TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

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I. Theoretical Calculations

Theoretical calculations showed that the 1,2-hydride shift reaction:

$$HMn(CO)_5 \longrightarrow (CO)_4Mn\text{-}C(O)H$$

is considerably more endothermic than the 1,2-methyl shift reaction:

$$CH_3Mn(CO)_5 \longrightarrow (CO)_4Mn\text{-}C(O)CH_3$$

This explains the apparent inability of hydride to migrate toward CO [1]. Quantum chemical calculations were performed on the oxidative addition of pentane onto $HPt(PPh_3)X$ (X = Cl,Br,I) complexes [2]. An extended Hückel MO analysis of H-H and C-H activation reactions by d^o ML_n species, such as Cp_2LuR was reported. For the systems considered a mechanism involving a transition state with an electron-deficient coordination mode was found to be reasonable [3]. A semiempirical study of oxygen transfer from oxo porphyrins to ethene was performed, based on EHT calculations augmented by VB analysis of the resultant wave functions [4]. The concerted [3+2] cycloaddition of an olefin to the oxygen ligands in OsO_4 - which is the first step in the oxidation of olefins to vicinal diols - has been analyzed from the frontier orbital point of view [5].

II. Hydroformylation and Related Reactions of CO

1. Hydrogenation of CO to Hydrocarbons and to Oxygen- or Nitrogen-containing Organic Compounds

Hydrogenation of CO to hydrocarbons was studied with Co(I) catalysts at 200-250°C in solution or supported on alumina silicates. The Co(I) catalysts were either prepared *in situ* from Co(II) trifluoroacetate or the complex CpCo(COD) was used. At low pressures significant amounts of olefins were formed [6]. Ruthenium(III) ions were incorporated into sulfonated linear polystyrene through an ion-exchange process and the reactions of these Ru(III) ions with CO and H_2 were studied. H/D Exchange was observed between O_2 and the benzene rings of the polystyrene backbone. Carbon monoxide and hydrogen reacted at 150° to give various aliphatic hydrocarbons and oxygen-containing compounds [7].

Benzene solutions of $[Rh(OEP)]_2$ in the presence of H_2 and CO catalytically produce formaldehyde and methanol when irradiated with 300 nm light. Formation of CH_2O probably occurs by the reaction between HRh(DEP) and HCORh(DEP) (formed in a thermal equilibrium) initiated by the homolytic cleavage of the Rh,C bond [8].

The formation of ethylene glycol and ethanol from synthesis gas in the presence of Ru carbonyl catalysts (240°C, 500 bar) is promoted by ammonium, phosphonium, and iminium halides. Highest activity for ethylene glycol formation was observed with $(Ph_3P)_2NCl$. The electron-accepting ability of the solvent had also a significant effect; solvents with acceptor numbers between 12 and 15 gave the best results [9]. The formation of ethylene glycol (and methanol) in N-methylpyrrolidone as solvent was markedly increased also by the addition of a large excess of imidazole compounds, especially benzimidazole [10]. Probably the amine is converted to an ammonium ion and acts as the cation of the catalytically active anionic Ru species [11]. Conversion of synthesis gas into C_2 oxygenated products was studied with 10:1 Ru:Rh mixed metal catalyst systems in AcOH as solvent. The Rh component mainly contributed to the activity of the catalyst and the Ru component enhanced its stability [12].

The effect of pressure on the conversion of CO + H_2 with Co and Rh catalysts to ethylene glycol was studied. In both cases the selectivity to ethylene glycol increased with H_2 partial pressure but was practically independent of CO partial pressure [13].

Different proposals for the mechanism of the formation of C_2 oxygenates from synthesis gas over oxide-supported Rh were presented in two polemic papers [14,15]. The synthesis of ethylene glycol from synthesis gas using a $Rh_4(CO)_{12}$ + N-methyl-2-pyrrolidone system as catalyst could be significantly accelerated by increasing the temperature. At 300°C and 2000 bar the turnover frequency for ethylene glycol was about 2000 h^{-1} with 70% selectivity. The reaction mixture was colorless [16]. In the hydrogenation of CO to ethylene glycol catalyzed by Rh-phosphine complexes (220-240°C, 500 bar) the selectivity of the reaction and the stability of the catalyst were found to be strongly dependent on the structure of the phosphine ligands. Best results were obtained with bulky alkylphosphines like PPr^i_3 [17,18] while arylphosphines and all types of phosphites led to the formation of the phosphidocarbonyl cluster anion $[Rh_9P(CO)_{21}]^{2-}$ and hence inhibited catalysis [18]. Rhodium complexes formed in situ from $Rh(CO)_2(acac)$ and a large excess of tri-n-alkylphosphines (10-40 moles/mole Rh) showed in addition significant catalytic activity in the hydrogenation of aldehydes to alcohols (at 80°C). 1,2-Dimethyl-2-imidazolidinone or tetraglyme were used as solvents [19]. By monitoring infrared spectra and conductivities it was observed that the yield of ethylene glycol from synthesis gas at 200°C and 200 bar increased with increasing concentration of $[Rh(CO)_4]^-$ in the reaction mixture. The tetracarbonylrhodate anion was, however, catalytically only active if a tertiary ammonium cation was also present; this probably acted as a proton donor [20].

