TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

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[x] No reprints available
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I. Theoretical Calculations

A theoretical study of some Co carbonyl complexes present in the catalytic cycle of hydroformylation (formylcobalt tricarbonyl, (η^2-ethylene)hydridocobalt tricarbonyl, and ethylcobalt tricarbonyl) was performed by means of ab inito Hartree-Fock and configuration-interaction calculations [1]. The potential energy profile of a full cycle of olefin hydrogenation with $Rh(PPh_3)_3Cl$ as catalyst has been determined by ab initio molecular orbital calculations. The profile was found to be smooth, without excessive barriers (the highest, olefin insertion is about 20 kcal) and without too stable intermediates [2].

The structure and epoxidation properties of Ti-tartrate asymmetric epoxidation catalysts have been studied by using the frontier orbital approach [3]. Qualitative VB considerations emphasize the radical character of the O transfer from Fe(IV)-oxo porphyrins to ethene yielding ethylene oxide [4]. The structure of oxo-iron porphyrins was studied theoretically by LCAO-MO-SCF calculations in relation to their stereospecific epoxidation properties [5].

It was found that the most stable structure of oxo-iron porphyrin is one in which the oxygen is inserted into the Fe-N bond. Alkene is coordinated perpendicular to the iron atom and the next step is a slipping motion of the alkene toward the oxygen [5] [6].

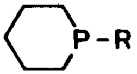
II. Hydroformylation and Related Reactions of CO

1. Hydrogenation of CO to Oxygen-containing Organic Compounds

The selective transformation of synthesis gas into ethylene glycol, C_1-C_3 alcohols, AcOH and acetate esters by Ru complexes dissolved in low melting phosphonium salts was reported [7]. 1-Alkylbenzimidazoles have been found to be very efficient promoters for ethylene glycol formation from synthesis gas in the presence of $Ru_3(CO)_{12}$ as catalyst at 240°C and 500 bar. It has been shown that $Ru(CO)_4$(1-alkylbenzimidazole) complexes play an important role in ethylene glycol formation [8]. A catalyst composed of $Ru_3(CO)_{12}$ and 1-methyl-3-ethylbenzimidazolium bromide showed high selectivity (44%) for ethylene glycol formation from synthesis gas at 150-220°C and 450 bar. The favorable effect of the imidazolium cocatalyst was attributed to its activity in promoting the condensation of formaldehyde to glycolaldehyde [9]. Hydrogenation of CO by a $Ru_3(CO)_{12}$ + PPNCl + acid catalyst system at 240°C and 500 bar was examined. Weak acids, especially carboxylic acids promoted the formation of both ethylene glycol and MeOH [10].

The activity of $Ru_3(CO)_{12}$ + alkali metal halide catalysts and their selectivity for ethylene glycol formation from CO + H_2 at 230°C and 300 bar is increased by addition of $Re_2(CO)_{10}$. Activity and selectivity also increases with increasing ionic radius of the metal [11]. Acetic acid is formed directly from synthesis gas in up to 95% selectivity using a Ru + Co + I + Bu_4PBr melt catalyst combination. The Ru component of the catalyst is responsible for the formation of MeOH which is transformed into MeI and then carbonylated to AcOH by cobalt carbonyls [12]. Addition of $Co_2(CO)_8$ as cocatalyst to the onium halide (e.g. PPNCl) promoted Ru systems which lead mainly to the production of alcohols (MeOH, EtOH) from CO + H_2, promotes the formation of acetic acid. With the best combination of reaction parameters selectivity to acetic acid exceeds 80%. The results may be explained by the independent action of Ru and Co carbonyls, probably no mixed-metal clusters are involved in the catalytic cycles [13]. The selectivity of ethylene glycol formation from synthesis gas in the presence of homogeneous Ru or Ru + Rh catalysts was significantly increased by amines, especially imidazole. It was suggested that Ru is mainly responsible for the formation of formaldehyde and Rh for its transformation into ethylene glycol [14]. Acetate esters of ethylene glycol were prepared with good selectivities from synthesis gas using Ru-Ru bimetallic homogeneous catalysts together with N-containing bases or alkali metal cations as promoters in AcOH as solvent. No hydrocarbons were formed and the C_1/C_2 ratio was between 1 and 2 [15].

Two dinuclear Rh complexes, $[Rh(CO)_3(PR_3)]_2$ (R = iPr or cyclopentyl) were isolated from the catalytic reaction mixtures of syngas conversion to ethylene glycol. Both complexes are active catalysts for the synthesis of ethylene glycol from CO + N_2 at 230°C and 470 bar [16]. In the conversion of CO + N_2 to ethylene glycol the Rh + PBu_3 catalyst system was found to be about 20 times more active under 1000 bar at 210°C than under 500 bar. This unusual pressure effect was considered to be due to the formation of catalytically more active non-cluster Rh species [17]. Carboxylic acids promote the formation of ethylene glycol from synthesis gas catalyzed by $Rh_4(CO)_{12}$ and PCy_3 at 220°C and 500 bar. Complexes of the type $Rh(OOCR)(CO)(PCy_3)_2$ were recovered from these reaction mixtures and could be used as catalysts for the reaction [18]. Complexes of the type $RhX(CO)L_2$ (X = arylcarboxylato or C_6F_5O; L = PCy_3 or PPr^i_3) were found to be more active catalyst precursors for the conversion of synthesis gas to ethylene glycol at 220°C and 510-540 bar than the corresponding $Rh_4(CO)_{12}$ + L systems. The complexes were reduced to $Rh(CO)_4^-$ and $Rh(CO)_3L^-$ under the reaction conditions; their catalytic activity was proportional to the initial rate of this reduction [19]. Catalytic activity of Rh + phosphine catalyst systems for the synthesis of ethylene glycol from synthesis gas depends on the structure of the phosphine. The rate of ethylene glycol formation increases with increasing electron-donating property of the alkyl substituent in phosphines of type iPr_2PR and (1) [20].



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The recently described homogeneous catalyst systems for ethylene glycol from synthesis gas composed of Rh carbonyls and substituted imidazoles (AS 1986, refs.10 and 11) have been investigated by high pressure IR spectroscopy. The mononuclear complex $HRh(CO)_3$(N-methylimidazole) was suggested to be the catalytically active species [21]. Hydrogenation of CO with $Rh_4(CO)_{12}$ as catalyst at 400 bar and 200°C was investigated in different amides as solvents. Dimethylimidazolinone yielded significantly higher selectivities for ethylene glycol than N-methylpyrrolidone [22].

See also [80,85,120].

2. Hydroformylation

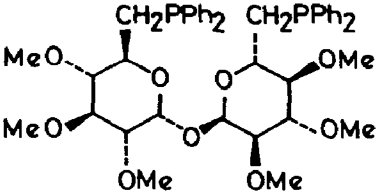
a) Co Catalysts

Hydroformylation of propylene trimers with Co carbonyl-Lewis base catalysts led to higher yield of alcohols and lower yield of high-boiling byproducts [23]. Hydroformylation of fluoro olefins $R_fCH=CH_2$ (R_f = F, CF_3, C_2F_5, C_3F_7, C_8F_{17}, C_6F_5) promoted by Co, Pt, Ru, or Rh carbonyl catalysts has been studied. Remarkable regioselectivity of the reaction was found in the case of trifluoropropene and pentafluorostyrene: Co catalysts yielded almost exclusively n-aldehydes whereas i-aldehydes were the main products with Rh catalysts. On the contrary, vinylfluoride gave 2-fluoropropanal exclusively, regardless of the metal catalyst species [24]. Activity of the mixed-metal cluster $Co_2Pt_2(CO)_8(PPh_3)_2$ for hydroformylation was found to be higher than that of the corresponding mononuclear Co-P and Pt-P complexes [25].

b) Rh catalysts

The mechanism of phosphine-modified rhodium-catalyzed hydroformylation of 1-hexene was studied by in situ IR spectroscopy. Reaction rate was limited by CO dissociation from the catalyst $HRh(CO)_2(PR_3)_2$ containing para-substituted triarylphosphines. Reaction rates and selectivities for linear aldehydes both increased with increasingly electron-withdrawing phosphines [26]. Deactivation of the catalyst in this system was shown to be due to the formation of an inactive dinuclear complex having bridging phosphido ligands [27]. The Rh-phosphite complexes $Rh(acac)L_2$ and

and $HRhL_4$ ($L = P(OPh)_3$) were used for the hydroformylation of methyl methacrylate and vinyl acetate. Reasonable yields were achieved even under very mild conditions: 40°C and 1 bar [28]. A new process was developed for the hydroformylation of propene using Rh complexes as catalysts modified by water-soluble phosphines. The catalyst is practically insoluble in the raw product butyraldehyde and may thus be separated simply by phase separation [29]. Isopropene was synthesized via hydroformylation of 2-butene to methylbutanal followed by dehydration of the aldehyde. Hydroformylation was carried out in the presence of a Rh + PPh_3 catalyst (P:Rh = 40:1) at 100°C; selectivity of methylbutanal formation was > 98% [30]. In the hydroformylation of methyl methacrylate with Rh-phosphine catalysts prepared in situ from $[Rh(NBD)Cl]_2$ and tertiary phosphines the regioselectivity was found to be very sensitive to the reaction conditions. Both the increase of the P/Rh ratio and the amount of Et_3N added increased the amount of branched aldehyde [31]. Hydroformylation of styrene catalyzed by Rh complexes of the ligand (2) gave the branched-chain aldehyde with 98.5% regioselectivity; other ligands like (3), and DIOP gave less selective catalysts [32].



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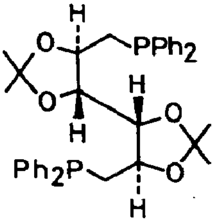
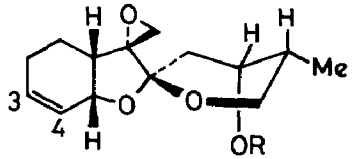


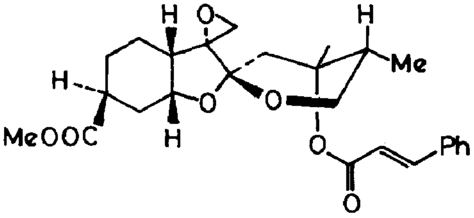
3

Hydroformylation of linear terminal alkenes bearing a PPh_2 group with Rh-PPh_3 catalysts led to the predominant formation of α-methyl aldehydes or alcohols. If the PPh_2 group was separated from the C=C double bond by only 1-3 CH_2 groups, alcohols were the main products but if this distance was 4 CH_2 groups hydroformylation stopped at the aldehyde stage [33]. The temporary incorporation of a coordinating phosphine residue [m-$(Ph_2P)C_6H_4CO$] into the tetracyclic phyllanthocin precursor (4a) directed the $[(COD)RhOAc]_2$-catalyzed hydroformylation of (4b) largely to the desired C(3) position [34].



4a; R = H

4b; R = m-(Ph$_2$P)C$_6$H$_4$CO



(+)-Phyllanthocin

Catalyst systems composed of $[Rh_2(\mu\text{-}L)_2(CO)_4]$ and PR_3 (L = triazolate, benzotriazolate or tetrazolate) have been used for the hydroformylation of 1-hexene at 80°C and 5 bar. In the case of the triazolate and benzotriazolate complexes catalytic activity decreased in the sequence $PPh_3 > P(OMe)_3 > P(OPh)_3$ whereas with L = tetrazolate the inverse order of reactivity was observed [35]. The complex $Rh_2(SBu^t)_2(CO)_2(L)_2$ containing the water soluble ligand L = $P(\underline{m}\text{-}C_6H_4SO_3Na)_3$ could be used as catalyst for the hydroformylation of olefins at 80°C and 8 bar in water/organic two-phase systems both with CO + H_2 as reagent and with CO alone. In the latter case water served as a solvent and hydrogen source simultaneously [36].

Catalytic activity of $HRh(CO)(PPh_3)_3$ in hydroformylation of 1-hexene (80°C, 5 bar) increased on the addition of $Cp_2Zr(CH_2PPh_2)_2$ or $[Cp_2Zr(CH_2PPh_2)]_2O$. The mixed-metal Rh-Zr complex $[Cp_2Zr(CH_2PPh_2)_2RhH(CO)PPh_3]$ was prepared and found to be a very effective hydroformylation catalyst [37]; it was found to be more active than $HRh(PPh_3)_4$ and also the linear/branched aldehyde ratio was higher than with Rh alone [38]. The Rh oxometalates $[(Ph_3P)_2Rh(CO)(MeCN)]_4SiW_{12}O_{40}$ and $[(Ph_3P)_2Rh(CO)]_4SiW_{12}O_{40}$ catalyze hydroformylation of olefins and oxidation of aldehydes by air to carboxylic acids in toluene suspension. These complexes act therefore as bifunctional catalysts activating CO and H_2 on the Rh centers and O_2 on the W centers [39]. The carbido clusters $Fe_4Rh_2C(CO)_{16}$ and $Ph_4P[Fe_3Rh_3C(CO)_{15}]$ were used as catalyst precursors for the hydroformylation of 1-pentene (100°C, 60 bar). The Fe_3Rh_3 cluster could be recovered after catalysis in 70-80% yield [40].

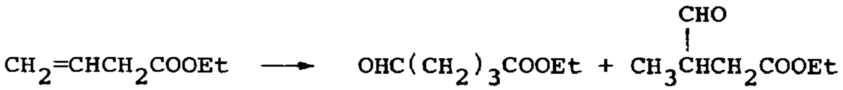
See also [24,37,60,89].

c) Other Metals as Catalysts

Hydroformylation of olefins was studied using $Tc_2(CO)_{10}$ or $Tc_2(CO)_{10}$ + PBu_3 as catalysts. The technetium-phosphine system proved to be more active than Mn- or Re-based catalysts but was a poor catalyst compared with Co or Rh compounds [41].

Propene was hydroformylated at 70-110°C and 10-20 bar using the cluster $(Et_4N)[HRu_3(CO)_{11}]$ as catalyst. Regioselectivity of the reaction depended on the solvent: in general ether solvents favored the formation of the linear aldehyde. Under optimum conditions 98.6% n-butanal was formed [42]. Hydroformylation (and consecutive hydrogenation) of internal olefins to give predominantly linear alcohols is catalyzed by Ru carbonyl "melt" catalysts, wherein the Ru carbonyls are dispersed in low melting point quaternary phosphinum salts. Mixed-metal catalysts composed of Ru and Co yield the corresponding aldehydes as the main products [43].

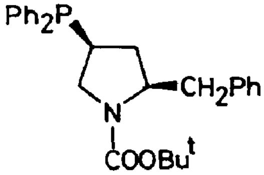
The <u>cis</u>-$[PtCl_2(PPh_3)_2]$ + $SnCl_2$ bimetallic system was used as catalyst for the hydroformylation of ethyl 3-butenoate; regioselectivity was 75-80% in favor of the linear aldehyde isomer (5). Ketones or aromatic hydrocarbons were the best solvents; in EtOH which strongly inhibits the reaction the acyl complex <u>trans</u>-$[PtCl(COCH_2CH_2CH_2COOEt)(PPh_3)_2]$ was recovered [44].



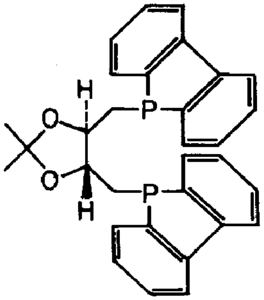
$$CH_2{=}CHCH_2COOEt \longrightarrow \underset{5}{OHC(CH_2)_3COOEt} + CH_3\overset{\displaystyle CHO}{\overset{|}{C}}HCH_2COOEt$$

5

Hydroformylation of olefins with $LPtCl_2$ + $SnCl_2$ catalysts (L = 6,7) or their polymer-supported analogs showed that the rates were lower in the case of the polymer-supported catalysts. In the case of styrene, good optical yields were only observed at partial conversion and short reaction times because of consecutive racemization of the 1-phenylpropionyl aldehyde formed [45].



6 (BPPM)



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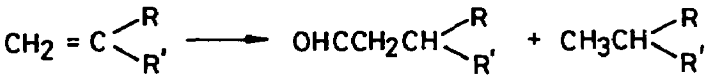
Hydroformylation of several olefins was carried out with the chiral catalysts [(-)-BPPM]$\mathrm{PtCl_2}$ + $\mathrm{SnCl_2}$ and [(-)BPPM]$\mathrm{Pt(SnCl_3)Cl}$ at 60°C and 200 bar. Enantioselectivities ranged between 70-85% but if the reaction was performed in triethyl orthoformate as solvent, enantiomerically pure (> 98%) acetals were obtained [46]. Vinylidene esters of type (8) have been hydroformylated with the chiral catalyst [$\mathrm{PtCl(SnCl_3)}$(R,R)-DIOP]. Highest optical induction (82%) was achieved in the case of (8; R = COOMe, R′ = $\mathrm{CH_2COOMe}$) [47].



8

See also [24,25,48,50,88].

d) Heterogeneous Systems (Supported Complexes)

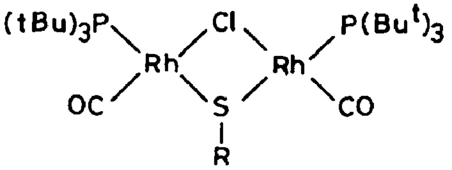
Polymer-supported M_3 and M_4 (M = Ru, Os) and $\mathrm{RuOs_3}$ anionic clusters were used as catalysts for the simultaneous hydrogenation and hydroformylation of 1-hexene. The supported clusters were more active than their homogeneous counterparts and Os clusters were more active than Ru clusters [48]. High activities and selectivities toward normal alcohols were achieved in the vapor-phase hydroformylation of ethene and propene on carbon-supported Ru-Co bimetallic catalysts derived from the mixed-metal clusters $\mathrm{H_3Ru_3Co(CO)_{12}}$, $\mathrm{HRuCo_3(CO)_{12}}$, and their $\mathrm{Et_4N^+}$ salts. Reaction conditions were 172-194°C and 1 bar [49]. Hydroformylation of ethene and propene (160°C, 1 bar) was carried out with catalysts prepared by impregnating SiO_2 gel with Rh, Fe, or bimetallic Rh-Fe carbonyl clusters. Catalysts prepared from $Rh_4(CO)_{12}$ or $[TMBA][Fe_3(CO)_{11}]$ (TMBA = trimethylbenzylammonium) showed negligible activity but hydroformylation activity was increased several hundred fold for catalysts derived from $FeRh_5$, $FeRh_4$, Fe_2Rh_4, and Fe_3Rh_2 carbonyl clusters [50].

Hydroformylation of propene was studied with $HRh(CO)(PPh_3)_3$ dissolved in liquid PPh_3 and condensed onto a porous support. Leaching of the catalyst was negligible. Propadiene inhibited the reaction [51]. Supported liquid-phase catalysts containing $HRh(CO)(PPh_3)_3$ dissolved in PPh_3 were used for the gas-phase hydroformylation of C_2-C_4 olefins [52]. Based on these bench-scale studies a large-scale SLPC plant for the hydroformylation of propene was designed [53].

Diphenylphosphine-substituted styrene oligomers were prepared and used as ligands for the Rh-catalyzed hydroformylation of propene. High selectivity for nPrCHO was achieved at lower P/Rh ratios than with PPh_3 [54]. Ethene was hydroformylated using a $HRh(CO)(PPh_3)_3$ liquid-phase catalyst supported on α-Al_2O_3. A stable activity level, which was highly dependent on the type of α-Al_2O_3, was reached in 24h on-stream time. Deactivation was probably caused by aldol products which leached out the catalyst [55].

Hydroformylation of 1-hexene using homogeneous catalysts and zeolite-supported Rh species was compared. The two systems behaved in most respects analogously: addition of phosphines reduced olefin isomerization and increased the amount of n-aldehyde, mercaptans acted as poisons except if large amounts of phosphine were present. The data suggest catalysis by dissolved or surface-bound Rh but are not consistent with intrazeolitic catalysis [56]. Zeolite-supported rhodium carbonyl catalysts were prepared from $Rh(allyl)_3$ and used for the hydroformylation of 1-hexene. The major conclusion drawn from the experimental results was that the observed activity has to be attributed to rhodium carbonyl complexes leached from the support and acting as homogeneous catalysts [57].

Rhodium complexes of sulfur-containing polymers prepared from poly(vinyl chloride) by partial substitution of the chlorine atoms with SR groups were found to be highly active catalysts for the hydroformylation of α-olefins at 60°C and 60 bar. The catalysts could be reused once again [58]. Several dirhodium complexes of the type (9) were anchored to diphenylphosphinated crosslinked polystyrene, to chloromethylated polystyrene, to silica and to alumina and used in this form as catalysts for the hydrogenation or hydroformylation of cyclohexene. Only minor metal leaching was observed and the catalysts could be reused ten times without structural changes [59].

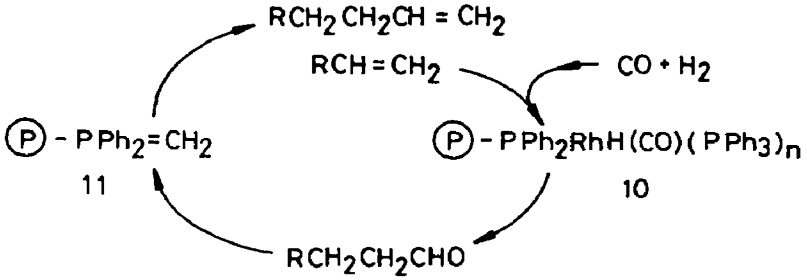


9; R = Ph, p-substituted Ph

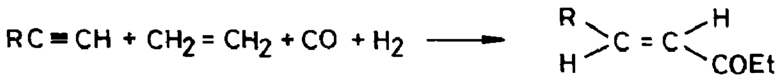
See also [45,60,83,88].

e) Modified Hydroformylations

Hydroformylation of a 1-alkene in a co-suspension of polystyrene-bound $HRh(CO)(PPh_3)_3$ (10) and a polystyrene-bound Wittig-reagent (methylenetriphenylphosphorane; 11) resulted in the formation of a homologous series of aldehydes according to the schematic cycle of reactions shown below:



The composition of the aldehydes did not follow the Schultz-Flory distribution. No reaction was observed if soluble $HRh(CO)(PPh_3)_3$ was used instead of (10) [60]. Cross-hydrocarbonylation of acetylenes with ethene, CO, and H_2 gives α,β-unsaturated ethyl ketones; the reaction is catalyzed by $Rh_4(CO)_{12}$ at 60 bar (H_2:CO = 5:1) and 90°C:



$$RC{\equiv}CH + CH_2{=}CH_2 + CO + H_2 \longrightarrow (R)(H)C{=}C(H)(COEt)$$

The reaction of terminal acetylenes proceeds with high stereo- and regioselectivity: the propionyl group will be linked to the less sterically hindered acetylenic carbon atom [61].

Hydroformylation of ethene with CO + H_2O in basic solutions containing $Fe(CO)_5$ as a catalyst (Reppe hydroformylation) was found to be second order with respect to $Fe(CO)_5$ and inhibited by CO. The reaction between $EtCOFe(CO)_3^-$ and $HFe(CO)_4^-$ to produce EtCHO and $Fe_2(CO)_7^{2-}$ was proposed as the rate-determining step. Propionaldehyde was the principal product if NaOH was used as the base, Et_3N facilitated the reduction to n-propanol [62].

See also [94].

3. Hydrocarbonylation (Homologation) of Alcohols, Aldehydes and Esters with CO + H_2

Homologation of MeOH to EtOH by synthesis gas is catalyzed by $Mn_2(CO)_{10}$ in the presence of K formate at 200°C and 200 bar according to the following stoichometry:

$$CH_3OH + 2\ CO + H_2 \longrightarrow CH_3CH_2OH + CO_2$$

The reaction between $Mn(CO)_5^-$ and methyl formate to form $MeMn(CO)_5$ is the rate-limiting step of the catalytic cycle. The catalyst is slowly deactivated due to the formation of Mn carbonate and Mn formate [63].

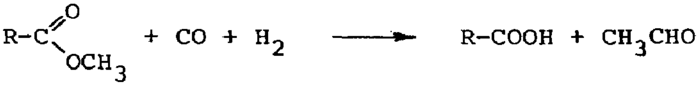
Hydrocarbonylation of PrOH, BuOH, and $iPrCH_2OH$ using Co carbonyls as catalysts was studied [64]. Methanol was homologated to EtOH in dioxane as solvent using a silica-supported poly-γ-mercaptopropylsiloxane-cobalt complex as catalyst. Conversion and selectivity were 88 and 89%, respectively [65]. The bi-, tri-, and quadridentate alkoxyethylphosphanes of the type $R_nP(CH_2CH_2OR')_{3-n}$ (R = Ph, Cy; R' = Me, iPr) were used as ligands in the hydrocarbonylation of methanol with CO + H_2, Co catalysts and I_2 promoter at 180°C and 300 bar. CoI_2 was found to be a more active catalyst than $Co(OAc)_2$ but due to the formation of HI the alkoxy groups of the phosphines were gradually split off and this led to deactivation [66].

The homologation of ethanol has been studied in the presence of Co-Ru catalysts. Reaction conditions were selected such that propanol and its derivatives were the main poducts. Homologation proceeded at least partially via hydroformylation of an olefinic intermediate [67]. Homologation of nPrOH and iPrOH to butanols with CO + H_2 was performed with Co + Ru mixed catalysts at 180°C and 430 bar. Best selectivities for C_4 alcohols were obtained at Co:Ru ratios of about 6. Both propanols were transformed into nBuOH and iBuOH suggesting an olefinic intermediate [68]. The four butanols were converted into C_5 homologous alcohols by CO + H_2 in the presence of Co + Ru binary catalysts and I_2 promoter. The best results were obtained with a Co/Ru ratio of approximately 5; the reactivity of butanols increased in the order primary < secondary < tertiary. Olefins were supposed as intermediates also in this case [69].

Methane formation accompanies the homologation of MeOH to EtOH with Rh catalysts [70].

Hydroformylation of paraformaldehyde and aqueous formaldehyde to give glycolaldehyde was performed in acetone at 90-140°C and 100-140 bar with selectivities up to 90% using $Rh_4(CO)_{12}$ as catalyst precursor and halides as promotors. The promotion ability of halides followed the trend Cl > I > Br > F [71]. Formaldehyde has been hydroformylated to glycolaldehyde with selectivities up to 95% with catalyst systems formed from $Rh_4(CO)_{12}$, a phosphine and an inorganic acid like HI or H_2SO_4 in DMF. Anionic species related to $[Rh_5(CO)_{14}(PPh_3)]^-$ were suggested as catalysts [72]. Paraformaldehyde has been hydroformylated to glycolaldehyde at 140 bar CO_2 + H_2 and 110°C with selectivity up to 95% in acetone as solvent using a catalytic system composed of $[Rh(CO)_2Cl_2]^-$ and $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$. A related catalyst system generated *in situ* from $Rh_4(CO)_{12}$, PPh_3, and halide ions showed comparable behavior [73]. Rhodium(I) complexes in the presence of phosphine amides having the structure $PPh_2(CH_2)_2C(O)N(Me)R$ (R = Me, $nC_{18}H_{37}$) were used for the hydroformylation of formaldehyde to glycol aldehyde. Such catalyst systems gave glycol aldehyde selectivities above 90% and did not need the use of nucleophilic (high boiling) solvents thus making product separation and catalyst recovery feasible [74]. Hydroformylation of formaldehyde to give glycolaldehyde was achieved by using $[Rh(\mu\text{-}SBu^t)(CO)(PPh_3)]_2$ as catalyst in the presence of an excess of PPh_3 at 80°C and 50 bar CO + H_2. The main side reaction was hydrogenation to methanol. Selectivity for glycolaldehyde strongly depended on the solvent; best results were obtained with HMPA [75].

Ruthenium carbonyl iodide systems could be used effectively for the homologation of formic esters to produce a mixture of oxygenates rich in acetates. Activity of these systems did not decrease strongly by passing from Me to higher alkyl derivatives [76]. Methyl esters react with synthesis gas in the presence of a Co-Li catalyst formed <u>in situ</u> from $Co(OAc)_2 \cdot 4H_2O$ and LiI at 180°C and 350 bar to give anhydrous acetaldehyde and a carboxylic acid:



$$R\text{-}C(=O)OCH_3 + CO + H_2 \longrightarrow R\text{-}COOH + CH_3CHO$$

Amines, especially NPh_3, enhance the rate. Acetaldehyde selectivity is above 95%. If Rh is used instead of Co, acetic anhydride and ethylidene diacetate are formed as byproducts [77]. Rhodium-based homogeneous catalysts were described for the homologation of esters under mild conditions (20-60 bars, 150-160°C) according to the following two alternative stoichiometries [78]:

$$2RCOOR + 2CO + 2H_2 \longrightarrow RCOOCH_2R + 2RCOOH$$

$$RCOOR + 2CO + 2H_2 \longrightarrow RCH_2COOH + RCOOH$$

A new catalyst system based on $Pd(OAc)_2$, MeI and Bu_4PI has been described for the hydrocarbonylation of methyl acetate to acetaldehyde:

$$CH_3COOCH_3 + CO + H_2 \longrightarrow CH_3COOH + CH_3CHO$$

Reaction conditions were relatively mild, 160°C and 35-70 bar. Acetone and ethylidene diacetate were observed as byproducts [79].

See also [95].

4. Coordination Chemistry Related to Hydroformylation

It was proposed that activation of metal carbonyl catalysts in the hydroformylation reaction results from loss of a CO ligand accompanied by the change in spin state from singlet to triplet [80].

A kinetic study of the reaction of $HCo(CO)_4$ with olefin giving $RCo(CO)_4$ at -80°C indicated that the loss of a CO ligand from $RCo(CO)_4$ to form $RCo(CO)_3$ is the slow step in low-temperature hydroformylation [81]. Infrared spectroscopic studies have shown that $YCCo_3(CO)_9$ (Y = H, Pr, Ph, Cl) complexes decompose under hydroformylation conditions (130°C, 40 bar CO + H_2) into $Co_2(CO)_8$ and $HCo(CO)_4$. Accordingly these latter species are the true catalysts if the above mentioned trinuclear complexes are applied as catalyst precursors [82]. According to IR and EXAFS data the structure of the cluster catalyst $Co_4(CO)_{10}(PPh)_2$ on SiO_2 was retained during hydroformylation of ethene at 130°C and 55 bar [83]. The formation of Rh carbonyl phosphine complexes active in hydroformylation from a Rh acetylacetonate complex was studied in situ by IR spectroscopy [84]. A catalytic cycle in which all the intermediate species are dinuclear has been put forward for the hydroformylation reaction catalyzed by $Rh_2(\mu\text{-}SR)_2(CO)_2L_2$ complexes (L = tertiary phosphines or phosphites). The proposal is based on experimental results and extended Hückel calculations [85]. The molecular structure of $Rh_2(\mu\text{-}SBu^t)_2\ [(\mu\text{-}Ph_2PCH_2)_2Zr(Cp)_2](CO)_2$, a bimetallic species which is active as a hydroformylation catalyst, has been determined [86].

