TRANSITION METAL DERIVATIVES IN ORGANIC SYNTHESIS

ANNUAL SURVEY COVERING THE YEAR 1976

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CONTENTS

Transition metal derivatives in organic synthesis, Annual Survey covering the year 1975 see J. Organometal. Chem., 126(1977)151-226.

I. GENERAL COMMENTS

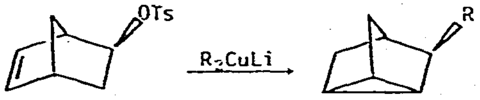
This annual survey covers the literature for 1976 dealing with the use of transition metal intermediates for organic synthetic transformations. It is not a comprehensive review, but is limited to reports of discrete systems that lead to at least moderate yields of organic compounds, or that allow unique 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

While organocuprates have been extensively employed as alkylating agents for a variety of substrates over the past several years, the structures of the complexes involved and the mechanism of the alkylation reaction remains somewhat obscure. Recent vapor depression and x-ray scattering studies suggest that "lithium dimethylcuprate" is dimeric in ether solution. Kinetic studies suggested a mechanism involving a reaction of this dimer with methyl iodide in which each copper atom provides one electron to produce the required oxidative addition and subsequent coupling [1]. In the reaction of lithium dimethyl cuprate with β-cholesteryl tosylate, a 1:1 mixture of product resulting from replacement of tosylate with retention of configuration, and of tricyclic material was obtained, indicating participation of the homoallylic double bond in the alkylation reaction had occurred. Similarly, tricyclic product resulted from alkylation of norbornenol tosylate (eq. 1). In the



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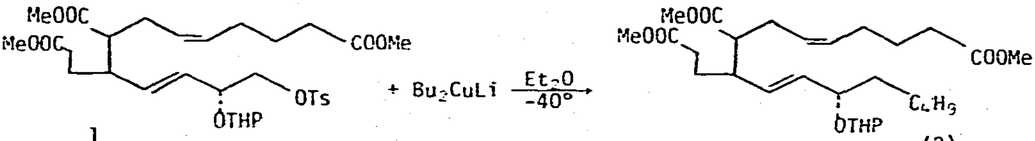
same paper, a synthesis of trans-trans farnesol from homogeranyl iodide and $(ROCH_2CH{=}C(CH_3))_2CuLi$ was reported [2].

Alkylation of aliphatic systems by organocopper reagents has been studied by several groups. Straight chain ω haloacids were alkylated by n-pentyl-, 2-phenethyl- and sec-butyl Grignard reagents using Li_2CuCl_4 as catalyst. High yields of fatty acids were produced [3]. Benzyl bromides were cleanly alkylated by treatment with the reagent resulting from the reaction of tetraalkylborates with cuprous halides. Little bibenzyl was produced [4]. Unsaturated ester **1** suffered no reductive elimination of tosylate upon treatment with lithium dibutylcuprate (eq. 2) [5]. Dihalocyclopropanes were treated sequentially with R_2CuLi, then an alkylhalide to produce dialkylation in a 1-pot procedure (eq. 3) [6]. A mixture of isomers, whose composition depended on the nature of the R groups, was obtained.



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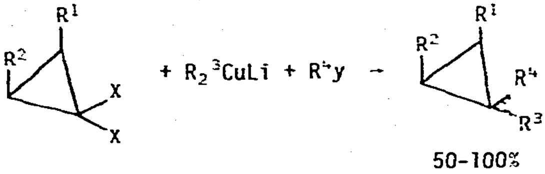


(3)

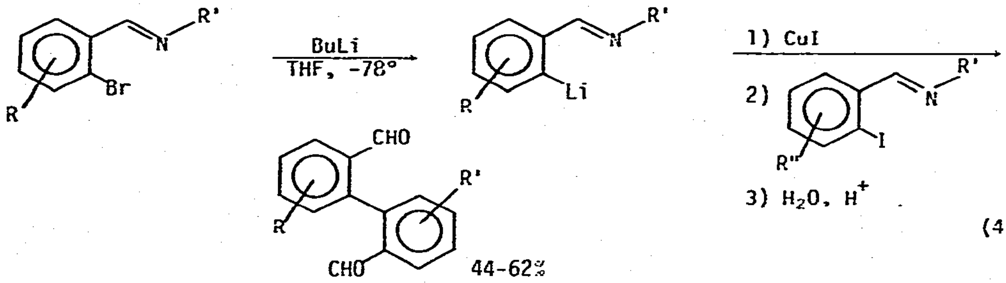
R^1 = Ph, $-(CH_2)_4-$, n-hexyl, $PhCH_2OCH_2$

R^2 = H

R^3 = n-Bu, s-Bu, t-Bu

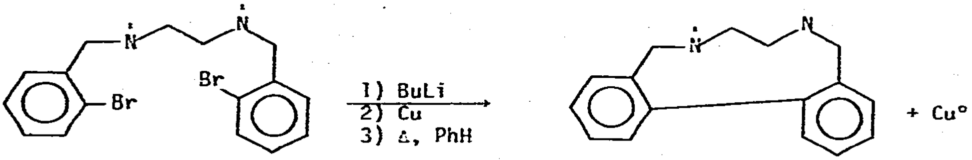
R^4y = MeI, EtI, AcBr, EtOH

Biaryl aldehydes and oxazolines were prepared by the coupling of o-halobenzaldehyde imines with o-copper benzaldehyde imines (eq. 4).



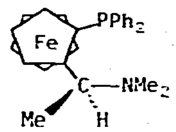
(4)

The reaction was homogeneous, proceeded at ambient temperatures, and allowed the synthesis of both symmetrical and unsymmetrical systems. The coupling proceeded even when the substrate halide was flanked by two ortho substituents [7]. A similar intramolecular coupling to produce macrocyclic materials has also been achieved (eq. 5) [8].



(5)

The cross coupling of aryl iodides with a variety of alkyl-, aryl-, and acetylenic Grignard reagents was catalyzed by $L_2Pd(Ph)I$. Yields from 40-80% were obtained [9]. Similarly, 1,8-diiodonaphthalene was converted to 1,8-diphenylnaphthalene by treatment with phenylmagnesium bromide in the presence of a catalytic amount of nickel(II) acetylacetonate [10]. The full experimental details of the L_2NiX_2 catalyzed cross coupling of Grignard reagents with aryl and vinyl halides has appeared [11]. Over sixty experiments are discussed. Use of a chiral phosphine-nickel complex to catalyze the reaction between vinyl bromide and α-phenethylmagnesium chloride produced coupling product in 86-98% yield and 57-60% optical yield. The chiral ligands studied were the unique ferrocenyl phosphines **2**-**5** [12]. Finally, allylic alcohols were alkylated and rearranged by treatment with aryl halides and a palladium(II) catalyst (eq. 6) [13].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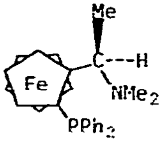
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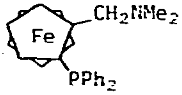
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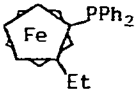
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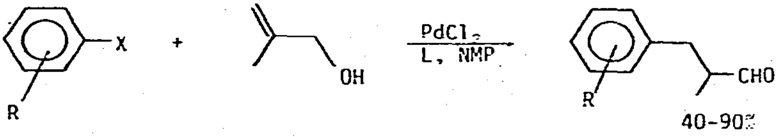
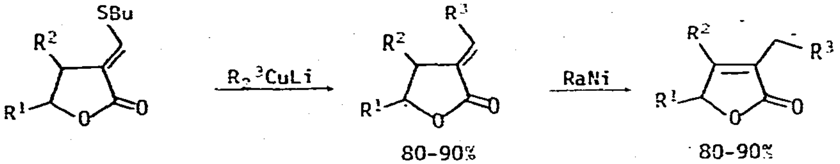


(6)

R = Me, OMe, OH, NO_2, COOEt, CHO, CN, COMe, t-Bu

The bromide in α-benzamino-β-bromoacrylates was alkylated by lithium dimethylcuprate in 52% yield with predominant retention of the stereochemistry of the double bond, and without subsequent conjugate alkylation. With lithium dibutylcuprate significant double bond isomerism was observed [14]. Similarly β-iodo vinylsulfones were alkylated by methyl-, butyl-, and phenylcopper in 70-90% yield [15]. α-Alkylidene-γ-butyrolactones and $\Delta^{\alpha,\beta}$-butenolides were prepared by alkylation of the corresponding vinyl sulfide (eq. 7) [16]. Enol phosphates were alkylated in a similar manner (eq. 8) [17]. In this case, lithium dimethylcuprate was unreactive, as were hindered enol phosphates.



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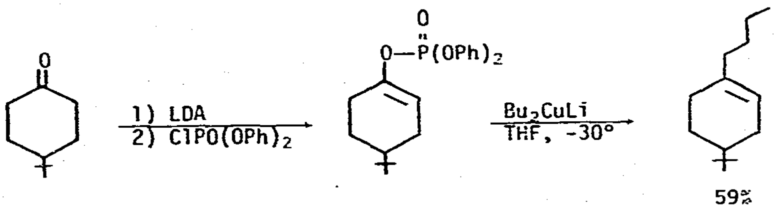

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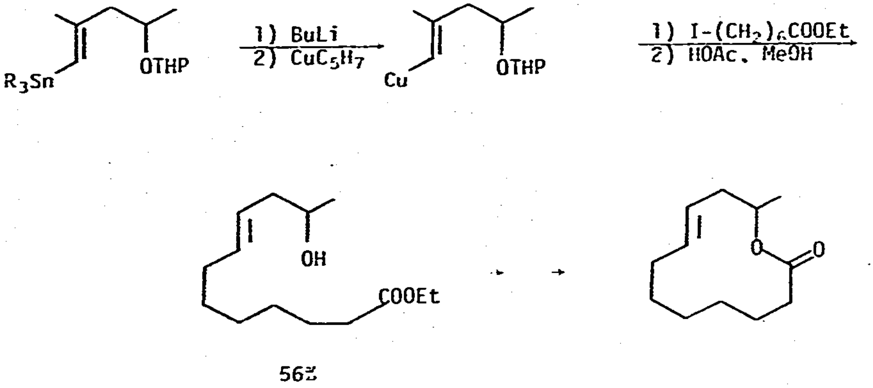
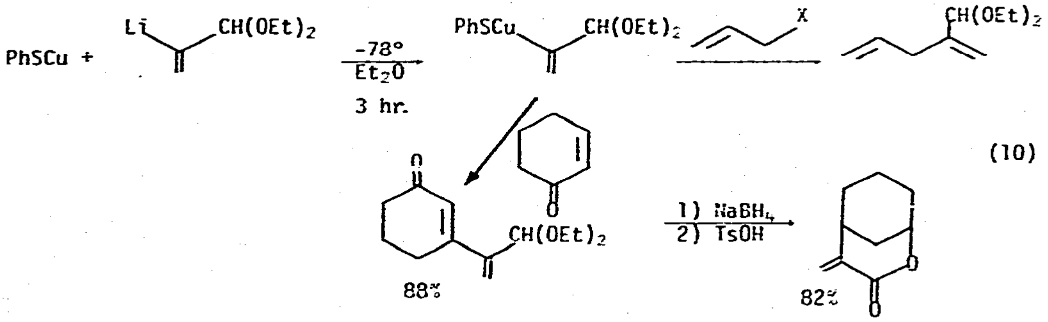
Vinyl copper complexes are also finding increased use in organic synthesis. A key step in the synthesis of ± 11-hydroxy-trans-8-dodecenoic acid lactone was the coupling of a functionalized vinyl copper species (prepared from the corresponding vinyl tin species) with an iodonitrile or ester (eq. 9) [18].



(9)

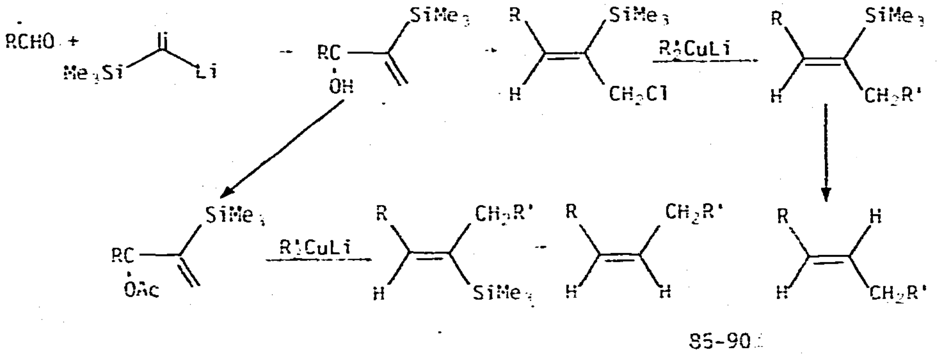
The acrolein-derived mixed vinylcopper complex **6** reacted selectively with allylic halides, while vinyl and benzyl halides were inert. Complex **6** also added 1,4 to conjugated enones, while the divinylcuprate $[(EtO)_2CH\text{-}C{=}CH_2)_2CuLi]$ added exclusively 1,2 (eq. 10) [19]. Vinyl Grignards were cleanly alkylated



(10)

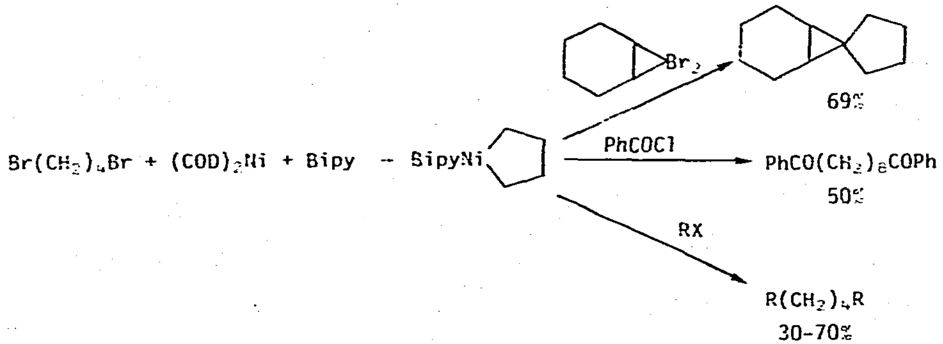
by alkyl iodides in the presence of cuprous iodide. Alkyl bromides were less reactive, and a small amount of olefin isomerization was observed [20]. Disubstituted alkynes were hydroborated with BH_2Cl and the resulting chlorodivinylborane was converted to the vinyl copper by treatment with methyl copper. Reaction of this complex with allylic chlorides or bromides, or alkyl iodides produced trisubstituted olefins in 48-97% yield. The reaction resulted in a net cis alkylation [21]. Similarly, treatment of trimethylsilylacetylenes with dichlorohexylborane, followed by sequential treatment with methyllithium, cuprous iodide, and triethylphosphite produce a vinyl copper complex which reacted with allyl and alkyl iodides in 70-94% yield to produce vinyl silanes [22]. Finally, treatment of terminal alkynes with diisobutyl aluminum hydride produced a trans vinyl alane. The compound coupled cleanly with aromatic bromides or iodides at 25° with a nickel(0) catalyst ($Ni(PPh_3)_4$) to produce 64-93% yields of the alkene with >99% trans stereochemistry [23].

Aldehydes were converted to either cis or trans disubstituted olefins in a sequence of steps involving alkylation of allyl halides or acetates with lithium dialkylcuprates (eq. 11). The reaction was stereospecific only if



(11)

isopropyl or cyclohexyl aldehydes were used. A stereospecific synthesis of disparalure was carried out in this fashion [24]. Hydrozirconation (with Cp_2ZrHCl) of 4-chlorocyclohexene followed by heating at 65° for 61 hrs. produced [3.1.0] bicyclohexane (45%) along with cyclohexene (26%) and chlorocyclohexane (15%) [25]. Bis(cyclooctadiene)nickel reacted with 1,4-dibromobutane and bipyridyl to produce a nickelocycle which reacted with a variety of organic halides to give both cyclic and noncyclic materials (eq. 12) [26]. Finally, the palladium(0) catalyzed alkylation of allylic



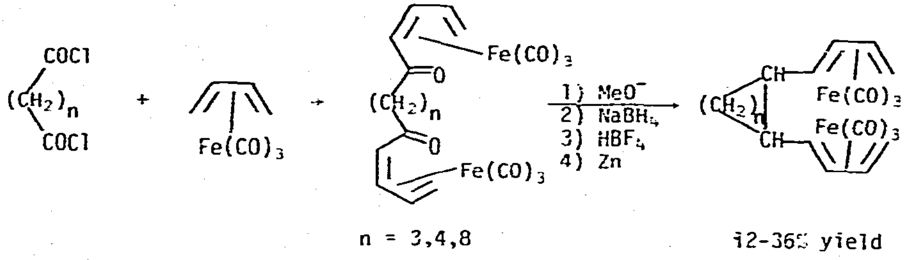
(12)

acetates by stabilized carbanions was reported. The reaction, a net Sn^2

displacement, went with complete retention of configuration and without competing eliminations. The stereochemistry of the allylic double bond was maintained, although geranyl and neryl acetates suffered some allylic transposition [27].

Several new conversions of acid chlorides to ketones have been reported. Treatment of cuprous iodide with one equivalent of methyllithium produced the well-known insoluble "MeCu". Treatment of this with an addition equivalent of a Grignard reagent produced a magnesium halide-dialkyl cuprate which reacted with acid halides to produce ketones in 80-100% yield. The reagent prepared in this manner was of comparable reactivity to lithium diorganocuprates, but easier to prepare, and more thermally stable. In addition, excess reagent was not required for high yields [28]. Treatment of manganous iodide with alkyllithium or Grignard reagents followed by treatment with an acid halide produced ketones in 60-91% yield [29]. Secondary and tertiary alkylketones were prepared from acid halides by treatment with the mixed cuprate $[\text{PhSCuR}]^{-}\text{Li}^{+}$ [30]. Treatment of trimethylsilylacetylene with potassium t-butoxide followed by cuprous iodide produced a reagent that converted acid chlorides into β-trimethylsilylynones in 30-65% yield. The reagent did <u>not</u> react with aromatic iodides [31]. Thioesters were converted to sulfoxides by treatment with lithium dialkylcuprates. The yields were better than with Grignard reagents, and the reaction went with clean inversion [32]. Treatment of $(RO)_2P(O)CH_2R'$ with butyllithium, then cuprous iodide, then an acid chloride produced $(RO)_2P(O)CH(R')(COR'')$ in 60-90% yields. This β-ketophosphorous compound was of use in Wittig reactions [33]. Finally, the reaction in eq. 13 was reported [34].

A procedure for the α-phenylation of conjugated enones has been developed, and depends upon the reaction of phenyl copper with the appropriate epoxytosylhydrazone (eq. 14) [35]. The stereospecific synthesis of α-methylene-γ-butyrolactones from cyclic unsaturated epoxides has been achieved, using the vinyl cuprate derived from the acetal of acrolein (eq. 15) [36].