The effect of tertiary phosphines on the hydrogenation of CO catalyzed by Ir carbonyl catalysts (250-270°C, 650-750 bar) has been investigated. Triarylphosphines such as PPh_3 enhanced the activity and selectivity for ethylene glycol formation, whereas trialkylphosphines mostly promoted methanol formation. The complex $Ir_2(CO)_6(PPh_3)_2$ was isolated from the reaction mixture and was found to have a high catalytic activity for ethylene glycol [21]. The clusters $[PtRh_5(CO)_{15}]^-$, $[Rh_5(CO)_{15}]^-$, and $[PtRh_4(CO)_{12}]^{2-}$ were used as catalysts for CO hydrogenation at 230°C and 1400-2000 bar. The results were compared with those obtained with catalysts composed of $Rh(acac)(CO)_2$ and $Pt(acac)_2$. Ethylene glycol was in most cases the favored product but Pt increased MeOH formation. The results suggest that Pt acts in the form of a mixed Pt-Rh cluster [22].

Both $RuO_2.xH_2O$ and $Ru_3(CO)_{12}$ have been found to be effective catalyst precursors for the conversion of CO + H_2 + NH_3 mixtures to N-methylformamides and Me_3N at 230°C and 340 bar. Probably formaldehyde is the primary reaction product. Water formed in the reaction participates in a water-gas shift reaction and subsequently leads to ammonium carbamate as byproduct. Rhodium, iridium and osmium carbonyls also showed some catalytic activity [23,24].

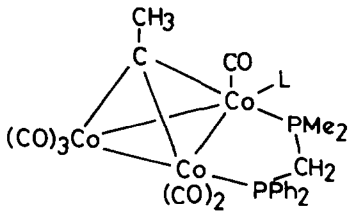
See also [201].

2. Hydroformylation

a) Co Catalysts

Capillary GC and GC-MS analysis of the alcohol mixture obtained by hydroformylation of C_{10-13} n-alkenes showed that all 24 alcohols that could be formed were present [25]. The rate of hydroformylation of propene using Co 2-ethylhexanoate as catalyst was decreased by py, $(iBu)_3N$ and $BuNH_2$; the inhibiting effect of these amines increased in the stated order. The same effect of the amines was noted on the rate of $HCo(CO)_4$ formation [26]. Cobalt 2-ethylhexanoate was found to be a more suitable catalyst for the hydroformylation of propene than Co dodecanoate because the regeneration of 2-ethylhexanoic acid was simpler than that of dodecanoic acid [27].

Hydroxycitronellol was prepared from 2,6-dimethyl-6-hydroxy--1-heptene by hydroformylation in the presence of a Co/phosphine catalyst [28]. The use of $Bu_2P(CH_2)_2SiMe(OMe)(CH_2)_2PBu_2$ as ligand in the hydroformylation of propene with Co carbonyl catalyst resulted in 97% selectivity for straight-chain products [29]. The aminophosphine-containing Co carbonyl complexes $[Co(CO)_3(Ph_2PCH_2CH_2NMe_3)_2](PF_6)_2$ and $[Co(CO)_3(Ph_2PCH_2CH_2NMe_2)]_2$ were tested as catalysts for the hydroformylation of 1-hexene. The ionic complex could be used also in an aqueous-organic solvent two-phase system but the activity of both catalysts was rather low [30]. The chiral cluster (1, L = (R)-(+)-PMePh(*o*-anisyl)) has been prepared and used as catalyst for the hydroformylation of styrene at 89°C and 80 bar CO + H_2. Under such conditions decoordination of the ligand L was observed and cluster (2) was obtained. No optical induction was reported [31].



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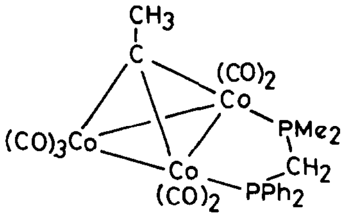

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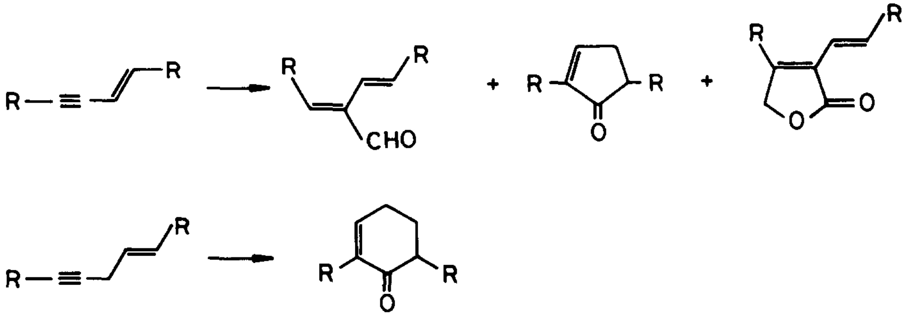
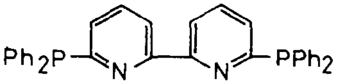
See also [43,45].

b) Rh Catalysts

The reaction of enynes with CO and H_2 in the presence of $Rh_4(CO)_{12}$ as catalyst at 100°C and 200 bar gave formyl dienes, cyclopentenones and unsaturated lactones [32] (R=Ph or *p*-substituted Ph):