5. Water Gas Shift Reaction

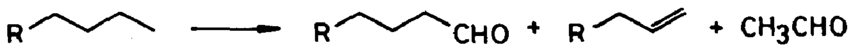
The water gas shift reaction is catalyzed by $Fe(CO)_5$, $M(CO)_6$ (M = Cr, Mo, W), and $Co_2(CO)_8$ in water at 180-220°C in the presence of alkali metal hydroxides, carbonates, or bicarbonates with a H_2 yield of at least 95%. Due to the formation of CO_2, alkalinity of the system decreases and leads to a drop in catalytic activity; this can be compensated by increasing the temperature [87]. Os, Ir, and Ru complexes supported on zeolites were successfully used for hydroformylation, hydrogenation and the water gas shift reaction [88]. The water gas shift reaction, the reduction of nitrobenzene or unsaturated carbonyl compounds, and the hydroformylation of olefins was studied with $Rh_6(CO)_{16}$ + amine or py catalyst systems. With pyridines as additives, unsaturated carbonyl compounds were hydrogenated at the C=C bond while diamines promoted the reduction of the C=O bond. In hydroformylation, consecutive hydrogenation of the aldehydes formed was favored by high concentration of additives [89].

6. Reduction with CO + H_2O

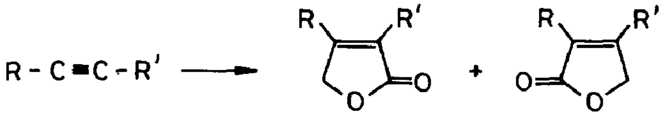
Dialdehydes and diketones were reduced to the corresponding diols with CO + H_2O in EtOH or $MeOCH_2CH_2OH$ at 180°C and 4 bar using $Fe(CO)_5$ or $Rh_6(CO)_{16}$ as catalysts. Benzoquinone gave quantitatively hydroquinone under these conditions [90]. Quinolines were hydrogenated selectively in the N-containing ring with CO + H_2O at 150°C and 60 bar in the presence of $Rh_6(CO)_{16}$ as catalyst. Isoquinolines were converted under the same conditions into N-formyl--1,2,3,4-tetrahydroisoquinolines. The formylation reaction was attributed to the higher basicity of the tetrahydroisoquinolines in comparison with tetrahydroquinolines [91].

7. Miscellaneous Reductive Transformations of CO and CO_2

n-Alkanes were regioselectively transformed under CO into aldehydes having one carbon atom more than the starting alkane, and 1-alkenes containing one carbon atom less with the simultaneous formation of acetaldehyde by photocatalysis in the presence of $Rh(CO)(PMe_3)_2Cl$:



The active species is presumably $Rh(PMe_3)_2Cl$ and the loss of catalytic activity with time is possibly due to the formation of $[Rh(PMe_3)_2Cl]_2$ [92,93]. Ruthenium-iodide systems have been found to catalyze the reaction of olefins, CO, and alcohols at 190°C to give esters and ketones. Ionic iodides like NaI yielded only esters, formation of ketones was promoted by covalent iodides like MeI [94]. A reaction analogous to MeOH homologation was described: $MeOSiEt_3$ reacts with HSiEt in the presence of $Co_2(CO)_8$ under CO pressure (50 bar) and 180-220°C to yield - along with large amounts of methane and $Et_3SiOSiEt_3$ - a mixture of saturated and unsaturated C_2-C_4 silyl ethers. The main products of homologation were CH_2=$CHOSiEt_3$ and $CH_3CH_2OSiEt_3$ [95]. Acetylenes were selectively converted into furan-2(5H)-ones (12) under water gas shift conditions (100°C, 100 bar CO, H_2O, THF, Et_3N) with $Rh_4(CO)_{12}$ as catalyst. Asymmetrically substituted acetylenes afforded two furanone structural isomers (12a) and (12b) [96].



12 a 12 b

The $[Ru(bpy)_2(CO)_2]^{2+}$/$[Ru(bpy)_3]^{2+}$/triethanolamine/DMF system reduces CO_2 to afford $HCOO^-$ under irradiation of light. In this system, the Ru carbonyl complex (which exhibits no electronic absorption band in the visible region) acts as catalyst and the other Ru complex as photosensitizer [97]. Mechanistic studies of the photoinduced reduction of CO_2 to CO mediated by $ReBr(CO)_3(bpy)$ in triethanolamine/DMF solvent mixtures were reported. The primary photoreduction product was $[ReBr(CO)_3(bpy)]^-$; its formation was inhibited by water or EtOH [98].

The controlled potential electrolysis of a CO_2-saturated H_2O/DMF solution containing $[Ru(bpy)_2(CO)_2]^{2+}$ or $[Ru(bpy)_2(CO)Cl]^+$ produces CO. If the solution is alkaline (pH 9.5) $HCOO^-$ is also formed [99]. The selectivity of the formation of formate in electrochemical reduction of CO_2 catalyzed by $[Ru(bpy)_2(CO)_2]^{2+}$ in MeCN solution was found to increase with increasing pK_a value of the proton source. Best results were achieved with $Me_2NH.HCl$ and PhOH [100]. In the presence of Me_2NH and $Me_2NH.HCl$ probably a carbamoyl Ru(II) complex is an intermediate of the reaction [101]. The complexes $[Pd(triphos)L](BF_4)$ (L = MeCN, $P(OMe)_3$,

PEt_3, $P(CH_2OH)_3$ and PPh_3 were shown to catalyze the electrochemical reduction of CO_2 to CO. Based on kinetic studies a mechanism for the reduction of CO_2 was proposed [102].

Group 6 metal pentacarbonyl chlorides $(CO)_5MCl^-$ and bridging hydrides $[HM_2(CO)_{10}]^-$ (M = Cr, Mo, W) have been found to be effective homogeneous catalyst precursors for the synthesis of formate esters from alkyl halides, CO_2 and H_2 in the presence of alkali metal carbonates at 150°C and 40 bar:

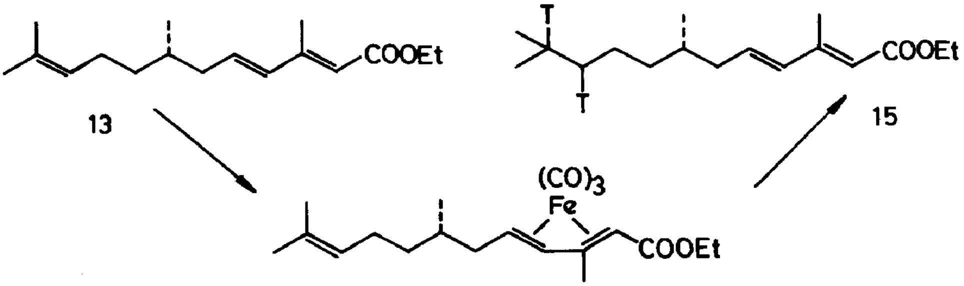
$$RX + CO_2 + H_2 \xrightarrow{NaY} HCOOR + NaX + HY$$

Selectivities were above 70%; main byproducts were the corresponding alcohols [103].

III. Hydrogenation and Reduction

1. H Exchange, D and T Labeling

Selective tritiation of the dodecatrienoate (13) was accomplished by transforming it into complex (14) and hydrogenating the latter with $^3H_2$ in the presence of $Rh(PPh_3)_3Cl$. Decomplexation with Ce^{4+} afforded the desired product (15) [104].



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14

Highly regioselective ortho tritiation of arylcarboxylic acids and of arylcarboxamides could be achieved in a single step by $RhCl_3$-catalyzed exchange with tritiated water [105].

See also [183].

2. Hydrogenation of Olefins

a) General

Homogeneous Pd complexes with S ligands were found to be 50-500 times more resistant to poisoning by thiophene in hydrogenation than complexes containing N ligands [106]. EXAFS investigation of homogeneous hydrogenation catalysts prepared by reduction of Ni and Fe acetylacetonates with $AlEt_3$ or $GaEt_3$ revealed the formation of amorphous metal carbide-like clusters [107].

Yb Complex catalyst see [253].

See also [166].

b) Ti and V Catalysts

The silica-supported titanium complex $[SIL-(CH_2)_3C_5H_4]_2TiCl_2$ is, after reduction with BuLi, an efficient and selective catalyst for the hydrogenation of 1-alkenes; it is more active and more selective toward 1-alkenes than the homogeneous analogues Cp_2TiCl_2+ BuLi, $(MeC_5H_4)_2TiCl_2$ + BuLi, and $[(MeO)_3Si(CH_2)_3C_5H_4]_2TiCl_2$ + BuLi [108]. Olefins were hydrogenated with homogeneous or supported catalysts obtained from BuLi and either $CpTiCl_2OC_6H_4R$ (R = H,Me, NO_2,Cl) or $CpTiCl_3$-alumina-silica gel reaction products. Activity of the catalysts increased with increasing donor propoerties of the ligands [109].

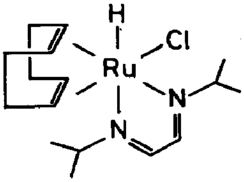
The V(II) complex CpVPr(dmpe) catalyzes the slow hydrogenation of olefins at room temperature [110].

See also [162].

c) Fe, Ru and Os Catalysts

Homogeneous gas-phase mixtures of ethene, H_2, and a catalytic amount of $Fe(CO)_5$ are transformed into active hydrogenation systems upon irradiation by near-UV light. The absorbed light generates a reservoir of $Fe(CO)_3(C_2H_4)_2$ which thermally dissociates and yields the active catalyst, $Fe(CO)_3(C_2H_4)$. The catalytic process is efficient in light with quantum yields (ethane per photon absorbed) around 20 [111].

Hydrogenation of cyclohexene catalyzed by different Ru(II) and Ru(III) complexes containing trichlorostannato and $NH(CH_2CH_2PPh_2)_2$ ligands was studied. Based on kinetic and NMR measurements it was concluded that the active catalyst was in all cases a Ru(II)-monohydride [112]. The Ru complex (16) catalyzes the hydrogenation of olefins at 80°C and 20 bar [113].



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Hydrogenation of styrene is catalyzed by $H_3Os_4(CO)_{12}$, $H_4Os_4(CO)_{12}$, $[H_2Os_4(CO)_{12}I]^-$, and $[H_3Os_4(CO)_{12}]^-$ in decalin solution at 140°C. Kinetic and spectroscopic evidence indicates that these tetranuclear clusters are not directly involved in the catalytic cycle but undergo fragmentation to produce low concentrations of lower nuclearity (probably mononuclear) species which are responsible for the observed catalytic activity [114].

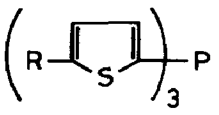
See also [48,88,165].

d) Rh and Ir Catalysts

Olefins were hydrogenated using pentamethylcyclopentadienyl complexes of Rh as catalysts in the presence of pyrazole or methylpyrazoles as additional ligands and Et_3N as a base. The complex $([Rh(C_5Me_5)(\text{dimethyl pyrazole})]_2(\mu\text{-}OH)_2(ClO_4)_2$ was found to be an effective hydrogenation catalyst also in the absence of base [115]. The catalytic activity of Rh complexes of Me methacrylate and 2-vinylpyridine copolymers in hydrogenation of olefins increased with increasing contents of Me methacrylate triads in the copolymer [116]. The Rh(III) complex $[Rh(2,2'\text{-biquinoline})Cl_2]Cl$ catalyzes the hydrogenation of olefins in alkaline MeOH solution but is inactive for the hydrogenation of nitro compounds [117]. Dicyano olefins NC-A-CN react with $Rh(CO)(PPh_3)_2(ClO_4)$ to give the dinuclear cationic complexes $[(PPh_3)_2(CO)RhNC\text{-}A\text{-}CNRh(CO)(PPh_3)_2](ClO_4)_2$ which are active catalysts for the hydrogenation of these dicyano olefins at 100°C (NC-A-CN = e.g. trans-$NCCH{=}CHCH_2CH_2CN$) [118]. The tetragonal coordination polymer $[\mathrm{Rh(diisocyanobiphenyl)_2{}^+Cl^-}]_n$ was tested as a catalyst for the hydrogenation of 1-hexene. The rather low catalytic activity could be increased by prehydrogenation. No evidence was found for homogeneous catalysis or metallic Rh particles [119]. Linear free energy relationships were successfully applied to alkene hydrogenations catalyzed by $[\mathrm{Rh(cyclooctene)_2Cl}]_2$ + 2-(N-alkylamino)pyridine and to $[\mathrm{Rh(cyclohexene)_2Cl}]_2$ + <u>para</u>-substituted triphenylphosphine catalyst systems [120].

The catalytic hydrogenation activity of $\mathrm{HRh(PPh_3)_4}$ and $\mathrm{HRh(CO)(PPh_3)_3}$ was found to be significantly influenced by the addition of phenyldibenzophosphole (DBP). The rate of hexene-1 hydrogenation increased in the case of $\mathrm{HRh(PPh_3)_4}$ as catalyst while $\mathrm{HRh(CO)(PPh_3)_3}$ was completely deactivated by already relatively small amounts (0.5 mole/mole) of DBP [121]. The cationic Rh complexes $[\mathrm{Rh(COD)L_2}]^+(\mathrm{OTs})^-$ (L = $\mathrm{Ph_2P(CH_2)_nPPh_2}$, n = 2,3,4, or L = (–)-DIOP) catalyze the hydrogenation of 1-heptene and Z-α-acetamidocinnamic acid. The tosylate anion increases the activity of the catalysts [122].

The mixture of dihydrides obtained in the reaction of H_2 with the water-soluble Rh(I) complex $\mathrm{RhCl(TPPTS)_3}$ (TPPTS = $\mathrm{P(\underline{m}\text{-}C_6H_4SO_3Na)_3}$ showed a very low catalytic activity for the hydrogenation of cyclopentene [123]. The complexes Rh(COD)Cl(L) (I), $[\mathrm{Rh(COD)(DAB)(L)}](\mathrm{ClO_4})$ (II), and $[\mathrm{H_2Rh(DAB)(L)_2}](\mathrm{ClO_4})$ (III) (L = $\mathrm{P(C_6H_4F\text{-}\underline{p})_3}$, DAB = $\mathrm{H_2NN{=}C(Me)C(Me){=}NNH_2}$) were tested as catalysts for the hydrogenation of 1-hexene. Complex (III) was found to be the most active, complex (I) showed an induction period [124]. The complex $[\mathrm{Rh_2(COD)CH(PPh_2)_3}](\mathrm{CF_3SO_3})_2\cdot\mathrm{Me_2CO}$ which contains two neighboring, coordinatively unsaturated Rh atoms catalyzes the hydrogenation of hexene-1. The rate of hydrogenation increased fivefold if one equivalent of $\mathrm{PPh_3}$ was added to the reaction mixture [125]. The catalytic activity of the complexes $\mathrm{HRh(CO)L_3}$ (L = 17) in hydrogenation of allylbenzene was found to be related to their NMR parameters [126].



17; R = H, tBu, $\mathrm{Me_3Si}$

The possibility to study homogeneously catalyzed reactions under reaction gas chromatographic conditions was demonstrated. Hydrogenation of alkenes with $Rh(PPh_3)_3Cl$ as catalyst and the aldol condensation of propionaldehyde were used as examples [127]. Homogeneous hydrogenation catalysts were prepared from Rh(I) complexes and phosphines of type PPh_2R based on polyethylene. These catalysts were shown to have about 80% of the activity of $Rh(PPh_3)_3Cl$ in the hydrogenation of various alkenes. The complexes dissolved at 90-100°C in hydrocarbons solvents but quantitatively precipitated and thus could be recovered at 25°C [128]. Attachment of $HRh(CO)(PPh_3)_3$ to phosphinated styrene-divinylbenzene polymers leads to complete loss of CO and H ligands; these species show catalytic activity in the hydrogenation of cyclohexene under room conditions [129].

Complexes of the composition MCl(L) (M = Rh, Ir; L = $HN(CH_2CH_2AsPh_2)_2$ were used as catalysts for the hydrogenation of cyclohexene. The activation parameters were determined [130]. The complexes $[M(L)(CO)(PPh_3)_2](ClO_4)$ (M = Rh, Ir) and $[H_2Ir(L)(CO)(PPh_3)_2](ClO_4)$ (L = trans-PhCH=CHCN, cinnamonitrile) show a low catalytic activity for the hydrogenation of cinnamonitrile [131]. The 1,4-dicyanobutene-bridged binuclear Ir complexes $[(CO)(PPh_3)_2IrLIr(PPh_3)_2(CO)](ClO_4)_2$ (L = cis- or trans-1,4-dicyanobutene-1 or trans-1,4-dicyanobutene-2) catalyze the hydrogenation of the corresponding free ligands to 1,4-dicyanobutane at 100°C [132].

See also [88,166,198,199]

e) Ni, Pd and Pt Catalysts

Supported Ziegler catalysts prepared by the reaction of Ni(II) 2-ethylhexanoate with Al_2O_3-SiO_2 treated with $AlEt_3$ or $NaAlH_2(OCH_2CH_2OMe)_2$ were found to be efficient catalysts for the hydrogenation of simple alkenes [133]. Homogeneous hydrogenation of styrene to ethylbenzene is catalyzed by the complexes [M(PNP)Cl]Cl.L (M = Ni, Pd, Pt; PNP = 1,1-bis(diphenylphosphino)-2,6-diaminopyridine; L = H_2O or EtOH [134].

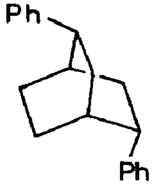
Catalysts obtained by complexing Pd with Schiff bases prepared from γ-aminopropyl silica and heterocyclic aldehydes, were used for hydrogenation of allylbenzene in MeOH solution in the presence of $NaBH_4$ [135]. Catalysts prepared by supporting the Pd complex of poly-γ-(m-diphenylphosphinophenyl)propylsiloxane or poly-γ-diphenylphosphinoundecylsiloxane on Si-Mg adsorbent, Al_2O_3, or SiO_2 were used for the hydrogenation of olefins. The activity of the catalysts decreased with increasing P:Pd ratio [136].

The complex $Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr_3)_2$ showed only little catalytic activity in the hydrogenation of styrene at 70°C and 50 bar. Its activity was, however, significantly increased if 2-10 equivalents of $SnCl_2 \cdot 2H_2O$ were added [137]. Supported Pt(II) phosphine complexes based on modified polystyrenes have been employed in the $SnCl_2$ co-catalyzed hydrogenation of styrene. The heterogenized catalysts could be reused upon addition of fresh $SnCl_2$ [138].

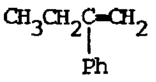
See also [177, 203, 204].

3. Asymmetric Hydrogenation of Olefins

The titanocene derivative $Cp^*_2TiCl_2$ containing the enantiomerically pure ligand Cp^* = (+)- or (-)- (18) was prepared and used as catalyst for enantioselective hydrogenation of the prochiral simple alkenes (19) and (20). Optical yields up to 95-96% were achieved at low temperatures (-75°C) [139].

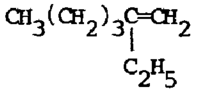


(+)-18



$CH_3CH_2\underset{\displaystyle Ph}{\underset{|}{C}}{=}CH_2$

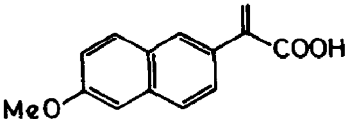
19



$CH_3(CH_2)_3\underset{\displaystyle C_2H_5}{\underset{|}{C}}{=}CH_2$

20

The unsaturated carboxylic acids $tBuC(=CH_2)COOH$ and $tBuC(Me)=CHCOOH$ were hydrogenated to the (R) enantiomers of the corresponding saturated carboxylic acids with 22-31% o.y. using $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ as catalyst [140]. Asymmetric hydrogenation of unsaturated carboxylic acids not containing an amide or a related group was achieved using Ru(II)-BINAP complexes as catalysts. Both α,β - and β,γ -unsaturated carboxylic acids (e.g. 21 and 22) could be hydrogenated with high optical yields (97% and 88%) at room temperature and 4-135 bar [141].



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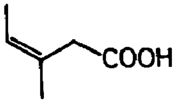

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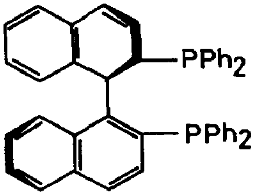
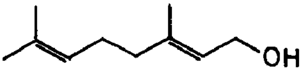


23, (R)-BINAP

Enantioselective hydrogenation of allylic and homoallylic alcohols was achieved with high optical yields (above 96%) with Ru(BINAP)(OOCR)$_2$ (R = Me, tBu) complexes as catalysts. The method was succesfully used for the hydrogenation of geraniol (24), nerol (25), homogenariol (26), and the alcohol (27); depending on the configuration of the chiral phosphine it was suitable for the synthesis of both saturated enantiomers [142].



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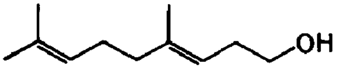

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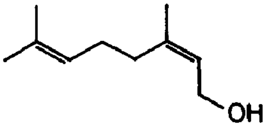

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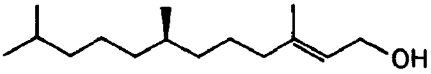

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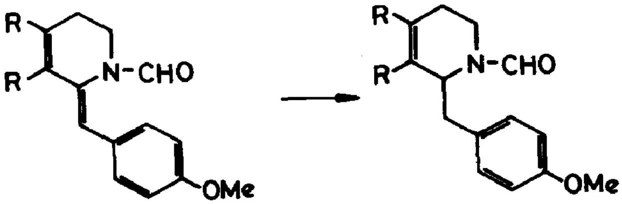
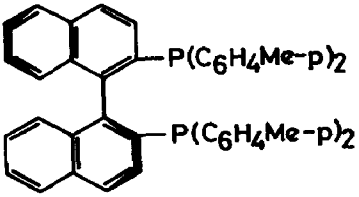
The enamides (28) were asymmetrically hydrogenated to the chiral tetrahydropyridine derivatives (29) using Ru(L)(OOCCF$_3$)$_2$ (L = (S)-tolbinap; 30) as catalyst at 30°C and 100 bar (chemical yield 100%, o.y. 97%) [143].



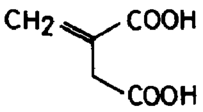
28 29

R = Me or R-R = (CH$_2$)$_4$



30

Itaconic acid (31) and related unsaturated dicarboxylic acids were asymmetrically hydrogenated with good optical yields using Ru-BINAP complexes as catalysts. Citraconic acid (32) and mesaconic acid (33) were, however, hardly hydrogenated; optical yields were much poorer also if the methyl esters of the dicarboxylic acids were used as substrates [144].



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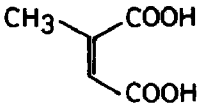

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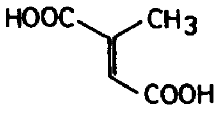
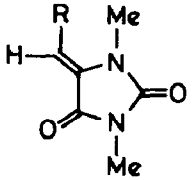


33

Asymmetric hydrogenation of unsaturated substituted hydantoins (34; R = iPr, Ph, *p*-substituted Ph) by $(Ph_3P)Co(dmg)_2$ or $(Bu_3P)Co(dmg)_2$ in the presence of chiral 2-quinuclidinecarboxamides (35; R′ = OEt, NHMe, and different chiral amino groups) was examined. Maximum optical yield was 82%; the results suggest that the chiral base acts as a proton donor [145].



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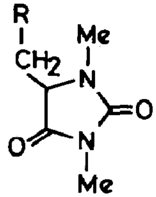

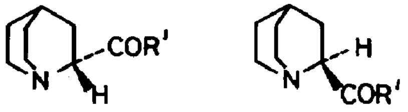

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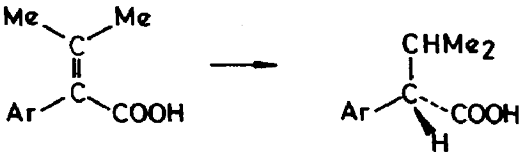
Asymmetric hydrogenation of methyl-(Z)-α-acetamidocinnamate (mac) catalyzed by $[Rh(dipamp)]^+$ has been examined. It was concluded that the predominant (S) enantiomer product is derived from the minor (less stable) $[Rh(dipamp)(mac)]^+$ adduct by virtue of its much higher reactivity towards H_2. The inverse dependence of o.y. on H_2 partial pressure was shown to be due to the rapid reaction of H_2 with the diastereomeric adducts which inhibits their interconversion [146]. Trisubstituted acrylic acids (36) were hydrogenated with high enantioselectivity (92-98%) to the corresponding (S)-carboxylic acids (37) using catalysts prepared in situ from

$[Rh(NBD)Cl]_2$, $AgBF_4$, and the chiral (aminoalkyl)ferrocenylphosphine ligands (38). Interaction between the dialkylamino group of the ligand and the carboxy group of the substrate are thought to be responsible for the high enantioselectivity [147].



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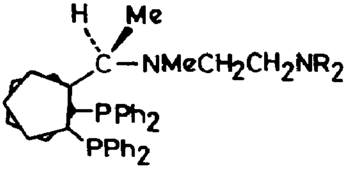
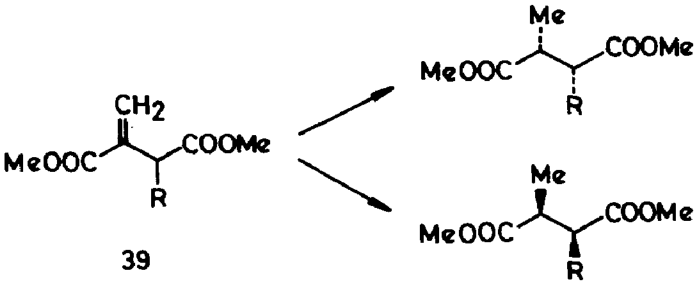


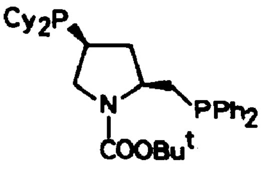
38

3-Substituted racemic itaconate esters (39, R = Me, Et, Ph, OMe) were hydrogenated in two steps to yield both enantiomers of the 3-substituted 2-methyl succinic esters (40) and (41). First, the racemic substrate was partially hydrogenated with $[Rh(dipamp)(NBD)]^+$ as catalyst to give the (S,S)-enantiomer (40) as the main product and then the remaining (kinetically resolved) substrate was hydrogenated with $[Rh(dppb)(NBD)]^{2+}$ as catalyst to produce the (R,R)-enantiomer (41) [148].



39 40 41

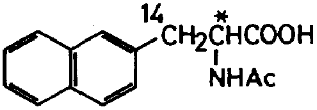
Unusually strong effects of H_2 pressure and Et_3N on the optical yields in asymmetric hydrogenation of itaconic acid catalyzed by cationic Rh(I) complexes of (42) were observed [149].



42

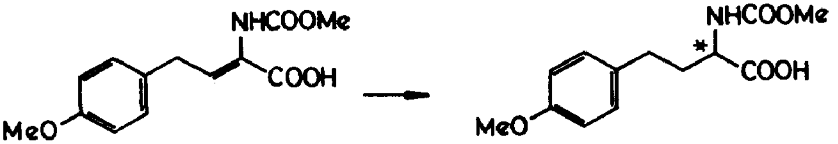
Monodehydropeptides with the dehydroamino acid fragment in the C-terminal or N-terminal position were asymmetrically hydrogenated using chiral Rh complexes as catalysts [150]. The kinetics of hydrogenation of Z-α-acetamidocinnamic acid with $[Rh(COD)L_2]$ $(O_3SC_6H_4Me\text{-}\underline{p})$ ($L_2 = Ph_2P(CH_2)_nPPh_2$, n = 2-4; or (-)-DIOP) were determined. The results support a mechanism according to which the catalyst first coordinates the olefinic substrate [151].

The unnatural labeled amino acids N-acetyl-D-(2,3-^{3}H)-3-(2-naphthyl)alanine and N-acetyl-D-(3-^{14}C)-3-(2-naphthyl)alanine were synthesized by asymmetric hydrogenation of their dehydro analogs using Rh(I) catalysts with (S,S)-BPPM as chiral ligand [152]. The ^{14}C-labeled D-alanine derivative (43) was prepared by asymmetric hydrogenation of the corresponding dehydro amino acid using the chiral catalyst Rh(I)-BPPM [153].



43

Asymmetric hydrogenation of the dehydroamino acid derivative (44) with Rh(I) phosphine catalysts was investigated using several different chiral phosphines as ligands. The highest enrichment for the (R) enantiomer of (45) was obtained with (S,S)-chiraphos, the highest enrichment for the (S) enantiomer with (R,R)-dipamp (46) [154].



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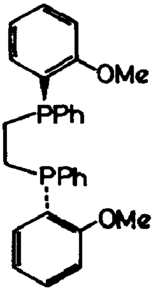
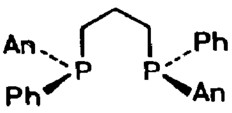


46

The new polydentate chiral phosphines (47-50, An = $\underline{o}$-anisyl) were prepared and used as ligands in homogeneous asymmetric hydrogenation with Rh(I) complexes. Ligand (47) was about as effective as dipamp in the hydrogenation of α-(acetylamino)acrylic acids [155].



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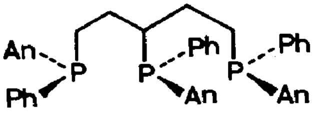

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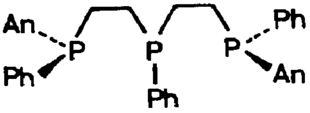

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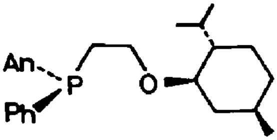
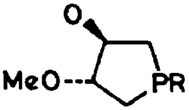
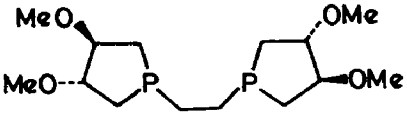


50

Rhodium(I) complexes of the chiral phospholanes (51,52) were used as catalysts for asymmetric hydrogenation of α-acetamidocinnamic acid. Highest o.y. was 17% [156].

