TRANSITION METAL DERIVATIVES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

TRANSITION METAL DERIVATIVES IN ORGANIC SYNTHESIS

I. GENERAL COMMENTS

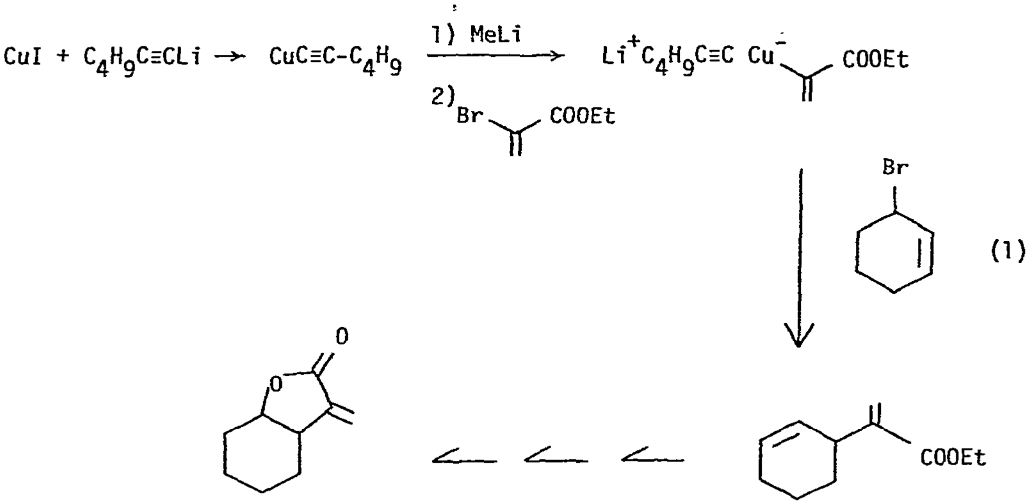
This annual survey covers the literature for 1974 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review, but is limited to reports of discrete systems that lead to at least moderate yields of organic compounds, or that allow unique 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. Alkylations

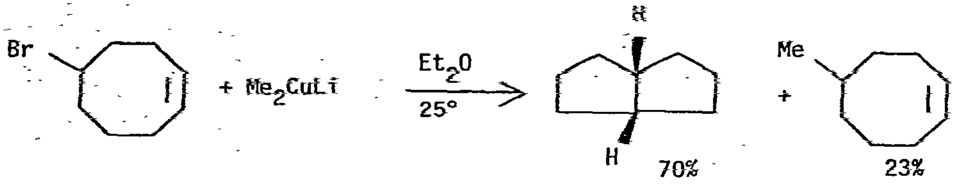
Organocuprate reagents continued to be exploited for their ability to selectively alkylate a variety of organic substrates. Organic dibromides of the type $Br-(CH_2)_n-Br$ (n = 3,4,5,6,10) were mono-alkylated by alkyl Grignard reagents and Li_2CuCl_4 to produce chain lengthened monobromides in 40-90% yield [1]. The use of mixed cuprates to allow efficient utilization of valuable organolithium reagents has been more fully developed. A convenient preparation of mixed cuprate $[PhSCu(t-Bu)]^-Li^+$ from thiophenol, Cu_2O and t-BuLi, and its use in the high yield t-butylation of 1-iodooctane, benzoyl chloride, and cyclohexenone has been reported [2]. Sec-butyllithium also worked well with this sytem. The selectivity of organic group transfer in reactions of mixed lithium diorganocuprates has been studied in detail[3]. With substrates of low reactivity, mixed cuprates containing a highly basic organic group, particularly t-butyl, may have advantages. The reaction of alkynyl-α-carbethoxyvinyl cuprate with allylic halides has been used to synthesize α-methylenelactones (eq. 1)[4]. Propargyl halides also reacted while benzyl, aryl, vinyl, and aliphatic halides were unreactive towards this complex. Chiral mercury alkyls have been used to generate mixed cuprate



(1)

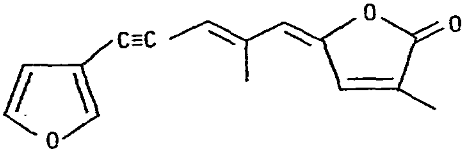
complexes. These reagents alkylated organic halides in ~25% yield, with 60-75% retention of configuration of the carbon originally bonded to mercury [5].

Lithium dimethylcuprate reacted with 5-bromocyclooctene to produce mainly bicyclic material, indicating transannular interaction between copper and this olefin (eq. 2) [6]. Similar results were obtained with other unsaturated cyclic halides and tosylates. Benzyl halides [7], 2-chlorotropone [8], and vinyl iodides [9] have also been alkylated by organocuprate reagents



(2)

under the usual conditions. The acetylene sesquiterpene freelingyne (1) has been synthesized by alkylation of the requisite iodoalkyne with lithium bis (2-furanyl)cuprate [10], while o-bromobenzoic acids have been alkylated by acetylacetone utilizing NaH and CuBr [11]. Conjugated enol ethers and esters reacted with lithium dimethylcuprate, undergoing replacement of the ether or ester by a methyl group (eq. 3) [12].



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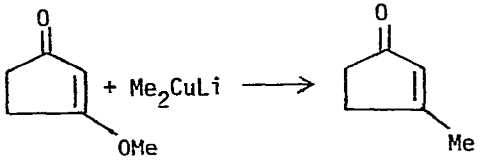
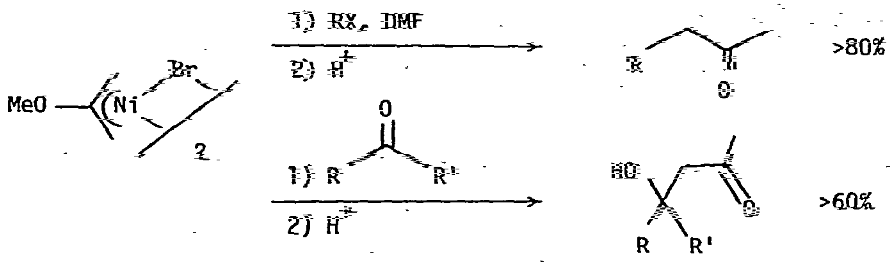


Several carbuxylic acid derivatives were reacted with organocuprates to produce ketones. Diacid halides of the type $ClCO(CH_2)_nCOCl$ reacted with t-butylmagnesium chloride and a Cu(I) catalyst to produce α,ω-di-t-butylketones [13]. Similarly, cyclopropane dicarboxylic acid chlorides were converted to the corresponding diketones by reaction with lithium dialkylcuprates [14]. Thioesters were also converted to ketones by similar procedures [15].

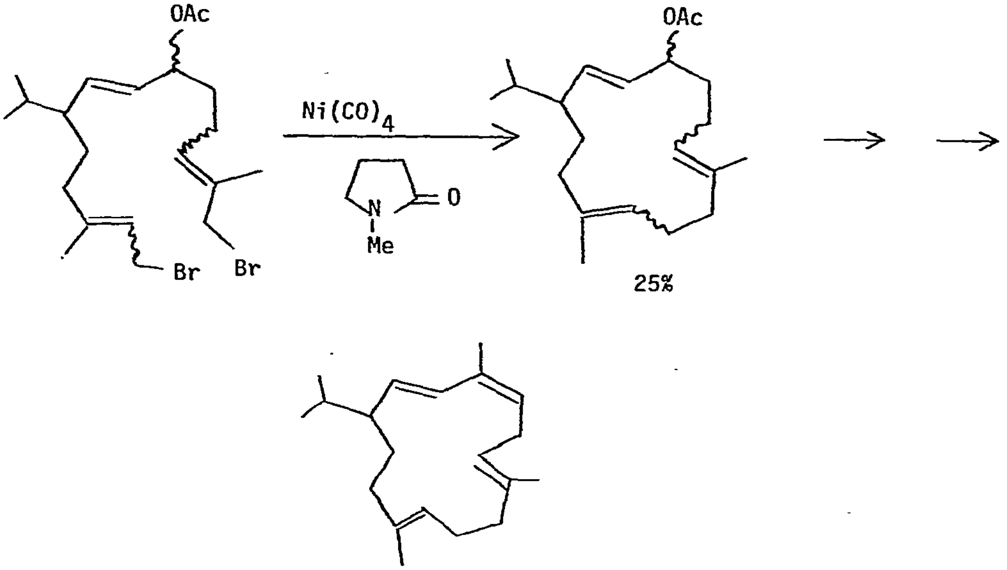
Oxidative coupling via organocopper compounds has recently been reviewed [16] as has the Ullmann synthesis of biaryls [17].

π-(2-methoxyallyl)nickel bromide was reacted with aryl, vinyl, allyl and alkyl halides to produce substituted methyl ketones, and with ketones and aldehydes to produce β-hydroxyketones in good yield (eq. 4) [18]. The reaction with vinyl halides proceeded with retention of geometry. Tocopherols



(4)

were synthesized by the alkylation of the appropriately substituted aryl bromide with the π-allylnickel halide complex containing the requisite isoprenoid side chain [19]. The stereochemistry of the reaction between π-allylnickel halide complexes and allylic halides has been studied, and the effects of substituents on the π-allyl ligand on the resultant geometry of the double bond in the coupling products has been detailed [20]. Cembrene (2), a 14-membered ring diterpene was synthesized using as a key step the nickel carbonyl coupling of a bis-allylic halide (eq. 5) [21]. Alkyldibromides of the type $Br(CH_2)_nBr$



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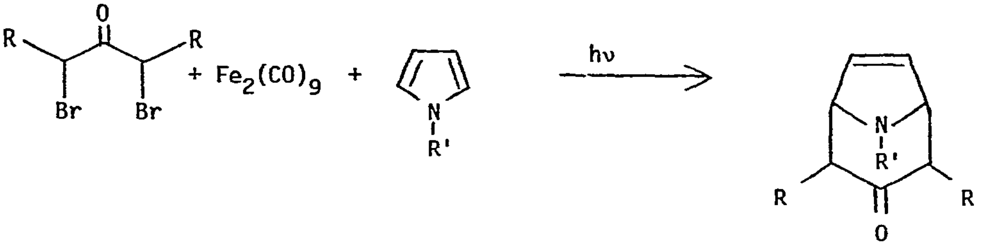
were cyclized to cycloalkanes by bis-cyclooctadiene nickel in the presence of dipyridyl. The system became catalytic upon addition of reducing agents such as isopropyl magnesium bromide [22]. Finally, chiral nickel(II) complexes were used to catalyze the reaction of Grignard reagents with organic halides, giving 30-90% yields of cross coupled products, with 8-14% enantiomeric excess [23].

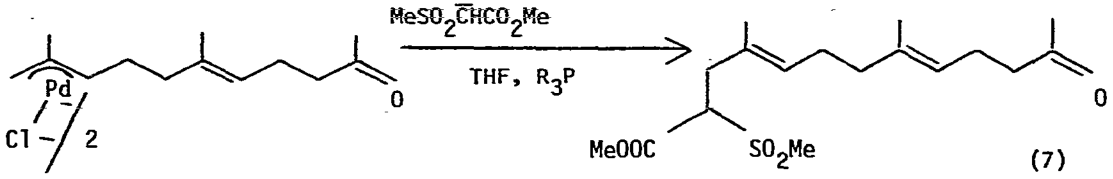
Several methods for the coupling of olefins with organic halides have recently been reported. Aryl and vinyl bromides reacted with olefins in the presence of $Pd(OAc)_2$, triphenylphosphine, and a tertiary amine to produce olefins in which a vinyl hydrogen of the original olefin had been replaced by the organic group of the halide, with ∿70% stereospecificity. The reaction is thought to proceed through an alkylpalladium intermediate [24]. The stereochemistry of this vinyl transfer has been studied [25]. The addition of allyl chloride to phenylacetylene to produce 1-phenyl-1-chloropentadi-1,4-ene was catalyzed by $PdCl_2 \cdot 2PhCN$ [26].

Several systems which promote the addition of dihalides to activated double bonds have been developed. Copper isonitrile complexes catalyzed the reaction of 1,1-dichloro-3-alkenes with ethyl acrylates to give vinylcyclopropanes [27], the reaction of o-bis-bromomethylbenzene with acrylates and maleates to give tetrahydronaphthalene derivatives [28], and the reaction of 1,3-diiodopropane with acrylates or maleates to give carboxycyclopentanes [29]. The reaction of α,α' dibromoketones with N-carbomethoxypyrrole and $Fe_2(CO)_9$ produced the tropane ring system in fair yield (eq. 6) [30].



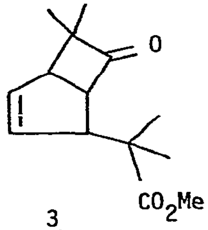
(6)

Olefins were reacted with $PdCl_2$ to form π-allyl palladium chloride complexes, which reacted with sulfur stabilized carbanions in the presence of tertiary phosphines to yield alkylated olefins (eq. 7). Attack occurred at the least hindered site of the π-allyl group [31,32].