Chemical oscillation was observed in the hydroformylation of propene with a Rh-phosphine catalyst. The most important requirement for oscillation to occur was the presence of a certain amount of butyraldehyde trimer in the liquid reaction mixture [33]. Hydroformylation of allyl alcohol with Rh-PPh_3 catalysts is accompanied by several side reactions and a rapid deterioration of catalyst activity. Using bidentate phosphines as promoters the formation of Ph_3PO and phosphonium compounds could be diminished [34]. Hydroformylation of $CH_2=CHCH_2OBu^t$ with a Rh carbonyl-PPh_3 catalyst followed by hydrogenation of the aldehydes and ether cleavage gave $HO(CH_2)_4OH$ in 75% overall yield [35]. Stoichiometric hydroformylation of 1-hexene with $HRh(CO)[(P(OPh)_3]_3$ has been studied using ^{31}P NMR. The CO-free complex $HRh[P(OPh)_3]_4$ was formed which could be converted back to the monocarbonyl by admitting CO to the reaction mixture [36]. Hydroformylation of 1-hexene was examined at 1-11 bar and 40°C with $Rh(acac)[P(OPh)_3]_2$ + $P(OPh)_3$ as catalyst. Very high n/i ratios were obtained at 1 bar; pressure increase caused a systematic drop of this ratio. IR examination of the reaction mixture suggested that $HRh(CO)[P(OPh)_3]_3$ was the active form of the catalyst [37]. The large ring binuclear Rh complexes $[Rh_2(\mu\text{-}L)_2(COD)_2]^{2+}$ and $[Rh_2(\mu\text{-}L)_2(CO)_4]^{2+}$ (L = 3) were prepared and used as catalysts for the hydroformylation of 1-hexene [38].



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Addition of tBuSH to $HRh(CO)(PPh_3)_3$ slightly increased its catalytic activity for hydroformylation of 1-hexene at 80°C and 5 bar. IR and NMR spectra showed the formation of the dinuclear complex $[Rh(\mu\text{-}SBu^t)(CO)(PPh_3)]_2$. The two Rh complexes probably act as catalysts by independent pathways [39]. Several substituted allylbenzenes were hydroformylated using the dinuclear Rh complexes $[Rh(\mu\text{-}SBu^t)(CO)L]_2$ (L = PPh_3, $P(OMe)_3$, $P(OPh)_3$) as catalysts. High yields of linear aldehydes were obtained at 80°C [40]. Low pressure catalytic hydroformylation of 1-hexene was performed using $[Rh(\mu\text{-}SBu^t)(CO)_2]_2$ and stoichiometric amounts of various diphosphines including $Cp_2Zr(CH_2PPh_2)_2$. The latter ligand furnished the most active catalyst system [41].

Nitrogen-containing cyclic olefins (N-substituted nortropidines and N-methyl-1,2,3,6-tetrahydropyridine) were hydroformylated with Rh + PR_3 catalysts prepared in situ. Regio- and chemoselectivity of the reaction was practically independent of the phosphine in the case of nortropidines; with the less basic tetrahydropyridine the selectivities were influenced by the phosphine ligand and by the presence of added bases such as Et_3N [42].

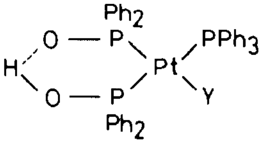
See also [106].

c) Other Metals as Catalysts

Hydroformylation of 1-hexene was investigated with the bimetallic catalyst $Cr(CO)_5(PBu_3)$ + $HCo(CO)_3(PBu_3)$. Linear alcohol production was most efficient if the Cr/Co ratio ranged between 50:1 and 100:1 [43].

Hydroformylation of ethene and propene is catalyzed by the Ru(O) complexes $Ru(CO)_3(PPh_3)_2$, $Ru(CO)_4(PPh_3)$ and $Ru_3(CO)_{12}$ under UV irradiation at ambient temperature and pressure. Hydrogenation of aldehydes and olefins was also observed under these conditions [44]. The $Co_2(CO)_8$ + $Ru_3(CO)_{12}$ bimetallic system showed an increased catalytic activity for the hydroformylation of olefins, compared with $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ alone. Alcohols were the best solvents for these mixed-metal catalysts. It was proposed that the synergistic effect might be explained by the high reactivity of $[HRu(CO)_4]^-$ against cobalt acyl complexes [45].

The platinum complex (4, Y=H) was found to catalyze the hydroformylation of heptene-1 and heptene-2 to give products of high linearity (90 and 60%, respectively). Along with C_8 aldehydes also C_8 alcohols and heptane were formed in comparable amounts. If ethene was used as substrate, the alkyl and acyl complexes (4,Y = Et) and (4,Y = EtCO) could be isolated. Catalysts formed in situ from $Pt(COD)_2$, Ph_2POH and a tertiary phosphine were also active and in the absence of a tertiary phosphine ethene produced mainly 3-pentanone under hydroformylation conditions [46].