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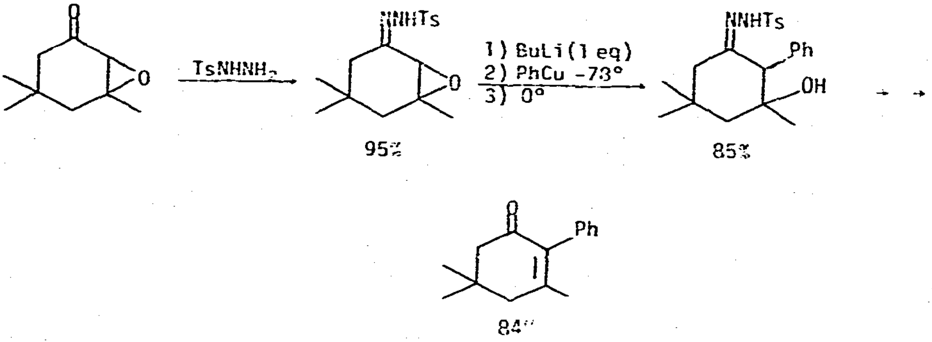

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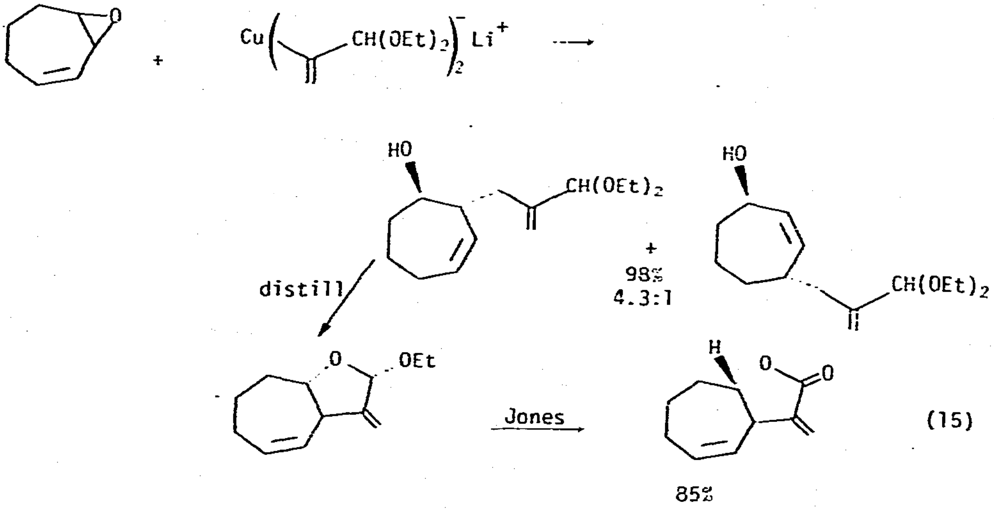

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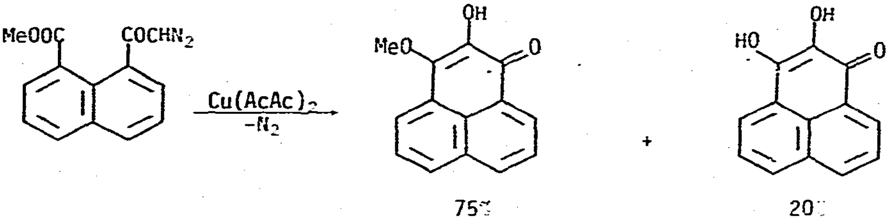
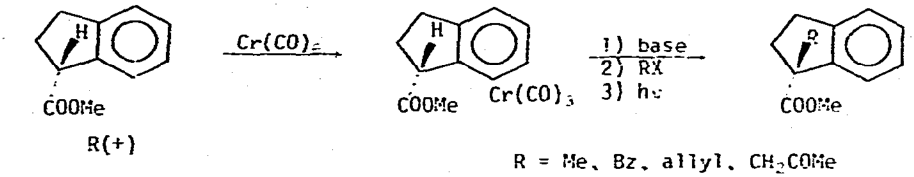
In a continuing study on the production of axial alcohols, 4-t-butylcyclohexanone was treated with n-butyllithium, sec-butyllithium, n-Bu_3CuLi_2 and sec-Bu_3CuLi_2 under a variety of conditions and the ratio of axial to equatorial alcohols produced was measured. In all cases the R_3CuLi_2 system gave the highest (90-97%) yield of axial alcohol, while RLi gave considerably lower (73-76%) yields [37]. Cupric acetylacetonate was used to catalyze the insertion of diazoketone into an adjacent ester in the substrate in eq. 16.



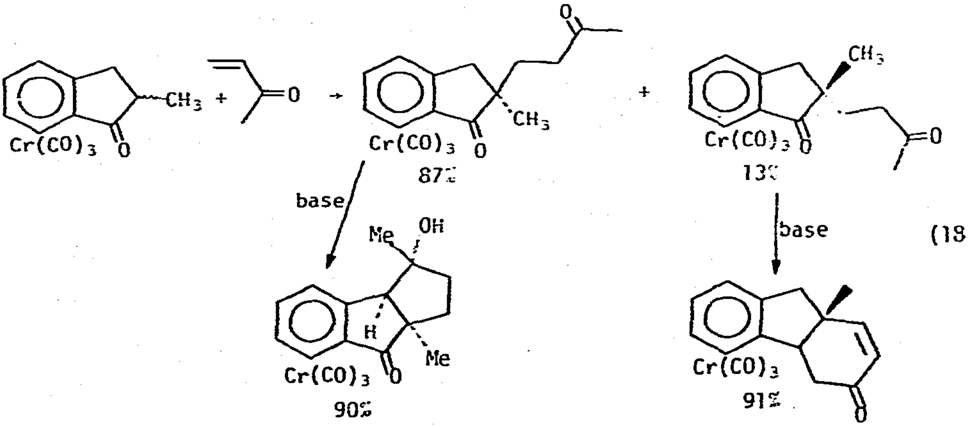
(16)

The stereospecific alkylation of indane-1-carboxylates was accomplished via the π-arene chromium tricarbonyl complex. The chromium blocked one face of the molecule and forced stereospecific alkylation of the ester anion from the face opposite the metal (eq. 17) [39]. Similarly, the chromium tricarbonyl



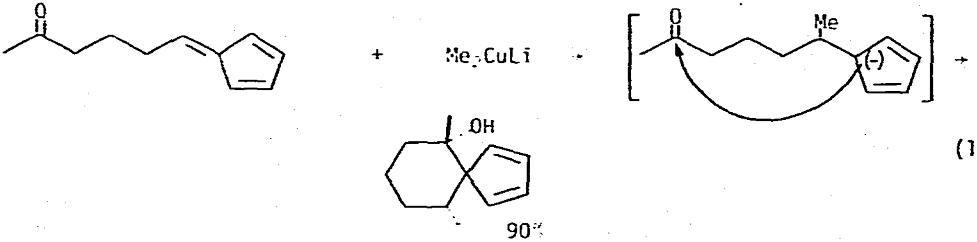
(17)

complex of 2-methylindanone reacted with methyl vinyl ketone primarily from the face opposite the metal carbonyl group. The resulting product was ring-closed in a new example of stereospecific activation of the α position of a ring complexed by chromium tricarbonyl (eq. 18) [40].



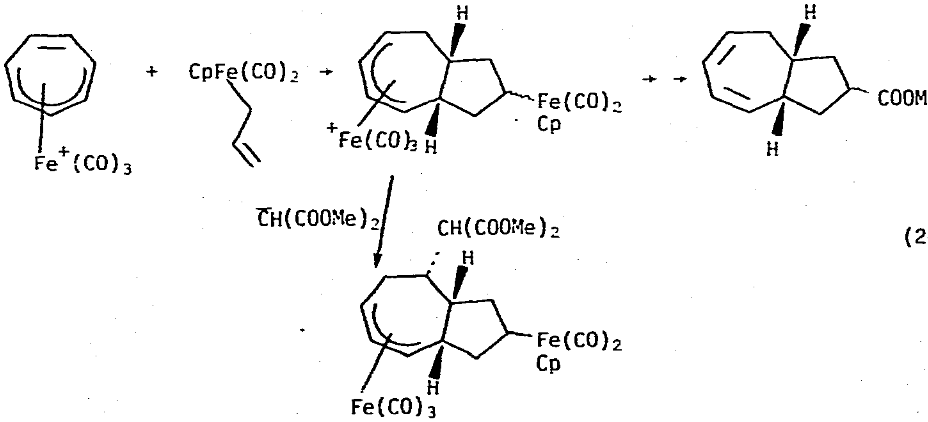
(18)

A new stereospecific synthesis of alkenyllithium reagents has been developed. Alkyl copper species added cis to terminal alkynes producing terminal vinyl copper species. Treatment with I_2 produced the vinyl iodide which was lithiated. The vinyllithium reagents produced in this manner were reacted with a variety of electrophiles [41]. Diphenyl(alkynyl)phosphines reacted with dialkylcuprates to produce diphenyl(vinyl)phosphines in which alkylation had occurred at the β-carbon of the alkyne, with clean cis stereochemistry [42]. Fulvenes were converted to spirovetivanes by treatment with lithium dimethylcuprate as in eq. 19 [43]. The full details of both the



(19)

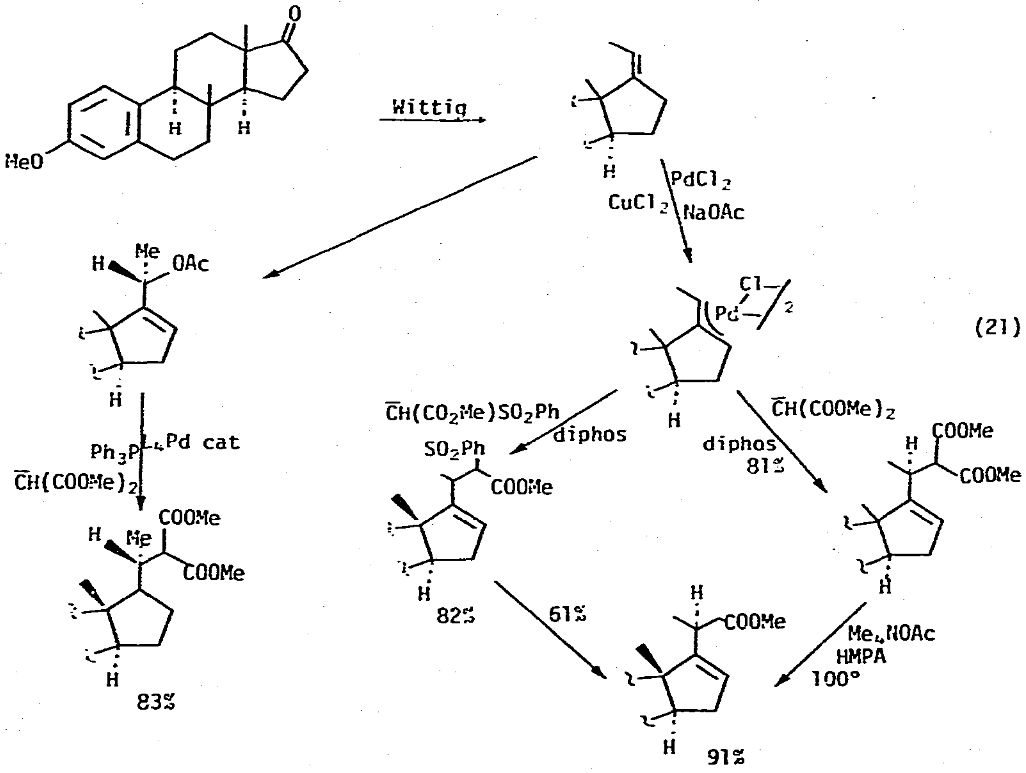
preparation and reactions of σ-allyl(cyclopentadienyl)iron dicarbonyl complexes have recently appeared [44]. The complexes were prepared by treatment of allyl halides with $CpFe(CO)_2^-$ or by treatment of cyclopentadienyliron dicarbonyl olefin cationic complexes with bases. The σ-allyl group underwent 3+2 cycloaddition reactions with substrates such as TCNE to produce five-membered ring systems. The azulene ring system was synthesized by the reaction of σ-allyliron complexes with π-cycloheptatrienyliron cationic complexes (eq. 20) [45]. Since the initial cyclization product contained



(20)

two iron atoms, further functionalization was possible, and was explored. A variety of olefins, including 1-octene, 1-hexene, styrene, methyl vinyl ketone, acrylonitrile and methylmethacrylate, reacted with esters of trichloroacetic acid in the presence of L_3RuCl_2 catalyst to produce 2,2,3-trichlorocarboxylic acid esters. The reaction was a homolytic cleavage-free radical addition of Cl· and ·Cl_2COOR across the carbon-carbon double bond [46]. The full experimental details of the reaction of π-allylnickel halides with quinones to produce allylhydroquinones, or enediones have been published [47]. The syntheses of Coenzyme Q_1 and Plastoquinone-1 are contained in that paper.

The alkylation of π-allylpalladium complexes by stabilized carbanions has been used to functionalize estrone methyl ether (eq. 21) [48], as well as cholestanone and testosterone (eq. 22) [49]. A new synthesis of π-allylpalladium chloride complexes by the reaction of vinyl mercurials with olefins in the presence of Li_2PdCl_4 has also been reported (eq. 23) [50].



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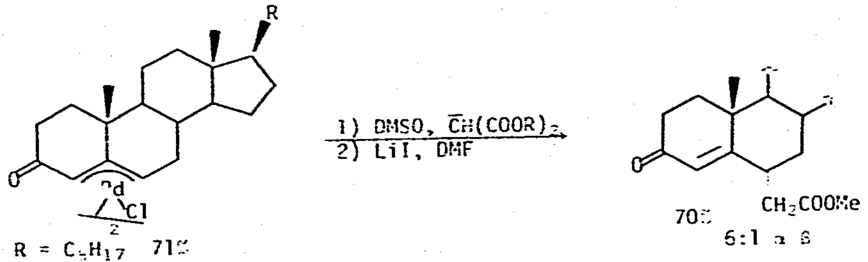
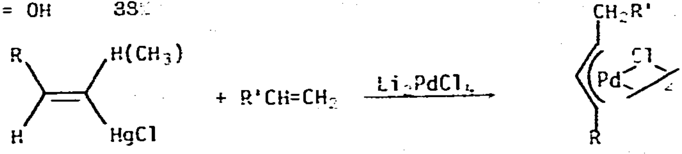
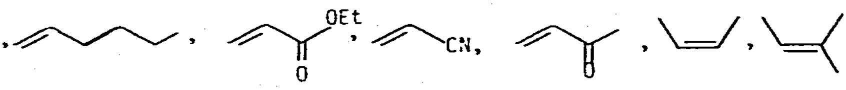


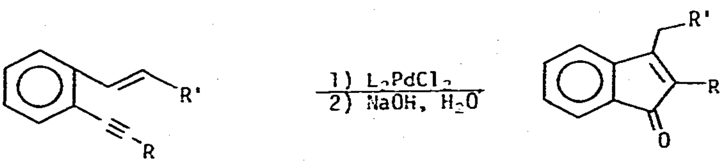
R = C_8H_{17} 71%
R = OH 38%



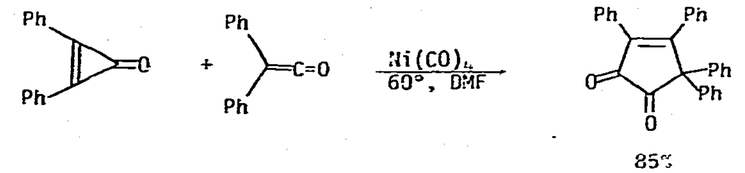
olefin = $H_2C=CH_2$,



Indenones were produced by the reaction of o-alkynylstyrenes with L_2PdCl_2 (eq. 24) [51]. The reaction was thought to proceed through a π-allylpalladium complex. The cis addition of $R_3Si-SiR_3$ to alkynes to produce cis $(R)R_3SiC=CSiR_3(R)$ tetra-substituted alkenes was catalyzed by L_2PdCl_2. The reaction went in 60-95% yield [52]. Nickel carbonyl catalyzed the reaction of diphenylcyclopropenone with diphenylketene to produce the tetraphenylcyclopentenedione (eq. 25) [53]. The palladium-catalyzed reaction



R'	Ph,	t-Bu,	Me,	Me
R	Ph,	Ph ,	Ph,	Me
%	54	35	15	30



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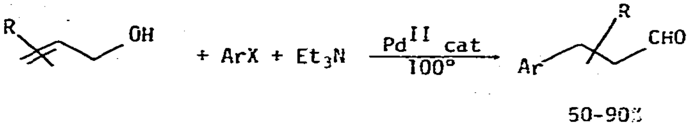
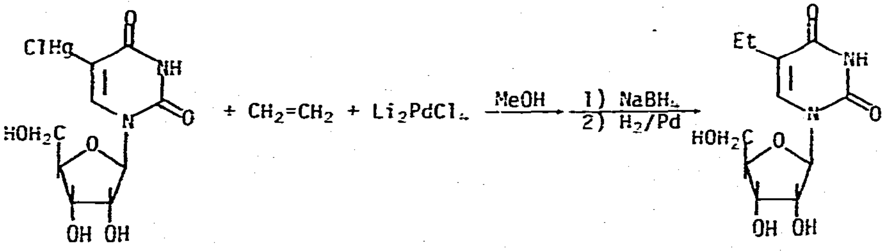
between aryl halides and allylic alcohols to produce aldehydes (eq. 26) has been studied extensively by two separate groups [54][55]. Lithium



(26)

chloropalladate was used to catalyze the reaction between alkenes and vinyl mercurials in the synthesis of 5-substituted pyrimidine nucleosides. In this fashion, 5-ethyluridine was prepared in 80% yield, while 2'-deoxy-5-ethyluridine was prepared in 68% yield. By the use of olefins other than ethylene, other functional groups were also introduced at the 5 position by this method (eq. 27) [56].



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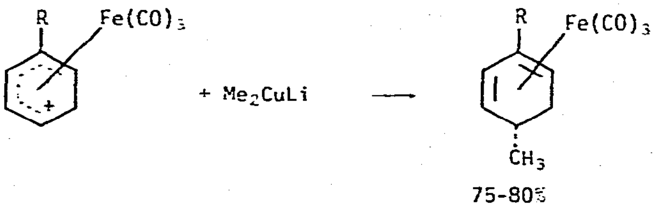
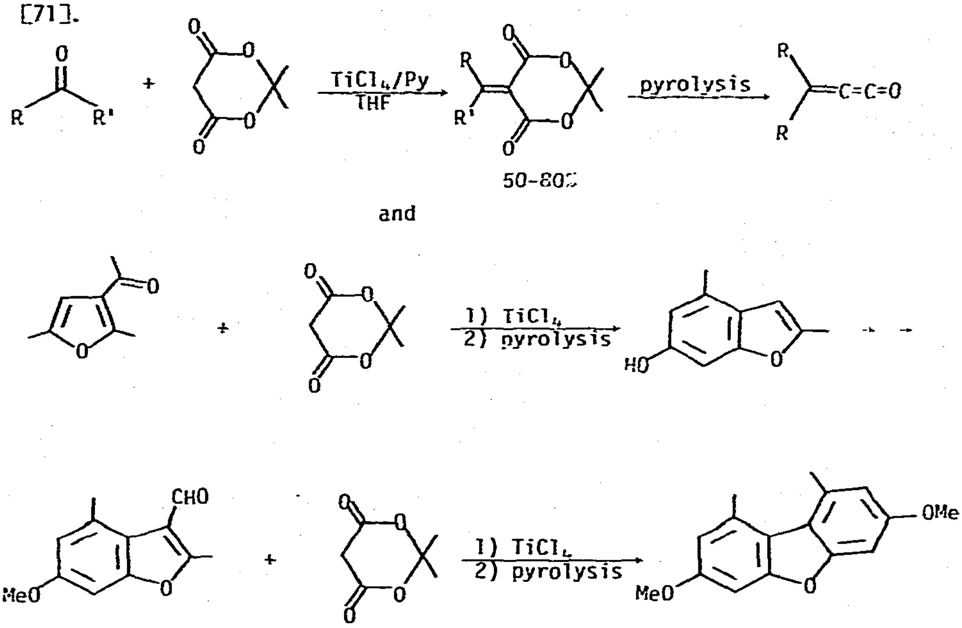
A variety of carbene reactions were catalyzed by transition metals. Thus dihalomethanes reacted with ethylene to give propene, and with propene to give isobutene (50% yields) under the influence of a nickel(0)-phosphine catalyst [57]. The reaction resulted from insertion of carbene into a vinylic C-H bond. Copper powder was used to generate carbenes from CH_2I_2, $CHClI_2$ and $Br_2CHCOOCH_3$ for reaction with olefins such as cyclohexene, cycloheptene, cyclooctene, styrene, stilbene and 1-hexene. Cyclopropanes were formed in fair to good yields [58]. Rhodium(II) carboxylates were used to catalyze the reaction between diazoacetates and alkenes to give cyclopropane carboxylic acids in quite high yield. For instance 3-hexene reacted with butyl diazoacetate to give 98% yield of the corresponding cyclopropane when rhodium(II) acetate was used as catalyst, while only a 15% yield resulted with copper triflate as catalyst [59]. A series of papers concerning metal salt catalyzed carbenoid reactions has been published [60-63]. In these, the following topics were discussed: (a) general considerations for copper catalyzed carbene transfer reactions; (b) mechanisms of cyclopropanation and allylic CH insertion by diazoesters in the presence of olefins and copper catalysts; (c) mechanisms of carbene dimer formation; (d) synthetic and structural aspects of copper salt catalyzed additions of $:C(COOMe)_2$ to olefins.

The 2+2 cycloaddition of norbornene with dimethylacetylene dicarboxylate was catalyzed by H_2RuL_4, and produced the exo adduct exclusively in 52% yield. Benzonorbornene behaved in a similar fashion. Norbornadiene underwent almost exclusive mono addition [64]. Cyclohexadienyliron tricarbonyl cationic complexes reacted with lithium dimethylcuprate to undergo methylation from the fact opposite the iron group (eq. 28) [65].



