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TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION, AND OXIDATION

ANNUAL SURVEY COVERING THE YEAR 1989*

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CONTENTS

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I. THEORETICAL CALCULATIONS

Based on density functional theory a theoretical study has been carried out on the CO dissociation of $HCo(CO)_4$ and the migratory insertion reaction $RCo(CO)_4 \longrightarrow RC(O)Co(CO)_3$ for R = H and CH_3, respectively. Energetics of intermediates and reaction steps involved in the hydroformylation reaction catalyzed by $HCo(CO)_4$ were calculated [1]. Computer-driven molecular graphics and van der Waals energy minimization were used to analyze the addition of H_2 to the major and minor diastereomer precursors for asymmetric catalytic hydrogenation of ethyl N-acetyl-α-amino-cinnamate with $[Rh((S,S)\text{-chiraphos})]^+$. Two of the eight possible modes of H_2 addition appear to be devoid of strong atom-atom interactions [2]. EHMO calculations were carried out on hydrogenation catalysts of the type $H_2MXL_2(C_2H_4)$ (X = Cl,Br,I; L = different ρ-substituted phenyls; M = Rh,Ir) [3].

II. HYDROFORMYLATION AND RELATED REACTIONS OF CO

1. Hydrogenation of CO to Hydrocarbons and to Oxygen-Containing Compounds

The CO hydrogenation activity of clusters $Cp_2Mo_2Fe_2S_2(CO)_8$ and $Cp_2Mo_2Co_2S_3(CO)_4$ supported on Al_2O_3, SiO_2, TiO_2, and MgO was evaluated. The surface compounds, e.g. $C_{5-8}Mo_2Fe_2S_{1.8}$ resulting from thermal decomposition were sulfur-tolerant CO hydrogenation catalysts [4]. The behavior of a $[RhMo_2Cp_3(CO)_6]$ cluster-derived catalyst in CO hydrogenation at 10 bar was studied and compared with a catalyst prepared by conventional impregnation of the support with metal salt solutions [5]. The roles of Co,Rh and Ru carbonyl complexes in the homogeneous hydrogenation of carbon monoxide have been discussed. The prevalence of ionic complexes or the potential for forming such species seem to be common for the most active systems [6].

A bimetallic Fe-Co/Al_2O_3 CO hydrogenation catalyst prepared by impregnation of γ-Al_2O_3 with $Cp(CO)_2Fe\text{-}Co(CO)_4$ showed 44% selectivity in olefin production at 280°C using a 2:1 = H_2:CO mixture at atmospheric pressure [7]. The bimetallic complex $CpFe(CO)_2\text{-}Co(CO)_4$ supported on γ-Al_2O_3 was more active in the hydrogenation of CO to olefins and methane than a similar catalyst prepared from a mixture of $Fe(CO)_5$ and $Co_2(CO)_8$ [8]. Zeolite-entrapped Os carbonyl clusters catalyze CO hydrogenation at 573K and 19 bar to give C_2-C_4 hydrocarbons in high yield [9]. Catalysts for the hydrogenation of CO to hydrocarbons were prepared by supporting osmium carbonyl clusters on MgO. Under CO and H_2 these clusters were transformed at 280-300°C into $[H_3Os_4(CO)_{12}]^-$ which was regarded as the precursor of the catalytically active species [10]. The homogeneous CO reduction catalytic system composed of $Ir_4(CO)_{12}$ and $AlCl_3$ was heterogenized by binding $Ir_4(CO)_{12}$ to a phosphine-functionalized Al_2O_3 or SiO_2 support and reacting the deposited cluster with $AlCl_3$. When a mixture of CO, H_2, and HCl was passed over this catalyst at 75-125°C, CH_4, CH_3Cl, CO_2, and H_2O were formed. In contrast to the homogeneous system, only traces of C_2 products were observed [11].

Rhenium carbonyl, $Re_2(CO)_{10}$, combined with a halide or acetate salt was found to catalyze the synthesis of MeOH and ethylene glycol from CO + H_2 at 700-750 bar and 290°C in N-methylpyrrolidinone as solvent. Lithium chloride was the most effective salt additive. Addition of $Ni(OAc)_2$ increased the formation of ethylene glycol [12]. A promotion effect of mixed halides on homogeneous ruthenium catalysis in direct synthesis of ethanol from H_2 and CO has been found. Thus the addition of PPNI or a hydrogen halide to the $Ru_3(CO)_{12}$-PPNCl system markedly enhanced both the rate of and the selectivity for ethanol formation at 240°C and 340 bar (cold) pressure of $CO:H_2 = 1:1$ [13]. The role of different Ru carbonyl species in the hydrogenation of CO was studied. It was shown that $[HRu_3(CO)_{11}]^-$ was responsible for the reduction of CH_2O to MeOH and $[Ru(CO)_3Cl_3]^-$ was active in the homologation of MeOH to EtOH [14]. In the $Rh(CO)_2(acac)$ + PR_3 (R = nBu,iPr) catalyzed hydrogenation of CO (220°C, 470 bar) the reaction rate and selectivity for ethylene glycol have been found to be much improved by the addition of N bases. In 1,3-dimethyl-2- imidazolidinone as solvent and with Et_3N as added base, ethylene glycol selectivity was higher than 80% [15].

See also [61,77].

2. Hydroformylation

a) Cobalt catalysts

Hydroformylation of *trans*-dodecene-6 at 80°C and 160 bar (CO + H_2) in Et_2O solution yielded a mixture of C_{13} aldehydes, >70% of which were formed from isomerized alkylcobalt carbonyl intermediates. If these aldehydes were prepared from 5-bromododecane and $NaCo(CO)_4$ under the same conditions, <10% isomer formation was observed. This difference underlines the role of alkylcobalt tricarbonyls in the isomerization process [16]. Hydroformylation of nonterminal alkenes was carried out with $Co_2(CO)_8$ + $P(C_{12}H_{25}$-$n)_3$ catalyst at 180°C and 30-45 bar. The product contained 70-74% *n*-alcohols; 5-12% of the alkenes was hydrogenated to alkanes [17]. Mathematical equations and nomograms describing the hydroformylation of C_{11}-C_{14} olefins in the presence of Co-phosphine catalysts were derived based on experimental data. These relationships can be used to optimize the yields of branched- or straight-chain alcohols [18].

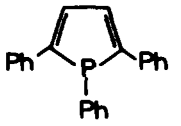
Propene was hydroformylated at 100-140°C and 40-100 bar using the cluster complex $HFeCo_3(CO)_{12}$ as catalyst. The catalyst decomposed under such conditions to $HCo(CO)_4$, $Co_2(CO)_8$, and $Fe(CO)_5$ and catalytic activity was probably due to $HCo(CO)_4$ [19]. The iron-cobalt cluster $(PhCH_2NMe_3)[FeCo_3(CO)_{12}]$ was used as catalyst for the hydroformylation of olefins at 120-160°C and 40-70 bar [20]. Phosphines strongly decreased the rate of the reaction [21]. Bimetallic clusters of the type $(NR_4)[FeCo_3(CO)_{12}]$ with different quaternary ammonium cations have also been tested as catalysts for the hydroformylation of 1-heptene. All complexes were highly active at 120°C and 40 bar [22]. The mixed-metal cluster $Fe_2Co_2(CO)_{11}(PPh)_2$ has been found to catalyze the hydroformylation of 1-pentene in 50-90% yield at 130°C. Based on *in situ* Cylindrical Internal Reflectance FT-IR and product analyses, a true cluster catalysis has been suggested. A *closo* → *nido* polyhedral transformation in the cluster was proposed as the entry point into the catalytic cycle [23].

The mixed-metal clusters $(PhCH_2NMe_3)[MCo_3(CO)_{12}]$ (M = Fe,Ru) were more active as catalysts for the hydroformylation of ethene at 130°C and 39 bar than the clusters $PhCCo_3(CO)_9$, $Co_4(CO)_{10}(PPh)_2$, or $Co_2(CO)_6(PBu_3)_2$ [24]. It was reported that the addition of $Ru_3(CO)_{12}$ in the $Co_2(CO)_8$-catalyzed norbornene hydroformylation not only accelerates the reaction but also improves the selectivity for 2-norbornanecarbaldehyde [25].

b) Rhodium Catalysts

The branched aldehyde isomer is the main product of styrene hydroformylation with $Rh_4(CO)_{12}$ catalyst; its amount decreases with increasing temperature (from 20 to 130°C) and decreasing CO and H_2 partial pressures (from 90 to 6 bar). These results have been rationalized on the basis that the branched alkylrhodium intermediate isomerizes to the linear one and this is favored by high temperature and low pressure [26]. The catalytic deuteroformylation of 1-hexene between 20-100°C and 80-140 bar $CO:D_2$ = 1:1 using $Rh_4(CO)_{12}$ has been studied. Results of MS and ^2H NMR analyses of the products indicated that at high temperatures a β-hydride elimination process occurs which is more significant for the branched than for the linear alkyl complexes thus accounting for the influence of the reaction parameters on the regio- and chemoselectivity of the reaction [27]. A flow diagram for the manufacture of 2-ethylhexanol by hydroformylation of propene with Rh carbonyl catalyst, followed by aldol condensation of the resultant butyraldehyde and hydrogenation of the condensation products was given [28].

The catalytic properties of Rh-phenyldibenzophosphole (DBP) and Rh-triphenylphosphine complexes have been compared by determining the kinetics of propene hydrogenation and hydroformylation. At low CO/H_2 partial pressure ratios the selectivity and the regioselectivity of the DBP complexes - contrary to the PPh_3 complexes - was essentially independent of p(CO) [29]. The influence of various parameters on the rate and product distribution of 1-hexene hydroformylation in the case of a Rh-1,2,5-triphenylphosphole (**1**) system has been studied. The activity and selectivity of the catalyst was independent of the phosphole ligand concentration [30].



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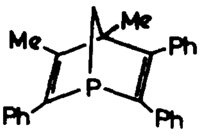
The hydroformylation of 1-hexene has been carried out using *in situ* catalysts generated from $[Rh(CO)_2Cl]_2$, Et_3N and phospholes at 80°C and 20 bar syn gas. The best result in n-heptanal selectivity was 84% with a total yield of aldehydes of 90% using 1,2,5-triphenylphosphole (1) [31]. The phosphanorbornadienes (2) and (3) were successfully employed as ligands in the hydroformylation of alkenes with Rh complexes; the catalysts formed *in situ* were more active than those containing PPh_3 [32].



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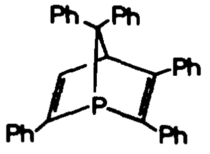

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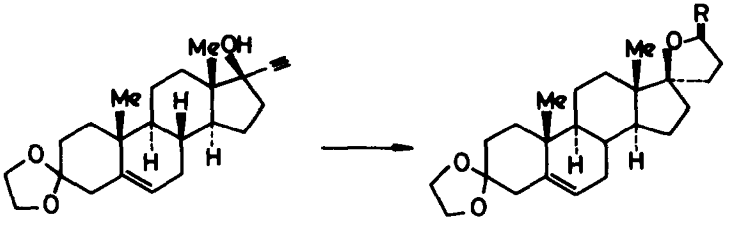
The above catalysts have been found useful also for the selective (80-94%) synthesis of 2-arylpropionaldehydes from styrene and substituted styrenes (*p*-iBu, *m*-PhO) at 25-40°C [33].

The inhibitory effect of α,β-unsaturated aldehydes in the low-pressure hydroformylation of olefins can be remarkably reduced by adding dppb [34]. The synthesis of perfumery chemicals by the hydroformylation of terpenes and other olefins has been examined under mild conditions using phosphine-modified Rh catalysts. The odors of the product aldehydes and their respective alcohols were given [35].

The kinetics of hydroformylation of allyl alcohol using $HRh(CO)(PPh_3)_3$ as catalyst have been investigated at 60-80°C. The rate was first order in catalyst, 1.5 order in H_2 partial pressure and showed a maximum with respect to CO partial pressure and allyl alcohol concentration [36]. A kinetic study of vinyl acetate hydroformylation using $HRh(CO)(PPh_3)_3$ catalyst in the temperature range 50-70°C has been performed. A first order dependence in H_2 and catalyst and a complex dependence in CO and substrate was found [37]. The hydroformylation reaction (15 bar, 80°C, $Rh_2(OAc)_4$, PPh_3) has been applied for the synthesis of lactol (**4**), which was oxidized to the lactone (**5**) with $Ru(PPh_3)_3Cl_2$ and N-methyl-morpholine N-oxide quantitatively [38].



4; R=H,OH **5**; R=O

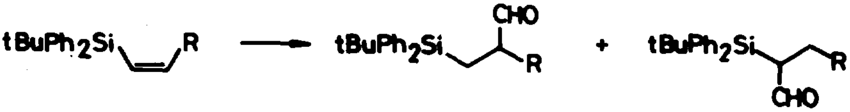
The hydroformylation of 1-vinyl-2-pyrrolidinone at 100°C and 80 bar using $[Rh(NBD)Cl]_2$ + PPh_3 catalyst precursors gave a 2:1 mixture of the branched:linear formyl products [39].

Hydroformylation of oleyl alcohol was carried out at 100°C and 51 bar over a catalyst consisting of the water-soluble Rh complex $HRh(CO)[P(C_6H_4SO_3Na\text{-}m)_3]_3$ dissolved in a film of water supported on a high-surface-area inorganic solid (SiO_2). The reaction took place on the water-organic interface [40]. The water-soluble complexes $HRh(CO)(P)_3$ and $[Rh(\mu\text{-}SR)(CO)(P)]_2$ (P = tris(*m*-sulfophenyl)phosphine; R = tBu, CH_2Ph, Me, Ph, C_6F_5; $(SR)_2$ = SCH_2CH_2S) have been prepared and used as catalysts for the hydroformylation of alkenes in a two-phase system. The dimeric complexes were found to be particularly suitable for this purpose [41]. The dinuclear Rh(I) complexes $Rh_2(SBu^t)_2(CO)_2L_2$ (L = phosphine or phosphite) were used for the low pressure hydroformylation of alkenes with CO + H_2 or CO + H_2O. Using tris(*m*-sulfophenyl)phosphine as ligand 96% selectivity for linear aldehyde was achieved with n-hexene-1 and the catalyst could easily be separated from the reaction product by decantation [42].

Hexene-1 was hydroformylated with the dinuclear Rh complexes $Rh_2(\mu\text{-}SBu^t)_2(Ph_2PXPPh_2)(CO)_2$ as catalysts (X = $(CH_2)_3$, 1,1'-ferrocenyl, 1,1'-ruthenocenyl, and $(CH_2)_4$). The first three complexes showed about the same catalytic activity whereas the complex with X = $(CH_2)_4$ was rather inactive [43]. Hexene-1 was hydroformylated at 80°C and 5 bar CO/H_2 using $\{Rh_2[\mu\text{-}S(CH_2)_3NMe_2]_2(COD)_2\}$ as catalyst precursor. The best result

(87% conversion and 93% linear heptanal) was obtained with a 40/1 molar ratio of PPh_3/Rh-dimer. The rhodium catalyst could be quantitatively recovered from the reaction mixture by adding dilute H_2SO_4 and reused without loss of activity [44]. Asymmetric hydroformylation of styrene by rhodium catalysts modified with aminophosphinephosphinite ligands has been studied. The best results (ee > 30%) were found with (1R,2S)-$PPh_2NMeCHMeCHPhOPPh_2$ and $Me_2C(NMePPh_2)HCH_2OPPh_2$ [45]. The nonchelating phosphine ligands $CH_3Si(CH_2CH_2PPh_2)_3$ (A) and $Si(CH_2CH_2PPh_2)_4$ (B) combined with $Rh(CO)_2(acac)$ have been used in the rhodium-catalyzed batch hydroformylation of 1-butene to yield 83% n-pentanal. In the continuous hydroformylation with ligand A, 88% selectivity in n-pentanal and a slow deactivation of the catalyst in 5 days have been observed [46]. The dinuclear Rh complexes $Rh_2X_2(CO)_n(\mu\text{-}Ph_2PCH_2PH_2)_2$ and $[Rh_2(\mu\text{-}Y)(CO)_n(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ (X,Y = Cl,I,CN; n = 2-4) were tested as catalysts. Under CO and H_2 these complexes catalyze the selective hydrogenation of alkynes to alkenes at low temperatures whereas at somewhat elevated temperatures they act as catalysts for the hydroformylation of olefins. If the latter reaction was performed in MeOH solution, the aldehydes were transformed into ethers and hydrocarbons [47].

Hydroformylation of tricarbonyl(η-styrene)chromium and related compounds using $HRh(CO)(PPh_3)_3$ as catalyst gave the corresponding α-arylaldehydes with high regioselectivity under mild conditions (30-50°C, 1-36 bar CO/H_2). Chiral rhodium and platinum catalysts with (-)-DIOP, (-)-BINAP and (-)-chiraphos gave up to 50% ee of the branched aldehydes [48]. Hydroformylation of t-butyldiphenylsilylalkenes with Z configuration (6) at 80°C using $HRh(CO)(PPh_3)_3$ as catalyst in the presence of a large excess of PPh_3 (50:1) gave β-silylaldehydes (7) with high (>96:4) regioselectivity. No diastereoselection was observed if the group R was a chiral substituent [49].



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c) Other Metals as Catalysts

Ethene hydroformylation in basic media was studied using different Ru compounds as catalysts at 15°C and 75 bar. Alkali halides and iodine were found to be effective promoters. IR and Ru K-edge EXAFS studies have shown that $[HRu_3(CO)_{11}]^-$ was the predominant species in active hydroformylation systems. Kinetic studies, however, indicated that mononuclear and possibly dinuclear fragments were responsible for catalytic activity [50]. The role of homogeneous and heterogeneous protonic and Lewis acids in catalytic hydroformylation and hydroesterification of pentene-1 using H^+ and H^- hydrido carbonyl ruthenium derivatives has been studied. It was found that the H^- hydrido carbonyl species were mainly involved in the activation of olefins and in the hydrogenation of the acyl intermediates to aldehydes and alcohols, whereas the H^+ hydrido iodocarbonyl derivatives were involved in the activation of alcohols and other oxygenated substrates, and in their carbonylation to esters [51].

The asymmetric hydroformylation of styrene with Pt-bisphosphine-$SnCl_2$ (or $CuCl_2$, or CuCl) catalytic systems has been studied (bisphosphine = BDPP, DIOP). At 20°C and P(CO) = $P(H_2)$ = 40 bar 88.8% ee for 2-phenyl propanal has been observed [52]. A new Pt-Sn couple has been produced by electroreduction of $Pt(DIOP)Cl_2$ using a soluble tin anode which showed remarkable regioselectivities for linear aldehyde formation in catalytic hydroformylation at 90°C and 100 bar CO : H_2 = 1:1. [53]. Unprecedented regioselective hydroformylation catalysts have been obtained by electroreduction of $Pt(DIOP)Cl_2$ using tin or iron anodes in an undivided cell. In the presence of such catalysts at 100 bar pressure and 90°C up to 90% 3-phenylpropionaldehyde and 98% n-heptanal were obtained from styrene and 1-hexene, respectively [54].

See also [19,20,21,22,23,24,25,48].

d) Heterogeneous Systems (Supported Complexes)

A supported cobalt carbonyl cluster catalyst has been prepared by treating chloromethylated polystyrene first with

$LiPPh_2$ and then with $BrCCo_3(CO)_9$. The catalyst was used for hydroformylation of olefins and showed no decrease in activity after 6 cycles [55]. Hydroformylation of 1-heptene with the Co-Ru bimetallic complex of polyaluminazane yielded branched aldehydes with 70% selectivity [56]. A seriesof anchored Rh-Co cluster catalysts were synthesized by the reaction of $Co_2Rh_2(CO)_{12}$ with various polymer supports, such as poly(2-vinylpyridine) and poly(styrene-maleic anhydride) and its aminated derivatives. These catalysts showed high activity, good selectivity, stability and reproducibility in hydroformylation [57]. Heterogeneous hydroformylation of 1-pentene has been studied on supported (SiO_2 or Al_2O_3) metal (Co, Ru, and Rh) catalysts. The activity of the metals increased in the stated order. In the presence of (-)-DIOP asymmetric hydroformylation was achieved over Rh/Al_2O_3 [58].

The catalytic hydroformylation of heptene-1 at 70°C and 30 bar total pressure has been studied using some rhodium(I) complexes anchored to 2% divinylbenzene-crosslinked phosphinated polystyrene as heterogenized catalysts [59]. 1-Hexene and 1-heptene were hydroformylated at 100°C and 60 bar using a silica-supported poly-γ-mercaptopropylsilaxane-rhodium complex as catalyst. Activity and selectivity of the catalyst strongly depended on the Rh:S ratio [60].

Rhodium and iron carbonyls entrapped in NaY zeolite were tested as catalysts for CO hydrogenation and olefin hydroformylation. $Rh_6(CO)_{16}$/NaY led to selective formation of olefin-rich C_2-C_4 hydrocarbons, while the bimetallic RhFe/NaY (synthesized from $[HFe_3(CO)_{11}]^-$/NaY and $Rh_4(CO)_{12}$) showed higher activity and selectivity for linear alcohol formation in the hydroformylation of ethene and propene [61]. Catalysts derived from $Rh_6(CO)_{16}$ on NaY and $Rh_6(CO)_{16}$ + $[HFe_3(CO)_{11}]^-$ on NaY gave a mixture of aldehydes as the main oxygenated products in the hydroformylation of propene. In contrast, bimetallic catalysts containing RhFe carbonyl clusters presynthesized inside the NaY zeolite supercages exhibited high yields and selectivities towards *n*-butanol [62,63].

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

The effects of catalyst components and reaction conditions on the activity of $Co_2(CO)_8$ - PPh_3(or dppe) - MeI systems for MeOH homologation have been studied. More than 85% selectivity to EtOH could be achieved for several combinations of the variables [64]. Acetaldehyde was produced by the rhodium-catalyzed reductive carbonylation of methanol approaching 90% selectivity beside acetic acid at 130-150°C and 70 bar synthesis gas pressure in the presence of dppp and CH_3I. If ruthenium was employed as a cocatalyst, acetaldehyde was hydrogenated *in situ* and ethanol was produced with the same selectivity and rate. Based on kinetics, isolated rhodium complexes, and modelling of assumed steps in the catalytic cycle, a reaction mechanism was postulated [65]. Dimanganese decacarbonyl catalyzes the homologation of MeOH to EtOH at 200°C and 300 bar synthesis gas ($CO:H_2$ = 3:1) in the presence of N-methylpiperidine according to the following stoichiometry:

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

The yield of ethanol is 75%; 15% methane is formed as the main byproduct and the minor liquid products include ethyl formate, acetaldehyde, n-propanol, and acetals [66].

In the synthesis of ethylene glycol from formaldehyde, CO and H_2 in N-methylpyrrolidone solution at 50-200 bar with $Rh(CO)_2(acac)$ as catalyst the highest yield of ethylene glycol + glycol aldehyde was achieved at 122-132°C [67]. Higher pressures and temperatures increased the formation of MeOH [68]. Hydroformylation of paraformaldehyde and aqueous formaldehyde to glycolaldehyde with homo- and hetero-metallic catalytic systems involving metal carbonyl species in different oxidation states has been investigated. Selectivity up to 80% was found at 90-140°C and 100-145 bar ($CO:H_2$ = 1:1) with chloride-promoted $Rh_4(CO)_{12}$ as catalyst precursor. Using optimized ratios of $[Rh(CO)_2Cl_2]^-/[Rh_5(CO)_{15}]^-/Cl^-$ allowed the selectivity to be increased up to 90% [69]. Formaldehyde reacts with synthesis gas

at 200°C and 50 bar over a NaY-supported $Ru_3(CO)_{12}$ catalyst to give EtOH and MeOH [70].
See also [14,190].

4. Coordination Chemistry Related to Hydroformylation

In the stoichiometric reduction of formaldehyde to methanol by $HCo(CO)_4$, (hydroxymethyl)- and (hydroxyacetyl)cobalt tetracarbonyl intermediates were isolated [71]. The composition of pyridine-modified cobalt catalysts used for hydroformylation was studied by IR-spectrometry. The results indicated the formation of $(pyH)^+[Co(CO)_4]^-$ and - possibly - $[Co(py)_6]$ $[Co(CO)_4]_2$ [72]. The structures of the supported clusters $Co_4(CO)_{10}(PPh)_2/SiO_2$ and $(PhCH_2NMe_3)[FeCo_3(CO)_{12}]$/ /polystyrene which have been used as hydroformylation catalysts were investigated by EXAFS. The results suggest that the cleavage of the metal-metal bonds is the first step towards the formation of the catalyst center [73].

An acylrhodium tetracarbonyl was observed and umambiguously identified by *in situ* infrared spectroscopy as an intermediate in the rhodium-catalyzed hydroformylation reaction at 25°C [74]. The water-soluble hydroformylation catalyst $HRh(CO)[P(C_6H_4SO_3Na\text{-}m)_3]_3$ did not lose a phosphine ligand under hydroformylation conditions (up to 200 bar CO + H_2) in the presence of a three molar excess of free phosphine. This is in contrast to $HRh(CO)(PPh_3)_3$ which under similar conditions is completely converted to $HRh(CO)(PPh_3)_2$ [75]. The catalytic activity of Rh-Y zeolite for hydroformylation of ethene was considerably enhanced by pretreatment of the fresh catalyst with H_2. On exposure to CO, two types of Rh carbonyl species were formed; $Rh_6(CO)_{16}$ and $Rh(CO)_2$; of these two only the Rh cluster reacted with ethene + H_2 to form some propionaldehyde [76].

5. Water-Gas Shift Reaction and Reduction with CO + H_2O

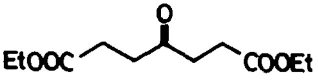
The formation of formaldehyde and formic acid as side products in the liquid phase water-gas shift reaction catalyzed by $K[Ru(III)(EDTA\text{-}H)Cl].2H_2O$ in the range of 7-34 bar CO and 40-80°C has been reported. CO insertion into the Ru - OH bond was proposed as the mechanism of HCOOH formation [77]. Catalysis of the water-gas shift reaction by anchored $Ru_3(CO)_{12}$ and $Rh_4(CO)_{12}$ at 120°C and p(CO) = 7 bar was studied. The highest activities were obtained with $H_2N(CH_2)_3Si(OEt)_3$-anchored $Ru_3(CO)_{12}$ on silica gel [78]. $Rh(COD)L_2^+$ and $Rh(NBD)L_2^+$ complexes (L = PPh_3, tri-*o*-, tri-*m*-, tri-*p*-tolyl phosphine) were tested as catalysts for the water-gas shift reaction in the presence of OH^-. The complexes containing L with larger cone angle were found to be more active [79]. A stable, moderately active homogeneous catalyst for the water-gas shift reaction formed from $RhCl_3$ in aqueous pyridine and other substituted pyridine solvents has been studied. The turnover frequencies for H_2 production were about 100 moles H_2/mole Rh.day at 100°C [80]. The heterogenized Rh catalyst $Rh(CO)Cl(PPh_2CH_2CH_2SiO_{3/2})_2 \cdot xSiO_2$ has been found active at 70°C for the water-gas shift reaction [81]. Using the $Pd(OAc)_2$-PPh_3-CF_3COOH/H_2O system for the homogeneous water-gas shift reaction and the hydroformylation of ethene to diethyl ketone, a cationic hydride complex, $[(PPh_3)_3PdH]^+$ has been characterized as the catalytically active palladium species [82].

A useful method for the preparation of 1,2,3,4-tetrahydroquinolines and 1,2,3,4-tetrahydroisoquinolines from quinolines and isoquinolines has been found using rhodium clusters under water-gas shift conditions. $Rh_6(CO)_{16}$ gave the best results (mostly more than 90% isolated yield) at 150°C and 56 bar CO pressure [83]. The complex $(\eta^4\text{-}Ph_4C_4C{=}O)(CO)_3Ru$ catalyzes the reduction of nitroarenes to anilines by CO and H_2O. High selectivities have been achieved at 105°C and 34.5 bar CO pressure in the case of nitrobenzenes substituted by electron-donating groups [84].

6. Hydroformylation-Related Reactions of CO

The Reppe-hydroformylation of ethene with CO, H_2O and $Ru_3(CO)_{12}$ as catalyst in the presence of a base at 150°C and 35 bar yielded 2-methylpent-2-en-1-al as the main product resulting from the condensation of propanal. Iodide and $M(CO)_6$ (M = Cr,Mo,W) carbonyls increased the activity of the catalyst. The most active combination was $Ru_3(CO)_{12}$-$W(CO)_6$-CsI-CsOH-MeOH [85]. Hydroformylation of propene with CO + H_2O in the presence of $Fe(CO)_5$ + trialkylamine catalysts has been studied. The effect of H_2SO_4 on the reaction was determined [86].

In the reaction of $KHFe(CO)_4$ with ethyl acrylate in ethanol at 70°C the formation of ethyl propionate and diethyl 4-oxopimelate (8) was observed in 27% and 40% yield (with respect to iron), respectively [87].



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Cyclopentanone derivatives were synthesized by hydrocarbonylation of 1,4- or 1,5-dienes with CO + H_2O using $Co_2(CO)_8$ or $[Rh(COD)Cl]_2$ as catalysts. Reaction conditions were 165-180°C and 120-180 bar with cobalt, and 120-140°C and 30 bar with rhodium catalyst. For example, diene (9) could be transformed with 47% overall yield into (10) and (11) (ratio 1:1.6), and diene (12) with 70% yield into (11). In both cases also the cyclohexanone derivative (13) was formed in minor amounts [88].

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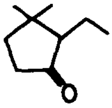

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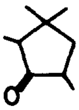

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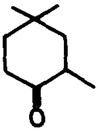

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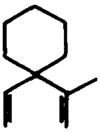
This synthetic method of "hydrocarbonylative cyclisation" was extended also to dienes of type (14) and (15) which gave - among others - cyclic ketones of type (16) and (17), and to the methylenecyclopropane derivative (18) which could be transformed into (19) [89].



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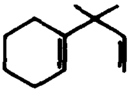

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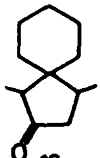

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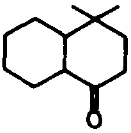

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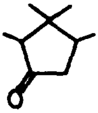
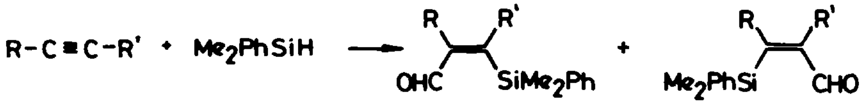


19

Cyclopentenene derivatives were obtained in moderate yields under hydroformylation conditions from enynes using $Rh_4(CO)_{12}$ as catalyst precursor [90]. Hydrocarbonylation of acetylene in an aqueous system containing palladium diacetate, PPh_3, and CF_3COOH gave acrolein, acrylic and propionic acid, and Et_2CO [91].

Ring opening siloxymethylation of acylic ethers has been achieved by a new catalytic system composed of $HSiR_3/CO/Co_2(CO)_8$ at 25°C and atmospheric pressure:

The reactivity of cyclic ethers decreased in the order of 4 > 3 > 5 >> 6 and 7-membered rings. The regio- and stereoselectivities of the reaction with substituted oxiranes have been investigated [92]. An efficient silylformylation of alkynes with Me_2PhSiH, catalyzed by $Rh_4(CO)_{12}$ in benzene solution under 30 bar CO at 100°C has been reported. Alkene (20) was the main product if R' = H; in some cases isomerization of (Z) to (E) alkenes was observed [93].



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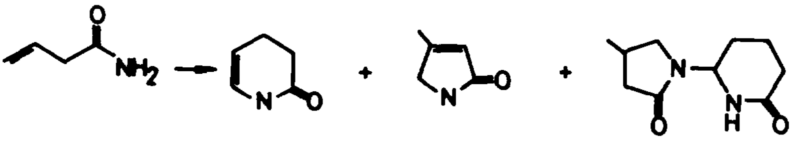
A remarkably selective catalytic synthesis of predominantly secondary amines by reaction of an amine with an ethene/syngas feed in the presence of $[Rh(CO)_2Cl]_2$ has been reported. Starting from $PrNH_2$, Pr_2NH was formed with 98% selectivity with respect to ethene at 60 bar and 115°C [94]. Nitrogen heterocycles were formed through intramolecular amidocarbonylation (80 bar 3 CO + H_2, 80°C) of alkenamides (e.g. 21) catalyzed by rhodium complexes (A: $Rh(PPh_3)_3Cl$ + 20 PPh_3; B: $Rh(PPh_3)_3Cl$ + 10 $P(OPh)_3$) [95]:



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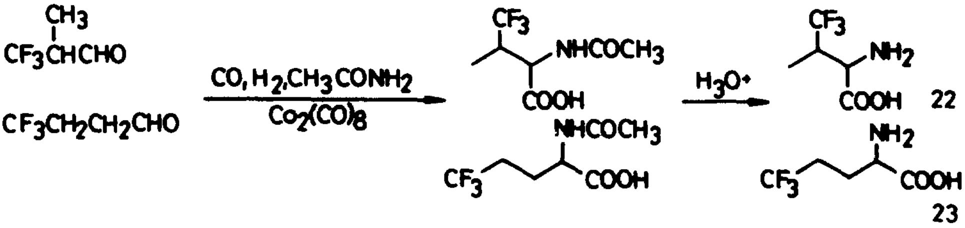
A:	92 %	8 %	–
B:	3 %	3 %	94 %

Ruthenium clusters, $Ru_3(CO)_{12}$, $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ have been found to catalyze the carbonylation of piperidine and other cyclic amines to the corresponding formamides using CO or CO_2 + H_2. In the case of $Ru_3(CO)_{12}$, carbamoyl clusters of the type $(\mu_2\text{-H})Ru_3(CO)_{10}(\mu_2,\eta^2\text{-OCNR}_2)$ have been isolated from the reaction mixture [96]. The trifluoro analogs (22–24) of valine, norvaline, and norleucine were synthesized through amidocarbonylation with CO, H_2, and acetamide in the presence of $Co_2(CO)_8$ as catalyst from the isomeric trifluorobutyraldehydes and by asymmetric hydrogenation from (Z)-N-benzoyldehydrotrifluoroleucine methyl ester with the chiral catalyst $[Rh(dipamp)(NBD)]ClO_4$ (dipamp: 24a) [97].



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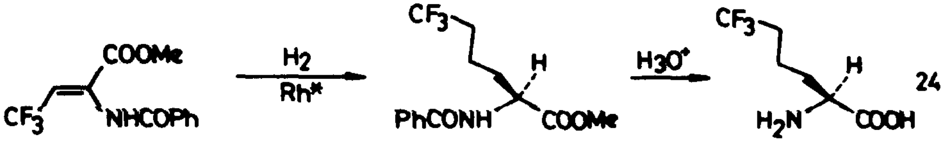

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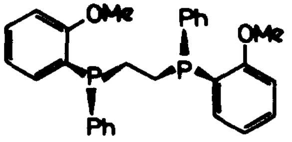


24 a

The ketene complex, $Co_2(CH_2{=}C{=}O)(CO)_7$ promotes in the presence of Zn the reductive methoxycarbonylation of CH_2Br_2 in THF at -40 – +20°C and 5 bar CO yielding methylacetate [98]. A practically useful one-step hydroxymethylation of benzyl halides in the presence of Na_2CO_3 using $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ as catalyst precursors has been found. An 88% yield of 2-phenylethanol was achieved at 110°C and 150 bar CO/H_2 = 1/2 [99]. A direct catalytic formylation of arylchlorides to aryl aldehydes (up to 95% yield in the case of benzaldehyde) by CO and HCO_2Na at 150°C and 5 bar using $(dippp)_2Pd(0)$ as catalyst has been reported. (Ar = Ph, 4-Me-C_6H_4, 2-Me-C_6H_4, 4-MeO-C_6H_4; dippp = $iPr_2P(CH_2)_3PPr^i_2$) [100].

$$ArCl + CO + HCO_2Na \longrightarrow ArCHO + NaCl + CO_2$$

See also [42].