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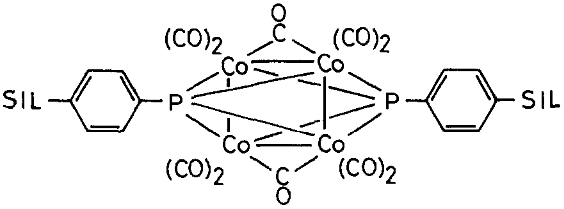
See also [187].

d) Heterogeneous Systems (Supported Complexes)

The supported tetranuclear Co-P cluster (5) was prepared and used as catalyst for the hydroformylation of olefins at 110-150°C and 20-60 bar. The activity of the catalyst did not decrease during repeated use (up to 10 times) [47].



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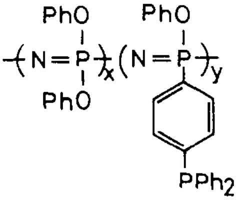
Phosphine-bearing polyphosphazenes (6) and (7) were used as carriers for cobalt hydroformylation catalysts. Both systems were transformed under the reaction conditions into soluble complexes which behaved like the homogeneous analogues $Co_2(CO)_8$ + XPR_2. Formation of HPR_2, benzene, benzyl alcohol and other degradation products was observed [48].



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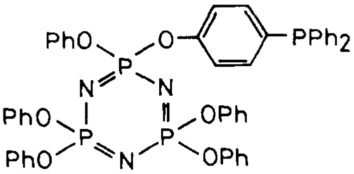

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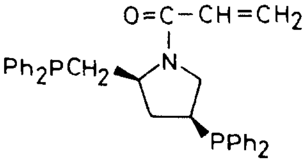
Hydroformylation of dicyclopentadiene was studied using catalyst systems obtained from $Rh_nCo_{4-n}(CO)_{12}$ (n = 0,1,2,4) clusters bonded to tertiary amines or commercially available tertiary amine resins. During the first hours of catalyst life hydroformylation was the slow step but later aldehyde hydrogenation became rate determining [49].

The industrial applicability of $HRh(CO)(PPh_3)_3$ dissolved in liquid PPh_3 and immobilized on a porous support by strong capillary forces, was tested for the hydroformylation of propene. Catalysts based on α-alumina supports were stable for 1500 h [50]. Polymeric aminophosphine ligands were prepared by reacting an amino group-containing divinylbenzene-styrene copolymer with $(Et_2N)_2PCl$. Complexes prepared from $[Rh(CO)_2Cl]_2$ and these ligands were used as catalysts for the hydroformylation of diisobutylene [51]. The catalyst containing the $-CH_2NHCH_2CH_2OH$ group as substituent on the aromatic ring was found to be the most active and selective for aldehyde formation [52]. The catalyst lifetime was studied for Rh-loaded, commercially available amine functionalized resins for the hydroformylation of dicyclopentadiene and the hydrogenation of the aldehyde formed [53]. A series of Rh(I) hydroformylation catalysts has been prepared by reacting $Rh(CO)_2(acac)$ with p-styryldiphenylphosphine-polyropylene copolimers. The supports were prepared by γ-radiation grafting the unsaturated phosphine onto polypropylene in different solvents. The supports prepared in THF showed good selectivities for normal aldehyde formation [54].

The activity of Rh-zeolite X and Y catalysts for hydroformylation was found to depend on their method of preparation. The rate dependence upon the partial pressures of CO, H_2 and propene were similar to that reported for homogeneous hydroformylation [55]. Rhodium zeolite A catalysts containing either surface Rh prepared by ion exchange or intrazeolitic Rh were applied as catalyst for the hydroformylation of hexene-1 in the vapor phase and in the liquid phase. The vapor-phase activity of the two catalysts was similar but in the liquid phase the ion-exchanged catalyst lost Rh more rapidly [56]. In situ Fourier transform IR studies of propene hydroformylation by a RhNaY zeolite catalyst were reported. The reaction proceeded in a homogeneous-like reaction pathway [57].

Polystyrene-divinylbenzene-based polymeric phosphines were used to heterogenize Pt catalysts for hydroformylation of α-olefins in the presence of $SnCl_2$. The catalysts displayed high selectivity (95%) to linear aldehydes [58]. Copolymerization of the phosphine (8) with styrene and divinylbenzene gave a phosphinated polymer which was loaded with $PtCl_2$ and $SnCl_2$. The resulting chiral complex catalyzed the hydroformylation of styrene. The resulting hydrotropaldehyde was of 70-75% enantiomeric purity [59].



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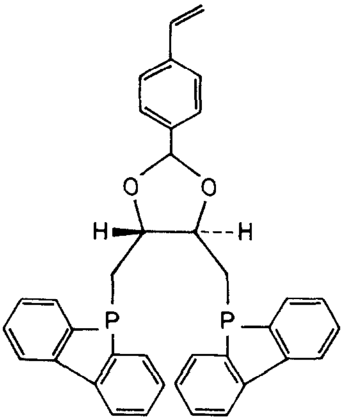
The chiral ligand (9) attached to linear or cross-linked polystyrene was used for asymmetric hydroformylation with Pt + $SnCl_2$ catalyst systems. Optical yields ranged between 0-70% in the case of styrene, vinyl acetate or N-vinylphthalimide as olefins. The catalysts could be reused several times without loss of enantioselectivity but their catalystic activity gradually decreased [60].