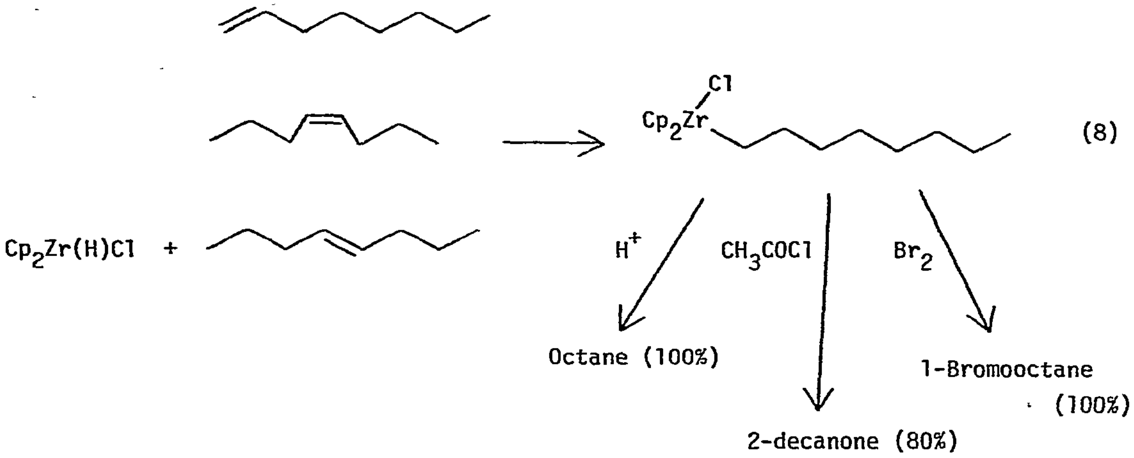
(7)

Low valent metals have been used to catalyze the reaction between strained ring compounds and olefins. The ring opening of 1,1-dimethylcyclopropene and subsequent reaction with acrylic, maleic, and fumaric esters to form 2-methyl-2-propenylcyclopropane·carboxylate esters was catalyzed by bis-(cyclooctadienyl) nickel [33]. Bis-(acrylonitrile)nickel was used to catalyze the cycloaddition of dimethyl maleate or fumarate with bicyclo[2.1.0]pentanes to produce substituted norbornanes. The stereochemistry of the adduct was the reverse of that encountered in purely thermal cycloadditions [34]. Norbornadiene was found to undergo a 2 + 2 cycloaddition with itself to produce exo-5-o-tolyl-2-norbornene with catalysis by $NiCl_2(PBu_3)_2$ and $NaBH_4$ in amine solvent [35]. A similar product, 5-phenyl-2-norbornene was formed by the reaction of norbornene with benzene catalyzed by $WCl_6{\cdot}EtAlCl_2{\cdot}EtOH$ [36]. Finally, bis (cyclopentadienyl)nickel reacted with two moles of dimethyl ketene to produce after Ce^{4+} oxidation, ketoester 3 in excellent yield [37].



3

Several methods for functionalizing olefins, based on metal hydride additions have recently been developed. Ethylene reacted with $RhH(CO)L_3$ or $CoH(N_2)L_3$ to produce an unstable σ-ethylrhodium(I) or -cobalt(I) complex. These were treated with acid halides to produce ethyl ketones in excellent yields. Longer chain olefins gave much poorer yields [38]. The use of polymer bound rhodium hydride and rhodium alkyl catalysts for the syntehsis of aldehydes (Oxo process) and ketones has been reviewed [39]. Of particular promise is the recently reported [40] uses of $Cp_2Zr(H)Cl$ to functionalize olefins. Treatment of a variety of terminal and internal alkenes with $Cp_2Zr(H)Cl$ produced a stable terminal Zr-alkyl complex, which reacted with a variety of electrophiles to produce substituted alkanes in excellent yields (eq. 8).



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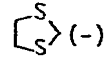
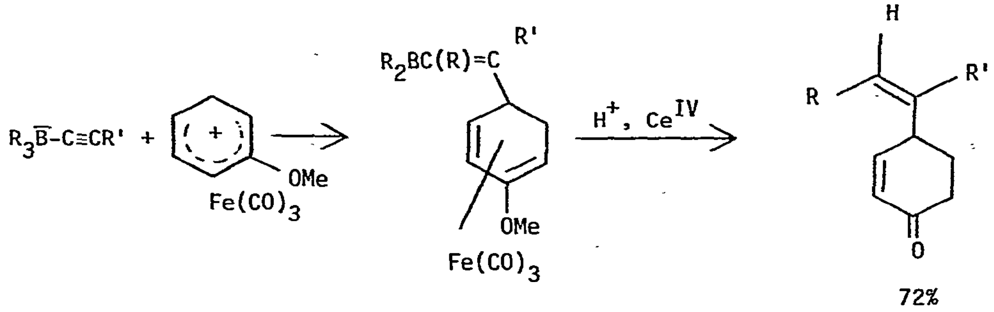
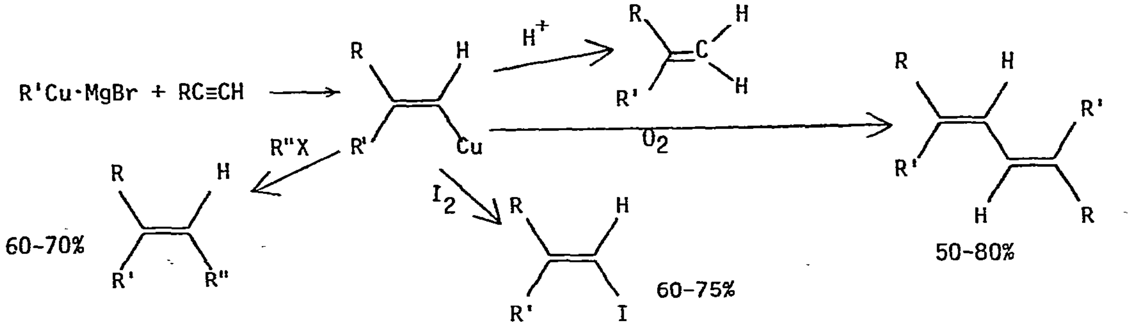
Nucleophilic attack on metal-complexed arenes has produced interesting synthetic transformations. The reaction of (chlorobenzene) chromium tricarbonyl with a variety of stabilized carbanions ($-C(R_2)CN$, $-C(R_2)COOEt$,) led, after oxidative decomposition, to the alkyl benzenes resulting from the replacement of the chloride by the carbanion. Simple anions such as $^{(-)}CH_2CN$,  and Ph $COCH_2(-)$ failed to produce appreciable amounts of product [41]. However, a different group has reported that phenoxide, aniline, and phenylmagnesium bromide similarly displace chloride from the above complex to produce diphenyl ether, diphenylamine and biphenyl, respectively, in excellent yield [42]. In this regard two improved syntheses of arene chromium tricarbonyl complexes are of some importance [43,44]. Ortho alkylation of benzaldehyde was achieved by orthometallation of the aldimine with palladium chloride followed by treatment with Ph_3P and an organolithium reagent. After hydrolysis 76-91% of the *o*-alkyl benzaldehyde was obtained [45,46]. The reaction of alkynyl borates with cyclohexadienyliron tricarbonyl complexes to produce substituted cyclohexenones has also been reported (eq. 9) [47]. In this regard the use of tertiary amine oxides as a mild reagent for the removal of Fe from stable Fe diene complexes without destruction of the organic ligand is of some interest [48].



(9)

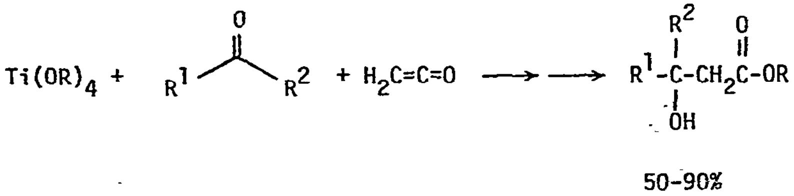
The addition of alkylcopper reagents to terminal alkynes produced vinyl cuprates regio-and stereospecifically. Several useful reactions of these intermediates were reported (eq. 10) [49,50]. The reaction of perfluoroalkylcuprates with propargyl bromides or alcohols resulted in allenes, produced by attack of the perfluoroalkyl group on the terminal acetylenic carbon with concommitant allene formation by displacement of Br or OH. Acetylenic iodides underwent



replacement of I by the perfluoroalkyl group to give perfluorosubstituted alkynes [51]. The copper-catalyzed addition of alkyl and arylsulfonyl bromides to phenylacetylene to produce α-bromo-β-sulfonyl styrenes has been reported [52].

Metal-catalyzed decomposition of α-diazoesters and ketones to produce carbenes was the subject of several studies. The reaction of styrene with ethyldiazoacetate catalyzed by the *chiral* cobalt complex *Bis*[(+)-Camphorquinone dioximato]Co(II) led to an overall 91% yield of the *cis* and *trans* 1-carbethoxy-2-phenylcyclopropanes. In both isomers the 1S,2S enantiomer was obtained in 70% excess [53]. The use of $CuSO_4$ or CuCl to catalyze the decomposition of diazoesters and ketones increased the yield of insertion of the carbene into cyclohexane from <1% in the absence of catalyst to 9-24% in the presence of catalyst. Diphenyl diazomethane did not insert under any conditions, indicating that conjugation of the copper carbenoid with a carbonyl group is crucial for intermolecular C-H insertion [54]. Cupric sulfate was also used to catalyze the reaction of methyl diazoacetate with $CH_3C{\equiv}C\text{-}SEt$ to give $CH_3C{\equiv}C\text{-}SCH_2COOMe$ in 35% yield [55].

Titanium compounds were used to promote several interesting organic reactions. The use of $LiAlH_4$ in conjunction with $TiCl_3$ to reductively couple ketones to symmetrical olefins was the key step in the conversion of retinal to β-carotene (85% yield). The reaction was general, and proceeded in high yield under mild conditions. Aldehydes were converted to *trans olefins*. The reagent also converted 1,2-diols to olefins [56]. The condensation of ketene with ketones to produce β-hydroxy esters (eq. 11) was catalyzed by



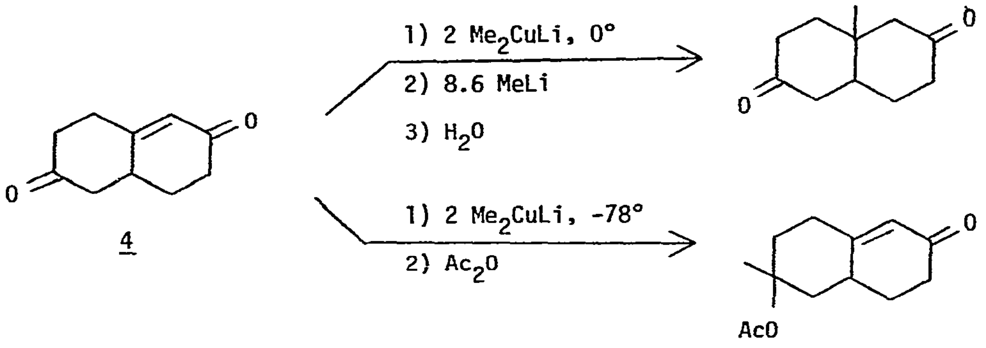
(11)

$Ti(OR)_4$. Sterically hindered 3° ketones resulted in lower yields, while easily enolized ketones failed altogether [57]. The condensation of active methylene compounds such as $(MeCO)_2CH_2$ [58] and $EtO_2CCH_2PO(OEt)_2$ and $CH_2[PO(OEt)_2]_2$ [59] with aldehydes and ketones to produce alkylidene compounds such as $R_1R_2C{=}C[PO(OEt)$ was promoted by $TiCl_4$. Yields were 50-90%. The reaction between benzylphenylsulfi anion and acetophenone to produce methyl stilbene was also promoted by $TiCl_4$ [60].

A general review entitled "Prescriptions and Ingredients for Controlled C-C Bond Formation with Organometallic Reagents" has recently been published [61].

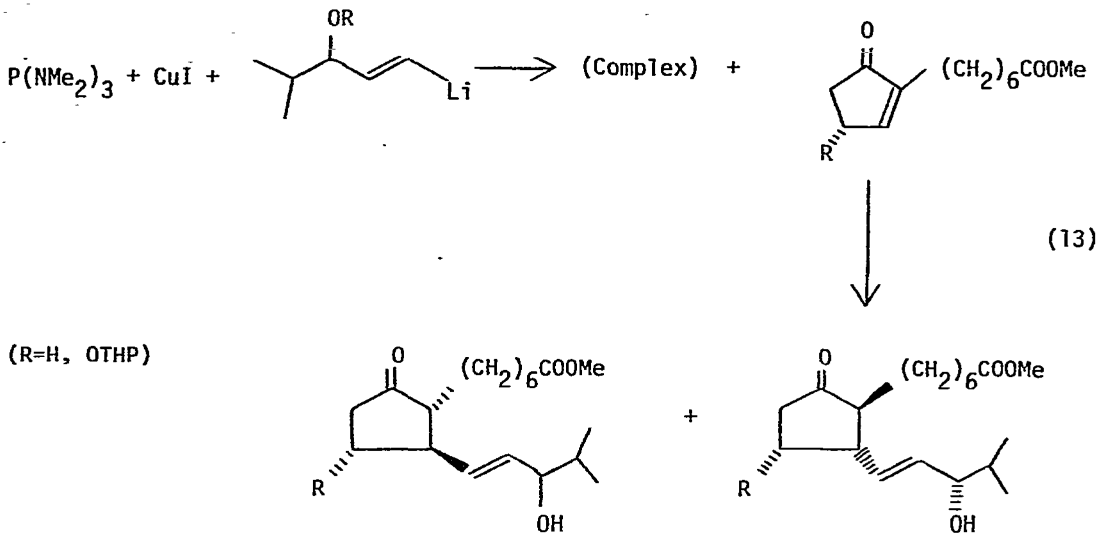
B. Conjugate Additions

Organocuprates continue to be the reagents of choice for effecting 1,4 addition to conjugated enones. In a thorough study [62] of the reaction of lithium dimethylcuprate with enedione 4 it was found that 1,4 addition to the conjugated ketone occurred at 0° in the presence of excess methyllithium while 1,2 addition to the saturated ketone predominated at -78° (eq. 12).