7. Reduction of CO_2

Powerful reducing agents for the reduction of several substrates, including CO_2 have been generated by irradiating $[W_2(CO)_{10}]^{2-}$ in the presence of Ph_3P. A plausible mechanism for the reduction of CO_2 to formate involving a 19-electron complex $[W(CO)_5PPh_3]^-$ was suggested [101].

Electroreduction of CO_2 to squaric acid is mediated by the rubredoxin-analogue $\{Fe(SR)_4\}^{2-}$ complexes {HSR = tBuSH, PhSH; $H_2S_2R_2$ = 1,2-benzenedithiol, 1,2-benzenedimethanethiol}. The process needs 1/2 electron per CO_2, but shows a short lifetime owing to the lack of stability of the iron complexes [102]. The reduction of CO_2 at 20°C and 1 bar to give CO_3^{2-} and CO by the 19e complex $CpFe(C_6R_6)$ (R = H or Me) has been reported [103]. Controlled potential electrolysis of CO_2-saturated dry MeCN containing $[Et_4N]_3[Fe_6Mo_2S_8(SEt)_9]$ and MeCOSEt produces $HCOO^-$ and $MeCOCOO^-$ with a current efficiency of 11 and 27%, respectively. Thus, the FeMoS cluster catalyzes the reductive CO_2 fixation reaction shown below [104]:

$$MeCOSEt + CO_2 + 2e^- \longrightarrow MeCOCOO^- + EtS^-$$

The kinetics of the catalytic reduction of CO_2 by H_2 to formic acid and formaldehyde and their decomposition to CO and H_2O in the presence of $K[Ru(III)(EDTA\text{-}H)Cl].2H_2O$ in aqueous medium have been investigated. The rates of formation of formic acid and formaldehyde showed first order dependence with respect to catalyst and dissolved CO_2 and H_2 [105]. The stoichiometric reduction of CO_2 to formic acid and formaldehyde by the same complex in the range of 5-70 bar CO_2 pressure and 40-80°C was first order in both the complex and dissolved CO_2. The formation of HCOOH and HCHO was found to be faster via CO_2 reduction than CO hydration and reduction [106]. Carbon dioxide was electrochemically reduced to MeOH in aqueous solution on a Ru-modified electrode. Ruthenium was fixed as a mercaptide on a conductive polymer prepared by electropolymerization of mercaptohydroquinone. The current efficiency for MeOH formation was almost 100%, traces of CH_4 and CO were formed [107]. The previously reported reduction of CO_2 with H_2 in the presence of Me_2NH to DMF catalyzed by several Ru, Os, Rh, Ir, and Pt complexes has been found to produce also Me_3N.DMF is the intermediate of the reduction of CO_2 and Me_2NH to Me_3N under such conditions [108]. Electropolymerized films of $[Co(v\text{-}tpy)_2]^{+-}$ (v-tpy = 4'-vinyl-2,2':6',2"-terpyridine) have been found active in the electrocatalytic reduction of CO_2 to formic acid. The polymer films lower the overpotential of CO_2 reduction in DMF by nearly 1.0 V [109]. The complex $IrCl(CO)(PPh_3)_2$ is an effective catalyst precursor for the synthesis of formamide from CO_2, H_2 and NH_3, and for the further reduction of formamide to methane [110]. Electroreduction of CO_2 to CO and HCOOH is catalyzed by $IrCl(CO)(PPh_3)_2$. Hydroxo and hydrido Ir(I) complexes are involved in the process [111]. The reduction of CO_2 by alkylsilanes to the methoxide level is catalyzed by Ir(CN)(CO)dppe at ambient temperatures and pressures. The overall reduction stoichiometry for Me_3SiH is shown below [112]:

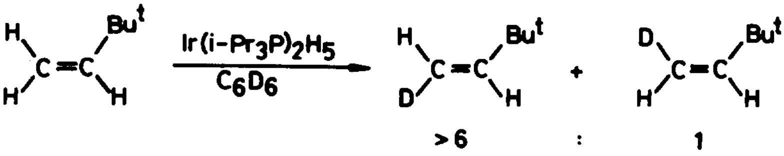
$$3Me_3SiH + CO_2 \longrightarrow CH_3O\text{-}SiMe_3 + Me_3Si\text{-}O\text{-}SiMe_3$$

Symmetrical ketones resulted is high yields along with Ni(II) in the reaction of alkyl halides with a Ni(0) complex obtained by electrochemical reduction of bpy Ni(II) salts in the presence of CO_2. The Ni(0) species can be electrochemically regenerated to give rise to a catalytic process [113].
See also [96,244].

III. HYDROGENATION AND REDUCTION

1. Deuteration and H/D Exchange

Catalytic deuteration of cycloalkene using $RhX(PAr)_3$ (X = halide) catalysts frequently gives rise to polydeuteration and scrambled addition of deuterium to the cycloalkenes substrate. These undesirable side reactions could be minimized by using small, electronegative aniono ligands and electron-withdrawing triarylphosphine ligands [114]. Alkenes were deuterated using the $[Rh(COD)Cl]_2$ + DIOP catalyst system. Significant deuterium scrambling and polydeuteration was observed due to the reversibility of intermediate Rh alkyl formation. Yields of specifically deuterated products were inferior to those obtained with Wilkinson-type catalysts [115]. A very high conversion of 1-pentene into deuterated pentanes and deuterated oligomers has been observed using methylalumoxane and (-)-(R)-EBTHI-ZrX_2 (X = CH_3; (R)-1',1"-bi-2-naphtolate; EBTHI = (-)-ethylenebis (4,5,6,7-tetrahydro)-(R)-1-indenyl) catalyst precursors between 25 and 40°C, and 9 bar of deuterium. The investigation of the products has shown that the *re* enantioface of the olefin is involved in deuteration but its *si* enantioface in dimerization and oligomerization [116]. Thermolysis of $(CH_3)_3SiH$ in the presence of $Os(PMe_3)_4(SiMe_3)(H)$ catalyst results in formation of $(CD_3)_3SiD$ (>90% D) after 4 days at 90°C. Deuterium is also incorporated into the coordinated phosphine, silyl, and hydride ligands of the catalyst. At least one Si-H bond is required for deuterium exchange into the silane alkyl groups [117]. Vinyl H/D exchange between terminal olefins and benzene-d_6 is catalyzed by $H_5Ir(i\text{-}Pr_3P)_2$ at 30°C. For substituted 1-alkenes H/D exchange was found to be stereoselective, with a preference for activation of the C-H bond *trans* to the larger substituent at the β-carbon [118]:



The kinetics of H-D exchange between α-methylstyrene and CD_3COOD catalyzed by $Li_2Pd_2Cl_6$ have been studied. Exchange proceeded at highest rates when reduction of Pd(II) took place and was much slower in the presence of benzoquinone as a Pd reoxidant. A hydride-allyl species with Pd in the formal oxidation state of IV was suggested as intermediate [119].
See also [326].

2. Hydrogenation of Olefins

a) Fe, Ru and Os Catalysts

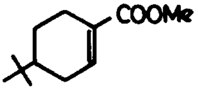
$Fe(stearate)_3$-$AlEt_3$ catalysts supported on iron and nickel hydroxides showed higher activity than the unsupported system in hydrogenation of cyclohexene and sunflower oil linoleates [120].

The kinetics of the homogeneous cyclohexene hydrogenation catalyzed by different ruthenium - (EDTA-H) complexes like $Na[Ru(EDTA\text{-}H)N_3].2H_2O$ and $[Ru(EDTA\text{-}H)NO]BF_4$ was studied. In comparison with earlier results the catalytic activity of the complexes increased with an increase in the π-acidity of the second ligand: $N_3^- < H_2O < PPh_3 < NO < CO < SnCl_3^- <$ olefin [121,122]. Several ruthenium (II) complexes of Ph_3P, 1-phenyldibenzophosphole, and 1-phenyl-3,4-dimethylphosphole have been investigated for their ability to catalyze the homogeneous hydrogenation of allylbenzene at 100°C and 7 bar H_2 pressure in a 1/1 ethanol/benzene solution [123]. The dinuclear Ru carboxylates, $Ru_2(OOCR)_4$ (R = Me, CF_3) have been used as catalysts for the hydrogenation of 1-alkenes [124]. The Ru(IV) complex $RuCl_2H_2(AsPh_3)_2$ obtained by the hydrogenation of $RuCl_3(AsPh_3)_2.CH_3OH$ intercalated into the interlamellars of montmorillonite clay catalyzes the hydrogenation of long chain unsaturated oils at room temperature and atmospheric pressure [125].

The cation $[H_5Os(PMe_2Ph)_3]^+$ has been shown to hydrogenate ethene and 1,5-cyclohexadiene. A facile catalytic hydrogenation of cyclohexene was found under 69 bar H_2 pressure at 25°C [126].
See also [1,215,216].

b) Rh and Ir Catalysts

The hydrogenation of cyclohexene catalyzed by $RhCl(SbPh_3)_3$, $RhCl(AsPh_3)_3$, or $[RhCl(Ph_2PCH_2CH_2AsPh_2]_2$ has been investigated [127]. The rate of hydrogenation of cyclohexene with $Rh(PPh_3)_3Cl$ as catalyst shows a maximum as a function of cyclohexene concentration. This effect was explained by assuming the formation of $RhCl(PPh_3)_2(cyclohexene)_2$ [128]. The complex $Rh[(Ph_2PCH_2CH_2CH_2)_2NH]Cl$ was prepared and used as a catalyst for the hydrogenation of cyclohexene [129]. The coordinatively unsaturated dinuclear complexes $[(iPr_2P(CH_2)_nPPr^i_2)Rh]_2(\mu\text{-}H)_2$ (n = 2,3) catalyze the hydrogenation of 1-hexene. Kinetic studies indicate that although a pathway involving dinuclear intermediates is also available, the active catalyst is a mononuclear species [130]. The rhodium phosphinosulfoxide complexes $(NBD)Rh(L)^+$ and $(COD)Rh(L)^+$ (L = $Ph_2PCH_2S(O)Ph$) catalyze the hydrogenation of olefins. The catalytically active species in these systems is probably the bis-ligand complex $[Rh(L)_2]^+$ which is formed *in situ* by a disproportionation reaction [131]. XeCl excimer laser (308 nm) irradiation of $RhH(CO)(PPh_3)_3$ accelerates the homogeneous hydrogenation of olefins under ambient conditions [132]. Olefins derived from methyl acrylate having a polar substituent like OH, COOR, or NHCOR at a chiral center situated in the α'-position were hydrogenated using cationic chelating Rh biphosphine complexes as catalysts. In all cases high anti-stereoselectivity was observed in the reduced product [133]. Hydrogenation of (25) using $Rh[P(C_6H_4R\text{-}p)_3]_3Cl$ complexes as catalysts furnished the *trans* cyclohexane derivative as the main product. The stereoselectivity of the reaction increased in the order R = Cl < H < Me < Me_2N [134].



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A heterogenized Rh(I) complex has been prepared by reacting $Rh(PPh_3)_3Cl$ with a functionalized polymer obtained from chloromethylated styrene-divinylbenzene copolymer and ethylene diamine. This polymer-supported complex was used as a catalyst for the hydrogenation of 1-octene at 1 bar and 30-35°C [135]. Hydrogenation of unsaturated hydrocarbons is catalyzed by $RhCl_3$ supported on an itaconic acid-divinylbenzene cation exchange resin having a macroreticular spherical structure. The selectivity of the catalyst is similar to that of an analogous homogeneous catalyst derived from linear macromolecules [136]. A heterogenized rhodacarborane was prepared by the copolymerization of carboranylstyrene, styrene, and divinylbenzene, followed by treatment with KOH in EtOH and then with $Rh(PPh_3)_3Cl$. The freshly prepared catalyst was highly active for the hydrogenation of 1-hexene [137]. Rhodium complexes supported on silica gel modified by P and N-containing ligands were prepared by treating silica gel containing $-(CH_2)_3NHR$ (R = H, PPh_2) groups with $[Rh(COD)Cl]_2$, $Rh(PPh_3)_3Cl$, or $RhCl_3.nH_2O$. These catalysts were used for the hydrogenation of allylbenzene [138].

The thermodynamics of the homogeneous hydrogenation of cyclohexene catalyzed by Ir(I) complexes, $IrCl(PPh_3)_2S$, IrCl(dppe)S, and $IrCl(dppe)PPh_3$ (S = solvent) have been studied in the temperature range 10-40°C and at 0.6-1 bar of H_2 partial pressure in ethanol/benzene [139]. The complex $[(COD)IrL](SbF_6)$ which contains the bidentate chelating ligand L = *o*-$BrC_6H_4PPh_2$ catalyzes the hydrogenation of 1-methylcyclohexene at 25°C and 1 bar H_2 in dichloromethane solution. The catalyst is more active in this case than $Rh(PPh_3)_3Cl$ in EtOH, which is very sluggish for trisubstituted olefins [140]. A heterogenized catalyst for hexene-1 hydrogenation prepared from $[IrCl(COD)]_2$ and solid polysiloxane-phosphine ligands has been reported. The initial rate of H_2 uptake showed first-order dependence on the metal and zero-order for 1-hexene [141].
See also [17,29,229,230].

c) Ni, Pd, and Pt Catalysts

Hydrogenation of olefins is catalyzed by $Ni(acac)_2$ in THF under irradiation by visible light. The reaction is apparently a homogeneous catalytic process; Ni(I) complexes generated by photoreduction react with H_2 to give Ni hydride complexes which are the actual catalysts [142].

Cationic Pd(II) complexes of ferrocenylphosphines $[(L)Pd(L')](ClO_4)$ (L = $Fe(C_5H_4PPh_2)_2$ or $CpFe(C_5H_3(CHMeNMe_2)PPh_2$-1,2), (L' = py or DMF) were prepared and used as catalysts for the hydrogenation of simple olefins at 30°C [143]. Polystyrene derivatives react with lithioferrocenes, lithium ferrocenyl phosphines and lithiated aminoferrocenes to give materials containing unstrained ferrocene fragments. Palladium(II) derivatives of these amine- and phosphine-containing materials are hydrogenation catalysts for olefins [144]. Alkenes, α,β-unsaturated aldehydes and cyclododecatriene were hydrogenated over $PdCl_2$-Tussah silk, $PdCl_2$-PVP (polyvinylpyrrolidone), and $PdCl_2$-PVP/Al_2O_3 catalysts. For most of the substrates the last one was found to be the most active [145]. Factors influencing the catalytic activity of palladium(II) complexes with poly(2-vinylpyridine) and poly(4-vinylpyridine) in the hydrogenation of unsaturated alcohols and aldehydes in water and ethanol have been discussed [146]. Supported palladium complex catalysts prepared from bromopyridinomethylated or N-diphenylphosphinopyridinomethylated divinylbenzene-styrene copolymers and $(PhCN)_2PdCl_2$ were used for the hydrogenation of mesityl oxide to 4-methyl-2-pentanone [147]. Palladium chloride supported on ion-exchange resins was used as catalyst for the hydrogenation of cottonseed oil. Catalysts based on strong-acid resins were more active than those based on strong-base resins [148].

The H_2PtCl_6 + $(C_8H_{17})_3N$ + $(iBu)_2AlH$ system was found to be a highly active catalyst for the hydrogenation of alkenes [149]. The heterobimetallic dihydride $Cp(CO)_2HRe-PtH(PPh_3)_2$ slowly catalyzes the hydrogenation of ethane and reacts stoichiometrically with alkynes to produce rhenium-alkene complexes [150].
See also [237].

d) Other Metals as Catalysts

The organometallic adducts prepared from metallic Sm and aromatic or multiolefinic hydrocarbons in ether solvents catalyze the hydrogenation of monoolefins [151].

The hydrogenation of olefins using Cp_2TiCl_2-iPrMgBr catalyst precursors has been studied [152]. The heterometallic hydride complex $Cp_2Ti(\mu\text{-}H)_2Al(Me)(\mu\text{-}H)_2TiCp_2$ is a highly active catalyst for the hydrogenation of 1-hexene [153]. The system $(Cp_2TiCl)_2$ + $LiAlH_4$ (Al:Ti = 0.25-1.5) catalyzes the homogeneous hydrogenation of allylbenzene [154].

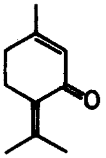
Hydrogenation of cyclohexene in DMF at 50°C and 1 bar with $Mo_2(OAc)_4$ as catalyst is first order in H_2 and catalyst and is independent of substrate concentration. Formation of a molybdenum hydride complex from $Mo_2(OAc)_4$ and H_2 was proposed as the rate-determining step [155].

Rhenium(V) complexes with thiophane and 2-propylthiophane were prepared and used as catalysts for olefin hydrogenation [156].

See also [143,144,150,211,213].

3. Asymmetric Hydrogenation of Olefins

The clusters $Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)\text{-DIOP}]_3$ and $Ru_4(CO)_8(OOCCH_2CH_2CH_2COO)_2[(-)\text{-DIOP}]_2$ showed catalytic activity and enantioselectivity in the hydrogenation of prochiral olefins (e.g. in the case of tiglic acid up to 50% optical yield was found) [157]. The cationic ruthenium complexes $\{RuX(arene)[(S)\text{-BINAP}]\}Y$ (X = Cl,Br,I; Y = Cl,Br,I,BF_4,BPh_4; arene = C_6H_6, p-$MeC_6H_4CHMe_2$) have been found to be efficient catalyst precursors for the enantioselective hydrogenation of various prochiral alkenic and ketonic substrates under 95-100 bar H_2 between 17 and 65°C. Thus methyl 3-oxobutanoate gave methyl (S)-3-hydroxybutyrate in 97-99% ee, and geraniol gave (R)-citronellol in 96% ee [158]. Piperitenone (26) was hydrogenated in the presence of chiral Ru hydride catalysts to give piperitone (27), menthone (28), and isomenthone (29). Starting from (27), which was only 42% optically pure, (28) was obtained with 80% enantioselectivity due to double asymmetric synthesis including kinetic resolution and catalytic asymmetric induction [159].



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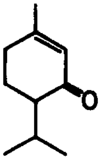

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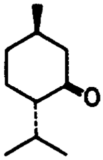

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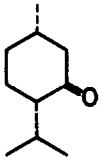

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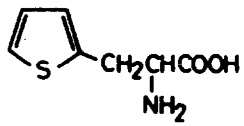
Available crystallographic data for chelate bisphosphine Rh complexes were used to explain structure-reactivity relationships in asymmetric hydrogenation of dehydroamino acids [160]. For the hydrogenation of dehydro aminoacids in various solvent mixtures with rhodium complexes containing chiral diphosphines, a linear correlation of log %S/%R with the solvophobicity parameter S_p has been found [161]. Asymmetric hydrogenation of (Z)-α-acetamidocinnamic acid, (Z)-α-benzamidocinnamic acid, and their esters was achieved using Rh(acac)[(-)-DIOP] as catalyst. Optical yields were in the range of 35-78% [162]. The optimization of asymmetric hydrogenation of 3-phenyl-3-butenoic acid catalyzed by Rh(I)-DIOP systems has been studied. The best optical yield (85% ee) was obtained in the presence of 5 mol% Et_3N in 75% aqueous methanol using a neutral Rh-DIOP catalyst [163]. The optically active selenienylalanines (S)-(**30**) and (S)-(**31**) were prepared by asymmetric hydrogenation of the corresponding acetylamido acrylic acids using *in situ* catalysts formed from $[Rh(NBD)Cl]_2$ and (+)-DIOP followed by hydrolysis of the N-acetylalanine derivatives [164].



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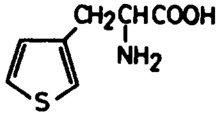
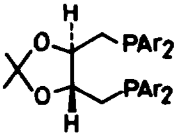


31

The influence of symmetrically and unsymmetrically substituted (R,R)-DIOP derivatives on optical induction in the hydrogenation of ethyl α-acylaminoacrylate and (Z)-methyl α-acylamino-cinnamate with $[Rh(modified\text{-}DIOP)(COD)]^+BF_4^-$ as catalyst precursor was studied. The optical yield obtained using an unsymmetrical DIOP ligand was fairly consistent with the value calculated by averaging the optical yields in the case of the corresponding symmetrical DIOPs. The ee vs. σ_p correlation shows that the ee decreases with rising electron donating ability of the substituent [165,166]. The rhodium complex of a modified DIOP analogue (32) has been found to give up to 96% ee in the catalytic asymmetric hydrogenation (1 bar 90°C) of itaconic acid and its derivatives bearing β-aryl groups [167].



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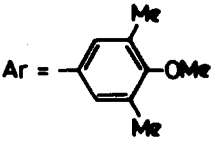
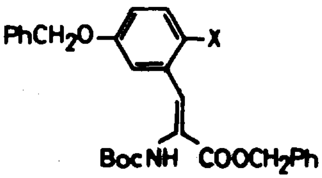
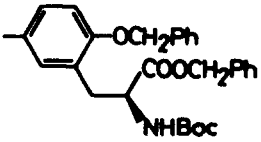


The (Z)-dehydrophenylalanine derivatives (33) and (34) were hydrogenated with better than 99% enantioselectivity to the corresponding (S)-phenylalanine derivatives using $[Rh(dipamp)]^+$ as catalyst in MeOH solution at 20°C [168].

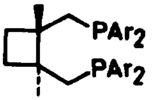


33; X = Br

34; X =



The enantioselective hydrogenation of α-acetamido acrylic acid in water has been studied using a rhodium catalyst associated with chiral sulphonated phosphines (35-37) and the analogous phosphine oxides (38-40). The best result (61% ee) was achieved with ligand 37 and $[Rh(COD)Cl]_2$ as catalyst precursor. With the phosphine oxides no enantioselectivity was observed [169].



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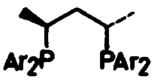

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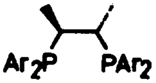

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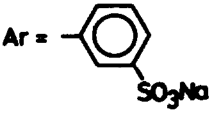

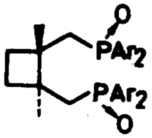

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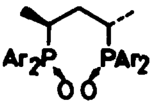

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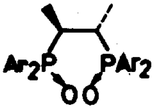
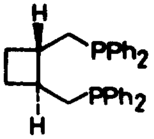


40

Sulfonation of (S,S)-cyclobutanediop (**41**), (S,S)-BDPP (**42**), (S,S)-chiraphos and (R)-prophos results in chiral water-soluble ligands. Rhodium(I) catalysts formed with these sulfonated diphosphines are efficient catalysts for the asymmetric hydrogenation of C=C (89% ee with α-acetamidocinnamic acid Me ester), C=O (22% ee with acetophenone), and C=N (58% ee with acetophenone benzylimine) bonds in aqueous-organic two-phase solvent systems [170].



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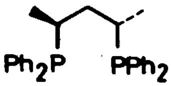
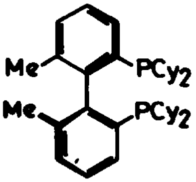


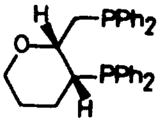
42

An *in situ* generated rhodium(I) catalyst containing 2,3-bis(dimethyl-phosphino)maleic anhydride as ligand gave 100% conversion and 70% ee in α-acetamido cinnamic acid hydrogenation, 81% conversion and 47% ee in acetophenone hydrogenation, and 46% conversion and 42% ee in acetophenone hydrosylation [171]. Rhodium(I) complexes of (R)- and (S)-BICHEP (**43**) catalyze the asymmetric hydrogenation of ethyl α-(benzamido)cinnamate and dimethyl itaconate with up to 98% yield and 98-99% ee [172].



(R)-(-)-43

The chiral diphenylphosphines (**44**) and (**45**) were prepared starting from D-glucose and used as ligands in the asymmetric hydrogenation of (Z)-α-N-acetylaminocinnamic acid catalyzed by Rh(I) complexes. Enantioselectivity was about 70% with phosphine (**44**) whereas phosphine (**45**) afforded a catalyst with only low enantioselectivity [173].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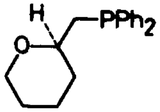
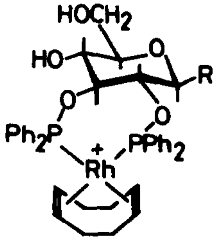
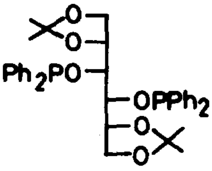

45

Rhodium(I) complexes of chiral bis-diphenylphosphines derived from D-glucose and D-galactose exhibited low to relatively high enantioselectivities in hydrogenation of Z-α-acetylaminoacrylic acid [174]. Rhodium(I)-[2,3-O-bis(diphenylphosphino)-β-D-glucopyranoside] chelates like (**46**) with free hydroxyl groups in the 4,6-positions have been found to be excellent catalysts in asymmetric hydrogenation of methyl (Z)-acetamidocinnamate [175].


46; R= OPh, Ph

The chiral ligands (**47**-**49**) have been prepared from the corresponding carbohydrates and were tested in asymmetric hydrogenation of prochiral olefins and acetophenone using $[Rh(COD)Cl]_2$ as catalyst precursor. Optical yields between 8 and 78% have been achieved [176].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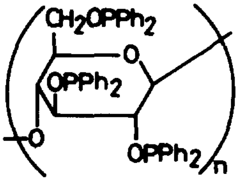
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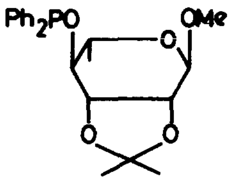
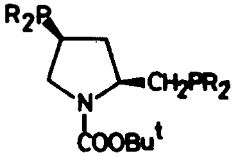
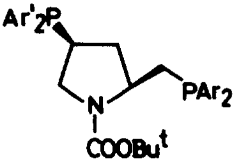

49

The BPPM-analogs (**50**; R = 2-, 3-, or 4-$MeOC_6H_4$) have been prepared and used as chiral ligands in the asymmetric hydrogenation of (Z)-PhCH=C(NHAc)COOH with Rh complexes as catalysts [177].



50

Rhodium complexes of pyrrolidinebisphosphines (51; Ar, Ar'= p-$Me_2NC_6H_4$ or Ph) bearing *para*-dimethylamino groups have been found to be much more effective (ee. up to 93%) than those with the analogous ligands 52 and 53 for the asymmetric hydrogenation of dimethyl itaconate [178].



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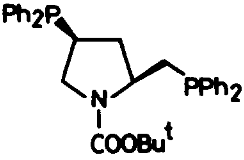

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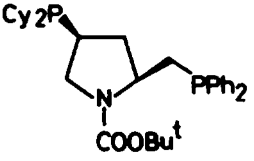
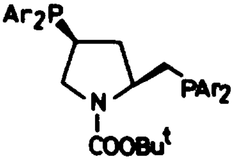
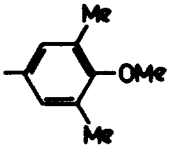


53

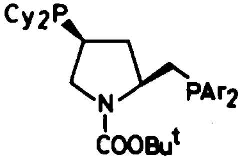
The chiral catalyst formed *in situ* from $[Rh(NBD)_2]ClO_4$ and the diphosphine ligand (54) was successfully used for the asymmetric hydrogenation of (Z)-2-acetamidoacrylic acid derivatives. The enantioselectivity of the new catalyst was generally higher than that of the structurally related BPPM-Rh catalyst; this was attributed to the electronic and steric factors of the substituents on the aromatic rings [179].



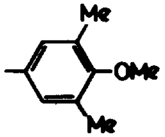
54; Ar =



Several substituted derivatives of the known chiral biphosphine BCPM (55; Ar = Ph) have been synthesized and tested as ligands in the asymmetric hydrogenation of itaconic acid with Rh complex catalysts. No significant improvement of activity or enantioselectivity could be achieved [180].



55 ; Ar =

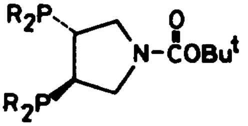


o-, m-, p-$MeOC_6H_4$

p- $Me_2NC_6H_4$

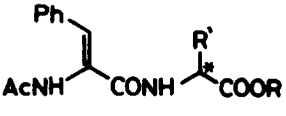
p- ClC_6H_4

It has been shown that the different stereoisomers of the diphosphine ligands (56; R = Me or Ph) deeply influence the enantioselective catalytic behavior of their rhodium complexes. A square planar rhodium complex $[LRh(COD)]^+$ (L = 56) with a phosphine ligand which bears phenyl groups in axial and methyl groups in equatorial position gives higher optical yields in α-(acetamino)cinnammic acid hydrogenation than its counterpart with the methyl groups axial and the phenyl groups equatorial [181].



56

The effect of solvent and temperature on 1,4-asymmetric induction in diastereoselective hydrogenation of dehydrodipeptides (57; R' = PCH_2, Me, iBu; R = H, Me) with Rh(I)-(58) catalysts has been investigated. The highest stereoselectivity (96% diastereomeric excess) was obtained in methanol-water solvent at 20-40^{o}C, white aprotic solvents such as DMF and THF gave comperatively low selectivity and reactivity [182].



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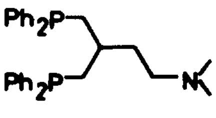


58

An earlier report on asymmetric hydrogenation of trisubstituted acrylic acids catalyzed by a chiral (aminoalkyl) ferrocenylphosphine-rhodium complex (AS 1987, ref.147) has been reviewed and discussed [183].

Hydrogenation of tetrasubstituted C=C double bonds in dehydroamino acids RC(Me)=C(NHCOPh)COR' (R = Me, Ph; R' = OMe, NHCHMePh, phenylalanine Me ester, methionine Me ester) has been achieved at 20°C and 1 bar using complexes of the type $[Ir(COD)(PhCN)(L)](ClO_4)$ (L = PCy_3, PPh_2(neomenthyl), PMePh(*o*-MeOphenyl)) as catalyst precursors. Optical yields were less than 27% [184].

See also [2,190].

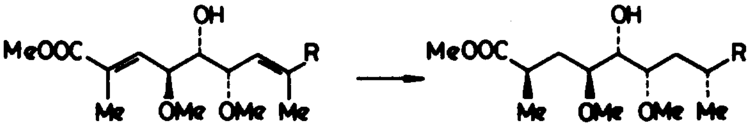
4. Hydrogenation of Dienes and Alkynes

Samarium and ytterbium were vaporized into frozen (77K) organic solvents (THF, benzene, or methylcyclohexane) and the low-valent highly dispersed species obtained in this way were used as catalysts for the hydrogenation of C_2-C_4 alkenes, alkynes and the partial hydrogenation of benzene to cyclohexene. Internal alkynes were hydrogenated more readily than terminal alkynes; Sm usually showed a greater activity than Yb [185].

The subcarbonyl species $Mo(CO)_3$ encaged in alkali metal cation-exchanged X and Y zeolites was found to catalyze a highly selective hydrogenation of butadiene to *cis*-2-butene [186].

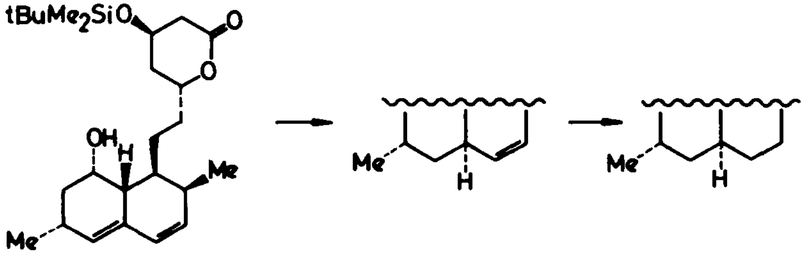
Terminal alkynes were selectively hydrogenated to alkenes in THF at 20°C and 1 bar H_2 pressure using $\{[P(CH_2CH_2PPh_2)_3]FeH(N_2)\}^+$ or $\{[P(CH_2CH_2PPh_2)_3]FeH(H_2)\}^+$ as catalysts [187]. Selective hydrogenation of t-butylacetylene [188] and diphenylacetylene [189] to the corresponding alkenes in the presence of $Ru_3(CO)_{12-n}(PPh_2H)_n$ (n = 2,3), $HRu_3(CO)_{10}(\mu\text{-}PPh_2)$, $HRu_3(CO)_9(\mu\text{-}PPh_2)$, $H_2Ru_3(CO)_8(\mu\text{-}PPh_2)_2$ and $HRu_3(CO)_7(\mu\text{-}PPh_2)_3$ at 120°C has been reported. (S,S)-2,3-Dimethyl succinic acid is formed with 96% ee *via* two consecutive 1,2-hydrogen additions to 1,3-butadiene-2,3-dicarboxylic acid catalyzed by a Ru-(R)-BINAP complex [190]. The complexes $OsHCl(CO)(PR_3)_2$ (PR_3 = $PMeBu^i_2$) catalyze the hydrogenation of PhC≡CH and $PhCH{=}CH_2$ in iPrOH at 50°C. Selectivities close to 100% were achieved for the hydrogenation of the alkyne to the alkene. Spectroscopic and kinetic evidences indicate that it is not the difference in the coordinating power of the substrates that is important in determining selectivities for the hydrogenation to the alkene but the tendency of the alkyne to undergo insertion to yield a vinyl intermediate [191].

The cationic Co(I)-complex $[Co(py)_6]^+$ has been found to be an active catalyst for the hydrodimerization of diphenyl acetylene at 20°C under H_2. From 1-hexyne and from 2-butyne not only the hydrodimer, but other hydrooligomers were also formed [192]. The dithiocarbonate complex $[Rh(S_2CO)(triphos)]BPh_4$ was used as catalyst precursor for the hydrogenation of alkynes and alkenes [193]. The kinetics of hydrogenation of hydroxy-terminated telechelic butadienes with $Rh(PPh_3)_3Cl$ as catalyst has been investigated. Due to the predominant 1,2-structural units the anionic prepolymer reacted twice as quickly as the radical prepolymer [194]. Kinetic and mechanistic studies have shown that in the presence of $RhCl(PPh_3)_3$ as catalyst selective homogeneous hydrogenation of 1,2(vinyl) addition units over 1,4(internal) addition units in polybutadiene (90% 1,2 addition, $\bar{M}_n$ = 10000) could be achieved between 20-50°C and at subatmospheric H_2 pressures. An inverse dependence with respect to the added $[PPh_3]$ and a first-order dependence on [Rh], [C=C] and $[H_2]$ at lower values was found [195]. Homogeneous hydrogenation of PhC≡CH catalyzed by $Rh(PPh_3)Cl$, $[Rh(COD)(PPh_3)_2]^+$, and $[Rh(COD)(dppe)]^+$ using *para*-hydrogen induced polarization has shown that for $Rh(PPh_3)_3Cl$, the addition of H_2 is reversible, whereas for the other two catalysts, H_2 addition in hydrogenation catalysis is irreversible (the catalytic cycle starts with the addition of alkyne) [196]. The chiral dienols (59; R = COOMe, CH_2CH_2OOCPh) were hydrogenated with 89-94% yield to the corresponding saturated products (60) at room temperature and 70 bar using $[Rh(dppb)(NBD)](BF_4)$ as catalyst [197].