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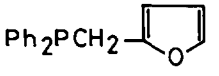
e) Modified Hydroformylations

Polynuclear Co carbonyl complexes containing phosphine ligands (Ph_2PH, Ph_2PR, Ph_3P, Bu_3P, dppe) were used as catalysts for the hydroformylation and consecutive hydrogenation of 1-tetradecene. Selectivity of pentadecanol formation was 31-34% [61].

See also [105].

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

The catalytic activity of $[Ru(CO)_3I_3]^-$ in homologation of MeOH, Me_2O, MeOAc, formates, and alkyl orthoformates was discussed [62]. The selectivity of acetaldehyde formation in the hydrocarbonylation of methanol with CoI_2 as catalyst (150°C, 200 bar CO + H_2) could be improved by adding diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1-6) to the catalyst system. The main species present under the reaction conditions was $[Co(CO)_xP_y][Co(CO)_4]$ (x + y = 5; P = a phosphine moiety) [63]. The influence of several furfurylphosphines and their phosphonium salts, and of furylphosphines on the homologation of methanol to ethanol was investigated using Co as catalyst metal and I_2 as promotor. The best results with respect to selectivity and conversion were obtained with the bidentate ligands (10) and (11) [64].



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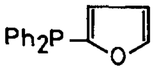

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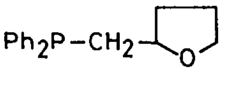
Homologation of MeOH to EtOH using the CoI_2 + $RuI_2(CO)_2(PPh_3)_2$ + NaI catalyst system was found to be second order in MeOH. The complex $[MePh_3P][RuI_3(CO)_3]$ was isolated from the reaction mixture and proved to be an active homologation catalyst also in the absence of cobalt [65]. The influence of (12) and (13) on the homologation of MeOH to EtOH was investigated using $Co(OAc)_2.4H_2O$ + $RuCl_3.3H_2O$ (20:1) as catalyst and I_2 as promoter. The potentially bidentate phosphine (12) gave a much more active catalyst system than the potentially tridentate phosphine (13) [66].



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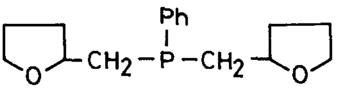

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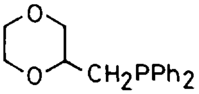
The ligand (14) was tested in the homologation of MeOH with Co + Ru catalyst and MeI promotor. Under optimum conditions selectivity of EtOH formation was about 60% but at high conversions large amounts of Et_2O were formed [67].



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Bifunctional catalysts composed of Co, I and a heterogeneous noble metal (Ru, Rh or Re) were tested for the homologation of MeOH [68]. Homologation of methanol to ethanol with CO + H_2 (200°C, 100 bar) was achieved with a Ru + Rh mixed-metal catalyst system. Neither of the metals alone were active, the most significant synergistic effect was observed at a Ru:Rh ratio of 6:1 [69]. In the homologation of EtOH to PrOH in the presence of Co, Ru and I with CO + $2H_2$ at 200°C and 450 bar, Co and Ru were found to be synergistic [70]. Homologation of benzyl alcohol to 2-phenylethanol could be performed with high selectivity (84-87%) using a $Co_2(CO)_8$ + $RuCl_3$ mixed-metal catalyst system, benzyl bromide as promoter, adding a small amount of water and working at a rather low reaction temperature (120°) [71].

Hydrocarbonylation of 2,2-dimethoxy propane at 170-180°C and 120 bar CO + H_2 using Rh and Co complexes has been studied. Rhodium complexes furnished mainly diethyl ether; with $Co_2(CO)_8$ acetaldehyde dimethyl acetal was the main product. Heavy byproducts were also formed, these consisted mainly of aldolization and crotonization products of acetaldehyde [72]. Hydroformylation of formaldehyde to glycolaldehyde and its hydrogenation to ethylene glycol using Co + Rh mixed-metal catalytic systems has been investigated at 110°C and 100 bar. Highest C_2 selectivities ($\approx$ 65%) were obtained with $CoCl_2.6H_2O$ + $Rh_4(CO)_{12}$ catalysts.Glycolaldehyde was found to be formed only in the first few hours of the reaction; later only hydrogenation of formaldehyde to methanol and of glycolaldehyde to ethylene glycol took place. This effect may be due to the presence of Co^{2+} which maintains the rhodium catalyst for some time in a relatively oxidized state [73]. The use of pyridine or substituted pyridines as solvents greatly enhanced the formation of glycol aldehyde in the hydroformylation of formaldehyde with $Rh(CO)(PPh_3)_2Cl$ as catalyst. Paraformaldehyde was used as substrate and the reaction was run at 70°C and 50 bar CO + H_2 [74]. Straight-chain carbohydrates such as trioses, tetroses, pentoses, and hexoses were obtained in good yields by reacting formaldehyde with CO + H_2 in the presence of $Rh(CO)(PPh_3)_2Cl$ and Et_3N at 120°C and 120 bar. Carbohydrate formation under such conditions was due mainly to an amine-catalyzed condensation of glycol aldehyde formed by the Rh-catalyzed hydroformylation of formaldehyde [75].

The ruthenium-catalyzed homologation of acetic acid to propionic acid with synthesis gas was shown to proceed through the following consecutive reactions: hydrogenation of acetic acid to ethanol (and esterification to ethyl acetate) and carbonylation of the alcohol to propionic acid. Alkyl iodides were also found in the reaction mixtures and probably played a role in the carbonylation process [76].