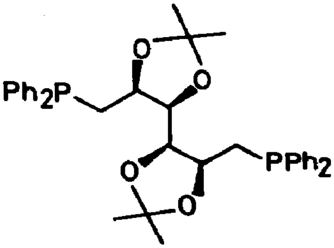




51; R = Me, CH_2Ph

52

The chiral bisphosphines (53-56) were prepared starting from mannitol and iditol. Homogeneous hydrogenation of acylated dehydroamino acids and esters using Rh(I) complexes formed in situ from $[Rh(NBD)_2]^+$ and these diphosphines furnished the corresponding amino acid derivatives with optical yields below 44% [157].



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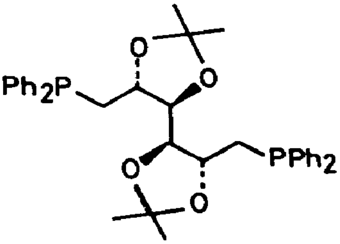

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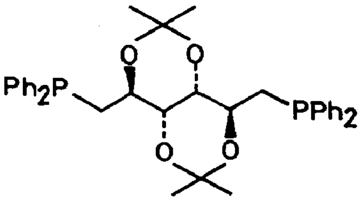

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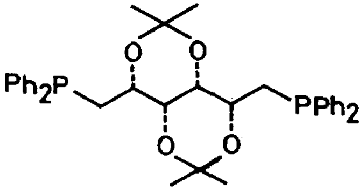
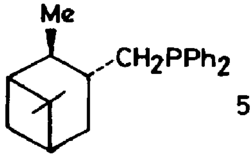


56

The new chiral monophosphines (57) and (58) were prepared and used as ligands for enantioselective hydrogenation of (Z)-α-acetamidocinnamic acid with Rh(I) complexes catalysts. Optical yields were below 30% [158].



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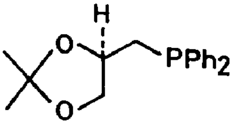
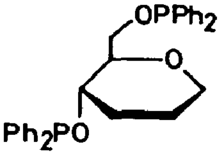


58

The two new diphenylphosphinites (59) and (60) prepared from D-glucose and D-xylose, respectively, were used in the form of their Rh(I) complexes in asymmetric hydrogenation of Z-α-acetamidocinnamic acid. The complex of (59) afforded (R)-, while the complex of (60) afforded (S)-N-α-acetylphenylalanine; best optical yield was 90% at -15°C [159].



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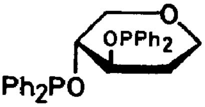
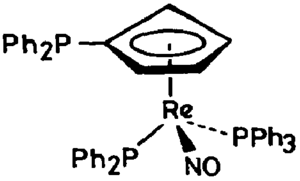


60

The unusual chiral bisphosphine (61) has been prepared and used as ligand in asymmetric hydrogenation of acetylated dehydroamino acids and their esters with Rh(I) complexes as catalysts. Optical yields ranged between 82 and 98% [160].



61

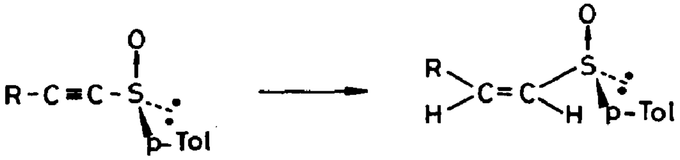
Rh(I)-phosphine complex catalysts prepared in situ from $[Rh(COD)(OOCR)]_2$ (with (+)-N-acetylphenylalanine as chiral carboxylato ligand) and different mono- and diphosphines gave catalytic systems with low enantioselectivity (optical yields 5-10%) for the hydrogenation of Z-α-acetamidocinnamic acid [161].

See also [122].

4. Hydrogenation of Dienes and Alkynes

The 1:1 complex of titanocene and tolane catalyses the hydrogenation of alkenes and alkynes to saturated hydrocarbons [162]. Canole oil was hydrogenated using mixtures of $(PhCOOMe)Cr(CO)_3$ and a heterogeneous Ni catalyst. At certain Cr:Ni ratios high reaction rates and low concentrations of trans isomers in the products were achiewed [163]. The reaction between $HMn(CO)_5$ and conjugated diolefins gives allylmanganese pentacarbonyls and - usually as minor products - monoolefins. This latter hydrogenation reaction is the predominant process with 1,3-cyclohexadiene. CIDNP effects observed suggest that radical pairs are formed as intermediates [164]. The complex $[HRu(COD)(PMe_2Ph)_3](PF_6)$ catalyzes the hydrogenation of alkenes and alkynes. The reactions are hydrogen diffusion-controlled. Addition of PMe_2Ph decreases the catalytic activity for alkene hydrogenation; in the presence of 2 moles of phosphine only hydrogenation of alkynes can be observed [165].

Performing hydrogenation of alkynes or alkenes with H_2 enriched in para hydrogen a CIDNP effect was observed with $[Rh_3Cl_2H_2(CO)_2((Ph_2PCH_2)_2PPh)_2]^+$ as catalyst although the reaction does not involve radical species as intermediates. It was shown that such an effect should be observed with para hydrogen-enriched H_2 in those cases when hydrogenation occurs via pairwise transfer of H atoms [166]. Acrylonitrile-butadiene copolymers were hydrogenated with $Rh(PPh_3)_3Cl$ as catalyst. Kinetic and spectral results were consistent with a mechanism in which the interaction of the catalyst with the C=C bond was the rate-determining step. Interaction of nitrile groups with the catalyst inhibited the reaction [167]. Olefins and polyenes were hydrogenated in an organic-water two-phase system using a catalyst prepared from $RhCl_3.3H_2O$ and triphenyl phosphine meta-trisulfonate (a ligand already industrially used for the two-phase hydroformylation of olefins). Qualitative studies suggested that the actual catalyst is not an analogue of $Rh(PPh_3)_3Cl$ but rather a colloidal dispersion of the ligand and yet unidentified Rh salts [168]. A series of supported Rh catalysts were prepared from $[Rh(COD)Cl]_2$ and styrene-divinylbenzene copolymers, functionalized with different amounts of phosphine groups, and were tested for the selective hydrogenation of dienes and acetylene. Partial hydrogenation of dienes was favored by an increase of the steric hindrance around the metal [169]. The chiral 1-alkynyl *p*-tolyl (+)-(S)-sulfoxides (62, R = C_3-C_6 n-alkyl, Me_3Si) were stereospecifically hydrogenated to the corresponding (E)-alkenyl sulfoxides (63) using $Rh(PPh_3)_3Cl$ as catalyst in benzene. Reduction with $LiAlH_4$ gave the isomeric (Z)-alkenyl sulfoxides [170].



62 63

1,4-Cyclohexadiene was selectively hydrogenated to cyclohexene using a homogeneous Ni catalyst generated from $Ni(acac)_2$, $Et_3Al_2Cl_3$, and PPh_3 in an aromatic hydrocarbon as solvent at 40°C and 1 bar [171] or with $Ni(acac)_2$ + $Al_2Et_3Cl_3$ catalysts anchored to phosphinated polystyrenes [172]. The complex $CpNiRu_3(\mu\text{-}H)_3$ catalyzes the hydrogenation of linear or cyclic dienes to monoenes. The cluster remains intact during the catalytic reaction [173]. Chelates of Pd, Rh, Ru, Co, or Ni chlorides with polyethyleneimine or polytriethyleneimine after reduction with $NaBH_4$ catalyze the hydrogenation of 1,3-pentadiene to pentane and isomeric pentenes. The reduction of these chelates with H_2 (5 bar, 85°C) also yields hydrogenation catalysts which, however, are less active [174].

Hydrogenation of unsaturated phopholipids by Pd di(sodium alizarine monosulfonate) proceeds rapidly under room conditions. The hydrogenation of polyunsaturated fatty acids gives a variety of natural and unsatural positional cis and trans isomers which are hydrogenated to saturated acids at longer reaction times [175]. Hydrogenation of 1,3-pentadiene over Pd complexes with macroporous anion exchangers gave in some cases monoolefins with 100% selectivity; n-pentane was observed only after the first step was complete [176]. The Pd(II) acetate complex of 2,2'-dipyridylmethane supported on polystyrene-divinilbenzene is an efficient catalyst for the hydrogenation of alkenes and alkynes [177].

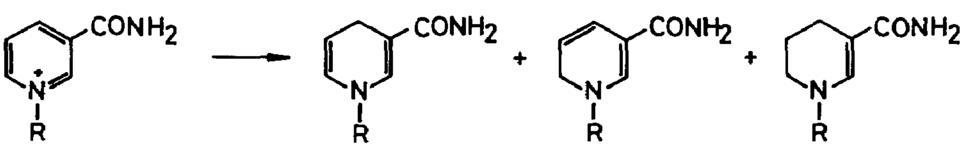
Complex catalysts prepared from H_2PtCl_6 by reacting it with aliphatic amines and then with $(iBu)_2AlH$ or Et_3Al were used to hydrogenate 1-hexene, 1,3-pentadiene and 3-heptyne to the corresponding alkanes [178].

See also [200, 204].

5. Hydrogenation of Arenes and Heterocyclic Compounds

Aniline was hydrogenated to cyclohexylamine using $Ru(OH)Cl_3$ as catalyst at 90-120°C and 20-100 bar. Cyclohexanol was also formed [179].

The catalyst system $Co(acac)_2 + Et_2Al(acac)$ was more active than $Co(acac)_2 + Et_3Al$ for the hydrogenation of benzene but less active for the hydrogenation of styrene [180]. Hydrogenation of coal-oil phenol under mild conditions with $Co(acac)_3 + Et_3Al + Al_2O_3$ catalyst gave cyclohexanol with high yields even in the presence of other aromatic compounds. The alumina support increased the activity of the catalyst [181]. Partial hydrogenation of N-substituted 3-carbamoylpyridinium salts (64; R = benzyl or iPr) was achieved by $(py)Co(dmg)_2Cl$ in MeOH at room temperature. Main products were the dihydropyridines (65) and no overreduction to tetrahydropyridines (66) was observed in the presence of $NaHCO_3$ [182].



64 65 66

The ion pair generated from $RhCl_3.3H_2O$ and Aliquat 336 in an aqueous-organic two-phase medium was shown to catalyze the hydrogenation of arenes at 30°C and atmospheric pressure under apparently homogeneous conditions. Sterically hindered benzenes yielded both cyclohexane and cyclohexene derivatives. Deuteration of arenes was found to be associated with both side-chain and ring-proton H-D exchange. Water proved to be essential for the reduction [183]. Polycyclic aromatic hydrocarbons and some of their derivatives were shown to undergo partial hydrogenation in the presence of $RhCl_3$-Aliquat 336 as catalyst. Chlorine and bromine substituents underwent hydrogenolysis when attached to the reacting moieties but remained unaffected when located on non-reacting aromatic rings [184].

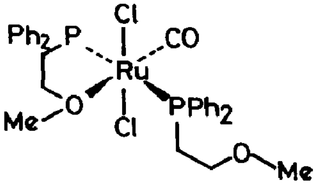
The reactivity of arenes in hydrogenation with a $Ni(acac)_2$ + $LiAlH_4$ catalyst increased in the following order: benzene < biphenyl < chrysene < naphthalene < phenanthrene < anthracene [185].

See also [198].

6. Hydrogenation of Carbonyl Compounds

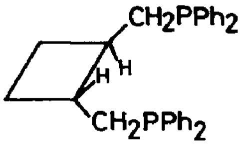
The neutral complex $H_4Ru(PPh_3)_3$ was shown to be a more active catalyst for hydrogenation of cyclohexanone to cyclohexanol and of 9-methylanthracene to its octahydro derivative than the anionic complex $[H_3Ru(PPh_3)_3]^-$ earlier described for these reactions. $H_4Ru(PPh_3)_3$ reacts with cyclohexanone also stoichiometrically to yield cyclohexanol and $H_2Ru(PPh_3)_3$; latter complex reacts with H_2 to regenerate the tetrahydride thus closing the catalytic cycle [186]. Hydrogenation of benzophenone using polyhydride complexes of tris(triphenylphosphine)ruthenium as catalyst has been studied. Six stoichiometric reactions were found to constitute a complex set of interconnected catalytic cycles; transformation of Ph_2CO into Ph_2CHOH takes place simultaneously over three different pathways

[187]. Asymmetric hydrogenation of β-keto carboxylic esters to β-hydroxy esters was carried out using Ru(BINAP)X_2 complexes (X = Cl,Br,I) as catalysts at 25°C and 100 bar in MeOH solution. Optical yields were in the range of 95-99% [188]. The Ru(II) complex (67) catalyzes the hydrogenation of acetaldehyde to ethanol at 150°C and 44 bar in toluene solution [189].



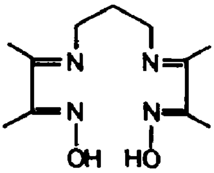
67

α,β-Unsaturated ketones have been hydrogenated to saturated ketones using $Ru_2(DIOP)_3Cl_4$ or $HRuL_2Cl$ (L = 68) as catalysts at 50-80°C and 4-40 bar. Reasonable optical yields were achieved with cyclic ketones; the best value was 62% [190].



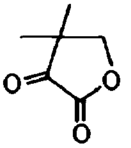
68

The rate of hydrogenation of benzil catalyzed by the (L)Co(dmg)$_2$ + quinine system was increased by increasing the basicity of the axial ligand L and by increasing H_2 pressure without affecting enantioselectivity. Chirality at Co (induced by substituting one Me group of the dmgH ligand by a Ph group) did not affect optical selectivity [191]. Benzil was hydrogenated with $[Co(LH)]^+$ (LH_2 = 69) as catalyst in water/n-propanol mixtures at different pH values. In the presence of py the rate of hydrogenation decreased with increasing pH which was attributed to the deprotonation of $[HCo(LH)(py)]^+$, an intermediate of the catalytic cycle [192]. If no py was present rate of hydrogenation increased with increasing pH probably because of the coordination of OH^- as axial ligand to $[HCo(LH)]^+$ [193].



69

Optical yields and reaction rates achieved in the asymmetric hydrogenation of ketopantolactone (70) using $[Rh(COD)Cl]_2$ and the bisphosphines (71) support the conclusion that the CH_2PR_3 group in position C2 is mainly responsible for the optical yield while the PR'_2 group in position C4 mainly influences the rate of hydrogenation [194].



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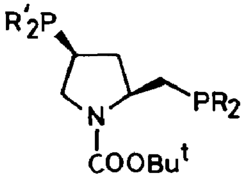


71

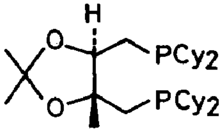
a) R = Ph, R' = Cy (= 42)

b) R,R' = Ph (= 6; BPPM)

c) R = Cy, R' = Ph

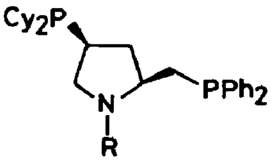
d) R,R' = Cy

The chiral bisphosphine (72) was also tested in the Rh(I) complex-catalyzed asymmetric hydrogenation of ketopantolactone (70). Both rate and o.y. were higher (72%) than in the case of DIOP [195].



72

The new chiral pyrrolidinebisphosphines (73) were synthesized and used as ligands in asymmetric hydrogenation of the α-keto ester MeCOCOOMe and the α-keto acetal $MeCOCH(OMe)_2$ with Rh(I) complexes as catalysts. Best optical yields were achieved with ligand (73a) in the case of the keto ester (87%) and with ligand (73d) in the case of the keto acetal (75%) [196].



73

R	R	
a) CONHMe	d) COOMe	
b) $CONHBu^t$	e) $COOBu^t$	(= 42)
c) CONHPh	f) COOPh	

The complexes [Ir(trans-CH_3CH=CHCHO)(CO)$(PPh_3)_2$]ClO_4 and Ir(ClO_4)(CO)$(PPh_3)_2$ catalyze the hydrogenation of trans-CH_3CH=CHCHO and CH_2=CHCHO, respectively, to the corresponding saturated aldehydes. The analogous complex containing the ligand trans-C_6H_5CH=CHCHO is, however, inactive [197].

See also [89, 96, 204].

7. Hydrogenation of Nitro Compounds

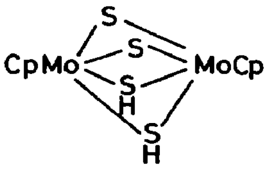
The ion pair formed from aqueous $RhCl_3$ and Aliquat 336 catalyzes the selective hydrogenation of olefinic C=C bonds of unsaturated aromatic or aliphatic nitro compounds in a two liquid phase system at 30°C. Nitrobenzene gives, under these conditions, a mixture of aniline and nitrocyclohexane [198]. The binuclear Rh(I) complex [$Rh_2Cl_2(COD)_2$(phenazine)] catalyzes the hydrogenation of alkenes and aromatic nitro compounds in the presence of $NaBH_4$ in DMF [199].

Conjugated double bonds and nitro groups were hydrogenated in benzene solution with trans-[$(PhCH_2CN)_2PdCl_2$] as catalyst [200]. Hydrogenation of aromatic and aliphatic nitro compounds was studied using trans-$Pd_2L_2X_2$ and trans-PdLL'Cl complexes as catalysts (LH = 2-benzoylpyridine, 2-benzylpyridine, $PhCH_2NMe_2$; L' = py, 2-picoline, 3,3-lutidine, PPh_3; X = OAc, Cl). Hydrogenation was best performed in DMF [201]. Palladium complexes supported on quaternary ammonium group-containing polystyrene resin showed good activity and selectivity in the hydrogenation of nitrobenzene. Activity of the catalysts decreased in the following order of Pd complexes: $PdCl_4^{2-} > PdBr_4^{2-} > PdI_4^{2-}$ [202]. Palladium complexes of poly ω-diphenylphosphinoalkylsiloxanes were prepared and used as catalysts for the hydrogenation of olefins and nitrobenzene [203]. The Pd(II) and Pt(II) complexes of azobenzene were used as catalysts for the hydrogenation of nitroaromatics, alkenes, alkynes, and aromatic carbonyl compounds in DMF solution. Anilines (im some cases phenylhydroxylamines), alkanes and alcohols were the products. The actual catalytic species was probably a hydrazo complex containing a metal-carbon bond [204].

See also [89].

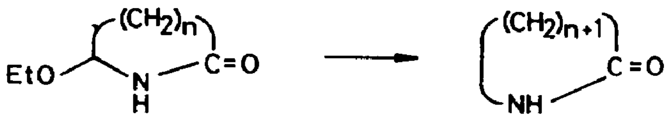
8. Miscellaneous Hydrogenations

Complex (74) catalyzes the hydrogenation of methyl bromoacetate to methyl acetate under room conditions. Turnover numbers are, however, very low (2.5-4) [205].



74

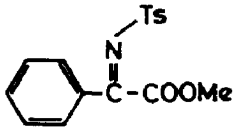
Alkoxy-substituted cyclic amides (75) are hydrogenolyzed under hydroformylation conditions with $Co_2(CO)_8$ as catalyst to the corresponding unsubstituted amides (76) [206].



75

76

The C=N double bond in (77) and analogous compounds was hydrogenated stoichiometrically using Na[Co(dmg)(py)], or catalytically with H_2 in the presence of the glyoximato Co complexes (78) and quininium salts. In the latter case enantioselectivity was observed and optical yields ranged between 5 and 20% [207].



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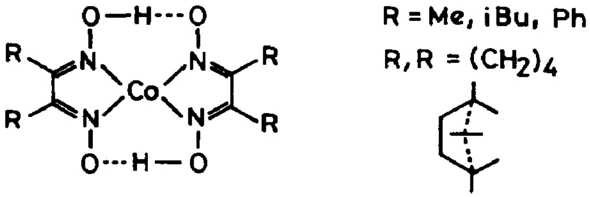


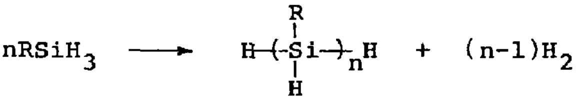
78

Imines were hydrogenated at room temperature and 1 bar H_2 using $Rh(PPh_3)_3Cl$ or $[Rh(PPh_3)_2(diene)]PF_6$ complexes as catalysts in alcohols as solvents. A water-Et_2O phase-transfer system was used in the case of a solid imine [208].

See also [70, 184].

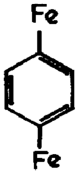
9. Dehydrogenation

Dehydrogenative coupling of primary organosilanes is catalyzed by Cp_2TiMe_2:

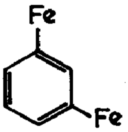


$$n\mathrm{RSiH_3} \longrightarrow \mathrm{H}\!\left(\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{-Si-}}}\right)_n\mathrm{H} + (n-1)\mathrm{H_2}$$

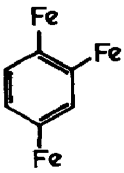
If the reaction is carried out in the presence of an olefin, evolution of H_2 is suppressed and hydrogenation of the olefin takes place. The complex $Cp_2Ti(\mu\text{-}H)(\mu\text{-}HSiHPh)TiCp_2$ (which is an intermediate in the reaction if R = Ph) is a good catalyst for the hydrogenation of olefins with H_2 [209]. The ferrocenylbenzenes (79) act as photocatalysts for the evolution of H_2 from MeOH in the presence of methyl viologen (MV^{2+}), triethanolamine, and colloidal Pt under irradiation with visible light. The highest quantum yield of the formation of MV^{+} was obtained at 480 nm where the intensity of solar light is largest [210].



79 a



79 b



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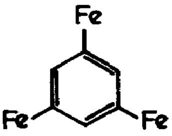
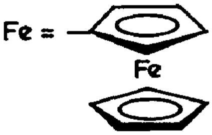


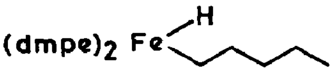
79 d



Irradiation of the complex (80) in dilute pentane solution at -30°C produced 1-pentene and the complexes (81), (82), and (83) [211].

$(\mathrm{dmpe})_2\mathrm{FeH_2}$

80



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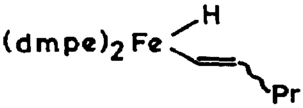
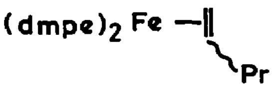


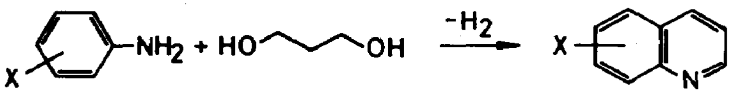
82, Z and E



83

Catalytic activity of iron cyano complexes such as $K_4[Fe(CN)_6]$, $K_4[Fe(CN)_5(Gly)]$, and $K_4[Fe(CN)_5(triGly)]$ in the dehydrogenation of NADH and ascorbic acid coupled with reduction of methylene blue was observed. The activities of these complexes of evolutionary importance increased in the stated order [212].

A homogeneous catalyst for the dehydrogenation of methanol was developed based on $Ru_2(OAc)_4Cl$ and PPh_3. Hydrogen evolution proceeded smoothly at MeOH reflux temperature without irradiation; the primary product was CH_2O which transformed gradually into $HCOOCH_3$ [213]. Primary alcohols undergo dehydrogenation followed by condensation to give esters and H_2 upon treatment with $H_2Ru(PPh_3)_4$ as catalyst at 180°C; similarly, 1,4- and 1,5-diols can be converted into the corresponding γ- and δ-lactones. This principle can be extended to ester formation from alcohols and aldehydes. All these transformations are even more effective in the presence of some H acceptor like acetone. Aldehydes can be transformed into carboxylic acids by this method if water and a H acceptor are present [214]. Quinolines (84) and indole derivatives (85) were prepared from anilines and 1,3-propanediol or glycols, respectively, by dehydrocyclization in the presence of $RuCl_3.nH_2O + PBu_3$ or $Ru(PPh_3)_3Cl_2$ as catalysts. N,N-Diarylpropylenediamines and N,N-diarylethylene diamines and their dehydrogenated imine derivatives were postulated as intermediates. The reactions proceeded at 180° with spontaneous H_2 evolution [215].



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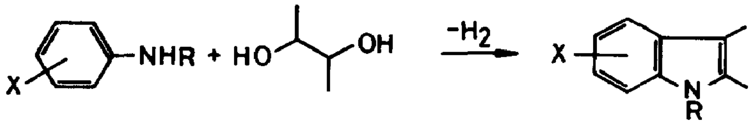


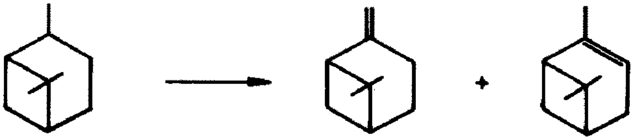
85

Dehydrogenation of aliphatic alcohols is catalyzed by $[Rh(bpy)_2]Cl$ in the presence of water and NaOH at 120°C. The reaction has been studied primarily with EtOH; besides H_2, acetaldehyde (and its condensation products), methane and CO_2 were formed. Latter products suggest that - at least in part - the following reaction takes place [216]:

$$C_2H_5OH + H_2O \longrightarrow CH_4 + 2H_2 + CO_2$$

The photocatalytic system composed of acetone and cis-[RhCl(CO)(dppm)]$_2$ was found to be quite effective for the production of H_2 from iPrOH. Pinacol was formed as byproduct and the selectivity of the reaction depended on the wavelength of irradiation [217]. Photocatalytic dehydrogenation of iPrOH is catalyzed also by trans-Rh(CO)(PPh$_3$)$_2$Cl; probably the unsaturated complex Rh(PPh$_3$)$_2$Cl is the catalytically active species [218]. Arenes were dehydrogenated to biphenyls at room temperature under irradiation in the presence of Rh(CO)(PMe$_3$)$_2$Cl. In the case of toluene the mixture of bitolyls formed contained the o,p'-isomer as the main product which suggests the existence of radical intermediates [219].

Secondary alcohols could be dehydrogenated to the corresponding ketones at 100°C under N_2 by refluxing in hexamethyldisiloxane in the presence of $H_5Ir(PPr^i_3)_2$ as catalyst. No H acceptor was necessary and H_2 was evolved; turnover numbers reached 150 [220]. Linear and cyclic alkanes can be selectively dehydrogenated to the corresponding alkenes with $H_2Ir(\eta^2\text{-OOCCF}_3)(PR_3)_2$ (R = CF_3, cy) both thermally (in the presence of the sacrificial H acceptor tBuCH=CH$_2$) or photochemically (when no H acceptor is required and H_2 is evolved). A key feature of the catalyst is that the chelating acetate group can open up to allow β-elimination to take place in the alkyl hydride intermediate [221]. The stoichiometric dehydrogenation of cycloalkanes to arenes by $[IrH_2(Me_2CO)(PPh_3)_2]^+$ with tBuCH=CH$_2$ as hydrogen acceptor could be improved by using the SbF_6 salt of the Ir complex in the substrate alkane as solvent. In this way, cyclohexane could be dehydrogenated to benzene and alkylcyclopentanes to the corresponding alkylcyclopentadiene complexes of Ir [223]. Pinane was converted to β-pinene (86) with high (> 95%) selectivity using tBuCH=CH$_2$ as H acceptor and $H_5Ir(PPr^i_3)_2$ as catalyst. Catalytic turnover number was about 10 [224].



86

Oxazolines (87, R = Ph, 2-furyl, 2-thienyl) were dehydrogenated to oxazoles (88) by treating with Ni peroxide in benzene at reflux [225].

87 88

The reactions of gas-phase Ni_1^+-Ni_{10}^+, Pd_1^+-Pd_4^+, and Pt_1^+, Pt_2^+ ions with n-butane have been investigated. Dehydrogenation reactions were the main processes, the dehydrogenating activity increasing in the order Ni < Pd < Pt [226].

10. Hydrogen Transfer Reactions

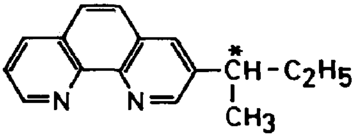
a) Hydrogenation of C=C Bonds

The complexes $Ru_4(CO)_{12}(C_6H_6O)$ and $Ru_3(CO)_{10}(C_6H_8O)$ have been obtained from the reaction of $Ru_3(CO)_{12}$ and cyclohex-1-ene-2-one; both complexes were found to be active catalysts for the transfer hydrogenation of cyclohex-1-ene-2-one to cyclohexanol by iPrOH [227]. Transfer hydrogenation of tert-butylethylene by iPrOH is efficiently catalyzed by $H_5Ir(PPr^i_3)_2$ at 30°C. The reaction shows autocatalytic behavior but the induction period can be eliminated by addition of acetone [228]. Hydrogen transfer from MeOH to the product was observed during dimerization of butadiene to octatrienes with Ni(O) complexes (formed from $Ni(acac)_2$, BuLi, and $(Me_2N)_3P$) as catalysts [229].

b) Hydrogen Transfer Reactions Involving >C=O and >CH-OH Groups

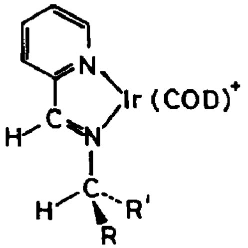
Oppenauer oxidation of secondary alcohols is efficiently catalyzed by SmI_2 at room temperature; the catalytic species is probably a diiodo-samarium aldolate generated in situ [230]. Lanthanide tri-2-propoxides, $Ln(OPr^i)_3$ (Ln = Nd,Eu,Gd,Dy,Er,Tm,Yb), are very efficient catalysts for the Meerwein-Ponndorf reduction of carbonyl compounds. The catalytic activity of $Gd(OPr^i)_3$ is about 1000 times as high as that of $Al(OPr^i)_3$ [231]. The Zr(IV) complexes Cp_2ZrH_2 and $Cp_2Zr(OPr^i)_2$ catalyze the Oppenauer-type oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds in the presence of an appropriate H acceptor such as benzaldehyde or cyclohexanone.

This hydrogen transfer proceeds in refluxing toluene and furnishes the desired enones in preparatively useful (> 80%) yields [232]. Hydrogen transfer from cyclohexanol to hexanal is catalyzed by heterogenized Ru(II) complexes bound to polycarboxylate matrices. Highest activity was obtained using terpolymers prepared from methyl methacrylate, butanediol diacrylate and bis(acrylato)bis (triphenylphosphine)Ru(II) complexes [233]. Kinetics and mechanism of oxidation of alcohols by hydrogen transfer to cyclohexanone, catalyzed by $HRh(PPh_3)_4$, were studied. Deuterium isotope studies indicated concerted hydrogen transfer as the rate limiting step [234]. The catalyst formed _in situ_ from $[Rh(COD)Cl]_2$ and (+)-(S)-(89) promotes the asymmetric transfer hydrogenation of acetophenone in iPrOH solution at reflux temperature; optical yields up to 31% were obtained [235].