59 60

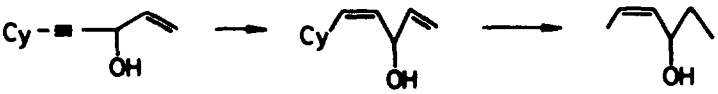
Solutions of syndiotactic 1,2-polybutadiene and a butadiene-styrene triblock thermoelastic elastomer containing $Rh(PPh_3)_3Cl$ or $[Ir(COD)(PMePh_2)_2](PF_6)$ catalysts were evaporated and then hydrogenated in bulk at 60°C and 0.4-3 bar [198]. Treatment of $[IrH_4(PMe_2Ph)_3]BF_4$ in CH_2Cl_2 with 2-butyne yields $[Ir(MeC_2Me)(PMe_2Ph)_3]BF_4$, *cis*-2-butene, and 1-butene. The latter complex reacts with H_2 to regenerate the starting complex and butane [199]. The diene (61) was hydrogenated in CH_2Cl_2 solution stereoselectively to a mixture of the *trans*-anellated monoene (62) and saturated product (63) under room conditions with $[Ir(COD)(py)(PCy_3)](PF_6)$ as catalyst. Addition of iPrOH (3 equiv) increased the chemoselectivity for the monoene to 90% [200].



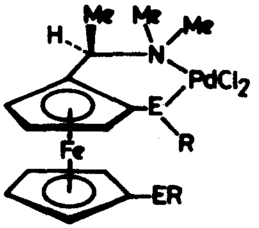
61 62 63

Modifying the boron-nickel catalyst formed from $Ni(OAc)_2$ and $NaBH_4$ (1:4) with about 2% aminoantipyrine gave a product which catalyzed the hydrogenation of 5-dodecyne to *cis*-5-dodecene with 95% yield and 94% selectivity [201]. A homogeneous solution was prepared from $Ni(OAc)_2$ and $NaBH_4$ in EtOH and used as a catalyst for the hydrogenation of alkynes to alkenes. The catalyst was active at 7-9°C and 1 bar and the yield of *cis*-alkenes was 91-95% [202]. An active catalyst for the *cis* hydrogenation of PhC CH, styrene and C_2D_4 has been obtained in the reaction of $Pd_2Cl_2(dppm)$ with $NaBH_4$. In these hydrogenations using para-enriched H_2, the observation of *para* hydrogen-induced polarization showed that the transfer of hydrogen to substrate occured pairwise and fast relative to proton relaxation [203]. The loss of Pd during the hydrogenation of 1,5,9-cyclododecatriene at 100°C and 20 bar using a $PdCl_2$ catalyst supported on divinylbenzene-styrene copolymers modified by different ligating groups was studied. The stability of Pd depended on the ligand atom and increased in the order C < P

< N < 0 [204]. Polymer-bound Pd complexes were prepared by treating phosphinated polystyrenes with $PdCl_2$. These complexes showed high selectivity for catalytic hydrogenation of cyclopentadiene to cyclopentene [205]. Nitrogen-containing divinylbenzene-styrene copolymer- supported Pd complex catalysts were prepared and tested for the hydrogenation of 1,5,9-cyclododecatriene in 1:1 benzene-EtOH at $100^{o}C$ and 20 bar. Catalysts containing chelating ligands displayed high catalytic activity [206]. An interlamellar montmorillonite-diphenylphosphinepalladium(II) complex gave excellent results as catalyst in the stereoselective hydrogenation of alkynes, enynes and dienes. Up to 98% *cis* selectivity in the hydrogenation of the triple bond has been reported. In case of unconjugated dienes the terminal double bond is preferentially hydrogenated without isomerization [207]. Palladium(II) acetate anchored via a bipyridine group in the interlammellar region of montmorillonite was found to hydropenate alkynes and alkynenes to cis-alkenes and alkadienes to alkenes regioselectively at room temperature and atmospheric pressure. Using a 1:100 catalyst:substrate ratio the yields were >95% [208].



The bimetallic Fe-Pd complexes (64; R = alkyl, benzyl, aryl; E = S,Se) were found to be effective catalysts for selective hydrogenation of 1,3-cyclooctadiene to cyclooctene at room temperature and 7 bar H_2 pressure [209].



64

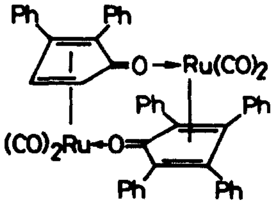
The hydrogenation of cyclooctadiene to cyclooctene in the presence of Pd(II) or Pt(II) complexes of ferrocenyl amine sulfides has been studied [210].
See also [125,126,145,148,237,255].

5. Hydrogenation of Arenes and Heterocyclic Compounds

Supported hydride complexes of Ti and Zr have been prepared by interacting Ti($CH_2Ph)_4$ or Zr(π-$C_3H_5)_4$ with SiO_2 and treatment with H_2. These catalysts were used for the hydrogenation of benzene at 90-150°C and of cyclohexene at 25°C [211]. The $MoCl_3$-LiCl-KCl and $NiCl_2$-LiCl-KCl salt melts promote the hydrogenation of anthracene (at 400°C for 1h with 98 bar H_2) and afford tetrahydro-, octahydro-, and dihydroanthracene as major products [212]. Cp_2ReH is an effective catalyst for the hydrogenation of cyclohexene, benzene, and ethyl acetate [213]. Aromatic and polynuclear aromatic compounds were hydrogenated at 50°C and 35 bar H_2 with a $BF_3 \cdot H_2O$ - $(MeCN)_2PtCl_2$ catalyst. Aryl ethers were hydrogenated and cleaved under these conditions [214].
See also [237].

6. Hydrogenation of Carbonyl Compounds

The catalytic hydrogenation of olefins, dienes, aldehydes and ketones in a polar solvent in the presence of $RuCl_2(L$-$L)_2$ (L-L = $Ph_2P(CH_2)_nPPh_2$, n = 4,5,6) has been studied [215]. The dimeric Ru complexes (**65**) and (**66**) catalyze the hydrogenation of cyclohexene and cyclohexanone (72°C, 12 bar) and the dehydrogenation of 2-octanol to 2-octanone (145°C, 1 bar N_2). At the end of the hydrogenation reactions the catalyst was present in the solution in the form of $(C_4Ph_4COH)(CO)_2RuH$ [216].



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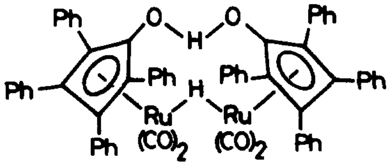
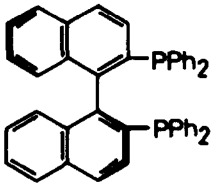


66

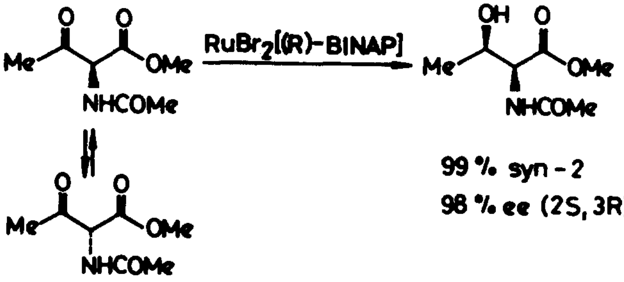
The dinuclear carboxylato clusters $Ru_2(CO)_4(\eta^2\text{-}OOCR)_2(DIOP)$ (R = Me, Et, CF_3) catalyze the hydrogenation of hydroxyacetone to 1,2-propanediol at 120°C and 40 bar; the enantiomeric axcess varies from 5 to 14% [217]. Catalytic asymmetric hydrogenation of the β-keto keto ester (67) was performed with $Ru_2Cl_4[(S)\text{-}BINAP)]_2$ as catalyst in the presence of Et_3N to give (68) in 90% yield [218].

67 68



69; (S)-BINAP

Stereoselective hydrogenation via dynamic kinetic resolution has been achieved in case of 2-substituted 3-oxo carboxylic esters and BINAP-Ru(II) catalysts at 15°C and 100 bar H_2. For example [219]:

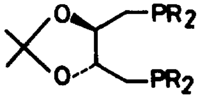


99 % syn-2

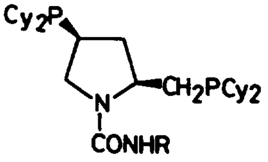
98 % ee (2S,3R)

The well-characterized silica surface-grafted cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OSi\ )]$ catalyzes the hydrogenation of saturated ketones at 130-170°C. IR-spectroscopic investigations prove that the cluster remains essentially intact under these conditions [220].

Asymmetric hydrogenation of acetophenone was carried out with a Rh-DIOP catalyst system modified by tertiary amines. It was found, that using triethanolamine instead of the more usually applied Et_3N significantly higher enantioselectivities could be achieved (up to 79%) [221]. A strong influence of the benzene-methanol solvent mixture composition and that of temperature on the enantioselectivity in the catalytic hydrogenation of acetophenone and acetophenonebenzylimine in the presence of rhodium(I)-BDPP complexes has been observed [222]. Rhodium(I) complexes of (70) and (71) showed high catalytic activity in hydrogenation of various kinds of prochiral ketones at atmospheric pressure and ambient temperature. Best optical yields were 66-76% [224].



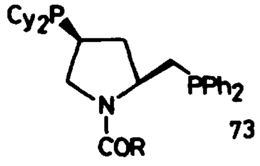
70 ; R = Et, iPr, Cy



71; R = Ph, Cy, tBu

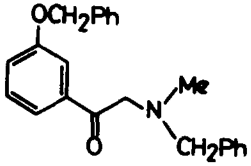
Neutral Rh catalysts prepared *in situ* from $[Rh(COD)Cl]_2$ and the chiral phosphines (2S,4S)-BCPM or MCCPM (73) were applied for the asymmetric hydrogenation of α-aminoacetophenone derivatives (72; R = H,Me,Et: R' = H,Et,$PhCH_2$) at 50°C and 20 bar in the presence of Et_3N in MeOH solution. Enantioselectivities between 81 and 97% were achieved [225].

72



BCPM; R = OBu^t
MCCPM; R = NHMe

In continuation of this work the asymmetric hydrogenation of aminoketone (74) which is a useful precursor for the synthesis of (R)-(-)-phenylephrine hydrochloride (75) (an adrenergic drug) has been investigated with Rh(I) catalysts prepared *in situ* from $[Rh(COD)Cl]_2$ and the chiral (2S,4S)-phosphines (76; R = OBu^t, $NHBu^t$, Bu^t, OPh, NHPh, Ph, OMe, NHMe, Me). Based on these results a practical synthesis has been developed for (75) using the (2R,4R)-phosphine (77) [226].



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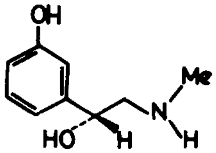

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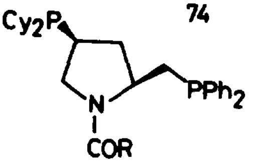

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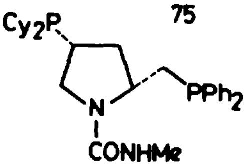
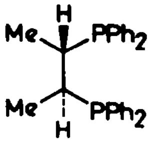


77

Homogeneous catalytic hydrogenation of aliphatic ketones with $Ir(ClO_4)(CO)(PPh_3)_2$ in $CHCl_3$ gave alcohols in 49-100% yield. Aromatic ketones gave low yields of alcohols, and other reduction products were also formed [227]. The iridium(I)-perchlorato complex $Ir(ClO_4)(CO)(PPh_3)_2$ catalyzes the hydrogenation of aldehydes to alcohols at $25^{o}C$ and 1 bar H_2 [228]. The selective hydrogenation of benzylidineacetone PhCH=CHCOMe by Ir-phosphine catalyst systems prepared *in situ* has been studied. Based on NMR spectroscopic evidence it was concluded that complexes of the type $IrH_5(PR_3)_2$ (R = alkyl or aryl) are catalysts for the hydrogenation of the C=C bond and $IrH_3(PR_3)_3$ type complexes catalyze the reduction of the C=O bond with a selectivity up to 100% [229]. The same hydrogenation was investigated also with cationic Ir-diphosphine complexes or with catalyst systems formed *in situ* from $[Ir(COD)Cl]_2$ and diphosphines. The following diphosphines were tested: dppe, dppp, dppb, (S,S)-chiraphos (78), (R)-prophos (79), (+)-DIOP (80) , and (S)-prolophos (81). Using *in situ* catalysts and an excess of diphosphine high (>90%) selectivities in unsaturated alcohol formation were obtained. Highest optical yield was 30% [230].



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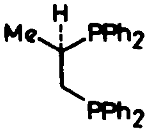

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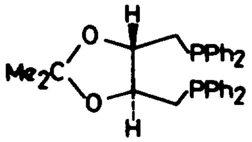

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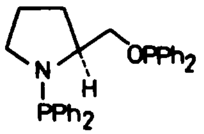
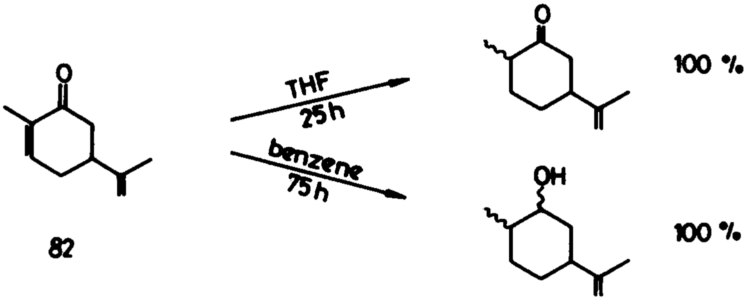


81

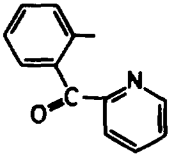
Conjugate reduction or complete 1,4- and 1,2-reduction of α,β-unsaturated ketones like (82) has been achieved at room temperature and 70 bar H_2 using $[(Ph_3P)CuH]_6$ as catalyst. Isolated double bonds were not hydrogenated [231].



See also [82,158,171,176,213,232,235].

7. Hydrogenation of Nitro Compounds

The dianion, $[H_2Ru_4(CO)_{12}]^{2-}$ showed excellent catalytic activity for the hydrogenation of nitrobenzene at 120°C and 20 bar (H_2 containing 5% CO). Its activity for benzaldehyde hydrogenation under the same conditions was moderate, under pure H_2, however, it was converted into a different Ru species of good catalytic activity [232]. Asymmetric hydrogenation of α-nitrocaprolactam in the presence of $PdCl_2$ and (S)-$PhCHMeNH_2$ in THF or glycol dimethyl ether gave (S)-α-aminocaprolactam. A dimeric azoxy lactam was identified as intermediate of the reaction [233]. Hydrogenation of nitroalkanes and aromatic nitriles to the corresponding amines has been achieved at 65-80°C and 40-120 bar using di- and mononuclear orthopalladated complexes of the type *trans*-$Pd_2L_2X_2$ and *trans*-$PdLL^1Cl$ (L = **83**,**84**, or **85**; L' = py,PPh_3; X = OAc,Cl) as catalyst precursors in DMF as solvent. The active catalytic species were found to be the corresponding mononuclear palladium hydride-DMF adducts [234].



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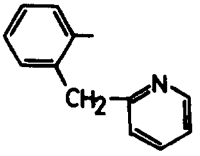

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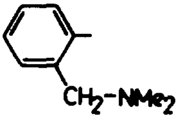
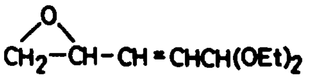


85

Hydrogenation of aromatic carbonyl and nitro compounds was carried out with a heterogenized catalyst prepared by reacting H-montmorillonite first with 3-aminopropyltriethoxysilane and then with $(PhCN)_2PdCl_2$. The red-colored catalyst was used at room temperature and atmospheric pressure and showed no activity for the hydrogenation of aliphatic nitro compounds [235]. Nitroaromatics were hydrogenated to amines at room temperature and atmospheric pressure with a heterogenized Pd(II) catalyst. The catalyst was prepared by treating montmorillonite first with $(EtO)_3Si(CH_2)_3NH_2$ and then with $(PhCN)_2PdCl_2$. Nitro groups were preferentially hydrogenated in the presence of chloro, aldehyde, and keto groups; the bromo group, however, was preferentially hydrogenolyzed in the presence of a nitro group [236]. Palladium(O) complexes of polymeric carriers containing chelating groups such as diketones, enaminoketones and diacylamines have been found to be effective catalysts for the hydrogenation at phenylacetylene, cyclohexene, toluene, nitrobenzene and α-nitroanthraquinone [237].Sodium selenite increases the catalytic activity of $MoCl_5$, $FeCl_2$, and $CuCl_2$, and decreases the catalytic activity of $NaAuCl_4$, AgCl, $CoCl_2$, $NiCl_2$, $PdCl_2$, and Na_2PtCl_6 in the reduction of nitrobenzene to N-phenylhydroxylamine and/or aniline with $NaBH_4$ in water [238]. The complex $[CpRu(C_6H_6)]PF_6$ increased, while the other Ru sandwich complex $[CpRu(Cp^*)RuCp^*]PF_6$ decreased the activity of the Pt(IV)-Alizarine Red complex catalyst for the hydrogenation of nitrobenzene to aniline [239].

8. Miscellaneous Hydrogenations

Hydrogenation of different epoxides in the presence of Pd(acac)$_2$ under 20 bar of H_2 at 50°C has been investigated. The order of reactivity of epoxides was (86) > styrene oxide >> propene oxide which indicates that the unsaturated substituent of the *epoxide plays an important role in the reactivity of the* epoxide ring [240].



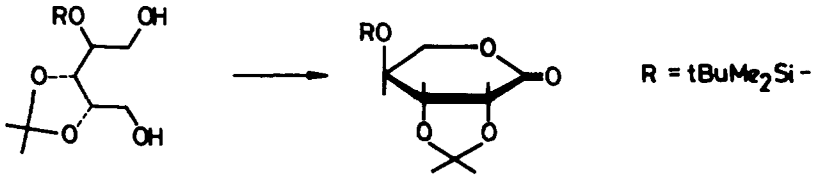
86

Fructose is readily hydrogenated at 100°C by 20 bar H_2 in N-methyl-2-pyrrolidinone in the presence of $H_2Ru(PPh_3)_4$. Among other products, the formation of glycerol proves the unprecedented homogeneous hydrocracking of the fructose C(3)-C(4) single bond. The selectivity for hydrocracking over simple hydrogenation to mannitol and glucitol could be dramatically improved (1:4 ⟶ 5:1) by the addition of KOH [241].
See also [222,234,236,338].

9. Dehydrogenation

The (tetraglyme)$_3$-$H_5PMo_{10}V_2O_{40}$ complex dissolved in 1,2-dichloroethane catalyzes the aromatization of cyclic dienes at 70°C in the presence of O_2 through oxidative dehydrogenation [242].p-Xylene was selectively dehydrogenated to 1,2-di-p-tolylethane in low yield under mercury lamp irradiation using $H_3PW_{12}O_{40}(H_2O)_n$ or $(Bu_4N)_3PW_{12}O_{40}$ as catalyst together with an equimolar amount of PtO_2, as hydrogen evolution catalyst. Under a slight overpressure of O_2 *p*-tolualdehyde and *p*-toluic acid were the products in moderate yields [243]. Irradiation of *fac*-HRe(bpy)(CO)$_3$Br and Et_3N in THF at <400nm results in catalytic evolution of H_2. No CO_2 reduction occurs if the reaction is conducted in a CO_2 atmosphere (cf. AS 1987, ref.86); CO does not inhibit the reaction [244].

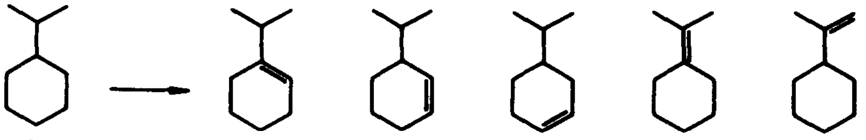
Iodosylbenzene in the presence of $RuCl_2(PPh_3)_3$ could be used for the dehydrogenation of secondary amines to imines [245]. Aldonolactones were prepared from protected alditols by dehydrogenation in the presence of $H_2Ru(PPh_3)_4$ as catalyst (toluene solution, 50°C). For example the protected arabinitol (87) was dehydrogenated to lactone (88) with 86% yield [246].


R = $tBuMe_2Si$-

87

88

Dehydrogenation of tetralin was studied in the presence of phthalocyanine and tetrapyridinoporphyrazine metal complexes. The dehydrogenation activity of phthalocyanine complexes increased in the order Cu < Ni < Co [247]. Carbonyl(halogeno)phosphine-rhodium complexes exhibit photocatalytic activities for 2-propanol dehydrogenation, yielding acetone and H_2. The photocatalytic activities of the chloride complexes with different phosphine ligands increase in the order $PPh_3 < P(iPr)_3 < PEtPh_2 < PEt_2Ph < PEt_3 < PMe_3$ [248]. Alkene and H_2 formation has been observed in catalytic dehydrogenation of alkenes with $RhCl(PR_3)_2$, photogenated from $RhCl(CO)(PR_3)_2$ by a high-pressure mercury lamp or by a Xe lamp. For example $RhCl(CO)(PMe_3)_2$ in cyclohexane yielded H_2 and cyclohexene (1402 and 1289 turnovers, respectively) at 68°C [249]. This latter complex has been found to be an efficient and general alkane photodehydrogenation catalyst with unusual selectivity. For example, quantum yields up to 0.10 and turnover numbers as high as 5000 were achieved with cyclooctane as substrate and starting from isopropylcyclohexane (89) the following olefins were formed at 50°C [250]:


89

5%

18%

42%

<0.5%

35%

Dehydrogenation of cyclic ethers such as THF and tetrahydropyran is catalyzed by a photocatalytic system composed of acetone and a Rh compound [251]. Photocatalytic dehydrogenation of cyclohexanol to yield cyclohexanone and H_2 using (TPP)RhCl was studied at reflux temperature (161°C). The rate of reaction was first order in catalyst concentration and correlated linearly with photointensity [252]. Tin(II)-coordinated Ir(III) complexes (formed *in situ* from $IrCl_3.3H_2O$ and $SnCl_2.2H_2O$) catalyze the dehydrogenation of MeOH to $CH_2(OMe)_2$ under high-pressure mercury lamp irradiation at reflux temperature. The complex $[IrH(SnCl_3)_5]^{3-}$ is regarded as the photocatalytically active species [253].

A slow catalytic dehydrogenation of 1,3-cyclohexadiene to benzene and H_2 has been observed at 80°C in the presence of *cis*-$[PtCl_2(SnCl_3)_2]^{2-}$. Trace amounts of dehydrogenation products were formed also from cyclohexene, cyclohexane and ethylbenzene [254].

See also [216].

10. Hydrogen Transfer Reactions (Organic Compounds as Reductants)

a) Hydrogenation of C=C Bonds

The reduction of α,β-unsaturated ketones by H-transfer from iPrOH and the hydrogenation of cyclohexadienes catalyzed by $MHCl(CO)(PPr^i_3)_2$ (M = Ru,Os) complexes has been reported. The activity of the catalysts in transfer hydrogenation was markedly increased by adding $NaBH_4$ [255]. $CoH(N_2)(PPh_3)_3$ was found to be an active hydrogen transfer catalyst in dihydronaphthalene disproportionation [256]. The Rh(III) complex py_3RhCl_3 has been found to be a versatile catalyst in the presence of NaOMe or KOH for the transfer hydrogenation of acetylenes to olefins, dienes to monoenes, α,β-unsaturated ketones to saturated ketones, Schiff bases to amines, and aromatic ketones to alcohols using iPrOH as H source. With catalyst systems formed *in situ* from $RhCl_3.xH_2O$ and chiral amines, enantioselective reduction of ketones took place but the optical yields were rather low [257]. Heterogenized complexes of Ru, Rh, Pd, and Pt were prepared by treating a chloromethylated styrene-divinylbenzene copolymer with Li_3P in THF and then with PPh_3 complexes of the metals. The polymer-bound Ru and Rh complexes catalyzed the reduction of 1-heptene by aqueous HCOOH and HCOONa at 40-100°C. The reduction was promoted by DMF [258]. Catalysts prepared from $Ni(acac)_2$ and $AlEt_3$ showed high activity in the hydrogen transfer between dihydroarenes [259]. See also [279].

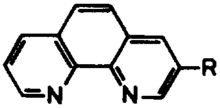
b) Transfer Hydrogenation of Ketones

Selective reduction of 2-haloacetophenone derivatives to the corresponding alcohols in 70-80% yield has been observed in the reaction with the acid-stable NADH model compound, 9,10-dihydro-10-methylacridine in CH_2Cl_2 in the presence of $TiCl_4$ at 25°C [260]. The Meerwein-Ponndorf type reduction of α,β-unsaturated aldehydes and ketones is catalyzed by Cp_2ZrH_2. Even sterically hindered enones such as *trans*-2-hexyl-2-decenal are reduced to the corresponding allylic alcohols in about 90% yield [261].

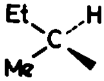
The mechanism of transfer hydrogenation of ketones to alcohols by iPrOH catalyzed by the $[HFe_3(CO)_{11}]^-$ anion under phase transfer conditions has been studied [262]. The Ru(II)-arene complex $[\{Ru(C_6H_6]\}_2(\mu\text{-}Cl)_3](ClO_4)$ is an active catalyst for the transfer hydrogenation of acetophenone by iPrOH [263]. Unsaturated aldehydes can be reduced at 30-80°C with good yields and excellent selectivities to the corresponding unsaturated alcohols by H transfer from $HCOONa/H_2O$ catalyzed by $RuCl_2(PPh_2C_6H_4SO_3Na\text{-}m)_2$ in aqueous/organic biphasic systems [264].

The coordinatively unsaturated complex $HCoL_3$ (L = $PPh(OEt)_2$) generated from $HCoL_4$ by photoirradiation catalyzes the H-transfer from secondary alcohols to ketones. Based on kinetic data it was concluded that the reaction is initiated by the coordination of the ketone to $HCoL_3$ [265]. The initial rates and the second order rate constants of catalytic hydrogen transfer from 1-phenylethanol to cyclohexanone and to 4-alkyl-substituted cyclohexanones with photogenerated $HCo[PPh(OEt)_2]_3$ have been determined. The transformation of the hydrido ketone cobalt complex into the alkoxo intermediate was found to be the rate-determining step

[266]. Substituted cyclohexanones were reduced to the corresponding alcohols using iPrOH as the H-source and Rh(I) complexes with phenanthroline and its substituted derivatives as catalyst precursors. It was found that 4,7-diphenyl phenanthroline and 4,7-dimethyl phenanthroline promote the formation of axial alcohols with high stereoselectivity (in some cases above 98%) [267]. The rhodium(I) catalyzed asymmetric transfer hydrogenation of acetophenone by iPrOH using chiral phenanthroline ligands (90) resulted in 24% ee as the highest optical yield [268].



90; R =



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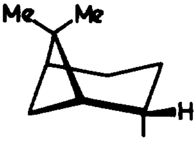
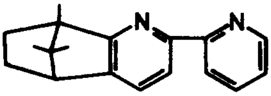


The optically active bipyridine (91) was prepared from (+)-camphor and used as a ligand in transfer hydrogenation of acetophenone with Rh(I) catalysts. Only a very low stereoselectivity was observed [269].

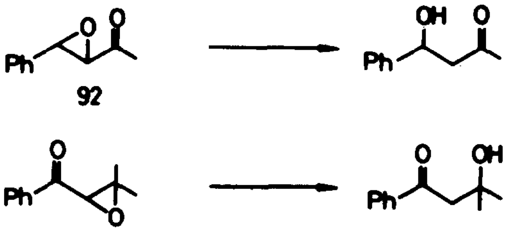


91

The complexes $(Cp^*M_2)_2$ and $[(Cp^*M)_2(\mu\text{-}Cl)_3]ClO_4$ (M = Ir,Rh) were found to be effective catalysts for the hydrogen transfer from iPrOH to PhCOMe in the presence of $iPrO^-$. The Ir complexes were less reactive that the Rh analogs [270]. Higher than 90% conversions and optical yields up to 84% have been obtained in catalytic hydrogen transfer from iPrOH to t-butyl phenyl ketone using {Ir(COD)(L)(I)] as catalyst precursor. (L = S-(+)-2-pyridinal-1-phenylethylimine) [271].
See also [257].

c) *Transfer Hydrogenation of Miscellaneous Organic Compounds*

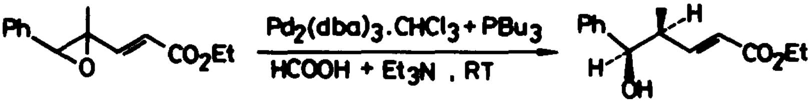
The reduction of α,β-epoxyketones like (92) and (93) to hydroxy ketones in excellent yields by triethylammonium formate in THF in the presence of a catalytic amount of $Pd(OAc)_2$ and dppe has been reported [272].



92

93

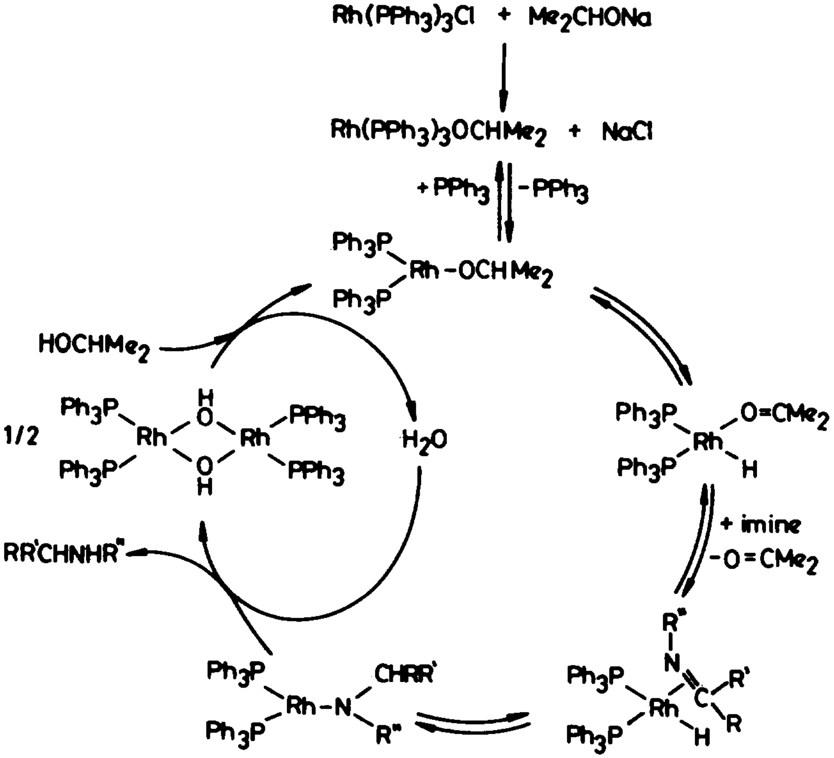
A selective hydrogenolysis of alkenyloxiranes (e.g.94) with triethylammonium formate catalyzed by $Pd_2(dba)_3.CHCl_3$ and PPh_3 has been reported [273].



94

99 %

Reduction of methylene blue by iPrOH is catalyzed by $Fe(CO)_5$. Kinetic oscillations were observed [274]. The catalytic cycle of the hydrogen transfer reaction from 2-propanol to imines forming secondary amines in the presence of $Rh(PPh_3)_3Cl$ and iPrONa has been elucidated [275]:



Aromatic nitro compounds were reduced to the corresponding amines by 2-mercaptoethanol in the presence of $[Fe_2M(O)(OAc)_6(py)_3]$ [M = Mn,Fe,Ni,Co] complexes. The same complexes catalyzed also the oxidation of thiophenol by O_2 to diphenyl disulfide. The catalytic activity of the complexes decreased in both cases in the stated order of metals [276]. Hydrogen transfer from 2-propanol to nitroaromatic compounds in the presence of $[Rh(NBD)(PPh_3)_2]^+$ was found to be first order in both substrate and catalyst [277]. Rhodium complexes immobilized on amino- or aminophosphine-modified silica gel catalyze the transfer hydrogenation of $PhNO_2$ to $PhNH_2$ with iPrOH or the same reduction in iPrOH with $NaBH_4$ as H-donor. Selective reduction of chloro- and bromonitrobenzenes to the corresponding haloanilines was observed [278].

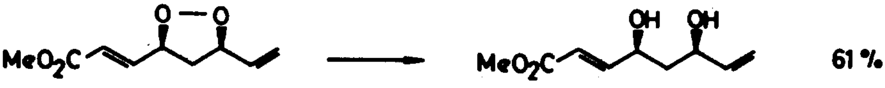
Hydrogenolysis of Ph_3P coordinated to transition metals in hydrogenation of cyclopentene by hydrogen transfer from pyrrolidine or 2-propanol was observed. The complexes $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_4$, $RuH_2(PPh_3)_4$, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ showed different activity. The relative preference between hydrogenation and hydrogenolysis was strongly affected by the hydrogen donors and by the complex catalysts [279].

The complex $(Cl_8TPP)FeCl$ has been found to be a very efficient catalyst for the photoreduction of carbon tetrachloride to chloroform by alcohols [280]. The transfer hydrogenation of CCl_4 in cyclohexanol with $Ru_3(CO)_{12}$ precatalyst (82°C, 35 bar CO) gave with more than 100 turnovers $CHCl_3$ and cyclohexanone [281]. Rhodium and palladium complexes, immobilized on aminophosphinylated silica gel or polymers containing heterocyclic amine groups, catalyzed the hydrodehalogenation of *gem*-dihalocyclopropanes by H transfer from iPrOH or $NaBH_4$. The use of $NaBH_4$ results in the replacement of both halogen atoms [282].
See also [257].

11. Reduction Without Molecular Hydrogen

a) *Stoichiometric Reduction with Low-Valent Transition Metal Complexes*

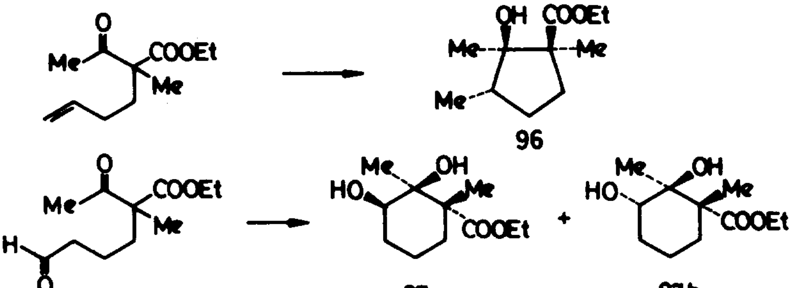
A general method for reduction of α-oxygenated esters, such as α-acetoxy, α-hydroxy esters to the corresponding deoxygenated esters using a SmI_2-THF-HMPA electron transfer system has been described. (R,R)-tartarates gave up to 99% isolated yields of (R)-malates [283]. SmI_2 mediated reduction of 1,2-dioxolanes at -78°C in THF under an inert atmosphere led to diols with retention of stereochemistry with good to excellent isolated yields [284]:



An 11-membered, unsaturated lactone benzoate was reduced with SmI_2 + THF + HMPA in the presence of pivalic acid to the pheromone ferrulactone (95) in 15% yield [285].

95

Highly functionalized five- and six-membered carbocycles (e.g. 96,97) have been prepared with high diastereoselectivity at three contiguous stereocenters by SmI_2-promoted intramolecular reductive coupling reactions in THF-alcohol solutions at $-78^{o}C$ [286].