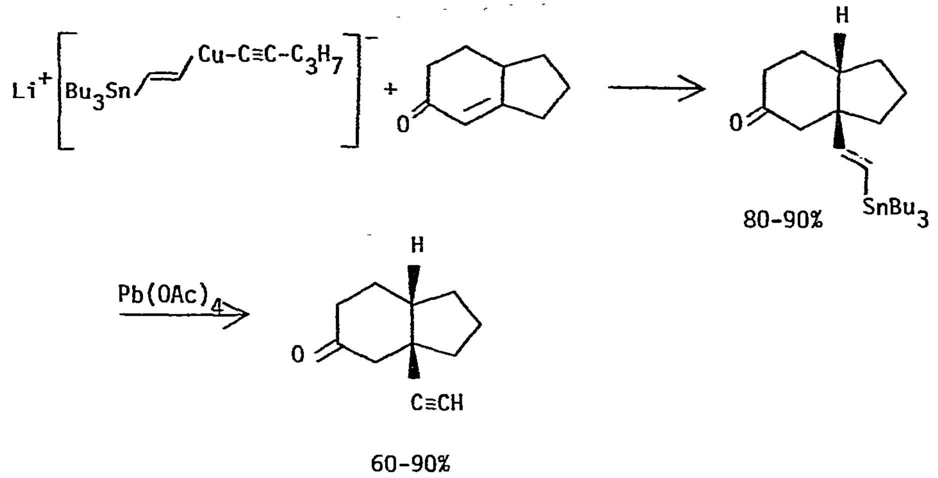
(12)

This is the first reported instance of predominant 1,2 attack by lithium dimethylcuprate when the possibility for 1,4 attack is present. The conjugate addition of lithium bis-(2-propenyl)cuprate to cyclohexenone has been reported, as has the oxidative coupling of the reagent to produce 2,4-dimethylpenta-1,4-diene [63]. Cyclohexenone reacted with the dialkylcuprate resulting from $CH_2{=}C(SiMe_3)Li$ and CuI to give the 1,4 adduct containing the vinyl trimethylsilyl group in greater than 90% yield [64]. A mixed hexamethyl phosphorous triamide-alkenyl cuprate reagent was used to synthesize members of the prostaglandins according to eq. 13 [65]. This use points out the remarkable selectivity and



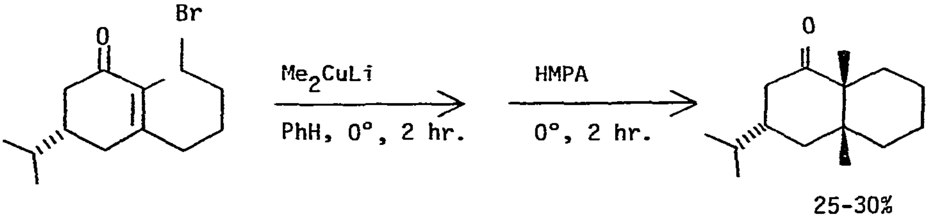
(13)

tolerance of functionality offered by organocuprate reagents. Alkynyl cuprates lack sufficient reactivity to transfer the alkynyl group to conjugated enones. To overcome this difficulty a mixed cuprate containing an ethynyl group equivalent (Bu$_3$Sn ) was synthesized and reacted with a variety of conjugated ketones (eq. 14) [66]. This reagent supplies a nucleophilic ethynyl group equivalent, and permits the facile introduction of an angular ethynyl group into fused ring systems.



(14)

Direct intramolecular alkylation of the enolate resulting from 1,4 alkylation of a cyclohexenone derivative by lithium dimethylcuprate was used to synthesize bicyclic products in moderate yield (eq. 15) [67]. Similar studies of intermolecular alkylations have also been reported [68]. Finally, dialkylcuprates were reported to monoalkylate pyridine in the 4 position in the presenc of methyl chloroformate to produce N-carbomethoxy-4-alkyl-4-hydropyridine in 56-86% yield. The alkyl groups studied were Me, Et, i-Pr, n-Bu, <u>sec</u>-Bu, Ph and <u>p</u>-tolyl [69].



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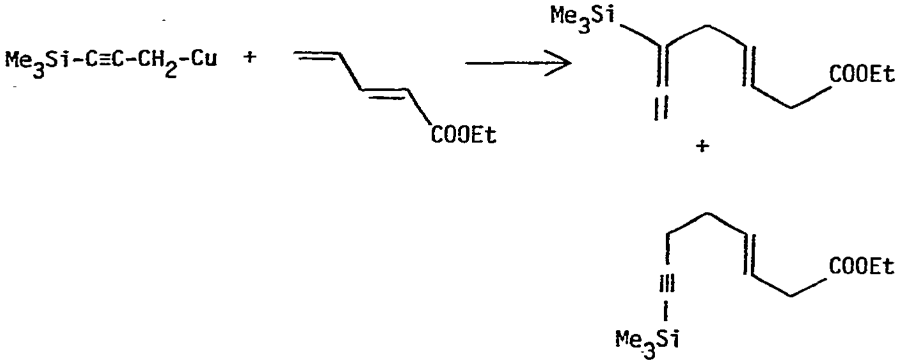
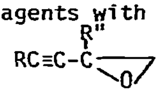
Monoalkylcopper(I) complexes have found increasing utility in organic synthesis. 1-Trialkylsilylcopper reacted with ethyl penta-2,4-dienoate to produce a 4:1 mixture of the 1,5 allenic and 1,5-acetylenic esters in overall

80% yield (eq. 16) [70]. The facile cleavage of the vinyl- and alkynyl trimethylsilyl group led to the free alkyne or allene.



(16)

Monoalkyl copper(I) complexes were reacted with 1-alkynyl sulfoxides (RS(O)C≡CR') to produce vinyl sulfoxides (RS(O)CH=CR'R") after hydrolysis of the vinyl copper species. The reactions went in high yields with almost exclusive cis stereoselectivity [71,72]. The related stereospecific addition of Grignard reagents to 1-alkynyl sulfides in the presence of Cu(I) halides has also been reported [73]. Excellent yields of the corresponding vinyl sulfides (RR'C=CHSMe) were obtained, again with high cis stereoselectivity.

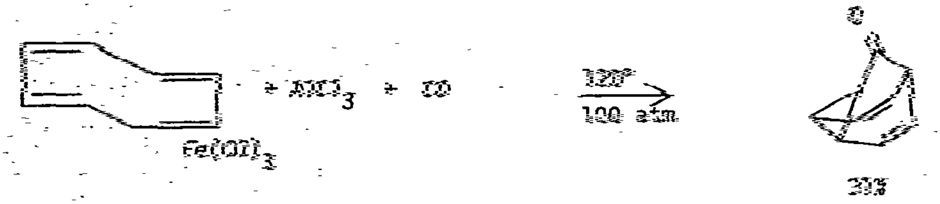
Copper catalyzed reactions of Grignard reagents with unsaturated epoxides resulted in predominantly 1,4 addition. Thus,  $RC{\equiv}C\text{-}\overset{R''}{C}(\text{-}O\text{-})CH_2$ reacted with R'MgBr-Cu to produce RR'C=C=CR"CH_2OH in greater than 90% yield (R=Me, Ph, $(EtO)_2CH$; R'=Et, Me_2CH, Bu, Ph, Me; R"=Me, Me_3C) [74]. Similarly, butadiene monoepoxide reacted with phenyllithium and $Cu(OAc)_2$ to give predominantly the 1,4 adduct [75]. The allenic ether $H_2C=C=CHOCH_3$ reacted with RMgX and CuX in a similar fashion to give $RCH_2C{\equiv}CH$ in 75-92% yield [76]. Ethylcrotonate reacted with $(PhC{\equiv}CH)Co_2(CO)_6$ to produce PhCH=CH-C(CH_3)=CHCOOEt in 45% yield. Acrylonitrile and crotonaldehyde were similarly reactive [77]. The oxidative coupling of ketones and enol esters by manganic acetate to produce 1,4-diketones has also been reported [78].

C. Carbonylations

Transition metal complexes offer one of the few methods for the carbonylation of organic substrates, and several new methods have been developed during the past year. The palladium(II) complex $PdCl_2(PPh_3)_2$ was used to catalyze the carbonylation of aromatic, vinyl, and heterocyclic aromatic halides, as well as aromatic acid halides. In the presence of a tertiary amine, CO (1200 psi), and H_2 at 80-150° the corresponding aldehydes were produced in 60-90% yields. This system was limited to substrates lacking β hydrogens [79]. When the same classes of halides were instead treated with CO, a primary amine and a tertiary amine at 100° in presence of the same catalyst the corresponding amide was obtained in 60-90% yield [80]. A palladium(0) catalyst was used to convert aryl, vinyl, and benzyl halides to the corresponding esters in 30-90% yield in the presence of CO, in alcohol and a tertiary amine [81]. Allyl chloride has been converted to the acid chloride by carbonylation in the presence of π-allylpalladium chloride complex catalysts [82].

The hydroformylation of olefins by CO and H_2 using $Rh_6(CO)_{16}$ has been studied. The active catalyst was shown to be $Rh(H)(CO)_3$ [83]. The use of Rh or Co catalysts with chiral ligands as hydroformylation catalysts with styrene and internal olefins has been studied. Cis-2-butene was converted to 2-methylbutanol with a 27% optical yield [84].

Iron carbonyl compounds have been used to both cyclize and carbonylate a variety of organic substrates. 5-Acetylindanone was prepared by the treatment of 1,2-bis(bromomethyl)benzene with $Fe(CO)_4^{=}$, followed by acetyl chloride, followed by $AlCl_3$ [85]. A similar cyclization-carbonylation was carried out on the cyclooctatetraene iron tricarbonyl complex (eq. 17) [86]. Strained olefins (eq. 18) [87] and cyclopropenes (eq. 19) [88] react with $Fe(CO)_5$ to form cyclic carbonylated products.



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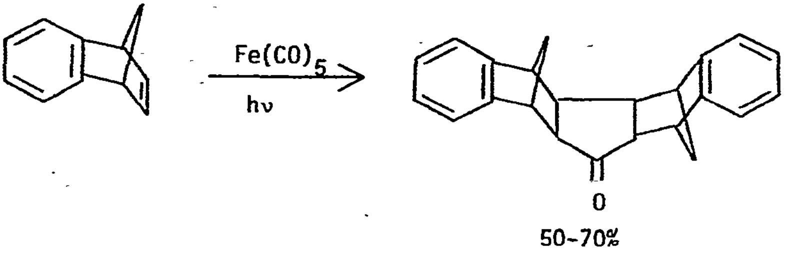

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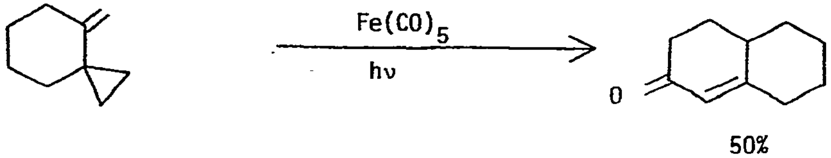
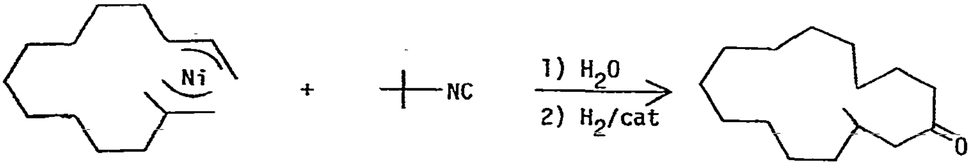


(19)

Cp_2TiCl_2 reacted with $Li(CH_2)_4Li$ followed by CO to produce cyclopentanone [89]. Muscone 5 resulted in 40% yield from the treatment of bis-π-allylnickel complex 4 with t-butyl isonitrile followed by hydrolysis and reduction (eq. 20) [90].



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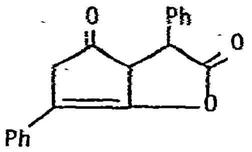
(20)

Phenylacetylene was carbonylated using $Rh_4(CO)_4Cl_2$ as catalyst to produce compound 6. No yields were reported [91].



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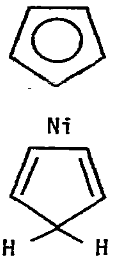
Vinyl cuprates reacted stereospecifically with CO_2 in the presence of $(EtO)_3P$ to produce α-ethylenic acids in high yield. HMPA was the solvent of choice [92]. The carboxylation of olefins by $Cu(CO)_3^+$ (formed in situ from Cu_2O and CO) in the presence of BF_3, CO and catalytic amounts of H_2O has been reported [93]. Rearrangements and carbon-carbon bond cleavage in these reactions, for which no yields were given, have been reported. A review on transition metal-carbon σ bond scission which contains reference to carbonylation reactions has recently appeared [94].