89

Alkyl phenyl ketones were reduced by asymmetric hydrogen transfer from iPrOH using Ir(I) complexes with chiral bidentate Schiff bases (90) as catalysts. Small amounts of KOH were necessary to obtain the catalytically active species; best optical yields were around 50% [236].



90

R = H,Me,Et,CH_2Ph

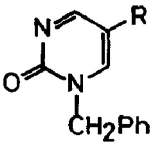
R' = H,Et,Ph, α-$C_{10}H_7$

Catalysts formed _in situ_ from $[Ir(COD)(OMe)]_2$ and different alkyl or aryl phosphines were used for the transfer hydrogenation of cinnamic aldehyde to cinnamyl alcohol with iPrOH as hydrogen source. Selectivity of the systems was very high, usually in the range between 90-100% [237].

See also [227].

c) Hydrogenation of C=N Bonds

The Meerwein-Ponndorf reduction of pyrimidin-2(1H)-ones (91; R = H,F,Cl,Br,I) using $Zr(OPr^{i})_4$ gave exclusively the 3,4-dihydro product (92) [238].



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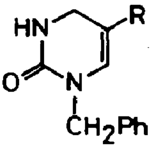


92

Transfer hydrogenation of benzylideneaniline by iPrOH is catalyzed by $Ru_3(CO)_{12}$ at reflux temperature. The trinuclear cluster $(\mu\text{-H})Ru_3(CO)_9)(\mu_3\text{-PhNCPh})$ has now been isolated from the reaction mixture and found to be catalytically active in the same reaction [239].

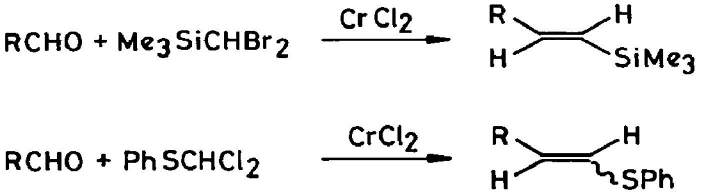
11. Reduction without Molecular Hydrogen

a) Stoichiometric Reduction with Low-Valent Transition Metal Complexes

Deoxygenation of epoxides to olefins was achieved by SmI_2 in THF-HMPA in the presence of N,N-dimethylaminoethanol or glutaric anhydride [240]. α,β-Epoxy esters were reduced at room temperature to β-hydroxy esters with retention of the configuration at the β-carbon atom using a SmI_2 + THF + HMPA system in the presence of N,N-dimethylaminoethanol. The same reagent was succesfully applied also for the synthesis of vinilogous (unsaturated) δ-hydroxy esters [241]. The reduction of organic halides by SmI_2 in THF to the corresponding alkanes was found to be effectively promoted by the addition of HMPA. Usually yields above 95% could achieved in this way, even in the case of chlorides [242].

Olefinic double bonds conjugated with aromatic rings could be reduced by PhYbI or Yb metal in MeOH. Isolated double bonds or aromatic systems were not affected under these conditions [243]. Performing the reduction in the presence of MeOD the deuterated reaction product was formed [244].

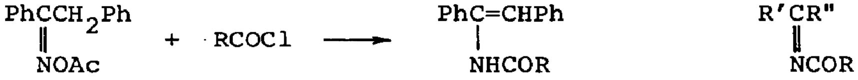
A Ti(O)-slurry prepared from $TiCl_4$ in THF with Mg or $LiAlH_4$ was used for the deoxygenation of unfunctionalized aromatic N-oxides; the parent heterocycles were formed in good yields [245]. The reduction of α-acetylenic ketones to the corresponding trans olefinic products was achieved with Cr(II) reagents; the yields ranged between 40-84% [246]. (E)-Alkenylsilanes (93) were obtained by reducing a mixture of aldehydes and $Me_3SiCHBr_2$ with $CrCl_2$ in THF. A combination of $CrCl_3$ and $LiAlH_4$ could be also employed as reductant. Reductive transformation of aldehydes into phenyl 1-alkenyl sulfides (94; E/Z-mixture) was also achieved by the same method [247].



93

94

Reductive acylation of O-acetylated oximes having activated hydrogens in α-position (e.g. 95) with $Fe_3(CO)_{12}$, acyl chlorides and Et_3N gave enamides (96) in good yield. If the oxime derivative contained no active hydrogen, N-acylimino compounds (97) were formed [248].



$$\underset{NOAc}{\overset{\|}{PhCCH_2Ph}} + RCOCl \longrightarrow \underset{NHCOR}{\overset{|}{PhC{=}CHPh}} \qquad \underset{NCOR}{\overset{\|}{R'CR''}}$$

95 96 97

A kinetic investigation of the stoichiometric hydrogenation of acetone to iPrOH by $[Ru(bpy)_2(CO)H]^+$ in buffered aqueous solutions has been carried out:

$$[Ru(bpy)_2(CO)H]^+ + (CH_3)_2CO \xrightarrow{H^+/H_2O} [Ru(bpy)_2(CO)(H_2O)]^{2+} + (CH_3)_2CHOH$$

The kinetic data support a mechanism involving general acid catalysis [249]. Low valent Co species, prepared in situ in THF by the reaction of $CoCl_2$ with $NaBH_4$/EtOH under CO, isomerize and reduce olefins; the extent of these reactions strongly depends on minor changes in the experimental procedure [250].

Reduction of the enol phosphate moiety in phosphonates of type (98) was achieved with an excess of lithium dibutylcuprate in THF at -78°C with good yields. The reaction occured selectively and with complete retention of configuration [251].

98

Methanol and/or MeI were reduced in aqueous NaOH to methane by Cu(I) complexes formed from Cu_2O and phenanthroline; yield of methane was $\leqslant 6\%$ [252].

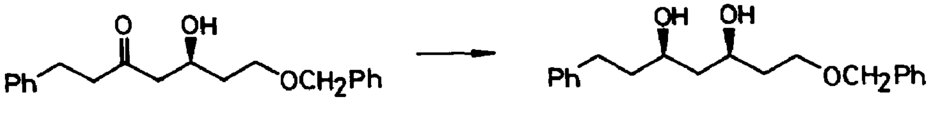
b) Inorganic Reductants in the Presence of Transition Metal Complexes as Catalysts

Several organolanthanide complexes catalyze the reduction of 1-hexene with NaH: Cp_3Ln (Ln = La,Pr,Nd,Sm,Tb,Y,Er,Yb, and Lu), L_2YCl (L = Cp or substituted Cp), and L'_2LnX (L'_2 = $C_5H_4CH_2CH_2O$ $CH_2CH_2C_5H_4$; L_n = La,Dy,Er,Y,Lu; X = Cl,tBu,$tBuCH_2$,Ph,MeC_6H_4, CF_3COO). The complex L'_2YCl also catalyses the hydrogenation of 1-hexene by H_2 in THF at 45°C [253].

Reaction of alkyl and aryl cyanides with iPrMgBr in the presence of Cp_2TiCl_2 followed by acid hydrolysis gave the corresponding aldehydes. A titanium hydride was proposed as the reductant in the process [254]. The C=C double bond of enedicarboxylate compounds like (99) could be reduced with $TiCl_4$ + $LiAlH_4$ + Et_3N in THF. Other double bonds did not react [255].

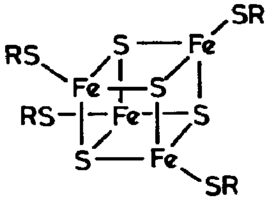
99

The β-hydroxy ketone (100) was reduced to diol (101) with $NaBH_4$ in the presence of $Ti(OPr^i)_4$ at -78°C. A syn-anti ratio of 87:13 could be achieved [256].



100 101

Reductive dehalogenation of α-halo ketones and esters was effectively achieved (yields 95-100%) using $PhSiH_3$ and catalytic amounts of $Mo(CO)_6$ and PPh_3. In the absence of PPh_3, the method was not catalytic with respect to $Mo(CO)_6$ and required 20-50 mole % of the metal carbonyl. A less efficient system comprised of $Pd(PPh_3)_4$ and Ph_2SiH_2 was also tested [257]. The Fe-S cluster (102) in cetyltrimethylammonium bromide micelles catalyzed the reduction of acridine derivatives (103) by dithionite; the reduction proceeded without side reactions and the reduction products could be reoxidized to the starting materials by anthraquinone-1,5-disulphonate [258].



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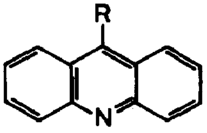

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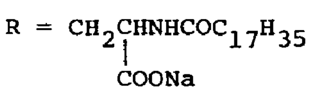
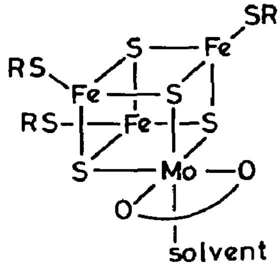


$$R = \underset{\displaystyle COONa}{CH_2CH}NHCOC_{17}H_{35}$$

R = $NHCOBu^t$, NHCOCy, $NHC_{12}H_{25}$

n-Pentyl azide was reduced by $Na_2S_2O_4$ in an aqueous Triton X-100 micellar solution containing methylviologen and the iron cubane clusters (104) and (105). Reduction products were $n\text{-}C_5H_{11}NH_2$, N_2, N_2H_4, and NH_3 if (104) was used as catalyst, while (105) catalyzed only the formation of $n\text{-}C_5H_{11}NH_2$ and N_2 [259].



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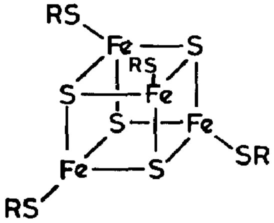
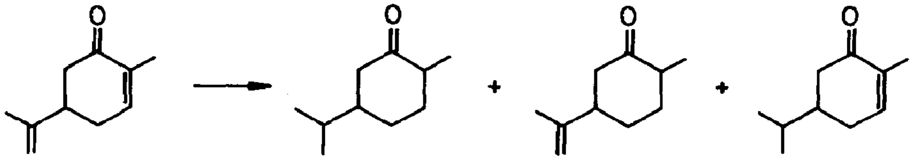


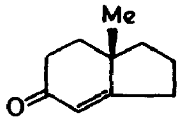
105; R = nC_8H_{17}


Tolan was reduced to stilbene with $NaBH_4$ using $Rh-PPh_3$ complexes as catalysts. With $Rh(CO)(PPh_3)_2Cl$ mainly cis-, whereas with $HRh(PPh_3)_4$ mainly trans-stilbene was formed [260]. Aldehydes could be selectively reduced to alcohols in the presence of ketones with a combination of Me_3SiCl and Ni boride (prepared in situ from Ni^{2+} and $NaBH_4$) in DMF or diglyme as solvent [261]. The system Zn + $NiCl_2$ (9:1) has been applied for the reduction of α, β-unsaturated carbonyl compounds at the C=C double bond. The rate of reduction was significantly increased by ultrasound [262]. Both C=C bonds of carvone (106) were reduced under such conditions, buth the reaction could be made selective by changing the reaction conditions: in the presence of amines dihydrocarvone (107) was the main product whereas with a Zn + $NiCl_2$ (1:1) reductive system primarily carvotanacetone (108) was formed [263].



106 107 108

Hydrindenone (109) was reduced by $HAl(iBu)_2$ in HMPA to the hydrindanones (110) and (111) in the presence of MeCu. The ratio of the cis and trans products depended on the amount of MeCu used [264].



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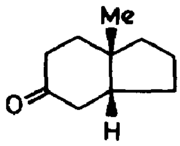

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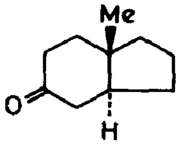


111

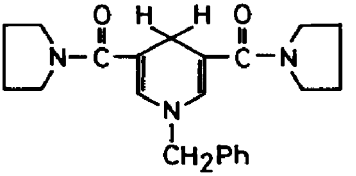
See also [207].

c) Organic Reductants in the Presence of Transition Metal Complexes as Catalysts

The clusters $[Fe_4S_4(SR)_4]^{2-}$ catalyze the reduction of nitro compounds, quinones, and N-oxide compounds to amines, hydroquinones, and deoxygenated compounds, respectively, in the presence of thiols in MeCN solution. The reactions proceed via one-electron transfer [265]. Nitrobenzene and m-dinitrobenzene are reduced to aniline and m-nitroaniline, respectively, by tBuSH in MeCN in the presence of $[Fe_4S_4(SPh)_4]^{2-}$. The thiol is oxidized to $PhSSBu^t$ and the cluster is transformed into the isomeric $[Fe_4S_4(SBu^t)_4]^{2-}$; following this the tBu-cluster is the effective catalyst and H-transfer takes place according the following stoichiometry [266]:

$$6\ tBuSH + ArNO_2 \longrightarrow 3\ tBuSSBu^t + ArNH_2 + 2H_2O$$

Acetylenic carbinols were deoxygenated in 35-85% yields by reduction of their $Co_2(CO)_6$ complexes with $BH_3 + Me_2S + CF_3COOH$ [267]. Reduction of substituted nitrosobenzenes by the NADH-model compound (112) is catalyzed by bivalent metal ions (Ni, Zn, Co, Fe, Mn, Mg, Ca). It was found that the metal ions form a complex with (112) according to a Michaelis-Menten saturation kinetics and promote hydride transfer to the substrate [268].

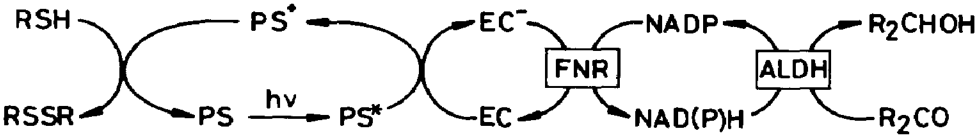

112

Preparation of 1-alkenes by the hydrogenolysis of terminal allylic carbonates and acetates with formates in the presence of Pd complexes has been described. Formic acid + Et_3N was a suitable reductant and $Pd_2L_3(CHCl_3) + PBu_3$ (L = dibenzylideneacetone) the best catalyst [269].

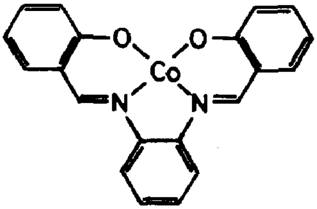
d) Electroreduction and Photoreduction

Secondary trichloromethyl carbinols and their ethers could be reduced by chemically- or electrochemically-generated $CrCl_2$ to form (Z)-monochlorovinyl compounds in one step. Tertiary carbinols favored the formation of dichlorovinyl compounds [270]. Water-soluble substrates like methylviologen were reduced by the nineteen-electron complexes $Cp\dot{F}e(CO)_2(PR_3)$ generated photochemically from $[CpFe(CO)_2]_2$ and PR_3 in the benzene phase of micellar or reverse micellar solutions [271].

Photohydrogenation of phenylacetylene and methylphenylacetylene was accomplished in cyclohexane/water using $(bpy)_3Ru^{2+}$ as photosensitizer, alkylviologens as charge relays, Na_2EDTA as sacrificial electron donor and a Pt or Pd colloid stabilized in the organic phase as hydrogenation catalyst [272]. Photoinduced reduction of ketones to alcohols by 2-mercaptoethanol which is transformed into the corresponding disulfide was performed in the following system: $[Ru(bpy)_3]^{2+}$ as photosensitizer (PS), methylviologen (or other bipyridinium salts) as electron carrier (EC), ferredoxin-NADP reductase (FNR) to reduce NADP, and alcohol dehydrogenase (ALDH) to reduce the ketone with the aid of NAD(P)H. The whole catalytic cycle is shown schematically below [273]:



Electrocatalytic reduction of benzyl chloride was performed at controlled potential in the presence of Co(saloph) (113) as catalyst. Only poor yields were achieved [274].



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Homogeneous catalytic electrochemical reduction of trans-1,2-dibromocyclohexane was investigated with several transition metal octaethylporphyrin complexes. The metalloporphyrins fell into two categories: Zn(OEP) and Cu(OEP) behaved as redox catalysts like polycyclic aromatic compounds whereas Ni, Fe, and Co(OEP) complexes gave rise to a catalysis which was several orders of magnitude more efficient [275].

IV. Oxidation

1) Catalytic Oxidation of Hydrocarbons or Hydrocarbon Groups with O_2

a) Oxidation of Alkanes

Kinetic results for the oxidation of pentadecane in the presence of $Ce(st)_3$, $Ni(st)_2$, and $Cr(st)_3$ catalysts were described [276]. Catalytic oxidation of pentadecane with O_2 to carboxylic acids was performed in two steps: first, ketones were obtained by using Cr or Ni stearates as catalysts; in the second step these ketones were transformed into carboxylic acids with $Mn(st)_2$ as catalyst [277].

Oxidation of cyclohexane to cyclohexanol and cyclohexanone by O_2 in the presence of (TPP)(imidazole)Fe(III)Cl and similar axial coordinated complexes of iron(III) porphyrins has been studied. These catalysts were found to be more active than hemin [278].

Hydrocarbons were hydroxylated by O_2 with (TPP)FeCl as catalyst, methylviologen as mediator, zinc amalgam as reducing agent and Ac_2O as acetylating agent. Probably $[(TPP)FeO]^+$ is the active species hydroxylating the C-H bond in a non-radical fashion. The system models native cytochrome P-450 [279]. The catalyst system composed of iron, Zn, AcOH, and py for the selective oxidation of saturated hydrocarbons with O_2 has been studied. Pyridine was found to be a unique solvent and could not be replaced by pyridine derivatives [280]. Cyclohexane was oxidized with O_2 using $Co(acac)_3$ fixed on silica as catalyst [281]. Oxidation of succinic acid by an oxygen-containing Co L-histidine complex was investigated; the substrate reacted in the form of its monoanion [282].

See also [302, 366].

b) Oxidation of Olefins

Based on kinetic measurements a mechanism was proposed for the oxidation of cyclohexene by O_2 catalyzed by a laminated $MoCl_5$-graphite compound [283].

Oxidation of isoprene to $Me_2C=CHCH_2OH$ and of $PrMeC=CH_2$ to $PrCMe_2OH$ by O_2 is catalyzed by a TPP complex of Mn(II) [284]. Kinetic results for the oxidation of olefins with O_2 in the presence of Mn porphyrin catalysts indicate that a ternary olefin-catalyst-O_2 complex is an intermediate of the reaction. In the case of cholesterol the rate-determining step in forming this intermediate is the reaction of O_2 with the catalyst, in the case of 1-hexene it is the coordination of the olefin to Mn [285].

Cyclohexene was oxidized with O_2 using $(L)FeO_2$ as catalyst (LH_2 = tetra-o-pivaloylphenylporphyrin). The catalytically active complex was prepared from (L)FeBr and KO_2 [286]. Oxidation of methyl linoleate micelles in aqueous dispersion by O_2 induced by iron salts and ascorbic acid have been studied. It was suggested that the initiating radicals were generated by the decomposition of hydroperoxides by Fe^{2+} and that ascorbic acid functioned as a reducing agent for the transformation of Fe^{3+} to the more reactive Fe^{2+} [287]. Oxidation of cyclohexene with O_2 is catalyzed by $[Ru(bpy)_2(PPh_3)(H_2O)]^{2+}$ in dry o-dichlorobenzene under room conditions. Reaction products are 2-cyclohexene-1-one, 2-cyclohexene-1-ol and (in minor amounts) cyclohexene oxide [288].

Co(II) fixed on a polyethylene-acrylic acid graft copolymer catalyzed the oxidation of cyclohexene by participating in chain initiation and decomposition to radicals [289]. Oxidation of octene-1 to octanone-2 by O_2 was achieved with two catalytic systems containing the heteropolyacids $H_{3+n}[PMo_{12-n}V_nO_{40}]$ (HPA). Either chlororhodium(III) complexes were used with HPA in alcoholic solvents at 60°C, or $PdSO_4$ with HPA in water-THF solvent mixtures at 20°C. With Rh catalysts the solvent was partly oxidized to aldehydes, esters and acetals [290].

Oxidation of cyclohexene to cyclohexanone with O_2 and $PdCl_2 + CuCl_2.2H_2O$ or $PdCl_2 + FeCl_3.3H_2O$ as catalyst has been investigated in different alcohols as solvents. Best results were achieved with $CuCl_2.2H_2O$ as cocatalyst and EtOH as solvent. If oxidation was carried out for longer times further oxidation to 2-cyclohexene-1-one and 3-ethoxy-2-cyclohexene-1-one was observed [291]. In the case of cyclopentene best yields of cyclopentanone were obtained at atmospheric pressure with $PdCl_2 + FeCl_3.6H_2O$, and under increased pressures of oxygen with the $PdCl_2 + CuCl_2.2H_2O$

catalyst system [292]. Oxidation of 1-octene to 2-octanone in a flow-type reactor using a $PdCl_2$ + $CuCl_2$ + HCl catalyst solution in aqueous $MeOCH_2CH_2OH$ gave significant amounts of chlorooctanes as byproducts. This could be avoided by using $PdSO_4$ + $H_{n+3}PMo_{12-n}V_nO_{40}$ (n = 6, 8) but this latter catalyst deactivated rather rapidly [293]. Linear-chain C_8-C_{10} terminal olefins could be oxidized to methyl ketones in high yields at 60-80°C in an aqueous-organic two phase system using $PdCl_2$ and cyclodextrins as catalyst. This catalyst system showed high substrate selectivity; yields were much lower in the case of C_{12}-C_{14} olefins [294]. Oxidation of terminal olefins with O_2 by a catalyst system consisting of acetone monoxime, CuCl, and $PdCl_2$ in anhydrous acetone gives the corresponding methyl ketones. Although the catalyst system is similar to that employed in the Wacker process, the mechanism of this oxidation is fundamentally different because if the reaction is performed in acetone containing $^{18}H_2O$ practically no ^{18}O is incorporated into the ketone [295]. The one-step synthesis of ethylene glycol monoacetate and diacetate from ethene, O_2, and AcOH using the $PdCl_2$-$CuCl_2$-$Cu(OAc)_2$ catalytic system was studied. An overall yield of 95% was achieved [296]. Reaction of 1,3-cyclohexadiene with O_2 in a biphasic system of hexane and acetic acid in the presence of LiOAc and catalytic amounts of $Pd(OAc)_2$, hydroquinone and Co(salen) results in a selective oxidation to yield (114) (highest yield 47%). This reaction consists of three different catalytic cycles: O_2 oxidizes hydroquinone to quinone (the Co complex acts as a catalyst), Pd(II) oxidizes the diene (and is reduced to an unidentified Pd(0) complex) and Pd(0) is reoxidized by quinone to Pd(II) [297].

114

Mono-, bi-, and tricyclic alkenes were oxidized with O_2 in THF containing $PdCl_2$ and CuCl to ketones. For example, (115) gave 85% (116). Linear polyenes were also oxidized with H_2O_2, NiO_2, NaOCl, Ag_2O, MnO_2, or $KMnO_4$ and the $PdCl_2$ + CuCl catalyst to ketones [298].

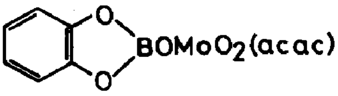
115 **116**

The liquid-phase oxidation of cyclohexene is catalyzed by the two-component catalyst system $[(Me_2SO)_5VO]^{2+}$ + $[Pt(SCN)_6]^{4-}$; maximum activity occurs at V/Pt = 2 [299].

See also [304, 306, 307, 312, 314, 329, 378, 517].

c) Epoxidation of olefins

Oxidation of cyclohexene by O_2 is catalyzed by a layered compound of graphite with $MoCl_5$. The catalyst participates in the decomposition of cyclohexyl hydroperoxide and the epoxidation of cyclohexene by this hydroperoxide [300]. The kinetics of epoxidation of cyclohexene in the presence of catalysts (117) and (118) were investigated. The B-O bonds were cleaved during epoxidation and more stable catalysts were obtained with a polymeric support, e.g. polystyrylboronic acid [301].



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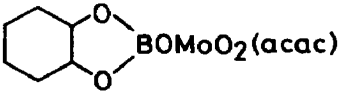

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Epoxidation of alkenes and hydroxylation of alkanes by O_2 and Zn as reducing agent were achieved with good yields (up to 50% based on Zn) and rates (up to 200 turnovers of the catalyst per hour) by using (TPP)MnCl as catalyst in the presence of 1-methylimidazole and acetic acid [302]. The liquid-phase oxidation of octenes by O_2 in the presence of Tc complexes was studied. Low yields of (mainly trans) epoxides were obtanied [303].

The iron bleomycin-mediated oxidation of cis-stilbene under aerobic conditions affords mainly cis-stilbene oxide and benzaldehyde. It was now shown by isotopic tracer experiments that for each of the oxidants tested, the benzaldehyde oxygen was derived primarily from O_2 while the source of oxygen in stilbene oxide depended on the oxidant used (O_2, H_2O_2, $NaIO_4$, or PhIO) [304]. The homogeneous oxidation of cis-cyclooctene with O_2 catalyzed by $K[Ru(H\text{-}EDTA)Cl].2H_2O$ was found to be first order in substrate and catalyst, and half order in O_2. Cyclooctene oxide was the chief product and a small quantity of 2-cyclooctene-1-ol was also obtained in the reaction [305]. Treatment of $[Ru(Me_2phen)_2(H_2O)_2]^{2+}$ (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) with Ce^{4+} resulted in the formation of the dioxo complex $[Ru(Me_2phen)_2(O)_2]^{2+}$ which was found to be an efficient catalyst for the oxidation of alkenes with O_2 to epoxides, alcohols, and carbonyl compounds [306]. Oxidation of olefins and alcohols with PhIO or air is catalyzed by trans-$[Ru(phen)_2(OH)(H_2O)](ClO_4)$ and trans-$[Ru(bpy)_2(OH)(H_2O)](ClO_4)$. Aldehydes, ketones, and epoxides are the reaction products. The Ru complex remains intact after these oxidative reactions [307]. Epoxidation of cyclohexene with O_2 is catalyzed by Ru(III)-EDTA in a 50% $EtOH/H_2O$ solution at 30°C. The reaction is first order with respect to catalyst and substrate and half order with respect to O_2. Both oxygen atoms are used for the formation of cyclohexene epoxide and the turnover numbers reach 200 min^{-1} [308].

Liquid-phase cooxidation of benzaldehyde and propene in the presence of Co(TPP) involves the formation of $Co(TPP)^{+\cdot}$ complexes with PhCOOOH which then react with propene to give propylene oxide. The induction period of O_2 consumption is influenced by substituents of the porphyrin ring [309]. The epoxidation of oleic acid with O_2 in the presence of benzaldehyde using Co^{3+} as the catalyst has been investigated and a reaction mechanism was proposed. The results indicated that the epoxidized oleic acid was formed by a series of free-radical reactions. Selectivity was 88% [311].

Oxidation of several mono- and nonconjugated diolefins with air and the catalyst $(MeCN)_2PdCl(NO_2)$ has been described. Nonbornene derivatives reacted by epoxidation of the strained double bond, other alkenes and dienes yielded methyl ketones [312].

See also [288].

d) Oxidation of Aromatics

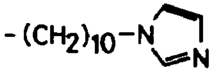
The use of Mn bromide + HBr catalysts for the air oxidation of the formylated derivatives of m-xylene and 1,3,5-trimethylbenzene to produce trimellitic anhydride and pyromellitic dianhydride was discussed [313]. The catalytic activity of $NiBr_2$, $MnBr_2$, and $CrBr_3$ in the oxidation of cyclohexene, α-alkenes, α-methyl styrene, and styrene at 120°C in aqueous cetyltrimethylammonium bromide by O_2 increased in the stated order of salts and alkenes and with decreasing concentration of the phase-transfer catalyst [314].

Ferrocene and ferrocene derivatives accelerate the oxidation of cumene and the decomposition of cumene hydroperoxide [315]. Catalysts prepared from hemin bound on 3 organosilicas (119) were used in liquid-phase oxidation of cumene by O_2. Activity of catalysts based on (119b) and (119c) (which contain imidazole groups) was higher than that of (119a) [316].

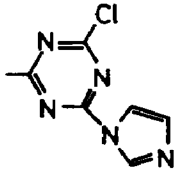
$(SiO_2)_n(CH_2)_3NHR$

119

119b, R =

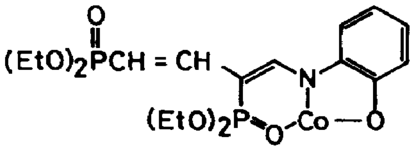


119c, R =



119a, R = H

The liquid-phase oxidation of o-xylene, catalyzed by Co(II) acetate in AcOH, has been studied at 130-150°C and 3 bar O_2. The first oxidation product was o-tolualdehyde which was oxidized to the main product o-toluic acid. In addition, nine other reaction products were found to be present in minor amounts [317]. The contribution of the reaction of peroxy radicals with Co(II) to chain propagation in the oxidation of alkylbenzenes with a $Co(OAc)_2$ + NaBr catalyst system was examined [318]. A polypropargyl methacrylate-Co^{2+} complex catalyzed the oxidation of m- and p-diethylbenzenes to mono- and diketones [319]. Mesitylene was oxidized to 3,5-dimethylbenzaldehyde in the presence of Co bromide catalysts activated with triethanolamine or py. The lower rate of consecutive oxidation of the aldehyde as compared with that of oxidation of mesitylene was attributed to the role of cooxidation reactions in the process [320]. Monomethyl terephthalate was prepared by air oxidation of methyl p-toluate using Co acetate + zirconium acetate as catalyst in AcOH at 120°C [321]. The Co complexes (120) and (121) were found to accelerate the liquid-phase oxidation of cumene [322].



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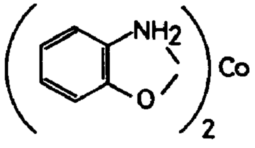
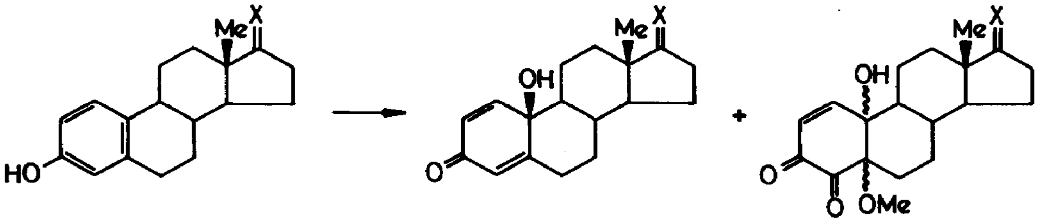


121

Estrone (122a, X = O) and estradiol (122b, X = H,OH) could be hydroxylated to the corresponding derivative (123) by O_2 in the presence of Co(salen) as catalyst. If the reaction was performed in MeOH, methoxylated byproducts (124) were also formed [323].