96

97a

97b

A rapid and mild deoxygenation of sulphoxides, sulphones, N-oxides and $(Bu_3Sn)_2O$ was found at room temperature by using a stoichiometric amount of SmI_2 in THF-HMPA [287].

The reduction of several *p*-substituted nitrobenzenes by Ti(O) has been reported. Substituted anilines and azobenzenes were observed as reaction products [288]. Both aliphatic and aromatic sulfoxides are readily deoxygenated to sulfides by $Cp_2Ti(CO)_2$ in THF at reflux temperature. Yields are in most cases better than 90% [289].

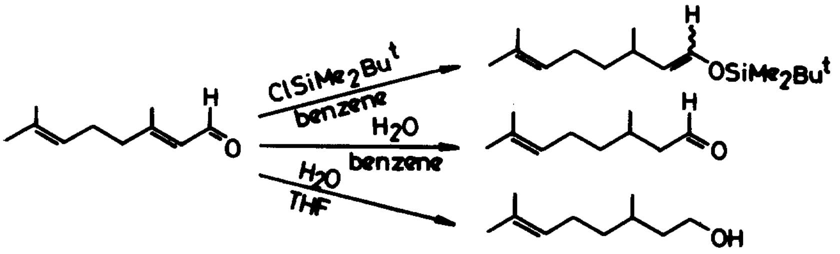
Metal nitrene complexes have been proposed as intermediates in reactions of nitroso compounds with $(Ph)(OCH_3)C{=}Cr(CO)_5$, $Cr(CO)_6$ or $Fe(CO)_5$ leading to the corresponding azo- and azoxy compounds [290]. The cyclopentadienones (**98a**, R = $SiMe_3$) and (**98b**, R = Ph) were reduced by $Cr(CO)_6$ in refluxing dioxane containing 1% water to the cyclopentenones (**99a**, R = H) and (**99b**, R = Ph) with 14 and 61% yield, respectively [291].


98

99

Trappings experiments provided support for an electron transfer mechanism proceeding in two one-electron steps in the Fe^{2+} reduction of N-aryl-O-pivaloylhydroxylamines [292]. A radical pair mechanism in hydrometalation and stoichiometric hydrogenation reactions of $cpFe(CO)_2H$ with conjugated dienes has been suggested based on kinetic results and CIDNP phenomena [293]. Norbornane-2-carboxaldehyde is converted by $Fe_2(CO)_9$ in refluxing Bu_2O to the alcohol with 68% yield. In hexane or THF at lower temperatures the corresponding ester is the main product [294]. Reduction of nitrobenzene to aniline by $Fe_3(CO)_{12}$ under triphase conditions (aqueous NaOH, benzene containing $PhNO_2$ + $Fe_3(CO)_{12}$, and solid chloromethylpolystyrene quaternised by tertiary amines) conditions has been studied [295]. The reduction of acetonitrile to dimethylamine has been observed in the reaction with $[(C_6Me_6)RuB_9H_{12}]$ [296].

Citral and some other α,β-unsaturated aldehydes gave good to excellent isolated yields of products of reductive silylation (**100**), regioselective conjugate reduction (**101**), and in some cases of one-pot reductions to the saturated alcohol (**102**) using $[(Ph_3P)CuH]_6$ as reductant at room temperature [297].



100

101

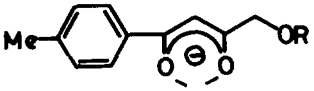
102

See also [302,303,304,305,308].

b) Inorganic Reductants in the Presence of Transition Metal Complexes

Enantioselective reduction of ketones (acetophenone, octanone-2, butanone-2) with $NaBH_4$ in cyclohexane in the presence of the chiral [*fac*-Λ-$L_3Ln(III)$] complexes (L = **103**; Ln =

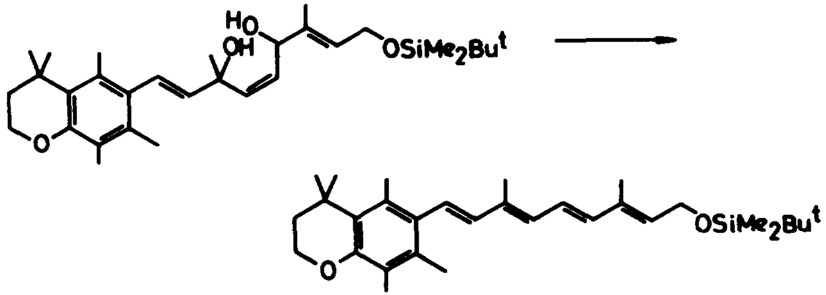
La,Pr,Gd,Er) has been reported. Highest optical yield was 84% [298].


103; R = ℓ-menthyl

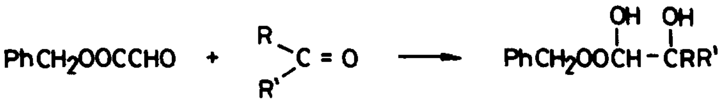
1-Phenalenol (**104**) has been prepared in 83% isolated yield from phenalenon at 0°C using $NaBH_4/CeCl_3$ for reduction [299].


104

Some disubstituted acetylenes were reduced to the corresponding olefins by iBuMgBr in the presence of Cp_2TiCl_2. The stereochemistry of the reaction was determined [300]. Epoxides can be reduced to the less substituted alcohols by hydrozirconation followed by hydrolysis. Addition of Cp_2MCl_2 (M = Ti,Zr) or $Ti(OBu)_4$ improves the regioselectivity [301]. The reduction of 2-ene-1,4-diols to 1,3-dienes by low-valent Ti compounds formed *in situ* from $TiCl_3$ and $LiAlH_4$ in THF was used for the preparation of aromatic retinoid analogs like (**105**; R = H,Et). The reaction yields *trans*-dienes in a highly stereospecific manner [302].

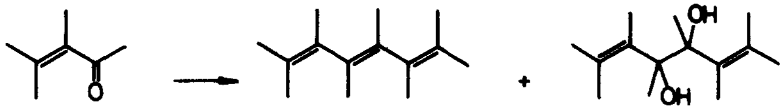

105

The procedure of deoxygenative inter- and intramolecular coupling of ketones and aldehydes to olefins on treatment with low-valent titanium compounds has been optimized. The best results were obtained by rapid addition of the substrate to a reagent prepared from a zinc-copper couple and 3 equiv of $TiCl_3(DME)_{1.5}$ per equivalent of carbonyl compound [303]. The low-valent titanium compound prepared form $TiCl_4$ and Zn in the presence of 1,2-dimethoxyethane reduces carbonyl compounds to 1,2-diols, the corresponding coupling products. Under suitable conditions (excess of glyoxalate) this method was successfully employed for the reductive cross coupling of glyoxylic acid benzyl ester and aldehydes or alcohols to yield α,β-dihydroxycarboxylic acid benzylesters (**106**; R = alkyl, aryl: R' = H,Me,Ph) [304].

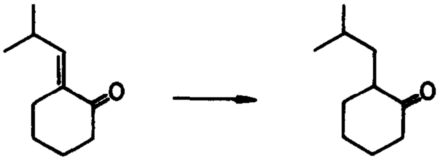


106

The reactive coupling of α,β-unsaturated ketones (**107**) by the $TiCl_4$-Mg reagent leads in most cases to 1,3,5-trienes (**108**) and bisallylic pinacols (**109**). It has now been found that in the presence of tBuOH hydrogenation of the C=C double bond takes place and thus, for example, (**110**) is transformed into (**111**) [305].



107 **108** **109**



110 **111**

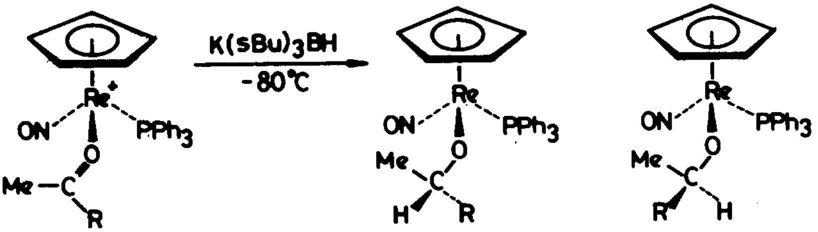
The synthesis of α-amino acids by reduction of α-oximino esters with $TiCl_3$ and $NaBH_4$ has been reported [306]. Mixtures of

MgH_2 and catalytic quantities of first row transition metal halides effectively reduce organic halides at room temperature in THF suspension. Quantitative conversions of chlorobenzene to benzene were observed in the presence of $NiCl_2$ and $FeCl_3$. Quantitative yields of decane from 1-chlorodecane were achieved in the presence of $TiCl_3.3THF$, $CrCl_3$, $MnCl_2$, and $FeCl_3$ [307].

The V(II) complex $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, prepared *in situ* from $VCl_3(THF)_3$ and zinc dust, is an effective reagent for the reductive coupling of aldehydes to 1,2-diols. The important advantage of this reagent is that it may be used for the intermolecular cross coupling of two different aldehydes to prepare unsymmetrical diols if the more reactive aldehyde is slowly added to the mixture of the less reactive aldehyde and the vanadium reagent [308].

Rapid ionic hydrogenation of hindered alkenes like $Me_2C{=}CMe_2$, with high yields at -75°C has been demonstrated using $CF_3SO_3/HMo(CO)_3cp$ [309].

Methyl ketone complexes of the chiral rhenium Lewis acid (**112**; R = Et,iPr,tBu,Ph) were reduced with high diastereoselectivity (80-98%) into alkoxide complexes (**113**) by a commercially available borohydride reductant. The alkoxide complex products could easily be transformed into organic alcohols or esters, and the rhenium fragment could be recovered in optically active form [310].

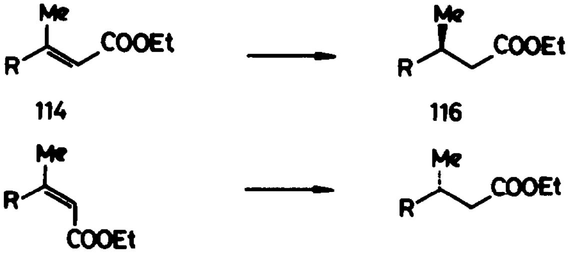


(+)-(*R*)-112 (+)-(*RS*)-113 (+)-(*RR*)-113

Oxiranes were deoxygenated to olefins by $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$ and $NaBH_4$ at 25°C. For example, *trans*-stilbene oxide and 2-octene-oxide gave 75% *trans*-stilbene and 30% 2-octene, respectively [311]. The catalytic activity of Mo-Fe-S cluster compounds for reduction of acetylene increased with increasing

Fe:Mo ratio and reached a maximum at Fe:Mo = 8. $(NH_4)_2WS_4$ alone or in combination with Fe compounds did not show catalytic activity [312,313]. The $Et_3NH^+H_2PO_2^-.nH_2O/RuCl_2(PPh_3)_3$ system selectively reduces aromatic and aliphatic ketones to the corresponding alcohols with excellent yields at room temperature. Nitro groups and isolated C=C double bonds are not attacked under these conditions [314]. The $Ru_3(CO)_{12}$-catalyzed reduction of *ortho*-nitrophenylallyl ether with carbon monoxide has been studied [315].

Alkynes were reduced to (Z)-alkenes in THF solution by SmI_2 in the presence of cobalt catalysts and a proton source [316]. Dimethoxyborane-transition metal salt systems were used for the reduction of a variety of functional groups. The $(MeO)_2BH$ + $CoCl_2$ system reduced nitriles and aldehydes, the $(MeO)_2BH$ + $NiCl_2$ system reduced nitriles, aldehydes, ketones, and olefins under mild conditions [317]. Imines, anils and enamines were reduced by $CoCl_2$ or $NiCl_2/NaBH_4/MeOH$ in THF at low temperatures to afford the corresponding amines in 64-82% yields [318]. The unsaturated carboxylic acid esters (**114**) and (**115**) (R = $PhCH_2CH_2$, $Me_2CH{=}CHCH_2CH_2$, iPr, Ph) were reduced to the saturated esters (**116**) and (**117**) with $NaBH_4$ in EtOH in the presence of catalytic amounts of $CoCl_2.6H_2O$ and the chiral ligand (**118**). Enantioselectivity of this system formed *in situ* exceeded in most cases 90% [319].



114

116

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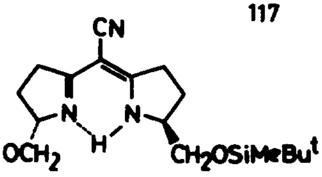


118

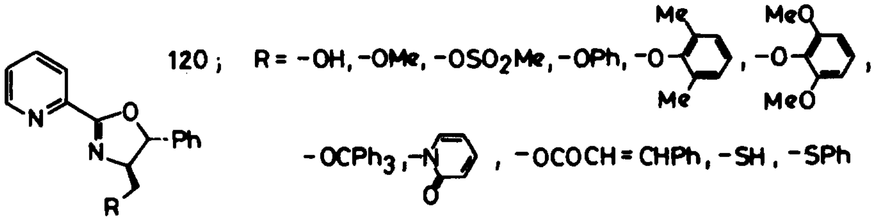
A simple procedure for selective reduction of the olefinic double bond in α,β-unsaturated carbonyl compounds using powdered aluminium and $NiCl_2.6H_2O$ in THF at room temperature has been described. Up to 95% isolated yields were achieved within 15 min reaction time [320]. A nickel reagent prepared from $NiBr_2$.DME, PPh_3, and $LiAlH_4$ has been found useful for the reductive desulfurization of mercaptans, thioethers, sulfoxides, and sulfones [321]. It has been found that $Ni(PPh_3)_4$ or $Pd(PPh_3)_4$ activate MgH_2 for the reduction of organic halides [322]. Selective removal of the O-bonded allyl protecting group with Bu_3SnH and $Pd(PPh_3)_2Cl_2$ catalyst, and reduction of the para-quinol ether group with $CrCl_2$ have been applied in transformations of phenolic peptides [323]. Grignard reagents have been found to reduce both hindered and unhindered alkyl halides to the corresponding alkanes in the presence of either (dppf)Pd(0) or $(dppf)PdCl_2$ in concentrations of 2 to 50 mol% (dppf = 1,1'-bis(diphenylphosphino)ferrocene) [324]. Acyl chlorides (e.g. 119) were selectively reduced by Bu_3GeH to aldehydes using $Pd(PPh_3)_4$ as catalyst [325].

119

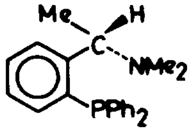
A reducing system, $NaBH_4$-Cu_2Cl_2/MeOH has been described for the dehalogenation of aryl halides, conjugate reduction of α,β-unsaturated esters, and deuterium labeling at 0°C. A transient copper hydride was assumed as the active reducing agent [326].
See also [255,278,282].

c) Reductions via Hydrosilylation

Rhodium(I) complexes of β-diketonates and related ligands were found to be catalysts for acetophenone hydrosilylation with Ph_2SiH_2 [327]. Up to 80% ee of (R)-1-phenylethanol from acetophenone has been achieved at 0°C in the enantioselective hydrosilylation with α-naphtylphenylsilane and subsequent acidic hydrolysis using an *in situ* catalyst composed from $[(C_2H_4)_2RhCl]_2$ and different 2-[2-pyridinyl]-1,3-oxazolines (**120**) as ligands [328].

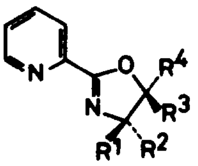


High activity and optical yieds up to 50% ee have been obtained in the asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 catalyzed by Rh(I), Ir(I), Pd(II), and Pt(II) complexes combined with (S)-amphos (**120a**) [329].



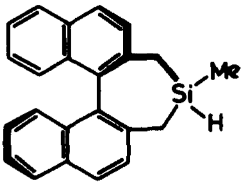
120a

Enantioselective hydrosilylation of ketones with 21 different *in situ* $[Rh(COD)Cl]_2$ + chiral pyridinyloxazoline (**121**; R^1 = H,Me,Et,Ph,Cy,Pr; R^2 = H,Me,Et,iPr,sBu,iBu,tBu, CH_2Ph, CH_2CH_2SMe, CH_2OH, CH_2OMe, bornyl; R^3 = H,Me,Ph; R^4 = H,OPh,bornyl) catalysts at 20°C has been reported. After hydrolysis, 1-phenylethanol was produced in the best case (H,sBu,H,H) with 83% ee from acetophenone [330].

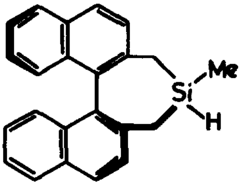


121

The optically pure binaphthyl cyclic silanes (R)-(**122**) and (S)-(**122**) have been prepared and used for the reduction of prochiral ketones in the presence of $Rh(PPh_3)_3Cl$ or $TiCl_4$ as catalysts. Optical yields ranged from 6 to 26% [331].

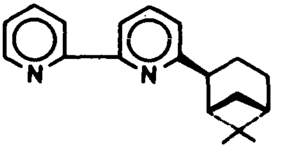


(R)-122



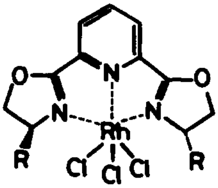
(S)-122

Optically active pyridinethiazolidones, pyridinethiazolines, pyridinimidazolines, Schiff bases and bipyridines have been tested as cocatalysts together with the procatalyst $[Rh(COD)Cl]_2$ in catalytic hydrosilylation of prochiral ketones with diphenylsilane. Optically active 1-phenylethanol was produced from acetophenone after hydrolysis of the silyl ether. The best optical purity of 72% was obtained with the pinanyl-substituted bipyridine (123) [332].



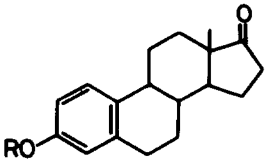
123

Chiral bis(oxazolinylpyridine)rhodium(III) trichloride complexes (124: R = iPr,sBu,tBu) were found to be effective catalysts for the asymmetric hydrosilylation of ketones with Ph_2SiH_2 between -20°C in the presence of Lewis acids. Extremely high enantioseletivities (94%) in the formation of secondary alcohols have been reported [333].

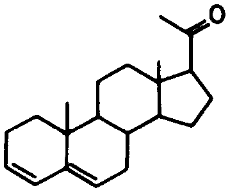


124

2- and 4-alkylcyclohexanols were produced through hydrosilylation of 2- and 4-alkylcyclohexanones with Ph_2SiH_2 in the presence of $RhCl(PPh_3)_3$ or other, similar complexes prepared *in situ*. The isomeric distribution of the alcohols was influenced by the position and size of the alkyl group, the catalyst concentration, the reaction temperature, and the type of P-ligand [334]. The reduction of steroid 17- and 20-ketones (**125** and **126**, respectively) with Ph_2SiH_2 and Rh-(+)- or (-)-DIOP catalysts has been reported. Asymmetric induction was only observed in the case of the 17-ketones (**125**) [335].

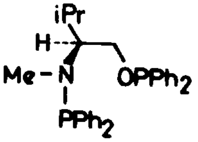


125 ; R = H, Me



126

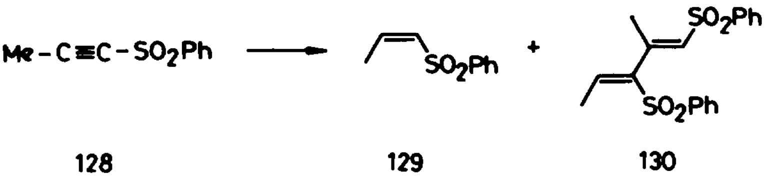
The enantioselective reduction of N-(α-methylbenzylidene) benzylamine to N-benzyl-α-phenylethylamine through hydrosilylation catalyzed by *in situ* generated chiral aminophosphine--phosphinite-rhodium catalysts has been studied. The best result (29% ee) was obtained using the ligand (**127**) [336].



127

Rapid *cis* reductions of acetylenes at room temperature using acetic acid, tetramethyldihydrodisiloxane, and a Pd(0) catalyst formed from $(dba)_3Pd_2.CHCl_3$ and Ar_3P in benzene have been reported [337]. Aromatic acyl fluorides can be reduced at 175°C under H_2/CO pressure to the corresponding aldehydes in the presence of $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ catalysts. Reductions with polymethylhydrosiloxane occur at lower temperature and give better yields than hydrogen [338]. The stereoselective reduction of acetylenic sulfones (e.g.**128**) to *cis* vinylic sulfones (**129**) was achieved by a

Cu(II) salt and Et_2MeSiH. The best results were obtained by the use of $Cu(BF_4)_2$. In some cases reductive coupling products (**130**) were also formed [339].



See also [297].

d) Electroreduction and Photoreduction

Up to 98% isolated yields of pinacols have been achieved in the samarium-catalyzed electrochemical coupling of aldehydes and ketones [340]. The reductive dehalogenation of halides with carbonylferrates derived from $Fe(CO)_5$ and cathodically-generated methoxide ion has been studied [341]. Electroreduction of $HOC_2H_4N_3$ on glassy carbon electrodes modified with $(NBu_4)_4[MoFe_3S_4(SPh)_3(o\text{-}O_2C_6Cl_4)]_2$ and $(NBu_4)_2[Fe_4S_4(SPh)_4]$ yields $HOC_2H_4NH_2$, N_2, N_2H_4, and NH_3 [342]. The two-electron photoreduction of 1,2-dichloroethane promoted by the $^1(\delta\delta^*)$ excited state of $Mo_2[O_2P(OPh)_2]_4$ gave ethene quantitatively [343]. See also [265,266,280].

IV. OXIDATION

1. Catalytic Oxidation of Hydrocarbons and Hydrocarbon Groups

a) Oxidation of Alkanes

Silica-supported 12-molybdophosphoric acid was found to be an effective catalyst for the partial oxidation of methane (mainly to CH_2O). The 12-molybdophosphoric acid Keggin unit itself was regarded to be responsible for the activity of the catalyst [344].

The ratio of lower to higher molecular weight carboxylic acids formed in the oxidation of hexadecane by O_2 and manganese acetate as catalyst decreased in the presence of polyethylene. Polyethylene itself was also oxidized in the process [345].

Azido(tetraphenylporphyrinato) complexes of Cr(III), Mn(III), and Fe(III) have been found to be active catalysts for the selective (88-92%) formation of tBuOH from isobutane and O_2 (7 bar) at 80°C in the absence of added co-reductants [346]. A huge increase in catalytic activity was observed when the *meso*-phenyl groups in the porphyrin ligand were replaced by pentafluorophenyl substituents. In the case of the Fe(III) complex the catalyst turnovers in 6 h could be raised from 130 to 2060 [347]. The complexes $Fe(F_{20}TPP)X$ ($X = N_3^-$, Cl^-, OH^- and 1/2 O^{2-}) have been found to be uniquely active catalysts for the selective air oxidation of propane to a mixture of isopropyl alcohol and acetone at temperatures as low as 100°C [348].

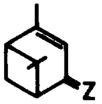
The mixed-metal complex $Ni(St)_2.Cr(St)_3$ displays higher catalytic activity than either of its components in the oxidation of pentadecane with O_2. This can be explained by the fact that the Cr component is a better chain initiator and the Ni component is a better oxidation catalyst [349].

See also [495,543].

b) Oxidation of Olefins

Cholesterol was oxidized with O_2 using as catalyst manganese acetate hematoporphyrinate immobilized on a morpholine-modified tetrafluoroethylene-perfluoro-3,6-dioxa-5-methyl-8-sulfonylfluoro-1-octene copolymer film. Although the immobilized catalyst was more active than the corresponding homogeneous catalyst [350], oxidation gave the same products whether the homogeneous or polymer-immobilized Mn-porphyrins were used. On the contrary, oxidation of anthracene gave anthraquinone in the homogeneous system but only peroxidic products with the immobilized catalyst [351]. The oxidation of aromatic olefins, with O_2 in the presence of $NaBH_4$ catalyzed by (TPP)MnCl has been studied. A mechanism was proposed which proceeds via the activation of olefins on (TPP)Mn(II) followed by reaction with O_2 to form the products

[352]. Ethylene glycol is formed directly from ethene, oxygen (air), and water by means of a Hoechst-Wacker type redox system which comprises thallium chloride and iron or copper chloride in aqueous solution. With iron chloride as cocatalyst the yield of ethylene glycol is 80-90% [353]. Highly selective oxidative cleavage of styrene into benzaldehyde by O_2 has been achieved at ambient conditions in the presence of catalytic amounts of $[RuCl(dppp)_2]ClO_4$ or *trans*-$[RuCl_2(dppp)_2]$. Complete supression or substantial inhibition of the catalytic activity was observed in the presence of free-radical traps [354]. Liquid-phase oxidation of 3-carene, α-pinene, and tetralin catalyzed by Co and Cu complexes at 5-100°C and 5 bar was studied. Allylic ketones were the major products [355]. Oxidation of α-pinene (**131**) by O_2 in liquid phase catalyzed by cobalt acetylacetonate has been studied at various temperatures and concentrations. A rate equation for the formation of products (**132**,**133**) was given [356].



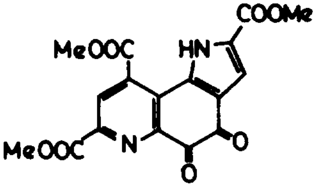
131; Z = H_2
132; Z = H,OH
133; Z = O

In the presence of PPh_3, Co(salen) catalyzes the oxidative hydration of styrene to α-phenylethanol in EtOH solution according the following reaction scheme:

$$PhCH{=}CH_2 + PPh_3 + CH_3CH_2OH + O_2 \text{ ---- } PhCH(OH)CH_3 + OPPh_3 + CH_3CHO$$

In toluene solution the Co(salen)/PPh_3 system catalyzes the oxidation of secondary alcohols to ketones in a much slower reaction [357]. Using a similar system, olefins could be hydrated to alcohols in moderate yields with O_2 and a secondary alcohol (as H-donor) in the presence of $Co(acac)_2$ as catalyst. The corresponding ketones and saturated hydrocarbons were formed as byproducts. Alcohol yields were higher if bis(trifluoroacetylacetonato)cobalt(II) was used as catalyst [358,359]. Moreover, also triethylsilane [360], or triphenylsilane [361] could be used as H-donors; in these cases, however, the corresponding silyl peroxides were formed as byproducts.

Reducing $Pd(OAc)_2$ with H_2 in the presence of 1,10-phenanthroline or 2,2'-bipyridine, catalytically active solutions were formed which catalyzed the oxidative acetoxylation of ethene to vinyl acetate, propene to allyl acetate and toluene to benzyl acetate at 1 bar O_2 and 25-90°C [362]. Cationic palladium nitro complexes have been found to catalyze effectively the selective oxidation of alkenes to ketones (e.g. 1-octene to 2-octanone) at room temperature and 1 bar O_2. Cyclic monoalkenes such as cyclohexene were also readily oxidized, but the corresponding ketone product was catalytically oxydehydrogenated to the α,β-unsaturated ketone [363]. The kinetics of oxidation of butene to methyl ethyl ketone were studied using a homogeneous $PdCl_2$-$CuCl_2$ catalyst in aqueous solution between 35 and 85°C. The reaction was found to be first order in butene, half order in $PdCl_2$ and negative first order with respect to $CuCl_2$ [364]. A kinetic study of cyclopentene mono-oxygenation by O_2 catalyzed by a $PdCl_2$-$CuCl_2$ complex in ethanol (AS 1987, Ref. 292) has shown that oxidation cannot be accounted for by conventional Wacker-type catalysis involving the reoxidation of Pd(0) by Cu(II). More probably the process is catalyzed by a Pd(II)-Cu(I) bimetallic complex, in which Cu(I) serves as a transient oxygen carrier and a Pd(II)OOH species oxygenates cyclopentene to cyclopentanone [365]. Oxidation of 1-octene to 2-octanone by O_2 was performed in a flow reactor with aqueous $PdCl_2$ containing $Cu(OAc)_2$ and $MeOCH_2CH_2OH$. 3-Octanone and 4-octanone were formed as minor byproducts [366]. Terminal olefins were oxidized to the corresponding 2-alkanones with O_2 in DMF/H_2O using $PdCl_2$ and the trimethyl ester of coenzyme PQQ (**134**) as a Wacker oxidation catalyst system. The *ortho*-quinone function reoxidizes the reduced palladium species generated *in situ* [367].



134

Cyclooctatetraene was oxidized to benzaldehyde by O_2 with a $PdCl_2$ - CuCl (1/10) catalyst in THF solution at 50-60°C with about

50% yield. 1,2-Epoxycyclooctatriene was proposed as an intermediate of this reaction [368]. The kinetics of ethene oxidation to β-haloethyl alkyl ethers and dialkyl acetals of acetaldehyde in MeOH or EtOH solutions by O_2 in PdX_2-CuX_2-LiX-HX (X = Cl,Br) systems has been studied. The rate constants were higher in EtOH than in MeOH [369]. The oxidation of 1-dodecene by oxygen at 50°C with a mixed $Pd(dba)_2$-silver nitrite catalyst in alcohols has been reported to give 2-dodecanone in good yield [370].

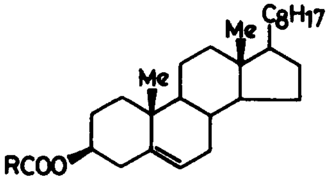
Copper(II) nitrate supported on Ampholite AKNB (an oxidized 2-methyl-5-vinylpyridine + *p*-divinylbenzene copolymer) catalyzes the oxidation of cyclohexene with O_2 to cyclohexene hydroperoxide with 95-100% selectivity [371].

See also [242,495].

c) Epoxidation of Olefins

The mechanism of catalytic epoxidation of propene with O_2 using Cr(III), Mn(III), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) p-tetratolylporphyrins in the presence of propionaldehyde has been studied [372,373]. The cooxidation of *cis*-octene-4 and butyraldehyde by O_2 in the presence of $MoO_2(acac)_3$ or $Co(acac)_3$ converted 68 and 40% of the olefin, respectively, into the epoxide. The *cis/trans* epoxide ratio was nearly independent of the aldehyde/olefin ratio [374]. The effects of catalyst and substrate concentration in the oxidation of cholesterol by air in the presence of (TPP)MnOAc and its substituted derivatives was studied [375].

Epoxidation of hexamethyldewarbenzene using (TPP)FeCl as catalyst was investigated [376]. Epoxidation of cyclohexene by O_2 is catalyzed by Ru(III) in aqueous solutions at 35°C. The following systems have been found to be active: $[RuCl_2(H_2O)_4]^+$ in water-ethanol or water-dioxane, and $[RuCl_2(H_2O)_2(HA)]$ (H_2A = ascorbic acid) in water-dioxane. Ethanol and ascorbic acid are cooxidized to acetaldehyde and dehydroascorbic acid, respectively [377]. Oxidation of cyclohexene with O_2 catalyzed by (salen)Ru(Im)Cl and (L)Ru(Im)Cl (Im = imidazole; L = bis(salicylaldehyde)*o*-phenylenediiminato) complexes is first order in both cyclohexene, O_2, and catalyst. The main reaction products are 2-cyclohexen-1-one and cyclohexene oxide [378]. Epoxidation of the cholesteryl esters (**135**; R = H,alkyl,CMe_3,Ph,OEt) with air in the presence of $(TMP)Ru(O)_2$ gave the β-epoxides (**136**) in high yields [379]. A catalyst : substrate molar ratio of about 1 : 25 was found to be optimal [380].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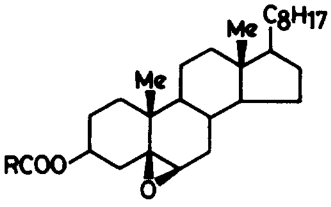

136

See also [398,551].

d) Oxidation of Aromatics

Oxidation of dialkyl arylmalonates, $PhCH(COOR)_2$ (R = alkyl) and its derivatives, by $Mn(OAc)_3$ in AcOH, alone or in the presence of O_2 or N_3^-, SCN^-, Br^-, Cl^- ions gave $PhCX(COOR)_2$ (X = OAc, N_3, SCN, Br, Cl) [381].

Hydroquinones have been found to be useful reductants for a one-step hydroxylation of aromatic compounds with O_2 in anhydrous organic solvents using an iron complex catalyst prepared *in situ* from $FeCl_3$, pyrocatechol, and pyridine. Anisole was the most reactive aromatic compound and t-butylhydroquinone the most effective reductant [382]. A highly selective and unusual benzylic oxidation by the iron-oxo species of the Gif^{IV} system ($Fe(OAc)_2$ + Zn + pyridine + AcOH in benzene under air) has been reported. Oxidation of ethylbenzene, diphenylmethane and benzylcyclopropane afforded solely the corresponding ketone without attacking tertiary or primary C-H bonds [383].

Organic bromides are formed as byproducts in the oxidation of methylbenzenes by O_2 with a $Co(OAc)_2$-NaBr or $CoBr_2$-NaOAc catalyst [384]. The effect of composition of $Co(OAc)_2.4H_2O$ + HBr + pyridine catalytic systems on the rate of p-xylene oxidation in anhydrous acetic acid at 120°C and 6 bar O_2 pressure has been studied.

Catalysts with the molar ratio Co:Br:py = 1:2:1-2 had the highest catalytic activity in the initial stage of the reaction [385]. The liquid-phase oxidation of p-xylene in the presence of water, catalyzed by phase transfer agent and $CoBr_2$ has been studied. A free radical mechanism implying bromine radicals as initiating species has been proposed [386]. Cyclohexylbenzoic acids were prepared by the oxidation of the corresponding cyclohexyltoluenes with O_2 in glacial AcOH using $Co(OAc)_2$ as catalyst and acetaldehyde as iniciator [387]. Molecular bromine is formed during the oxidation of *p*-xylene by O_2 in AcOH solution in the presence of Co-Mn-bromide catalysts. This is caused by Co(III) which oxidizes Br^- to Br_2 [388]. Cobalt ions supported on a diethyl vinylphosphonate-acrylic acid copolymer catalyze the oxidation of ethylbenzene to PhCHMeOOH , PhCOMe, and PhCHMeOH. Pretreating the catalyst with PhCHMeOOH or $RCMe_2OOH$ (R = Me,Ph) increased the selectivity for PhCHMeOOH to 99% [389].

Addition of N-methyl-2-pyrrolidinone increased the rate and selectivity of the air oxidation of toluene and cumene to hydroperoxides catalyzed by $Ni(acac)_2$ [390]. The role of higher oxidation state Pd complexes in the selective oxidation of aromatic rings by O_2 exemplified by reactions of benzene and PhOAc were discussed [391]. In the catalytic oxygenation of benzene at 25°C by simultaneously added H_2 and O_2 in the presence of Pd and Cu species, phenol or benzoquinone were obtained as the major products [392]. The oxidative polymerization of toluene and its analogs catalyzed by a Cu_2Cl_2 - $AlCl_3$ - O_2 system has been reported [393].

See also [243,351,352,362].

2. Catalytic Oxidation of O-Containing Organic Compounds with O_2

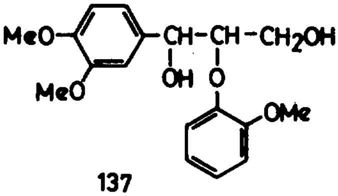
a) Oxidation of Alcohols

NaCe(IV)Y zeolite can be used for oxidative cleavage of 2,3-dimethyl-2,3-butanediol to acetone. Its activity can be restored by O_2 and it is therefore a regenerable glycol-cleaving oxidant [394].