The decarbonylation of both α- and β-diketones to monocarbonyl complexes by $Rh(Cl)(PPh_3)_3$, $Rh(Cl)(CO)(PPh_3)_2$, and $RhCl_3 \cdot 3H_2O$ in toluene has been reported [95]. Finally, the decarboxylation of tryptophan to tryptamine catalyzed by $Cu(OAc)_2$ or $Zn(OAc)_2$ in solvents such as HMPA, DMSO, ethylene glycol or phenol has been studied [96]. The reaction proceeds through a metal chelate complex.

D. Oligomerization

The use of $Pd(PPh_3)_2$ (maleic anhydride) to dimerize isoprene has been reported. The dimerization occurred exclusively tail to tail to produce 2,7-dimethyl-1,3,7-octatriene [97]. Similar results were obtained using $Pd(AcAc)_2$, Ph_3P and m-methoxybenzaldehyde [98]. 2-Ethyl-1,3-butadiene is similarly dimerized. The maleic anhydride complex also catalyzed the codimerization of isoprene and 1,3-butadiene to give mainly (70%) 7-methyl-1,3,7-octatriene, as well as some (30%) 2-methyl-1,3,7-octatriene. (Cyclopentadienyl)cyclopentadiene nickel 7 catalyzed the dimerization of ethene to 1-butene at 145° [99]. The reaction led to an 80% yield of dimers consisting of >90% 1-butene. During the reaction the cyclopentadienyl group remained coordinated while the cyclopentadiene group was labile.

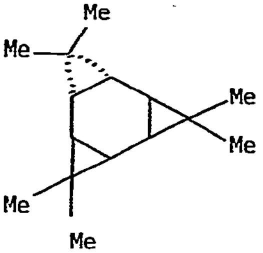


7

The photodimerization of norbornene and related olefins [100] and of cyclohexene, cyclopentene,and cycloheptene [101] using Cu(I) trifluoromethanesulfonate as a catalyst led to a marked increase in yields compared to other Cu(I) complexes studied. This complex also led to mixed photodimerizations. The photodimerization of N-vinylcarbazole was catalyzed by $Cu(ClO_4)_2 \cdot 6H_2O$ [102]. The quantum yield was greater than 1, suggesting a chain mechanism. At concentrations greater than 0.05 M, polymer rather than dimer was obtained. The synthesis of cyclobutanes from photochemical, metal catalyzed, and cation radical induced dimerization of olefins has recently been reviewed [103].

The ring opening of bicyclobutane and its addition to methyl acrylate was catalyzed by bis(cyclooctadiene)nickel [104]. The products were a 63:37 mixture of cis and trans 1-allyl-2-carbomethoxycyclopropane in 62% overall yield. Norbornadiene was dimerized to produce exo-5-o-tolyl-2-norbornene in 70% yield using $NiBr_2(Bu_3P)_2$ in R_2NH [105]. 1,1-Dimethylcyclopropene was cyclotrimerized to 8 in 100% yield by $Pd(PPh_3)_4$ at 40-45° [106].

The cyclic dimerization of butadiene to produce mixtures of 1,5-cyclooctadiene and 4-vinylcyclohexene was catalyzed by $CoCl(PPh_3)_3$ at 60° [107]. Butadiene and 2-vinylfuran were copolymerized by a mixture of $Ni(AcAc)_2$, $P(OPh)_3$ and Et_3Al to give furan 9 in 90% yield [108]. Butadiene reacted with



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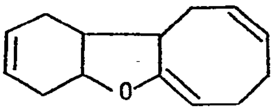
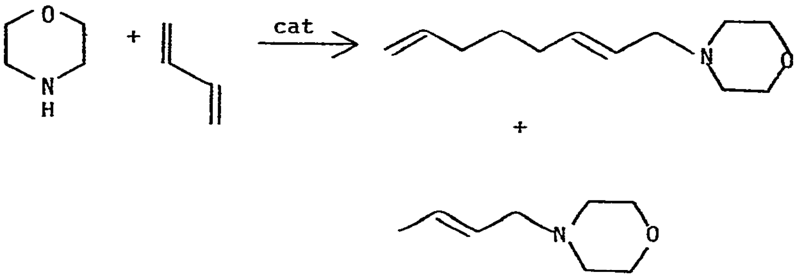


9

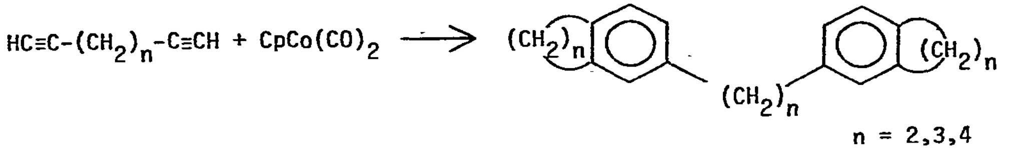
the N-methylimine of benzaldehyde in the presence of a $Pd(NO_3)_2/PPh_3$ catalyst to produce N-methyl-2-phenyl-3,6-divinylpiperidine [109]. Morpholine reacted with butadiene in the presence of a $Ni(AcAc)_2/P(O-\langle\;)_3$ catalyst to give a mixture of N-(2-butenyl)morpholine (32%) and the morpholine terminated linear dimer (51%) (eq. 21) [110]. A similar reaction between butadiene and nitroalkanes in the presence of a mixed Pd(0)-phosphine complex catalyst led to nitroalkanes containing the 1,6-octadiene side chain in the α-position [111]. Both of these reactions appear to involve π-allylpalladium intermediates, and depend on the presence of phosphites for catalytic activity.



(21)

The copolymerization of butadiene and ethylene to produce mixed hexadienes was catalyzed by $Ni(Ph)(Cl)(PPh_3)_2$ in the presence of $BF_3 \cdot Et_2O$. The reaction kinetics of this process were studied [112]. The polymerization of cyclohexadiene with ethylene in the presence of an Ni catalyst to produce methylvinyl cyclohexenes and butenylcyclohexenes has been reported. Cycloheptadiene and cyclooctadiene copolymerizations with ethylene were also studied [113]. Finally the reaction of benzcyclopropane with butadiene to give vinylindane (64%) and 1-phenyl-2,4-pentadiene (26%) under catalysis by Ag^+ has been reported [114].

The oligomerization of alkynes by transition metals has been the subject of much recent study, and has resulted in the synthesis of some very unusual cyclic organic compounds. Terminal alkynes such as $HC{\equiv}C\text{-}CR_2OH$ were cyclotrimerize to 1,3,5 tri(-CR_2OH) benzenes in 56-84% yield by $NiBr_2(Bu_3P)_2$ [115]. Cyclopentadienylcobaltdicarbonyl was used to convert α,ω-dialkynes to benzocycloalkanes (eq. 22) [116]. Other unusual alkyne cyclizations are depicted in eq. 23 [117], 24 [118] and 25 [119].



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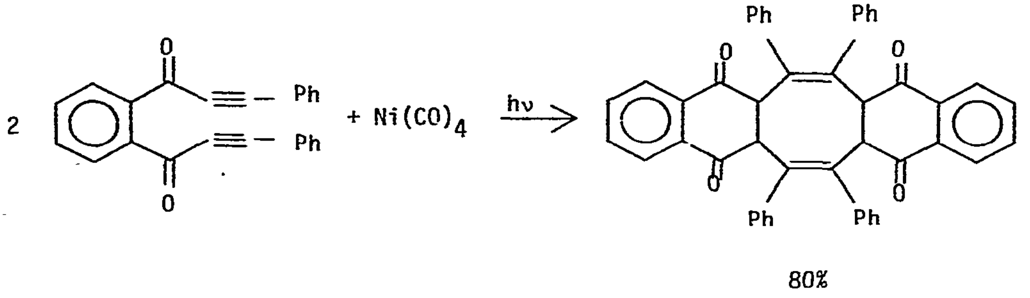

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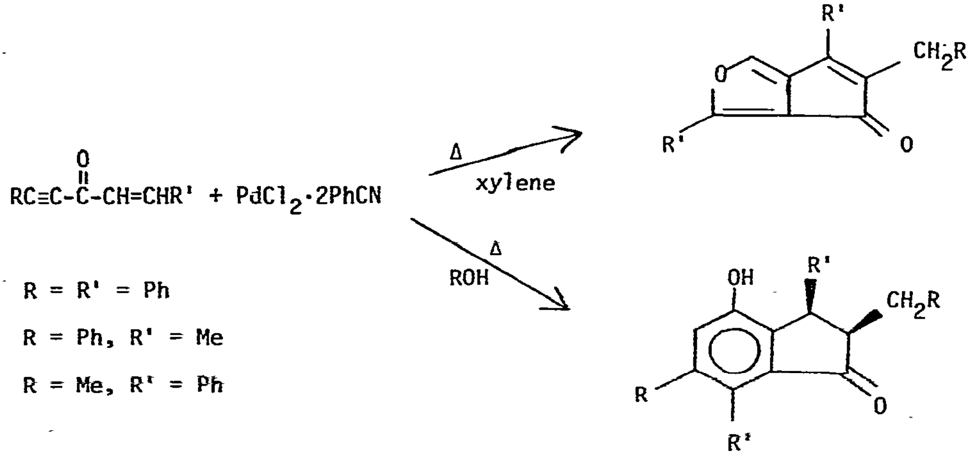

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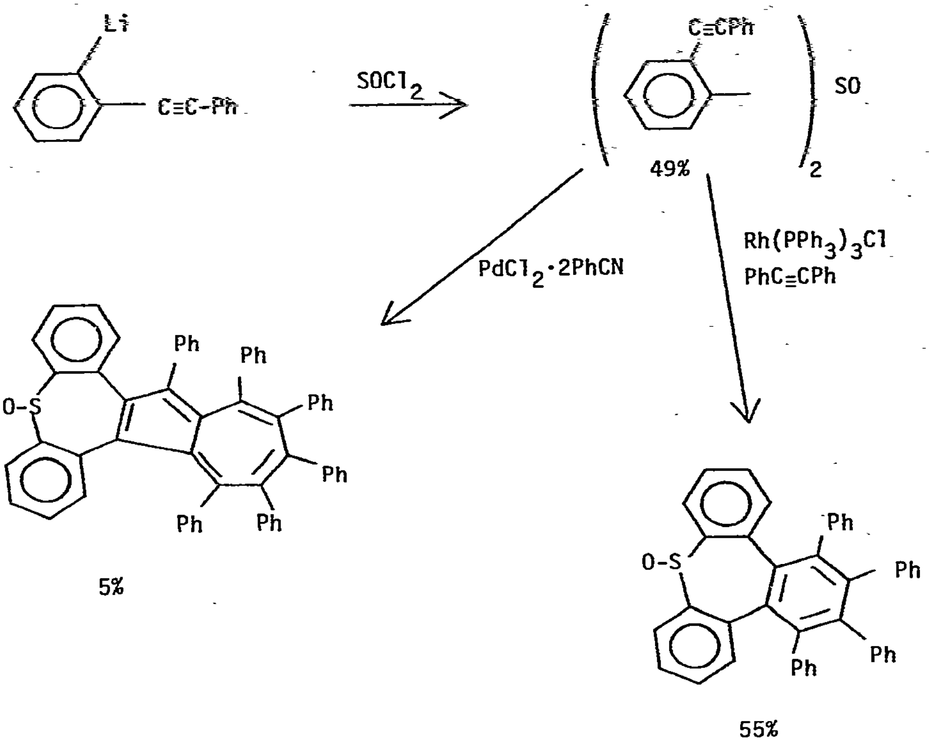
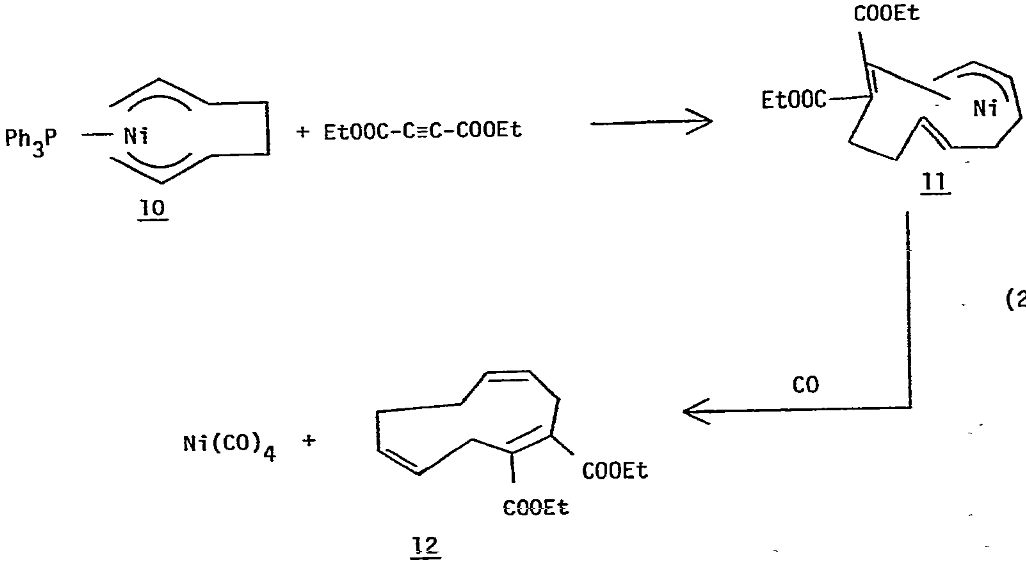