(28)

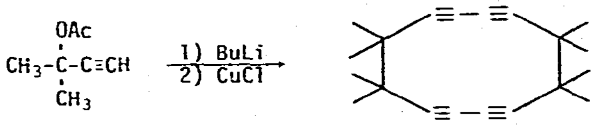
Titanium tetrachloride was used to promote a variety of aldol type condensation reactions. The cross aldol condensation of silyl enol ethers with carbonyl compounds containing other functional groups (i.e., ketoesters, α-haloaldehydes) was reported in full detail [66]. The silylenol ether of 3-pentanone was condensed with (+)-2-methylbutanal using titanium tetrachloride to produce (+)-manicone (4,6-dimethyl-oct-4-ene-3-one) in 83% yield and 97% optical purity [67]. β-Alkoxyesters were produced in high yield from the titanium tetrachloride promoted reaction of acetals with ketene alkyltrimethylsilylacetals [68]. Allyltrimethylsilanes reacted with a variety of aldehydes and ketones in the presence of titanium tetrachloride to produce homoallylic alcohols resulting from alkylation of the carbonyl group by the allyl group. With unsymmetrical allylsilanes, allylic transposition was observed [69]. A similar reaction resulted with α-ketoesters, with attack occurring exclusively at the ketone carbonyl. When chiral esters were used, 16-55% optical induction at the newly reacted chiral center was observed [70]. Finally, the $TiCl_4$ promoted condensation of ketones with β-diesters was used to develop a synthetic approach to dibenzofurans (eq. 29) [71].



(29)

The free radical addition of ketones to alkenes was affected by heating the reactants in the presence of PbO_2, MnO_2 or CuO. Thus, acetone reacted with 1-octene to produce 2-undecanone in 70% yield. The reaction is thought to proceed by generation of $CH_3COCH_2\cdot$ which added to the olefin. The thus-formed alkyl radical then abstracted H• from another molecule of acetone to allow the reaction to proceed [72]. Acetylacetone reacted with 1-heptene using $Mn(OAc)_3$ as catalyst to give heptyl-acetylacetone in 60% yield by a similar radical pathway [73]. In a similar fashion $Mn(OAc)_3$ was used to promote the reaction of benzene with nitromethane to produce $PhCH_2NO_2$[74].

Several new methods for the symmetrical coupling of organic halides have been developed. Aliphatic halides such as 1-octylbromide were coupled by electrochemical reduction of iron or nickel acetylacetonate in the presence of triphenylphosphine. The transition metals were electrochemically reduced to metal(0) species which were stabilized by the added triphenylphospine. The low valent metals then coupled the organic halides [75]. A wide variety of aryl mercuric halides were coupled by heating with copper powder and palladium chloride catalyst in pyridine. The systems from Ph^-, 2-MeO-Ph, 4-MeO-Ph, $4\text{-}H_2NPh$-, $4\text{-}NH_2OCPh$, 2-furyl, and 2-thiophenyl coupled cleanly, while 4-AcO-Ph, 4-COOH-Ph and mesityl- failed [76]. Cycloalkanes were produced from α,ω-dihalides by treatment of the corresponding diGrignard reagents with silver(I) salts. Thus cyclobutane (84%), cyclopentane (80%), cyclohexane (55%), norbornane (82%), tetralin (70%), cis-decaline (57%), trans-decalin (67%), and [4.2.0] tricyclooctane (61%) were produced from the corresponding dihalides. The reaction was not suitable for formation of rings larger than six-membered [77]. Dimerization of β-ketoesters or β-diesters at the α position was effected by silver oxide in DMSO [78]. Cyclotetramerization of propargyl acetate **6** was carried out by treatment with n-butyllithium followed by cuprous chloride (eq. 30). The resulting cycloalkyne had an unusual PES spectrum which suggested that the C≡C's are bowed, rather than linear [79].



(30)

6 5%

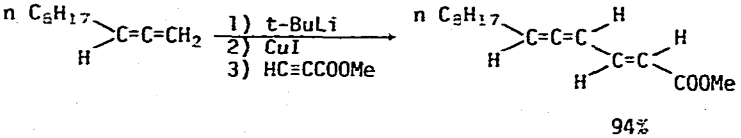
Aromatic amines were dimethylated by treatment with formaldehyde in ethanol in the presence of $KHFe(CO)_4$ [80]. This same iron complex promoted the reaction of glutaraldehydes with primary amines to produce N-alkylpiperidines in 40-90% yields [81]. Polystyrene was treated with molybdenum hexacarbonyl to produce polymer bound (benzene) molybdenum tricarbonyl complexes. These were studied as catalysts for Friedel-Crafts alkylations and acylations.

These catalysts worked only with stabilized or tertiary carbonium ions, and rates were considerably slower for polymer-bound catalysts compared to homogeneous systems [82]. Finally, the alkylation and arylation of unsaturated compounds with the aid of transition metal complexes has been reviewed [83].

B. Conjugate Addition

The mechanism of the conjugate addition of lithium dialkylcuprates has been intensively studied recently. It had been proposed that electron transfer processes were important in this reaction, and the use of lithium organocuprate additions as models for electron transfer processes has been reviewed [84]. These ideas have been extended in a series of papers studying electron transfer from lithium dialkylcuprates to diarylketones and β-cyclopropyl-α,β-unsaturated ketones, in which detection of radical anion intermediates was attempted [85-87]. In a subsequent study, it was demonstrated that the enolate resulting from conjugate addition of lithium dimethylcuprate to 3-methylcyclohexenone was a lithium enolate, not a copper enolate [88].

Treatment of lithium tetraalkylborates with cuprous halide produce the corresponding copper tetraalkylborate. This reagent added 1,4 to acrylonitrile to produce saturated alkylnitriles. Reaction with α,β-cyclopropyl-γ,δ-unsaturated ketones resulted in a 1,6 addition with opening of the cyclopropyl ring [89]. Lithium diallenylcuprates were prepared and added 1,4 to acetylenic esters. In this fashion a pheremone for a bean parasite was synthesized (eq. 31). This reagent also reacted cleanly with alkyl halides to produce substituted allenes [90]. Lithium dicyclopropylcuprate added 1,4 to conjugated enones and ynones, and cleanly alkylated β-halo-α,β-unsaturated ketones without subsequent 1,4-addition (eq. 32) [91]. Functionalized cyclopropyl cuprate



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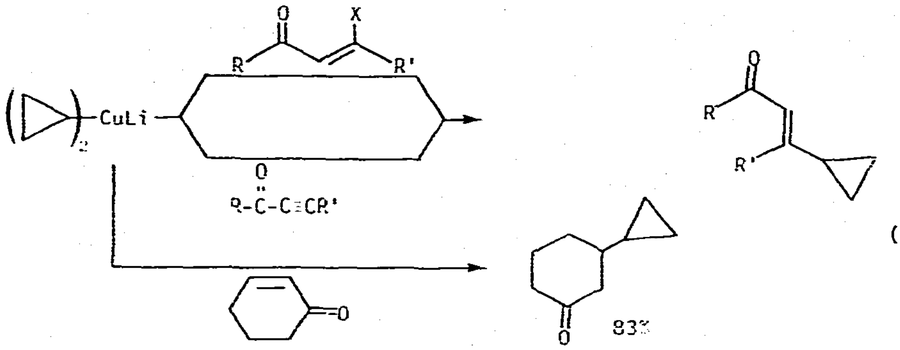
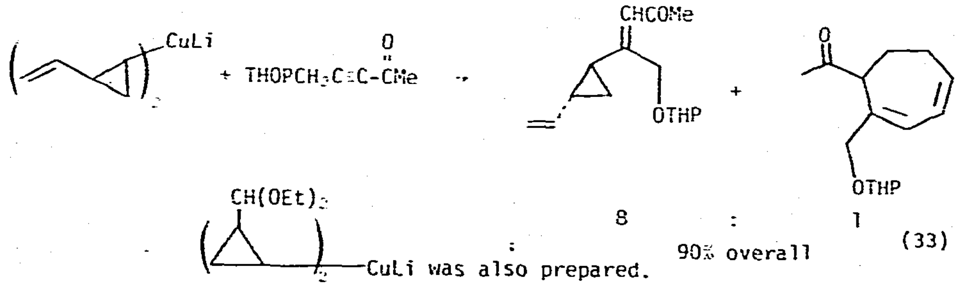


(32)

reagents were also synthesized [92] and used in the synthesis of ring-fused cycloheptatrienes (eq. 33) [93].



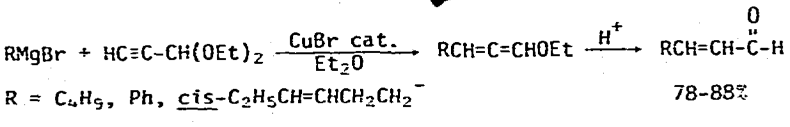
8 : 1

90% overall

(33)

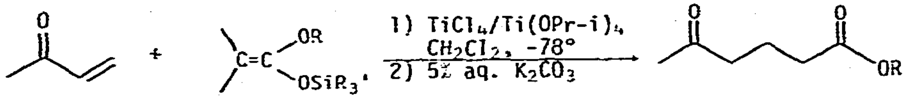
was also prepared.

Lithium dialkylcuprates reacted with propargyl acetates to produce allenes (90%) in an overall Sn^{2}' displacement of the acetate [94]. Similarly ferric chloride catalyzed the reaction of alkyl Grignard reagents with propargylic chlorides to produce allenes, again with a net Sn^{2}' displacement [95]. Cuprous bromide was used to catalyze the reaction of Grignard reagents with the acetal of propynal, producing allenic enol ethers which hydrolyzed to the alkylated acrolein (eq. 34) [96]. The preparation of δ ketoesters by the 1,4-addition of o-silanated ketene acetals to conjugated ketones was promoted by $TiCl_4$-$Ti(OPr\text{-}i)_4$ (eq. 35) [97]. Silyl enol ethers added 1,4 to α,β-unsaturated ketones or acetals under similar conditions [98].



$$RMgBr + HC{\equiv}C\text{-}CH(OEt)_2 \xrightarrow[Et_2O]{CuBr\ cat.} RCH{=}C{=}CHOEt \xrightarrow{H^+} RCH{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \qquad (34)$$

$R = C_4H_9$, Ph, $\underline{cis}$-$C_2H_5CH{=}CHCH_2CH_2^-$ $\qquad$ 78-88%



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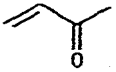
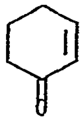
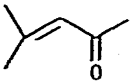
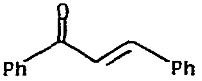
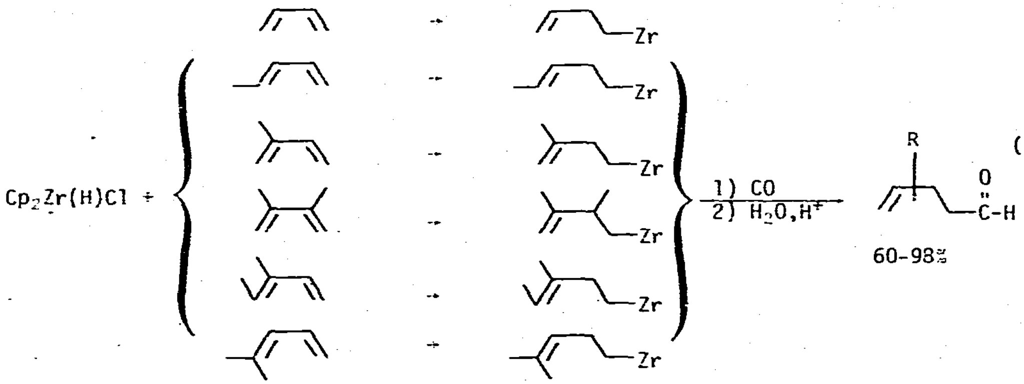
, ,  and  worked well.

C. *Acylation*

The metal catalyzed acylation of simple olefins has been subjected to extensive investigation recently. Ligand stabilized platinum(II)-group IVB metal halide complexes were studied as catalysts for the homogeneous carbonylation of α-olefins to carboxylic acid esters with up to 98% selectivity for the linear esters. The best catalyst systems were found to be $(Ph_3As)_2PtCl_2/SnCl_2$, $(Ph_2AsCl)_2PtCl_2/SnCl_2$, and $[(PhO)_3P]_2PtCl_2/SnCl_2$. The activity was highly dependent upon the coordinated ligand's structures. The effects of olefin structure, nucleophile, temperature, pressure and catalyst structure were studied [99]. In a more detailed study of the conversion of 1-heptene to methyl octanoate, up to 76% yield with 87% selectivity for linear ester was achieved with $(Ph_3P)_2PdCl_2/10\ SnCl_2$ as a catalyst. This reaction was relatively insensitive to temperature, CO pressure, solvent, and coreactant, but was significantly influenced by the nature of the catalyst and the olefin. The rate was fastest with α olefins, intermediate with branched α-olefins, and slowest with internal olefins [100]. The catalytic methoxycarbonylation of both cis and trans-2-butene by $PdCl_2/CuCl_2/CO/O_2$ in methanol was carefully investigated. The initial methoxypalladation was found to be stereospecifically trans. In contrast, addition of one equivalent of sodium acetate resulted in exclusive cis methoxypalladation [101]. As an extension of these studies, palladium(II) carbonylation of terminal and branched α olefins and cycloolefins was investigated. Again treatment of alkenes with carbon monoxide in methanol with a Pd^{2+}/Cu^{2+} catalyst system resulted in up to 83% conversion to the β-methoxyester, if excess copper was used. Oxidation of carbon monoxide to carbon dioxide competed. However, addition of sodium acetate to this catalyst system led to production of 1,2-diesters in 60-90% yield. With cyclic olefins, the product was predominantly diester regardless of conditions [102]. When styrene was treated with carbon monoxide in ethanol with $(Ph_3P)_2PdCl_2$ as catalyst, ethyl-2-phenylpropionate was the sole product. With (+ DIOP)$PdCl_2$ as a catalyst, ethyl-3-phenylpropionate (lacking a chiral center) was the sole product [103].

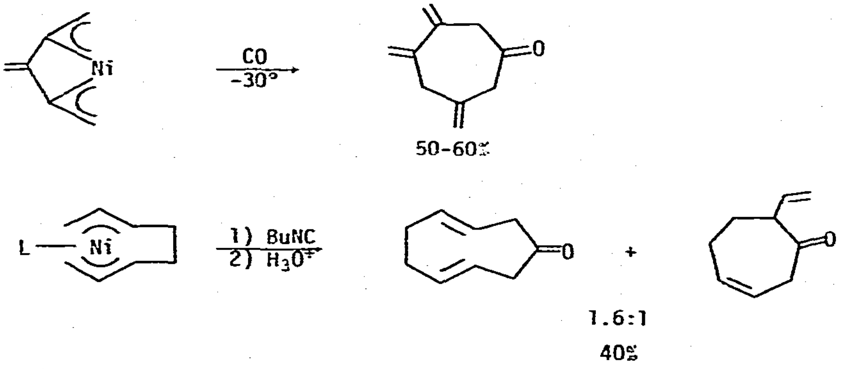
The monoacylation of 1,3-dienes to γ,δ-unsaturated aldehydes was effected by hydrozirconation ($Cp_2Zr(H)Cl$) followed by carbonylation and acidic isolation. Only monoacylation products were obtained, and terminal aldehydes were the sole products. Hydrozirconation occurred exclusively on the less substituted double bond in unsymmetrical systems (eq. 36) [104]. (+)-α-Pinene was hydroformylated to (+)-2-formylbornene using dicobaltoctacarbonyl as catalyst (5% catalyst, 120°, 1:1 H_2/CO, 300 bar) while use of a rhodium catalyst with (-)-α-pinene produced (+)-3-formylpinane [105]. Hydroformylation of 1-pentene using $L_3Rh(H)CO$ as a homogeneous catalyst produced a 3.3 to 1 ratio of linear to branched aldehydes. When the same catalyst was attached to a polystyrene support with high (40%) phosphine loading, the ratio increased to 16.1 to 1 at 120° [106]. Use of $L_2RuH_2(CO)_2$ as a homogeneous hydroformylation catalyst produced, in 80% conversion, a 2:1 ratio of terminal to branched aldehydes [107]. Finally, the use of a rhodium hydroformylation catalyst with the chiral phosphine ligand (-)-2,3-o-isopropylidene-2,3-dihydroxy-1,4-bis (5H-dibenzophospholyl)butane led to aldehydes with a 44% optical yield [108].



(36)

The cyclization of 4-pentenal to cyclopentenone, the formal intramolecular addition of an aldehyde across an olefin, was catalyzed by $(Ph_3P)_3RhCl$ in the presence of ethylene. The reaction went in 72% yield with 96% conversion. Use of other catalysts, such as $(olefin)_2Rh(AcAc)$ led to insertion of ethylene to produce mixtures of heptenones as well as isomerized starting material [109]. Treatment of 4-ethoxy-2-butanone with methyl iodide and carbon monoxide, with $(Ph_3P)_3RhCl$ as catalyst produced mixtures of levulinic acid and ethyl levulinate in moderate yield [110]. Polystyrene-bound $(Ph_3P)_2Rh(CO)Cl$ catalyzed the carbonylation of methyl iodide to methyl acetate [111]. The kinetics and mechanism of carbon monoxide insertion into complexes of the type $L_2M(R)X$ where M is nickel, palladium or platinum, has been reported in extensive detail. Preparation and spectral data for 62 different complexes were presented[112]. Finally, benzyl, aryl, vinyl and heteroaromatic halides were converted to the corresponding carboxylic acids by carbon monoxide and $(Ph_3P)_4Pd$ catalyst under phase transfer conditions. The catalyst had high activity, and high turnover [113].

A variety of metal π-complexes were reacted with carbon monoxide to form cyclic ketones. The bis-π-allylnickel complex resulting from allene coupling reacted with carbon monoxide to produce an unsaturated cycloheptanone while that from dimerization of butadiene produced a cyclooctenone along with a cyclononadienone (eq. 37) [114]. The iron tricarbonyl complexes of cycloheptatriene and cyclooctatetraene reacted with H^+ then hydride, then carbon monoxide to produce bicyclic ketones in fair yield (eq. 38) [115]. The



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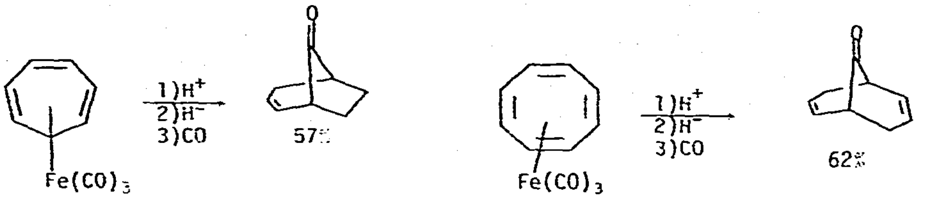
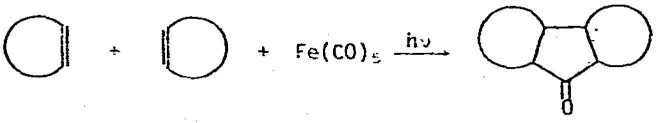


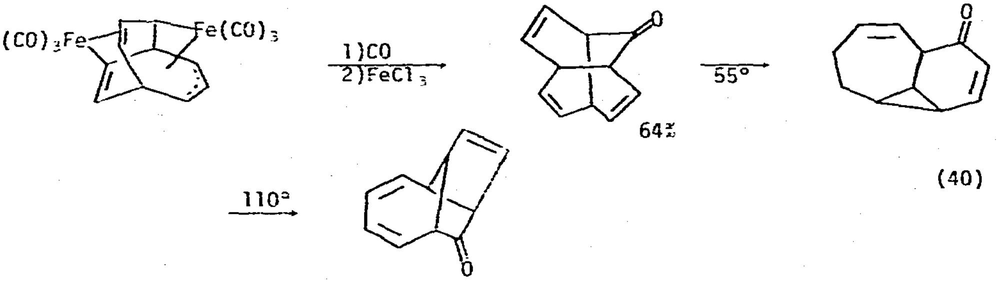
(38)

stereospecific cyclic ketone formation with iron(0) (eq. 39) has been reviewed [116]. The bis iron complex of a bicyclic olefin underwent



(39)

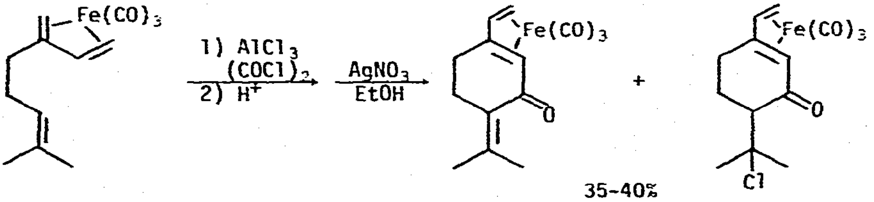
carbonylation to produce a bicyclic trienone which underwent several different thermal rearrangements (eq. 40) [117]. The substituted butadiene iron tri-



(40)

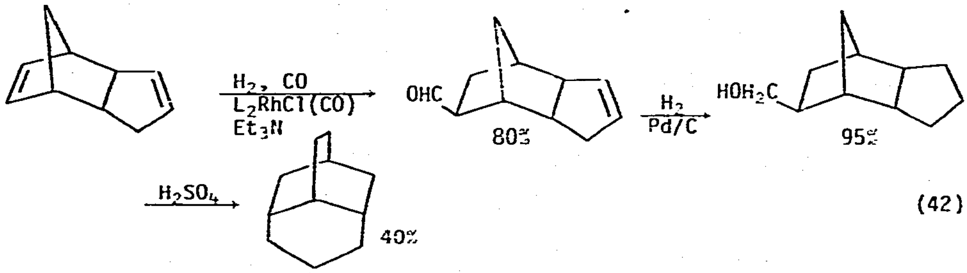
carbonyl complex in eq. 41 was carbonylated by oxalyl chloride to produce a mixture of cyclohexenones [118].