The oxidation of benzoin to benzil in the presence of air, pyridine-N-oxide or p-benzoquinone at 30^{o}C with $[MoO(SPh)_4]^-$ catalyst was studied and catalytic cycles were proposed for benzoquinone and for pyridine-N-oxide [395]. The mixed-type heteromolybdic acid $H_8SiMo_{10}Sn_2O_{40}$ was used as a catalyst for the oxidation of EtOH to acetaldehyde with O_2. Highest selectivity was achieved at 240^{o}C [396].

The catalytic oxidation of fructose to erythrose by O_2 promoted by Fe^{3+} and of **141** to **142** promoted by the Co^{2+} complex of 6,6'-bis(benzoylamino)-2,2'-bipyridine was described [397]. The kinetics of oxidation of allyl alcohol by O_2 catalyzed by Ru(III)-EDTA was investigated in the pH range 1.0-3.0 at 35^{o}C in aqueous solution. The main product was acrolein at pH 1.0-2.0 and epoxy propionaldehyde at pH 2.0-3.0 [398].

Secondary alcohols can be oxidized at 75^{o}C with O_2 to the corresponding ketones with bis(trifluoroacetylacetonato)cobalt(II) as catalyst. If the reaction is performed in the presence of a 4A molecular sieve to remove the water formed in the process, the yields are almost quantitative [399]. The lignin model compounds (**137**) and (**138**) were oxidized at 170^{o}C and 35 bar (4% O_2 in N_2) using Co(II), Mn(II), and Co(II) + Mn(II) as catalysts, or with stoichiometric amounts of Co(III). Predominantly products formed by C_{α}-C_{β} bond cleavage were formed [400].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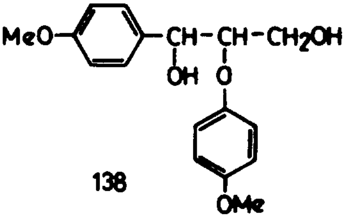
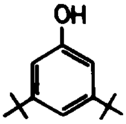

138

See also [357,377].

b) Oxidation of Phenols

Tetrabutylammonium salts of heteropolyvanadate and isopolyvanadate have been used to catalyze the oxidation of (**139**) and (**140**) with O_2. A reaction mechanism was proposed [401].



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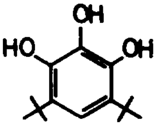
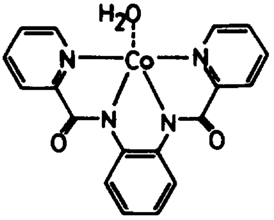


140

Substituted phenols like (**141**) were efficiently oxidized to the corresponding quinones (**142**) by O_2 at room temperature and atmospheric pressure using the cobalt(II) complex (**143**) as catalyst [402].

141

142
(100%)

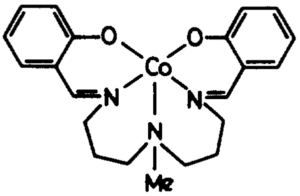


143

In the oxidation of (**141**) by O_2 catalyzed by different Co(TPP) catalysts containing substituents on the *para*-position of the phenyl groups the activity of the catalysts decreased in the order MeO > Me > H > Cl > CN. If Mn(TPP)Cl was used as catalyst, the activity and selectivity could be significantly increased by the addition of $NaBH_4$. An even better system was obtained from Fe(TPP)Cl and $NaBH_4$ in the presence of a small amount of pyridine [403].

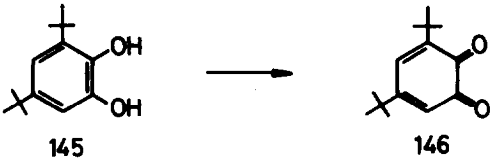
The mechanism of oxidation of hindered phenols by O_2 catalyzed by Co Schiff-base complexes was studied using electrochemical methods to determine the role of the redox reactions of Co in the process. The results rule out a simple chain reaction initiated by the interaction of Co(II) and O_2 [404]. In the catalytic O_2 oxidation of 2,6-dimethylphenol to form 2,6-dimethyl-1,4-benzoquinone, the high-spin cobalt (II) complex, (**144**) (S = 3/2), shows a maximum increase of the initial rate at ~1000 G, while the low-spin cobalt complex, cobalt(II)salen (S =

1/2), in a 1 : 10 ratio with pyridine, shows a maximum decrease of the initial oxidation rate at ~800 G [405].



144

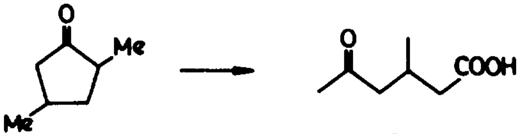
Selective oxidation of (**145**) to (**146**) with O_2 using Cu(II) and Co(II) complexes of poly(4-vinylpyridine) as catalysts has been achieved. The results were compared to those obtained with the corresponding homogeneous Cu(II)- and Co(II)-pyridine catalysts [406]. The Cu(II) complexes of 3,4-dimethoxycinnamic acid and of 3,5-dimethoxycinnamic acid alsocatalyze the oxidation of (**145**) to the corresponding *o*-quinone (**146**) by O_2 [407].



Kinetic experiments have shown that the tetranuclear oxocopper(II) complex $(py)_3Cu_4Cl_4O_2$ initiates and catalyses the oxidative coupling of 2,6-dimethylphenol by O_2 in nitrobenzene at 25°C [408]. High yields of trimethyl-p-benzoquinone from 2,3,6-trimethylphenol have been achieved by oxidation with O_2 in the presence of a catalytic amount of $CuCl_2$/amine-HCl in alcoholic solution at ambient temperature [409,410]. Several Cu-amine-cellulose polymers have been found to be excellent reusable heterogenized catalysts for a variety of autoxidations of organic substrates: phenols to quinones, benzoin to benzyl, coupling of terminal acetylenes to 1,3-diynes, bromination of ketones with LiBr, and coupling of *o*-phenylene-diamine with aldehydes to benzimidazoles [411].
See also [397].

c) Oxidation of Aldehydes and Ketones

The ring-opening oxidation products of cyclic ketones (keto esters or diesters) were formed in a stoichiometric or catalytic reaction on treatment with a solution of $VO(OEt)_3$ or $VO(OEt)Cl_2$ in ethanol under O_2 at room temperature [412]. The vanadium complexes $VO(acac)_2$, $VO(OPr^i)_3$ and $H_{3+n}(PMo_{12-n}V_nO_{40})$ were tested as catalysts for the oxidative cleavage of ketones by O_2. At room temperature in the presence of O_2 they cleave benzylic ketones $PhCH_2COR$ (R = Me,Et) to give the corresponding carboxylic acids and benzaldehyde [413]. The oxidation of ketones with a heteropolyacid, $H_5[PMo_{10}V_2O_{40}]$, and O_2 at 60°C and 1 bar has been demonstrated in the case of substituted cycloalkanones, 1-phenyl alkanones and alkyl ketones. For example, (**147**) was transformed into (**148**) with 94% yield [414].



147 **148**

An experimental study has shown that stable steady states and one-peak periodic oscillations are possible in the cobalt-catalyzed benzaldehyde oxidation by O_2 in a two-phase continuous reactor at 52°C [415]. The kinetic parameters of the oxidation of benzaldehyde by O_2 catalyzed by polymer-supported Co(III) were determined [416]. Oxidation of C_2-C_5 aldehydes with O_2 in benzene catalyzed by Rh(I) chelate complexes has been investigated. Two complexes were isolated from the reaction products: the catalytically active $(anthranilate)Rh(CO)_2(OH)(OOCEt)$ and the catalytically inactive $[Rh_3O(EtCOO)_6(H_2O)_3]^+$ [417].

Oxidation of cyclohexanone by O_2 in the presence of NH_3 or Et_3N is catalyzed by the phenanthroline complex of Cu(II). α-Hydroxycyclohexanone was the most probable primary product which decomposed to the α-diketone or to adipic acid [418]. The high pressure-high temperature oxidation of cyclohexanone by O_2 in an aqueous system was strongly catalyzed by Ag^+, Fe^{3+}, and Cu^{2+} ions.

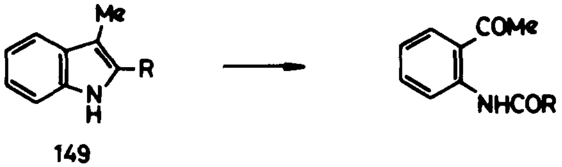
From a detailed study of the copper-catalyzed oxidation it was concluded that the enol of cyclohexanone is not an intermediate of the reaction [419].
See also [374].

d) Miscellaneous Oxidations

Manganese(II) acetate tetrahydrate dissolved in nonanoic acid is easily oxidized by air to Mn(III) at 95°C. This oxidation is accompanied by the oxidative decarboxylation of the carboxylic acid and the formation of alkyl, alkoxy, and alkylperoxy radicals [420]. The rate of oxidation of 2-substituted 1,3-dioxolanes with O_2 and catalyzed by cuprate in the presence of 18-crown-6 increased in the order of substituents Me < H < Ph [421].

3. Catalytic Oxidation of N-Containing Organic Compounds with O_2

NADH was oxidized by O_2 in the presence of vanadate, ascorbate, and phosphate. Ascorbate reduces vanadate to vanadyl, autoxidation of vanadyl produces superoxide which initiates a free radical chain reaction resulting in the oxidation of NADH [422]. The reaction of indoles with O_2 in acetonitrile in the presence of bis(acetylacetonato) oxovanadium(IV) has been investigated. High yields were achieved in the oxidative ring cleavage of 3-methylindole (**149**; R = H) and 2,3-dimethylindole (**149**; R = Me) [423].

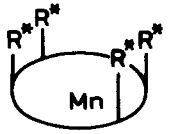


149

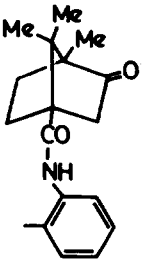
The asymmetric dioxygenation of racemic N-acetyl-tryptophan methyl ester (**150**) with predominant generation of (R)-(**151**) was achieved in 23.3% ee using the α,α,α,α-stereoisomer (**152**) of the

Mn complex of 5,10,15,20-tetrakis[*o*-(L-(-)-camphanoylamido)phenyl] porphyrin as catalyst [424].

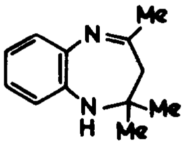
150 **151**



152 ; R* =



A similar enantioselective dioxygenation (k_L/k_D = 1.17) of (**150**) catalyzed by the achiral catalyst (TPP)Mn incorporated into a carrier protein, bovine serum albumin, has also been reported [425]. The diazepine derivative (**153**) is oxidized by O_2 in the presence of $MnCl_2$ to (**154**) in 40% yield [426].



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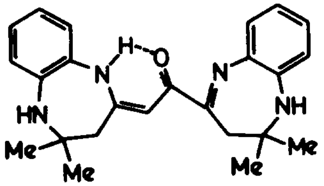
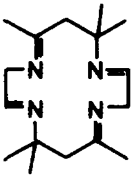


154

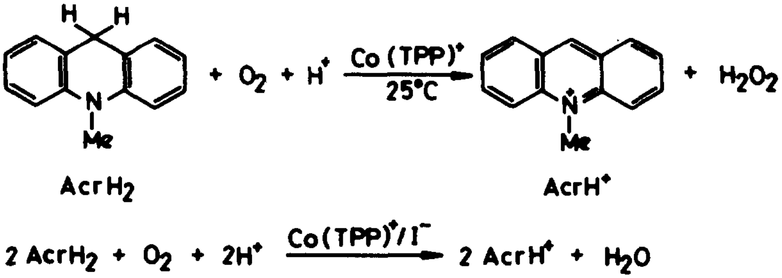
N,N-dimethylaniline was efficiently oxidized in acetonitrile in the presence of several iron complexes [Fe(salen)OAc, $[Fe(salen)]_2O$, (TPP)FeOAc, $[Fe_3O(OAc)_6(H_2O)_3]Cl$ and the simple iron salts $FeCl_3$ and $Fe(ClO_4)_3$ under O_2 (1 bar) at 60°C to give a product mixture of N-methylaniline, N-methylformanilide, N-(4-dimethylaminobenzyl)-N-methylaniline, and 4,4'-methylenebis (N,N-dimethylaniline) [427]. A note appeared reporting similar results using 3- and 4-substituted N,N-dimethylanilines [428]. Oxidative degradation of deoxytetranucleotides by O_2 mediated by Fe(II)(peplomycin) (a derivative of bleomycin) or Co(III) (peplomycin) + $h\nu$ has been reported [429]. Oxidation of NADH and ascorbic acid by O catalyzed by [Fe(L)(MeCN)](BF) (L = **155**) is accompanied by self-organizing space-time phenomena, i.e. the processes shows oscillatory behavior [430].



155

Dibenzylamine was oxidized to N-benzylidinebenzylamine by O_2 at atmoshperic pressure and 80°C in the presence of $Ru(PPh_3)_3Cl_2$ and $Ru(DMSO)_4Cl_2$ as catalysts [431].

Cobalt Schiff base complexes promote the oxygenation of nitroalkanes to give the corresponding carbonyl compounds. Thus, oxidation of $PhCHMeNO_2$ using (salen)CoOH as catalyst in alcohol solutions gave the corresponding benzoic acid esters and acetophenone [432]. The two-electron and four-electron reduction of dioxygen with 10-methylacridan ($AcrH_2$) catalyzed by metalloporphyrins in the presence of $HClO_4$ has been reported. Oxidation of $AcrH_2$ was first order each in $AcrH_2$, O_2, and $[Co(TPP)]^+$ [433].



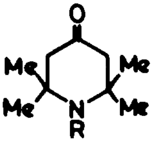
Solutions of *mer*-$RhCl_3(DMSO)_3$ in N,N-dimethylacetamide under an O_2/H_2 mixture catalyzed the concomitant formation of $AcN(Me)CH_2OOH$ and H_2O_2 at 50°C [434].

The catalyst system $PdCl_2 + CuCl_2 + CF_3COOH$ was used for the oxidation of unsaturated amines and related compounds of the type $CH_2=CH(CH_2)_3CH=CHCH_2NRR'$ ($RR'N = Me_2N$, piperidino, morpholino, AcNMe, succinimido, etc.) with O_2 in THF to the corresponding ketones $MeCO(CH_2)_3CH=CHCH_2NRR'$ [435].

Oxidation of 1-benzyl-1,4-dihydronicotinamide and its 1-aryl analogs by O_2 in aqueous solution is catalyzed by Cu^{2+}. A concerted 2-electron-transfer route involving a substrate-Cu^{2+} complex was proposed for the oxidation mechanism [436]. N-acetylhistamine was oxidized by O_2 in the presence of Cu(II) and ascorbate to (156) as the main product [437].

156

A kinetic study was reported on the oxidation of the aminoketones (157) by O_2 in the presence of alkali and Cu(II)-phenanthroline complexes. The primary oxidation products were either a nitroso compound (if R = O˙) or an α-diketone (if R = H) [438].



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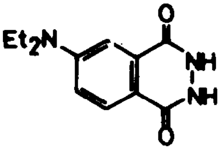
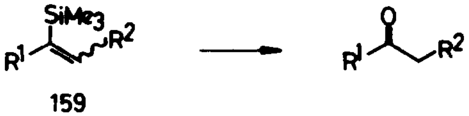
The chemiluminescent oxidation of the aminophthalhydrazide (158) by H_2O_2/O_2 is catalyzed by Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} [439].



158

4. Catalytic Oxidation of Si-, S-, or Cl-Containing Organic Compounds with O_2

The reaction of various vinylsilanes (159; R' = nBu, nC_8H_{17}, $PhCH_2CH_2$, $AcCH_2CH_2CH_2$; R^2 = Me, Et, nBu, OMe) with O_2 catalyzed by bis(2-ethoxycarbonyl-1,3-butanedionato)cobalt(II) in iPrOH solution at 75°C has been found to be a useful and convenient method for the preparation of ketones in 82-91% yields [440].



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The formation of mixed ligand complexes was confirmed by electronic spectra in the oxidation of cysteine by O_2 catalyzed by Fe(II,III) complexes of L-histidine [441]. Ruthenium(VI) dioxo porphyrin species in benzene stoichiometrically oxidize thioethers to sulfoxides. The reaction becomes catalytic under O_2 but the turnover numbers are low [442].

Based on experimental O_2 consumption in the oxidation of 2-mercaptoethanol to disulfide at 25°C, water-soluble polymeric metal phthalocyanines (MPc) showed the following order of reactivities (mole thiol/mole MPc unit.min): NiPc(70) < FePc(420) < CoPc(630) [443]. Cobalt complexes of low-molecular-weight and polymeric phthalocyanines were prepared on the surface of SiO_2, γ-Al_2O_3, and active charcoal and used as catalysts for the oxidation of 2-mercaptoethanol. Polymeric phthalocyanines exhibited a higher catalytic activity as compared with low-molecular-weight phthalocyanines [444]. Oxidation of 2-mercaptoethanol by O_2 was investigated kinetically in the presence of Co(II) phthalocyanine supported on latex particles by means of polymeric quaternary ammonium salts. This immobilized catalyst had the same activity as the corresponding homogeneous system [445]. Autoxidation of 1-decanethiol to di-1-decyldisulfide at 35°C under O_2 catalyzed by cobalt phthalocyaninetetrasulfonate on cationic latexes has been studied [446]. Oxidation of sodium mercaptides RSNa (R = Et,Pr,Bu) by O_2 in the presence of homogeneous and heterogeneous Co-phthalocyanine catalysts gives the corresponding disulfides as the major propducts; prolonged oxidation leads to RSO_2Na and RSO_2SNa [447]. The catalytic properties of the derivatives of (octahydroxyphthalocyanine)cobalt in the oxidation of Et_2NCS_2Na by O_2 were studied. The reaction rate increased with increasing concentration of the free acid Et_2NCS_2H [448,449].

Allyl chloride was oxidized to epichlorohydrin with O_2 in DMF in thee presence of dialkyl phthalates and $MoO_2(C_8H_{16})$ catalyst. Addition of $ROCH_2NEt_2$ (R = substituted naphthyl groups) increased the yield of epichlorohydrin [450]. Liquid-phase oxidation of *o*-chlorotoluene by O_2 under mild conditions (1 bar, 95°C) in the presence of $Co(OAc)_2$ amd NaBr (1:1.1) gave *o*-chlorobenzoic acid in high yield (100% conversion, 97-98% yield). Minor amounts of *o*-chlorobenzaldehyde were also formed; at low conversions, however, aldehyde selectivities of up to 50% could be achieved [451]. 2,4-Dichlorotoluene was oxidized to 2,4-dichlorobenzoic acid with O_2 in the presence of $Co(OAc)_2$ + $Mn(OAc)_2$ + NaBr. Best results *were achieved at 150-180°C with Mn:Co = 1:4 and metal :* Br^- = 1:1-2. The main products of oxidation were $2,4\text{-}Cl_2C_6H_3COR$ (R = OH, H) [452,453].
See also [276].

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

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

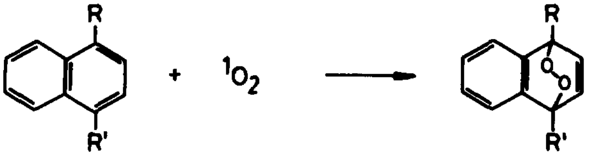
The oxidation of benzene to phenol has been studied in a two-phase system at 40°C using V_2O_5, H_2O_2 and picolinic acid [454].

The oxidation of methacrylic acid esters to pyruvic acid esters was carried out with aqueous H_2O_2 in MeCN in the presence of catalytic amounts of Cr compounds such as $Cr(acac)_3$, $Cr(OAc)_3 \cdot H_2O$, or CrO_3 (the latter preferably together with equimolar amounts of Et_3N). Best selectivities and yields were in the range of 70 to 95% [455]. The influence of various nitrogen bases on the yields of cyclohexanol and cyclohexanone in cyclohexane oxidation with H_2O_2 using chloro-tetratolylporphyrinatochromium(III) as a catalyst at 30°C has been investigated. A correlation between the pKa value of the bases and the total yield of products has been found. The highest yields were observed in the presence of imidazole and 4-aminopyridine

[456]. The mechanism of oxidation of alkanes by tBuOOH in the presence of $Cr(CO)_6$ has been studied. It was found that the hydroperoxide oxidizes $Cr(CO)_6$ to Cr(VI) [457]. The 1:1 molar mixture of tBuOOH and pyridinium chlorochromate is a highly effective oxidant for the conversion of 1,4-cyclohexadienes into 2,5-cyclohexadien-1-ones. For example, (**160**) was oxidized to (**161**) with 87% yield [458].

160 **161**

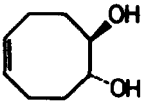
The naphthalenic endoperoxides (**162**; R'R' = Me, CH_2CH_2COONa or CH_2CH_2COOH) were prepared by oxidizing the appropriate naphthalene derivatives with H_2O_2 in the presence of $Na_2MoO_4.2H_2O$ (a chemical source of singlet oxygen). Yields were almost quantitative [459].



162

Alkyl-substituted phenols were easily oxidized to the corresponding *p*-benzoquinones by H_2O_2 in acetic acid in the presence of the heteropolyacids $H_3PM_{12}O_{40}.nH_2O$ and $H_4SiM_{12}O_{40}.nH_2O$ (M = Mo, W). The role of heteropolyacids was mainly to catalyze the hydroxylation of the benzene ring, the hydroquinones thus formed were easily oxidized further [460]. Alkynes were oxidized to carboxylic acids and/or ketones by H_2O_2 in the presence of $(cetylpyridinium)_3PM_{12}O_{40}$ or Na_2MO_4 (M = Mo,W) as catalysts and $Hg(OOCCF_3)_2$, in an aqueous-organic two-phase system under vigorous stirring at 40°C. The heteropolyacids were found to be more efficient [461]. Hydrogen peroxide oxidation of ethylbenzene in refluxing MeCN catalyzed by Keggin anions

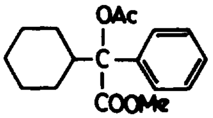
$[PW_{12}O_{40}]^{3-}$ gave acetophenone in moderate yield [462]. Olefins can be cleaved into carboxylic acids by H_2O_2 in the presence of catalytic amounts of H_2WO_4 in refluxing tBuOH solution. This oxidative cleavage probably proceeds over 1,2-diols and their subsequent dehydrogenation to α-ketols [463]. The optimum conditions for the preparation of tartaric acid by oxidation of maleic acid with H_2O_2 in the presence of Na_2WO_4 were determined. The yield of tartaric acid was 87% [464]. 1,5-cyclooctadiene was oxidized to the diol (163) by H_2WO_4-H_2O_2 [465].



163

Catalytic oxidation of cyclohexane to cyclohexanone and cyclohexanol in low yield (13%) has been observed with tetrakis(2,6-dinitrophenyl)porphinatomanganese(III) chloride and iodosylbenzene at room temperature. Under similar conditions (TPP)MnCl and (F_{20}TPP)MnCl gave 17% and 9% yields, respectively [466]. Oxidation of cyclohexane to cyclohexanol and cyclohexanone by H_2O_2 is catalyzed by (TPP)MnCl immobilized on SiO_2 modified by 3-imidazolylpropyl groups. In homogeneous solution (TPP)MnCl is inactive even in the presence of imidazole or imidazole and SiO_2; the imidazole group has to be chemically bonded to the silica surface [467]. An optically active tetraarylporphyrin macrocycle, 5α, 10β, 15α, 20β-tetrakis[(R)-1,1'-binaphth-2-yl]-porphyrin ($TBNPH_2$) has been synthesized and metallated into (TBNP)MnCl. This compound showed a very high catalytic efficiency (up to 2800 turnovers in 80 min) and moderate enantioselectivity (15-40% ee) for asymmetric epoxidation of a variety of unfunctionalized olefins like styrene, with hypochlorite as oxidant in a two-phase system [468]. High-valent manganese carboxylates, $[Mn_4O_2(O_2CR)_6(H_2O)_2]$ (R = CPh_3 or CMe_3), catalyzed the hydroxylation of cyclooctane and adamantane and the epoxidation of cyclooctene employing either tBu_4OOH or PhIO [469]. The kinetics of the Mn(III)-catalyzed oxidation of unsaturated carboxylic acids by acidic bromate in the presence of Hg(II) as a bromide-ion scavenger have been studied. The catalytic effect of Mn(II) was attributed to the formation of a Mn(II)-substrate π-complex which is oxidized to a Mn(III)-substrate π-complex by bromate [470]. Cyclohexyl- triphenyltin, $C_6H_{11}SnPh_3$, was hydroxylated on the cyclohexyl group with PhIO as oxidant and $(F_{20}TPP)Mn(OAc)$ as catalyst. This system provided a 22% conversion of the substrate to a mixture of *cis*- and *trans*-hydroxy derivatives; the main product was the *trans*-2 isomer [471].

Electron transfer agents such as N,N,N',N'-tetramethylphenylenediamine, ferrocenes, and phenothiazines promote the hydroxylation of benzene with H_2O_2 in the presence of Fe^{2+}. Phenol yields of 80% or higher (based on H_2O_2) were achieved under optimized conditions [472]. Alkenes were oxidized by H_2O_2 and $Fe(ClO_4)_2$ as catalyst. Reactivity increased in the order methane < ethane < cyclohexane < n-hexane < isopentane and the regioselectivity of the reaction was primary:secondary:tertiary carbon = 1:11:15 [473]. Oxidation of (**164**) with the reagent system $H_2O_2/Ac_2O/Fe(MeCN)_6^{2+}$ gave, among other products, the ring-hydroxylated compounds (**165**; R = H, R' = 3-OH or 4-OH; R = OH, R' = H) [474].



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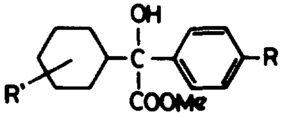
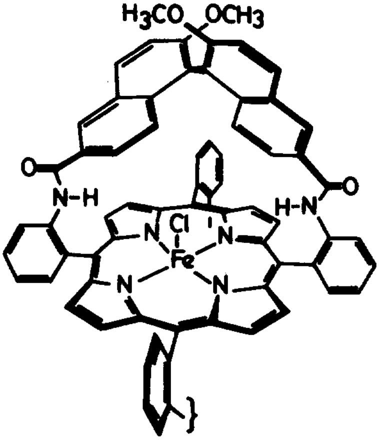


165

Phthalocyaninatoiron complexes may be prepared inside the pore structure of large pore zeolites X or Y by sequential introduction of the components followed by assembly inside the void space of the zeolite. Such complexes catalyze the oxidation of alkanes by PhIO and because of steric constraints inside the zeolite crystallites prefer to oxidize toward the end of the long molecular axis of the substrates [475]. Monooxygenation of cyclohexane to cyclohexanol with iodosobenzene and some of its substituted derivatives using (TPP)FeCl as catalyst has been investigated. All iodosobenzene derivatives studied were found to be less active than iodosobenzene itself [476]. Isotope effects were determined for the hydroxylation of cyclohexane and perdeuterocyclohexane with various iron porphyrin catalysts [477]. The perfluorinated iron-porphyrin complex $(F_{28}TPP)FeCl$ catalyzes the oxidation of cyclooctane, benzene, and phenol by H_2O_2. The main products are cyclooctene oxide, phenol, and 1,4-benzoquinone, respectively. The catalyst proved to be remarkably stable under the reaction conditions [478]. Pyrene, benzpyrene, and benzanthracene were oxidized in homogeneous solution by *m*-chloroperoxybenzoic acid in the presence of a bifacially hindered porphinatoiron complex as catalyst. The peroxyacid was unreactive in the absence of the catalyst. Phenols and quinones were the oxidation products [479]. Asymmetric hydroxylation of ethylbenzene to 1-phenylethanol (41% ee of the R enantiomer) was achieved at $0^{o}C$ in CH_2Cl_2 with iodosylbenzene using the chiral binaphthyl iron porphyrin (166) as catalyst [480].



166

The kinetics of oxidation of maleic and fumaric acids by N-bromosuccinimide in aqueous AcOH catalyzed by Ru(III) have been studied in the presence of $Hg(OAc)_2$. The reaction was first order in oxidant and fractional order in substrate [481]. Deuterium isotope effects suggest that in the oxidation of toluene by Cr(VI) in the presence of Ru(IV), σ-complex or ion-radical pair formation is the rate-determining step. In the case of chlorotoluenes, however, C-H bond cleavage in the methyl group was found to be rate determining [482]. Oxidation of substituted cinnamic acids by Ce(IV) and catalyzed by Ru(III) in aqueous acidic medium is zero order in Ce(IV), first order in Ru(III), and fractional order in substrate. The rearrangement of a Ru(III)-substrate π-complex into a σ-complex was suggested as the rate-determining step [483]. A highly selective (>99%) oxidation of cyclohexane to cyclohexanone and of ethers, both cyclic and linear, to lactones and esters has been found using oxidants such as LiOCl, PhIO, H_2O_2 and persulfate together with ruthenium(II) complexes as catalysts in a water-CHCl system. Up to 1 turnover per minute at room temperature was achieved with hypochlorite as oxidant [484]. The $SiRu(H_2O)W_{11}O_{35}^{5-}$ has been used as catalyst for the liquid phase oxidation of alkenes and alkenes with various primary oxidants, including $KHSO_5$, $NaIO_4$, tBuOOH, and PhIO at 50°C [485]. Application of the RuO_4-catalyzed oxidation for oxidative cleavage of the tetrasubstituted double bond in (**167**) using RuO_2 and $NaIO_4$ furnished the triketone (**168**) in quantitative yield [486].

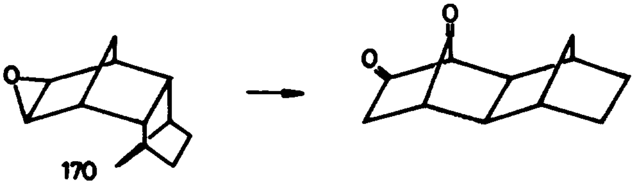
167 **168**

The ruthenium-catalyzed oxidation of various bicyclic or tricyclic alkanes (e.g.**169**) by $NaIO_4$ (i.e. with *in situ* generated RuO_4 as catalyst) resulted in preferential hydroxylation of the tertiary position [487].

169

90 %

Under similar conditions epoxides with the norbornane skeleton like (**170**) could be oxidized with the same reagent to β-diketones. The reaction was accompanied by a Wagner-Meerwein rearrangement [488].



170

80 %

The kinetics of the OsO_4-catalyzed oxidation of cyclohexene and of α-pinene with Me_3NO in aqueous t-BuOH are first order in total Os, first order in oxidant and zero order in alkene but are strongly dependent on which alkene is used. The reaction of cyclohexene is inhibited by pyridine and α-pinene. Oxidation of *trans*-stilbene in the presence of α-pinene results in a slight (3%) asymmetric induction [489]. Asymmetric dihydroxylation of alkenes can be achieved by the OsO_4-catalyzed oxidation with N-methylmorpholine N-oxide in the presence of chiral alkaloids (e.g. dihydroquinidine) which at the same time increase the reaction rate. It was now shown that the highest optical yields can be observed at much lower alkaloid concentrations than those which are necessary to reach the highest reaction rates. Kinetic evidence for a 1:1 alkaloid-OsO_4 complex as the asymmetry-inducing oxidant has been provided [490]. As a further proof the 1:1 complex of (dimethylcarbomyl)dihydroquinidine with OsO_4 has been isolated and its structure determined by X-ray and NME methods [491]. Highly improved enantioselectivities could be achieved by slightly modifying the original procedure for the asymmetric dihydroxylation of olefins with the N-methylmorphholine N-oxide/OsO_4/ dihydroquinidine 4-chlorobenzoate system in an acetone/water mixture (AS 1988,ref.169). Based on mechanistic investigations it was shown that two catalytic cycles are operating simultaneously and only one of these gives high enantiomeric excess. The essential modification is that the olefin has to be added very slowly to the well-stirred reaction mixture [492]. Under such "slow addition conditions", a wide variety of functionalized and unfunctionalized olefins were efficiently converted to the corresponding *cis* vicinal diols with 80-95% yield and 50-89% ee [493].

The oxide clusters $[(Cp^*Rh)_4V_6O_{19}]$ and $[(Cp^*Rh)Cl(MeCN)_2]_2[Mo_6O_{19}]$ catalyze the oxidation of cyclohexene with t-BuOOH at 70°C to give mainly allylic oxidation products and selectively epoxycyclohexane, respectively [494]. The oxidation of various hydrocarbons (octene-1, octene-2, styrene, cyclohexene, adamantane and cyclohexane) by hypochlorite at 20°C or by O_2 (1 bar) at 50°C in the presence of $[Rh(dppe)_2]BF_4$ catalyst has been reported [495].

The $PdCl_2$ complex-catalyzed cyclopentene oxidation using t-BuOOH as the oxygen donor has been studied. Methanol was found to be the most effective solvent (23.7% yield of cyclopentanone)

[496]. The complex formed between $PdCl_2$ and COD in aqueous acetone was used as catalyst in the oxidation of 1,5-cyclooctadiene with H_2O_2. Eight volatile oxidation products were formed among which cycloocten-4-one was the major one [497].

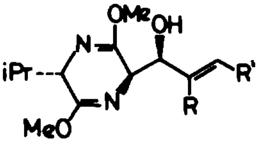
In the hydroxylation of benzene, fluorobenzene, anisole, and nitrobenzene by Cu^+-H_2O_2 the OH radical generated in a Fenton-type reaction was found to be the major reactive species that reacted with the aromatic compounds [498].

The Ag^+-catalyzed oxidation of maleic acid with $S_2O_8^{2-}$ in water was found to be first order in both oxidant and catalyst but independent of the concentration of the substrate [499]. Oxidation of terephthalic acid with peroxodisulfate and Ag(I) as catalyst has been studied kinetically. A free radical mechanism was proposed [500].
See also [195,515,536,537,543,553,579,647,648,649,651,655].

b) Epoxidation of Olefins

The classical Sharpless epoxidation (tBuOOH + $Ti(OPr^i)_4$ + (+)-or (-)-diethyl tartrate + molecular sieve; see AS 1987, ref.397) of allylic alcohols has been successfully applied in the following cases:

- The bislactim ethers (**171**; R = H,Me; R' = H,Me,Ph) gave the anti and/or syn epoxides (**172**) and (**173**). In some cases stereoselectivity was almost 100% [501].



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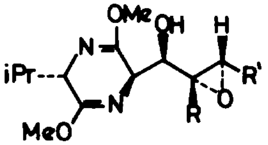

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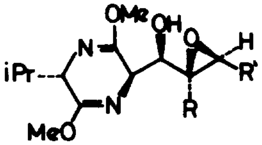


173

- Epoxidation of (**174**) in CH_2Cl_2 solution at -25°C gave (**175**) with 76% chemical and 92% optical yield [502].

174 175

- Divinylcarbinol (176) gave the epoxy alcohol (177) in 58% yield and 97% enantiomeric purity [503].

176 177

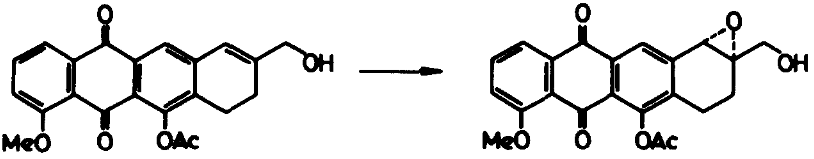
- Epoxidation of the allylic alcohols (178; R = H,Me,iPr) at -20°C gave the corresponding epoxyalcohols (179) in good yields with excellent enantiomeric purity [504].