Li
C≡C-Ph
SOCl₂
C≡CPh
SO
49%
2
PdCl₂·2PhCN
Rh(PPh₃)₃Cl
PhC≡CPh
O-S
Ph
Ph
Ph
Ph
Ph
Ph
5%
O-S
Ph
Ph
Ph
Ph
55%

(25)



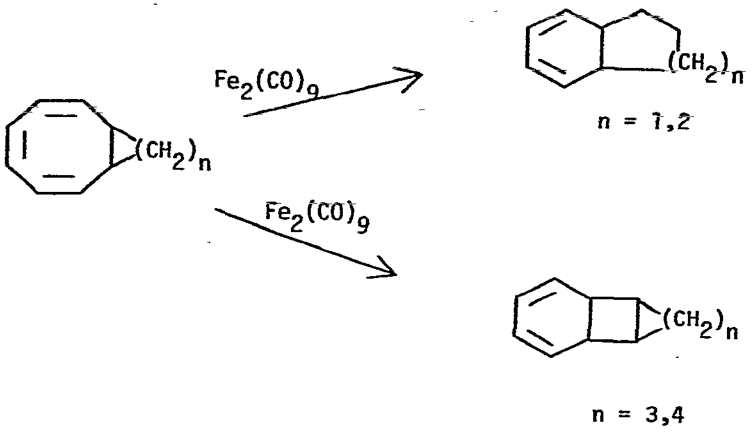
Ph₃P
Ni
10
+ EtOOC-C≡C-COOEt
COOEt
EtOOC
Ni
11
CO
Ni(CO)₄
+
COOEt
COOEt
12

(26)

A model for the nickel(0) catalyzed cyclooligomerization of butadiene and alkynes has been developed [120]. The α,ω-octadieneoylnickel-triphenylphosphi complex 10 was treated with EtOOCC≡CCOOEt to produce complex 11, which was isolated in 30% yield and characterized. Treatment of this complex with CO produced $Ni(CO)_4$ and the cyclooligomer 12 (eq. 26). Similar intermediates are inferred to be involved in the catalytic cyclooligomerizations of butadienes and alkynes. The oligomerization of acetylenes on transition metal complexes has recently been reviewed [121].

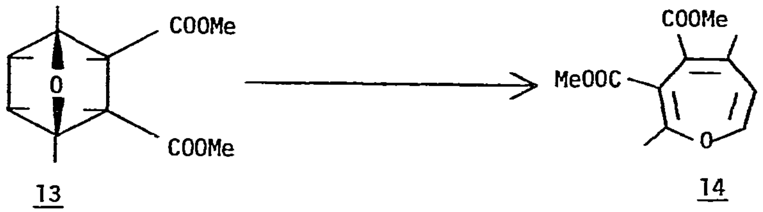
E. Rearrangements

The use of transition metals to catalyze rearrangements in strained ring system is a rapidly expanding area of research. A careful investigation of the rearrangement of bicyclo[3.1.0]hex-2-enes to a mixture of carbomethoxycyclohexadienes by $RhCl(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$ was found to require O_2 to proceed at a moderate rate [122]. Since this observation puts the structure of the catalytically active species in doubt, current hypotheses concerning the mechanism of this reaction will require some revision. Cuprous chloride was used to catalyze the reaction of diazomethane with phenycyclobutane to produce 4-phenyl [3.1.0]bicyclopentane. Ring opening of this compound was best effected by ZnI_2 catalyst to produce 3-phenylcyclopent-1-ene. Rhodium and silver catalysts were found to be less regiospecific than zinc [123]. The effect of metal carbonyls on the rearrangements of bicyclo[6.n.0]trienes has been reported [124]. The results are summarized in eq. 27. The conversion of cytooctatetraene oxide to 1-formylcycloheptatriene was catalyzed by a variety of transition metal compounds [124].

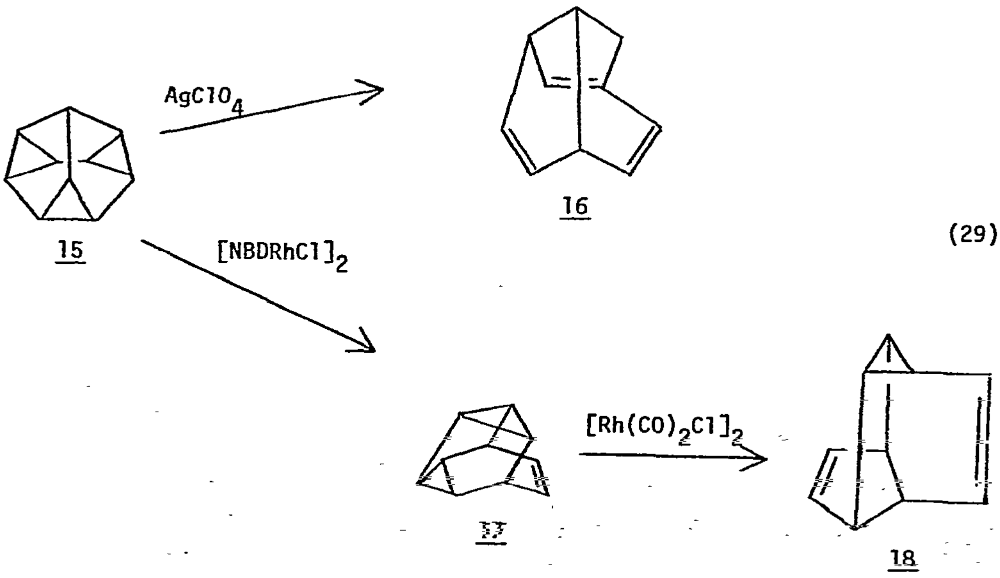


(27)

Metal catalyzed rearrangements of oxoquadricyclanes formed the basis of a new oxepine synthesis. Thus compound 13 reacted with either $PtCl_2\cdot 2PhCN$ or $[Rh(CO)_2Cl]_2$ to form oxepine 14 in 60-70% yield (eq. 28) [125]. Diademane (15)

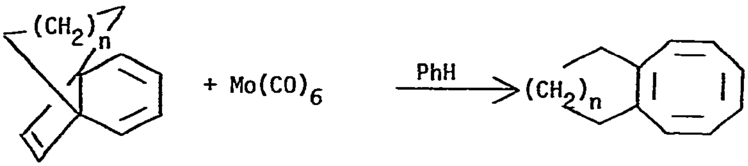


(28)



(29)

was rearranged to triquinacene (16) by $AgClO_4$ while norbornadiene rhodium chloride dimer as catalyst caused snoutene (17) to be produced (eq. 29) [126]. In turn snoutene was further rearranged to tetracyclodecadiene 18 by $[Rh(CO)_2Cl]_2$ as catalyst [127]. A careful study of the mechanism and stereochemistry of the Ag(I) catalyzed rearrangement of 1,3 disubstituted [4.1.0.0] tricycloheptanes to predominantly substituted bicyclo [3.2.0] hept-6-ene products has appeared [128]. Treatment of [4.4.2]propella-2,4,11-triene with $Mo(CO)_6$ in dry benzene resulted in isomerization to 1,2-tetramethylene cyclooctatetraene (eq. 30). Studies with the homologous [5.4.2] propellatriene showed that the rearrangement was general, and positionally specific [129]. The rearrangement depicted in eq. 31 was catalyzed by $PdCl_2 \cdot 2PhCN$ [130].



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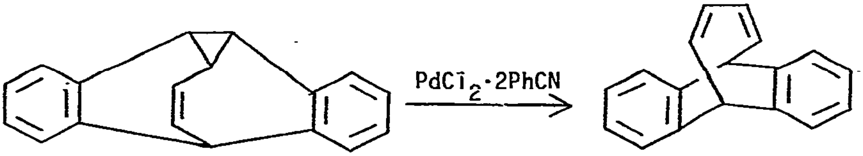
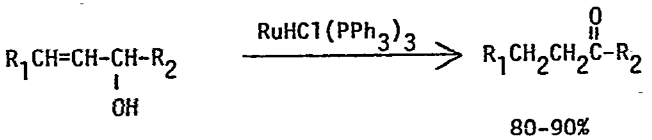


(31)

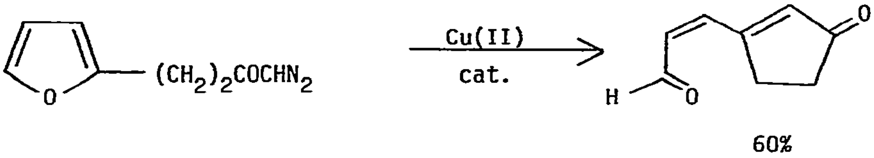
Trans-stilbene oxide was rearranged to $PhCOCH_2Ph$ in 88% yield using $RhCl(PPh_3$ at 210° [131]. The use of $RuHCl(PPh_3)_3$ to catalyze the rearrangement of allylic alcohols to saturated ketones via the initially formed enol (eq. 32) was a high yield process [132]. A mixture of H_2PtCl_6 and $SnCl_2$ was reported to rearrange γ,δ unsaturated esters to β,γ unsaturated esters in alcohol solvents, and to reduce them to saturated esters in acetic acid solvents [133]. Copper(II) salts



$$R_1CH{=}CH{-}\underset{OH}{\underset{|}{C}H}{-}R_2 \xrightarrow{RuHCl(PPh_3)_3} R_1CH_2CH_2\overset{O}{\overset{\|}{C}}{-}R_2 \qquad (32)$$

80-90%

were used to catalyze the decomposition of diazoketone 19 to rearranged keto-aldehyde 20 in fair yield (eq. 33) [134]. Dibenzylidene cyclohexanones were rearranged to phenols by $IrCl(CO)(PPh_3)_2$ at 250° (eq. 34) [135]. Thirteen examples of this rearrangement were cited.



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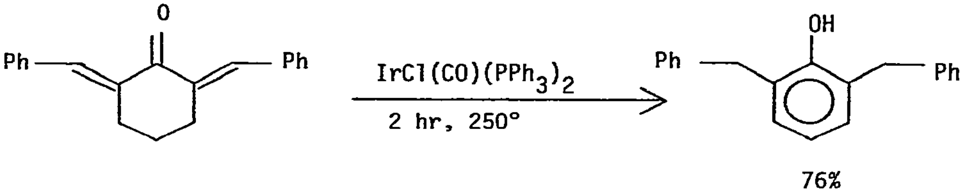
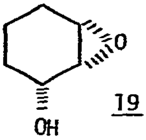


(34)

(Diphenylcarbene)pentacarbonyltungsten(o) reacted with ethyl vinyl ether at 37° to produce 1,1-diphenyl-2-ethoxycyclopropane in 65% yield. With 2-methylpropene,1,1-diphenylethene was obtained in 76% yield, while 2-butene led to 1,1-diphenyl-1-propene in 54% yield. In the last two cases the source of the methylene fragment was clearly the alkene. These experiments demonstrated the scission of the carbon-carbon double bond of the alkene and the combination of the resulting methylene fragment with the diphenyl carbene group of the initial tungsten complex [136].

III. OXIDATIONS

Transition metals have traditionally played a major role in the oxidation of organic substrates. Many new and useful oxidizing systems have recently been developed. Solid nickel peroxide, readily obtained from nickel salts and NaOCl in basic solution, oxidized PhCH(OH)CH(OH)Ph in ether or benzene to benzil in 98% yield. No C-C bond cleavage was observed [137]. Sodium tungstate catalyzed the oxidation of diazines and diazanaphthalene, some of which were decomposed by peracids, to the corresponding <u>bis</u>-N-oxides. The reaction proceeded <u>via</u> the mono N-oxide [138]. Similarly, $Mo(CO)_6$ or $Mo_2(dpm)_2$ catalyzed the reaction of t-butylhydroperoxide with substituted azobenzenes to give the corresponding azoxy derivatives. The yields in this reaction compared favorably with those obtained from oxidations using peroxyacids [139]. The dioxygen complex of palladium, $Pd(O_2)(PPh_3)_2$ caused the deoximation of ketoximes, producing ketones in high yield. The reaction even worked well with the oximes of camphor and pinacolone [140].