Dialkylacetylenes were cyclodimerized to tetraalkylcyclopentenones by nickel carbonyl in concentrated hydrochloric acid [119]. A precursor to 4-homotwistane was synthesized by the $L_2Rh(Cl)CO$ catalyzed hydroformylation



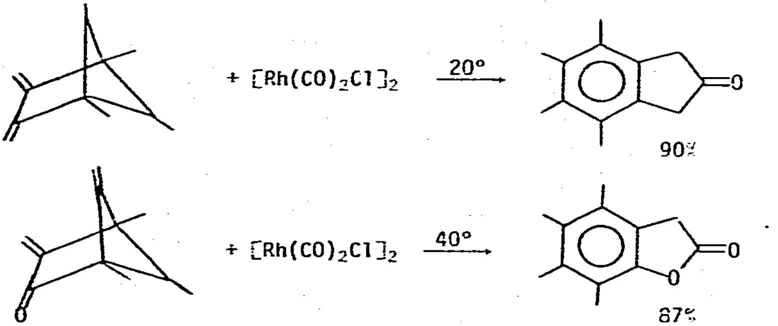
(41)

of cyclopentadiene dimer (eq. 42) [120]. The rhodium carbonyl chloride dimer reacted with several polycyclic systems to produce cyclic ketones



(42)

(eq. 43) [121]. Benzene and anisole were converted to the corresponding 4-benzoic acid upon treatment with 1:1 acetic acid/acetic anhydride in the presence of sodium palladium(II) malonate [122]. Finally, tris(methyldiphenylphosphine)rhodium(I) chloride acted as a decarbonylation catalyst of aldehydo sugars (eq. 44) [123].



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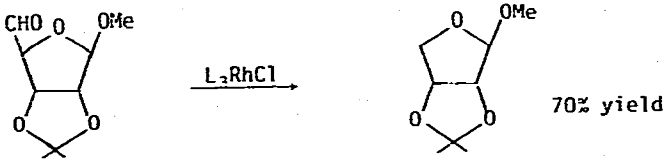
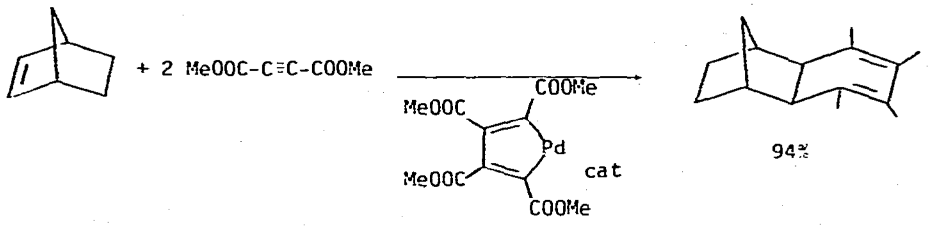


(44)

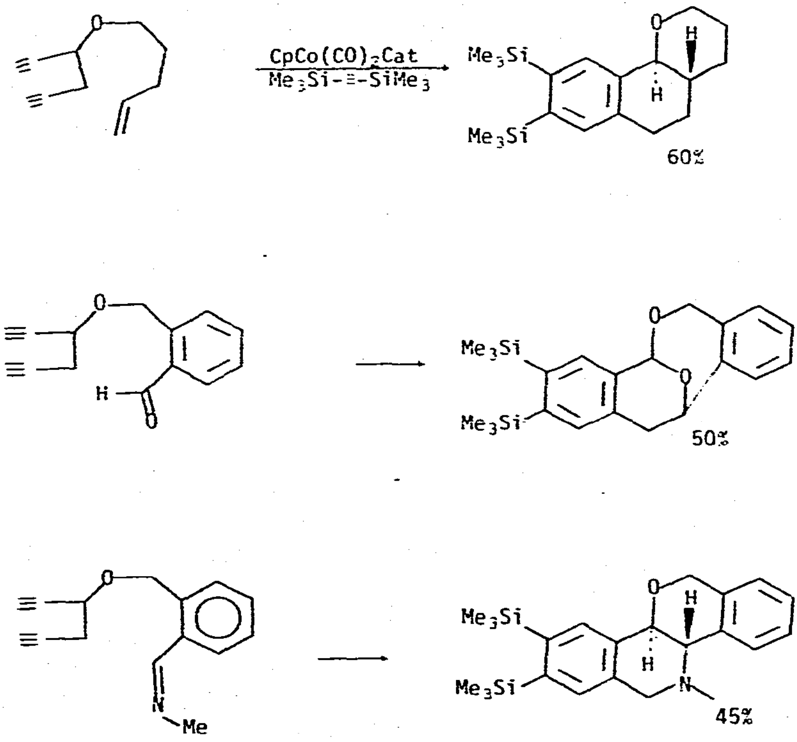
D. Oligomerizations

Transition metal catalyzed oligomerizations of alkynes continued to be actively studied. The palladium(II) induced oligomerization of acetylenes has recently been reviewed [124]. Nickelocene (Cp_2Ni), $Cp_2Ni_2(CO)_2$ and $Cp_3Ni_3(CO)_2$ were dispersed on silica gel, then heated at 80-120° under vacuum. The resulting materials catalytically trimerized acetylene to benzene at room temperature, catalyzed H_2-D_2 exchange, and catalyzed the reduction of ethene and benzene. They were inactive as oxocatalysts however [125]. The palladiocycle formed by the cyclodimerization of dimethylacetylene dicarboxylate was found to be a highly specific catalyst for the cocyclodimerization of norbornene with dimethylacetylene decarboxylate (eq. 45) [126].



(45)

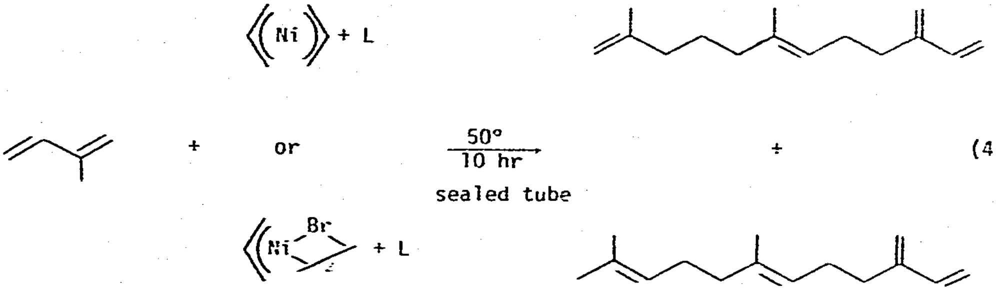
The intramolecular cyclotrimerization of alkynes by CpCo(CO)$_2$ was used to synthesize several rather complex polycyclic materials in one step. These reactions are summarized in eq. 46 [127].



(46)

Polymer supported palladium chloride was used to catalyze the codimerization of alkynes with allylic halides to produce 1,4-pentadiene derivatives in high yield. The reaction worked well with both mono- and disubstituted alkynes [128]. Terminal alkynes were hydroaluminated with diisobutylaluminum hydride, and the resulting vinyl alane coupled to vinyl halides using either nickel(0) or palladium(0) catalysts. Conjugated dienes were formed in 50-80% yield with >95% EE stereochemistry [129]. Di- and trisubstituted vinyl iodides were dimerized by treatment with an organolithium reagent in the presence of a manganese(II) catalyst in ether at -20°. The yields of symmetrical 1,3-butadienes were 70-90% by this procedure [130]. The net dimerization of alkynes to 1,3-butadienes was accomplished by conversion of the alkyne to the vinyl mercurial compound. Treatment with lithium chloropalladate in HMPA produced the symmetric 1,3-diene in essentially quantitative yield, with very high stereospecificity. Furthermore, a variety of functional groups were tolerated by this procedure [131].

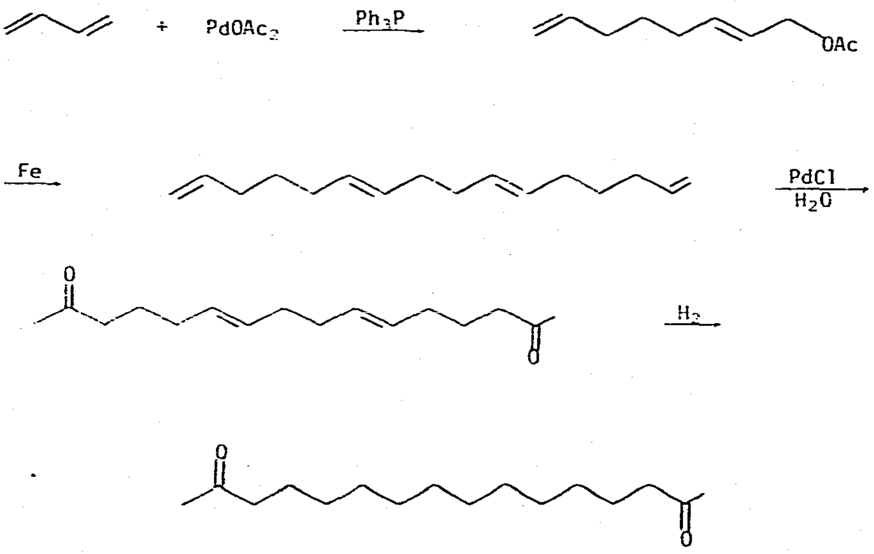
The linear trimerization of isoprene was catalyzed by both *bis*-π-allylnickel and *bis*-π-allylnickel halide complexes with a variety of ligands (eq. 47).



(47)

The catalysts produced over 90% trimeric material. The isomer distribution could be drastically altered by changing the nature of the ligand, from 93:7 (terminal olefin to farnesene) to 17:83 [132]. Isoprene was reductively dimerized by treatment with formic acid, triethyl amine and one per cent "LPd" catalyst. The reaction produced 40-80% yields of head to tail dimers, consisting of a mixture of double bond isomers [133].

Butadiene was dimerized to an octadienyl acetate, which was coupled to a hexadecatetraene by treatment with iron metal. The terminal olefins were oxidized to ketones by palladium chloride/water, and the internal olefins catalytically reduced to produce 2,15-hexadecadione, a muscone precursor (eq. 48) [134]. Butadiene was copolymerized with a large number of oxygen substituted alkynes by a nickel zero catalyst to produce cyclodecenes after reduction (eq. 49). The reaction was also applied to α,ω-dialkynes [135].



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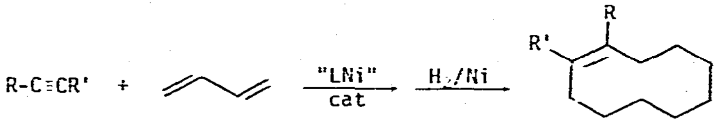
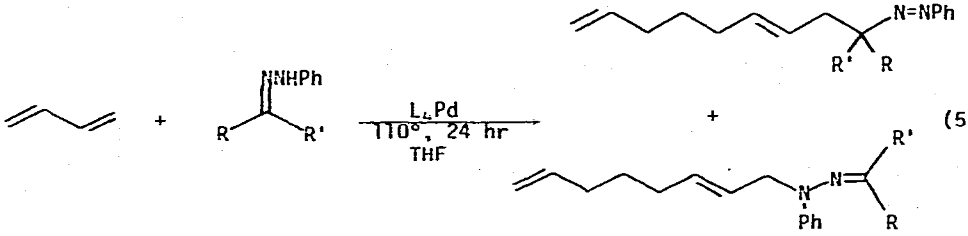


(49)

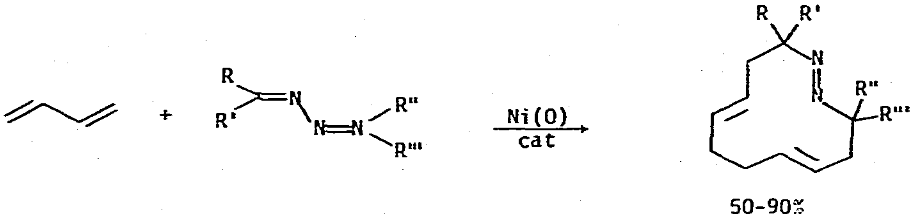
R's = CH_2OMe, $(CH_2)_2OTHP$, $(CH_2)_3COOMe$, etc.

Butadiene was copolymerized with ketone phenylhydrazones by a tetrakis phosphine palladium(0) complex in 60-90% yield, as a mixture of isomers (eq. 50) [136]. Cyclooligomerization of butadiene with bis-hydrazones using a nickel(0) catalyst produced a variety of 1,2-diaza-1,5,9-cyclododecatrienes (eq. 51) [137].



(50)

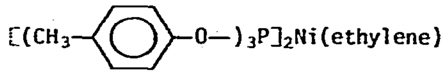
60-90%

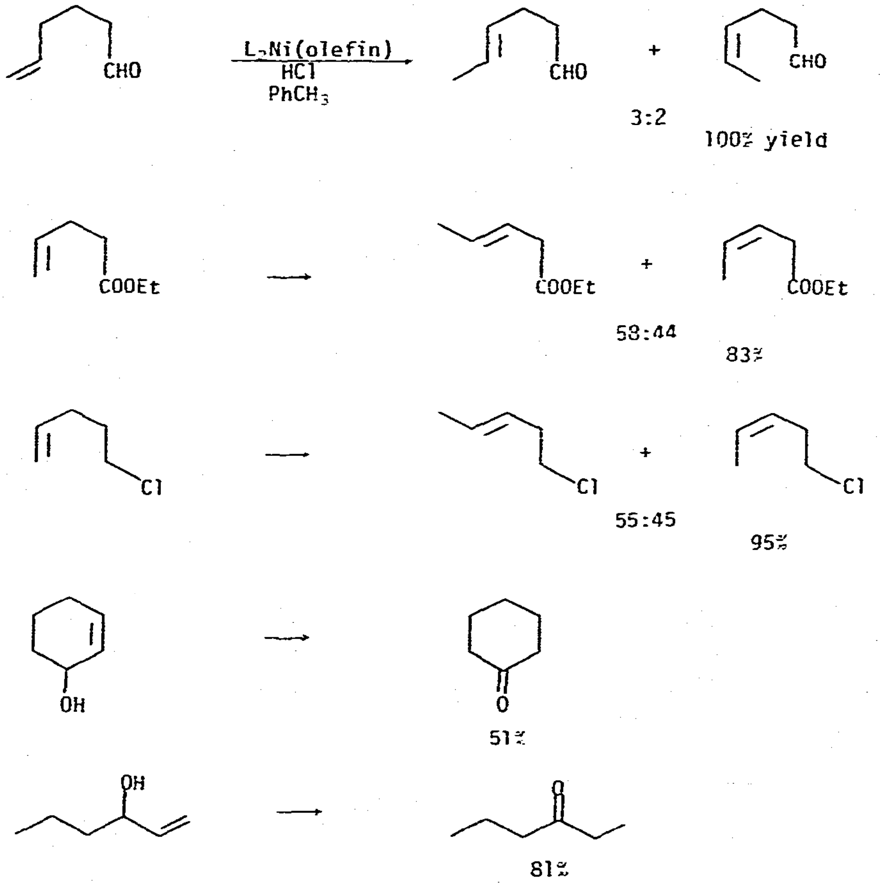


(51)

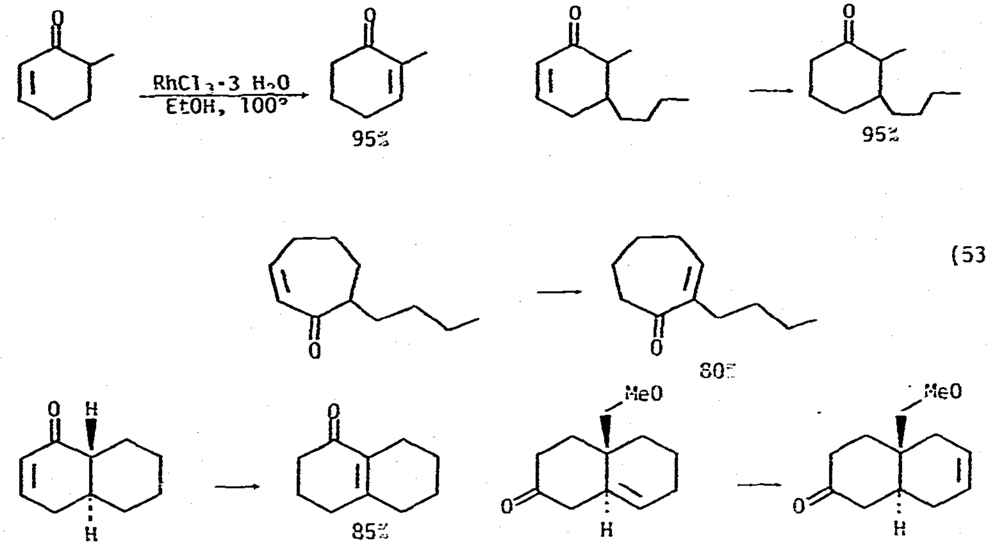
Brominated polystyrene was treated with L_4Ni to produce polymer-bound bis-(triphenylphosphine)phenylnickel bromide via an oxidative addition. Treatment of this solid phase supported organonickel complex with boron trifluoride etherate produced material that was a good catalyst for olefin dimerization [138]. The cationic platinum complex $Pt(CH_3CN)_4(BF_4)_2$, prepared by treating platinum chloride with silver tetrafluoroborate in acetonitrile, dimerized branched olefins in nitromethane [139]. Cycloolefins including cyclobutene, cyclopentene, cycloheptene, cyclooctene and norbornene were converted to polyalkenomers with greater than 90%, cis stereochemistry by treatment with the olefin metathesis catalyst $Ph_2C{=}W(CO)_5$ at 25-40° [140]. Iron pentacarbonyl or bis-cyclooctadiene nickel cyclotrimerized α,α'-dibromoacetophenone to 1,2,3-tribenzoylcyclopropane in 70% yield [141].

E. Rearrangements

The rearrangement of 1,2-olefins to 2,3-olefins was catalyzed by  in toluene solution in the presence of hydrogen chloride. The rearrangement went no further, even in cases where the potential for conjugation existed. The same catalyst system isomerized allylic alcohols to carbonyl compounds [142]. These transformations are summarized in eq. 52. Rhodium trichloride trihydrate was used to isomerize unsubstituted cyclic conjugated ketones to substituted conjugated ketones by heating in a sealed tube in ethanol at 100°. This remarkable transformation was quite general and went in excellent yield (eq. 53) [143]. Potassium t-butoxide and iron pentacarbonyl, molybdenum hexacarbonyl, palladium chloride, or tris(triphenylphosphine)rhodium trichloride in HMPA was used to effect double bond rearrangements in high yield. For example, 1,5-cyclooctadiene isomerized cleanly to 1,3-cyclooctadiene with this catalyst [144].