178 179

- Epoxidation of the primary allylic alcohol (180) furnished (181); after esterification with 3,5-dinitrobenzoyl chloride the corresponding enantiomerically pure ester was isolated in 45% overall yield [505].

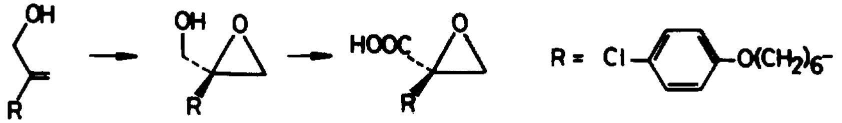
180 181

- The tetracyclic allyl alcohol (182) was transformed with high optical yield (96%) into the epoxy alcohol (183) [506].



182 183

- Finally, allylic alcohol (184) gave epoxide (185) which by oxidation with NaIO$_4$ in the presence of RuCl$_3$ as catalyst was transformed into the oxiranecarboxylic acid (186) [507].

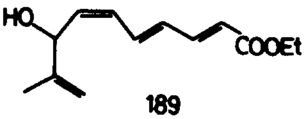


184 **185** **186**

Catalytic Sharpless oxidation of the racemic secondary allylic alcohol (**187**) with L-(+)-diisopropyl tartrate/tBuOOH/ /Ti(OPr^i)$_4$ to 50% conversion gave (by kinetic resolution) the epoxy alcohol (**188**) [508].

187 **188**

Using the same Sharpless-system, the allylic alcohols (**189**-**191**) were transformed into the corresponding epoxides (**192**) retaining the unaltered triene structures [509].



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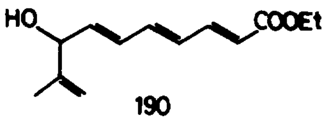

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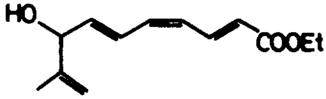

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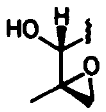

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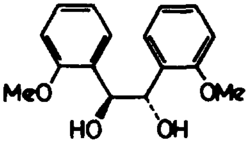
In order to gain insight into the nature and composition of this asymmetric epoxidation catalyst, Ti complexes with three "tartrate-like" ligands, (3R,4R)-diisopropyl 3,4-dihydroxyadipate, (2S,4S)-diisopropyl 2,4-dihydroxyglutarate, and (2S,5S)-diisopropyl 2,5-dihydroxyadipate were studied. The relationships between catalyst intramolecular fluxional equilibration, torsion ring strain, alkoxide exchange rate, reaction rate, and face selectivity have been explored [510]. Furthermore, experiments with linked bis-tartrate esters as ligands furnished arguments against the sole intermediacy of a monomeric titanium-tartrate in the parent system [511]. Asymmetric epoxidation of prochiral allylic alcohols (up to 96% ee), and asymmetric oxidation of prochiral sulfides to sulfoxides (up to 84% ee) with BuOOH + $Ti(OPr^i)_4$ + the optically active diol (**193**) as chiral catalyst have been reported [512].



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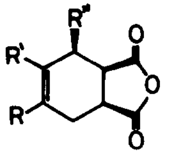
Rapeseed oil has been epoxidized by isopropylbenzene hydroperoxide and vanadium acetylacetonate as catalyst. Epoxide yield was 27%; rate equations for several steps of the epoxidation mechanism were established [513]. Catalysts have been prepared for the hydroperoxide epoxidation of cyclohexene by impregnating cellulose phosphate with solutions of vanadium(V). Highest activity of the catalysts was observed if the solution had a pH of about 1.8; the catalysts were not selective above pH 3.5 [514].

Styrene was oxidized by $NaNO_2$ in the presence of $[Cr(salen)(H_2O)_2]Cl$ or $[Cr(salen)(ONO)(H_2O)]$ to a mixture of styrene oxide, benzaldehyde, and formaldehyde in poor yields [515].

Epoxidation of cyclohexene by tBuOOH was investigated in the presence of $Mo(CO)_6$ in benzene solution and with $Mo(CO)_6$ anchored on various polymers. The catalyst on polystyrene showed a much higher activity than $Mo(CO)_6$ used under homogeneous conditions [516]. Epoxidation of 1-cyclohexen-3-ol and 1-cyclopenten-3-ol with 1-methyl-2-cyclopentenyl hydroperoxide in the presence of $Mo(CO)_6$ gave stereospecifically the *cis*-epoxy alcohols. The analogous epoxidation of 1-cyclohexen-4-ol, however, gave both the *cis*- and *trans*-epoxy alcohols [517]. Cyclohexenedicarboxylic anhydrides (**194**; R,R',R'' = H,Me) were epoxidized with 3-methylcyclopentene hydroperoxide and $Mo(CO)_6$ as catalyst to give the corresponding *cis*-epoxy anhydrides (**195**) stereospecifically in 50-60% yield [518].



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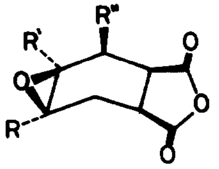
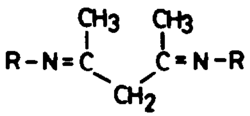


195

Rapeseed oil and the Me esters of its fatty acids were epoxidized in the liquid phase with cumyl hydroperoxide and Mo acetylacetonate as catalyst. Decomposition products of cumyl hydroperoxide inhibited the reaction [519]. Epoxidation of 1-octene by tBuOOH in the presence of Mo salts is inhibited by the reaction products. The inhibiting effect increases in the following order: epoxides < alcohols < diols << tetrols [520]. Among several molybdenum chloro nitrosyl complexes studied, $MoCl_2(NO)_2(HMPA)_2$ was the most active in the epoxidation of octene-1 with tBuOOH [521]. Bimetallic complexes $M_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]_3$ ($M = Eu^{3+}$, Sm^{3+}, and Y^{3+}) were found to be active cocatalysts in cyclohexene epoxidation with cumene hydroperoxide at 80°C [522]. Modifying MoO_2L_2 (L = propanediolate) with $Ph_2Si(OH)_2$, Et_3SiOH, or poly(dimethylsiloxane) increased its catalytic activity in the epoxidation of propene with cumene hydroperoxide [523]. The complex MoO_2Cl_2[3-(diethoxyphosphinyl) camphor] catalyzed efficiently the epoxidation of a wide range of alkenes by tBuOOH at 0-35°C. In the case of polybutadiene all of the backbone double bonds were epoxidised and the terminal ones remained unreacted [524]. The dioxomolybdenum complexes *cis*-MoO_2L_2 (H_2L = 196-198) were used as catalysts for the epoxidation of olefins using tBuOOH as oxidant [525].



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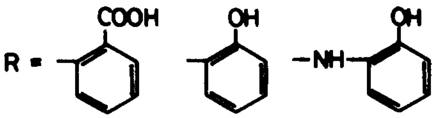

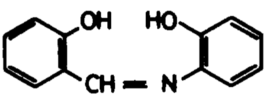

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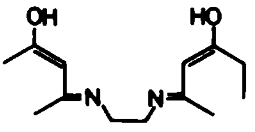


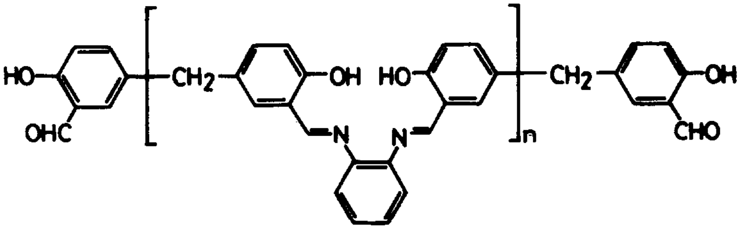
198

The epoxidation of alkenes with H_2O_2 was carried out in the presence of a catalyst formed *in situ* from molybdenum blue and $(Bu_3Sn)_2O$ in $CHCl_3$. With some olefins like styrene or cyclohexene, Me_3N had to be added to the reaction mixture to achieve good yields [526]. Epoxidation of 1-octene by H_2O_2 in the presence of molybdenum tungsten carbide, $(MoW)_2C$, has been studied. Under optimum conditions the selectivity of the reaction was 78% [527].

The epoxidation of α,β-unsaturated carboxylic acids with H_2O_2 catalyzed by tris(cetylpyridinium)12-tungstophosphate at 60-65°C gave up to 90% yield (75% isolated yield) of epoxy acids [528]. A mathematical model has been developed for the epoxidation of 1-octene with H_2O_2 catalyzed by a heteropoly complex formed *in situ* from $Na_2WO_4.2H_2O$ and H_3PO_4 in a phase-transfer system containing $(PhCH_2)(n\text{-}C_8H_{17})_3N^+Cl^-$ and 1,2-dichloroethane as organic solvent. A mechanism was proposed [529].

Binuclear Mn(II)-Schiff base complexes catalyze the epoxidation of olefins with iodosylbenzene as an oxidant in acetonitrile-water solvent mixture at room temperature [530]. The epoxidation of alkenes by hypochlorite catalyzed by Mn(III)-tetraarylporphyrins in a two-phase water/dichloromethane system is accelerated by lowering the pH of the aqueous phase. Using trapping experiments it was shown that the rate-determining step involves the formation of the active oxo-manganese species $[(P)MnO]^+$ [531,532]. The kinetics of epoxidation of norbornene, *cis*-cyclooctene, and cyclohexene with NaOCl and $(Me_{12}TPP)MnCl$ have been determined in a homogeneous (wet dichloromethane) solution. The rate did not change on addition of even large amounts of 4'-imidazol-1-ylacetophenone [533]. The factors ruling the catalytic activity of Mn(III)porphyrins in olefin epoxidation carried out at 0°C under two-phase conditions with ClO^- and/or HOCl as oxidant have been investigated using cyclooctene and 1-dodecene as model olefins [534]. Alkene epoxidation with 30% H_2O_2 and $[(Cl_8TPP)Mn(III)]^+$ is strongly enhanced by the addition of lipophilic carboxylic acids and lipophilic imidazole or pyridine ligands [535]. Potassium hydrogen persulfate, $KHSO_5$, is an efficient oxidizing agent in olefin epoxidation and alkene hydroxylation with Mn porphyrin complexes as catalysts. Very inert saturated hydrocarbons can be oxidized at room temperature with a conversion rate in the range of 0.1-4 cycles per min [536]. A supported Mn-porhyrin catalyst has been prepared by absorption of Mn[*meso*-tetra(4-N-methylpyridiniumyl)porphyrin](Cl)$^{4+}$.4Cl^{-} on silica, and has been found very efficient as compared to similar homogeneous catalysts for cyclo-octene epoxidation and for alkane hydroxylation by PhIO [537].

Iron and Mn complexes of 5,10,15,20-tetrakis (2,6-difluorophenyl)porphyrin were found to be highly active catalysts for the epoxidation of olefins with hypochlorite. The Mn complex was especially efficient in the presence of pyridine for epoxidation of α-methylstyrene (turnover number 200,000) whereas the Fe complex did not need an additional nitrogen base and was superior for the epoxidation of cycloalkenes [538]. The water-soluble magnesium monoperoxyphthalate has been described as a very efficient reagent for the epoxidation of alkenes under phase-transfer conditions in the presence of Fe- or Mn-porphyrins as catalyst. The best results were obtained with (Cl$_8$TPP)MnOAc (turnover rates as high as 1600 epoxide/catalyst/min for styrene epoxidation at 0^{o}C) [539]. Alkenes were epoxidized with PhIO in methylene chloride as solvent at room temperature using Mn, Cr, and Fe complexes of the polymeric Schiff base ligand (**199**) as catalyst. The Mn-containing catalyst was the most active [540].



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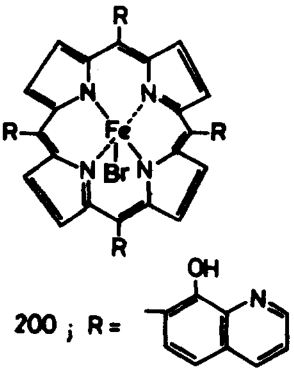
The four conformational isomers of 5,10,15,20-tetrakis (3,5-di-*tert*-butyl-2-nitrophenyl)porphyrin were separated and converted to their Fe and Mn complexes. These metalloporphyrins catalyze the epoxidation of styrene by OCl^{-} [541]. The epoxidation of norbornene, cyclohexene and adamantylideneadamantane with C_6F_5IO using variously substituted tetraphenylporphyrin complexes of chloroiron(III), chloromanganese(III) and chlorochromium(III) as catalysts has been studied with respect to the effects of metal and porphyrin substituents on selectivity and regiochemistry [542]. Membrane-spanning steroidal iron(III) and manganese(III) metalloporphyrins containing four cholenic acid moieties have been shown to be active and site selective catalysts for the epoxidation (with PhIO) and hydroxylation (with O_2 + ascorbic acid, or with $NaIO_4$) of sterols, fatty acids, and hydrocarbons [543]. Iron-porphyrin (200) and manganese-salen (201) type complexes containing additional functional groups which can bind Cu^{2+} have been prepared and used as epoxidation catalysts with PhIO as oxidant. These catalysts showed in the presence of Cu^{2+} a strong selectivity for epoxidizing such olefins (e.g.202) which can be fixed by coordination in an appropriate position for oxygen transfer [544].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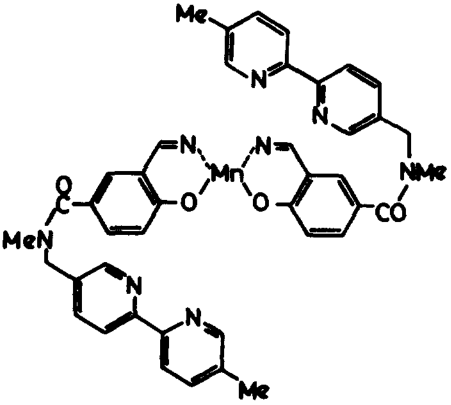
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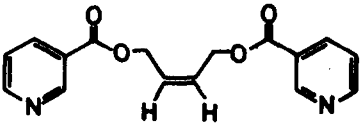
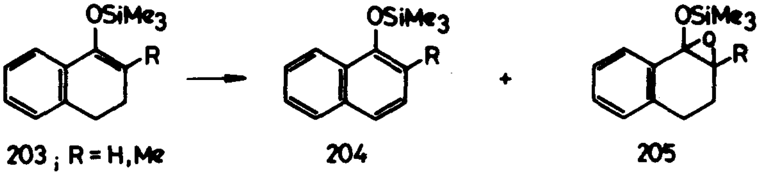
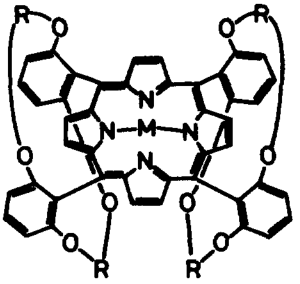

202

(Br_8TPP)FeCl has been used as catalyst for epoxidation of nine structurally different alkenes with C_6F_5IO as oxygen donor. Nearly quantitative yields were obtained [545]. The homolytic and heterolytic scission of organic hydroperoxides by (TPP)FeCl and its relation to olefin epoxidation has been studied. It was found that two separate oxidizing agents are produced in the reaction. In the absence of imidazole, (TPP)FeCl cleaves the hydroperoxides homolytically to alkoxy radicals and (TPP)Fe(=O); both species oxidize the hydroperoxide to peroxyl radicals which epoxidize *cis*-stilbene nonstereospecifically. In the presence of imidazole, (TPP)FeCl cleaves the hydroperoxides heterolytically to alcohol and $[(TPP)Fe(=O)]^+$, which epoxidizes *cis*-stilbene stereospecifically [546]. Oxidation of (203) with PhIO and $(F_{20}TPP)FeCl$ as catalyst gave mainly the aromatized product (204) along with the epoxide (205). This system mimics aromatase cytochrome P 450 [547].



The "twin coronet" iron porphyrins (206) and (207) (M = FeCl) which have binaphthalene pockets on their both faces have been prepared and applied as catalysts for the epoxidation of styrene and substituted styrenes with iodosobenzene. Using (206) as catalyst, 80% excess of the (R) enantiomer was obtained in the catalyst, 80% excess of the (R) enantiomer was obtained in the epoxidation of *o*-nitrostyrene [548].



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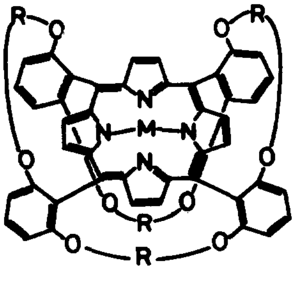

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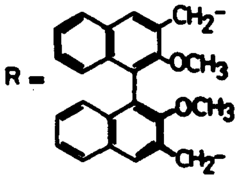
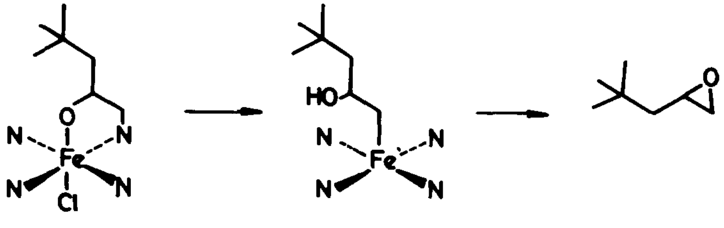
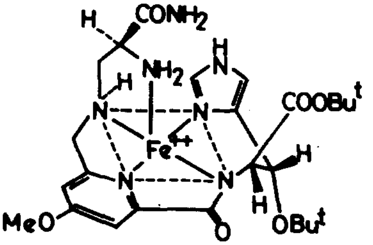


The N-alkyl metalloporphyrin (208), which is formed from $(Cl_8TPP)FeCl$ during alkene epoxidation using 4,4-dimethylpentene and C_6F_5IO is converted by $Na_2S_2O_4$ into the β-hydroxyalkyl σ-metalloporphyrin (209). When treated with a strong base this forms the epoxide (210) [549].



208 209 210

The epoxidation of alkenes with iodosylbenzene catalyzed by iron(III) Schiff base chelates has been studied. Up to 12% yield has been achieved at $45^{\circ}C$ in the case of norbornene [550]. *cis*-β-Methylstyrene was epoxidized either with the Fe(III) + H_2O_2 or with the Fe(II) + O_2 + 2-mercaptoethanol systems using bleomycin or an analogous synthetic molecule (211) as ligand to give the epoxide (212) with 45-51% enantioselectivity. No enantioselectivity was observed with *trans*-β-methylstyrene as substrate [551].



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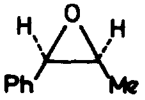


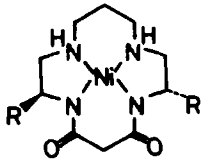
212

A highly efficient epoxidation of olefins with 2,6-disubstituted pyridine N-oxides in the presence of ruthenium porphyrins has been reported. Thus up to 9000 turnover and 100% yield of epoxide was achieved at $30^{\circ}C$ in benzene for styrene using 2,6-dichloro pyridine N-oxide together with $(TMP)Ru(O_2)$. Similar results were found in the case of (TMP)Ru(CO) and $(F_8TPP)Ru(O_2)$

catalysts as well [552]. The $[Ru(III)(salen)(X)(Y)]^n$ complexes $[(X)(Y) = (CN)_2$; $(PPh_3)(PBu_3)$; $(PPh_3)(py)$; $(PPh_3)(N_3)$; (PPh_3)(tosylate anion)] catalyze the oxidation of alkenes by PhIO at room temperature. With norbornene and cyclooctene, epoxides were formed. In the case of styrene and stilbene, oxidative cleavage of the C=C bond was the major reaction pathway [553]. The complexes $[RuCl(LL)_2]^+$ [LL = dppp or $Ph_2(CH_2)_2$(2-py)] were tested as catalyst for the epoxidation of various olefins with PhIO, NaOCl, or H_2O. A kinetic study was performed for the system PhIO/$[RuCl(dppp)_2](ClO_4)$ and the decomposition of an alkene-Ru-oxo species was proposed as the rate-determining step [554,555].

Epoxidation of propene with *m*-chloroperoxybenzoic acid in the presence of Co tetratolylporphyrin has been investigated. The results suggest that a porphyrin radical cation is the active form of the catalyst [556].

The Ni(II) complexes (213; R = CH_2Ph, CH_2CHMe_2, iPr, H) were found to catalyze the oxidation of alkenes to epoxides and aldehydes with NaOCl under phase-transfer conditions [557].



213

Selective ketonization or selective epoxidation of olefins were observed under mild conditions using tBuOOH and $KHSO_5$ with either $[(diphoe)Pt(CF_3)(CH_2Cl_2)]BF_4$ or $(diphoe)Pt(CF_3)OH$ (diphoe = *cis*-1,2-bis(diphenylphosphino)ethylene) as catalyst [558]. The epoxidation of 1-octene with H_2O_2 using $[(diphosphine)Pt(CF_3)(solv)]^+$ and $[(diphosphine)Pt(CF_3)(OH)]$ type complexes has been studied at 25°C. Diphosphine complexes with rigid, five-membered chelate rings proved to be the best catalysts [559].

See also [469,494,621,622.623,624,625,811].

c) Oxidation of O-Containing Functional Groups

The synthesis of 1,2-quinones from the corresponding phenols, naphthols, anthracenols, and phenanthrols by a combination of the transition metal complexes $Ti(OPr^i)_4$, $VO(acac)_2$, $Zr(acac)_4$, or $Zr(OPr)_4$ and tBuOOH or $[Mo(O_2)_2O]$.py.HMPA has been described [560].

Polymer supported catalysts prepared from Nafiol 551 (the K salt of the solid-state superacid reagent Nafion-H) and Cr(III) or Ce(IV) were found to be effective catalysts for the oxidation of secondary alcohols to the corresponding ketones with tBuOOH. Oxidations were carried out in benzene or chlorobenzene solution at 80-85°C [561]. The mechanism of the Cr(III)-catalyzed oxidation of allyl alcohol by Ce(IV) in acid solution was studied and the rate laws for both the uncatalyzed and the catalyzed paths were determined. The slow step of the catalyzed process was the oxidation of a Cr(III)-alcohol complex by Ce(IV) [562]. Molybdenum complexes were used to catalyze the oxidation of terpene alcohols by tBuOOH. The reactivity sequence of the alcohols tested was isoborneol > borneol, neomenthol > menthol > isomenthol [563]. Alcohols were oxidized by tBuOOH in the presence of Br_4MoO^- supported on different carriers. The best carrier for Br_4MoO^- as an oxidation catalyst was a modified silica [564].

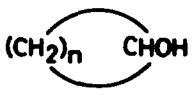
Oxidation of formaldehyde to CO_2 by H_2O_2 in dilute aqueous solutions is greatly accelerated by Fe^{2+}. Methanol (used as stabilizer of formaldehyde solutions) is also oxidized under such conditions to CO_2. These reactions are of significance in environmental chemistry [565]. Oxidation of ascorbic acid by $Cr(dien)(O_2)_2.H_2O$ (dien = diethylenetriamine) is catalyzed by Fe(II), Fe(III), and VO_2^{2+}. Addition of EDTA completely blocks the reaction in the case of Cu(II) and VO_2^{2+} and greatly retards it in the case of Fe(II) or Fe(III) [566].

Oxidation of 2-methylcyclohexanol to the corresponding ketone by $KBrO_3$ in acidic solutions and catalyzed by Ru(III) is first order in Ru(III) and the substrate, and zero order in bromate and H^+. The proposed mechanism involves the formation of a complex between the substrate and Ru(III) which decomposes in the rate-determining step to a Ru(III) hydride and the product. Bromate reoxidizes the hydride to the starting complex in a fast step [567]. The kinetics of the Ru(III)-catalyzed oxidation of cycloheptanol by acidic solutions of $KBrO_3$ in the presence of mercuric acetate as scavenger have been determined. The disproportionation of a complex between $[RuCl_2(H_2O)_4]^+$ and cycloheptanol into a Ru(III) hydride and the reaction product was proposed as the rate-determining step [568]. The kinetics of oxidation of ethylene glycol and glycerol by an acidic solution of N-bromoacetamide in the presence of Ru(III) chloride as catalyst and $Hg(OAc)_2$ as scavenger at 30-50°C have been reported. The main products of oxidation were acids [569]. Oxidation of diacetone alcohol by Ce(IV) is catalyzed by Ru(III). Based on kinetic measurements it was proposed that the rate-determining step of the reaction is the oxidation of a Ru(III)-diacetone alcohol complex by Ce(IV) to a Ru(IV) complex [570]. The oxidation of cyclohexanol to cyclohexanone by $[Fe(CN)_6]^{3-}$ is catalyzed by chlororuthenium complexes in aqueous alkaline solutions. Below pH 11 the reaction is limited because of the decomposition of the catalyst in its reduced state [571]. The rates of oxidation of mandelic acid by N-bromoacetamide were measured in the absence and in the presence of Ru(III). The catalyzed process involves the rapid reversible formation of an adduct between the catalyst and mandelic acid which reacts with the oxidant in a slow step [572]. The Ru(VI)-catalyzed oxidation of alkoxy-substituted 2-ethoxy ethanols by $[Fe(CN)_6]^{3-}$ in alkaline solution was found to be zero order in oxidant and first order in Ru(VI) [573]. Propanol and butanol are oxidized by alkaline $[Fe(CN)_6]^{3-}$ and Ru(VIII) catalyst to the corresponding carboxylic acids. The reaction is first order in Ru [574].

The kinetics of the uncatalyzed and catalyzed oxidations of acetophenones by N-bromosuccinimide in the presence of Ru(III) have been determined. The catalyzed reaction was first order in oxidant and fractional order in substrate and catalyst; the rate of oxidation increased with electron-attracting substituents on the aromatic ring [575]. The kinetics of the Ru(III) chloride-catalyzed oxidation of benzaldehyde and substituted benzaldehydes by trichloroisocyanuric acid in acid medium were determined [576]. Oxidation of chalcones by acid bromate and catalyzed by Ru(III) was found to be first order each in chalcone and Ru(III), and zero order each in H^+ and BrO_3^-. A radical mechanism involving the chalcone and Ru(III) in the slow step was proposed [577]. The kinetics of the homogeneous oxidation of ascorbic acid to dehydroascorbic acid, cyclohexane to cyclohexanol [578], and cyclohexanol to *cis*-1,3-cyclohexanediol [579] by hydrogen peroxide catalyzed by Ru(III)-EDTA-ascorbate complexes have been studied at 15-40°C.

Cobalt Schiff base complexes catalyze the oxidation of *p*-substituted benzyl alcohols to the corresponding benzaldehydes by tBuOOH. The catalytically active species is a $(tBuOO)Co^{III}(L)$ (L = Schiff base ligand) complex [580]. Rhodium(III)-chloride catalyzes the oxidation of alcohols to the corresponding carbonyl compounds by diperiodato cuprate. The oxidation is first order in Rh(III) and alcohol and zero order in cuprate [581].

Allylic alcohols can be selectively oxidized to the corresponding unsaturated carbonyl compounds by $K_2S_2O_8$ and catalytic amounts of $NiSO_4$ in a two-phase system (CH_2Cl_2/aqueous NaOH). The active species in this catalytic oxidation is nickel peroxide which is formed *in situ* from Ni^{2+} and the oxidant [582]. The kinetics of 2,4-di-*t*-butylphenol oxidation with H_2O_2 in the presence of bis(ethylenediamine)copper(II) as catalyst have been studied. Based on initial rates first order dependence in H_2O_2, phenol and catalyst were found. Spectroscopic evidence supported the intermediacy of a Cu(II):en:H_2O_2 = 1:2:1 and a Cu(II):en:phenol:H_2O_2 = 1:1:1:1 complex (en = ethylenediamine) [583]. The oxidation of ascorbic acid by H_2O_2 in the presence of Cu^{2+} ions has been investigated. A chain mechanism was proposed [584]. The very slow oxidation of ascorbic acid to dehydroascorbic acid by Cr(diethylenetriamine)$(O_2)_2$ is catalyzed by Cu(II) and VO^{2+}. This catalytic effect is due to the formation of Cu or VO complexes of the ascorbate anion which are then rapidly oxidized by Cr(IV) [585]. Oxidation of cycloalkanols (**214**) by $Pb(OAc)_4$ using $Cu(OAc)_2$ as catalyst afforded the corresponding cycloalkanones, alkenals $CH_2{=}CH(CH_2)_{n-2}CHO$ and (for n = 6,7) the oxabicycloalkanes (**215**) [586].



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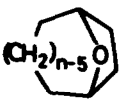
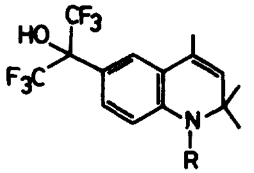


215

The oxidation of phenols by persulfate in the presence of Ag^+ has been studied at different temperatures. Various thermodynamic parameters for the oxidation of monosubstituted phenols have been determined [587]. The kinetics of the Ag(I)-catalyzed oxidation of formic acid by the [ethylenebis(biguanidine)]Ag(III) cation in perchloric acid media were determined [588].
See also [38,395,478,460,607,624,685].

d) Oxidation of N-Containing Organic Compounds

Phosphotungstic acid is an efficient catalyst for the N-oxidation of pyridine, alkylpyridine, and pyridinecarboxylic acids by H_2O_2 at room temperature [589]. Oxidation of the secondary amine (216) with H_2O_2 in the presence of Na_2WO_4 gave the nitroxide (217) [590].

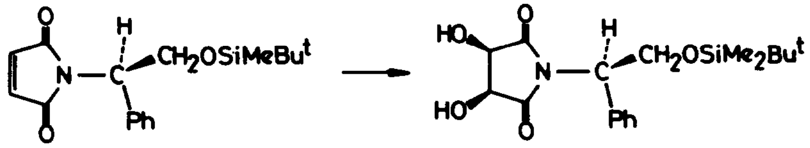


216; R = H
217; R = O·

Oxidation of glycine by Ce(IV) sulfate in the presence of Mn(II) ions has been found to be first order in both oxidant and substrate concentrations [591]. The Mn^{2+}-catalyzed oxidation of lumogallion by H_2O_2 is first order in the substrate-Mn^2 complex and changes from first to zero order in H_2O_2 as the concentration of the oxidant increases [592]. Oxidation of indigo carmine by H_2O_2 is catalyzed by Mn(II)-histidine complexes. At high reactant concentrations the reaction is inhibited by the complex formation between the reactant and the catalyst [593].

Oxidation of leucine with H_2O_2 in the presence of Fe^{2+} (Fenton reagent) gave isovaleraldehyde, α-ketoisocaproate, isovalerate and isovaleraldehydeoxime. Radical scavengers did not inhibit aminoacid oxidation [594]. The catalytic activity of Fe ions in the chemiluminescent oxidation of luminol by monobasic aliphatic peroxy acids is increased by the addition of 1,10-phenanthroline [595]. Oxidation of aromatic amines by H_2O_2 is catalyzed by tetraphenylporphyrin complexes of Fe^{3+}, Co^{2+}, Ni^{2+},

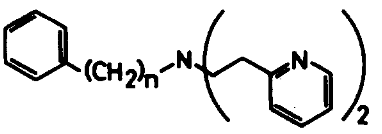
Mn^{3+}, and Cu^{2+}; the activity of the catalysts strongly decreases in the stated order. Highest rates were obtained in the oxidation of *o*-dianisidine with TPP-Fe^{3+}. A radical mechanism was discussed [596]. Oxidation of glycine, α-alanine, leucine, phenylglycine, and phenylalanine by N-bromosuccinimide in the presence of $Hg(OAc)_2$ and Ru(III) as catalyst in aqueous AcOH yields aldehydes, ammonia and CO_2. Kinetic measurements showed that oxidation was first order in oxidant and fractional order in substrate [597]. The kinetics of oxidation of $EtNH_2$, $BuNH_2$, $iPrNH_2$, Et_2NH and Et_3N by chloroamine-T were studied in alkaline medium catalyzed by Os(VIII) and in acid medium catalyzed by Ru(III). The two catalyst systems followed similar kinetics. Mechanisms were proposed for both cases [598]. The maleimide (218) was catalytically osmylated (OsO_4 + N-methylmorpholine-N-oxide) to yield the *cis*-diol (219) [599].



218

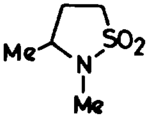
219

The kinetics of the oxidation of asparagine with chloroamine-T catalyzed by Cu(II)) have been investigated. The results proved that the reactions proceeds through both uncatalyzed and catalyzed pathways [600]. Oxidation of indigo carmine by $S_2O_8^{2-}$ is catalyzed by Cu(II). The reaction is first order in substrate [601]. Hydroxylation of one of the pyridine rings in *ortho* position occured when compound (220) bonded in a Cu(I) complex was oxidized with PhIO [602].



220

Alkanesulfonamides were oxidized by $Na_2S_2O_8$-$AgNO_3$-$CuSO_4$ in water. $R(CH_2)_3SO_2NH_2$ (R = Me,Et,Pr) was oxidized regioselectively to $RCO(CH_2)_2SO_2NH_2$, and $Me(CH_2)_3SO_2NHMe$ gave (221) and (222) [603].



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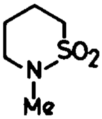
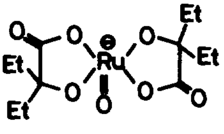


222

The oxidation of picolinic acid hydrazide by $K_2S_2O_8$ in the presence of $AgNO_3$ takes place in two consecutive steps. The primary oxidation product is picolinoyl diimide which is further oxidized to picolinic acid and N_2 [604].
See also [245,439,498,655,749,764].

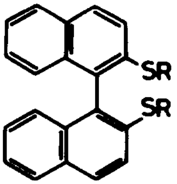
e) Oxidation of P-, S-, Se-, and Cl-Containing Organic Compounds

Oxygen atom transfer from a variety of oxygen atom donating heterocyclic amine oxides and sulfoxides, including pyridine N-oxide, nicotinamide N-oxide, DMSO, diphenyl sulfoxide, and biotin S-oxide in either CH_2Cl_2 or THF to oxidize triphenyl phosphine to triphenylphosphine oxide by using an oxo-bridged Mo(V) complex $Mo_2O_3(dtc)_2I_2(THF)_2$ as catalyst was reported (dtc = $C_5H_{10}NCS_2^-$) [605]. Technetium thiolato complexes, $TcO(tmbt)_3(py)$, $(Ph_4As)[TcO(tmbt)_4]$ and $TcO(SPh)_3py$ have been found to catalyze the oxidation of PPh_3 by DMSO at 22°C in MeCN (tmbt = 2,3,5,6-tetramethylbenzenethiolato) [606]. Primary and secondary alcohols and PPh_3 were oxidized to aldehydes, ketones, and Ph_3PO, respectively, in the presence of the Pr_4N^+ salt of the Ru(V) complex (223) as catalyst and excess N-methylmorpholine N-oxide in acetonitrile at room temperature [607].