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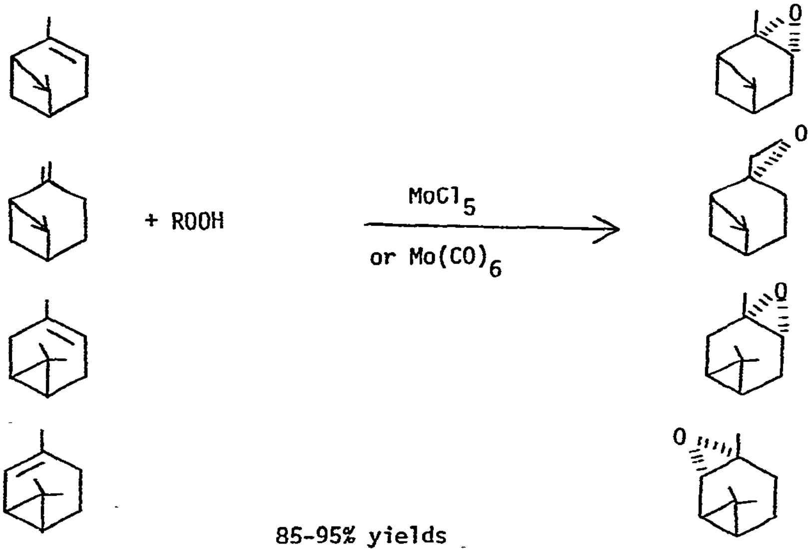


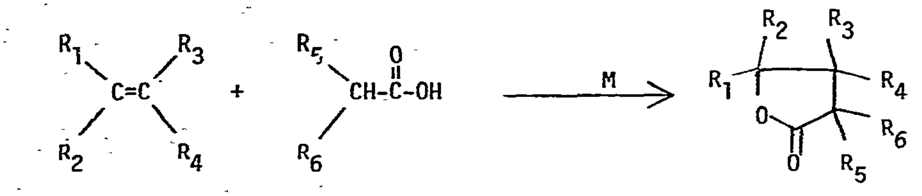
(35)

85-95% yields
high stereoselectivity

Several new systems for the oxidation of olefins have been developed. Cyclohexene was oxidized to 19 by $CpV(CO)_4$ in good yield, and 99% stereoselectivity [141]. Similarly, $MoCl_5$ or $Mo(CO)_6$ catalyzed the epoxidation of a variety of olefins by hydroperoxides in high yield and high stereoselectivity (eq. 35) [142], as did Mo or V acetylacetonate complexes [143]. Catalysts for epoxidation of olefins by hydroperoxides have been reviewed [144].

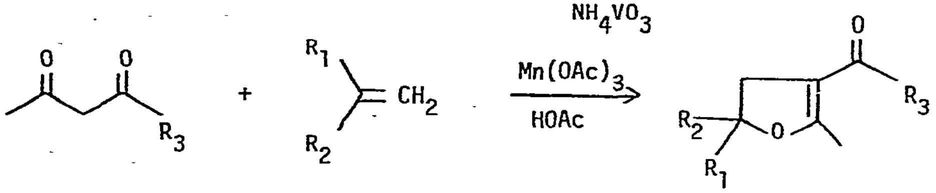
The oxidation of olefins to ketones by molecular O_2 has been catalyzed by $RhH(CO)(PPh_3)_3$ or $RhCl(PPh_3)_3$. The reaction between 1-hexene, 1-heptene or 1-octene and O_2 to produce the methyl alkyl ketone proceeded at ambient temperature and pressure in benzene. Mechanistic arguments concerning the structures of the intermediates involved were made [145]. The use of a $PdCl_2$ catalyst in aqueous sulfolane oxidized 3,3-dimethylbut-1-ene in >90% yield [146]. The study of the $CuCl_2$ promoted oxidation of olefins to chloroacetates or diacetates by $PdCl_2$ in acetic acid were extended to other metals such as $RhCl_3$, $IrCl_3$ and $PtCl_2$, which proved to be the best catalyst for the above transformation [147]. Silver oxide (Ag_2O) was used to catalyze the oxidative carboxylation of olefins, alcohols and saturated alkanes by carbon monoxide in sulfuric acid at room temperature. This system converted appropriate substrates to tertiary carboxylic acids in high yields. Since the reaction proceeded via carbonium ions its use was restricted to substrates which produced stable 3° carbonium ions upon protonation [148]. Dialkyloxalates were prepared in good yield by oxidative carbonylation in the presence of alcohols and dehydrating agents, using a palladium based redox system and molecular oxygen [149].

The metal catalyzed oxidative addition of activated methylene compounds to olefins has been used to synthesize several interesting heterocyclic compounds. Carboxylic acids reacted with olefins in the presence of $Mn(OAc)_3 \cdot 2H_2O$, $Ce(OAc)_4$ or NH_4VO_3 to produce γ-lactones in 25-55% yields (eq. 36). Twenty-three lactones were prepared in this fashion [150]. Similarly β-diketones or β-oxoesters were added to olefins using $Mn(OAc)_3 \cdot 2H_2O$ catalyst to produce carbonyl substituted furans in high yield (eq. 37). The same catalyst was used to effect the addition of cyclohexanone to isopropenyl acetate to produce 2-acetonylcyclohexanone in moderate yield [151].



(36)

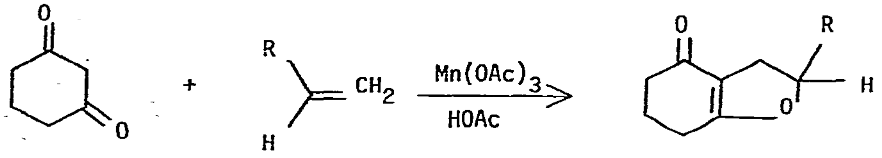
M = $Mn(OAc)_3 \cdot 2H_2O$ 25-55%
$Ce(OAc)_4$
NH_4VO_3



R_3 = Me, OEt

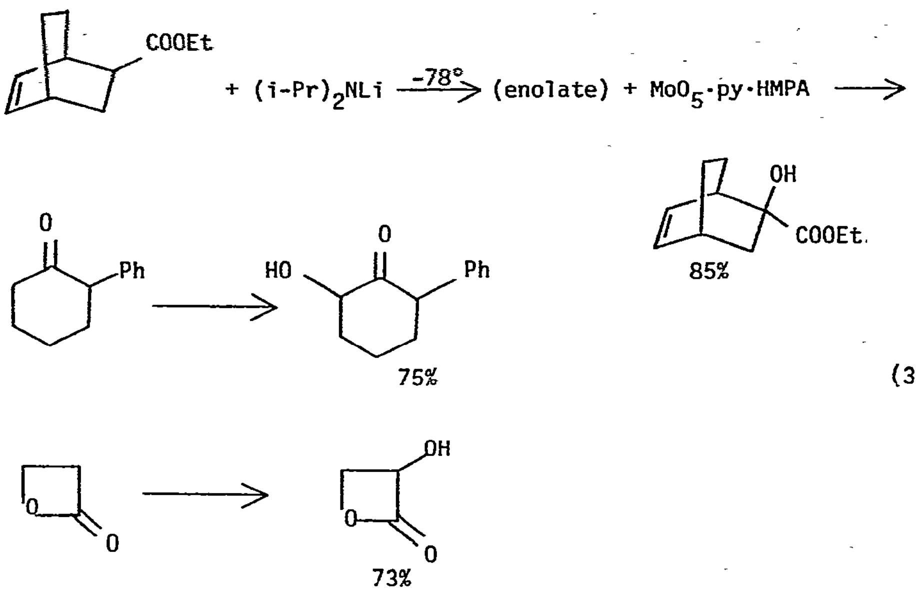
R_1 = Ph, Me, C_6H_{13}
R_2 = Me, H, Pr

(37)



R = Me, Pr

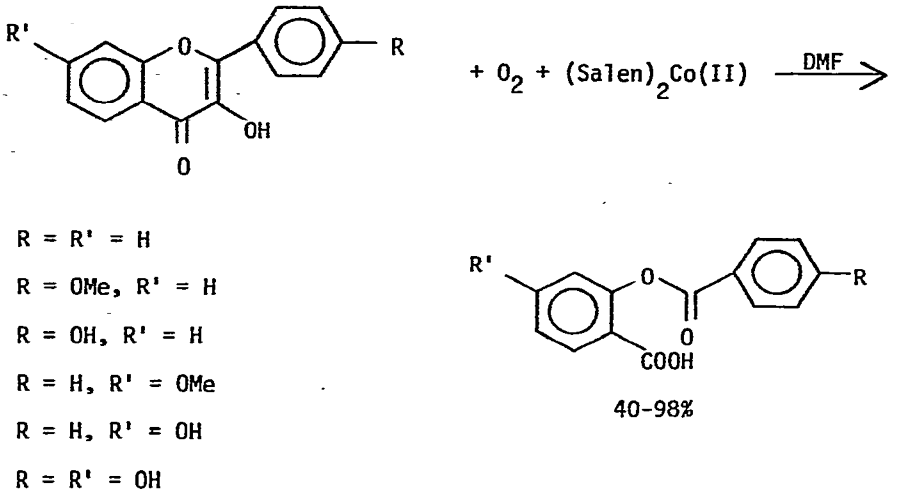
Several new methods for the oxidation of active methylenes have recently een developed. An extremely useful and promising procedure for the -hydroxylation of esters, ketones and lactones having α protons consists of orming the lithium enolate of the carbonyl compound with lithium diisopropyl mide, followed by treatment with a slight excess of the MoO_5·pyridine·HMPA omplex. The α-hydroxy carbonyl compounds were obtained in 50-80% yield [152]. xamples of this procedure appear in eq. 38. N-acylpiperidines were oxidized t the α position by RuO_4 to produce the corresponding 2-piperidones and/or



(38)

the 2,6-piperidiones [153]. Cobalt(II) naphthenate was used to catalyze the O_2 oxidation of cyclohexene to cyclohexen-3-ol in greater than 80% yield. The reaction proceeded via a radical process [154]. Picolines and methyl quinolines were oxidized to carboxy pyridines and quinolines by $PdCl_2$ and H_2O_2. In the absence of $PdCl_2$, N-oxides were obtained with picolines [155].

Terminal alkynes were oxidatively chlorinated to alkynyl chlorides by $CuCl_2/FeCl_3$ mixtures in 4 M aq NH_4Cl [156]. The selective remote oxidation of alkyltrifluoroacetates by Fe(II)-$Et_3N{\rightarrow}O$ complexes in trifluoroacetic acid has been reported [157]. Thus, 1-octyl trifluoroacetate was oxidized at the 7 position to give 1,7-bis(trifluoroacetoxy)octane with 72% position selectivity. Evidence for both polar and steric influences on this selectivity was presented. Catechol was oxidatively cleaved to 1-carboxy-4-carbomethoxybutadiene by O_2 in methanol using CuCl as a catalyst [158]. 3-Hydroxyflavones were oxidatively cleaved to phenyl benzoates by O_2 using (salen)$_2$Co(II) catalyst in DMF (eq. 39). The reaction was fairly general and went in moderate to high yield [159].



(39)

R = R' = H

R = OMe, R' = H

R = OH, R' = H

R = H, R' = OMe

R = H, R' = OH

R = R' = OH

IV. REDUCTION

Catalytic transfer hydrogenation has been used in stereoselective reductions of ketones to alcohols. The degree and direction of stereoselectivity depended on the conditions used. Thus, 4-t-butylcyclohexanone and cholestanone were reduced using $(NH_4)_2IrCl_6$ as catalyst and isopropanol as the hydrogen source in aqueous piperidine to give 23-30% axial alcohol. When the same reaction was run in aqueous dimethylsulfoxide with the same systems. 66-78% axial alcohol was obtained. Use of anhydrous dimethylsulfoxide led to ethers of the ketone and the alcohol used as a hydrogen source [160]. This study was extended to other metal catalysts and 4-t-butyl-, 3-t-butyl-, 2-methyl-, and 3,3,5-trimethylcyclohexanones as substrates [161]. Ruthenium based catalysts were the best of the complexes studied. Catalytic transfer hydrogenation has been reviewed [162,163].

A new copper-hydride reducing agent, Cu(H)(nBu)Li, has been developed [164]. This complex reduced aldehydes and ketones to alcohols, while esters were not reduced. Conjugated ketones were reduced to saturated ketones, while primary, secondary and tertiary alkyl halides, tosylates and mesylates were reduced to the corresponding hydrocarbons. All reductions proceeded in high yield, and no alkyl group transfer was observed. Treatment of bis-cyclopentadienyltitanium dichloride with sodium in benzene led to a species characterized as $[CpTi]_{1-2}$. This complex reduced aldehydes, esters and epoxides to the corresponding hydrocarbons in moderate yield [165].

The asymmetric hydrogenation of α-oxocarbonyl compounds using a chiral cobalt complex has been reported [166]. The complex used was a bis—dimethylglyoximato cobalt(II)-quinine complex, which reduced α-diketones to α-hydroxyketones with moderate optical yields. α-Ketoesters were reduced to α-hydroxy esters with 30-80% optical yields using R_2SiH_2 as the reducing agent and $CODRhCl_2$ in the presence of a series of chiral phosphines as the catalyst [167].

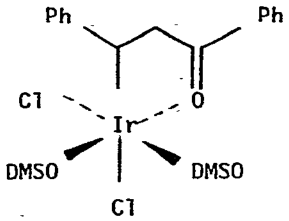
Iron carbonyl compounds have been used to effect the reductive alkylation of amines by aldehydes. Aniline was converted to dimethylaniline in quantitative yield by treatment with formaldehyde in ethanol for 1-2 days at 28° in the presence of CO and $KFe(H)(CO)_4$ [168]. Use of $Fe(CO)_5$ led to monoalkylation, aniline and formaldehyde producing methylaniline in 91% yield, while cyclohexanone and cyclohexylamine led to dicyclohexylamine in quantitative yield [169]. Secondary amines were reacted with alkyl aldehydes in the presence of $KFe(H)(CO)_4$ to produce tertiary amines in 60-80% yields [170].