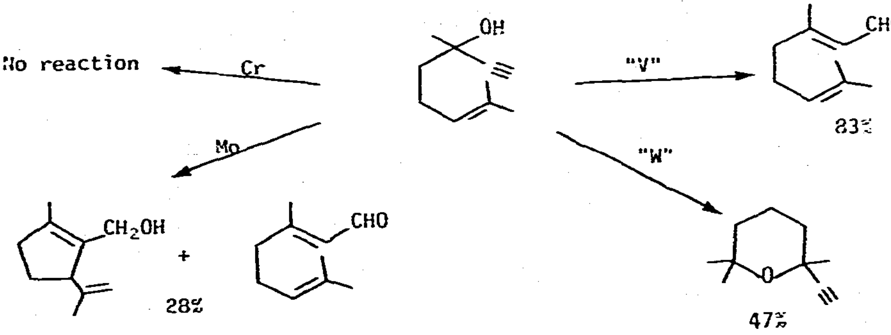


(52)



(53)

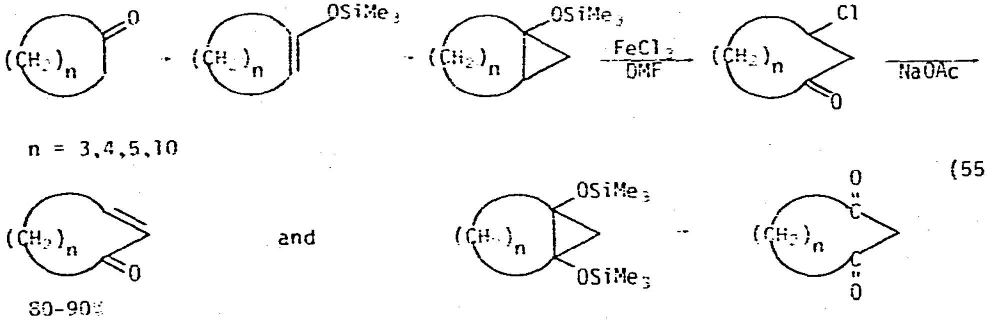
Three separate groups independently reported the use of silylvanadate complexes to catalyze the rearrangement of propargyl alcohols to unsaturated aldehydes. Treatment of diphenyldichlorosilane with Na$_3$VO$_4$ in xylene or aqueous acetone produced a polymeric catalyst of composition (---Ph$_2$SiO-V=O)$_x$ which was air stable, insoluble in xylene but soluble in aqueous acetone. This catalyst rearranged propargyl alcohols to unsaturated aldehydes. Similar catalysts prepared from chromium, molybdenum or tungsten catalyzed rather different rearrangements (eq. 54) [145]. The silylvanadate catalyst prepared



(54)

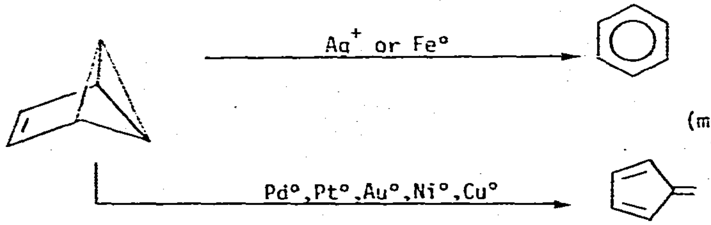
from a variety of silanes and having the composition [R$_3$SiO]$_3$VO effected the same propargyl alcohol-unsaturated aldehyde rearrangement as the polymeric vanadate catalysts discussed above. This rearrangement was used to produce a variety of isoprenoid aldehydes [146]. A variety of steroidal 17-ethynyl alcohols were rearranged to the 17-(=CHCHO) functionality by $(Ph_3SiO)_3VO$ catalyst in refluxing xylene in high yield. A variety of functional group arrays in the A and B rings was tolerated by this catalyst system [147].

Molybdenum hexacarbonyl catalyzed the rearrangement of epoxides to carbonyl compounds in refluxing DME. Thus styrene oxide was converted to benzyl aldehyde in 58% yield, while stilbene was converted to benzyl phenyl ketone in 80% yield [148]. Palladium acetylacetonate and triphenylphosphine catalyzed the rearrangement of butadiene-monoxide to 2-butenal [149]. A ring expansion procedure involving the ferric chloride assisted cleavage of siloxy cyclopropanes has been developed (eq. 55) [150].



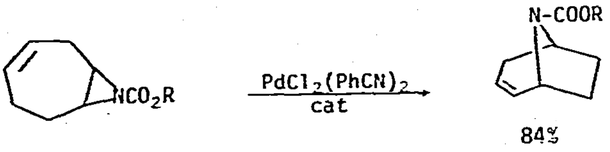
(55)

Transition metal catalyzed rearrangements of small ring compounds was the subject of a recent review [151]. Several of these arrangements were recently reported and are summarized in eqs. 56-58.

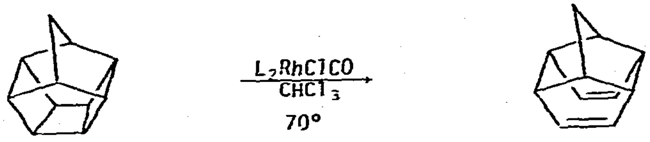


(mechanistic study)

(56)
[152]



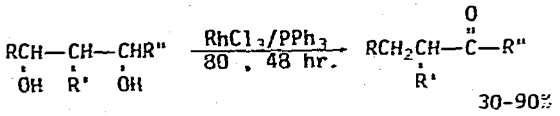
(57)
[153]



(58)
[154]

(inert to Ag)

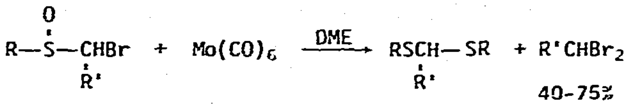
Several miscellaneous rearrangements involving transition metals have also been reported. A 1:1 mixture of triphenylphosphine and rhodium trichloride rearranged 1,3-diols selectively to monoketones (eq. 59).



$$\underset{OH}{RCH}-\underset{R'}{CH}-\underset{OH}{CHR''} \xrightarrow[80\ ,\ 48\ hr.]{RhCl_3/PPh_3} RCH_2\underset{R'}{CH}-\overset{O}{\overset{\|}{C}}-R'' \quad 30\text{-}90\% \qquad (59)$$

R's = H, Me, alkyl

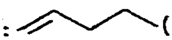
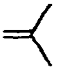
Yields decreased as the steric hindrance increased, and substitution at the 2 position also decreased reactivity [155]. Molybdenum hexacarbonyl converted α-halosulfoxides to thioacetals (eq. 60)[156]. Curpic acetate catalyzed the photolytic rearrangement of $CH_3CH_2CH_2CH_2CH(ONO)CH_3$ to $CH_2{=}CHCH_2CH_2CH(OH)CH_3$, a reaction which proceeded by a free radical mechanism [157].

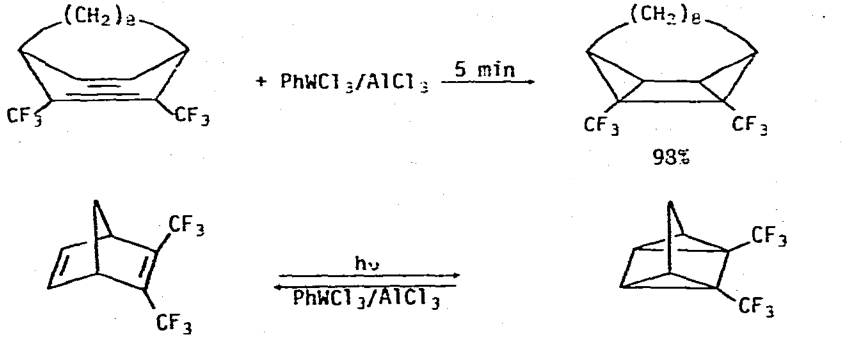


$$R-\overset{O}{S}-\underset{R'}{CHBr} + Mo(CO)_6 \xrightarrow{DME} RSCH\underset{R'}{}-SR + R'CHBr_2 \quad 40\text{-}75\% \qquad (60)$$

R = aryl, n-Pr R' = H, Et, Me

The olefin metathesis reaction continued to be intensively investigated. A review entitled "Olefin Metathesis, a versatile tool in Petro and Polymer Chemistry," has appeared [158]. Mechanistic aspects of olefin metathesis has also been reviewed [159]. The metathesis of long-chain olefins over $EtAlCl_2/W$ or Mo complex catalysts gave 8-11% of the desired olefin as a cis-trans mixture. Some of these mixtures had insect sex pheremone activity [160]. A metathesis catalyst for 1-hexene and 2-pentene was prepared from tungsten hexachloride and a variety of cycloalkylsilanes [161]. The metathesis of 1-hexene was also catalyzed by a mixture of tungsten hexacarbonyl and tetraalkyl tin. The reactivity decreased in the following order:

R = Et > Bu > Ph > Me > Me_3SiCH_2. Products that inhibited the reaction were produced by 5-decene [162]. A thorough study of the tungsten hexachloride-ethyl aluminum dichloride catalyst system for olefin metathesis has been made. When aromatic solvents were used, alkylation of solvent competed. This catalyst system was made to produce exclusively monosubstituted benzenes at thermal equilibrium [163]. The metathesis of olefins containing -COOR, -OCOR, -OR, -CN, -COR and -CONR groups was effected by $WCl_6/Me_3Al_2Cl_3$ and $Mo(OEt)_2Cl_3/Me_3Al_2Cl_3$ catalyst systems [164]. The metathesis of 1-decene with 1-tetradecene with a catalyst of $L_2Mo(NO)_2Cl_2/EtAlCl_2$ in chlorobenzene produced a mixture of C_{18}, C_{23}, and C_{28} olefins, from which muscalure, the sex pheremone for the house fly, was isolated by chromatography [165]. The metathesis of 1,5-cyclooctadiene with 4-methyl-4-octene using a $WCl_6/EtAlCl_2$ catalyst produced a 10:15:6 mixture of 4,9-dimethyl-4,8-dodecadiene, 4-methyl-4,8-dodecadiene, and 4,8-dodecadiene in 60% yield as a mixture of cis-trans isomers [166]. Treatment of 1-methylcyclobutene with the tungsten carbene complex $(CO)_5W{=}CPh_2$ produced a polyolefin which was mostly polyisoprene, with 85% Z stereochemistry and some imperfect alternation. This was the first catalyst to cause metathesis of trisubstituted olefins [167]. The $PhWCl_3/AlCl_3$ catalyst was the first to form cyclobutanes by a metathesis reaction, and also the first to do the reverse, cleave cyclobutanes to diolefins (eq. 61) [168]. Finally, the mechanism of olefin metathesis involving tungsten carbene complexes has been studied in detail. The order of olefin reactivity was: (49), (10), (1), (0).



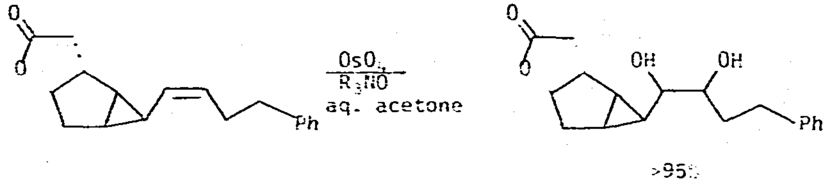
(61)

A complex mechanistic scheme to accommodate all observations was presented [169].

III. OXIDATION

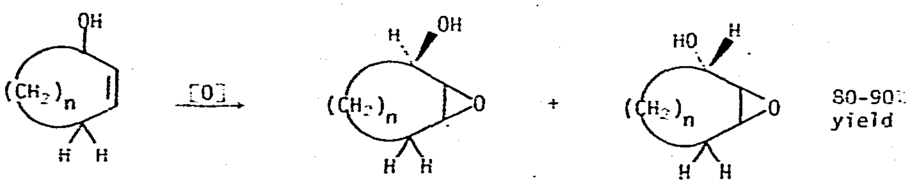
Several new oxidizing systems for the conversion of alcohols to aldehydes or ketones have been developed. Chromium trioxide was mixed with an anion exchange resin, Amberlyst A-26, and the resulting resin was a remarkably effective oxidation reagent for primary and secondary alcohols to aldehydes or ketones. The substrate alcohol was simply stirred with the resin in refluxing solvent, filtered and evaporated when reaction was complete. No acids or by-products were detected [170]. Chromium trioxide/HMPA was also an effective oxidizing agent for activated (allylic or benzylic) primary or seconday alcohols. A 2:1 oxidant to substrate ratio was found most effective. The oxidation of geraniol to geranial resulted in 10% double bond isomerism [171]. The complex $RuCl_2L_3$ was found to catalyze the oxidation of primary, secondary and allylic alcohols, but not homoallylic alcohols, by tertiary amine oxides, to aldehydes or ketones. In this manner cyclododecanol (100%), 1-dodecanol (80%), citronellol (90%), geraniol (81%) and carveol (94%) were oxidized in good yield [172]. Uranium hexafluoride was used to oxidize methyl ethers to ketones. Methyl cleavage always resulted. Thus methyl benzyl ether produced benzaldehyde (78%) while methyl cyclohexyl ether was oxidized to cyclohexanone (86%). Benzyl and benzhydryl ethers always oxidized to give the phenyl ketone, even with 2-o-nitrophenethyl-benzhydryl ether. This reagent also converted dimethyl- and tosylhydrazones to ketones in 60-90% yield, while aldehydes reacted to give acid fluorides in lower (40%) yields [173].

The oxidation of olefins to vicinal diols was effected by t-butylhydroperoxide and tetraethylammonium hydroxide in t-butanol, with osmium tetroxide present in catalytic amounts. This was claimed to be the best method when the substrates and products were stable to base, since it was catalytic in osmium, and neater than with metal chlorate catalysts or hydrogen peroxide which tend to over-oxidize. A wide variety of olefins, including terminal, internal, cyclic, tri- and tetrasubstituted and styryl systems, as well as oleic acid and oleyl alcohol were successfully oxidized [174]. The catalytic oxidation of olefins to diols by osmium tetroxide using amine oxides to regenerate the osmium catalyst has also been reported. Seven cases were reported, including the sensitive system in eq. 62. N-methylmorpholine-N-oxide was the best reagent [175].



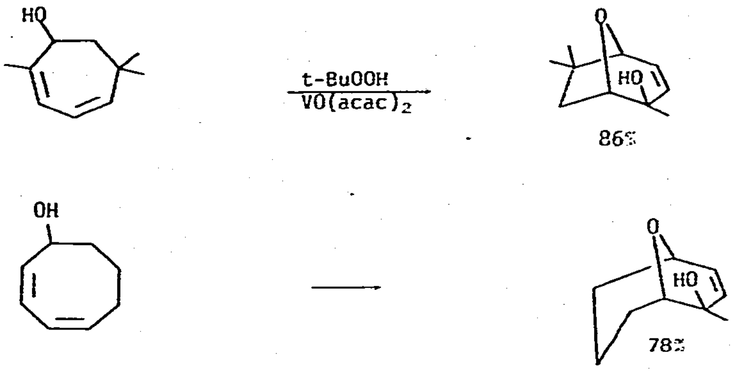
(62)

The cobalt(III) acetylacetonate catalyzed epoxidation of olefins was studied. It was claimed that allylic oxidation went via a hydroperoxide while epoxidation resulted from direct activation of molecular oxygen, and proceeded via a radical chain process [176]. The epoxidations of cyclic allylic alcohols by m-chloroperbenzoic acid and t-butylhydroperoxide/ VO(AcAc)$_2$ were compared. The metal catalyst system strongly favored formation of the syn epoxyalcohol (eq. 63) [177]. The same catalyst system was responsible for the unusual transannular epoxidation presented in eq. 64. This catalyst was usually regioselective for allylic double bonds. The reaction was shown to go via a syn 2,3-epoxy-4-enol, followed by a stereospecific rearrangement to product [178].



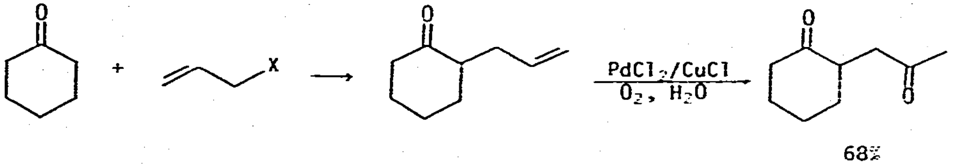
n = 2	99	5
n = 3	99	39
n = 4	97	99
n = 5	91	99
[O] =	t-BuOOH/VO(acac)$_2$	MCPBA

(63)



(64)

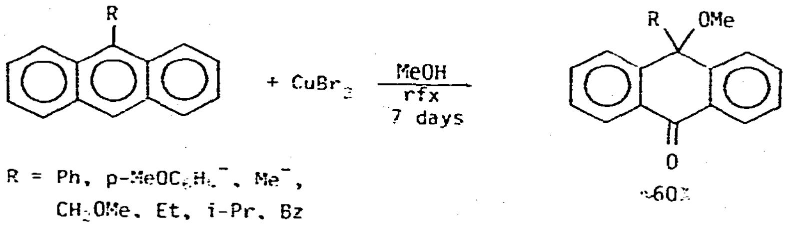
The disubstituted double bond of isoprene was epoxidized with peracetic acid, then oxidatively chlorinated by cupric chloride to produce 4-chloro-2-methyl-2-butenal in 80% yield [179]. This was an intermediate in the synthesis of vitamin A acetate. Ketones were α-alkylated with allylic or homoallylic halides to produce 4,5 or 5,6-unsaturated ketones. The double bond was then oxidized with a $PdCl_2$-CuCl/DMF/O_2 catalyst system to produce 1,4 or 1,5 ketones (eq. 65) [180]. The oxidation of olefins catalyzed by oxygen complexes of transition metals has been reviewed [181].



(65)

Cyanohydrins were prepared by the oxidation of nitrile anions with MoO_5·Py·HMPA [182]. 3,3-Dimethylcyclopentanone was oxidized to 4,4-dimethyl-2-cyclopentenone in 70% yield using chloranil and palladium chloride [183]. Ruthenium tetroxide was used to oxidize N-benzylpyrrolidine to N-benzylsuccinimide. This procedure was used as an alternative to the von Brawn degradation for assignment of stereochemistry for cyclic amines [184]. Primary amines were oxidized by simply mixing the amine and palladium chloride or gold chloride in water, and distilling to dryness. Indoline was oxidized in indole in 83% yield by stirring with palladium chloride in methanol with added triethylamine [185]. O-phenylene diamine (1,2-diaminobenzene) was oxidized the cis,cis-mucononitrile by molecular oxygen with a cuprous chloride catalyst in pyridine solvent [186]. Substituted o-phenylendiamines underwent a similar oxidative cleavage, as did 1,2-diaminonaphthalene [187]. The same catalyst/solvent system effected the cleavage of phenol to the monomethyl ester of muconic acid [188].

Cupric bromide oxidized 9-substituted anthracenes to the substituted quinol via electron transfer oxidation to the radical cation (eq. 66) [189].



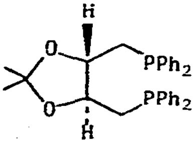
(66)

Benzyl amine substituted polystyrene or cross-linked polyamides with aniline substituted acrylamide groups were treated with cobaltous-4,4',4'',4'''-tetraaminophthalocyanine and coupled with cyanuric chloride. This material coupled 2-mercaptoethanol to the disulfide. This catalyst was more active than similar soluble catalysts, the activity depended on the nature of the support, and the supported catalysts were not deactivated as easily as homogeneous catalysts [190]. The use of active manganese dioxide oxidations in organic chemistry has been reviewed [191].

IV. REDUCTION

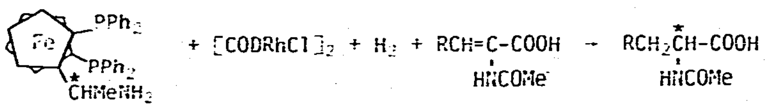
The full experimental details of catalytic hydrogenations of olefins using cationic rhodium(I) complexes have been published. The evolution of the catalyst systems employed $[RhH_2L_nS_x]^+$ and $[RhLnHSy]^+$, their isolation and identification of the catalytic species involved, and the hydrogenation of olefins by these catalysts are presented in detail [192]. The use of these catalysts for the selective hydrogenation of alkynes to *cis* alkenes has also been reported [193]. Cationic *bis*(phosphine) cyclooctadiene iridium(I) complexes were found to be excellent precursors for very active olefin hydrogenation catalysts. They effected reduction very rapidly at 0° and one atmosphere of hydrogen [194]. Butadiene monoxide was hydrogenated using tris(phosphine)rhodium(I) chloride complexes as catalysts. Alkyl or aryl epoxides were unreactive, while phenylcyclopropane was hydrogenalized. It was suggested that π-coordinating ability of the substrate was required for reduction to occur [195]. The reduction of olefins, styrenes and acrylates to saturate systems was effectively catalyzed by a homogeneous system consisting of H_2PtCl_6-$SnCl\cdot 2H_2O$ and HBr/H_2O in isopropanol [196]. Treatment of nickel(II) salts with lithium, sodium or potassium naphthalenide in THF or HMPA produced a metal catalyst that was more active than Raney nickel for the hydrogenation of safrole, cyclohexene, benzonitrile and furfural [197]. In contrast to previous reports, the palladium on carbon catalyzed reduction of 9α-fluorohydrocortisone-21-acetate, and 1,2-didehydro-9α-fluoro-16α-methylhydrocortisone-21-acetate produced the 5β configuration [198]. The addition of titanium tetrachloride to a stoichiometric amount of lithium aluminum hydride and olefin or alkyne led to reduction to alkane in 80-90% yield [199]. Extensive discussion and data on catalytic hydrogenation is contained in three recently published papers. The influence on reaction rates by the ratio of metal catalyst to carrier, by solvents and by acidity [200], poisoning by nucleophiles [201], and poisoning and promotion by cations [202] were all considered. The hydrogenation of alkenes on oxide catalysts has been reviewed [203].