Reaction of methyl acetate and synthesis gas at 170°C and 330 bar with a catalyst charged as CoI_2 + LiI + NPh_3 (molar ratio 2.5:1.5:1) resulted in the formation of acetaldehyde and acetic acid according to the following stoichiometry:

$$\mathrm{MeCOOMe + H_2 + CO \longrightarrow MeCHO + MeCOOH}$$

Acetaldehyde was obtained in 98% yield; minor amounts of methane and ethyl acetate were the only byproducts [77]. Homologation of methyl acetate with CO + H_2 using rhodium chloride/methyl iodide based catalyst systems under mild conditions (150-160°C, 40-60 bar) was reported. The activity of the catalyst was significantly increased by the addition of phosphine oxides. Predominant reaction under such conditions was the formation of propionic acid:

$$\mathrm{CH_3COOCH_3 + 2CO + 2H_2 \longrightarrow CH_3CH_2COOH + CH_3COOH}$$

In combination with Ru mainly the alcohol moiety was transformed into its next homologue [78]:

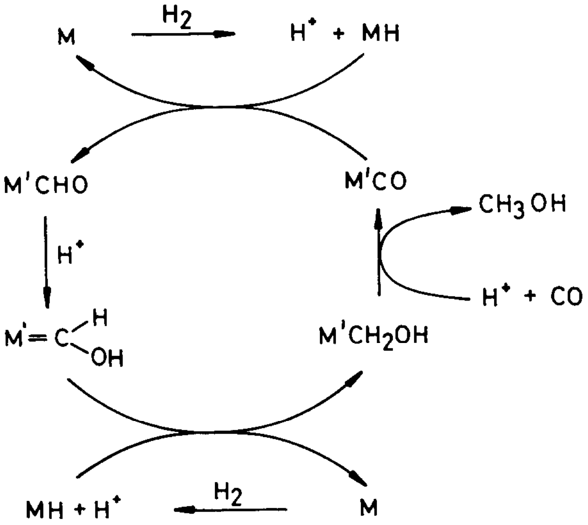
$$\mathrm{2CH_3COOCH_3 + 2CO + 2H_2 \longrightarrow CH_3COOC_2H_5 + 2CH_3COOH}$$

The effect of Lewis acids on the homologation of methyl acetate to ethyl acetate with ruthenium carbonyl iodide catalysts was investigated. Al and Sb derivatives favored the carbonylation steps of the reaction resulting in high (72%) selectivities to acetic acid; Ti derivatives favored carbonylation + hydrogenation increasing ethyl acetate selectivity up to 70% [79]. The homologation of methyl esters with synthesis gas in the presence of iodine-promoted ruthenium catalysts has been examined. The predominant pathway of the reaction depended on the nature of the iodine promoter employed: with LiI the main reaction was the formation of ethyl esters whereas with MeI acyl reduction was the most important process [80]. Homogeneous Co + Ru catalysts were tested for the reductive carbonylation of carboxylic esters in the presence of iodine promoters at 200°C and 420 bar ($2H_2$ + CO). Homologation of the alkoxy moiety was promoted by Ru (especially in the case of ethyl esters), and a combination of ionic iodide with iodide was found to be the most effective [81]. Ruthenium-assisted, Rh-based catalyst systems were found to be superior to the usual Ru-based or Co-based catalysts for the homologation of esters with CO + H_2. Both the alcohol and the carboxylic acid part of the ester could be transformed into its higher homologue [82].

Hydrocarbonylation of lactones catalyzed by Rh and Co complexes at 230°C and 180°C, respectively, and 200 bar has been investigated in the presence of I_2 as promoter. Formation of the homologous lactone was observed only with Co catalysts (14-48% yield), Rh catalysts furnished only mono- and dicarboxylic acids [83].

4. Coordination Chemistry Related to CO Hydrogenation and Hydroformylation

Based on model studies with isolable complexes of Ru and Os it was suggested that the homogeneously catalyzed hydrogenation of CO occurs via successive intermolecular additions of H^- and H^+ to coordinated CO. A catalytic cycle based on these steps is shown on the next page [84]:



A quantitative relationship was found between the effect of bases on the deprotonation of $HCo(CO)_4$ and their inhibiting effect on the hydroformylation reaction [85]. The acylcobalt tetracarbonyls $nPrCOCo(CO)_4$ and $iPrCOCo(CO)_4$ react with H_2 or $HCo(CO)_4$ to yield nPrCHO and iPrCHO, respectively. These reactions are part of the catalytic cycle in the industrially important hydroformylation of propene. The kinetic results support the conclusion that under the conditions of catalytic hydroformylation ($> 100^{\circ}C$ and > 100 bar $CO + H_2$) the reaction with H_2 is mainly responsible for aldehyde formation [86]. The reaction of $HCo(CO)_4$ with ethyl acrylate under CO results under kinetically controlled conditions ($< 10^{\circ}C$) in the branched-chain alkyl Co carbonyl complex; under thermodynamical control ($> 25^{\circ}C$) the alkyl complex is transformed into the straight-chain acyl Co carbonyl. This effect agrees with the known influence of temperature on the distribution of isomeric aldehydes in the catalytic hydroformylation of ethyl acrylate [87].