Palladium chloride was treated with sodium borohydride to produce a catalyst which, in the presence of hydrogen, reduced carbon-carbon double bonds, carbon-nitrogen double bonds and nitrogen-oxygen double bonds, but did not hydrogenolyze C-N or C-O functional groups. Thirty cases were studied with this catalyst [171]. The kinetics of the reduction of a variety of alkynes to alkanes by $NaBH_4$ catalyzed by $PdCl_2 \cdot 2DMSO$ have been reported [172]. The reduction of a series of methylbutadienes by hydrogen using $NaBH_4$ treated $RhCl(PPh_3)_2DMSO$ complexes as catalysts led to small amounts (∿2 %) of alkane, and various mixtures of all possible monoene products [173]. Data for the hydrogenation of a number of alkynes over Co-Fe, Co-Ni, Fe-Ni and Co(III)AcAc-Co(II)AcAc complex catalysts has been collected [174]. Finally, the complex $HRh[(+)\text{-diop}]_2$

where diop = 2,3-O-isopropylidine-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane was prepared from the ligand and $RhCl_3 \cdot 3H_2O$ in ethanol in the presence of formaldehyde and KOH. This complex has potential application for the induction of chirality in the hydrogenation of prochiral olefins [175].

Conjugated carbonyl compounds were reduced to saturated carbonyl compounds by the mixed hydrido-cuprate $Li^+Cu(H)(R)$ where R was 1-pentynyl, t-BuO-, or PhS-. Other normally reducible functional groups were unaffected by the reagent. The reducing ability of the hydridocopper species depended on the nature of R, with the 1-pentyne complex being more strongly reducing than the PhS- or t-BuO- complex [176]. The chromous complex $Cr(ethylenediamine)_2(OAc)_2$ also reduced α,β-unsaturated ketones to saturated ketones in methanol [177]. The reaction was quite general and went in 50-80% yield. The reductions were shown to involve electron transfer. Copper catalyzed the hydrogen reduction of acrylaldehyde to propanal, while a Cu/Cd catalyst converted the same substrate to allyl alcohol in the presence of H_2 [178]. Cadmium alone showed no catalytic activity. Catalytic transfer hydrogenation was also used to reduce conjugated ketones to saturated ketones [179]. Isopropanol was used as the hydrogen source, with $(NH_4)_2IrCl_6$ as the catalyst in DMSO. The compounds PhCH=CHCOR with R being Ph, t-Bu, and -CH=CHPh, were reduced to the completely saturated ketones in 65-95% yields. With chalcone, complex 19 was an isolated intermediate. Aqueous $TiCl_3$ reduced unsaturated diketones and ketoesters under mild conditions, but failed to reduce unsaturated diesters [180]. An example of the synthetic utility of this reagent is shown by the high yield reduction of steroidal diketone 20 (eq. 40).

The complex $(\pi\text{-allyl})Co[P(OMe)_3]_3$ was a remarkably active catalyst for the reduction of aromatic compounds to hydrocarbons at 25° and less than 760 mm of hydrogen pressure [181]. This catalyst is unparalleled for mildness of conditions required for this type of reduction. The nonheterocyclic aromatic ring of quinolines and isoquinolines was completely reduced by H_2 with a PtO_2



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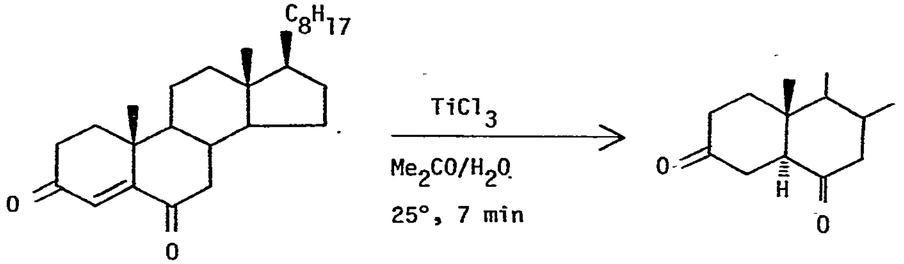
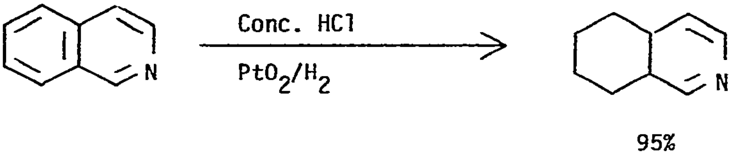


20

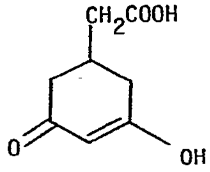
(40)

catalyst in conc. HCl (eq. 41) [182], while the pyridine ring remained unsaturated. Anthracene or anthraquinone was reduced to 9,9,10,10-tetradeuterio-9,10-dihydroanthracene by D_2 with a $Co_2(CO)_8$ catalyst in a CO atmosphere [183].



(41)

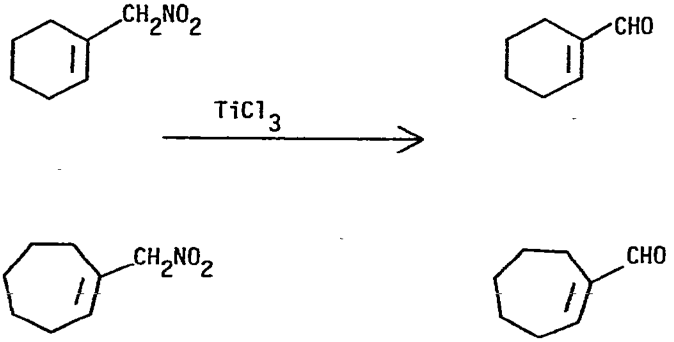
3,5-dihydroxyphenylacetic acid was reduced to cyclohexenone 21 in 77% yield by H_2 with a rhodium on alumina catalyst [184].



21

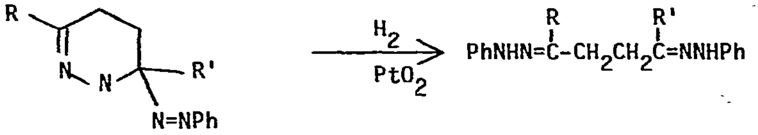
Vinyl and aryl bromides have been reduced to the corresponding hydrocarbons by isopropylmagnesium bromide and $CpTiCl_2$ [185]. Potassium tri-(sec-butyl)-borohydride and CuI were used to reduce alkyl, vinyl, aryl and benzyl chlorides, bromides and iodides to the corresponding hydrocarbons in 70-98% yield [186]. The same reagents reduced ketones to alcohols, and aryl esters to benzyl alcohols. The use of Cr(II) salts in the reduction of organic halides as well as unsaturated systems, epoxides, acyloxyketones and nitro compounds, has been reviewed [187]. Alcohols were reduced to the corresponding hydrocarbons by treatment with dicyclohexylcarbodiimide followed by hydrogenation over palladium on carbon [188]. The alcohols reduced in this fashion were 1, 2, 3 and 4 octanol, decanol and tetradecanol, borneol, menchol, and β-phenylethanol.

Aromatic nitro compounds were reduced to anilines by aqueous $TiCl_3$ at room temperature under reduced pressure [189]. Thus nitrobenzene, o-methyl-, o-chloro, p-methoxy, p-carbomethoxy-, and p-cyanonitrobenzene were reduced in 80-96% yield. The same reagent was used to reduce (1-cyclohexenyl)- and (1-cycloheptenyl)nitromethane to the conjugated aldehyde in ~55% yield (eq. 42) [190]. 2,6-dinitroanilines were selectively reduced to 2-amino-6-nitroanilines in 60-90% yield by H_2 in dimethoxyethane, using palladium on carbon as a catalyst [191].



(42)

The metals Cu(I), Cu(II) and Ag(I) were used to catalyze the homogeneous reduction of linear, substituted and cyclic nitro alkanes to oximes in good yield by hydrogen in the presence of ethylenediamine [192]. Both Cu(I) and Cu(II) salts were more active catalysts than Ag(I) salts. Catalytic activity was sensitive to structure, basicity of solvent, and availability of π-acceptor ligands, and was thought to involve a heterolytic cleavage of H_2 by the metal. The reductive cleavage of 22 by hydrogen with PtO_2 as catalyst (eq. 43) was reported [193].



(43)

22

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

V. FUNCTIONAL GROUP PREPARATIONS

A. Halides

Ferric chloride has been used to catalyze the exchange of tertiary organic chlorides with iodide ion to produce quantitative yields of tertiary organic iodides [194]. Only tertiary and benzylic chlorides reacted, while primary and secondary chlorides were inert. Allylic chlorides were converted to allylic bromides or iodides in 72-90% yield by treatment with excess HX at 40-80° with Cu_2Cl_2 as the catalyst [195]. Aromatic compounds were chlorinated by $PtCl_6^{=}$ in aqueous acetic acid [196]. Chlorobenzene was chlorinated predominantly in the meta and para positions (1:1) with little ortho attack being observed. Similarly, $PtBr_6^{=}$ led to bromination of aromatics. A modified Sandmeyer reaction was used to convert 3-aminopyridine and 3-amino-2,6-lutidine into the corresponding 3-bromo- or chloro compound [197]. The substrate was treated with $NaNO_2$ and HX with Cu_2X_2 as catalyst.

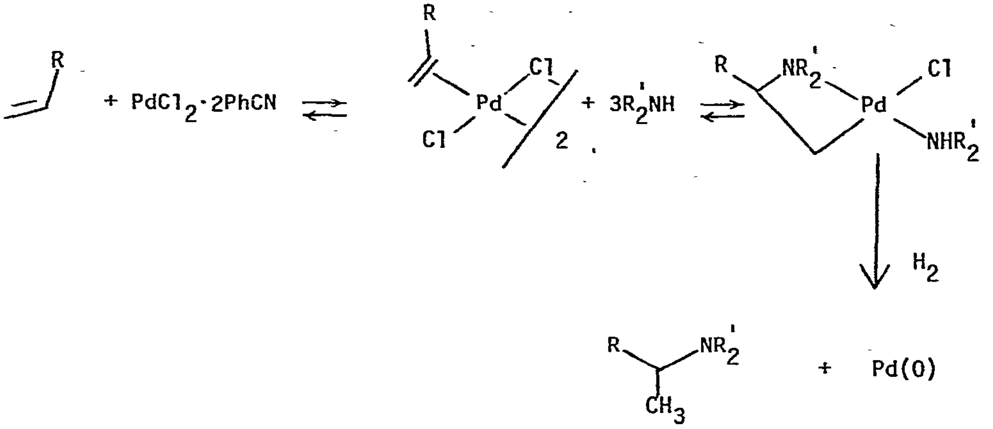
B. Amides, Nitriles

Palladium chloride catalyzed the hydrolysis of nitriles to amides in aqueous solution [198]. The reaction went in 60-80% yield, except with aceto-, propio-, and benzonitrile, for which the yields were 20-30%. Similarly, the complex $[(NH_3)_5RuCl]Cl_2$ was used to assist in the hydrolysis of nitriles to amides in 60-90% yield [199]. Although the ruthenium complex was recovered in usable form, the procedure required several operations including two AgO oxidations and two Zn/Hg reductions. The hydrolysis of 2-cyano-8-hydroxyquinoline to the corresponding amide was catalyzed by Ni(II), Co(II) and Cu(II) salts [200]. The hydrolysis involved initial complexation by the metal, and proceeded at a rate of 2×10^5 faster than in the absence of catalyst.

The reaction of aryl halides with cyanide ion to produce benzonitriles was catalyzed by both $(Ar_3P)_3Ni$ and $Ni(Ar)(X)(PAr_3)_2$ complexes [201]. Benzaldehyde oximes were converted to benzonitriles by treatment with triethylamine, dicyclohexylcarbodiimide and $CuSO_4 \cdot 5H_2O$ [202]. The reaction worked well with substituted benzaldehyde oximes as well as naphthaldehyde oximes.

C. Amines

Aryl iodides were treated with $CuN(SiMe_3)_2$ in refluxing pyridine producing the silyl protected aryl amines $ArN(SiMe_3)_2$ in 30-60% yields. Methanolysis produced the free aryl amine [203]. Secondary amines reacted with isolated olefins in the presence of palladium chloride to produce tertiary amines in high yield after reduction of the intermediate complex [204]. This reaction, an overall amination of olefins, proceeded best with terminal and nonsterically hindered olefins and secondary amines. Primary amines and NH_3 did not lead to synthetically useful amounts of product. The stereochemistry of the addition of amines to olefins with the above system was shown to be trans [205]. The reaction was thought to proceed as in eq. 44.



(44)

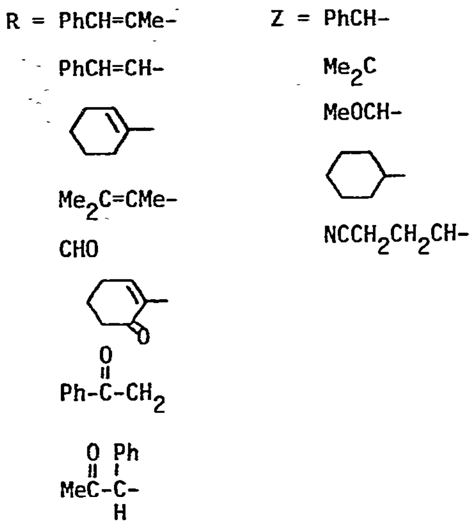
D. Ethers, Esters

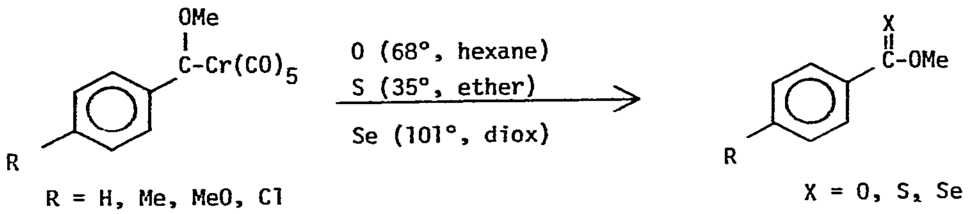
Copper was used to catalyze the reaction of allyl chloride with alcohols to produce allyl ethers [206]. Alkyl, benzyl, allyl and propargyl alcohols reacted under these conditions to produce the corresponding allyl ethers in 35-100% yield. With unsymmetrical allylic halides mixtures of products resulting from allylic transposition resulted. Allyl alcohol itself was converted to diallyl ether in 83% yield by treatment at 135° in an autoclave with $Fe(CO)_5$ in pentachloroethane solvent [207].