The use of chiral catalysts for the asymmetric reduction of unsaturated substrates, particularly amino acid precursors, continued to be actively investigated. The chemical and physical properties of $[Rh(COD)(+)DIOP]^+ClO_4^-$ (DIOP = structure 7), a very active catalyst for the asymmetric reduction of N-acetyl-1-phenyl-1-aminopropene in 92% optical yield, were investigated [204]. The use of a Rh(Cl)(+)DIOP catalyst for the reduction of β-substituted



7

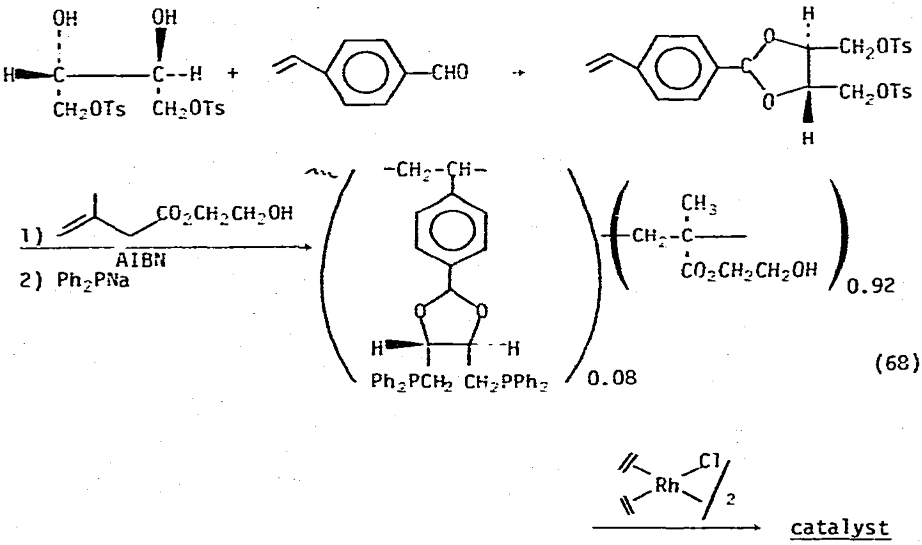
α-amidoacrylic acids produced alanine derivatives in up to 95% optical yield. The optical yield was influenced by the stereochemistry of the double bond, the para substituent of the N-benzoyl group, and by esterification of the carboxylic acid group [205]. A catalyst prepared from the cyclooctadiene rhodium chloride dimer and a chiral ferrocenyl phosphine ligand was used to catalyze the reduction of α-acetamidoacrylic acids to α-amino acids in 86-94% yield and 52-93% optical yield (eq. 67) [206]. A chiral phosphine



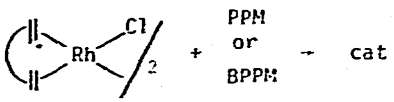
(67)

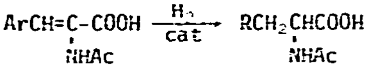
86-94% yield
52-93% optical yield

was constructed on a polymer support and treated with bis-ethylene rhodium chloride dimer to give a solid phase supported catalyst that reduced α-acetamidoacrylates to α-amino acids in yields and optical yields comparable to homogeneous systems. However this insoluble catalyst was easier to recover from reduction mixtures and recycle than were similar homogeneous systems (eq. 68) [207]. Two new chiral phosphine ligands have been



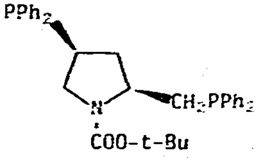
synthesized and used to prepare chiral rhodium catalysts for reductions as above (eq. 69) [208]. Asymmetric catalysis by chiral rhodium complexes in



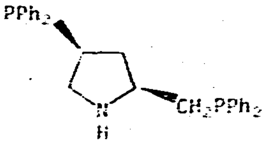


$$\underset{NHAc}{ArCH{=}C\text{-}COOH} \xrightarrow[cat]{H_2} \underset{NHAc}{RCH_2CHCOOH} \qquad (69)$$

85-97% yield
83-91% optical yield



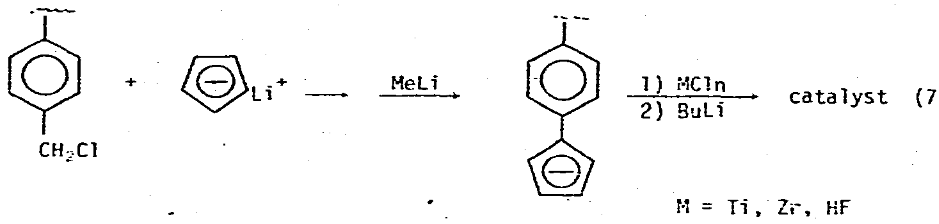
BPPM



PPM

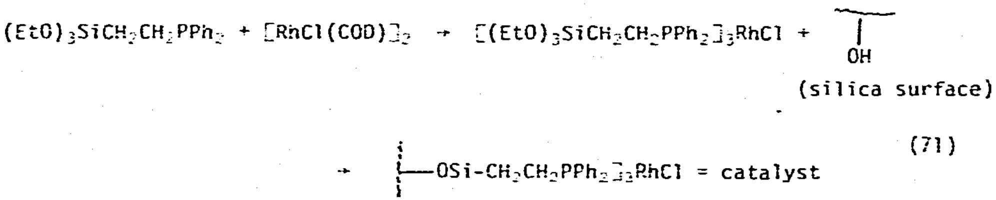
hydrogenation [209,210] and hydrosilation [210] has been reviewed. The use of platinum(II) complexes containing chiral phosphines for catalysis of asymmetric hydrosilation of 2,2-disubstituted prochiral olefins with methyl dichlorosilane was found to produce fair yields of hydrosilation, but only very low (0.5-5.0%) optical yield [211]. The use of nickel(II) complexes with $R\text{-}Bz\text{-}\overset{Ph}{P}\text{-}Me$ as ligands gave slightly better (up to 21%) optical yields [212].

Polymer-anchored homogeneous hydrogenation catalysts and their uses in multistep reactions has been reviewed [213]. A procedure for the preparation of polymeric organophosphorus ligands for attachment of catalysts to insoluble supports has been developed. Polystyrene was lithiated with butyllithium-TMEDA, and then treated with chlorodiphenylphosphine. The radial distribution and per cent phosphorus incorporation was controlled by controlling reaction conditions [214]. A catalyst for the selective reduction of conjugated diolefins to monoolefins at 30° and one atmosphere of hydrogen was prepared by treatment of polystyrene bound iminodiacetate (Chelex 100) with palladium chloride dihydrate [215]. Rhodium hydrogenation catalysts attached to soluble polystyrene bound phosphine ligands were analogous in all ways to homogeneous catalysts of the same type [216]. Use of insoluble polystyrene support produced catalysts three times less active than soluble supported catalysts [217]. Upon treatment of polymer-bound cyclopentadienyltitanium complexes with butyllithium, a catalyst which reduced olefins to alkanes in the presence of hydrogen was produced (eq. 70).



(70)

The polymer used was either 2% or 20% cross-linked polystyrene-divinylbenzene copolymer. Electron microscopy of the resin bound catalyst showed an even distribution of catalyst throughout the polymer bead. The rate of reduction by polymer-bound catalyst was 20-30 times greater than that of the corresponding homogeneous catalyst [218]. Silica supported rhodium and iridium hydrogenation catalysts were prepared as in eq. 71.



$$(EtO)_3SiCH_2CH_2PPh_2 + [RhCl(COD)]_2 \rightarrow [(EtO)_3SiCH_2CH_2PPh_2]_3RhCl + \underset{\text{OH}}{|}$$

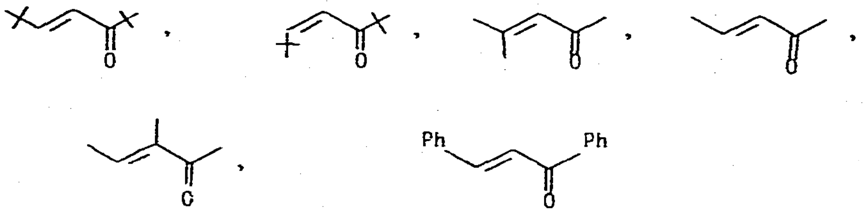
(silica surface)

$$\rightarrow \vdots\!-\!OSi\text{-}CH_2CH_2PPh_2]_3RhCl = \text{catalyst} \qquad (71)$$

These catalysts both reduced and isomerized 1-hexene. Internal olefins reduced only slowly. Added mercaptans did not inhibit the rhodium catalyst, but did slow the rate of reduction by iridium catalysts. Dithiols poisoned both systems [219]. The cyclooctene rhodium(I) chloride dimer was treated with a variety of phosphines to produce catalysts which promoted the homogeneous transfer hydrogenation of olefins, with dioxane as the hydrogen source. The activity of the catalyst depended on the phosphine, with alkyl phosphines being most reactive. A ratio of two phosphines per rhodium gave the best results. Styrene and cyclopentene were the best acceptors [220].

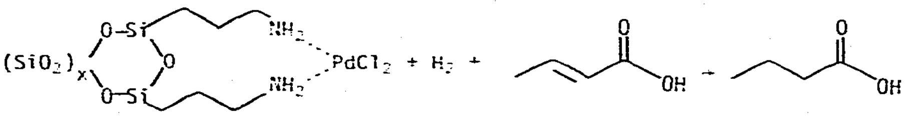
Cationic rhodium(I) complexes such as $[(NBD)RhL]^+A^-$ were catalysts for the reduction of dienes to monoolefins. 2,4-Hexadiene, 2-methylbutadiene and 2,3-dimethylbutadiene were studied. Both 1,2 and 1,4 reduction were observed [221]. Palladium chloride in DMF was used to homogeneously catalyze the reduction of alkynes and conjugated dienes to monoenes. Alkynes reduced cleanly to cis olefins in high yield, while unsymmetrical dienes gave mixtures of monoene products [222]. Treatment of phenylmethylacetylene with two moles of butyl Grignard and one mole of cuprous iodide resulted in production of cis-1-phenylpropene in quantitative yield. The reaction was claimed to proceed via a copper hydride species produced from the decomposition of the initially formed butyl copper complex [223]. Acetylenic sulfides were reduced to cis vinylsulfides by reduction with a "copper hydride" species prepared by treating cuprous bromide with lithium trimethoxyaluminum hydride [224]. The use of metal clusters to catalyze the reduction of triple bonds has been reviewed [225]. The full experimental details on the use of π-allylcobalt phosphine complexes as hydrogenation catalysts for aromatic compounds have appeared [226]. The activity of the catalyst depended on the nature of the phosphine, with activity increasing in the following order: $P(OMe)_3 < P(OEt)_3 < PMe_3 < P(O\text{-}i\text{-}Pr)_3$. As the activity of the catalyst increased, the lifetime decreased.

Conjugated ketones, esters, amides and nitriles were cleanly reduced to the saturate ketone,etc., by treatment with $NaHFe_2(CO)_8$. The yields were routinely high. With conjugated ketones containing additional unsaturation, only the conjugated double bond was reduced [227]. Similarly, conjugated ketones and aldehydes were reduced to saturated ketones or aldehydes under oxo conditions (H_2, CO, 140°, $Co_2(CO)_8$ catalyst). The reaction was 100% selective for the double bond, and carbon monoxide was required for the reaction [228]. Conjugated ketones underwent a clean 1,4 reduction when treated with a reagent prepared by reduction of cuprous iodide by lithium aluminum hydride. The optimum stoichiometry was 1:4:1 $LiAlH_4$:CuI:enone. The reaction was completely regiospecific, and proceeded in quite high yield (70-95%). The reagent was claimed to be better than that produced from lithium aluminum hydride and titanium trichloride. Cyclohexenone did not reduce, and cis olefins were slower than trans [229]. The active reducing agent was thought to be H_2AlI [230]. The scope of the reaction is summarized in eq. 72. Unsaturated acids were selectively catalytically



(72)

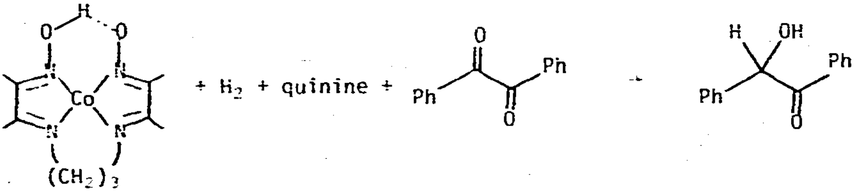
reduced in the presence of esters by a catalyst of palladium bound to an aminopolysiloxane (eq. 73) [231]. Substituted acrylonitriles were cleanly hydrosilated using a L_3RhCl catalyst. Ethyl acrylate under similar



(73)

conditions produced a variety of undesired products [232].

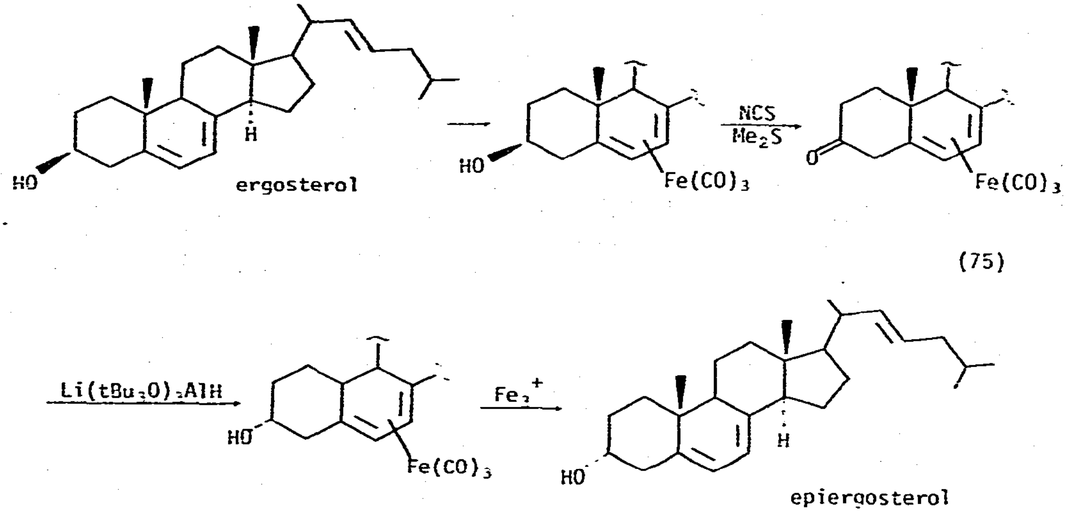
Ketones were cleanly reduced to alcohols upon treatment with sodium hydride and ferric chloride in THF solvent [233]. Benzil was reduced to benzoin with 10-65% enantiomeric excess by hydrogen, using a chelated cobalt catalyst and a one to four molar excess of quinine over catalyst (eq. 74)



(74)

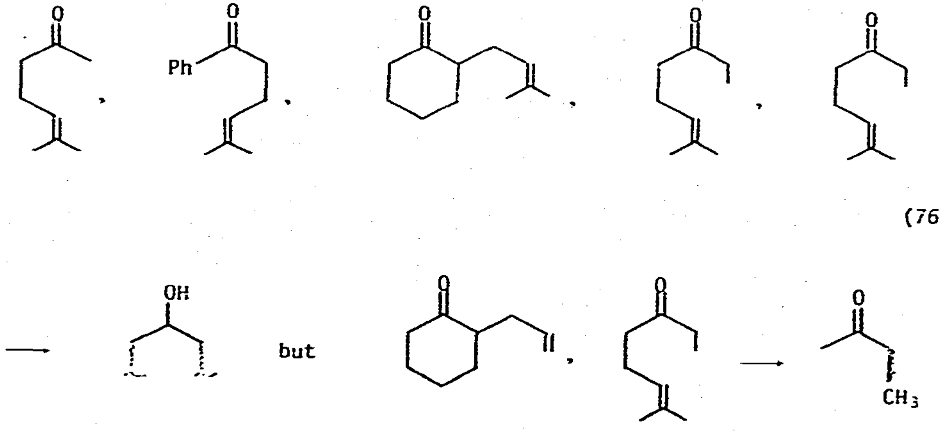
[234]. Para-substituted benzils were reduced to benzoins in 82-92% yield using either vanadium dichloride or titanium trichloride. These reagents also reduced quinones to hydroquinones in good yield [235]. Ergosterol was converted to the previously unknown epi ergosterol through a sequence involving protection of the B ring diene system as the iron tricarbonyl complex followed by an oxidation-reduction sequence (eq. 75) [236].

The kinetics and mechanism of transfer hydrogenation from indane, tetralin and dioxane to aldehydes catalyzed by L_4RuH_2 complexes was studied [237]. The order of reactivity of hydrogen sources was: 2,4-dihydrofuran, tripropyl amine > benzyl alcohol > cyclohexanol > tetralin > dioxane. With pentanal as substrate only 30% reduction was observed [238].



(75)

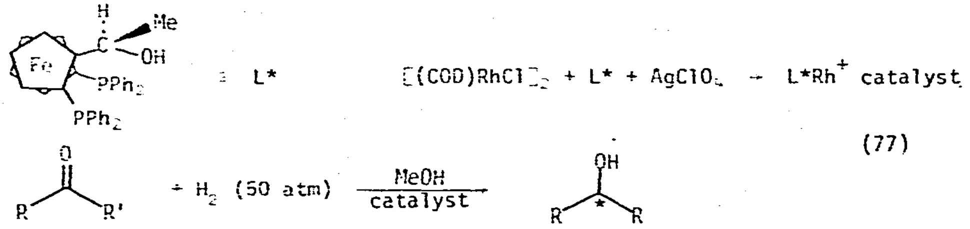
The reduction of the carbonyl group of nonconjugated unsaturated ketones without reduction of the double bond was catalyzed, in some cases, by chromium promoted Raney nickel in the presence of hydrogen (110 psi). However, closely related systems, as well as conjugated ketones, suffered carbon-carbon double bond reduction under the same conditions (eq. 76) [239].



(76)

Cinnamaldehyde underwent clean reduction of the carbonyl group without concomitant reduction of the olefin upon treatment with ferric chloride/ sodium hydride in THF. However, nonconjugated olefinic ketones were reduced to the saturated alcohol, and olefins as well as phenylacetylene were reduced to the saturated hydrocarbon by the same reagent [240].

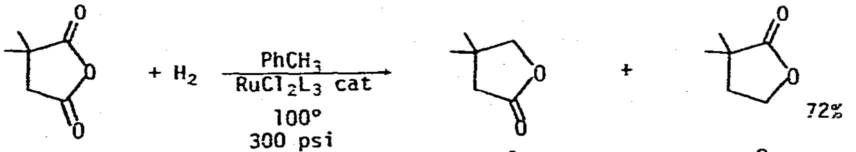
The chiral rhodium(I) complex catalysts $L_2RhCl(solvent)$, where the ligand was (S)(-) or (R)(+) benzylphenylmethylphosphine were effective for the reduction of phenyl ketones to alcohols in greater than 95% yield, and up to 58% optical yield. The reduction proceeded by a catalytic hydrosilation of the ketone, followed by hydrolysis of the trialkylsilylether to produce the alcohol. A variety of silanes were examined as reducing agents. Dialkylketones underwent the same reduction, in greater than 95% yield and up to 43% optical yield [241]. The catalyst prepared from a chiral ferrocenyl phosphine, (cyclooctadiene)rhodium(I) chloride dimer, and silver perchlorate catalyzed the reduction of ketones to alcohols by hydrogen. Yields were 70-100%, with 15-83% optical yields (eq. 77) [242].