223

In the oxidation of (−)-*sec*-octyl-p-tolyl sulfide with tBuOOH and oxotitanium complexes of N-salicyclidene L-amino acids double asymmetric induction takes place and the reaction affords the corresponding sulfoxide with 24% enantiomeric excess [608]. Enantioselectivity of up to 80% has been achieved in the $Ti(OPr^i)_4$/(+)-diethyl tartrate/H_2O = 1/2/1 mediated oxidation of 2-substituted 1,3-dithianes to the corresponding 1-oxides by cumene hydroperoxide [609]. In the asymmetric oxidation of β-hydroxy sulfides to the corresponding sulfoxides with tBuOOH-$Ti(OPr^i)_4$-(R,R)-diethyl tartrate the presence of the OH group in the substrate does not play a significant role in determining the extent of enantioselection. This is in marked contrast to the asymmetric epoxidation of allylic alcohols performed by the same system and indicates some important difference in the oxidation mechanism [610]. The racemic thioethers (224); R = Me; R_2 = CH_2, $(CH_2)_2$, -CH=CH- were asymmetrically oxidized to the monosulfoxides (225) with tBuOOH in the presence of $Ti(OPr)_4$ and (+)-diethyltartrate. These compounds may serve as starting materials for the preparation of enantiomerically pure (224; R = H) [611].



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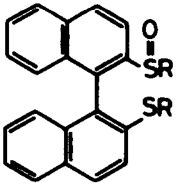


225

Oxidation of dimethyl sulfoxide by K_2FeO_4 is catalyzed by OsO_4 in alkaline solutions. The rate is zero order in oxidant, fractional order in substrate and first order in catalyst [612]. Oxidation of Bu_2S, Ph_2S, PhMeS and $(PhCH_2)_2S$ to the corresponding sulfoxides by N-methylmorpholine N-oxide catalyzed by $RuCl_2(PPh_3)_3$ in DMF was reported. According to spectral studies 1:1 complexes were formed between the sulfides and the Ru complex. The kinetics of the reaction have been studied [613]. The kinetics of the Os(VIII)-catalyzed oxidation of MeSPh to MeS(O)Ph by bromamine-B in alkaline medium have been determined [614].

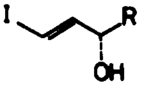
The oxovanadium(V) complexes VO(L)(OMe)(MeOH) (L = salicylidene-L-aminoacid, where aminoacid = L-alanine, L-phenylalanine, L-valine, and L-leucine) catalyze the asymmetric oxidation of MeSPh by tBuOOH to the corresponding sulfoxide. Highest optical yield (14%) was achieved with the valine complex [615]. Kinetic studies of the vanadium(IV)-catalyzed oxidation of DMSO by H_2O_2 in water and aqueous MeOH or EtOH showed that the reaction is first order in oxidant and substrate [616].

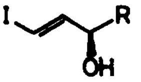
Asymmetric oxidations of alkyl aryl selenides to the corresponding optically active selenoxides under Sharpless oxidation conditions has been studied. Moderate to low chemical yields and up to 32.7% ee were achieved at -15°C using $Ti(OPr^i)_4$, diethyl tartrate and tBuOOH [617]. Oxidation of $MeSeC_6H_2R_3$-2,4,6 (R = iPr, tBu) according the Sharpless procedure in the presence of (+)- or (-)-diethyl tartrate in CH_2Cl_2 gave the corresponding (R)- and (S)-selenoxides, respectively. If the oxidations were performed in Et_2O as solvent the selenoxides with opposite configurations were obtained [618]. The combination of iron(II) bis(picolinate), H_2O_2, PhSeSePh, and a hydrocarbon substrate (cyclohexene, n-hexane, 2-Me-butane, adamantane, ethylbenzene) in py/AcOH reacted stoichiometrically to give the PhSe derivatives of the substrate at room temperature [619]. In the oxidation of mono-, di- and trichloroacetic acids by chloramine-T the catalytic effect of Ir(III) + V(IV) is greater that that of Ir(III) and V(IV) employed alone. This effect is explained by the Ir(III)-substrate complex reacting with the protonated chloramine-T-V(IV) complex in the rate-determining step [620].
See also [471,498,512,655,778,796].

f) Kinetic Resolution by Asymmetric Epoxidation

The Sharpless asymmetric epoxidation procedure (tBuOOH + $Ti(OPr^i)_4$ + L-(+)-diisopropyl tartrate) has been used for the kinetic resolution of racemic allylic alcohols by several groups. The following examples were described:

- Optically pure (E)-γ-iodo allylic alcohols (226; R = Me, pentyl, Cy, Ph, CH_2OCH_2Ph) have been prepared in excellent yields [621].

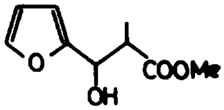




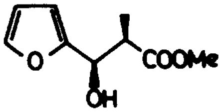
99 % ee

226

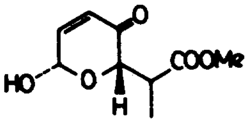
- Resolution of racemic trimethylsilyl secondary allylic alcohols Me$_2$SiCH=CHCHROH (R = alkyl, Ph, alkoxyalkyl) and R^{1}CH=C(SiMe$_3$)CHR^{2}OH (R^1 = H,Bu; R^2 = pentyl, Me) proceeded with very large and synthetically satisfactory rate differences for the two enantiomers [622]. The method has been successfully applied also for the kinetic resolution of different furylcarbinols. Using catalytic (20 mole%) or stoichiometric amounts of Ti(OPr^i)$_4$ 33-42% isolated yields (based on racemic furylcarbinol) with 95-99% ee of the slow-reacting enantiomer were achieved [623]. In one specific case, *syn*-(227), the resolution provided (2R,3R)-(227) in 45% yield which could be readily separated from the oxidation product (228) by column chromatography [624].



syn - 227



(2R,3R)-227



228

- Oxidation of racemic 2-thienylcarbinols (229; R = H,Me; R' = alkyl,Ph) with the Sharpless reagent proceeded to nearly 50% conversion (to an unidentified polymeric product) and the unconverted alcohol (230) had an optical purity higher than 95% [625].

229

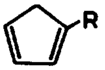
230

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

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

The kinetics of the Ce(IV) oxidation of malonic acid in sulfuric acid-perchloric acid media have been determined and a mechanism was proposed which involves decarboxylation as the rate-determining step [626]. Oxidation of malonic acid and its dimetyl ester by Ce(IV) has been found to be first order both in substrate and oxidant [627]. The kinetics and mechanism of oxidation of butylmalonic acid and its diethyl ester by cerium(IV) sulfate have been studied. The reactive species were shown to be $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$ [628].

Oxidation of ethene, propene, and 2,3-butylene glycol and pinacol with chromic acid in $HClO_4$ medium in first order each in glycol and oxidant. Oxidation rates increase in the stated order of glycols [629]. Oxidation of Me ricinoleate with H_2CrO_4 followed by epoxidation gave methyl 9,10-epoxy-12-oxooctadecanoate [630]. Oxidation of cyclopentadienes (**231**; R = nBu, n-octyl) with pyridinium chlorochromate gave the corresponding cyclopentanones (**232**) [631].



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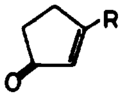
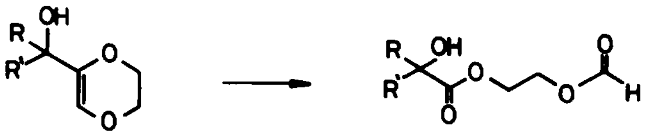


232

The allyic alcohols (**233**; R,R' = alkyl or cycloalkyl) undergo regiospecific oxidative cleavage with pyridinium chlorochromate at the dioxene double bond to give the α-hydroxy esters (**234**). Extension of this reaction to α,β-unsaturated ketones (**235**) affords the α-keto esters (**236**) [632].



233 234

235 236

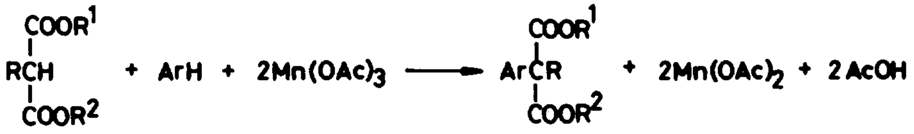
Treating the olefinic esters Me 10-undecenoate and *cis*-Me 9-octadecenoate with Ag_2CrO_4 and I_2 under anhydrous conditions gave the α-iodo ketones $ICH_2CO(CH_2)_8COOMe$ and 9(10)-iodo-10(9)-oxo-octadecanoate, respectively. In aqueous media, however, iodohydrins were formed [633]. Disubstituted internal olefins were selectively oxidized to α-chloro ketones (237) with excellent yields with CrO_3 + Me_3SiCl in CCl_4. Unsymmetrical olefins produced a mixture of both geometrical isomers possible. The actual oxidizing species is probably polyoxochromium dichloride [634].

237

UV irradiation of aqueous solutions of polytungstates in the presence of C_1–C_6 alkanes gave mixtures of alcohols, aldehydes, and acids. Thus, cyclohexane underwent 6% conversion to give mainly cyclohexanone, some cyclohexanol, and traces of adipic acid [635].

The kinetic parameters characterizing the oxidation of both sodium valerate of normal isotopic composition and sodium (2-D_2)valerate with manganate in aqueous NaOH solutions have been determined [636]. Oxidation of 1,2,4,5-tetraethylbenzene with aqueous alkaline $KMnO_4$ gave a mixture of $(KOOC)_n(HOOCCO)_{4-n}C_6H_2$ (n = 0–2), *p*-$C_6H_2(COOK)_4$, and $(COOK)_2$ [637]. A convenient one-step synthesis of 2-alkyl-2-hydroxy-3-oxocarboxylic esters ROOCC(OH)R'COR" (R,R' = Me,Et; R" = Me,Et,Pr,Bu,tBu; R'R" = $(CH_2)_4$) by $KMnO_4$ oxidation of the readily available α,β-unsaturated esters ROOCCR'=CHR" was described [638]. The oxidation of 12-oxo-(Z)-9-octadecenoic acid with alkaline $KMnO_4$ gave *erythro*-9,10-dihydroxy-12-oxooctadecanoic acid and 9,12-epoxyoctadeca-9,11-dienoic acid as minor and major products, respectively [639]. The kinetics of oxidation of cycloalkenes with cetyltrimethylammoniumpermanganate in CH_2Cl_2 have been studied. The relative rates of oxidation versus ^{13}C NMR chemical shifts, vertical ionization potentials, and strain energies were determined. The results suggest that MnO_4^- may act as a 1,3-dipole [640]. Kinetic characteristics of the disproportionation and oxidation of manganate(V) oxide were found to account for the observed product, - diols in basic solutions and ketols under neutral conditions - in permanganate-olefin reactions [641]. Evidence was found for the existence of the metastable manganate(V) ester intermediate in the permanganate oxidation of *endo*-dicyclopentadiene [642].

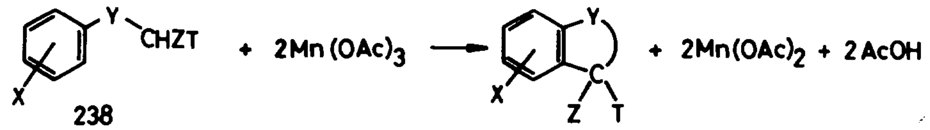
The synthesis of α'-acyloxy enones from enones by oxidation with manganese(III) acetate in presence of manganese(II) carboxylates or carboxylic acids has been reported [643]. Radical cations of benzo[*a*]pyrene and its 6-substituted derivatives have been generated by one-electron oxidation with $Mn(OAc)_3.2H_2O$ [644]. Oxidation of malonic acid esters by $Mn(OAc)_2$ in the presence of electron-rich aromatic substrates at 20-80°C yields aryl-substituted malonic esters (aromatic malonylation):



$$\underset{COOR^2}{\overset{COOR^1}{RCH}} + ArH + 2Mn(OAc)_3 \longrightarrow Ar\underset{COOR^2}{\overset{COOR^1}{C}}R + 2Mn(OAc)_2 + 2AcOH$$

The reaction has been investigated with a large number of aromatics and malonic esters and several side reactions (acetoxylation, oxidative coupling,etc.) were observed. The extent of these depends on the ionization potential of the aromatic compound and on the steric properties of the malonic acid derivatives [645]. Manganese(III) acetate in AcOH at 50-80°C induces oxidative cyclization of α-arylalkyl or α-(aryloxy)alkyl

β-dicarbonyl compounds (238; X = H, 3- or 4-OMe, 2,3- or 3,4-CH=CHCH-, 2-Ph, 4-NO_2, 4-NHAc: Y = $(CH_2)_3$, $(CH_2)_2$, CH_2, $O(CH_2)_2$, $O(CH_2)_3$: Z = COOEt; T = COOEt, CN, COMe). The reaction is favored by high electron density of the aromatic carbon atom α to the carbonylalkyl substituent [646].



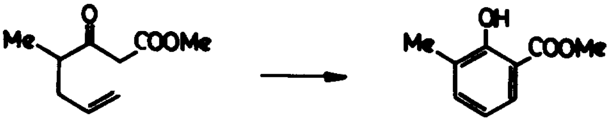
238

α-Diketones or α-hydroxy ketones have been obtained in good yields by treating olefins with a well-ground mixture of $KMnO_4/CuSO_4.5H_2O$ in CH_2Cl_2 containing catalytic amounts of *terc*-butyl alcohol/water at room temperature [647]. Various γ-lactones resulting from a 5-exo cyclization in the oxidative free-radical cyclization of allylic β-diesters with $Mn(OAc)_3$-$Cu(OAc)_2$ have been described [648]. Allyl acetoacetate (239, R = COMe) and allyl malonate (239, R = COOMe) are oxidized in acetic acid by $Mn(OAc)_3.2H_2O$ in the presence of $Cu(OAc)_2$ to 3-oxa bicyclo (3.1.0)-2-hexanone derivatives (240) [649].

239

240

Treatment of 3-oxo-6-heptenoate esters like (241) with $Mn(OAc)_3.2H_2O$ and $Cu(OAc)_2.H_2O$ gave the corresponding salicylate esters, e.g. (242). If the heptenoate ester contained an OH group in δ position, oxidative cyclization with $Mn(OAc)_3.2H_2O$ resulted in the formation of epoxides, see (243) → (244) [650].



241

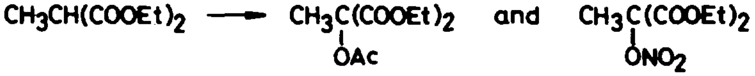
242

243 244

A mild synthesis of spiro[4,4]nonane compounds (245) in 68-72% yield was achieved by oxidative free radical cyclisation using one equiv. manganese(III)acetate and one equiv. copper(II)acetate in 0.1 M acetic acid [651].

245

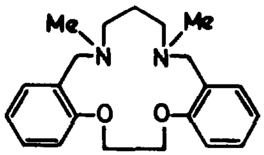
Iron (III) salts oxidize the α-position of malonic esters via the corresponding radicals. For example, methylmalonate (246) is oxidized by $Fe(ClO_4)_3.9H_2O$ in Ac_2O at 5^oC to give the corresponding α-acetoxy derivative (247) in 60% yield; iron(III) nitrate affords under similar conditions (247) and the α-nitrato derivative (248) in approximately equal amounts (40 and 44%) [652].



$$CH_3CH(COOEt)_2 \longrightarrow \underset{OAc}{CH_3C(COOEt)_2} \text{ and } \underset{ONO_2}{CH_3C(COOEt)_2}$$

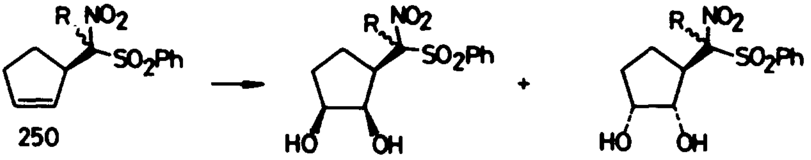
246 247 248

Stirring $[Ru^{VI}(L)(O)_2](ClO_4)_2$ with styrene for 12 h at room temperature produced benzaldehyde with a 40% yield, based on the amount of metal complex used [653]. Ruthenium-oxo complexes of the ligand L (249) are powerful oxidizing agents and active catalysts for the oxidation of organic substrates. Thus, *trans*-$[Ru(L)(O)_2]^{2+}$ oxidizes alcohols to the corresponding carbonyl compounds, stilbene, styrene, and toluene to benzaldehyde, cyclooctene to cyclooctene oxide, etc. On the other hand, *trans*-$[Ru(L)(O)(H_2O)]^{2+}$ catalyzes the same oxidations by PhIO as oxidant [654].



249

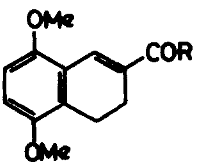
A preference of *syn* dihydroxylation to an allylic CHR_2 substituent of 3-substituted cyclopentenes (250; 0 = R) through osmylation with OsO_4 or OsO_4 + Me_3NO has been observed. By contrast, bulkier substituents (R = Me) gave rise to a striking reversal of selectivity [655].



250

R = H	92 %	8 %
R = Me	≤ 5 %	≥ 95 %

Asymmetric oxidation of hydronaphalenes (251; R = OMe,Me) with OsO_4 and the chiral diamine (253) gave the diols (252) [656].



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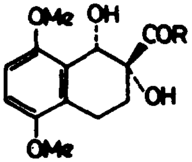

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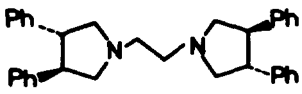
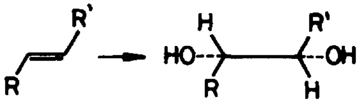
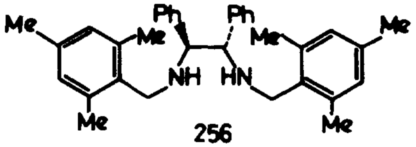


253

The enantioselective vicinal hydroxylation of terminal and E-1,2-disubstituted olefins (254; R,R' = Ph,H; Ph,Me; Me,COOMe; Ph,COOMe; R = R' = Ph; Et; MeOOC) by an equimolar mixture of OsO_4 and the chiral ligand (256) gave 80-95% isolated yields and 82-98% ee of the diols (255). The chiral ligand and Os were recovered with >80% efficiency [657].

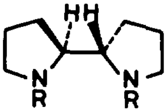


254 255



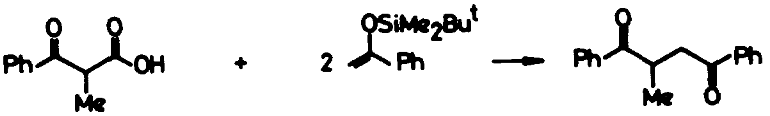
256

Up to 92% ee has been observed in asymmetric dihydroxylation of alkenes by osmylation with OsO_4 at -78°C using *N,N'-dialkyl-2,2'-bipyrrolidines* (257) *as chiral ligands* [658]. *In* this case also the structure of the Os(VI) glycolate ester-diamine complex prepared from [OsO_4(257; R = neohexyl)], and stilbene could be determined [659].



257; R = C_1-C_5 alkyl

The effect of NaBr on the allylic oxidation of olefins by Co(III), Mn(III), and Ce(IV) acetates in AcOH has been studied. Sodium bromide strongly accelerated the oxidation of cyclohexene by these oxidants to give cyclohex-2-enyl acetate in good yield [660]. Aliphatic and aromatic conjugated dienes were smoothly oxidized by $Co(OAc)_3$ in AcOH to give vicinal diol derivatives. Cyclooctadiene was converted under such conditions into the corresponding allylic acetate [661]. Kinetic data and Hammett plots were determined for the oxidation of *para*-disubstituted deoxybenzoins $RC_6H_4CH_2COC_6H_4R'$ (R = MeO,Cl,Br,NO_2,H; R' = H,Cl,Br,tBu,OMe) with $Co(OAc)_3$ [662]. Kinetic, selectivity and *isotope-effect studies were carried out on the oxidation of* benzene and methylbenzenes (1-5 Me groups) with Co(III)-AcOH-CF_3COOH solutions [663]. Manganese(III) tris(2-pyridine*carboxylate) was used as oxidant in the addition reaction of the β-keto carboxylic* (258) *acids to olefinic compounds* [664].



258

The kinetics of oxidation of p-toluic acid by $Co(OAc)_3$ have been studied in water or chlorobenzene as solvent. Cation radicals were proposed as intermediates [665,666].

Ethene oxidation by $Pd(NO_n)_{2-m}Cl_mL_2$ (where n = 2,3; m = 0,1,2; L = CH_3CN, CD_3CN) in $CHCl_3$ was studied by IR and ^1H NMR spectroscopy. Nitrito and nitrato complexes gave acetaldehyde whereas nitro complexes led to nitroolefin as main product. Based on identified intermediates suggestions for the key steps were made [667].
See also [458,668,670,712,790].

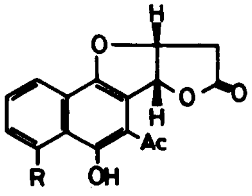
b) Epoxidation of Olefins

Second-order rate constants were determined for the epoxidation of alkenes (norbornene, *cis*-cyclooctene, cyclohexene) with the following oxochromium(V) porphyrins: $(Me_{12}TPP)Cr(O)(ClO_4)$ $(Cl_8TPP)Cr(O)(ClO_4)$, $(F_8TPP)Cr(O)(ClO_4)$, and $(TPP)Cr(O)(ClO_4)$. The yield of *exo*-norbornene oxide was theoretical; *cis*-stilbene did not yield epoxide but mainly diphenylacetaldehyde [668]. From the dynamics of epoxidation of a series of alkenes by $(Br_8TPP)Cr(O))(ClO_4)$ it has been concluded that the rate-determining step involves the formation of a charge-transfer complex [669]. Epoxidation of styrene with $MoO(O_2)_2$.HMPA is an autocatalytic process: styrene oxide forms a complex with the oxidant which is more reactive than the oxidant itself. Besides styrene oxide, benzaldehyde and formic acid are also formed [670]. The epoxidation of cyclohexene using resin-fixed phosphorus(V)-molybdenum(VI) mixed oxo derivatives has been studied [671]. The asymmetric epoxidation of simple prochiral olefins with molybdenum(VI)(oxo-diperoxo) complexes has been studied. Excellent optical purity (95.4% ee) was achieved from *trans*-2-pentene using $MoO(O_2)_2$(S)-piperidine-lactamide as oxidant and 2S,3S-butadienol as additive [672].

High-valent ruthenium(IV) and -(VI) oxo complexes of octaethylporphyrin (DEP), [(OEP)Ru(O)(EtOH)] and $[(OEP)Rh(O)_2]$ oxidize olefins to epoxides [673].
See also [630,654,650,792].

c) Oxidation of O-Containing Functional Groups

Oxidation of gallic acid with Ce(IV) starts with the formation of a complex which disproportionates into Ce(III) and an *o*-benzoquinone-type oxidation product. Ultimately the reaction affords HCOOH and CO_2 [674]. The kinetics of oxidation of L-rhamnose by Ce(IV) have been determined [675]. The kinetics of oxidation of *o*-, and *m*-methoxymandelic acids to the corresponding benzaldehydes by Ce(IV) have been studied. The overall rate constants have been determined [676]. The rate of oxidation of benzalacetophenone by Ce(IV) in H_2SO_4-AcOH mixtures is increased by electron releasing substituents and decreased by electron withdrawing substituents in both aromatic rings of the substrate [677]. Oxidation of glyceraldehyde by Ce(IV) sulfate in sulfuric acid solution was found to be first order both with respect to Ce(IV) and substrate [678]. The kinetic parameters of the oxidation of D-galactose, D-glucose, D-mannose, L-arabinose, D-ribose, D-xylose, D-fructose, and L-sorbose with Ce(IV), Cr(VI), and vanadium(V) were determined [679]. The kinetics of the oxidation of oxalic acid by Ce(IV) in sulfuric acid medium have been studied voltammetrically. The reaction is first order both in oxidant and substrate. A probable mechanism has been suggested [680]. Oxidation of (259) by ceric ammonium nitrate gave the rearranged hemiketal (260) [681].



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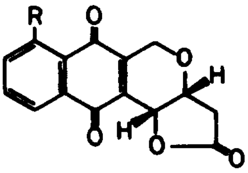


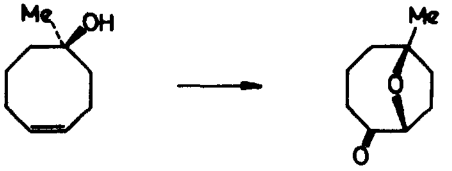
260

R = H,OMe.

Oxidation of benzyl alcohol with VO_2^+ leads to benzaldehyde. Kinetic studies of the reaction were carried out [682]. Oxidation of alcohols, aldehydes, ketones, and acids by V_2O_5 has been investigated in non-aqueous solvents. Alcohols were found to be more resistant to oxidation in organic solvents than in water, aldehydes were more difficult to oxidize than ketones, and acids reacted only to a very limited extent [683]. Effect of pressure on the rates of oxidation of monosaccharides with vanadium(V) in perchloric acid has been studied. A mechanism involving formation of a radical by hydrogen transfer in the rate-determining decomposition of a monosaccharide-vanadium(V) complex was proposed [684]. Oxidation of L-sorbose with vanadium(V) in aqueous perchloric acid is first order in substrate, catalyzed by HSO_4^-, and third order with respect to H^+. The effect of Ru(III) chloride as a homogeneous catalyst is small [685]. The kinetics of oxidation of aldopentoses to aldotetroses by vanadium(V) have been determined in perchloric acid solutions. Sodium hydrogen sulfate catalyzes the reaction. The values of the activation parameters and the HSO_4^- catalysis suggest that the configuration at C(2)-C(3) is important [686]. Kinetic investigations of the oxidation of propiophenone by vanadium(V) in aqueous acetic acid medium have been carried out. It was concluded that the reaction is ion-dipole and that the oxidant attacks the keto form rather than the enol form of the ketone [687]. The kinetics of oxidation of oxalic acid by peroxovanadate ions were determined [688].

The use of ultrasound improved the yields in pyridinium chlorochromate oxidation of primary and secondary alcohols to the corresponding carbonyl compounds [689]. Alcohols were oxidized to carbonyl compounds by adding the alcohol in a small amount of CCl_4 to a solution of CrO_3 and $(Me_3Si)_2O$ in pyridine at room temperature. Allylic alcohols were oxidized without C,C-bond cleavage [690]. Trimethylammonium chlorochromate has been used for the oxidation of α,β-unsaturated alcohols to the corresponding carbonyl compounds in 70-95% yield [691]. The dienals $CH_2{=}CHCMe{=}CHCHO$ and $CH_2{=}CHC({=}CH_2)CH_2CHO$ were prepared by oxidation with pyridinium chlorochromate from the corresponding dienols [692]. Alcohols were oxidized by potassium chlorochromate supported on alumina or silica gel. Benzyl and secondary alcohols in nonpolar solvents gave the best yields [693]. Several supported oxidant reagents have been prepared by the deposition of $K_2Cr_2O_7$ on $AlPO_4$, BPO_4, and $AlPO_4$-BPO_4 supports and used in the oxidation of OH groups of sterols [694]. Supported $K_2Cr_2O_7$ reagents have been tested for the oxidation of secondary alcohols, e.g. of menthol to menthone. The most active reagents were obtained from solid supports with large surface areas or with microcrystalline solids [695,696]. Oxidation of cholesterol and 16,17α-epoxy-

5-pregnen-3-ol-20-one with pyridinium chloro-chromate gave a mixture of products having the 5-en-3-one and the 4-en-3,6-dione structure. Using a large excess of pyridinium chlorochromate 16,17α-epoxy-4-pregnen-3,6-dione could be prepared in 83% yield [697]. Transannular oxidative cyclization of cyclooctenols with pyridinium chlorochromate in dichloromethane was applied for the preparation of the cyclic ethers (261) and (262). The corresponding methyl ethers were inert under these conditions [698].



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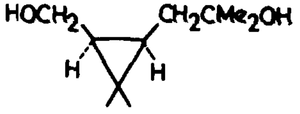
262

The cyclopropane derivative (263) was oxidized by pyridinium chlorochromate to give the lactones (264) and (265) [699].



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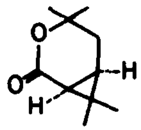

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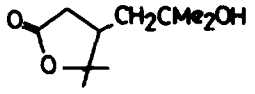

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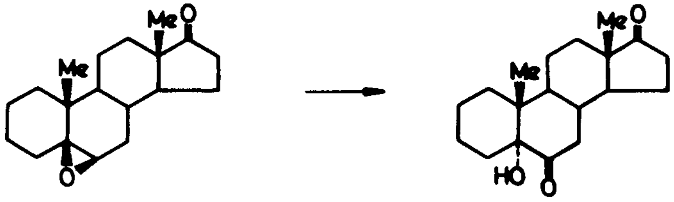
Oxidation of aldehydes RCHO (R = Ph, alkyl, cycloalkyl) with pyridinium chlorochromate in the presence of NaN_3 gives carbamoyl azides $RNHCON_3$ and/or acyl azides $RCON_3$ [700]. Acetals of benzaldehyde and substituted benzaldehydes with aliphatic alcohols were oxidized with chromic acid in aqueous acetic acid to the corresponding esters. Oxidation was first order in both acetal and Cr(VI) [701]. The kinetics of the liquid-phase oxidation of isobutyraldehyde with $K_2Cr_2O_7$ in AcOH were determined at 25-45°C [702]. Oxidation of tartaric acid with pyridinium chlorochromate was first order with respect to both substrate and oxidant [703]. The kinetics of the oxidation of oxalic and malonic acids by

Cr(VI) in acidic (H_2SO_4) solution have been determined. Mechanisms which involve rate-determining complex formation between the reactants were suggested [704]. Epoxide (266) could be oxidized by CrO_3 to the hydroxy ketone (267). The corresponding 3-Cl substituted derivative was, however, unreactive [705].

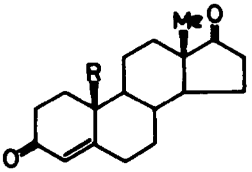


266 **267**

Manganese(III) acetate oxidizes veratryl alcohol to veratraldehyde and 1-(3,4-dimethoxyphenyl)-2-phenylpropanol to veratraldehyde, 1-phenylethanol, and acetophenone at physiological temperatures and pH values. These reactions are regarded as models for the biological oxidation of nonphenolic lignin components [706]. The stoichiometry and kinetics of the oxidation of 2-hydroxy acids by Mn(III) in aqueous solutions of perchloric acid were determined. Radical formation in the electron transfer from acid to Mn(III) was proposed as the rate-limiting step [707,708]. The kinetics of the oxidation of quinol (H_2Q) to benzoquinone by $Mn(bpy)_2^{3+}$ ions in aqueous perchlorate media have been studied. The involvement of intermediates such as $Mn(bpy)_2HQ^{2+}$ and $Mn(bpy)_2(OH)HQ^+$ was suggested [709].

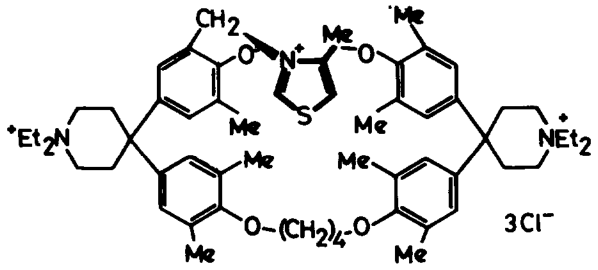
Allylic and benzylic alcohols were selectively oxidized to the corresponding carbonyl compounds by manganates under phase-transfer catalysis conditions [710]. The kinetics of oxidation of several monosacharides and polyhydric alcohols with permanganate in buffered solutions were studied. Aldosugars with *threo* configuration were more reactive than sugars with *erythro* configuration [711]. Aromatic alcohols, aldehydes, and alkylbenzenes may be oxidized to the corresponding acids with high yields by $KMnO_4$ in aqueous solutions of surfactants. The oxidation of alcohols and aldehydes proceeds under mild conditions, while the oxidation of alkylbenzenes requires higher temperatures [712]. The oxidation of acetaldehyde by permanganate obeys a rate law which is first order in aldehyde, permanganate and $[H^+]$ [713].

D-Galacturonic acid is oxidized by Fe^{3+} to formic acid and a fragment which has an additional carboxylic group [714]. The known oxidative couplings of phenols with $FeCl_3$ have been found to be faster and more efficient in the solid state than in solution. The reactions in the solid states were accelerated by irradiation with ultrasound [715]. Iron, cobalt, zinc and copper nitrates supported on silica gel have been found to be efficient in cleaving and oxidizing primary and secondary ethers to the corresponding aldehydes and ketones in refluxing CCl_4 or isooctane under N_2. Silica gel was essential for efficient oxidation. Overoxidation of the formed aldehydes to carboxylic acids has not been observed [716]. The peroxoiron(III) porphyrin complex $[(F_{20}TPP)Fe(O_2^{2-})]^-$, prepared *in situ* from $(F_{20}TPP)FeCl$ and KO_2 in the presence of 18-crown-6, oxidizes 4-androstene-3,17,19- trione (**268**) with 85% yield to 10β-hydroxyestr-4-ene-3,17-dione (**269**). If the oxidation was performed with the oxoferryl porphyrin cation radical $[(F_{20}TPP^{+\cdot})Fe(=O)]^+$, prepared *in situ* from $(F_{20}TPP)FeCl$ and *m*-chloro perbenzoic acid, the product was the carboxylic acid (**270**) [717].



268 ; R = CHO
269 ; R = OH
270 ; R = COOH

The kinetics of oxidation of L-ascorbic acid by $[Fe(CN)_6]^{3-}$ were studied. The reaction was first order in both oxidant and substrate; hydrogen ions showed a retarding influence [718]. Oxidation of *o*-, *p*-, and *m*-hydroxyacetophenones by $[Fe(CN)_6]^{3-}$ is first order each in substrate and oxidant [719]. A new thiazolium macrocycle (**271**) has been found to be a very efficient catalyst for the oxidation of 2-naphthaldehyde to 2-naphthoic acid at 30°C by potassium ferricyanide. A saturation kinetics and a large acceleration as compared to simple thiazolium salts have been observed [720].



271

A kinetic study of the oxidation of several alcohols by $[Ru^{IV}O(bpy)_2(ER_3)]^{2+}$ (ER_3 = PPh_3, PEt_3, PCy_3, $AsPh_3$, PPr^i_3) in H_2O, MeCN, and CH_2Cl_2 showed that both the hydrophobicity of the alcohol and the nature of ER_3 affect the reaction rate [721].

The osmium(VII) salt $(Ph_4P)(OsO_4)$ functions as a stoichiometric oxidant for benzylic and allylic alcohols, oxidizing primary alcohols to aldehydes and secondary alcohols to ketones. In contrast to RuO_4^-, OsO_4^- does not catalyze the oxidation of these alcohols by N-methylmorpholine-N-oxide [722]. Oxidation of alcohols, diols, and α-hydroxy acids to the corresponding carbonyl compounds by Os(VIII) in aqueous alkaline medium is first order in substrate and oxidant. No evidence for a complex formation has been found [723]. Oxidation of *m*-cresol by OsO_4 in alkaline medium was found to be first order each in oxidant and substrate. This result and the dependence on OH^- indicate the formation of a complex between the substrate and $[OsO_4(OH)_2]^{2-}$ [724].

Oxidation of aromatic secondary alcohols (272; X = H,Me, OMe,Br,Cl,F,NO_2; R = Me,Ph with $Co(OAc)_3$ in the presence of NaBr at 50-70°C gave the corresponding ketones in 84-97% isolated yields [725].

$$X{-}C_6H_4\underset{\displaystyle OH}{\underset{|}{C}}HR \longrightarrow X{-}C_6H_4\underset{\displaystyle O}{\underset{\|}{C}}R$$

272

Aliphatic aldehydes are oxidized by Ni(IV) periodate in aqueous alkaline solution to the corresponding carboxylic acids. The reaction is first order in both Ni(IV) and aldehyde [726].