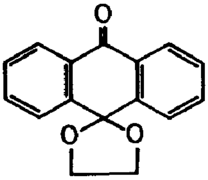


122 123 124

Factors affecting the activity of homogeneous Pd catalysts in allylic, vinylic, benzylic, and aromatic ring oxidation have been discussed. Low oxidation states seem to favor allylic or benzylic oxidation and oxidative coupling of aromatic rings whereas ring oxidation is favored by high oxidation state systems [324]. The use of zinc acetate in conjuction with $Pd(OAc)_2$ in benzylic acyloxylation of toluene in a high boiling carboxylic acid (e.g. lauric acid) as solvent at 170°C under continuous O_2 stream resulted in the improved catalytic production of the corresponding benzyl carboxylate compared to that of $Pd(OAc)_2$ alone [325]. Benzene reacts with O_2 to give phenol at 180°C in the presence of $Pd(OAc)_2$, acetic acid, phen, and CO; under optimum conditions 5-10 moles of

PhOH are formed per mole of Pd. All four components of the unusual catalyst system are essential; lack of CO leads to the formation of biphenyl, in the absence of phen benzoic acid is the main product and no reaction takes place if AcOH is not present [326].

The catalytic oxidation of benzene by the copper + ascorbic acid + O_2 system was improved by using MeOH as solvent; under such conditions phenol and hydroquinone were formed but not catechol. The turnover number of the catalyst exceeded 2 [327]. The kinetics of the liquid-phase oxidation of anthracene to anthraquinone by O_2, with $CuBr_2$ as catalyst and ethylene glycol as solvent, has been studied at 120-160°C. Acetal (125) was identified as an intermediate of the reaction [328].



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See also [353].

2. Catalytic Oxidation of O-containing Functional Groups with O_2

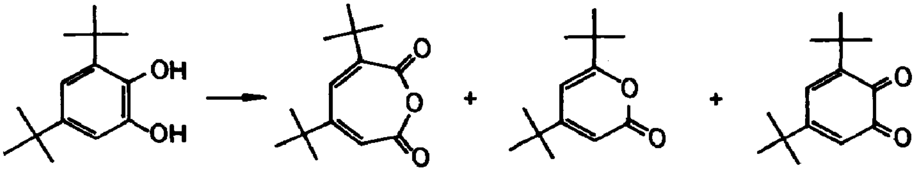
a) Oxidation of Alcohols

The uranium (IV) complex $(TPP)UCl_2$ was found to catalyze the oxidation of cholesterol [329]. Different porphyrin complexes of Mn, Fe or Cu adsorbed on the anion-exchange resin Amberlite IRA 900 catalyzed the oxidation of MeOH to CH_2O. Highest activity was observed with the Mn^{3+} complex of tetrakis(sulfophenyl)porphine [330]. Primary and secondary alcohols could be oxidized to aldehydes and ketones, respectively, by O_2 at 65°C in the presence of the trinuclear Ru carboxylate complexes $[Ru_3O(COCR)_6L_3]^n$ (L = Me, Et; L = H_2O, PPh_3; n = 0, +1) [331]. The biomimetic complex Cu(II)-py_4, an analog of the enzyme galactose oxidase, catalyzes the oxidation of monohydroxyacetone by O_2. The data indicate that the process involves three pH-separable pathways, two of which include concerted catalysis by free (excess) pyridine [332].

See also [554].

b) Oxidation of Phenols

The heteropolyvanadates $[PV_{14}O_{42}]^{9-}$, $[MnV_{13}O_{38}]^{7-}$, and $[NiV_{13}O_{38}]^{7-}$ catalyze the oxidation of (126) in MeCN solution to give the products (127-130). Labeling experiments with $^{18}O_2$ revealed that the oxygen atoms in products (127) and (128) come from dioxygen and not from the oxyanions present in the polyvanadates [333]. In the presence of V(acac)(L) (LH_2 = tetrachlorocatechol) (126) is easily oxidized by O_2 in CH_2Cl_2 to afford (127), (128), and (129). The V complex first reacts with (126) and the complex formed in this step reacts with O_2 to give the products [334].



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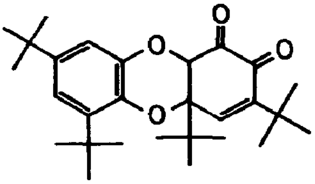

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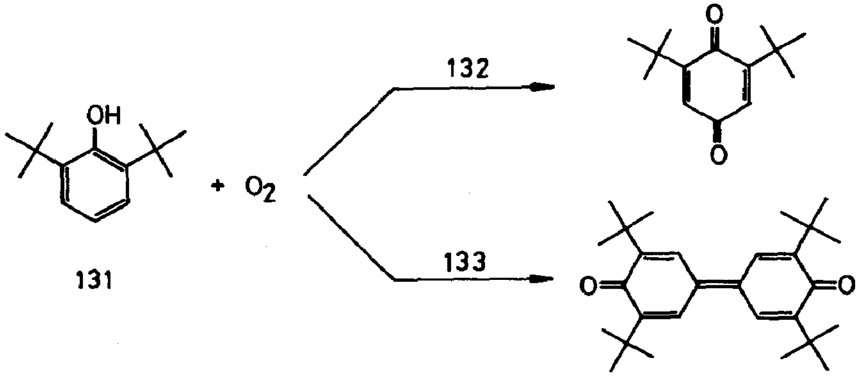
Oxidation of 2,6-di-tert-butylphenol (131) by O_2 was used as a test reaction to study the catalytic activity of a Mn porphyrin fixed on zeolite. The catalyst regenerated electrochemically gave good selectivities for the corresponding diphenoquinone (135) [335]. Oxidation of (131) by O_2 is catalyzed by the Co complex (132) and by the Mn complex (133); Co catalyzes the formation of the corresponding benzoquinone (134) while Mn promotes the formation of the analogous diphenoquinone (135). It has now been found, that an applied magnetic field influences the rates of both reactions: weak magnetic fields increase and very strong magnetic field decrease the rate of oxidation [336].



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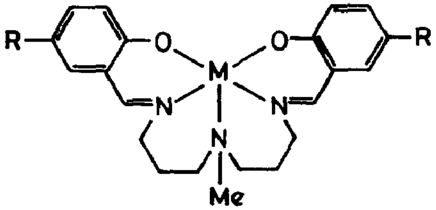
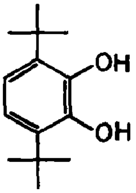


132; M = Co, R = H

133; M = Mn, R = NO_2

Oxidation of 3,6-di-tert-butylpyrocatechol (136) in MeOH solution with O_2 catalyzed by $Mn(OAc)_2.4H_2O$ gave the ortho quinone derivatives (137-139) [337].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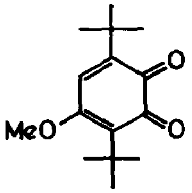
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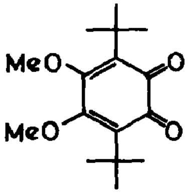
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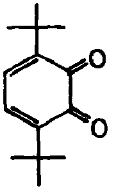
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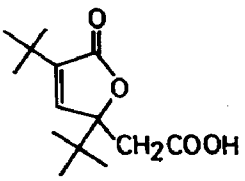
Oxidative ring opening of (126) with O_2 using $FeCl_2$ + bpy + py or $FeCl_2$ + py catalyst systems was studied. Highest yield of (141) was obtained at a $FeCl_2$:bpy:py ratio of 1:1:23 [338]. Oxygenation of (126) is catalyzed in THF/water, DMF or DMF/water by Fe(III) salts without the addition of any ligands (like py, bpy, etc.). Main products are (127) and (129) [339]. The 3,5-di-t-butylcatecholato [DTBC] iron complex $[Fe(DTBC)_3]^{3-}$ reacts in organic solvents reversibly with O_2 to form a ternary iron-catechol-oxygen complex. Repeated oxygenation and deaeration cycles, however, lead to the oxidation of the organic ligand; the yield of oxidized products (127, 129, 141, and 142) depends strongly on the solvent used [340].



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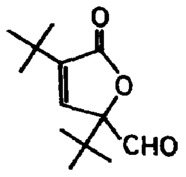
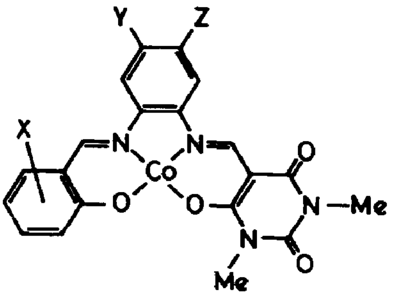


142

Oxidation of 2,3,6-trimethyl phenol using $RuCl_3$ as catalyst furnished trimethyl-p-benzoquinone in 90% yield. For the oxidation of 2,3,4-trimethoxy phenol to 2,3-dimethoxy-p-benzoquinone by air $CuCl_2$ was a useful catalyst. For the conversion of trimethoxybenzenes to the corresponding dimethoxy-p-benzoquinones, H_2O_2 + $[Fe(CN)_6]^{3-}$ was the most effective agent [341]. Oxidation of α-naphthol by O_2 catalyzed by different Co tetraphenylporphyrin complexes was studied. The main product was α-naphthoquinone. The activity of the catalysts having different substituents at the para position increased in the order COOH < H < OMe [342]. Oxidation of hydroquinone by O_2 is catalyzed by a Co-bpy complex; the rate increases on addition of imidazole or PPh_3. Oxidation follows Michaelis-Menten kinetics [343]. Non-symmetric Schiff base Co(II) complexes of the type (143) have been prepared and used as catalysts for the oxidation of (131) by O_2 to the corresponding benzoquinone (134). Their catalytic activity did not differ significantly from that of Co(salen) and similar symmetric Schiff base complexes [344].

Several Pd cluster complexes catalyze the oxidation of hydroquinone to p-benzoquinone but are much less active in the oxidation of ubiquinol (144). The most active catalyst is $[Pd_{10}(bpy)_4(O_2)_3](OAc)_2$ [345].



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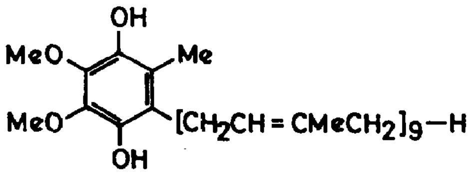
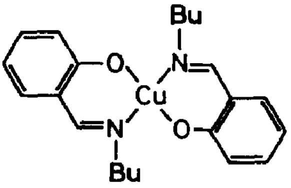


144

Oxidation of catechol to o-quinone by air is catalyzed by the dinuclear copper complex Cu(o-hydroxycinnamate)$_2$. Oxidation stops at this stage [346]. Several Cu(II) chelates were examined as catalysts for the oxidation of hydroquinone to benzoquinone by O_2. Bicyclic ones, such as (145) were more active than tricyclic ones, such as (146) [347].



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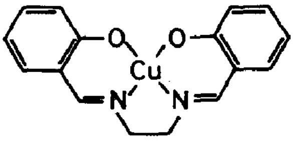
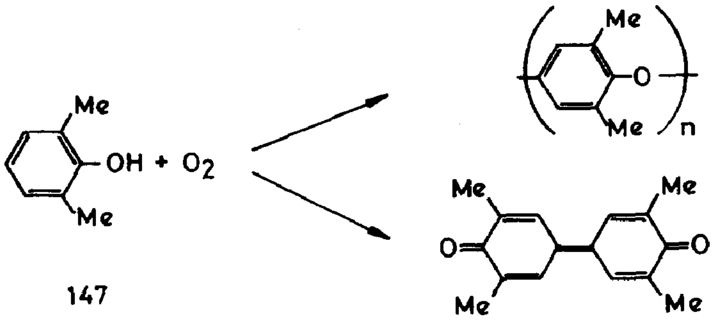


146

The dimeric Cu(I) complex $LCuCl_2CuL$ (L = N,N,N',N'-tetraethylethylenediamine) catalyzes the oxidation of 2,6-dimethylphenol (147) by O_2. At temperatures below -30°C the diphenoquinone (149), at higher temperatures the polymer (148) is formed as main product [348].



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148

149

See also [297].

c) Oxidation of Aldehydes and Ketones

Cerium(IV) was found to be the active form of Ce catalysts in the liquid-phase oxidation of aldehydes with O_2 [349].

Kinetics of acetaldehyde oxidation to AcOH with $Mn(OAc)_2$ as catalyst was studied under operating conditions of the industrial process. Kinetic models useful for reactor design were obtained [350]. Recycling of $Mn(OAc)_2$ catalyst in the oxidation of acetaldehyde to AcOH improved the yield of the latter and reduced formic acid production [351]. Oxidation of 2-arylpropionaldehydes by O_2 to 2-arylbutyric acids was performed with yields above 80% using $Mn(st)_2$ as catalyst in decane solution at room temperature and 8 bar. The reaction proceeded by a radical chain mechanism [352].

Liquid-phase oxidation of acetaldehyde to peracetic acid and of p-methoxytoluene to the corresponding aldehyde with O_2 in the presence of Co phthalocyanine as catalyst was studied [353]. The effects of particle size and degree of cross-linking on the oxidation of acetaldehyde by O_2 to peracetic acid in the presence Co ions fixed on ion-exchange resins was investigated both experimentally and theoretically [354]. A tubular-wall reaction lined with Co-complexed ion-exchange membrane catalyst was used for the oxidation of benzaldehyde to perbenzoic acid [355].

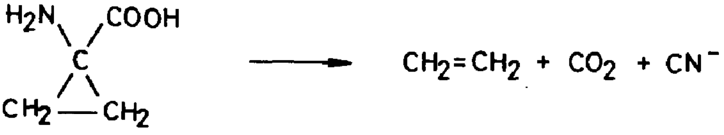
See also [309, 310].

d) Miscellaneous Oxidations

Ethylenediamine di(o-hydroxyphenylacetic)acid and diethylenetriamine pentaacetic acid were found to inhibit almost completely ascorbate oxidation catalyzed by Fe ions. The two chelating agents prevented Fe^{2+}/Fe^{3+} redox cycles [356]. Oxidation of ascorbic acid catalyzed by Cu^{2+} ions is retarded by disulfides like cystine or oxidized glutathion. Evidence suggests that this is due to the formation of stable Cu complexes [357]. The rate constant of the oxidation of vitamin C by air catalyzed by Cu^{2+} was determined in the pH range of 3-10 [358].

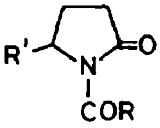
3. Catalytic Oxidation of N-containing Organic Compounds

A rate law for the oxidation of adrenaline catalyzed by oxovanadyl(IV) was determined [359]. Alkylpyridines were oxidized to the corresponding carboxylic acids using Co or Mn rosinates as catalysts. Yields were moderate [360]. Oxidation of alanine and phenylalanine to pyruvic acid and phenylpyruvic acid, respectively, with O_2 using metal ion complexes of pyridoxal as catalysts has been described. Catalytic activity of the metal ions increased in the order Cu(II) < Co(II) < Mn(II). The amino group was eliminated in the form of hydroxylamine and no H_2O_2 was formed [361]. Oxidation of (150) in the presence of 1-benzyl-3-carbamoyl-1,4-dihydropyridine, Mn^{2+}, and flavin mononucleotide yields ethene. The system mimics biological ethene formation in plant tissues [362].



150

Oxidation of histidine with O_2 catalyzed by (TPP)Co, (TPP)FeCl or (TPP)FeOH, fixed on silica gel was studied. A correlation was established between the activity of the complexes and their state on the carrier [363]. Pyrrolidinones (151; R = Ph,PhNH; R′ = H,COOMe) and piperidinones (152; R = H, Me, Ph) were prepared by the oxidation of the corresponding pyrrolidines and piperidines with Fe^{2+} and H_2O_2 or with O_2 and $Fe_3O(OAc)_6(py)_3$ [364].



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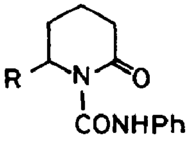
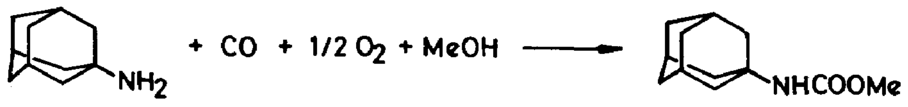


152

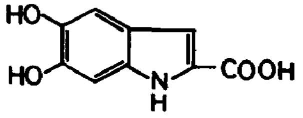
The oxidation of diethylamine by O_2 catalyzed by $[RuCl_2(H_2O)_4]^+$ or a Ru(III)-EDTA complex was investigated. The reaction was first order with respect to catalyst and substrate concentration and independent of O_2 concentration. The major products were the corresponding imine, N-hydroxethylamine and acetaldehyde [365].

Oxidation of 1-adamantylamine with O_2 in MeOH in the presence of CO and using Co(salen) as catalyst gives the corresponding carbamate (153) as a result of oxidative carbonylation. Under the same conditions diphenylmethane and anthracene exhibit only oxidation to benzophenone and anthraquinone, respectively [366].



153

Oxidation of N-benzylamines $RCONHCH_2Ph$ (R = Me, Ph, 2-ClC_6H_4) by O_2 in the presence of $Co(OAc)_2$ and NaBr gave mainly benzoic acid and $RCONH_2$. A radical chain mechanism was proposed [367]. Autoxidation of (154) in the presence of Co^{2+} or Cu^{2+} ions leads to a mixture of oligomers the major of which has been isolated as the acetyl and methyl ester derivative (155) [368].



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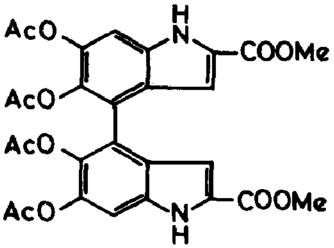
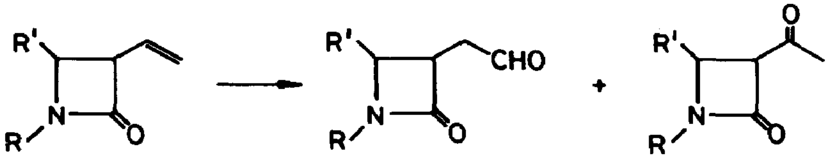


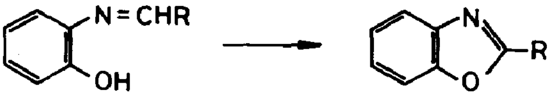
155

Oxidation of α-vinyl-β-lactams (156, R and R' phenyl or substituted phenyl) with $PdCl_2$ + CuCl + O_2 gave the corresponding aldehydes (157) as main products instead of the usual methyl ketones (158). This anomalous reaction could probably be explained by postulating that Pd coordinates with the carbonyl group or the β-lactam as well [369].



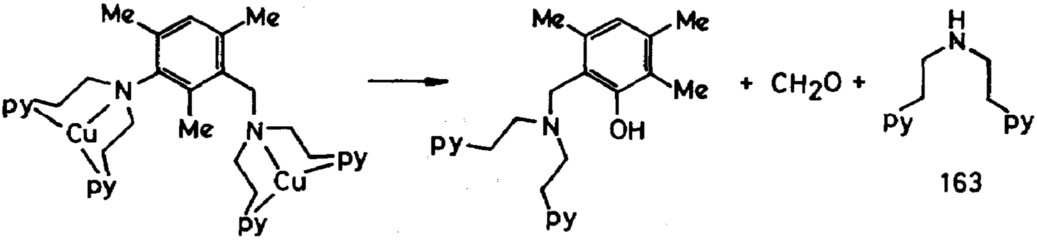
156 157 158

N-alkylidene-2-hydroxyanilines (159, R = phenyl or substituted phenyl) are oxidized by O_2 to 2-substituted benzoxazoles (160) in good yields when initiated by CuCl in py. The reaction rate is independent of substrate concentration, indicating that oxidation of Cu(I) is rate-limiting [370].



159 160

Oxidation of the dicationic Cu complex (161) with O_2 in CH_2Cl_2 solution gave after decomplexation with aqueous ammonia the hydroxylated product (162), CH_2O, and the amine (163) [371].

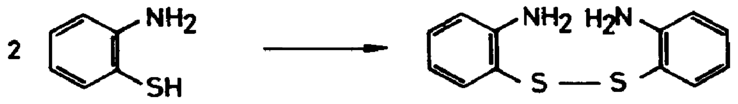


161 162 163

See also [372, 376].

4. Catalytic Oxidation of S-, Sn-, or B-containing Organic Compounds

Oxidation of 2-hydroxynaphthaldehyde thiosemicarbazone by O_2 is catalyzed by Mn(II). The compound is oxidized yielding a deep blue fluorescence [372]. Oxidation of thiols RSH (R = $HOCH_2CH_2$, dodecyl) by O_2 in the presence of Co(II) phthalocyanine tetrasodium sulfonate and a quaternary ammonium bromide polymer was studied. Poly-(quaternary ammonium salts) increased the activity of the Co(II) catalyst [373,374]. Cobalt phthalocyanine, along with Et_3N or py as promoter, was used as catalyst on different supports for the oxidation of EtSH [375]. Some ortho-substituted anilines were oxidized at room temperature with O_2 in the presence of $Co(ClO_4)_2 \cdot 2H_2O$ as catalyst. 2-Aminothiophenol was transformed quantitatively into its disulfide (164) whereas 2-aminophenol gave several oxidation products depending on the solvent. Two compounds have been identified: 2-aminophenoxazine-3-one (165) and 2,2'-dihydroxyazobenzene (166) [376].



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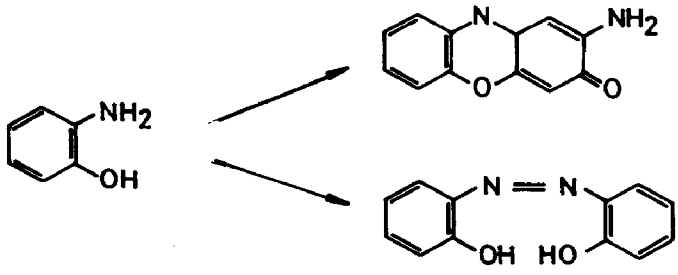

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166

The allylic tributyltin derivatives (167) and (168) were oxidized by O_2 in THF solution in the presence of $FeBr_3$ as catalyst at -78°C. The mechanism proposed (formation of organoiron intermediates and insertion of O_2 into the Fe-C σ-bond) explains the formation of two different carbonyl compounds; an allyl radical intermediate can be excluded since this would lead to the same product in both cases [377].

167

168

Hydroboration-oxidation of olefins to alcohols by $NaBH_4$ and O_2 is catalyzed by (OEP)RhCl or (TPP)RhCl:

$$>C=C< + O_2 + BH_4^- \longrightarrow H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH + >BO$$

First, BH_4^- transforms the catalyst into a Rh hydride and the olefin into an alkylborane; in the second step the Rh hydride is oxidized by O_2 back to Rh(III) and the alkyl borane is oxidized with retention of configuration to an alkylborate. For example, 1-methylcyclohexene is transformed in a one-pot reaction into (E)-2-methylcyclohexanol with 100% regioselectivity and 98% stereoselectivity [378].

5. Catalytic Oxidation of Organic Compounds with Organic or Inorganic Oxidants

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

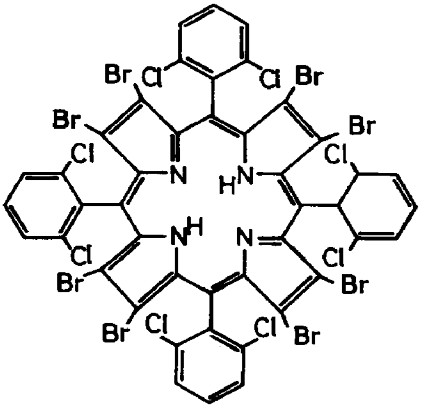
Oxidation of benzylic CH_2 groups or alcohols to carbonyl compounds was achieved with 70% aqueous tBuOOH in the presence of catalytic amounts of CrO_3 in CH_2Cl_2 at room temperature. Both oxidations were preparatively useful procedures [379, 380]. Alkenes could be converted into α,β-unsaturated carbonyl compounds with tBuOOH and catalytic amounts of CrO_3. This new type of allylic oxidation was especially useful for the transformation of cycloalkenes. Epoxides were formed in minor amounts as byproducts [381]. Although tBuOOH and pyridinium dichromate do not effect allylic or benzylic oxidations independently, a combination of the two turned out to be a good reagent system for these transformations at 25°C in dry benzene. Thus, for example, tetralone (169) was obtained from tetraline in 78% yield [382].

169

Oxidation of methylnaphthalenes (170, R = H, Me) with tBuOOH in $CHCl_3$ in the presence of $MoO_2(acac)_2$ gave naphthoquinones (171) [383].

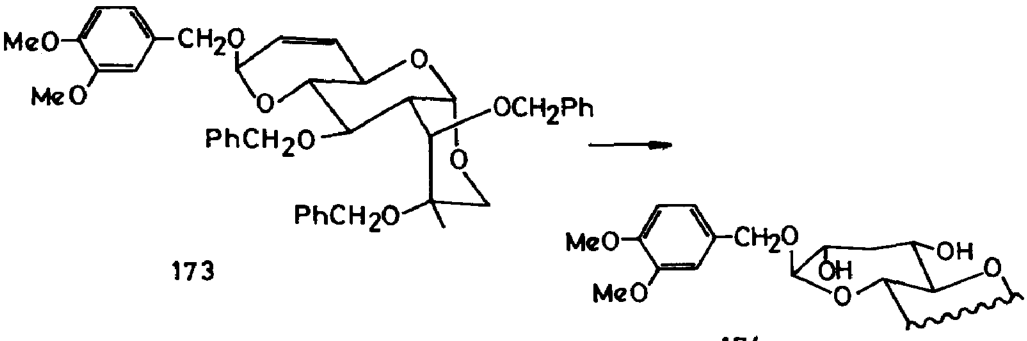
170 171

The Bu_4N^+-salts of the transition metal-substituted heteropolytungstate complexes, $[PW_{11}(M)O_{39}]^{5-}$ (M = Mn,Fe,Co,Cu), catalyze the oxidation of alkanes to alcohols and ketones by tBuOOH in benzene as solvent at 65°C. The reactions appear to be homogeneous [384]. Oxidation of propene by H_2O_2 was studied using (TPP)FeOH on α-alumina as catalyst [385]. Oxygenation of biphenyl with $[Fe(MeCN)]_6^{2+}$ + H_2O_2 + Ac_2O yielded 2- and 4-acetoxy derivatives. The system models heme-containing monooxygenase enzymes [386]. The (L)FeCl and (L)FeOH complexes of the halogenated tetraphenylporphine (L = 172) were applied as catalyst for hydroxylation of nornbornane and epoxidation of 4,4-dimethyl-1-pentene with F_5C_6IO as oxidant. The new catalysts were much more robust than the corresponding TDCPP complexes and practically not susceptible to "suicide inhibition" under the conditions applied [387].



172

Oxydation of styrene by H_2O_2 in a two-phase system and catalyzed by metal salts is remarkably promoted by the addition of quaternary ammonium salts as phase-transfer agents. Using $RuCl_3.xH_2O$, the chief product is benzaldehyde whereas with $PdCl_2$ mainly acetophenone is formed [388]. Oxidation of styrene and stilbene by IO_3^- in aqueous AcOH or ClO_4 catalyzed by Os(VIII) or Ru(III) is zero order in oxidant and first order in both substrate and catalyst [389]. The kinetics of the Ru(III) and Os(VIII) catalyzed oxidation of benzilic acid by $Tl(OAc)_3$ in aqueous AcOH-$HClO_4$ media were determined [390]. Enoside (173) was hydroxylated with methylmorpholine N-oxide and OsO_4 as catalyst to give the diol (174) in 62% yield [391].



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174

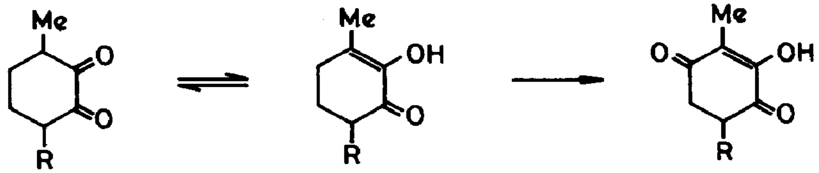
Oxidation of hexene-1 to hexanone-2 by benzoquinone and $PdCl_2$ as catalyst was performed in a formamide microemulsion using a hexene-1:water ratio of 1.56:1 (w/w), $C_9H_{19}-C_6H_4-(OCH_2)_8OH$ as surfactant and iPrOH as cosurfactant. The main feature of this novel Wacker-oxidation was the absence of an induction period [392]. Oxidation of ethene to vinyl acetate using $PdCl_2$ as catalyst and benzophenone as oxidant was found to be first order with respect to catalyst and zero order with respect to oxidant [393].

The effect of Cu^{2+} ions on the oxidation of styrene and (E)-propenylbenzene by $S_2O_8^{2-}$ in AcOH was investigated. Cu(III) acted as electron transfer agent and the resultant alkene radical-cation was converted into hydroxy acetates with good yield [394]. Dimethylanisoles (175) in which one of the Me groups is *meta* and the other is *ortho* or *para* are regiospecifically oxidized in high yield to the *ortho*- and *para*-substituted aldehydes (176) by Cu(II) and $K_2S_2O_8$ [395]:

175

176

The two 3,6-dialkyl-1,2-cyclohexanediones (177; R = Me, iPr) were oxidized with Cu(II) acetate and I_2 to the corresponding 3-hydroxy-1,4-benzoquinone derivatives (178) [396].