$[(COD)RhCl]_2 + L^* + AgClO_4 \rightarrow L^*Rh^+$ catalyst

(77)

The acid halides of substituted benzoic acids were reduced to aldehydes by treatment with triethylsilane and a cis L_2PtCl_2 catalyst at 120°. This system tolerated halogen, -OMe, and nitro groups on the aromatic ring. Cinnamoyl chloride was reduced in 65% yield, while aliphatic acid halides were reduced in 2-20% yield. The active catalyst was thought to be L_2PtHCl formed by oxidative addition of the silane, followed by reductive elimination of triethylsilyl chloride [243]. The least hindered carbonyl group of an acid anhydride was preferentially reduced by hydrogen (300 psi) at 100° using a $RuCl_2L_2$ catalyst in toluene solution. Lithium aluminum hydride led to predominant reduction of the most hindered carbonyl (eq. 78) [244]. The Fischer-Tropsch



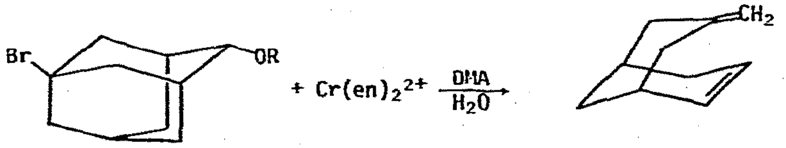
(78)

1 : 9
(19 : 1) with $LiAlH_4$

synthesis was the subject of a review [245]. The reduction of carbon monoxide to methane by hydrogen at 140° and two atmospheres pressure was catalyzed by $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ clusters. The rate was very slow, a 1% conversion (3 to 5 catalyst turnovers) in 3-5 days being observed. Added triphenylphosphine increased the rate, but led to production of ethane and propane as well. Added trimethyl phosphite increased the rate three fold, and maintained the specificity [246].

Cholestenol was hydrogenalized to cholestene in 65% yield by reduction with 4:1 lithium aluminum hydride-titanium tetrachloride. This reagent was especially effective for hydrogenolysis of tertiary steroidal allylic alcohols [247]. Benzaldehyde was reduced to toluene, and acetophenone to ethylbenzene using catalytic transfer hydrogenation. The catalyst was 10% palladium on carbon with a small amount of ferric chloride added. The hydrogen source was cyclohexene or limonene [248]. Palladium on carbon was used to convert 2-phenyl-2-methylbutanal to t-butylbenzene in 84% yield [249]. High vacuum cocondensation of chromium atoms (from vaporized chromium) and epoxides led to conversion of epoxides to olefins. In this fashion, cyclohexene oxide was converted to cyclohexene (86%), 1-methylcyclopentene oxide to 1-methylcyclopentene (100%) and 3-phenyl-1-propene oxide to allylbenzene (100%). Disubstituted epoxides gave mixtures of cis and trans alkenes [250].

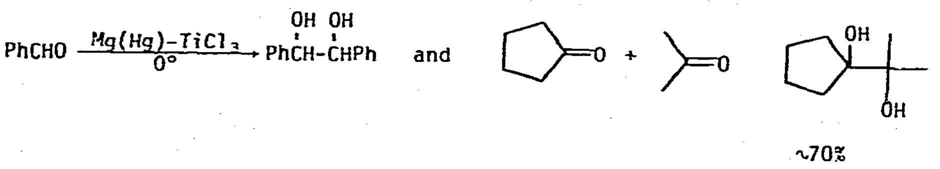
Aryl and vinyl halides were reduced to the hydrocarbons by isopropylmagnesium chloride in the presence of 1% manganous chloride [251]. Treatment of α-haloketones with molybdenum hexacarbonyl in refluxing DME led primarily to reduction to the ketone. Aldol type condensation products (20-50%) were also observed. Chromium and tungsten carbonyls were much less reactive [252]. α-Haloketones were cleanly reduced to the corresponding ketones in 80-96% yield by vanadium dichloride in aqueous THF [253]. Chromous ion induced the reductive fragmentation presented in eq. 79 [254].



(79)

Aromatic diazonium salts were reduced to anilines by vandium dichloride in aqueous THF [255]. Aromatic nitro compounds were reduced to aromatic amines using hydrogen and $RuCl_2L_3$ as a catalyst. The kinetics and mechanism of the reaction were studied in detail. This catalyst system tolerated Cl, Br, OH, OMe and CN substitution on the ring, but reduced conjugated esters. Nitroquinoline was cleanly reduced to aminoquinoline. Meta-dinitrobenzene was reduced to meta-nitroaniline (73%) 2,4-dinitrotoluene to 2-amino-4-nitrotoluene (19%) and 1,3-dinitronaphthalein to 1-nitro-4-aminonaphthalein (71%) [256]. Coordination of nitriles to $(NH_3)_5Co^{3+}$ increased the rate of reduction by sodium borohydride (6 min vs no reaction in 10 days) and the rate of Michael addition of acetylactone anion to acrylonitrile [257]. Sulfoxides were reduced to sulfides (thioethers) by $MoOCl_3/Zn/THF$ or $VCl_2/H_2O/THF$ in 78-91% yield [258]. The same transformation was effected by lithium aluminum hydride/titanium tetrachloride in ether at room temperature. The yields were 80-90% for this mild reductive procedure [259].

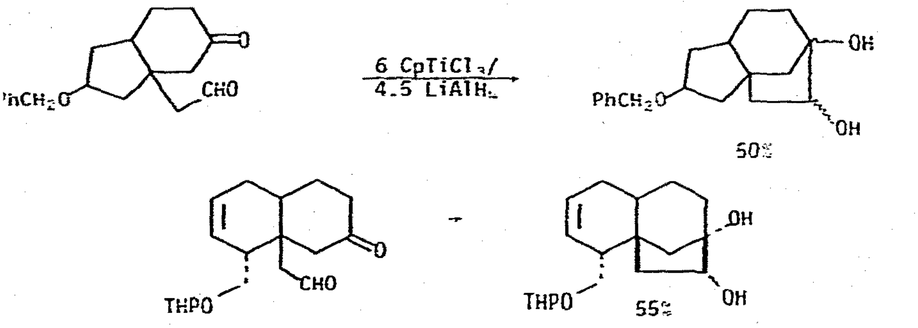
Vicinal dihalides were reductively eliminated to olefins by treatment with "titanium II", produced from lithium aluminum hydride and titanium trichloride. The yields were quite high, and cyclic systems worked well also. Benzyl bromide and allyl bromide were dimerized to bibenzyl and biallyl by this reagent while benzal chloride was converted to stilbene [260]. Allyl ethers were reduced to the parent olefins with allylic transposition by the lithium aluminum hydride/titanium tetrachloride reagent [261]. Two new titanium-based reagents for intermolecular and intramolecular pinacol coupling of ketones and aldehydes have been developed. The reagent from amalgamated magnesium/titanium tetrachloride coupled alkyl ketones and aldehydes in 84-95% yield. Mixed couplings also were successful (eq. 80).



$$PhCHO \xrightarrow[0°]{Mg(Hg)-TiCl_3} PhCH(OH)\text{-}CH(OH)Ph$$

(80)

The reagent prepared from 6 $CpTiCl_3$ and 4.5 lithium aluminum hydride was effective for intramolecular coupling reactions (eq. 81) [262]. The titanium trichloride/lithium aluminum hydride reagent cyclized 1,4-diphenyl-1,4-butanedione to 1,2-diphenylcyclobutene (61%) and 1,6-diphenyl-1,6-hexanedione to 1,2-diphenylcyclohexene (35%) in an intramolecular pinacol type coupling [263]. The reagent generated by the treatment of titanium trichloride with potassium metal proved to be superior to that from titanium trichloride and lithium aluminum hydride for the reductive dimerization of ketones to symmetrical olefins. This reagent converted diiospropyl ketone to tetraisopropylethylene in 40% yield, which was very high for this reaction. The reagent also converted pinacols to a mixture of cis and trans olefin isomers [264]. Mixed pinacol couplings between acetone and other ketones to produce 1,1-dimethyl olefins was achieved by use of a four-fold excess of acetone over the other ketone, and use of the reagent produced from treatment of titanium trichloride with lithium. Yields of the mixed pinacol coupling with acetone were: adamantanone (63%); 4-t-butylcyclohexanone (55%); 3-cholestanone (54%); cycloheptanone (50%), 1-indanone (71%); acetophenone (65%). Benzophenone and fluorenone cross coupled to other ketones with 1:1 stoichiometry [265].



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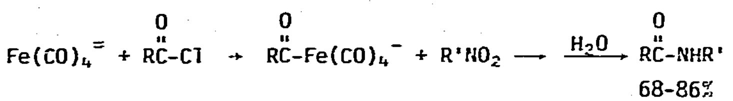
V. FUNCTIONAL GROUP PREPARATIONS

A. Halides

A review entitled "Hydrozirconation: A New Transition Metal Reagent for Organic Synthesis" has appeared [266]. The addition of $Cp_2Zr(H)Cl$ to olefins to produce terminal alkylzirconium complexes, alkynes to produce disodium tetracarbonylferrate, produced amides in good yield (eq. 83) [274].

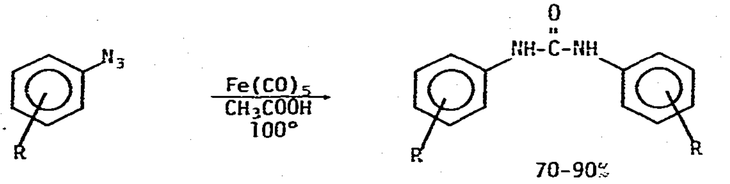


$$Fe(CO)_4^{=} + RC(=O)\text{-}Cl \rightarrow RC(=O)\text{-}Fe(CO)_4^{-} + R'NO_2 \longrightarrow \xrightarrow{H_2O} \underset{68\text{-}86\%}{RC(=O)\text{-}NHR'} \quad (84)$$

R = Me, Et, Ph, Bu, hexyl

R' = Ph, Me

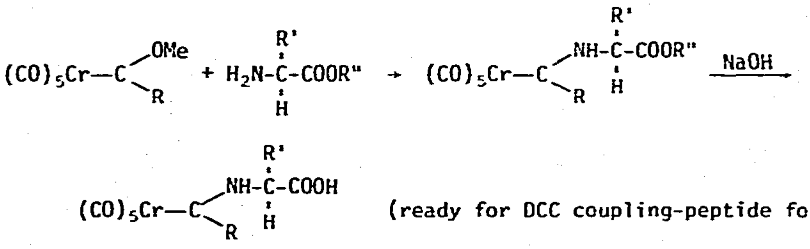
Aromatic azides were coupled to symmetrical ureas by treatment with iron pentacarbonyl in acetic acid (eq. 85) [275]. Finally, chromium carbene



(85)

R = H, 3-Me, 4-Me, 3-Cl, 4-Cl, 3-OMe, 4-OMe

complexes have been used as amino protecting groups in polypeptide synthesis. The complex withstands DCC coupling conditions and is cleaved by trifluoroacetic acid (eq. 86) [276].

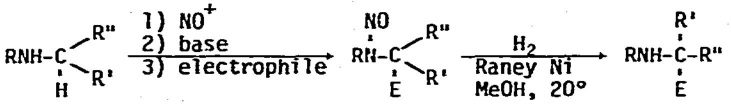


(86)

(ready for DCC coupling-peptide formation)

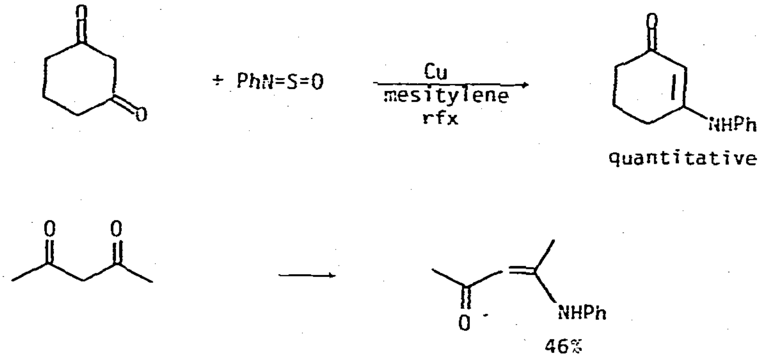
C. Amines, Alcohols

Electrophilic attack at the α-position of amines was effected by conversion to the N-nitrosamine, removal of the thus activated α-proton with base, and reaction of the carbanion with an electrophile. The amine was regenerated by treatment with hydrogen and Raney-nickel. This denitrosation was compatible with acid labile groups (eq. 87) [277].



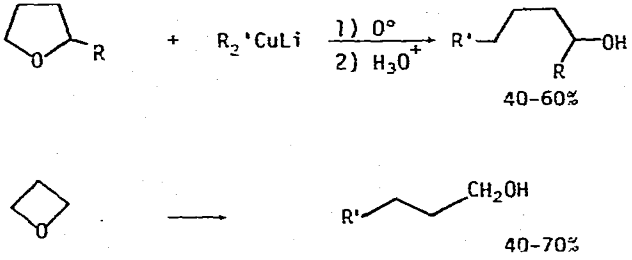
(87)

β-Diketones were converted to β-amino-α,β-unsaturated ketones by treatment with PhN=S=O and copper powder in refluxing mesitylene (eq. 88). Copper salts did not catalyze this reaction. 1,4-Diketones were converted to N-phenylpyrroles under these condition [278].



(88)

Allyl ethers were used as protecting groups for alcohols because they were stable to both acid and base, but easily cleaved in high yield by treatment with palladium on carbon catalyst in refluxing aqueous acidic methanol [279]. Tetrahydrofurans and oxetanes were alkylated and ring opened by treatment with lithium dialkylcuprates or organolithium reagents plus 10% cuprous iodide (eq. 89) [280].



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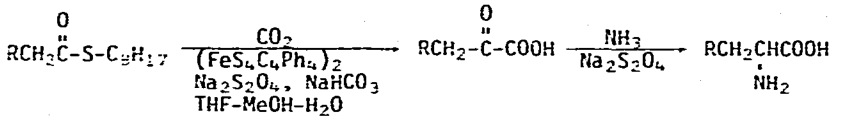
D. Ethers, Esters, Acids

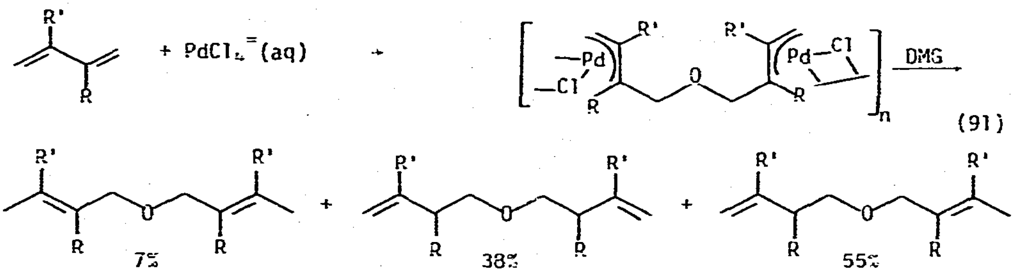
Aryl aldehydes reacted with a catalytic amount (3%) of sodium tetracarbonyl ferrate in THF to produce 70-90% yields of benzyl benzoates. The reaction resembles a Cannizzaro reaction in which an aromatic aldehyde disproportionates to a benzoic acid and a benzyl alcohol, which then condense to form the ester [281]. Thioethers were carboxylated by carbon dioxide in the presence of $(FeS_4C_4Ph_4)_2$ to produce α ketoacids, which were easily converted to αaminoacids (eq. 90) [282]. Aromatic hydrocarbons reacted with potassium



$$RCH_2\overset{O}{\overset{\|}{C}}-S-C_8H_{17} \xrightarrow[\substack{(FeS_4C_4Ph_4)_2\\ Na_2S_2O_4,\ NaHCO_3\\ THF-MeOH-H_2O}]{CO_2} RCH_2-\overset{O}{\overset{\|}{C}}-COOH \xrightarrow[Na_2S_2O_4]{NH_3} RCH_2\underset{NH_2}{C}HCOOH \quad (90)$$

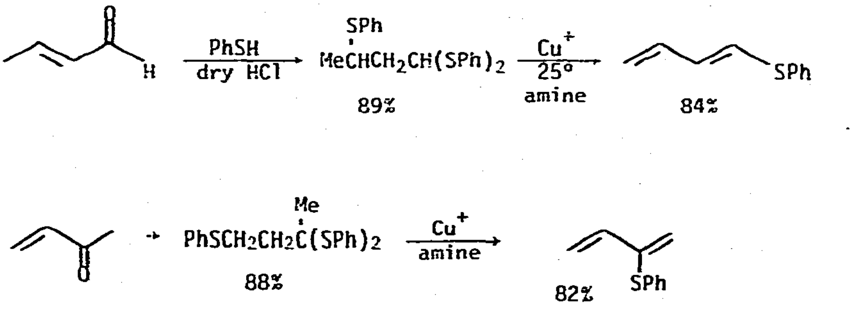
R = Ph, 73%; H, 70%; HO_2CCH_2, 51%

peroxydisulfate in glacial acetic acid in the presence of palladium acetate catalyst to produce aryl acetates. The yield was 200-900% based on catalyst, and 10-30% based on substrate. With monosubstituted aromatics, which usually favor ortho-para substitution, meta acetoxylation was observed. Excess acetate favored side chain acetoxylation [283]. Butadiene was coupled to give mixtures of dibutenylethers by aqueous chloropalladium (eq. 91) [284].



(91)

The preparation of 1,3-dienes with sulfur substitution for Diels-Alder reactions was accomplished by the treatment of conjugated aldehydes or ketones with thiophenol and dry HCl, followed by desulfurization with cuprous triflate (eq. 92) [285]. Aryl iodides were converted to aryl

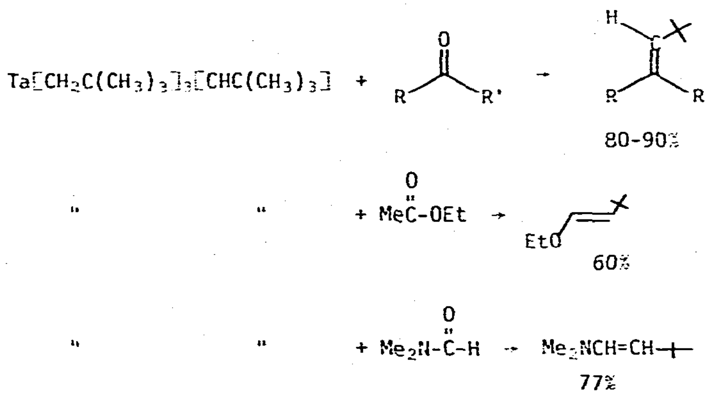


(92)

trifluoromethyl thioethers by treatment with $CuSCF_3$, prepared from copper metal and $Hg(SCF_3)_2$. The aryl iodide could contain additional ester, amine, or halogen functionality [286].

E. Olefins, Ketones

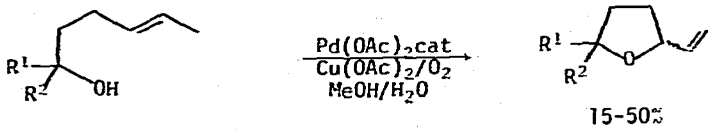
Copper oxide in quinoline was used to decarboxylate vicinal diacids to olefins at 180°. In this fashion endo norbornane-2,3-dicarboxylic acid was decarboxylated to norbornene in 52% yield. The yields of this method were considerably higher than for other methods including the use of lead tetraacetate, and electrochemical decarboxylation [287]. Ketones were converted to t-butyl alkenes by treatment with Ta[CH$_2$C(CH$_3$)$_3$]$_3$[CHC(CH$_3$)$_3$] (eq. 93). This reagent behaved like a Wittig reagent, transferring the "carbenoid" ligand [CHC(CH$_3$)$_3$]. High yields were obtained with unhindered alkyl and aryl ketones, while hindered carbonyls did not react [288]. Cupric acetate catalyzed the hydrolysis of N-methylhydrazones at pH 5.4 in water. The procedure tolerated γ esters, α-SCH$_3$, and ketals [289]. Tosylhydrazones as well as N-methylhydrazones were cleaved to the ketone in 78-96% yield using molybdenum trichloride or molybdenum hexaflucride [290]. The synthesis of t-butyl ketones by the use of [PhSCu—+—]$^-$Li$^+$ was investigated [291]. Secondary nitro alkyls were converted to the corresponding ketone by treatment with vanadium dichloride in DMF in 65-75% yield. Primary nitroalkyls were converted to aldehydes, which condensed and gave only poor yields [292].