Triarylphosphines undergo P-C bond scission under hydroformylation conditions ($190^{\circ}C$, 140 bar $CO + H_2$) in the presence of $Co_2(CO)_8$ to give a variety of hydrogenolysis and CO insertion products. Aryl group scrambling is also observed when PR_3 and PR'_3 are subjected to the above conditions. In the presence of an olefin the phosphorous-aryl bond cleavage proceeds at a much slower rate [88]. Formation of clusters was found to be the cause for deactivation of rhodium carbonyl catalysts used in hydroformylation.

Oxygen strongly promoted cluster formation. Clustering occured in steps, the relatively small clusters formed in the beginning still could undergo declusterification which resulted in partial reactivation of the catalyst [89].

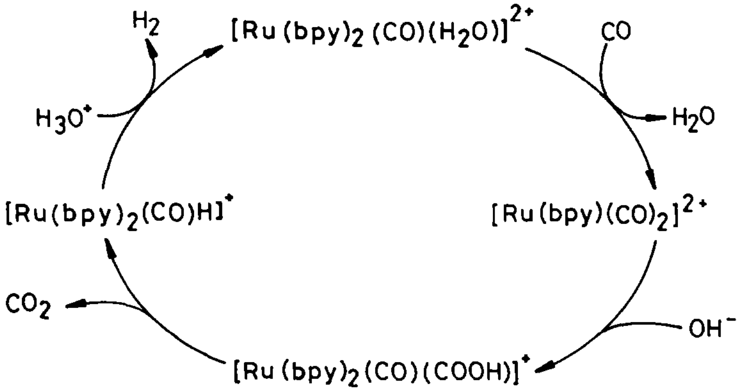
The mechanism of hydroformylation catalyzed by Pt-Sn complexes has been studied by investigating stoichiometric reactions of the complexes possibly involved in the catalytic cycle. It was concluded that $SnCl_2$ may act in several ways as a co-catalyst: as a Lewis acid, as the source of $SnCl_3^-$, and as a ligand bonded to Pt [90].

5. Water gas shift reaction

The water gas shift reaction is catalyzed by $HFe(CO)_4^-$ in a 9:1 mixture of DMF and water under CO if irradiated with a tungsten--halogen lamp. The suggested mechanism involves the reductive elimination of H_2 from a dinuclear intermediate [91]. The cluster hydride anion $[HFe_3(CO)_{11}]^-$ adsorbed on hydrated Na-Y zeolite showed a very high catalytic activity for the water-gas-shift reaction at 60-180°C. Kinetic and spectroscopic studies indicated that the reaction between H_2O and the cluster was rate-determining [92]. The synergetic effect of mixed metal carbonyls of Group VIII metals in the homogeneous water gas shift reaction has been studied. The most pronounced synergism was found in the case of Fe/Ru mixed metal carbonyls which were about two orders of magnitude more active than the individual metal carbonyls alone. About 50% increase of activity was observed with Fe/Ir systems [93].

Amines increase the catalytic activity of $Ru_3(CO)_{12}$ for the water gas shift reaction. It was shown, that primary and secondary amines yield highly active systems, but the amines react with CO_2 to form carbamates. Tertiary aliphatic amines do not give active catalyst systems. The best choice was pyridine which furnished a moderately active catalyst and was inert towards CO_2 [94]. Reaction of $Ru_3(CO)_{12}$ with bpy yields a dark blue complex which is a very active catalyst for the water gas shift reaction at room temperature. The catalyst is insoluble in polar or nonpolar solvents; it reaches its highest catalytic activity only after a relatively long induction period [95]. The complex $[Ru(bpy)_2(CO)H]PF_6$ has been prepared and its protonation (which leads to H_2 formation) investigated kinetically. This reaction is probably the rate-determining step in the water-gas shift reaction catalyzed by

$[Ru(bpy)_2(CO)Cl]^+$ [96]. The water-gas shift reaction catalyzed by bis(bpy)-carbonyl-Ru(II) complexes has been investigated. All the species involved in the catalytic cycle (which is shown below) have been isolated or characterized by spectroscopic methods [97].

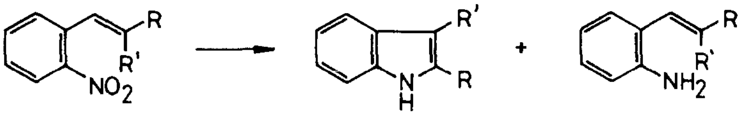


For a correction of AS 1985 ref. 66 see [98].

See also [23,105].

6. Reduction with CO or CO + H_2O

Reduction of ketones to secondary alcohols was achieved with CO + H_2O at 105°C and 30 bar using (η^4-$Ph_4C_4CO)(CO)_3Ru$ as catalyst in THF solution. The reaction was accelerated by addition of Na_2CO_3 [99]. The A_1 symmetry ν_{CO} vibrations of the carbonyl complexes $Mo(L)(CO)_4$ (L = substituted derivatives of phen), were determined. A correlation was found between these values and the catalytic activity of the systems composed of $Ru_3(CO)_{12}$ or $Rh_6(CO)_{16}$ and the corresponding phen derivatives in the hydrogenation of nitrobenzene with CO + H_2O [100]. The reduction of nitrobenzenes to the corresponding anilines was achieved with a series of Ru and Os phosphine complexes using H_2, H_2 + CO or CO + H_2O at 120°C and 70 bar in 2-ethoxy-ethanol as solvent. Addition of KOH increased the turnover numbers. The reaction was best carried out under water gas shift conditions [101]. Reduction of *o*-nitrostyrenes (15) to indole derivatives (16) by CO is catalyzed by $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Rh_6(CO)_{16}$ at 220°C and 80 bar in toluene solution. In small amounts also amines (17) are formed by hydrogen abstraction [102].