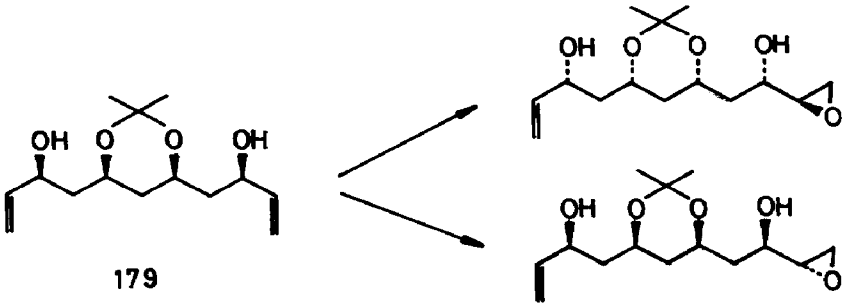


177 178

See also [298, 500, 515, 517].

b) Epoxidation of Olefins

Application of 3A or 4A molecular sieves (zeolites) in the Ti(IV)-catalyzed asymmetric epoxidation of allylic alcohols enables the use of only 5-10 mole % Ti(OPr^i)$_4$ instead of the stoichiometric amount required by the original procedure. The principal function of zeolites is the elimination of adventitious water in the reaction mixture. This improved method is especially useful for the epoxidation of low molecular weight alcohols [397]. The divinyl polyol (179) undergoes epoxidation with group and face selectivity with the <u>pro</u>-S and <u>pro</u>-R selective Scharpless reagents Ti(OPr^i)$_4$ + tBuOOH + L-(+)- or D-(-)-diisopropyltartrate, respectively, to give (180) or (181). The minor enantiomers produced in these reactions are selectively "destroyed" by a fast second epoxidation (kinetic resolution); accordingly very high levels of enantiomeric purity ($>$ 99.99999%) may be obtained [398].



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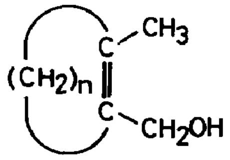
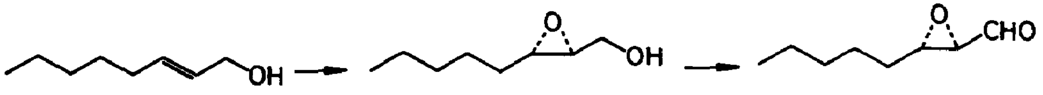
179

Sharpless epoxidation of mixtures of the cis- and trans-2-methylcycloalkenylmethanols (182) with 0.6 equivalents of the $Ti(OPr^i)_4$ + (+)-diisopropyltartrate + tBuOOH reagent produced a mixture of epoxy alcohols and unconverted allylic alcohols. In the case of 12- to 14-membered cycloalkenes the recovered alcohols were optically active; the 15- and 16-membered cases were racemic [399].



182; n = 10 - 14

The two diastereomeric epoxyoctanals (184) and (186) were prepared from the stereoisomeric octenols (183) and (185) by Sharpless epoxidation followed by oxidation with CrO_3 [400].



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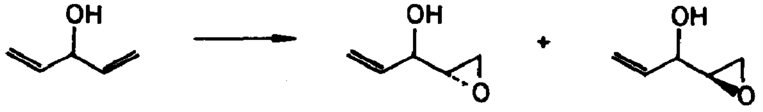
186

Sharpless asymmetric epoxidation of a few achiral substrates like (187) has been examined and shown to provide monoepoxy alcohol products of type (188) whose enantiomeric purity increases as the reaction proceeds toward completion. This result is in accord with a mathematical model based on the assumption that the asymmetric synthesis of (188) is coupled with the kinetic resolution operating during the second epoxidation process [401].

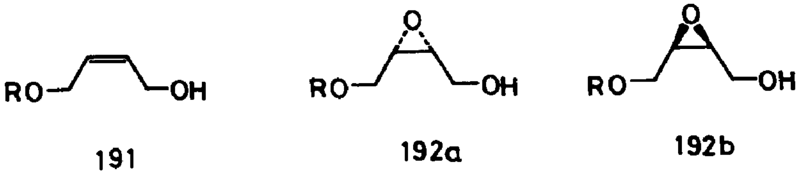


187

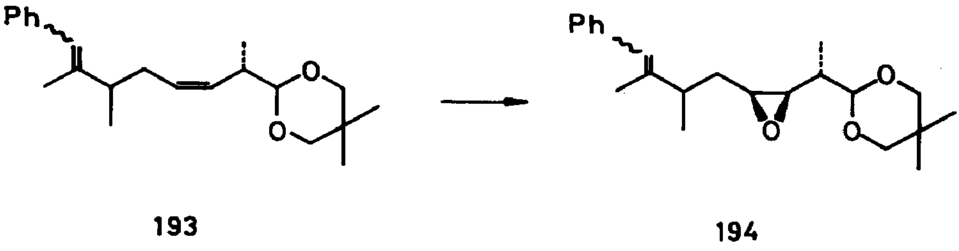
188

Catalytic asymmetric epoxidation of tiglyl alcohol (189) using tBuOOH, D-(-)-diethyl tartrate and $Ti(OPr^i)_4$ gave the epoxy alcohol (190) in over 50% yield [402].

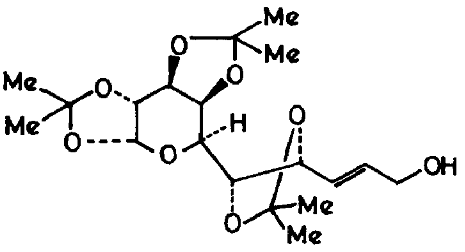
The chiral epoxides (192a) and (192b) ($R = 4\text{-}BrC_6H_4CH_2$) were prepared enantiomerically pure from the allyl alcohol (191) by Sharpless epoxidation with tBuOOH, $Ti(OPr^i)_4$, and (+)- or (-)-diisoporpyltartrate, respectively, in the presence of a 4A molecular sieve in 70-73% yield [403].



The acetal (193) was epoxidized with tBuOOH in the presence of $TiCl_{3.25}(OPr^i)_{0.75}$ as catalyst to give the anti-epoxide (194) in 80% yield [404].



Sharpless epoxidation of the decenopyranose (195) with diisopropyl L-(+)-tartrate gave epoxides (196a) and (197b) in a 5:1 ratio; use of the D-(-)-tartrate gave the two epoxides in a ratio 1:4 [405].



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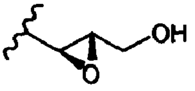

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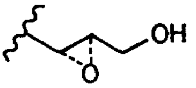
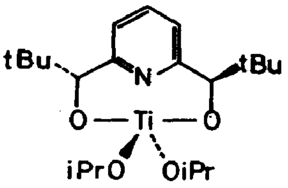


196 b

The Ti(IV)-pyridinediol complex (197) was studied as an asymmetric epoxidation catalyst modeling titanium-tartrate catalyst systems. The sign of induction depended on the alkyl group of the hydroperoxide oxidant; trityl hydroperoxide transformed allyl alcohol (198) into epoxide (199) - predicted by the model - with 64% o.y. [406].



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198

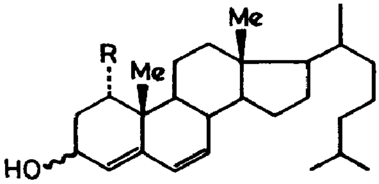
199

In the asymmetric epoxidation of homoallylic alcohols, a combination of Zr(OPr^i)$_4$, (+)-dicyclohexyltartramide, and tBuOOH was found to give good enantiomeric selectivities (up to 77%) especially for (Z)-homoallylic substrates like (200) [abs. configuration of (201): 3R,4S]. Analogous Ta or Hf catalysts showed poor enantioselectivity [407].

200

201

Unsaturated ketones possessing a neighboring OH group were stereoselectively epoxidized with tBuOOH in the presence of VO(acac)$_2$ as catalyst. The reaction was applied to steroidal substrates [408]. The dienols (202; R = H,OH) were transformed into the epoxycholestanols (203) by tBuOOH in the presence of $VO(acac)_2$ [409].



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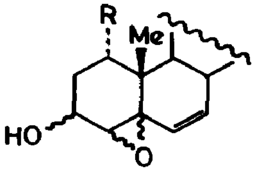
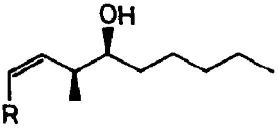


203

All possible diastereomeric epoxides were synthesized starting from the homoallylic alcohols (204) and (205) using the following epoxidizing agents: V^{5+} + tBuOOH, $MoO_2(acac)_2$ + tBuOOH, MoO_5.HMPA, or WO_5.HMPA [410].



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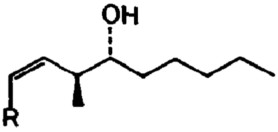
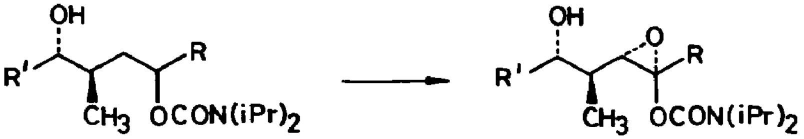


205

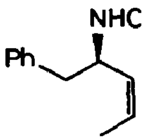
R = Me, nBu

The enol carbamates (206; R = H,Me; R' = Me,Ph,iPr,tBu) were diastereoselectively epoxidized to (207) with BuOOH using $VO(acac)_2$ as catalyst in dry CH_2Cl_2 [411].



206 207

Molybdenum complexes of the type MoO_2L_2 (L = 8-hydroxyquinoline, ethylene-1,2-bissalicylimine, etc.) have been applied as catalysts for the epoxidation of ethene by tBuOOH. Addition of cyclohexeneoxide improved selectivity and reproducibility [412]. Hydroxy and acetoxy derivatives of dicyclopentadiene were epoxidized in good yields with H_2O_2 in the presence of $(cetylpy^+)_3(PMo_{12}O_{40})^{3-}$. For hydroxy derivatives the orientation of the OH group determined the selectivity of the reaction. Regioselectivity in the epoxidation of acetoxy derivatives was opposite to that of the hydroxy derivatives [413]. Epoxidation of fatty acid esters was carried out with 30% aqueous H_2O_2 in the presence of a Mo oxide catalyst (prepared by fixing molybdenum blue on charcoal) and Bu_3SnCl in PrOH at 50°C. The method could be used also for the epoxidation of various vegetable oils [414]. The kinetics of hydroperoxide decomposition during the epoxidation of castor oil with cumyl hydroperoxide using Mo or V acetylacetonates as catalysts was studied [415]. The stereochemistry of epoxidation of allylic amides has been investigated. Using the $Mo(CO)_6$ + tBuOOH epoxidation reagent both (Z)- and (E)-allylic amides (208 and 209) gave preferentially the threo epoxides [416].



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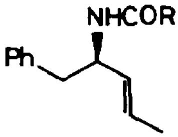


209

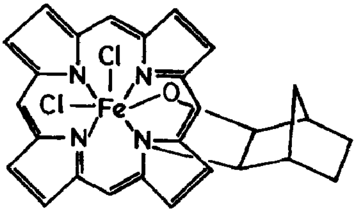
Tungsten boride (W_2B_5) was used as catalyst for the epoxidation of 1-octene with H_2O_2. The effect of different reaction parameters on the reaction was determined [417]. The highest turnovers reported so far in the epoxidation of olefins with H_2O_2 were obtained using $[MeN(n\text{-}octyl)_3][HWO_4]$ as catalyst complexed with anionic or neutral lipophilic phosphorous ligands containing the P=O subunit (e.g. $PhPO_3H_2$). The reactions were performed under homogeneous conditions in dioxane solution at 70°C with 70% H_2O_2 [418].

Several dienes were epoxidized with aqueous NaOCl using three different manganese porphyrins with different degrees of steric constraint: (TPP)Mn(OAc), (TTMPP)Mn(OAc), and (TTPPP)Mn(OAc). Selectivity for epoxidation of the less hindered double bond increased with the more hindered catalysts; this selectivity was also higher for nonconjugated than for conjugated olefins [419]. The high valent Mn-oxo porphyrin species formed from the reaction of *p*-cyano-N,N-dimethylaniline N-oxide with [(TDMPP)Mn(imidazole)]Cl has been shown to be the principal active agent in the epoxidation of cyclooctene. Epoxidation is not rate controlling and the Mn-oxo complex is partly used for the oxidation of *p*-cyano-N,N-dimethylaniline [420]. A kinetic study of the epoxidation of 2,3-dimethyl-

-2-butene by tBuOOH in the presence of (TPP)MnCl and imidazole has been carried out. Formation of the epoxide was found to be always first order, the yield of epoxide was about 60%. In a side reaction imidazole was also oxidized, presumably to its N-oxide [421]. Kinetic data indicate that the reactivity order of olefins in the catalytic epoxidation with NaOCl + (TPP)MnOAc + py is not directly related to olefin nucleophilicity. Pyridines and N-substituted imidazoles which act as axial ligands in olefin epoxidation with $KHSO_5$ + (TPP)Mn(OAc) are slowly oxidized to the corresponding N-oxides [422]. Two different oxidizing species, (TMP)Mn(O)Cl and (TMP)Mn(O)(H_2O), with different stereospecificities are formed from (TMP)MnCl and m-chloroperbenzoic acid. The Mn(V) species epoxidizes olefins in a stereoretentive manner whereas the Mn(IV) species transfers oxygen by a non-stereoretentive pathway [423]. In competitive experiments styrene increased the rate of epoxidation of aliphatic alkenes by (TPP)MnCl + NaOCl. This effect is caused by phenylacetaldehyde, a side-product of styrene epoxidation [424].

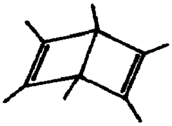
Epoxidation of cyclohexene by tBuOOH is catalyzed by Tc compounds, e.g. $Tc(PPh_3)_2Cl_4$. Addition of ionol increases the yield [425].

In the oxidation of propene by H_2O_2 in the presence of $(PP)Fe^{2+}.OH$ on α-alumina as catalyst (PP = protoporphyrin IX) propylene oxide was formed via allyl alcohol. The mechanisms of formation of propanal and acetone were also discussed [427]. Oxidation of propene with H_2O_2 over hemin supported on α-alumina at 160°C gave mainly propylene oxide along with some acetone, propionaldehyde, and allyl alcohol [428]. In contrast to earlier reports epoxidation of olefins by tBuOOH has been observed to be catalyzed by (TMP)FeCl. Significant epoxidation occured, however, only at low hydroperoxide/Fe ratios because excess of hydroperoxide reacted with the intermediate oxene $>$Fe=O and resulted in evolution of O_2 [429]. Upon epoxidation of but-1-ene in CH_2Cl_2 with PhIO and (TPP-Cl-p)FeCl at -10°C, the starting catalyst was progressively transformed into a new complex and, after treated with HCl, an N-alkylated porphyrin with the structure N-CH(COOH)Et could be isolated. This proves that in certain cases N-alkylporphyrins deriving from the binding of the pyrrole nitrogen to the more substituted vinylic carbon of alkenes may be formed during epoxidation [430]. During the (TDCPP)FeCl-catalyzed epoxidation of nornbornene (and other alkenes) by C_6F_5IO the hemin catalyst is converted to an N-alkylhemin species of type (210) resembling that formed during suicide inhibition of cytochrome P-450. This alkylhemin is, however, a catalyst for epoxidation and its formation does not result therefore in inhibition [431].



210

An iron tetraphenylporphyrin modified by binaphthyl groups was used for the epoxidation of olefins with PhIO in the presence of 1,5-diphenylimidazole. Due to the extremely large steric requirements of the binaphthyl groups the catalyst showed significant shape selectivity in favor of sterically less hindered olefins when used for the epoxidation of olefin mixtures [432]. A porphyrinatoiron(III) complex, Fe(ChP)Cl, containing a porphyrin ligand having four cholesteryl groups as substituents (ChP) has been incorporated into a synthetic phospholipid membrane and used as catalyst for the epoxidation of polyunsaturated sterols and fatty acids with PhIO. Epoxidation occurred primarily at the double bond closest to the hydrophobic terminus of the molecule [433]. The rearrangements of alkenes (211) and (212) were observed during their epoxidation with m-chloroperbenzoic acid and (TPP)FeCl as catalyst. Since these rearrangements are known to proceed through the intermediacy of alkene cation radicals the result was interpreted in terms of electron transfer from alkene to the high-valent iron intermediate [434].



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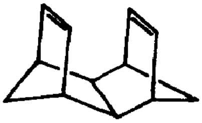
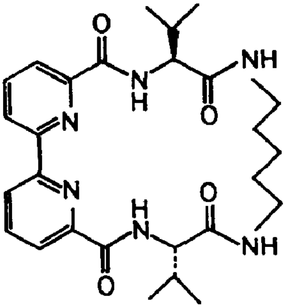


212

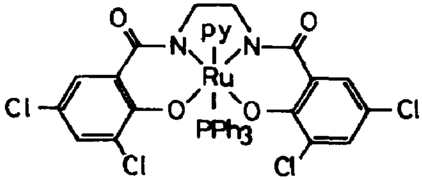
Epoxidation of cis- and trans-stilbene by $KHSO_5$ in $MeCN/H_2O$ catalyzed by Fe(III)- or Mn(III)-bleomycin complexes has been reported. The data support a metal-oxo species as oxygenating agent

[435]. The Fe(III) complex of the chiral bipyridine derivative (213) was used as catalyst for epoxidation of olefins using PhIO as oxidant. No enantioselectivity was observed with styrene as a prochiral model substrate [436].



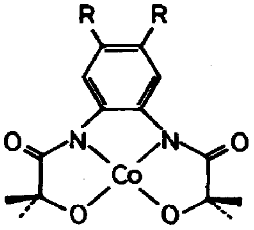
213

The $RuCl_3$-catalyzed epoxidation of cyclohexene and 1-octene by N-methylmorpholine N-oxide was found to be first order in catalyst and oxidant and variable order in olefin [437]. The Ru(IV) complex (214) acts as a catalyst for alkene epoxidation by PhIO. Styrene yielded selectively styrene epoxide; with cyclohexene, both the C-H and C=C bonds were attacked, cyclohexene oxide and cyclohex-2-en-2-one were formed in approximately equal amounts [438].



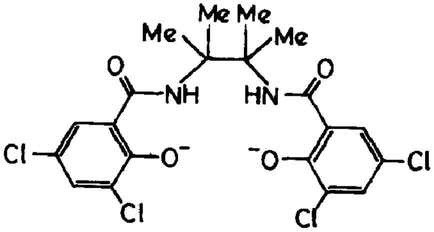
214

Styrene has been catalytically oxidized to styrene oxide and phenylacetaldehyde with iodosoarenes using anionic square planar Co(III) complexes like (215) as catalysts. The presence of vacant sites on the metal center seems to be important; an analogous di-aquo complex was inactive as catalyst [439].



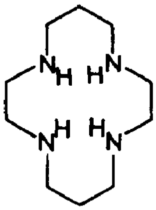
215; R = H,Cl

Epoxidation of olefins with tBuOOH or PhIO was investigated using the Co(II) complex of (216) as catalyst. The mechanisms of the two reactions were found to be different: a radical chain mechanism was proposed for epoxidation with tBuOOH whereas there was no evidence for radicals in the case of PhIO [440].



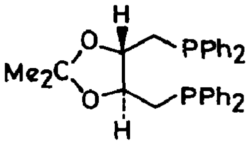
216

Nickel(II) complexes of several macrocyclic ligands have been examined as catalysts for olefin epoxidation using PhIO as oxidant. Epoxide yields were generally low (below 30%) and a large part of the oxidant was used up in oxidizing the ligands and solvents (MeCN or CH_2Cl_2). The catalytic efficiency of Ni(II)cyclam was investigated in most detail [441].

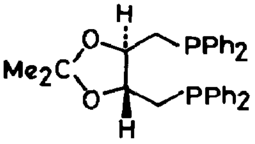


216a; cyclam

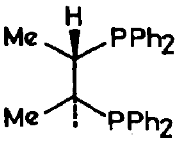
Platinum(II) complexes of the type $PtL_2(CF_3)X$ containing chiral diphosphines (L = (+)-DIOP (217a), (+)-chiraphos (218) or (+)-prophos (219); X = Cl, OH) have been used as catalysts for the asymmetric epoxidation of unfunctionalized olefins like propene or 1-octene with diluted H_2O_2. The best enantiomeric excess was 41% [442].



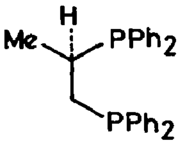
217a; (+)-DIOP



217b; (-)-DIOP

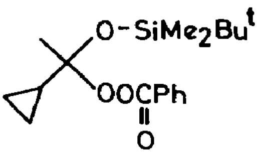


218; (+)-chiraphos



219; (+)-prophos

A new epoxidation method using the siloxyalkyl peroxybenzoate (220) as oxidant and $Cu(OOCCF_3)_2$ as catalyst was described. Regioselective epoxidation of all-trans-farnesol (221) (at position 6,7 or 10,11-depending on the conditions) was accomplished by the intramolecular version of this method [443].



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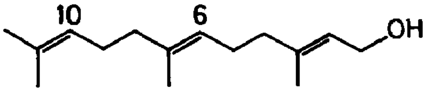


221

See also [304, 381, 387, 445, 449, 471].

c) Oxidation of O-containing Functional Groups

Oxidation of hydroquinones and naphthalenediols to 1,4-quinones with H_2O_2 was performed in the presence of a Cr(VI) compound with the approximate composition $(Bu_3SnO)_2CrO_2$. This catalyst was adsorbed on charcoal and used for the oxidation of dihydrovitamin K_1 to vitamin K_1 [444].

Secondary alcohols were oxidized to ketones and olefins epoxidized by tBuOOH in the presence of substituted ammonium salts of $[MoOBr_4]^-$. The selectivity of the reaction depended on the structure of the substituted ammonium cation: ammonium counterions containing no H gave only alcohol oxidation; ammonium ions containing H exhibited epoxidation activity too [445]. Oxidation of acetylacetone by H_2O_2 is catalyzed by a Mo(VI) complex containing 2,2,4,4-tetrahydroxy-3-pentanone as ligand [446]. Oxidation of secondary alcohols to ketones by tBuOOH is catalyzed by

$[(\text{cetyl})py^+]_3(PMo_{12}O_{40})^{3-}$. Primary hydroxy groups are not affected under such conditions [447]. Aliphatic secondary alcohols were oxidized to ketones by tBuOOH in the presence of $Mo(CO)_6$ and cetylpyridinium chloride with high yields. Primary OH groups were not affected by this procedure [448]. Oxygenation of alkenes and alkanes was performed with N-methylmorpholine N-oxide (MMNO) and catalytic amounts of $[TPP(Mn)]^+(ClO_4)^-$, and stoichiometrically with the isolated complex $[(MNNO)_2(TPP)Mn]^+(ClO_4)^-$. Product distributions for the two oxidation were similar [449].

Oxidation of ascorbic acid by H_2O_2 is catalyzed by the trinuclear complex $[Fe_2CrO(OAc)_6(H_2O)_3]^+$. During oxidation, destruction of the complex also takes place and this leads to a decrease in catalytic activity [450, 451]. 3,5-Di-tert-butylcatechol (126) is oxidized by peracetic acid (actually a mixture of AcOOH, AcOOH, AcOH, H_2O, and H_2O_2) to the lactone (141). It was shown that the yield of (141) is increased by adding Fe(III) acetate as catalyst [452].

Secondary alcohols are oxidized to ketones by N-methylmorpholine N-oxide and a catalytic amount of $RuCl_3.3H_2O$ or $Ru(PPh_3)_3Cl_2$ as catalyst. Spectral studies revealed that a Ru(V)-oxo species is formed <u>in situ</u> which reacts with the substrate in the rate-determining step [453,454]. Alcohols were oxidized to aldehydes or ketones with N-methylmorpholine N-oxide and $(Bu_4N)(RuO_4)$ or $(Pr_4N)(RuO_4)$ as catalysts. The reaction was preferably carried out in CH_2Cl_2 in the presence of molecular sieves (to eliminate water) and resulted in 70-98% yields of the corresponding carbonyl compounds [455]. Secondary alcohols poorly soluble in water could be oxidized with high yields to the corresponding ketones by $NaIO_4$ using RuO_2 as catalyst and a quaternary ammonium salt as phase transfer agent. Care had to be taken, however, to avoid uncontrolled exothermic oxidations [456]. Benzyl alcohols were oxidized selectively to the corresponding benzaldehydes by CCl_4 and Na_2CO_3 at reflux temperature with a combination of $RuCl_3.3H_2O$ and didecyldimethylammonium bromide (DDAB) as catalyst:

$$PhCH_2OH + CCl_4 + Na_2CO_3 \longrightarrow PhCHO + CHCl_3 + NaHCO_3 + NaCl$$

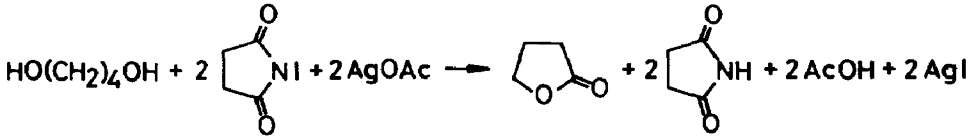
The Ru salt is insoluble in CCl_4 but in the presence of DDAB it gave a clear brown solution; in the absence of DDAB no reaction was observed and the highest reaction rate was obtained at a DDAB : Ru = 2:1 molar ratio [457]. The kinetics of the Ru(III)-catalyzed oxidation of benzyl alcohol by bromamine-T in perchloric acid was determined [458]. Oxidation of 1,2-butanediol and 1,3-butanediol by $[Fe(CN)_6]^{3-}$ using RuO_4 as catalyst was studied. Kinetic results suggest that hydride ion is transferred from the diol to Ru within a complex which then decomposes yielding aldehyde in the slow step [459]. Kinetics of the Ru(III)-catalyzed oxidation of diethylene glycol and ethyl diethylene glycol by N-bromosuccinimide have been investigated. Oxidation products were the corresponding aldehydes [460]. Oxidative cleavage of cyclic allylic alcohols and α,β-unsaturated ketones to diacids or ketoacids by $NaIO_4$ and RuO_4 (as catalyst) was reported. The stereochemistry of the starting materials was conserved as shown for the allylic alcohol (222) [461].

222

The kinetics of the Ru(III)-catalyzed oxidation of aldoses by N-bromosuccinimide in aqueous AcOH was determined [462]. Phenols were oxidized to p-quinones by PhIO using $RuCl_2(PPh_3)_3$ as catalyst. If hydroquinones were oxidized in this way, the Ru complex had little effect on the reaction [463]. The kinetics of oxidation of ascorbic acid to dehydroascorbic acid by H_2O_2 catalyzed by Ru(III)--EDTA was studied. Ruthenium(III) is reduced to ruthenium(II) in the rate-determining step and is reoxidized by H_2O_2 [464].

The kinetics of the OsO_4-catalyzed oxidation of benzylphenylglycolic acids by alkaline $[Fe(CN)_6]^{3-}$ was studied in 30% aqueous tBuOH. The proposed mechanism involves the formation of a complex between Os(VIII) and the acid anion which rapidly decomposes and the reduced Os species is reoxidized by $[Fe(CN)_6]^{3-}$ [465]. Rate constants were determined for the oxidation of benzoin and some of its derivatives by $[Fe(CN)_6]^{3-}$ in the presence of OsO_4 in aqueous tBuOH [466].

Diols are oxidized to lactones with N-iodosuccinimide and silver acetate in refluxing benzene solution according the following stoichiometry:

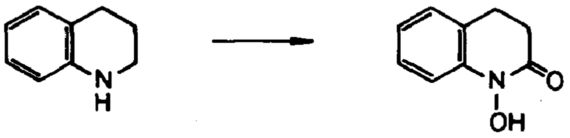


Hydroxy aldehydes are formed as intermediates [467].

See also [341, 380, 471].

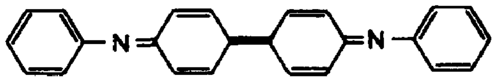
d) Oxidation of N-containing Organic Compounds

Oxidation of 1,2,3,4-tetrahydroquinolines (223, and substituted derivatives) to the corresponding hydroxamic acids (224) was succesfully carried out with H_2O_2 and Na_2WO_4 as catalyst. Isolated yields were between 52-85% [468].



223 **224**

The TcO_4^- ion oxidizes diphenylamine in the presence of Cu^{2+} as catalyst to the diquinonediimine (225). The catalytic activity of Cu^{2+} is probably due to the formation of a complex between this cation and protonated diphenylamine [469].



225

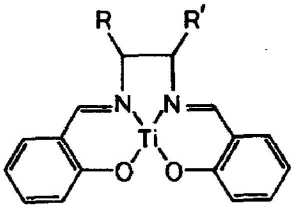
Oxidation of L-catecholamines to the corresponding quinones by H_2O_2 catalyzed by $[Fe(tetpy)(OH)_2]^+$ ions anchored to poly(D-glutamate) or poly(L-glutamate) was carried out. The activity of the two enantiomeric catalysts was practically identical if the iron/polymer ratio was low but catalysts having a higher iron content did show significant enantioselectivity [470]. Anhydrous $FeCl_3$ catalyzes in dry MeCN the demethylation of N,N-dimethylaniline,the epoxidation of olefins and the oxidative cleavage of 1,2-diols by H_2O_2. The products closely parallel those that result from their enzymatic oxidation by cytochrome P 450 [471]. The catalytic effect of Fe(III) on the oxidation of o-dianisidine by $S_2O_8^{2-}$ in the presence of phen was described; this reaction could be used for the determination of iron [472]. Oxidation of 3,5-diaminobenzoic acid dihydrochloride by H_2O_2 is very effectively catalyzed by Fe(III); this reaction can be used for the determination of Fe(III) [473]. (TPP)FeCl and (TPP)MnCl were found to be very effective catalysts for the oxidation of nitroso compounds to nitro compounds by PhIO, even at -78°C. Other oxygen donors like peroxides or NaOCl were less efficient in combination with these two metal porphyrins [474].

The kinetics and mechanism of oxidation of murexide by periodate catalyzed by K_2IrCl_6 was studied [475].

See also [364, 411, 416].

e) Oxidation of P-, S-, or Se-containing Organic Compounds

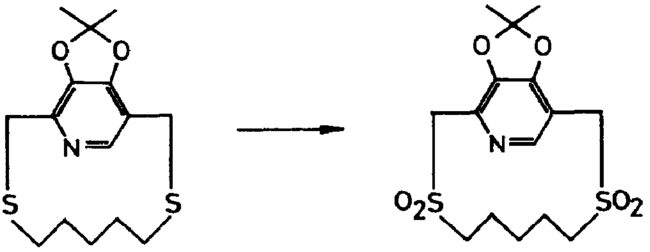
Cyclopropyl phenyl sulfide was oxidized to the corresponding sulfoxide by tBuOOH with 73% chemical yield and 95% o.y. using a catalyst formed in situ from $Ti(OPr^i)_4$, (R,R)-diethyl tartrate, and H_2O in CH_2Cl_2 [476], The binuclear Ti(IV) complex Cl(L)TiOTi(L)Cl (L = N,N'-disalicylidene-(R,R)-cyclohexanediamine) catalyzes asymmetric oxidation of PhSMe with Ph_3COOH to give the corresponding (R)-sulfoxide with 53% o.y. Enantioselectivity of the reaction is highly solvent dependent, the best result was obtained in MeOH [477]. Thioanisole was oxidized by H_2O_2 in the presence of the chiral Ti complexes (226; R = R' = H,Me,Ph; RR' = $(CH_2)_4$ or their $HClO_4$ adducts. Low enantiomeric excesses of PhS(O)Me were obtained [478].