β-Alkoxyketones and β-ketoacetals were prepared by the treatment of a variety of acetals with trimethylsilyl ethers at low temperatures in the presence of $TiCl_4$ [208]. Eq. 45 summarizes the scope and utility of this reaction, and illustrates its tolerance to various functional groups. Silver trifluoroacetate was used to convert 7,7-dibromonorcarane to the 7-bromo-7-trifluoroacetoxy compound in 90% yield [209].

The chromium carbene complexes 22 were converted to the corresponding esters, thioester. or selenoesters by treatment with O_2, S_8 or Se (eq. 46) [210].

$$ROSiMe_3 + Z(OMe)_2 \xrightarrow[-78°]{TiCl_4} \underset{60\text{-}100\%}{MeOZR} \qquad (45)$$

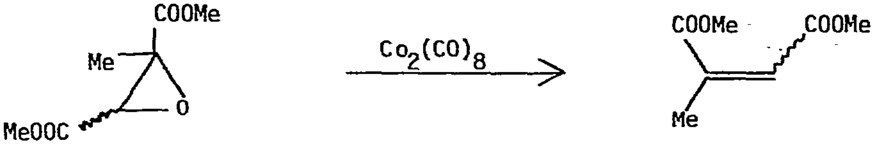




(46)

E. Olefins

Ferric chloride and butyllithium were used to deoxygenate epoxides, converting them to olefins in 57-92% yield [211]. The reaction was carried out at -78° in THF/hexane, and proceeded smoothly with styrene oxide, cis and trans stilbene oxide, cyclohexene oxide, 1-nonene oxide and indene oxide. Dicobalt octacarbonyl was used to convert epoxide 23 to the corresponding olefin in high yield and stereoselectivity (eq. 47) [212]. In a similar manner 2-benzoyl aziridines were deaminated to the α,β-unsaturated ketone in 65-94% yield by FeI_2 at room temperature [213].



23

trans

cis

cis

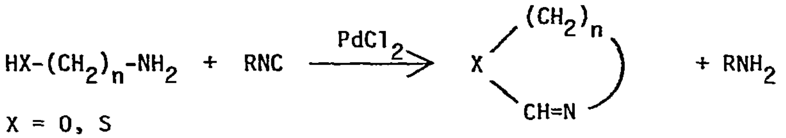
trans

95%

(47)

F. Heterocycles

Several new and useful heterocyclic syntheses which rely on transition metals have been developed. Palladium chloride was used to assist the reaction of isonitriles with aminoalcohols or aminothiols to produce 2-oxazolines or 2-thiazolines in 70-85% yield (eq. 48) [214]. The reaction was thought to



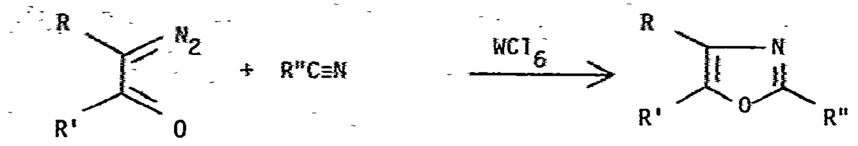
X = O, S

n = 2,3

70-85%

(48)

proceed through a Pd(II) carbene complex [215]. A similar reaction between nitriles and aminoalcohols to produce 2-oxazolines with catalysis by transition metal salts has been reported [216]. Substituted oxazols were produced in 20-66% yield by the reaction of α-diazoketones and nitriles in the presence of WCl_6 (eq. 49). The reaction was thought to involve a tungsten-carbene intermediate [217].

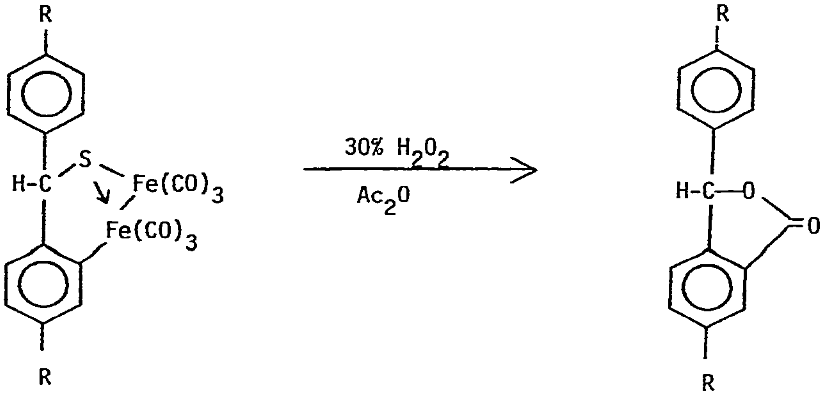


(49)

R = Ph, OMe   R" = Me, Et, vinyl

R' = Ph, H

Flavones were prepared in ∿80% yield by the $Pd(OAc)_2$ ring closure of o-hydroxychalcones in acetonitrile [218]. The reaction proceeded by phenoxy-palladation of the conjugated double bond followed by elimination of a palladium hydride species. Oxidation of the iron complex 24 by H_2O_2 in acetic anhydride produced lactones in moderate yield (eq. 50) [219].



(50)

24

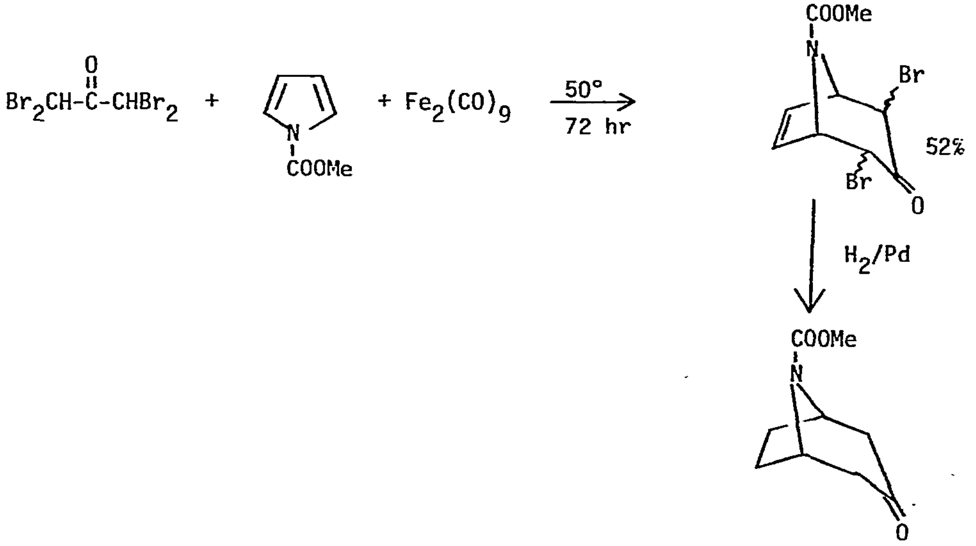
45-75%

R = H, Me, OMe

Terminal alkynes reacted with a variety of nitriles in the presence of $CoCl_2 \cdot 6H_2O$ to give substituted pyridines in ∿60% yields [220]. The ring was formed from two alkyne units and the -C≡N unit of the nitrile. Since the alkynes could unite in two different fashions, mixtures of positional isomers were obtained. Chromium carbonyl complexes were used to synthesize and stabilize novel dihydropyridines whose instability had made them previously unavailable for extensive chemical investigations [221].

Palladium black was used to catalyze the reaction between primary amines and 1,4-dihydroxybut-2-ene to produce N-substituted pyrroles in high yield [222]. The same catalyst was used to effect the alkylation of secondary amines by alcohols. The reaction of ethyl diazoacetate with acetylacetone produced 2-carbethoxy-3,5-dimethylfuran in 68% yield [223]. The reaction was catalyzed by $Rh_2(OAc)_4$ and proceeded smoothly at 25°. The same complex catalyzed the reaction of the diazoester with phenol, thiophenol, and aniline to give insertion products.

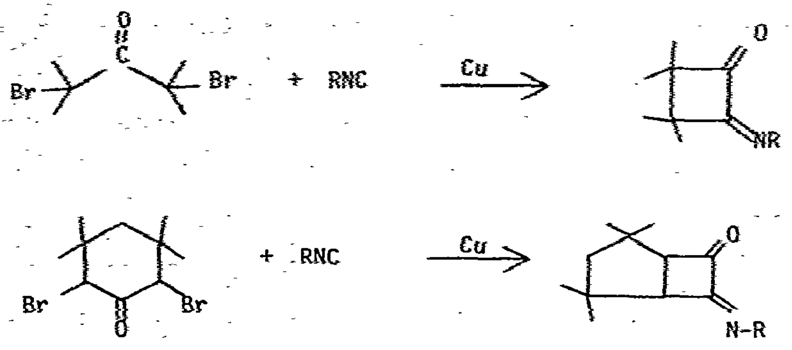
The ring system of the tropane alkaloids was synthesized from N-carbomethoxypyrrole and α,α,α',α'-tetrabromoketones, using $Fe_2(CO)_9$ to cause this condensation (eq. 51) [224]. This provides a simple approach to this important ring system.



(51)

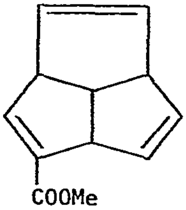
G. Miscellaneous

Isonitriles were reacted with α,α'-dibromoketones using a copper catalyst to produce α-iminocyclobutanones (eq. 52). The reaction went in 44-90% yield with both cyclic and acyclic ketones [225].



(52)

An efficient synthesis of (-)-triquinacene-2-carboxylic acid 25 consisting of a seven-step conversion of (cyclooctatetraene)$Fe(CO)_3$ has been reported [226]. The conversion went in 20% overall yield and was claimed to be "perhaps the most direct and efficient synthetic approach to the triquinacene ring system yet devised."



25

Hydrogen-deuterium exchange in alcohols was catalyzed by tris-(triphenylphosphine)ruthenium dichloride [227]. Thus heating alcohols in a large excess of D_2O at 200° in the presence of the catalyst led to incorporation of D at C_1 of the alcohol.

VI. REVIEWS

A book entitled "Organometallics in Organic Synthesis", of 160 pages has appeared [228]. A review on organic synthesis using transition metal compounds, including a discussion of oxidative additions, insertions, and cyclizations has been published [229]. Reactions of coordinated ligands have been treated in a review with 47 references [230]. The stereochemistry of organo-transition metal complexes has been presented in a review with 40 references [231]. Asymmetric hydrogenation, hydrosilation, hydroformylation, oligomerization and several other reactions catalyzed by chiral transition metal complexes, particularly rhodium were treated in a review with 98 references [232]. A review with 145 references on catalysis by coordination compounds has appeared [233]. The metallation of C-H bonds of aromatic and aliphatic compounds to C-M bonds followed by substitution reactions as been discussed [234].

The use of disodium tetracarbonylferrate ($Na_2Fe(CO)_4$) to convert organic halides to aldehydes, ketones, acids, esters, amides and alkanes, and acid halides to aldehydes and ketones has been covered by a review with 16 references [235]. This paper discusses the scope and limitations of the above reactions. The use of cyclopentadienyliron dicarbonyl complexes as potential reagents for organic synthesis has been reviewed [236]. The paper discusses metal assisted cycloadditions, organometallic condensations and demetallations.

The organic chemistry of platinum complexes has been discussed [237]. The activation of unsaturated hydrocarbons by platinum, the formation of platinum carbene complexes, and a carbonium ion model for reactivity were all considered. Organocobalt chemistry related to vitamin B_{12} has been reviewed [238]. A review on applications of chromium(II) salts to organic synthesis has appeared [239].

The organic chemistry of low valent titanium has been reviewed [240]. These reagents have been used to reduce oximes and nitro compounds to ketones, sulfoxides to sulfides, conjugated enediones to 1,4-diketones, and α-haloketones to ketones. Under proper conditions aldehydes and ketones were reductively coupled to produce olefins.

A review covering the diyne reaction of 1,4-, 1,5-, 1,6- and 1,7-diynes via transition metal complexes has appeared [241].

Approaches to the synthesis of pentalenes via metal complexes has also been reviewed [242]. Cyclooctatetraene reacted with $Ru(CO)_4(SiMe_3)_2$ in refluxing octane to produce pentalene complexes containing two Ru's *via* transannular ring closure in 30% yield. The physical characteristics of the complexes were reported.

The role of electron transfer mechanisms in organometallic catalytic reactions was reviewed [243]. Reactions including oxidative additions, reductive eliminations, β-eliminations, homocoupling of RMgX by Ag(I), Fe catalyzed reactions of Grignard reagents and cross coupling reactions of organocopper complexes were considered.

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