(93)

F. Heterocycles

Several new approaches to cyclic ethers using transition metals have been developed. Tetrahydrofurans and dihydropyrans were synthesized by the palladium catalyzed cyclization of γ-hydroxyolefins (eq. 94). The reaction was thought to proceed via palladium assisted nucleophilic attack on the carbon-carbon double bond [293]. Endo-brevicomin was synthesized from 6,7-dihydroxynon-1-ene by a similar intramolecular nucleophilic attack on a complexed olefin (eq. 95) [294]. Diphenyl ethers were converted to

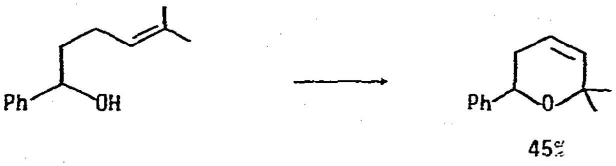


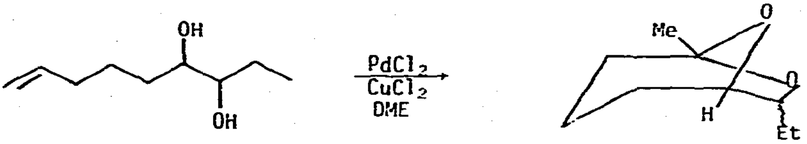
R^1 = Ph, Me

R^2 = Ph, Me, Et, H

but

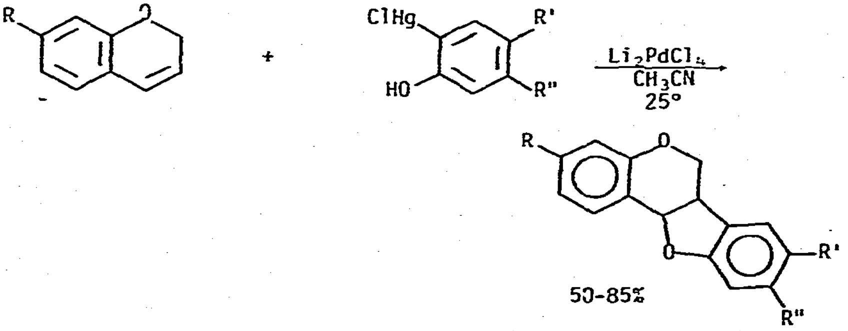
(95)





45% (Endo Brevicomin)

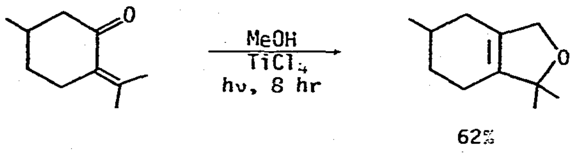
dibenzofurans in 40-50% yield by treatment with oxygen at 150° in the presence of palladium acetate catalyst [295]. Chromenes reacted with 2-mercurated phenols to give ring-fused diethers (eq. 96) [296] upon treatment



(96)

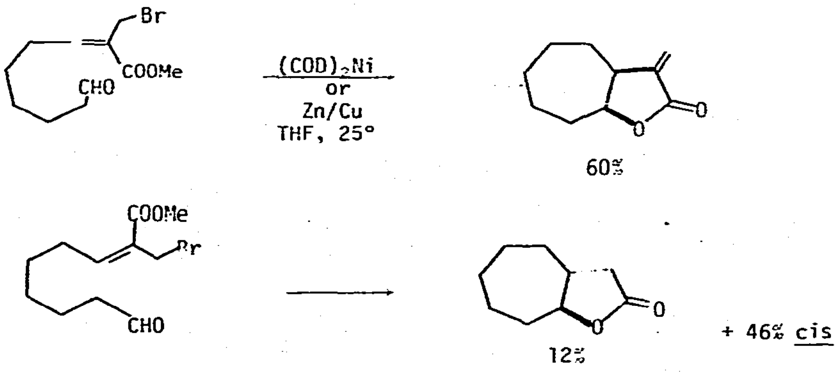
50-85%

with lithium chloropalladate in acetonitrile. Conjugated ketones were cyclized to furans by photolysis in methanol with titanium tetrachloride catalyst (eq. 97) [297].



(97)

Primary and tertiary propargylic alcohols were chloromercurated, and the thus-formed vinylmercurial was treated with carbon monoxide and lithium chloropalladate to give β-chlorobutenolides in good yield [298]. Ring fused α-methylene-γ-butyrolactones were prepared by reductive cyclization of ester containing open chain bromoaldehydes. Cyclooctadiene nickel or zinc copper couple were the reducing agents of choice (eq. 98) [299]. A key step in the synthesis of a model for vernolepin was the conversion of a cyclic alkynol to an α-methylene-γ-butyrolactone by treatment with carbon monoxide, thiourea, and palladium chloride (eq. 99) [300]. Conjugated



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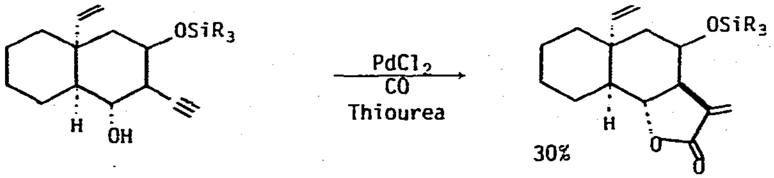
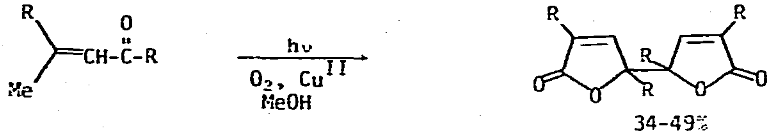
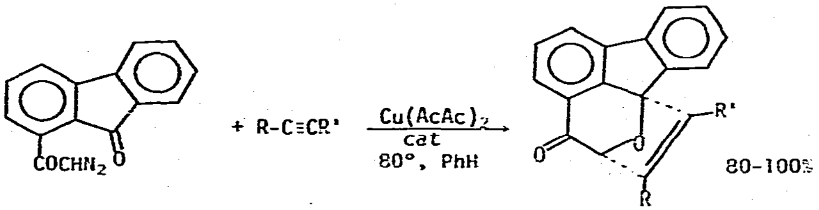


(99)

ketones were photochemically cyclized and dimerized to bis-butenolides in the presence of a copper catalyst (eq. 100) [301]. The cupric acetate catalyzed decomposition of a diazoketone in the presence of added alkyne was used to prepare the oxo-ketone in eq. 101 [302].

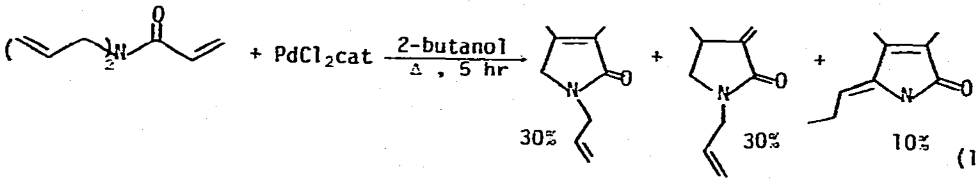


(100)

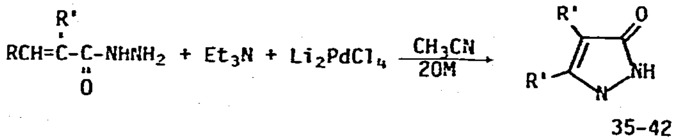


(101)

Copper acetylides reacted with imine oxides to produce β-lactams in 20-60% yield as a mixture of isomers [303]. Diphenylphthalimides were produced from the reaction of diphenylcyclopropenones with RN=S=O when treated with nickel carbonyl in DMF [304]. N,N-diallylamides of conjugated acids reacted with a catalytic amount of palladium chloride to produce a variety of cyclic amides (eq. 102) [305]. Conjugated acid hydrazides were similarly cyclized to pyrazolones by lithium chloropalladate and triethyl amine in acetonitrile (eq. 103) [306].

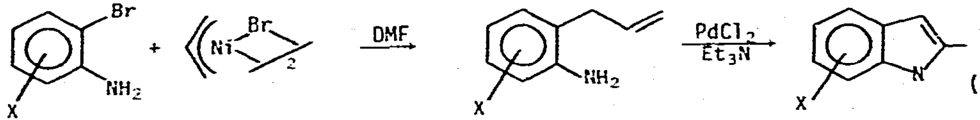


(102)



(103)

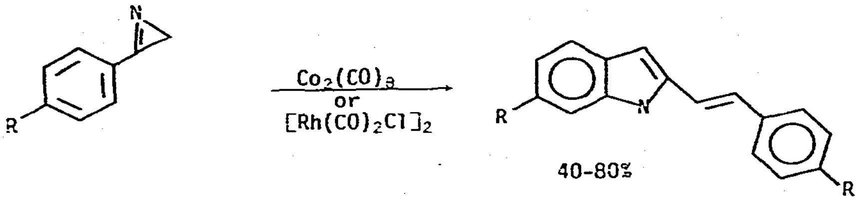
The conversion of 2-bromoanilines to indoles was achieved by reaction with π-allylnickel halide complexes to produce 2-allylanilines, followed by palladium assisted intramolecular amination of the side chain olefin to produce the 2-methyl indole. Both reactions tolerated a wide array of functionality in the aromatic ring. The isoquinoline ring system was formed in a similar fashion starting with 2-bromobenzylamine (eq. 104) [307]. 2-Phenyl-1-azirines reacted with dicobalt octacarbonyl [308] or rhodium dicarbonyl chloride dimer [309] to produce 2-sytrylindoles



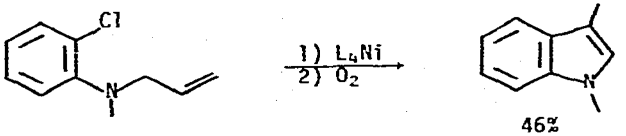
70-90% yields

(104)

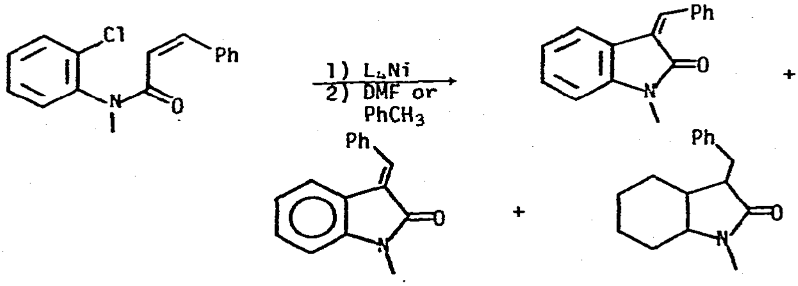
(eq. 105). Indoles substituted in the 3 position were prepared by treatment of 2-chloro-N-allylanilines with L_4Ni complexes, followed by oxidation (eq. 106) [310], while 2-chloroanilides of unsaturated acids produced 2-indanones (eq. 107) [311].



(105)

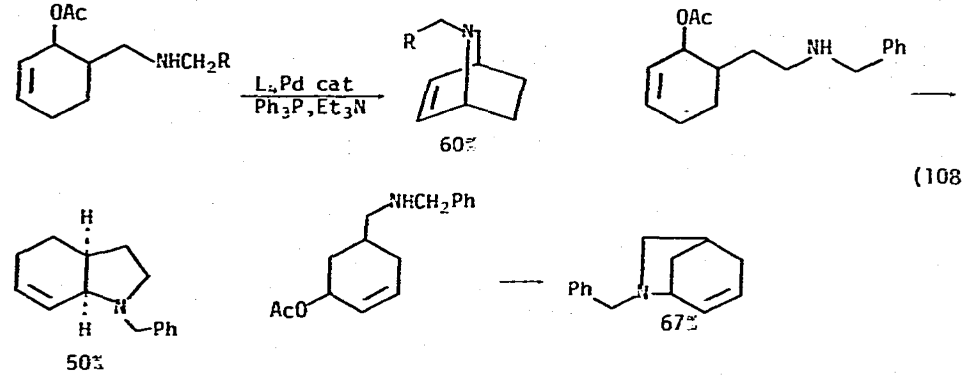


(106)

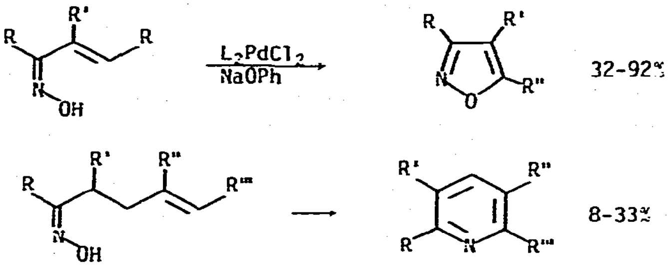


(107)

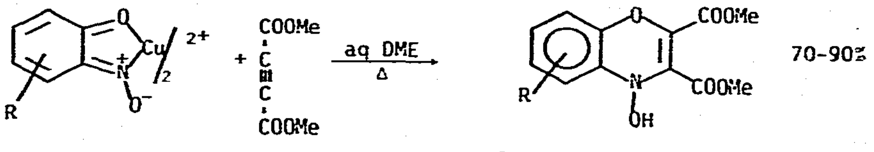
Palladium zero complexes were used to catalyze intramolecular aminations of allyl acetates with amino side chains. In this fashion the mesembrine and quinuclidine skeletons were synthesized (eq. 108) [312]. Terminal alkynes were cyclodimerzied with nitriles using cobaltocene as catalyst to give mixtures of 2,4,6- and 2,3,6-trisubstituted pyridines. Acetylene itself reacted in a similar fashion to produce 2-substituted pyridines in moderate yield [313]. α,β-Unsaturated oximes were cyclized to isoxazoles (40-92%) and γ,δ-unsaturated oximes to pyridines (8-50% yields) upon treatment with L_2PdCl_2 and excess sodium phenoxide, or palladium chloride/sodium carbonate (eq. 109) [314]. Other miscellaneous heterocyclic forming reactions are described in eqs. 110-113.



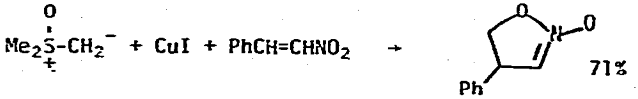
(108)



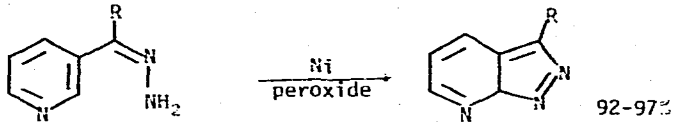
(109)



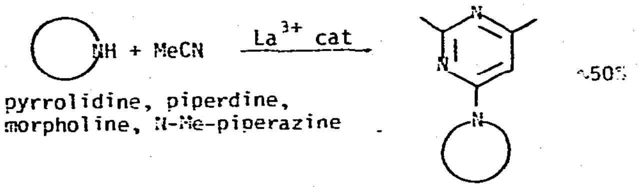
(110) [315]



(111) [316]



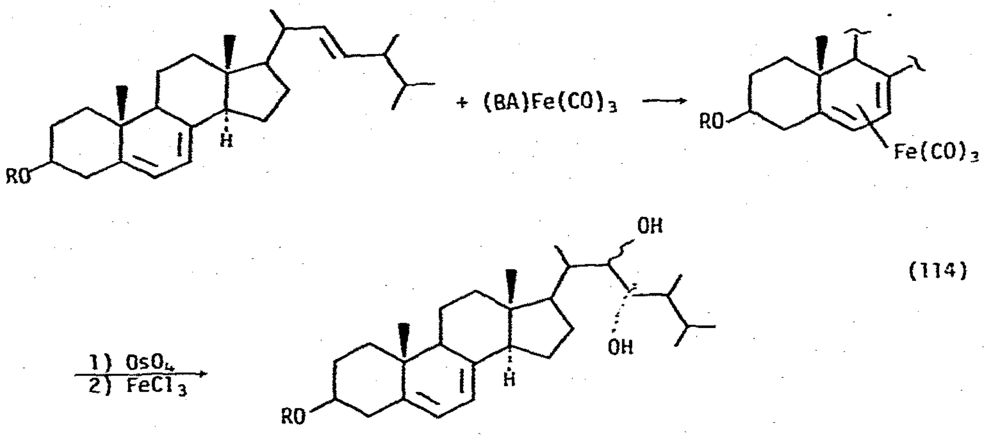
(112)
[317]



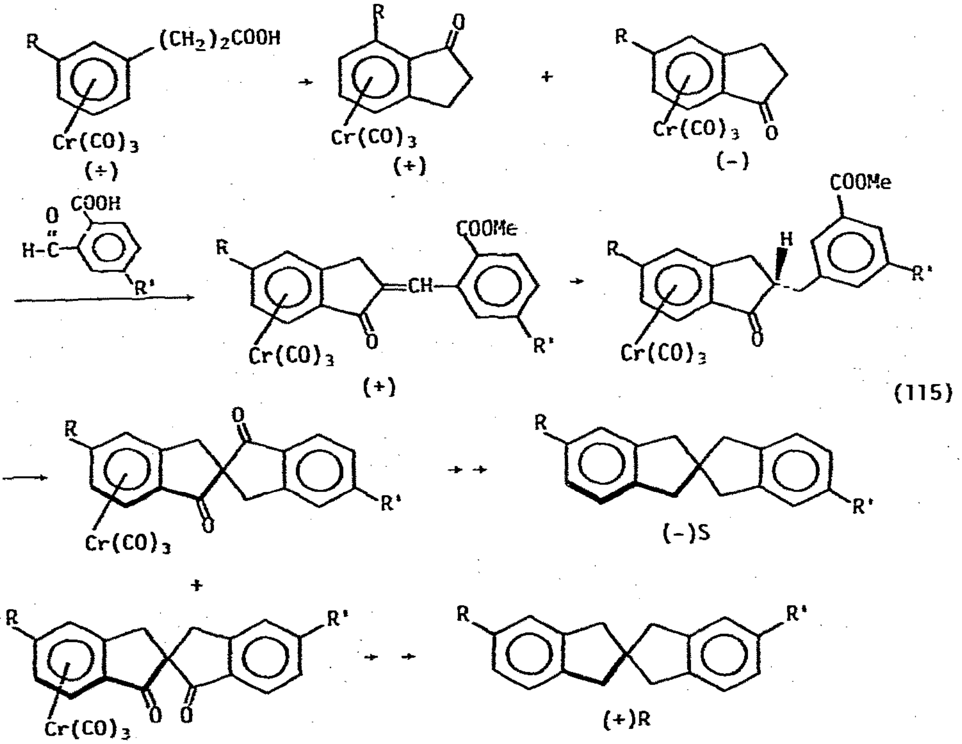
(113)
[318]

G. Miscellaneous

Treatment of RCuMgX with sulfur dioxide followed by hydrolysis produced RSO_2H in essentially quantitative yield. When an isolation using bromine was used, RSO_2Br was obtained [319]. In the attempted functionalization of high molecular weight noncrosslinked polyvinylchloride by treatment with Ph_2PLi in refluxing THF, complete halogen replacement was observed, but breakdown of the polymer backbone was also noted. The product consisted of short chain (10-12 units) polymers [320]. Allyl chloride reacted with sulfur dioxide in the presence of nickel carbonyl to give low yields of diallylsulfone [321]. Palladium chloride and sodium acetate in acetic acid deallylated N-allylamides in 60% yield. The reaction produced π-allylpalladium acetate [322]. The B-ring diene system in ergosterol was protected as the $Fe(CO)_3$ diene complex. Subsequently the side chain olefin was converted to the diol by oxidation with osmuim tetroxide. The iron protecting group was then removed by treatment with ferric chloride (eq. 114) [323]. Finally, 2,2'-spiro-bis-indanes were prepared from arene chromium tricarbonyl complexes (eq. 115) [324].



(114)



(115)

VI. REVIEWS

Transition metals in organic synthesis was the topic of both a review [325] and a book [326]. The reaction between α,α'-dihaloketones, $Fe_2(CO)_9$, and olefins has been reviewed [327]. Palladium catalyzed organic reactions were the subject of a review with 300 references [328]. The interaction of organometallic derivatives with organic halides has been treated [329]. Homogeneous catalysis was the subject of three reviews [330,331,334]. Solvent effects on reactivity of organometallic compounds has been considered [332]. Oxidative addition reactions were the topic of a review with 102 references [333] as well as part of a more extensive consideration of organometallic reactions [335]. A review with 136 references discussed homogeneous solution catalysis by small molecules and enzymes [336]. Mechanisms of heterogeneous catalysis were reviewed [337]. Mechanistic aspects of olefin metathesis [338] as well as transition metal carbene complexes and their synthetic applications were reviewed [339]. Organocopper reagents were treated in a review with 38 references [340]. Uses of activated metals in organic and organometallic synthesis were presented in a review with 107 references [341] while the uses of activated manganese dioxide in organic chemistry was presented in a mammoth (488 references) review [342]. Finally, a review entitled "Organometallic Chemistry - Part I. The Transition Elements" has been published [343].

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