226

The rates of oxidation to sulfones of three sulfoxides, Bu_2SO, PhMeSO, and Ph_2SO, with H_2O_2 in the presence of catalytic amounts of $MoO_2(acac)_2$ have been measured in EtOH [479].

The dithiapyridinophane (227) was oxidized at 60-85°C with H_2O_2 in the presence of $Na_2WO_4 \cdot 2H_2O$ mainly to the disulfone (228); the corresponding monoxide, dioxide and trioxide were formed in minor amounts as byproducts [480].



227 228

Sulfur or selenium derivatives of pentacovalent phosphorus like Ph_3PS or $(EtO)_2PhPSe$ could be transformed into the corresponding oxides by oxidation with $(Bu_4N)^+(IO_4)^-$ and (TPP)MnCl as catalyst. Yields were further improved by the addition of imidazole [481]. Oxidation of the selenides (229) with the Sharpless reagent (tBuOOH + $Ti(OPr^i)_4$ + diisopropyltartrate) afforded the corresponding selenoxides (230) with moderate optical yields (18-40%) [482].

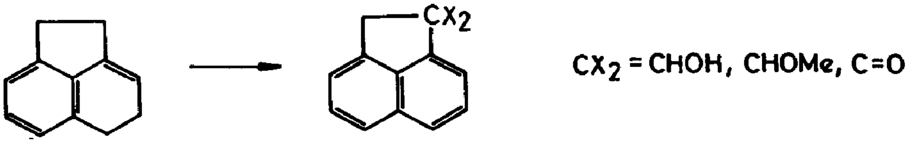
X = H, OMe

229 230

6. Stoichiometric Oxidation of Organic Compounds with High Valent Transition Metal Complexes

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

The kinetics and mechanism of the oxidation of both saturated and unsaturated cyclic hydrocarbons by $Ce(ClO_4)_4$ were studied [483]. Oxidation of carboxylic acids by Ce(IV) involves the formation of an intermediate complex the decomposition of which is rate determining [484]. Cerium(IV) in aqueous methanesulfonic acid was found to be a useful reagent for the oxidation of alkylaromatic or polycyclic aromatic compounds to the corresponding aldehydes, ketones or quinones. The resulting Ce(III) solution could be reoxidized electrolytically [485]. Oxidation of anthracene with $Ce(OOCCF_3)_4$ in alcohols as solvents gave anthraquinone and 9-alkoxyanthracenes. Yield of alkoxylation was highest in the case of MeOH and decreased with increasing molecular weight and in the case of secondary or tertiary alcohols [486]. Oxidation of (231) and (232) with Ce^{4+} yields different products although both reactions proceed by a SET-mechanism. This suggests that the two substrates are transformed into different radical cations by electron abstraction [487].



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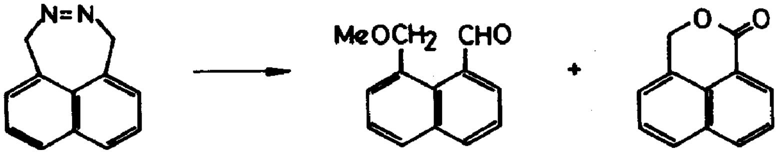
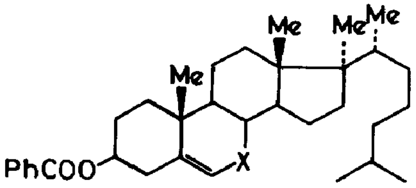


232

Oxidation of benzylic hydrocarbons, e.g. PhEt, Ph_2CH_2 etc. in benzene with pyridinium chlorochromate gave the corresponding carbonyl compounds in 60-88% yield [487a]. Methyl trans-2-octadecenoate was oxidized at the allylic position by CrO_3 in $AcOH-Ac_2O$-benzene to give trans-$Me(CH_2)_{13}COCH{=}CHCOOMe$ with 75% yield [488]. Pyridinium chlorochromate in refluxing CH_2Cl_2 was an effective reagent for allylic and benzylic oxidations of activated methylene groups to yield the corresponding ketones; e.g. (233a) was oxidized to (233b) with 54% yield [489].



233 a, X = CH_2

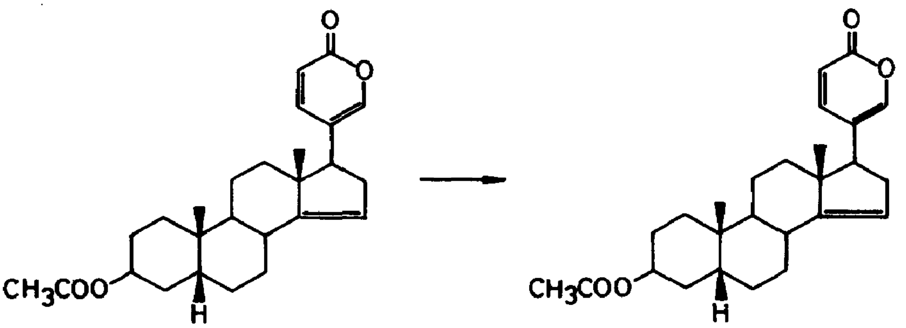
233 b, X = CO

Polycyclic hydrocarbons were oxidized by CrO_3 in CH_2Cl_2/AcOH/Ac_2O to alcohols or ketones. Thus, for example, 5α-androstane (234) was converted to (235) in 47% yield [490].

234

235

Olefin (236) could be oxidized in the allylic position to ketone (237) with CrO_3-$(py)_2$ complex in methylene chloride in 41% yield [491].

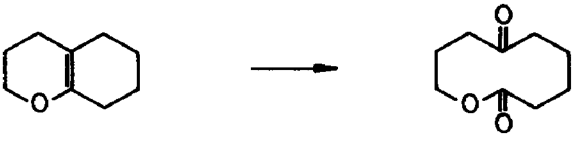


236

237

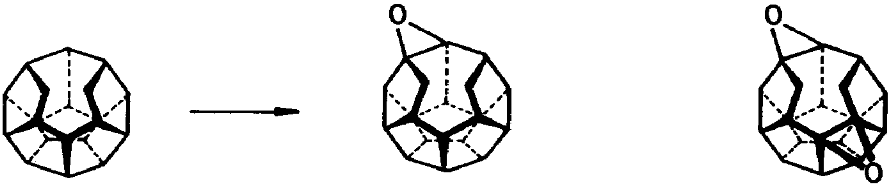
Pyridinium chlorochromate has been found to be a selective reagent for the oxidative cleavage of enol ethers to esters (e.g. 238) or keto lactones (e.g. 239) in high yields [492].

238



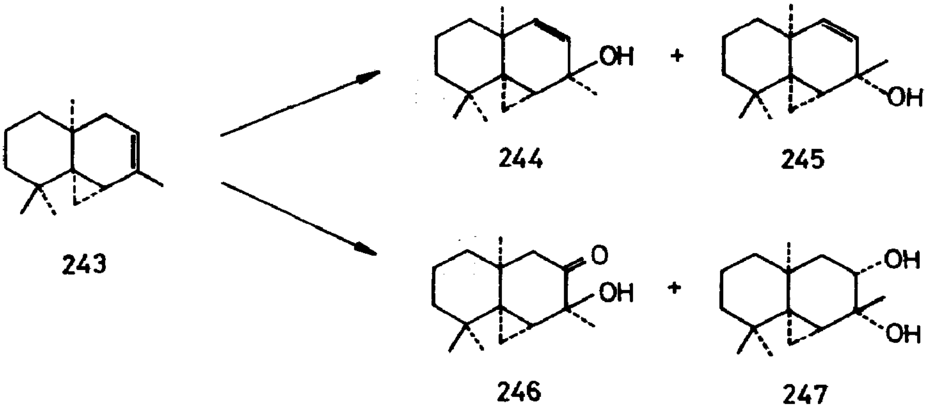
239

Secododecahedrene (240) was transformed by Na_2CrO_4 and $AcOH/Ac_2O$ regiospecifically into the diepoxide (242). The mono-epoxide (241) is an intermediate of this unusual reaction [493].



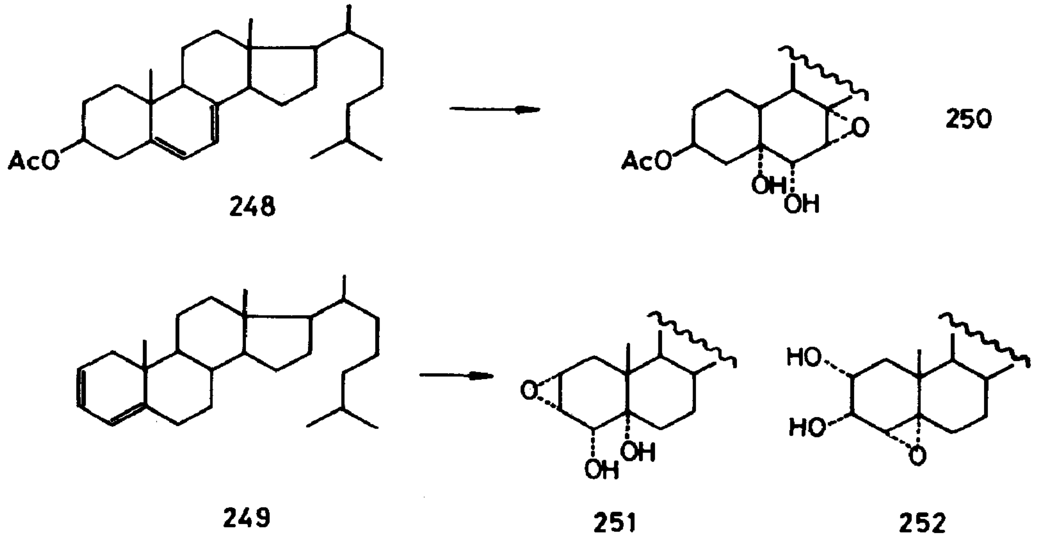
240 **241** **242**

Oxidation of carboxylic acids by $(MeBu_3N)(MnO_4)$ shows general acid catalysis, the carboxylic acid being at the same time both reducing agent and catalyst. A probable explanation of this can be the intermediate formation of permanganic acid as a very active oxidizing agent [494]. The kinetics and mechanism of the oxidation of unsaturated carboxylic acids by $(MeBu_3N)(MnO_4)$ has been studied in CH_2Cl_2 solutions. It was proposed that the reaction is initiated by the formation of an olefin-Mn π-complex which then rearranges into a Mn(V) cyclic diester and then undergoes a rapid (free radical)reduction to Mn(III) [495]. The kinetics of oxidation of C_2-C_5 carboxylic acids by $KMnO_4$ in aqueous H_2SO_4 have been studied. $HMnO_4$ was proposed to be the reactive species [496]. The kinetic isotope effect of ^{14}C in the oxidation of $EtCOO^-$ with $KMnO_4$ (at the α- and β-carbon atoms), as well as that of T in $CH_3CHTCOO^-$ in the same reaction was determined [497]. Potassium permanganate supported on silica gel was found to be an effective reagent for the oxidative fission of C=C double bonds at room temperature. The reaction could be performed in a chromatographic column [498]. Oxidation of thujopsene (243) with $KMnO_4$ results in the formation of several neutral products. In dry acetone (244) and (245), in aqueous acetone (246) and (247) are formed as main products [499].



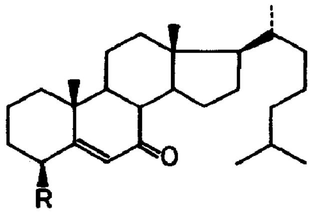
243 244 245 246 247

Oxidation of the steroidal dienes (248) and (249) with $KMnO_4$-$NaIO_4$ gave the epoxydiols (250) and (251,252), respectively [500].



248 250 249 251 252

Oxidation of di- and trisubstituted olefins with Mn(III) acetate in the presence of α-cyanoacetamide gave a wide range of products including butenolides, butenamides, pyrrolones, and pyrrolidones. These reactions also produced glycols or ketones by direct oxidation of the olefins [501]. The mechanism of oxidation of alkenes with Mn(III) acetate in the presence of AcOH yielding lactones and 1,2-diacetates has been investigated. Three distinct processes were identified [502]. Cholestenone (253; R = H) was oxidized by $Mn(OAc)_3$ in $EtCOOH-(EtCO)_2O$ to give the lactone (254) and the esters (253; R = AcO, EtCOO) [503].



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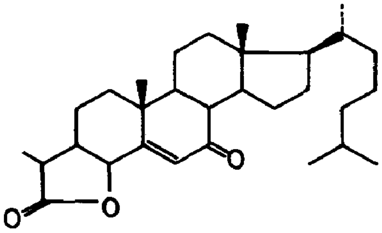
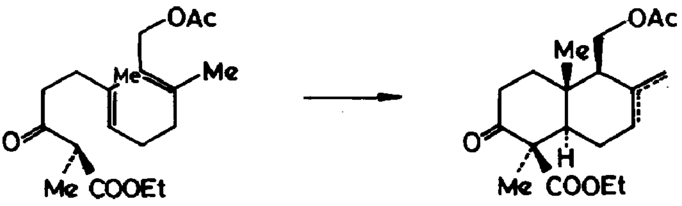


254

Oxidative cyclization of unsaturated β-ketoacids, β-ketoesters and malonic acids with $Mn(OAc)_3 \cdot 2H_2O$ has been applied for the preparation of several polycyclic compounds like (255) and (256). The new rings were formed either through cations [504] or radicals [505] as intermediates.



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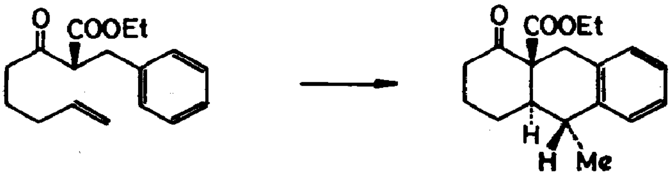
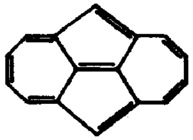


256

The complexes LMnO (L = tetra-*p*-methoxyphenyl or tetra-*p*--methoxycarbonylphenyl porphyrinato) prepared from LMnCl with PhIO, oxidize hydrocarbons [506].

Oxidation of 9,10-dialkylanthracenes with $[(phen)_3Fe](PF_6)_3$ has been investigated. Oxidation took place mainly at the alkyl groups and yielded hydroxymethyl and aldehyde derivatives [507]. The oxidation of Illinois No.6 coal proceeded readily with Ru(VIII) to provide a mixture of aliphatic and aromatic carboxylic acids [508]. The selective cleavage of the olefinic C=C bond of hydroxyaryl alkenes by RuO_4 was studied. Whereas phenols were rapidly oxidized with fragmentation, the aromatic nuclei of their O-trifluoroacetates were unaffected under dry conditions [509]. The Ru(VI) complex *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2O_2]^{2+}$ rapidly oxidized organic compounds with unactivated C-H and C=C bonds at room temperature in MeCN solution; for example cyclohexane was oxidized to cyclohexanone or styrene to benzaldehyde and styrene oxide [510].

Oxidation of the nonbenzenoid aromatic hydrocarbon isopyrene (257) with OsO_4 gave the *cis*-1,2-dihydroxy compound (258). Conversion of (257) into (258), albeit in lower yield, was also achieved with $KMnO_4$ under phase-transfer conditions [511].



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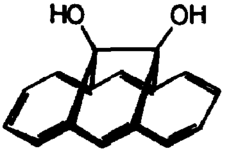
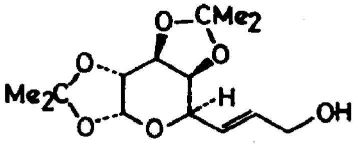


258

Osmylation of unsaturated carbohydrate derivatives like (259) with OsO_4 resulted in the preparation of synthetically useful octose derivatives e.g. (260) [512].



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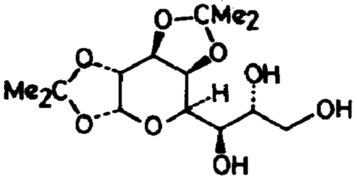
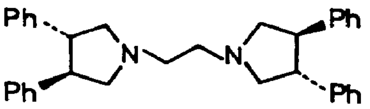


260

Enantioselective cis dihydroxylation of di- or trisubstituted trans-olefins was achieved by using OsO_4 in the presence of the chiral amine (261). Since both enantiomers of (261) are readily available, this method allows the synthesis of both enantiomers of the diols [513].



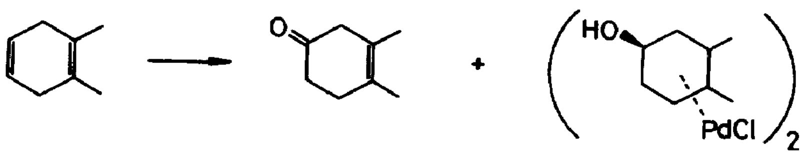
261

Oxidation of p-xylene with Co(III)-acetate at 120°C produces 4-methylbenzaldehyde, 4-methylbenzyl alcohol and 4-methylbenzyl acetate in about 50% total yield. Addition of water decreases, addition of p-toluic acid increases the yield of oxidized products [514].

Hydrocarbons (even methane) could be oxidized to trifluoroacetates using $Pd(OAc)_2$ as oxidant in CF_3COOH as solvent at 80°C:

$$\text{R-H} + \text{Pd(OAc)}_2 \xrightarrow{\text{CF}_3\text{COOH}} \text{R-OOCCF}_3 + \text{Pd(O)}$$

Since esters can be hydrolyzed to alcohols the overall reaction can be regarded as hydroxylation of a hydrocarbon. For p-xylene and toluene, attack on the ring rather than the benzylic position accounted for 90-97% of the monotrifluoroacetate esters suggesting that radical pathways are not involved in the reaction. Using $K_2S_2O_8$ as cooxidant, the oxidation could be made catalytic in Pd(II) [515]. Oxidation of toluene, p-xylene, mesitylene, and durene by Pd(II) was examined in CF_3COOH and AcOH-NaOAc. Two mechanisms were proposed [516]. 1,2-Dimethyl-1,4-cyclohexadiene (262) reacts with $(MeCN)_2PdCl_2$ and $CuCl_2$ in aqueous acetone at 20°C in the presence of $NaHCO_3$ to give the π-allyl Pd complex (264) and the Wacker oxidation product (263) [517].



262 263 264

Saturated carboxylic acids having H at the α carbon atom are oxidized by $CuSO_4$ under hydrothermal conditions; CO_2 is evolved and lower carboxylic acids and ketones are formed. Metallic Cu precipitates [518]. Oxidation of unsaturated β-keto esters like (265) with $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ leads to bicyclic products such as (266). This oxidative cyclization proceeds by a free radical mechanism and both oxidants act by abstracting hydrogen from a tertiary carbon atom [519].

265 266

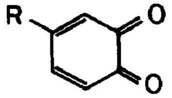
See also [548, 567, 597, 598].

b) Epoxidation of Olefins

A peroxo-molybdenum complex prepared from $(cetylpyridinium)_3(PMo_{12}O_{40})$ and aqueous H_2O_2 was used as oxidant for the epoxidation of olefins, the oxidation of alcohols to the corresponding carbonyl compounds, and the oxidation of diols to lactones. The used oxidant could be partly regenerated with H_2O_2 [520]. The Ru(V) oxoalkyl $(Me_3SiCH_2)_3Ru(O)Ru(O)(CH_2SiMe_3)_3$ reacts stoichiometrically with propene to give epoxide [521]. The Pd superoxo complexes formed from $Pd(OAc)_2$ or $Pd(OOCEt)_2$ and H_2O_2 in chloroform oxidize ethene to ethylene oxide and propene to propylene oxide and acetone. Rates of oxidation are rather high [522].

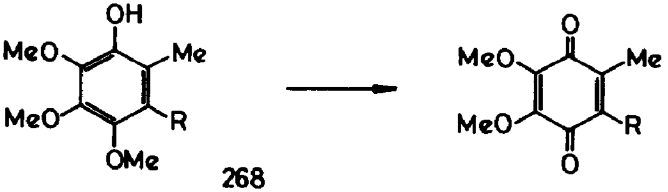
c) Oxidation of O-containing Functional Groups

The ortho-benzoquinones (267, R = CH=CHCOOH, CH_2CH_2COOH, CH_2CH_2COOMe, $CH_2CH(NH_2)COOH$) were prepared by ceric ammonium nitrate oxidation of the corresponding catechols [523].



267

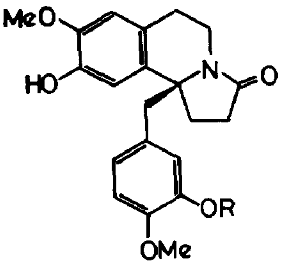
Oxidation of (268, R = $(CH_2CH{=}CMeCH_2)_9H$) with $Ce(NH_4)_2(NO_3)_6$, preferably in the presence of 2,6-pyridinedicarboxylic acid, gave the corresponding ubiquinone (269) in 85% yield [524].



268 **269**

Dihydroxy fumaric acid is oxidized by U(VI) [525].

The kinetics of oxidation of several diols and polyols with vanadium(V) have been studied in perchloric acid. The results supported $V(OH)_2^{3+}$ as the main oxidizing species [526]. Oxidation of acetoin with vanadium(V) in $HClO_4$ solution was found to be first order in V and acetoin, and second order in H^+. Formation of a radical by H atom transfer in the decomposition of an acetoin - vanadium(V) complex was suggested as the rate-determining step [527]. Oxidation of phenols (270) with VOF_3 gave the coupling products (271) in 63-67% yield [528].



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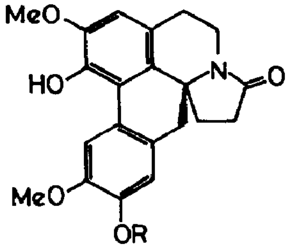
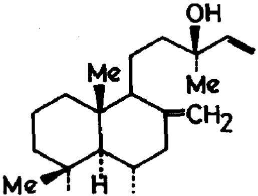


271

R = H, Me

Rate constants were determined for the oxidation of L-(+)-tartaric acid with $K_2Cr_2O_7$ in acid medium. Formation of an intermediate Cr(V) species was detected spectrophotometrically [529]. The kinetics of oxidation of α-hydroxy acids by acidic dichromate has been determined. A reaction path involving the formation of a cyclic chromate ester which decomposes in the rate-limiting step by oxidative decarboxylation, was suggested [530]. Oxidation of ascorbate by Cr(VI) was studied by EPR and relatively long-lived Cr(V) species were identified [531]. The catalytic effect of carboxylic acids on the oxidation of linalool to citrals with $(NH_4)_2Cr_2O_7 + H_2SO_4 + H_2O$ in benzene was studied. The most efficient carboxylic acid was tBuCOOH [532]. The oxidation of acetaldehyde to acetic acid by Cr(VI) in aqueous $HClO_4^-$ was found to be first order in substrate, $HCrO_4^-$, and H^+ [533]. Oxidation of larixol (272) by $Na_2Cr_2O_7 + H_2SO_4$ in AcOH gave among other products (273; two steroisomers) and (274) [534].



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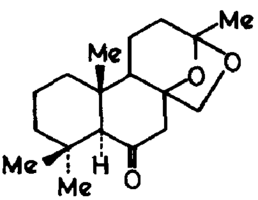

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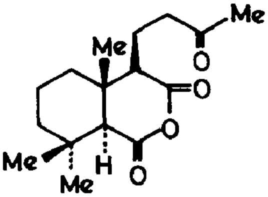
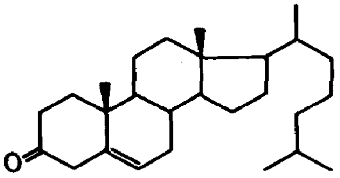


274

Methyl esters may be prepared by oxidizing aldehydes and an excess of MeOH in dry THF by pyridinium dichromate. In fact, methyl hemiacetals are being oxidized under such conditions [535]. Pyridinium bromochromate was found to be an efficient oxidant for alcohols; benzyl alcohol was converted to benzaldehyde with 78% yield [536]. Quinolinium chlorochromate selectively oxidized primary alcohols in the presence of secondary alcohols; if longer reaction times were used, also the secondary alcohols were oxidized to the corresponding carbonyl compounds [537, 538]. Oxidation of cholesterol with pyridinium chlorochromate gave ketone (275) [539].

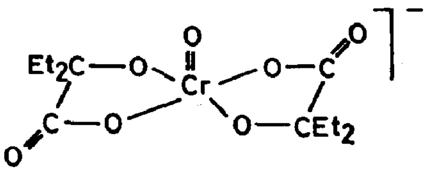


275

Oxidative rearrangement of enynols (e.g. 276) induced by pyridinium dichromate was employed for the synthesis of enynones (277). Good yields could be achieved only in the case of cyclic alcohols [540].

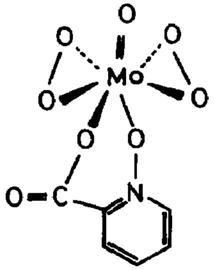
276 **277**

Ascorbic acid is rapidly oxidized to dehydroascorbic acid by the Cr(V) chelate (278) in solutions buffered by the ligand acid. Oxidation proceeds by single-electron steps [541].



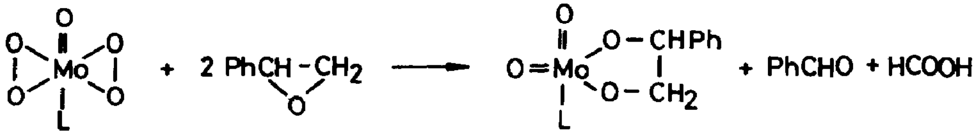
278

The kinetics of oxidation of ascorbic acid by molybdozirconophosphoric acid was determined [542]. The Mo-picolinate N-oxido complex (279) oxidizes alcohols in dichloroethane solution to the corresponding carbonyl compounds at 50°C with very high yields. This oxidant is equally effective for primary and secondary alcohols; in the case of geraniol, double-bond epoxidation is a competing reaction [543].



279

Styrene oxide is oxidized by the diperoxomolybdenum(VI) complex (280, L = HMPA) to benzaldehyde and formic acid according to the following stoichiometry [544]:



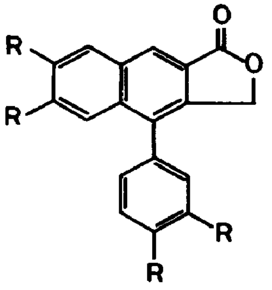
280

The kinetics of oxidation of α-hydroxy acids by Mn(III) were determined. The order of reactivity was benzilic > mandelic > lactic acid [545]. Oxidative cyclization of ω-unsaturated-β-dicarbonyl compounds like (281) with Mn(III) acetate affords 2-substituted phenols (282). If the terminal carbon atom of the alkene is substituted by alkyl groups, the ring closure leads to cyclopentanone derivatives with low yields [546].

281

282

The initial rate of oxidation of sodium hydrogen tartrate by $KMnO_4$ and the decomposition of the intermediate Mn(III) species was studied [547]. Stable solutions of Mn_2O_7 in CCl_4 have been prepared and used for the oxidation of organic compounds between -20 and -80°C. Primary alcohols were oxidized to carboxylic acids, secondary alcohols to ketones, olefins to carboxylic acids (with rupture of the C=C bond) and ethers to esters or lactones (transformation of the α-methylene group into a carbonyl function). Yields were generally high (70-90%) [548]. Bis(pyridine)silver permanganate has been found to be a useful oxidant for the preparation of 1-phenylnaphthalene lactones (283; R,R = OMe, OMe or OCH_2O groups) from the corresponding diols [549].



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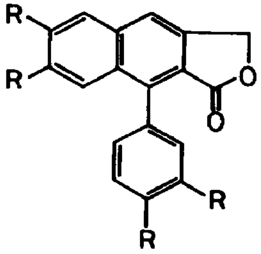
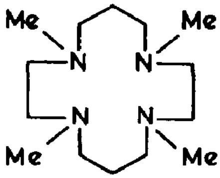


283b

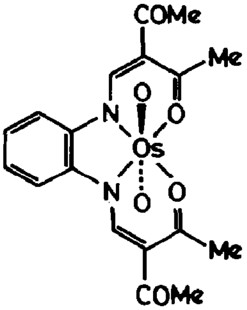
Kinetic and spectroscopic evidence was reported for the formation of an intermediate Fe(III) oxalate-ascorbate complex during the oxidation of L-ascorbic acid by $K_3[Fe(C_2O_4)_3]$ [550].

The kinetics of oxidation of alcohols by $[(bpy)_2(py)Ru(O)]^{2+}$ has been studied. The reactions were first order in alcohol and in oxidant. Spectral evidence and isotope data suggested that oxidation occured by a two-electron, hydride transfer [552]. Primary alcohols are oxidized to aldehydes by cis-$[Ru(bpy)_2(L)(O)]^{2+}$ complexes (L = PPh_3, PEt_3) in aqueous solution. More hydrophobic alcohols are oxidized faster which suggests that prior to oxidation the alcohol hydrophobically associates with the cis-phosphine ligand, thus increasing the concentration of the alcohol in the vicinity of the oxo site [553]. The Ru(VI) complex $[Ru(TMC)(O)_2](PF_6)_2$ oxidizes benzyl alcohol to benzaldehyde and also catalyzes with low turnover numbers the oxidation of benzyl alcohol with O_2 to benzaldehyde. The Ru(IV) complex $[Ru(TMC)O(MeCN)](ClO_4)_2$ acts similarly but is a weaker oxidant [554].



286; TMC

The Os(VI) complex (287) oxidizes benzyl alcohol to benzaldehyde in the presence of PPh_3. In the absence of PPh_3 no reaction occurs, the actual oxidant is the Os(IV) complex (288; L = Ph_3PO) which is formed from (287) and PPh_3 [555].