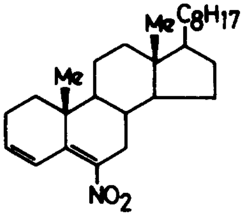
The kinetics and mechanism of the oxidation of ascorbic acid (H_2A) by Cu(II) were studied using the stopped-flow method. An intermediate complex with the composition ClCu(HA) is formed in the presence of Cl^- [727]. The kinetics of oxidation of ethylene glycol, 1,2-propanediol and tetrahydrofurfuryl alcohol by periodatocuprate(III) have been studied in alkaline medium. The order in Cu(III) was found to be unity and that in alcohol to be 1.3. A mechanism involving free radicals was proposed [728,729]. Copper(II) nitrate supported on silica gel efficiently oxidizes secondary alcohols and primary benzyl and allyl alcohols to the corresponding ketones and aldehydes under mild conditions (e.g. in refluxing CCl_4) [730].
See also [400.412,654,770].

d) Oxidation of N-Containing Organic Compounds

The oxidation of aniline, *o*-toluidine, 2,5- and 2,6-dimethylaniline, 2,4,6-trimethylaniline, and diaminodurene by Ce(IV) in aqueous perchloric acid proceeds via quinone imine and quinone intermediates. The kinetics of these reactions have been investigated [731]. The mechanism of the oxidation of N-alkyl derivatives of 1-aminonaphthalene and 4,4'-diamino-1,1'-binaphthyl by Ce(IV) sulfate in aqueous sulfuric acid was analysed by means of currentless potential-time curves [732]. In the oxidation of 4-piperidones by Ce(IV), $Ce(SO_4)_2$ is the active species and an enol intermediate is not involved [733]. The oxidation of L-serine, L-threonine, and L-aspartic acid with Ce(IV) in $HClO_4$ showed first order kinetics with respect to amino acid and fractional order with respect to Ce(IV). The formation of a Ce(IV)-amino acid complex was shown [734]. Oxidation of β-hydroxy nitrosamines by Ce^{4+} has been studied. Cyclohexylethanol-nitrosamine gave cyclohexylamine as the main product [735]. N^1-phenylbiguanidine, PhHNC(=NH)NHC(=NH)NH_2, in oxidized by Ce^{4+} to guanylurea, $H_2NCONHCONH_2$, 1,4-benzoquinone, and NH_3; if MnO_4^- is used as oxidant CO_2 is formed instead of benzoquinone. The kinetics of both reactions are first order in substrate and independent of oxidant concentration; hydrolysis of phenylbiguanidine was proposed as the rate-determining step [736].

Vanadyl sulfate and Na orthovanadate oxidize NADH in the presence of dithioerythrol, dithiothreol, and cysteine but not in the presence of glutathione. Thiourea inhibits the reaction [737].

The kinetics of oxidation of several substituted N-methyl-4-piperidones by Cr(VI) in the presence of sulfuric acid in aqueous acetic acid have been determined. The reactions were first order each in oxidant and substrate and second order in H_3O^+ [738]. Phenylbiguanidine, $PhNHC(=NH)NHC(=NH)NH_2$ was oxidized by Cr(VI) or Ce(IV) in sulfuric acid media to give 1,4-benzoquinone and carbamidoylurea, $NH_2CONHC(=NH)NH_2$ [739]. The oxidation of acetophenone oxime and its *para*-substituted derivatives by Cr(VI) was studied at 30°C. The products indicate that the reaction is an oxidative hydrolysis [740]. The chromic acid oxidation of 6-nitrocholesta-3,5-diene (273) gave the oxidized products (274), (275), and (276) [741].



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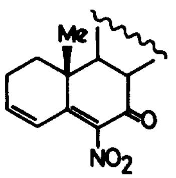

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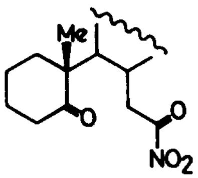

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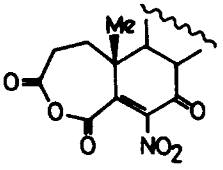
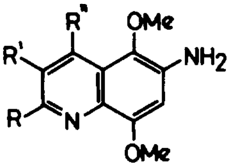


276

Halogenated pyridines (277; Ar = Ph, Cl- or NO_2-substituted phenyls) were oxidized with CrO_3 in AcOH or H_2SO_4 to give the respective ketones (278) [742].

277 278

Oxidation of the 6-amino-5,8-dimethoxyquinolines (279; R,R' = H,Me; R'' = H,Me,OMe,OEt,Cl) with $K_2Cr_2O_7$ gave the corresponding 8-methoxyquinoline-5,6-diones (280). In one case, the coupled product (281) was formed [743].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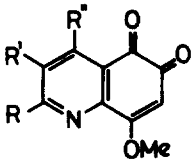
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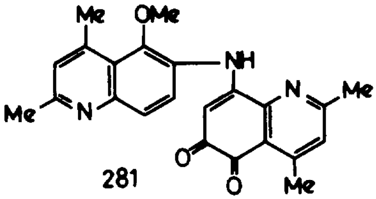
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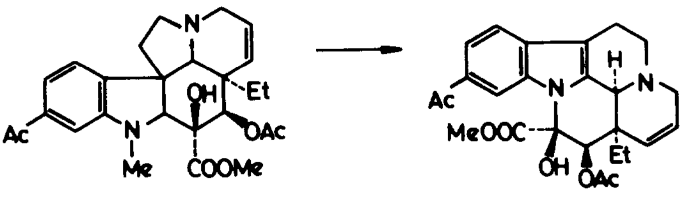
Oxidation of tertiary amines by $(Me_2N)_3POCrO(O_2)_2$ or $(Me_2N)_3POMoO(O_2)_2$ in $CHCl_3$ gives the corresponding N-oxides in good yield. Kinetic and spectroscopic results suggest a mechanism having some single-electron-transfer character [744].

The semicarbazones of aromatic ketones and aldehydes were oxidized by $Mn(OAc)_3$ to the corresponding carbonyl compounds. The carbonyl compounds could be regenerated in this way with about 80% yield [745]. Oxidation of vindoline (282) with MnO_2 gave a rearranged product, the vincine derivative (283) in 7% yield, among other oxidized vindoline derivatives [746].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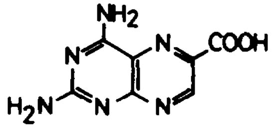
283

It has been found that in the reaction of toluidines and $KMnO_4$ in neutral aqueous solution the isolated yields of (N-acylamino)benzoic acids were low but MnO_2 was produced almost quantitatively due to the catalytic effect of the amides [747]. The one-pot oxidation and nitrosation of β-alkanolamines, $RCH(OH)CH_2NHR'$, with $KMnO_4$ in aqueous AcOH followed by treatment with $NaNO_2$ gives β-keto nitrosamines, $RCOCH_2N(NO)R'$ [748]. The same compounds may be prepared also from β-hydroxy nitrosamines by oxidation with $KMnO_4$-$CuSO_4.5H_2O$ in benzene or CH_2Cl_2 [749]. The kinetics of glutamic acid oxidation by $KMnO_4$ in acidic medium was determined in the absence and in the presence of Na dodecyl sulfate. The surfactant enhances the reaction rate without changing the reaction mechanism [750]. The kinetics and mechanism of oxidation of DL-alanine by $KMnO_4$ in sulfuric acid medium were studied. The reaction was first order in both reactants. Activation parameters were evaluated [751]. Imines, RCH=NR', have been oxidized to nitrones, RCH=N(O)R', in reasonable yields with $KMnO_4$ under phase-transfer conditions. It was found that water is necessary for the formation of the nitrone [752]. The carboxylic acids (284) and (285) were prepared by the $KMnO_4$ oxidation of the corresponding 6-(2-furyl)-substituted pteridines [753].



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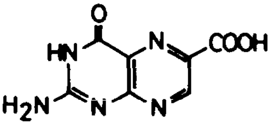

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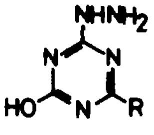
yields 2,3-diaminophenazine. The nonprotonated form of the substrate is the most active in this reaction; monoprotonation lowers the rate constant by a factor of about 5000 [754]. Oxidation of methyl indole-3-acetate with $FeCl_3$ in the presence of Pr_2NH gave methyl α-(dipropylamino)-indole-3-acetate in >90% yield [755]. The kinetics of oxidation of triethylenetetramine by $[Fe(CN)_6]^{3-}$ were investigated spectrophotometrically. The reaction was first order in both reactants [756]. The effect of substitution on the rate of oxidation of various dihydropyridines by $[Fe(CN)_6]^{3-}$ has been examined. The results were consistent with an initial electron removal in the rate-determining step [757]. Oxidation of diphenylamine by $K_3[Fe(CN)_6]$ leads to an orange-colored product. Kinetic investigations were used to establish the mechanism of formation of this product [758]. Oxidation of N-benzyl-1,4-dihydronicotinamide by $[Fe(CN)_6]^{3-}$ in acidic solution is not influenced by the presence of O_2. This is in contrast with the results obtained in alkaline media [759]. The oxidation of the same compound by $[Fe(CN)_6]^{3-}$ on active carbon is first order in substrate and independent of oxidant concentration [760]. Oxidative coupling of the hydrazino triazines (286; R = NMe_2, pyrrolidino, morpholino) with N,N-dialkylanilines using $[Fe(CN)_6]^{3-}$ gave the respective azo compounds (287; R' = Me, CH_2CH_2OH; R" = H, Me) [761].



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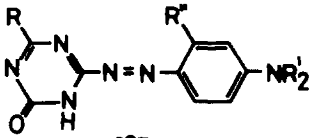


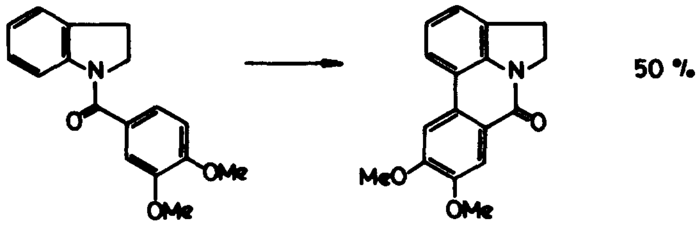
287

The oxidative demethylation of N,N-dimethylaniline and *para*-substituted N,N-dimethylanilines by oxo(phosphine) ruthenium(IV) complexes has been reported (R = Ph, Et).

$$[Ru(bpy)_2(O)(PR_3)]^{2+} + Me_2NPh \longrightarrow [Ru(MeCN)(bpy)_2(PR_3)]^{2+} + MeHNPh + CH_2O$$

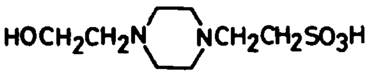
The reactions were first-order in both substrate and oxidant [762].

Rate data were determined for the oxidation of *p*-amino-N-ethyl-N-(β-hydroxyethyl)aniline with $Co(NH_3)_6Cl_3$ [763]. The silver and gold colloid-catalyzed oxidation of two *p*-phenylenediamines by $[Co(NH_3)_5Cl]^{2+}$ has been studied in aqueous solution. The silver-catalyzed oxidation is of complex character because the chloride of the Co complex inhibits the reaction whereas the organic compounds reduce the silver chloride formed to silver [764]. N-acylindolines (e.g. 288) were oxidized by $Pd(OAc)_2$ in refluxing glacial acetic acid leading to precursors of pyrrolophenanthridone alkaloids [765].



288

Tertiary amines such as (289) or N,N-dimethylethanolamine are oxidized by $(batho)_2Cu(II)$ (batho= 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate). The amines are dehydrogenated to iminium species which hydrolyze to secondary amines and aldehydes [766].


289

The oxidation of aryl hydrazines by copper(II) sulfate has been used for aryl radical generation in a new method of oxidative and reductive arylation of alkenes [767]. A kinetic study of the oxidation of uric acid with ammonia Cu(II) complexes confirmed a mechanism involving complexation of $[Cu(NH_3)_3]^{2+}$ with uric acid dianion followed by rate-determining electron transfer from Cu(II) to give uric acid anion radical [768].
See also [A52,728].

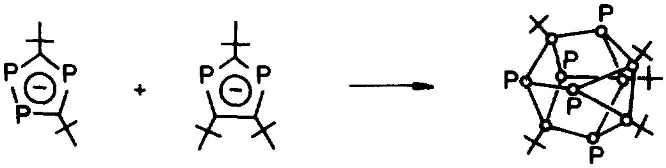
e) Oxidation of Si-, Sn-, P-, S-, and Halogen-Containing Organic Compounds

Carbon-silicon bond cleavage at room temperature and in quantitative yields in the oxidation of benzylic silanes by cerium(IV) ammonium nitrate has been reported. Kinetic results support a one-electron transfer mechanism [769].

Allylstannanes (290) were easily oxidized with $CuBr_2$ in the presence of water, alcohols, NaOAc, and amines to give the corresponding allyl alcohols, ethers acetates, and amines (291; X = OH, OR, OAc, NHR). In most cases regioisomer (291b) was the main product [770].


290 291a 291b

The oxidation of PPh_3 by *trans*-$[Ru(L)(O)_2]^{2+}$ in MeCN is first order in both reactants [771]. The kinetics of chromic acid oxidation of phenylphosphinic acid indicate the formation of an anhydride between $HCrO_4^-$ and phenylphosphinic acid. The data are not sufficient to decide whether phosphinic acid reacts in its "active" $PhP(OH)_2$ form or in its "inactive" PhPH(O)OH form [772]. A novel pentaphosphorus cage compound $P_5C_5(t\text{-}Bu)_5$ (292) has been prepared by oxidation of a mixture of the lithium salts of 1,2,4-triphosphacyclopentadienyl and 1,3-diphosphacyclopentadienyl with $FeCl_3$ or $CoBr_2$ [773].



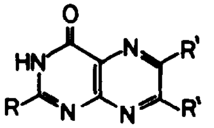
292

The kinetics of the oxidation of substituted phenyl methyl sulfides by vanadium(V) indicated in some cases the enhancement of resonance by steric effects [774].

The kinetics of oxidation of MeSPh by Cr(VI) in aqueous acetic acid have been investigated. The reaction is accelerated by oxalic acid; this is explained by considering the rate-determining formation of a ternary complex of oxalic acid, chromium(VI), and MeSPh [775]. The kinetics of the oxidation of several organic sulfides (aryl methyl, alkyl phenyl, dialkyl, and diphenyl) with pyridinium fluorochromate to the corresponding sulfoxides have been determined. The reaction was found to be first order with respect to the sulfide and the oxidant [776]. Reaction mechanism was proposed for the oxidation of thioglycolic acid by chromate [777]. Mercapto carboxylic acids (mercaptoacetic acid and cysteine) were oxidized to the corresponding disulfides by the diperoxochromium(IV) derivative of diethylenetriamine with a stoichiometry of RSO : Cr(IV) 5:1. The reaction was dramatically catalyzed by dissolved iron [778]. Gutathion has been oxidized by chromium(VI) in neutral aqueous solution and a chromium(III) complex of the oxidized glutathion has been isolated [779]. The mechanism of glutathione oxidation by chromate was investigated by ESR spectroscopy. Evidence was found for the involvement of the glutathione radical and a Cr(V)-glutathione intermediate [780]. Oxidation of DMSO by Cr(VI) in aqueous acetic acid in the presence of $HClO_4$ is first order in oxidant and substrate, and second order in H^+. Chloride ions inhibit the reaction [781]. Dimethyl sulfoxide is oxidized to dimethyl sulfone by chromic acid in aqueous acid medium. The reaction is first order each in oxidant and substrate. Added Mn(II) retards the reaction; this effect is eliminated by 1,10-phenanthroline [782].

Stoichiometric oxidation of several substituted phenyl methyl sulfides to sulfoxides was performed at -15°C with $MnO(O_2)_2(HMPA)$ in 1,2-dichloroethane in the absence and in the presence of $Hg(OOCCF_3)_2$. The rate of oxidation was significantly enhanced by the Hg^{2+} ion; this effect is probably an electrophilic catalysis taking place in the transition state of the O-transfer process [783]. The anionic Mo peroxo complexes $(Bu_4N)[MoO(O_2)_2L]$ (HL = picolinic acid or its N-oxide) were tested in nonpolar organic solvents as oxidants for the oxidation of thio ethers or alcohols [784].

The kinetics of the oxidation of several alkyl and aryl sulfides by MnO_4^- to yield sulfoxides were studied. A mechanism involving a one-step electrophilic oxygen transfer from MnO_4^- to the sulfide was proposed [785]. The kinetics of the oxidation of thiourea by MnO_4^- were studied by the stopped-flow technique. The reaction was found to be first order in both MnO_4^- and Mn^{2+} and thus showed autocatalytic behavior [786]. Oxidation of 2-thiolumazines (293; R = SH; R' = H,Me,Ph) by $KMnO_4$ in basic media led to the formation of the corresponding sulfonates (R = SO_3K) [787].


293

The kinetics of the anaerobic oxidation of cysteine to cystine by Fe(III) have been determined by a stopped-flow high-speed spectrophotometric method. Reproducible data were only obtained between pH 8.6 and 11.6 [788]. The kinetics of oxidation of thiourea by $Fe(ClO_4)_3$ were studied in the presence of bipyridine. The reaction was first order both in substrate and oxidant and was found to be inhibited by MeOH [789].

Kinetic and mechanistic studies of the oxidation of olefins, sulfides, and sulfoxides by $[Ru(IV)(bpy)_2(O)(PR_3)](ClO_4)_2$ (R = Et,Ph) complexes have been conducted in both methylene chloride and acetonitrile. On the basis of labeling experiments and kinetic evidence a mechanism was proposed involving a two-electron, oxygen atom insertion into the substrate. An [(oxidized substrate)Ru(III)] complex has been isolated and characterized in the case of styrene oxidation [790].

2-Mercaptoethanol is oxidized by Co(II)-tetrasulfophthalocyanine to 2-hydroxyethyl disulfide. The kinetics of the reaction were investigated [791]. The Pd-peroxo and Co-superoxo complexes $Pd(PPh_3)_2O_2$ and $Co(salpr)O_2$ oxidize sulfides and epoxidize olefins in the presence of acyl halides or anhydrides. Metal-oxo complexes seem to be the ultimate species mediating these oxidations [792]. Thiophene is oxidized by Pd(II) aquachloro complexes in aqueous solution to thienol. A kinetic study indicated a π-thiophene-Pd(II) complex as intermediate [793]. A kinetic study of the oxidation of thiophene by Pd(II) salts in aqueous solution in the presence of chloride ions has been carried out. The activity of Pd species decreased in the order $Pd^{2+} > PdCl^+ > PdCl_2 >> PdCl_3^-$ [794].

The oxidation of 2,2'-bithiophene by copper(II) trifluoromethanesulfonate in MeCN yielded an electroconductive polythiophene triflate $[(-C_4H_2S-)(CF_3SO_3)_{0.2}]_n$ [795]. The kinetics of oxidation of DMSO by diperiodatocuprate(III) in an aqueous alkaline medium have been studied. The reaction was first order with respect to both substrate and oxidant and was strongly accelerated by traces of Os(VIII) [796].

Oxidation of perfluoro olefins with $KMnO_4$ in absolute acetone yields α-hydroxy ketones [797]. Oxidation of phenacyl halides by vanadium(V) is first order each in oxidant and substrate. The reactions are acid-catalyzed [798].
See also [442,655].

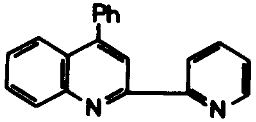
7. Electrooxidation and Photooxidation

Ceric methanesulfonate in aqueous methanesulfonic acid is an excellent mediator for the electrooxidation of alkyl aromatics and polycyclic aromatics to aldehydes, ketones, and quinones. The properties of this medium are ideal for electrochemical regeneration, giving current efficiences up to 89% [799].

The cationic Nb(V) species $[Nb(\eta^5-Me_3SiC_5H_4)_2I_2]^+$ was shown to be an effective catalyst for the electrochemical oxidation of PPh_3 to $OPPh_3$ in the presence of water [800].

Oxidation of 2,6-di-*tert*-butylphenol by O_2 using a poly (pyrrole-manganese-porphyrin) coated electrode as catalyst was described. The catalyst was reactivated by controlled-potential electrolysis [801]. Electrocatalytic epoxidation of *cis*-4-cyclohexene-1,2-dicarboxylic acid has been studied in the presence of Mn tetrakis(N-methyl-4-pyridyl)porphine. A mechanism was proposed [802].

Indirect electrooxidation using RuO_4 and chloride ion as recycling mediators has been reported for the oxidation of dissopropylidene-D-glucose to the corresponding ulose [803]. Olefins and ketones were oxidized electrocatalytically using the system $Ru(H_2O)(bpy)(trpy)^{2+}$ as catalyst. Cyclohexene was oxidized selectively to cyclohexenone, isosafrole to piperonal, acetophenone and deoxybenzoin to benzoic acid [804]. High-valent ruthenium-oxo complexes $[Ru^{VI}(Hdmg)_2(H_2O)(O)]^{2+}$ and $[Ru^{VII}(H_2dmg)_2(OH)(O)]^{4+}$ act as catalysts in the electrocatalytic epoxidation of cyclohexene and cyclooctene to the corresponding epoxides [805]. Two Ru complexes containing the ligand (L = 294), $[Ru(trpy)(L)(H_2O)]^{2+}$ and $[Ru(bpy)(L)(py)(H_2O)]^{2+}$ were prepared and found to be catalytically active for the electrochemical oxidation of secondary alcohols to ketones and allylic or benzylic primary alcohols to aldehydes. No further oxidation to carboxylic acids occurred [806].



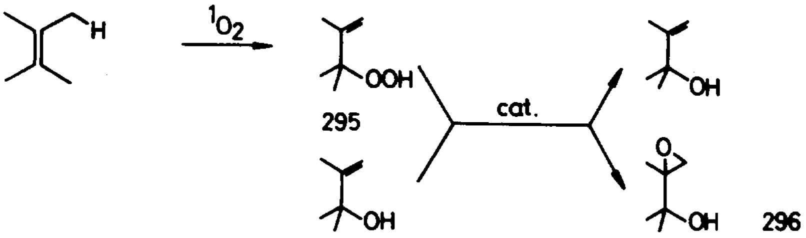
294

Electrooxidation of ascorbic acid on Pt-Nafion in the presence of Fe^{3+} as mediator has been studied. It was shown that the reaction between Fe^{3+} and ascorbic acid took place within a very narrow zone close to the surface [807].

Oxidation of *p*-xylene to terephthalic acid and toluene to benzoic acid with O_2 was carried out using electrochemically generated Co(III) acetate as catalyst. KBr was used as activator [808]. Cobalamine (vitamin B12) and Co phthalocyanine immobilized on graphite electrodes were used for the electrocatalytic oxidation of cysteine [809].

In the electrocatalytic oxidation of benzene with O_2 using a Cu(I)/Cu(II) redox couple as mediator, hydroquinone was obtained with a current efficiency of about 40%. Electrolysis with continuous extraction of the oxidation products yielded *p*-benzoquinone with a current efficiency of 50% [810].

Photooxygenation of alkenes in the presence of $Ti(OR)_4$ (R = iPr,tBu) catalysts was found to be a convenient and efficient "one pot" synthesis of epoxy alcohols. First, singlet oxygen transforms the olefin into its allylic hydroperoxide (295) which is subsequently converted via Ti-catalyzed intermolecular oxygen transfer into its epoxy alcohol (296) (cf. the Sharpless-epoxidation). $VO(acac)_2$ and $MoO_2(acac)_2$ could also be used as catalysts in this reaction [811].



Isobutylene was oxidized photocatalytically with O_2 on SiO_2-supported Mo, W, and Re ions as catalysts. Acetone was the only product [812]. Primary and secondary, saturated and unsaturated alcohols were photocatalytically oxidized to the corresponding aldehydes and ketones in the presence of heteropolytungstates with near UV and visible light. There was no sign of decomposition of the catalysts after 20 photocatalytic cycles [813]. The polyoxotungstate $[n\text{-}Bu_4N]_4[W_{10}O_{32}]$ has been found to be an efficient and selective initiator of hydrocarbon autoxidation. In a typical reaction at 21°C under air, isobutane gave ca. 100% yield of tBuOOH based on consumed isobutane after irradiation (λ > 300 nm) [814]. The polyoxometalates $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ and $[W_{10}O_{32}]^{4-}$ activated by near UV or blue light oxidize alkanes, alkenes, alcohols, ketones, and N-alkylacetamides at comparable rates. Functionalization of groups remote from the usually activating carbonyl group can also be accomplished [815].

The quantum yields in the photochemical hydroxylation of benzoic acid by H_2O_2 are increased by the addition of $FeCl_3$. It has been proposed that benzoic acid acts as a sensitizer in the reduction of Fe(III) to Fe(II) and the latter catalyzes hydroxylation by H_2O_2 (Fenton's reagent) [816]. The reaction could be effectively sensitized by methylene blue [817]. A novel photooxidation of hydrocarbons (adamantane, cyclohexane, cyclododecane) into a mixture of the corresponding alcohols and ketones sensitized by N,N'-dimethyl-2,7-diazapyrenium dication in the presence of Fe^{3+} as catalyst has been described [818]. Photochemical oxidation of hexane to hexanol and hexanone, and of cyclohexene to cyclohexene oxide, 2-cyclohexen-1-ol and 2-cyclohexen-1-one by O_2 using $(F_{20}TPP)Fe$ or (TPP)Mn catalysts together with Sn(IV)- or Sb(V)-porphyrins as photosensitizers has been described [819]. The mechanism of photooxidation of cyclohexene by an aqueous UO_2^{2+}-polymolybdate system was studied. The photoactive species was the excited UO_2^{2+} ion [820].

V. REVIEWS

Homogeneous catalysis by transition-metal complexes. 348 refs. [821].

Heterogenization of homogeneous catalysts on ion exchangers. 40 refs. [822].

Catalysts of organic polymer-bound Pd and Rh complexes. 42 refs. [823].

Transition metal templates as catalysts for selective organic transformations. 90 refs. [824].

Synthesis of alcohols from synthesis gas. 78 refs. [825].

Synthesis of acetaldehyde from synthesis gas. 47 refs. [826].

Synthesis of ethylene glycol. 48 refs. [827].

Production of ethylene glycol by hydroformylation of formaldehyde. [828].

Chemistry of C_1 compounds. X. Use of carbon monoxide in organic synthesis. 19 refs. [829].

Hydroformylation of higher olefins. Raw-material problems and use of products. 22 refs. [830].

The Ruhrchemie/Rhone-Poulenc (RCH/RP) process - latest variant of the fifty-year-old hydroformylation reaction. 10 refs. [831].

The use of dinuclear templates to perform the hydroformylation reaction. [832].

Industrially relevant homogeneous catalysis utilizing platinum group metal complexes. 12 refs. [833].

Chemistry of Co-Ru mixed metal complexes: carbonylation and metalloselective substitution reactions (homologation, hydroformylation). 15 refs. [834].

Homogeneous catalysis of organic reactions by complexes of metal ions. Reactions involving CO, hydroformylation, hydrocarboxylation. 182 refs. [835].

Studies in chemical and electrochemical coal conversion: final technical report, August 1, 1984 - July 31, 1987 (hydroformylation, water gas shift reaction) [836].

Homogeneous catalysis by ruthenium carbonyl clusters. 136 refs. [837].

Metal cluster compounds. Part 3. Chemistry and importance; homogeneous and heterogeneous catalysis. 166 refs. [838].

Homogeneous catalysis in Germany: past and present (carbonylation, oxidation). 6 refs. [839].

Reduction of CO_2 with platinum metals electrocatalysts. 25 refs. [840].

The homogeneous activation of C-H bonds by high valent early d-block, lanthanide, and actinide metal systems. 128 refs. [841].

Alkane activation processes by cyclopentadienyl complexes of Rh, Ir, and related species. 61 refs. [842].

Homogeneous catalysis. Part 1. Carbon-hydrogen activation with carbenoid chelate complexes. 67 refs. [843].

Cobaloximes as catalysts. 54 refs. [844].

Structure and reactivity of Rh(II) complexes (hydrogenation catalysts). 41 refs. [845].

Transition metal catalyzed reductions of organic molecules by molecular hydrogen and hydrides, an overview. 51 refs. [846].

Catalytic applications of transition-metal complexes with sulfide ligands (hydrogenations and redox reactions). 93 refs. [847].

Synthetic applications of enantioselective organotransition-metal-mediated reactions (asymmetric hydrogenation and hydrosilylation). 107 refs. [848].

Asymmetric hydrogenation of β-keto carboxylic esters. A practical, purely chemical access to β-hydroxy esters in high enantiomeric purity. 2 refs. [849].

Chemical multiplication of chirality: science and applications (asymmetric hydrogenation). 40 refs. [850].

Asymmetric homogeneous catalysis. 24 refs. [851].

Enantioselective hydrogenation of allylic and homoallylic alcohols. 13 refs. [852].

Catalytic hydrogenation by hydrogen transfer. 38 refs. [853].

Transfer hydrogenation reactions catalyzed by transition metal complexes. 163 refs. [854].

Reactions of hydrocarbons with transition metal polyhydride complexes (hydrogenations, dehydrogenations). 87 refs. [855].

Some recent advances in alkane functionalization: metal phosphine catalysts and mercury photosensitization (homogeneous dehydrogenation). 33 refs. [856].

Uses of low-valent titanium reagents in organic synthesis. 196 refs. [857].

Oxidation and reduction. 478 refs. [858].

Alkane oxidation studies in Du Pont's Central Research Department. 54 refs. [859].

Metal-catalyzed oxidations of unsaturated hydrocarbons by molecular oxygen: the use of multi-step catalysis. 30 refs. [860].

Liquid-phase oxidation of aromatic compounds in the presence of metal bromide catalysts. 16 refs. [861].

Studies on homogeneous catalysis in oxidation. 20 refs. [862].

Modern concepts of the mechanism of epoxidation of olefins. 388 refs. [863].

Transition-metal-catalyzed epoxidations. 364 refs. [864].

Kinetics and mechanism of hydroperoxide epoxidation of olefins on polymeric catalysts. 10 refs. [865].

Homogeneous catalysts for epoxidation by hydroperoxides. 59 refs. [866].

Catalytic asymmetric epoxidation and kinetic resolution: modified procedure including *in situ* derivatization. 2 refs. [867].

Iron redox reactions and lipid peroxidation. 14 refs. [868].

Shape-selective oxidation of hydrocarbons. 71 refs. [869].

Oxygenation of hydrocarbons by porphyrin complexes. 183 refs. [870].

Metalloporphyrin catalysis of the nonchain oxidation of olefins. 37 refs. [871].

Are intermediates with metal-carbon bond involved in the oxygenation reactions catalyzed by metalloporphyrins? 67 refs. [872].

Role of Co(II) porphyrin in autoxidation processes. 11 refs. [873].

Recent applications of oxochromium amine complexes as oxidants in organic synthesis. 80 refs. [874].

12-Heteropoly acids as catalysts in acid-base and oxidation reactions. 74 refs. [875].

Ruthenium and osmium oxo complexes as organic oxidants. 31 refs. [876].

Transition metal complexes of nitrogen oxides (catalytic oxidations). 48 refs. [877].

Transition metal dioxygen complexes as intermediates in homogeneous catalytic oxidations. 130 refs. [878].

Copper-dioxygen chemistry: a bioinorganic challenge. 53 refs. [879].

List of Abbreviations

acac	acetylacetonate

AS	Annual Survey on Hydroformylation, Reduction and Oxidation
BDPP	see Fig. 41
BINAP	see Fig. 69
Boc	*tert*-butoxycarbonyl, $-COOBu^t$
BPPM	see Fig. 52
bpy	2,2'-bipyridine
Br_8TPP	*meso*-tetrakis(2,6-dibromophenyl)porphinato
chiraphos	see Fig. 78
Cl_8TPP	*meso*-tetrakis(2,6-dichlorophenyl)porphinato
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl, η^5-C_5H_5
Cp^*	pentamethylcyclopentadienyl, η^5-C_5Me_5
Cy	cyclohexyl
cyclobutanediop	see Fig. 41
dba	dibenzylideneacetone
DIOP	see Fig. 80
DME	1,2-dimethoxyethane
dmgH	dimethylglyoxime
dppb	1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
dppm	bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$
dppp	1,3-bis(diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$
ee	enantiomeric excess
F_8TPP	*meso*-tetrakis(2,6-difluorophenyl)porphinato
$F_{20}TPP$	*meso*-tetrakis(pentafluorophenyl)porphinato
HMPA	hexamethylphosphoric triamide
$Me_{12}TPP$	see TMP
NBD	norbornadiene
o.y.	optical yield
phen	1,10-phenathroline
PMB	*p*-methoxybenzyl
prophos	see Fig. 79
py	pyridine
RT	room temperature
salen	N,N'-bis(salicylidene)-ethylenediaminato
St	stearate, $nC_{17}H_{35}COO-$
TMP	*meso*-tetramesitylporphinato
TPP	*meso*-tetraphenylporphinato

triphos	$MeC(CH_2PPh_2)_3$
trpy	2,2':6'2"-terpyridine

Metal index

Ti	154, 211, 260, 288, 289, 300-307, 331, 501-512, 560, 608-611, 617, 618, 621-625, 811, 857
Zr	116, 211, 261, 301, 560
V	242, 308, 401, 412-414, 422, 423, 454, 494, 513, 514, 560, 566, 585, 615, 616, 620, 682-688, 737, 774, 798, 811
Nb	800
Cr	48, 85, 290, 291, 307, 323, 346, 347, 349, 372, 373, 439, 455-458, 482, 515, 540, 542, 561, 562, 566, 585, 629-634, 668, 669, 679, 689-705, 738-744, 772, 775-782, 874
Mo	4, 5, 85, 104, 155, 186, 212, 238, 242, 309, 312, 313, 342-344, 374, 395, 396, 413, 414, 450, 459-461, 494, 516-527, 560, 563, 564, 605, 670-672, 744, 784, 811, 812, 820
W	85, 101, 243, 312, 313, 460-465, 527-529, 589, 590, 635, 812-815
Mn	66, 276, 307, 345-347, 350-352, 372, 373, 375, 381, 388, 400, 403, 420, 424-426, 452, 453, 466-471, 530-544, 591-593, 596, 636-651, 660, 664, 706-713, 736, 745-753, 782, 783, 785, 797, 801, 802, 819
Tc	606
Re	12, 150, 156, 213, 244, 310, 812
Fe	4, 7, 8, 19-24, 43, 61-63, 73, 86, 87, 102-104, 120, 143, 144, 183, 187, 209, 210, 238, 262, 274, 276, 280, 290, 292-295, 307, 311-313, 324, 341, 342, 346-348, 353, 372, 373, 376, 382, 383, 397, 403, 427-430, 441, 443, 472-480, 538-551, 565, 566, 571, 573, 574, 594-596, 612, 619, 652, 714-720, 754-761, 773, 778, 788, 789, 807, 816-819, 868
Ru	6, 13, 14, 24, 25, 38, 43, 50, 51, 56, 58, 65, 70, 77, 78, 85, 96, 105-108, 121-125, 157-159, 188-190, 215-219, 232, 239, 241, 245, 246, 255, 258, 263, 264, 279, 281, 296, 314, 315, 354, 377-380 398, 419, 431, 442, 481-488, 507, 552-555, 567-578, 597, 598, 607, 613, 653, 654, 673, 685, 721, 722, 762, 771, 790, 803-806, 834, 837, 876
Os	9, 10, 108, 117, 126, 191, 220, 255, 489-493, 598, 599,

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