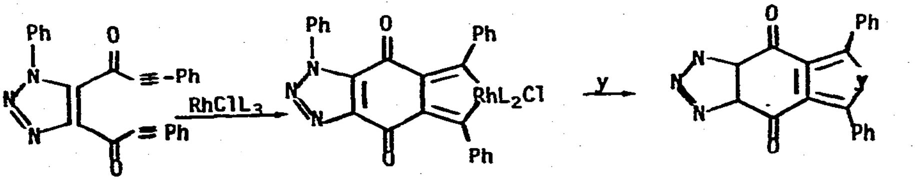
[316]



(113)
[317]



(114)
[318]



y = O,S, Se

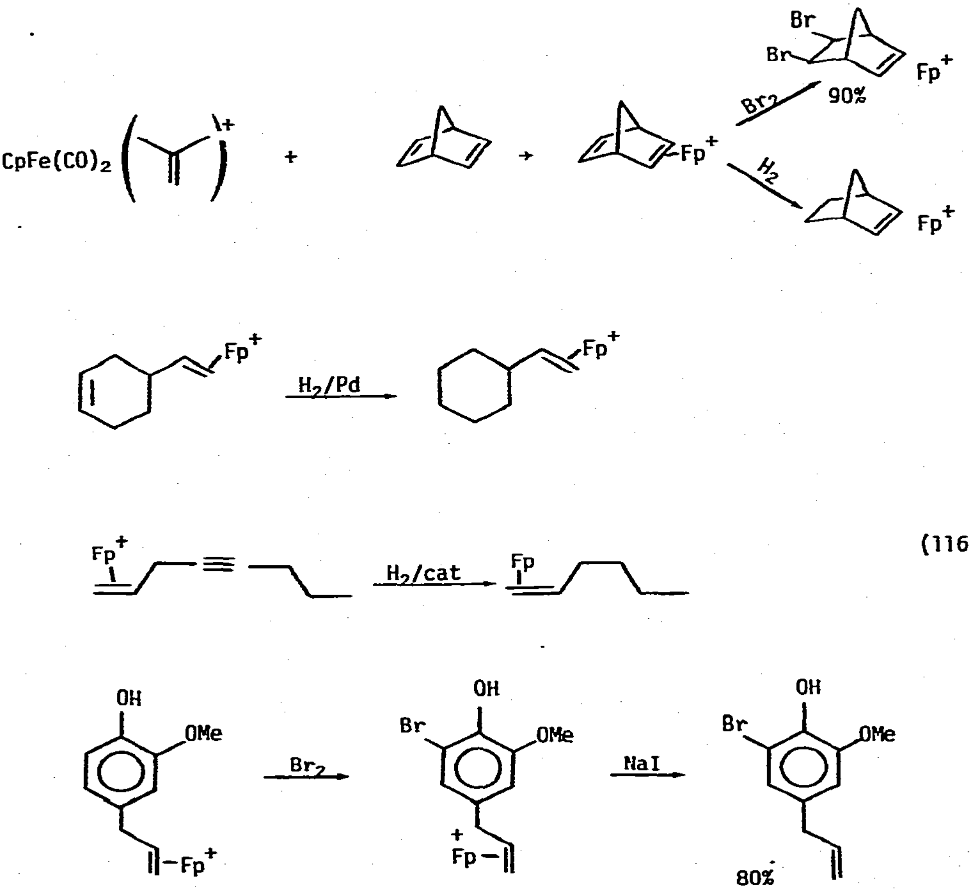
(115)
[319]

G. Miscellaneous

Two very useful examples of the use of transition metals as protecting or directing groups in organic synthesis have been reported. Racemic 1-endo-indanol or 1-endotetralol was complexed to chromium hexacarbonyl to give the arene chromium tricarbonyl complex. These complexes were resolved, and the secondary alcohol was oxidized to a ketone group, producing chiral chromium complexes of 1-indanone and 1-tetralone respectively, in which the chromium was coordinated to one face of the molecule. These complexes were then α-alkylated, reduced, or reacted with Grignard reagents. In all cases the reagent attached exclusively from the face opposite the chromium to give high optical yields in all cases. The organic compound was freed from the metal by exposure to sunlight [320]. In the second case, the cyclopentadienyliron dicarbonyl cation was used as an olefin protecting group. Treatment of a variety of olefins with [cyclopentadienyliron dicarbonyl (2-methylpropene)]$^+$ led to olefin exchange at the metal. In polyolefins, the less substituted and/or more strained double bond preferentially coordinated. The new iron-olefin complex withstood bromination, hydrogenation, and acetoxymercuration, but the olefin was easily freed from the iron by treatment with sodium iodide. The utility of this system is summarized in eq. 115 [321,322].

It was found that $MnCl_2$ complexed preferentially to some alcohols, forming an isolable complex which allowed easy regeneration of the alcohol. This procedure was used to separate a commercial mixture of cis and trans 4-t-butylcyclohexanol, technical geraniol, and cyclododecanol-cyclododecanone mixtures [323].

The 3-isopropoxyacetals of a variety of α,β-unsaturated carbonyl compounds were prepared in good yield using $Ti(i\text{-}PrO)_4$ and $TiCl_4$[324]. Dialkyl carbodiimides were prepared in 72-93% yield by the reaction of primary amines and isonitriles with silver oxide, and palladium chloride catalyst [325]. The nickel chloride catalyzed reactions of aromatic halides with a variety of



(116)

nucleophiles were studied with regard to effects of added metals, ligands, temperature and nucleophiles [326]. Iron pentacarbonyl deoxygenated oximes to imines in fair yield [327]. Azoxyalkanes were produced by the reaction of dichloroamines and aromatic nitroso-compounds using cuprous chloride [328].

VI. REVIEWS

Homogeneous catalysis by transition metal complexes has been treated in a review with 187 references [329]. A long and very detailed article, including some experimental discussion, on substitution reactions using organocopper reagents has been published [330]. Addition of hydrogen cyanide to monoolefins catalyzed by transition metals has been reviewed [331]. The use of disodium tetracarbonyl ferrate in organic synthesis has been treated in two separate reviews [332,333]. A review of homogeneous catalytic activation of C—H bonds has appeared [334]. Organometallic reactions involving hydro-nickel, palladium and platinum complexes have been reviewed [335]. The activation of Grignard reagents by transition metal compounds has been treated in a review with 65 references [336]. The selectivity in catalysis by alloys has been presented in a review with 181 references [337].

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