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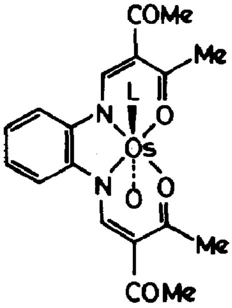
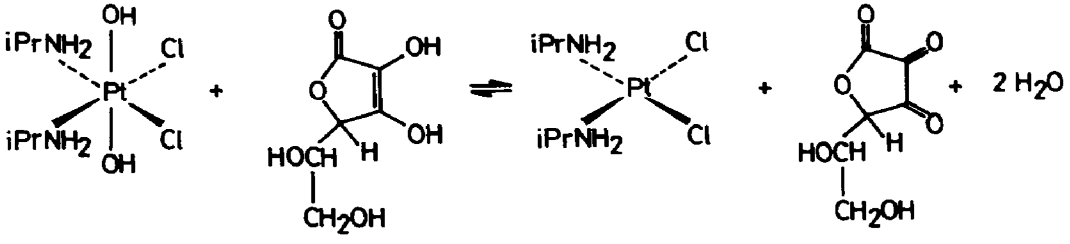


288

Oxidation of formate by 12-tungstatocobaltate(III) is catalyzed by alkali metal cations [556]. Oxidation of 2,6-disubstituted phenols by (py)(salen)$Co(O_2)$ was studied in $CHCl_3$ and MeOH. The composition of products depended on the solvent used [557].

The rates of oxidation of benzaldehyde and six substituted benzaldehydes by Ni(III) were measured in aqueous AcOH. Homolytic cleavage of the aldehydic C-H bond was proposed as the slow step [558]. The kinetics of oxidation of some aliphatic alcohols by a Ni(IV)-periodate complex has been studied. A mechanism involving complex formation between Ni(IV) and the alcohol followed by its dissociation in the rate determining step was suggested [559].

The anti-cancer drug platinum complex (289) oxidizes ascorbic acid to dehydroascorbic acid in an equilibrium reaction. A two-electron redox process has been proposed for this reaction [560].



289

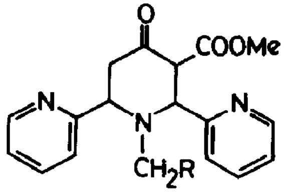
The kinetics and mechanism of oxidation of D-fructose by py_4Cu^{2+} in the presence of free py were studied. An enediol anion was proposed as the reacting species and the rate of enolization as the rate determining step [561]. The oxidative coupling of 2,6-dimethylphenol by Cu(II) complexes of polystyrene-bound 4-(N,N-dimethylamino)pyridine was studied. The selectivity for polyphenylene oxide formation exceeded 95% [562].

Succinic acid, several α-hydroxy acids (lactic acid, malic acid, glycolic acid, and tartaric acid), and some 1,2-glycols were oxidized with Ag(II) perchlorate in acidic media. The carboxylic acids furnished CO_2 and organic products containing one carbon atom less than the substrate, and glycols were oxidized to the corresponding aldehydes. The oxidations were first order both in Ag(II) and substrate [563].

See also [400].

d) Oxidation of N-containing Organic Compounds

The kinetics of oxidation of nitroanilines with Ce(IV) in aqueous perchloric acid was determined [564]. The oxidation of oxipiperidinecarboxylate esters (290; R = Ph, 2-pyridyl) by $Ce(SO_4)_2$ gave (291) and the dehydrogenation products (292) and (293) [565].



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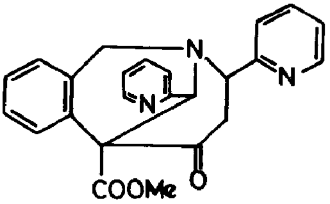

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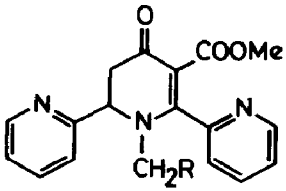

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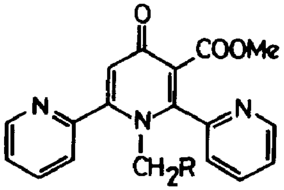
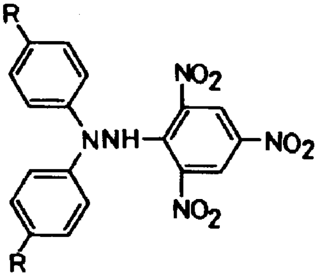


293

Kinetics of oxidative deamination-decarboxylation of L-proline and L-hydroxyproline by vanadium(V) was studied and a mechanism was proposed [566].

The kinetics of oxidation of <u>trans</u>-stilbene and indene by Cr(VI) and vanadium(V) were determined [567]. Oxidation of aromatic primary amines by CrO_2Cl_2 in CCl_4 or $CHCl_3$ resulted in the formation of intermediate solid adducts, which on hydrolysis gave azobenzenes, 1,4-benzoquinones and 1,4-benzoquinone derivatives [568]. Magnetic and IR measurements revealed that the adducts contain Cr(IV) with 1,4-benzoquinone imines and di-imines as ligands [569].

Oxidation of glycine by permanganate ion in aqueous phosphate buffers proceeds by a noncatalytic and a catalytic route in which colloidal MnO_2 formed as a reaction product is the catalyst. Based on kinetic experiments mechanisms for both reactions paths were suggested [570]. The kinetics and mechanism of the permanganate ion oxidation of different 3-pyridinyl-2-propenoates has been studied. The reaction was found to be first order both in substrate and oxidant [571]. The hydrazines (294; R = H, NO_2) were oxidized to the corresponding hydrazils (295) by $KMnO_4$ in CH_2Cl_2 in the presence of Bu_4NBr [572].



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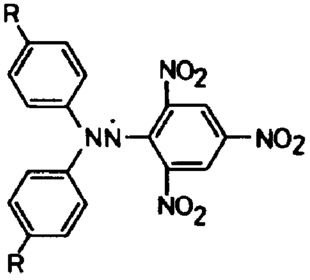
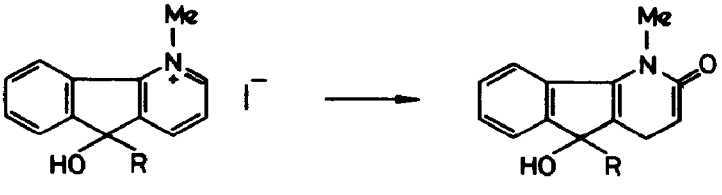


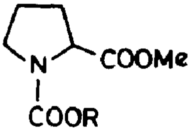
295

Oxidation of diphenylamines by alkaline $[Fe(CN)_6]^{3-}$ in aqueous MeOH is first order in oxidant and substrate. Diphenylaminyl radicals are formed as intermediates which can be detected by ESR spectroscopy [573]. Oxidation of benzylamines with alkaline hexacyanoferrate was also found to be first order in both substrate and oxidant. A radical intermediate was characterized by ESR spectroscopy [574]. Oxidation products of PhNRR′ (R = Me,Et; R′ = H,R) were characterized as PhNRCHO (R = H,Me) [575]. Oxidation of pyridinium salts by $K_3Fe(CN)_6$ gave the corresponding 2-pyridones; thus for example azafluorenones (297) were prepared from azafluorene salts (296) [576].



296 297

N-Alkylamides containing a donor group α or β to the amide N or a donor alkyl function in the acyl group were oxidized smoothly by RuO_4 to the corresponding imides [577]. N-Alkyllactams were oxidized with RuO_4. Four- and eight-membered lactams were oxidized at the exocyclic carbon to produce N-acyllactams, while five- and six-membered lactams underwent endocyclic oxidation to yield cyclic oxidation to yield cyclic imides. Seven-membered lactams yielded mixtures of the two products [578]. The N-protected proline esters (298, R = $PhCH_2$, p-$O_2NC_6H_4$, CCl_3CH_2, and tBu) were oxidized with RuO_4 to the corresponding pyroglutamic esters (299). The group $PhCH_2OOC$ was unstable under these conditions but the other protective groups remained intact and could be removed after oxidation without racemization [579].



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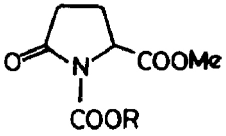
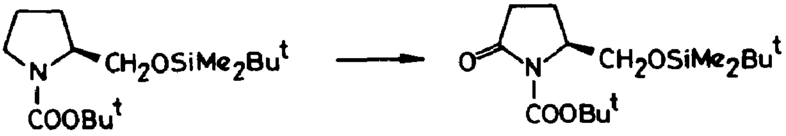


299

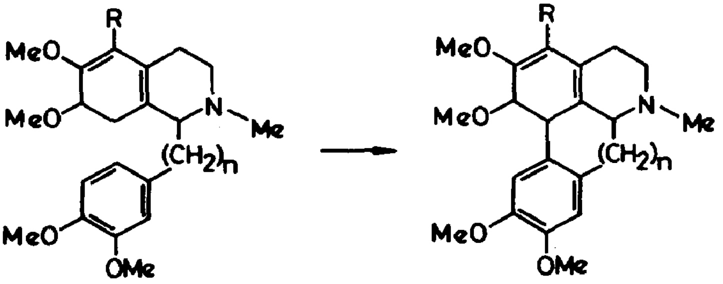
Oxidation of the L-prolinol derivative (300) with RuO_4 gave the pyrrolidone (301) [580].



300

301

Oxidative coupling of phenylalkyltetrahydroisoquinolines (302) to compounds having the aporphine or homoaporphine skeleton (303) was successfully carried out using $Ru(OOCCF_3)_4$ as oxidizing agent. Yields of this biomimetic reaction were around 70% [581].

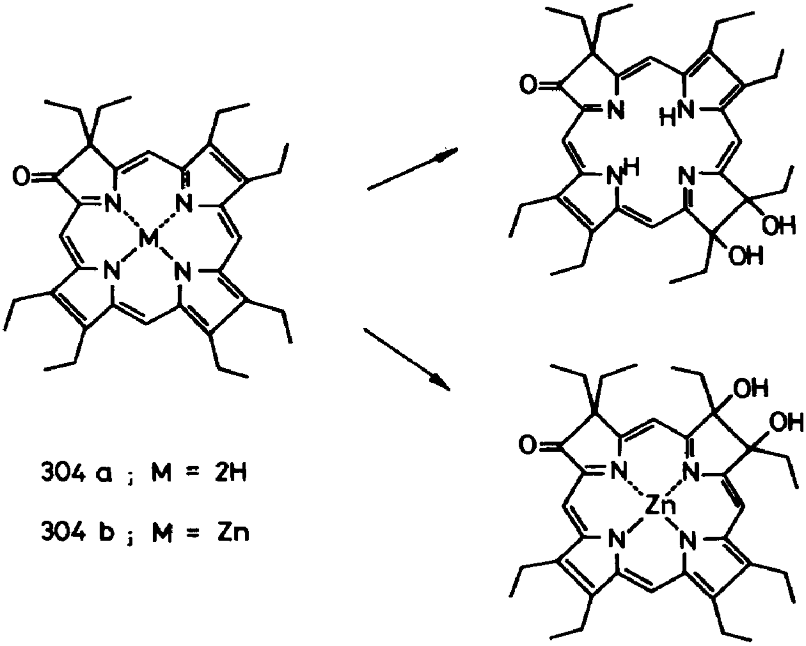


R = H, OMe
n = 1,2

302

303

The oxochlorin (304a) reacts with OsO_4 to yield the bacteriochlorin (305), the Zn complex (304b), however, transforms exlusively into the isobacteriochlorin (306) [582].



304 a ; M = 2H

304 b ; M = Zn

305

306

Oxidation of methylquinolinecarboxylic acids by Ni peroxide in aqueous base gave the corresponding dicarboxylic acids [583].

Oxidation of p-phenylenediamine with $AgNO_3$ in aqueous acid solution showed an induction period; this induction period was not observed if clusters of Ag were present. In dilute solutions the main reaction was first order in both reactants [584]. The kinetics of oxidation of benzaldoxime and some substituted benzaldoximes by Ag(III) have been determined [585].

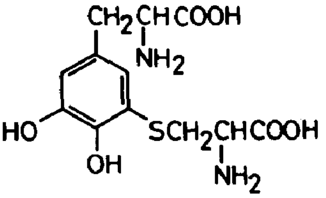
Oxidizing octaethylporphyrin with $Na(AuCl_4)$ transformed one of the ethyl groups into a chlorovinyl (-CH=CHCl) group [586].

See also [487, 589, 596].

e) Oxidation of P-, S-, Si-, or B- containing Organic Compounds

The Fe(II)-porphyrin complex (TPP)Fe reacts with amine N-oxides to form a not fully characterized oxoiron(IV) species which, in turn, oxidizes Ph_3P to Ph_3PO at $-56^{\circ}C$ [587]. The water soluble phosphine $P(C_6H_4SO_3Na)_3$ is oxidized by $RhCl_3.3H_2O$ in water to the corresponding phosphine oxide; the O atom originates from a water molecule and Rh(III) is reduced to Rh(I) [588].

A one-step synthesis for the cysteine-DOPA derivative (307) was achieved by adding cysteine to dopaquinone (308), which was generated *in situ* by oxidation of DOPA with ceric ammonium nitrate in H_2SO_4 [589].



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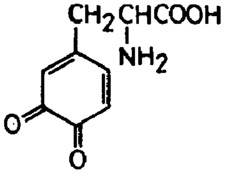


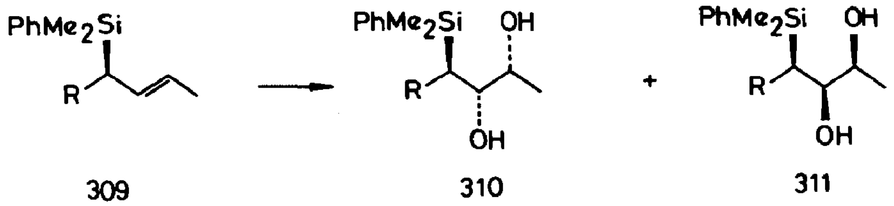
308

Vanadium(V) oxidizes thiols like cystein or glutathion and is reduced to V^{4+}. Vanadium(V)-thioester intermediates were proposed as intermediates [590]. The kinetics of cooxidation of substituted phenyl methyl sulfoxides and oxalic acid with Cr(VI) in the presence of $HClO_4$ was determined. Oxidation products were sulfones and CO_2 [591]. The Cr(V) complex (278) rapidly oxidizes thiolactic acid and cysteine to the corresponding disulfides. Oxidation proceeds by single-electron steps [592]. Dimethylsulfoxide is oxidized by MnO_4^- to dimethylsulfone in the presence of excess pyrophosphate (pyr) according the following stoichiometry:

$$2\ \mathrm{DMSO} + \mathrm{MnO_4^-} + 4\ \mathrm{H^+} \xrightarrow{\mathrm{pyr}} 2\ \mathrm{DMSO_2} + [\mathrm{Mn(pyr)_3}]^{3+} + 2\ \mathrm{H_2O}$$

The rate-determining step is the attack of MnO_4^- at the sulfur atom of DMSO [593]. Oxidation of thioglycolic acid by acidic $[Fe(CN)_6]^{3-}$ gave dithiodiglycolic acid. The reaction rate was first order in substrate, oxidant, and acid [594]. Dimethyl sulfide is oxidized to dimethyl sulfoxide and the latter to dimethyl sulfone by $[(bpy)_2(py)Ru(O)]^{2+}$. Both reactions occur by oxygen atom transfer; the ratio of reaction rates is 120 in favor of sulfide oxidation [595]. The kinetics of oxidation of 2-mercaptopyridine to the corresponding disulfide with $Ag(cyclam)^{2+}$ follows a second-order rate law. Probably a penta-coordinated species is involved in the electron-transfer reactions [596].

Hydroxylation of the chiral allylsilanes (309) with OsO_4 gave the diastereomeric diols (310) and (311); the ratio (310):(311) increased with increasing R group (Me < Pr < Ph). A similar trend was noted in case of the *cis* isomers of (309) [597].



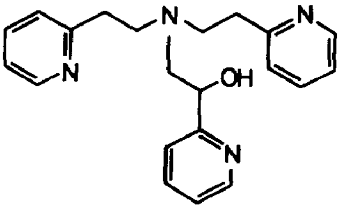
Oxidation of trialkylboranes containing primary alkyl groups with pyridinium chlorochromate in CH_2Cl_2 provides the corresponding aldehydes in good yields. The combination of this procedure with the hydroboration of terminal alkenes represents a direct convenient method for the transformation of alkenes into the corresponding aldehydes [598]. Cycloalkylboranes, prepared by hydroboration of cycloalkenes, were oxidized to ketones with aqueous $H_2Cr_2O_7$ [599].

7. Electrooxidation and Photooxidation

Organic compounds were oxidized by Ce(IV) and the Ce(III) formed regenerated by anodic oxidation. This Ce-catalyzed electrooxidation was applied for the oxidation of dimedone to 3,3-dimethylglutaric acid and of xylenes to tolylaldehydes [600]. Electrochemical oxidation of anthracene to anthraquinone in MeOH solution was shown to be catalyzed by Ce-loaded carbon fiber electrodes [601].

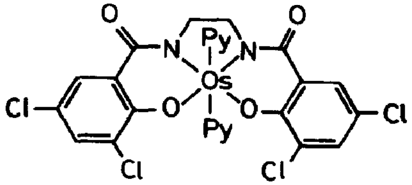
Regeneration of dichromate used in the oxidation of alcohols by anodic oxidation was described. The alcohols oxidized were benzyl alcohol, cinnamyl alcohol, allyl alcohol, cyclohexanol, and borneol [602]. The preparation of benzaldehyde by electrochemical oxidation of toluene in the presence of $MnSO_4$ was described [603].

The Ru(IV)-monooxo complexes *trans*-[Ru(TMC)O(X)](ClO_4) (TMC = 286, X = Cl^-, NCO^-, N_3^-) catalyze the electrooxidation of benzyl alcohol to benzaldehyde. The catalysts gradually lose their activity during the course of electrooxidation; this is due to their decomposition during the period that they are in the Ru(V) oxidation state [604]. The complex $[Ru(III)(L)(H_2O)]^{2+}$ (LH = 312) was shown to catalyze the electrooxidation of iPrOH to acetone and the epoxidation of olefins by PhIO [605].



312

Electrooxidation of alcohols to the corresponding carbonyl compounds in the presence of the Os complex (313) led to the discovery of several catalytic systems which are formed via the degradation of the chelating ligand. The principal species in the catalytically active solutions have been identified [606].



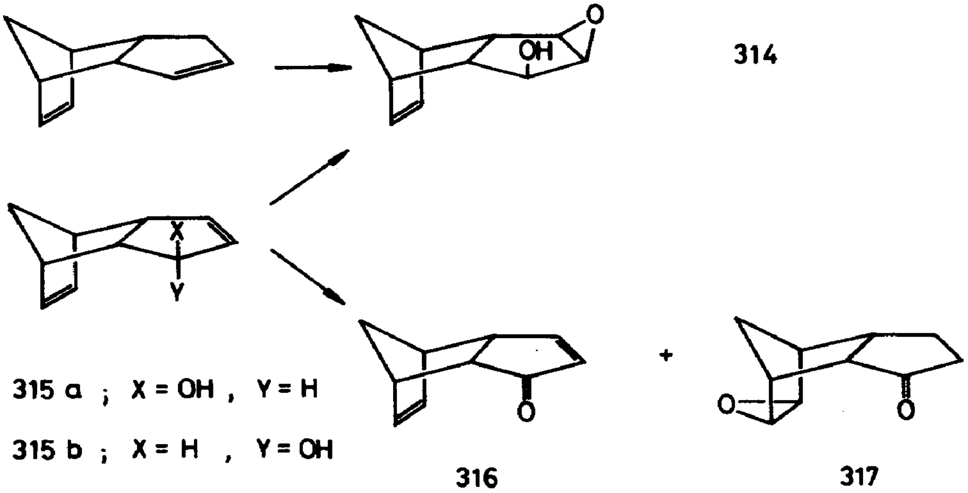
313

Arylthiomethyltrimethylsilanes could be oxidized by indirect electrooxidation using a Ni^{3+}/Ni^{2+} redox couple with cyclam as ligand [607]:

$$Ar\text{-}S\text{-}CH_2\text{-}SiMe_3 + ROH \longrightarrow Ar\text{-}S\text{-}CH_2\text{-}OR + Me_3Si^+ + H^+$$

Oxidation of 1-alkenes to methyl ketones and of cycloalkanes to the corresponding cyclic ketones proceeds smoothly with a catalytic system composed of $Pd(OAc)_2$ and benzoquinone, combined with electrochemical oxidation. Selection of the solvent is important; best results were obtained in MeCN and DMSO [608]. The oxidative properties of Pd(II) ions in the electrooxidation of formic acid on Pd anodes have been discussed [609]. Anodic oxidation of 1,3-cyclohexadiene mediated by $Pd(OAc)_2$ and hydroquinone in acetic acid was shown to produce either trans- or cis-1,4-diacetoxycyclohex-2-ene depending on the conditions [610]. Electrolysis of a propene-saturated AgOAc solution at 0-20°C in the presence of py led to a red Ag(II) complex which reacted with propene to give propylene oxide and Ag(I); ethene and butenes could be oxidized in this way too. Some higher olefins were subjected to such oxidation in presence of an anionic detergent [611].

Oxidation of cycloparaffins with O_2 could be photochemically promoted by ceric ammonium nitrate. The method was especially efficient and selective for the transformation of adamantane into 1-adamantanol [612]. Photooxidation of cyclohexene using air and visible light is catalyzed by titanyl and vanadyl tetraphenylporphyrin monomers and dimers. Oxidation products were epoxy cyclohexene, 2-cyclohexene-1-ol, and 2-cyclohexene-1-one [613]. Photooxygenation of dicyclopentadiene in the presence of Ti(OPr^i)$_4$ gave the *exo*-hydroxy epoxide (314) in 70% yield. Sharpless epoxidation of the allylic alcohols (315) with tBuOOH and VO(acac)$_2$ as catalyst gave quantitatively (314) starting from the *exo*-alcohol (315a) but only dienone (316) and epoxy enone (317) from the *endo*-alcohol (315b) [614].



314

315 a ; X = OH , Y = H

315 b ; X = H , Y = OH

316

317

Photochemical and thermal oxidation of amino acids with Cr(VI) has been studied. In both cases Cr(V) was an intermediate of the reactions [615]. Secondary alcohols were photooxidized to the corresponding ketones in the presence of the tungstate polyanions $[PW_{12}O_{40}]^{3-}$ and $[W_{10}O_{32}]^{4-}$ in homogeneous systems using H_2O/MeCN or MeCN as solvent. Photooxidation of the organic substrates was accompanied by the photoreduction of these polyanions and the catalytic cycle was closed by reoxidation of the reduced polyanions by O_2 [616]. Photocatalytic oxidation of alcohols to the corresponding carbonyl compounds with O_2 in the presence of heteropolytungstates like $[PW_{12}O_{40}]^{3-}$ in acetonitrile or water solution was studied. Strong alcohol precomplexation was observed and high turnover numbers (> 1000) could be achieved [617].

Hydrocarbons could be oxidized with $(TPP)Mn(ClO_4)$ or $(TPP)Mn(IO_4)$ under irradiation. The oxidation proceeded either stoichiometrically when the Mn complex was transformed into (TPP)MnCl or (TPP)MnI, respectively, or catalytically in the presence of excess $(R_4N)(ClO_4)$ or $(R_4N)(IO_4)$. Oxidation products were alcohols, aldehydes, ketones, and epoxides [618]. Photooxidation of phenol by O_2, Fe^{3+}, or $C(NO_2)_4$ is catalyzed by bpy complexes of Cr(III) in aqueous solutions [619]. Photochemical oxidation of ascorbic acid to dehydroascorbic acid is catalyzed by Pt-loaded TiO_2 in an aqueous solution of $(bpy)_3Ru^{2+}$. The system uses ascorbic acid as a sacrificial agent for the efficient evolution of H_2 from water [620]. Photolysis of <u>trans</u>-$[Os^{VI}(TMC)(O)_2]^{2+}$ or of $(Ph_4As)[Os^{VI}(CN)_4(O)_2]$ with PPh_3 or $(PhCH_2)_2S$ in MeCN resulted in the formation of Ph_3PO and $(PhCH_2)_2SO$, respectively [621]. The irradiation of phenol in acetonitrile under O_2 in the presence of chlorocuprates (Cu:Cl = 1:8) gave p-benzoquinone and catechol; the latter compound was the main product [622]. Alkylbenzenes were photooxidized by air at room temperature in the presence of $Pt[NPhNC(S)SMe]_2$ as catalyst precursor. For example, p-xylene was transformed mainly into p-tolyl benzaldehyde; p-methyl benzylalcohol and p-toluic acid were formed in minor amounts [623].

V. Reviews

Recent achievments, trends and prospects in homogeneous catalysis. 45 refs. [624].

Metalloporphyrins as biological and chemical catalysts. 41 refs. [625].

Homogeneous catalysis by metal clusters. 116 refs. [626].

Supported metal catalysts prepared from molecular metal clusters; organometallic surface chemistry. 42 refs. [627].

Catalysis by oxide-supported porphyrins and phthalocyanine complexes. 40 refs. [628].

Study of organometallic complexes of Rh fixed to oxide supports. 38 refs. [629].

Lanthanides in organic synthesis. 200 refs. [630].

Catalyst recycle in homogeneous catalytic reactions. 99 refs. [631].

Surface analogs of metal carbonyl adducts and their possible role in CO hydrogenation. 135 refs. [632].

Advances in hydroformylation catalysis [633].

Advances in the hydroformylation of olefins containing functional groups. 157 refs. [634].

Rhodium complex-catalyzed olefin hydroformylation reaction. 85 refs. [635].

Homogeneous catalysis in water (hydroformylation). 29 refs. [636].

Coal and biomass-based chemicals via carbonylation, hydroformylation, and homologation reactions. 26 refs. [637].

A new route to coordination catalysis by electrogeneration of organo transition metal active species (hydroformylation). 28 refs. [638].

The characterization and catalytic applications of heteronuclear cluster compounds of Fe, Ru, and Os (water gas shift reaction). 82 refs. [639].

Studies on mixed-metal clusters containing Co, Ru, and Rh and on the catalytic reactivity of homogeneous Ru-Rh and Ru-Co systems (MeOH homologation and water gas shift reaction). 63 refs. [640].

Catalytic C-C bond formation by carbonylation of organic substrates (results since 1984). 114 refs. [641].

Phase-transfer reactions catalyzed by metal complexes (reductions, carbonylations). 21 refs. [642].

Homogeneous catalysis of hydrogen isotope exchange. 21 refs. [643].

Activation mechanism of alkanes, arenes, and H_2 in aqueous Pt(II) halide solutions. 41 refs. [644].

Metal-containing polymeric catalysts for hydrogenation. 98 refs. [645].

Homogeneous hydrogenation: stereoselectivity due to intramolecular interactions. 71 refs. [646].

Catalytic asymmetric hydrogenation with homogeneous transition metal complexes. 34 refs. [647].

The use of platinum metal complexes in asymmetric catalysis. 21 refs. [648].

Supported asymmetric hydrogenation catalysts. 86 refs. [649].

Homogeneous catalytic hydrogenation, transfer hydrogenation and nitrobenzene carbonylation reactions with $Ru_3(CO)_{12}$ as catalyst. 24 refs. [650].

Anionic carbonyl clusters as homogeneous and supported catalysts in hydrogenation and transfer hydrogenation reactions. 13 refs. [651].

Activation and selective functionalization of alkanes by some soluble transition metal systems (dehydrogenation). [652].

Activation of H_2 by Ru(II)-chelating phosphine complexes, and activation of O_2 by Ru(II) porphyrin complexes: an update. 47 refs. [653].

Metal-centered oxygen atom transfer reactions. 545 refs. [654].

Autoxidation route of organic compounds through metal-ion and bromide catalysis. 25 refs. [655].

Metalloporphyrins: efficient catalysts for oxidation reactions in two-phase systems. Comparison with biological systems. 38 refs. [656].

Catalytic oxidation and fine chemicals. 19 refs. [657].

Asymmetric oxidation mediated by organometallic species. 47 refs. [658].

Liquid-phase oxidation of aromatic hydrocarbons catalyzed by variable-valence metal ions. 20 ref. [659].

Recent methods for the oxidation of alcohols to carbonyl compounds. 34 refs. [660].

Cerium(IV) oxidation of organic compounds. 255 refs. [661].

Heteropolytungstate complexes as homogeneous oxidatively resistant catalysts for difficult selective organic oxidations. Functionalization of alkanes [662].

Reactions with Mn(III) acetate - oxidations. 144 refs. [663].

The oxidation of organic compounds by active MnO_2. 769 refs. [664].

Direct O atom transfer reactions from O_2 catalyzed by dichlorotetraaquaruthenium and Ru(III)-EDTA ions [665].

Catalytic oxidation of olefins to glycols via O_2 with an osmium-copper system. [666].

Oxidations by Co compounds. 347 refs. [667].

Oxidation of organic compounds with Ni peroxide. 97 refs. [668].

Oxidation using Pd compounds. 110 refs. [669].

Roles of Pd in liquid-phase oxidation. 24 refs. [670].

Selective catalytic oxygenation of hydrocarbons with O_2 at room temperature - a completely inorganic mimic of monooxygenase enzymes (Pd catalysts). [671].

Oxidations of organic compounds catalyzed by Cu- and Co-amine complexes. 68 refs. [672].

Silver carbonate on celite oxidations. 261 refs. [673].

List of Abbreviations

acac	acetylacetonate
AS	Annual Survey of Hydroformylation, Reduction, and Oxidation
BINAP	see Fig.(23)
BPPM	see Fig.(6)
bpy	2,2'-bipyridine
chiraphos	see Fig.(218)
COD	1,5-cyclooctadiene
Co(salen)	see AS 1986, Fig.(169)
Cp	cyclopentadienyl
Cy	cyclohexyl
cyclam	1,4,8,11-tetra-azacyclotetradecane; see Fig.(216a)
DIOP	see Fig.(217)
dipamp	see Fig.(46)
dmgH	dimethylglyoxime
dmpe	bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
dppb	bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$
HMPA	hexamethylphosphoric triamide
NBD	nornbornadiene
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinato
o.y.	optical yield
phen	1,10-phenanthroline
prophos	see Fig.(219)
SIL	silica
st	stearate, $nC_{17}H_{35}COO$
TDCPP	5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato
TDMPP	5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrinato

tetpy	2,2′:6′,2″:6″,2‴-tetrapyridyl
TMC	1,4,8,11-tetramethyl cyclam; see Fig.(286)
TMP	5,10,15,20-tetramesityl porphyrinato
TPP	5,10,15,20-tetraphenylporphyrinato
TPP-Cl-p	5,10,15,20-tetrakis(p-chlorophenyl)porphyrinato
triphos	$PhP(CH_2CH_2PPh_2)_2$
Ts	p-toluenesulfonyl(tosyl), p-$CH_3C_6H_4SO_2$-
TTMPP	5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato
TTPPP	5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrinato

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