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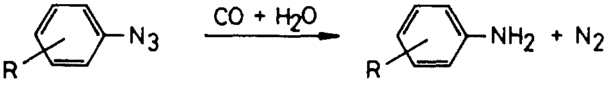
Hydrogenation of α,β-unsaturated carbonyl compounds with CO + H_2O and $Rh_4(CO)_{12}$ catalyst supported on polymers containing amine moieties was studied. The C,C double bonds were hydrogenated selectively. The resin-supported catalysts were generally more effective than the homogeneous one [103]. Azidoarenes (18) were readily transformed to aniline derivatives in good yields with CO + H_2O and $RhCl_3.3H_2O$ catalyst under mild conditions (20 bar, 150°C). $PdCl_2$ was less active as catalyst [104].



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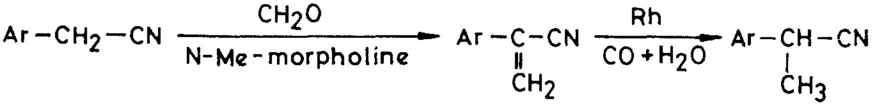
Reduction of various functional groups and carbonylation of olefins with CO + H_2O using $Rh_6(CO)_{16}$ + amine catalysts was studied. The activity and selectivity of the catalyst systems strongly depended on the structure of the amine component. The ethylene diamine containing catalyst showed high catalytic activity for the water gas shift reaction; N-alkylated diamines were the best additives for the reduction of aldehydes. With pyridines, α,β-unsaturated aldehydes were hydrogenated to saturated aldehydes; N-alkyldiamine systems gave high yields of alcohols from olefins via hydroformylation and reduction [105]. Arylacetonitriles can be transformed with formaldehyde into 2-arylpropionitriles under water gas shift conditions (200°C and 100 bar) in the presence of $RhCl_3.3H_2O$ as catalyst precursor. The role of the Rh catalyst is to hydrogenate the 2-arylacrylonitrile formed in the base-catalyzed reaction [106]:



$$\mathrm{Ar-CH_2-CN} \xrightarrow[\text{N-Me-morpholine}]{\mathrm{CH_2O}} \mathrm{Ar-\underset{\underset{\displaystyle CH_2}{\|}}{C}-CN} \xrightarrow[\mathrm{CO+H_2O}]{\mathrm{Rh}} \mathrm{Ar-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CN}$$

Nitrobenzene derivatives p-$RC_6H_4NO_2$ (R = Me, Cl) were reduced to the corresponding anilines with CO in aniline solution in the presence of NiX_2L_2 (X = Cl, Br; L = PR_3, R = Me,Et,Ph) or $NiI_2(PhNH_2)_4$ as catalyst precursors at 150-180°C and 20 bar. The aniline solvent was simultaneously converted to diphenylurea [107]:

$$RC_6H_4NO_2 + 3CO + 2PhNH_2 \longrightarrow RC_6H_4NH_2 + CO(NHPh)_2 + 2CO_2$$

Nitrobenzene and para-substituted nitrobenzenes were reduced by CO with good yields to anilines in the presence of a $Pd(OAc)_2$ + PPh_3 (1:4) catalyst in aqueous AcOH. The analogous reduction of $PhNO_2$ in BuOH + H_2SO_4 (1:5) gave p-$HOC_6H_4NH_2$ [108].

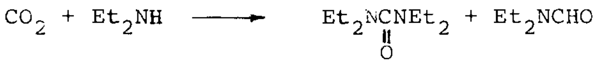
7. Miscellaneous Reductive Transformations of CO and CO_2

The formation of MeOH from CO and H_2O is catalyzed by $Mo(CO)_6$ at temperatures below 150°C [109]. The reduction of CO or CO_2 with Everitt's salt ($K_2Fe[Fe(CN)_6]$) to methanol (see A.S. 1985 refs. 79,80) could be performed in a catalytic manner by reducing the Prussian blue (formed in the stoichiometric reaction) electrochemically and using for this a commercial solar cell as energy source [110]. Electrocatalytic reduction of CO_2 to MeOH at an Everitt's salt-mediated electrode in EtOH solution in the presence of 1,2-dihydroxybenzene-3,5-disulfonato (tiron) ferrate(III) has been studied. The formation of an intermediate Fe(III)-tironethyl formate complex was established [111]. The reduction of CO_2 to MeOH on Pt electrodes modified with Everitt's salt was studied in the presence of different Fe and Cr complexes as homogeneous catalysts. Highest current efficiency was achieved with $[(H_2O)(C_2O_4)_2Cr]^-$ [112]. Methyl formate coordinated to the metal was proposed as an intermediate [113].

Carbon monoxide and carbon dioxide were electrochemically reduced to MeOH in the presence of the following metal complexes as homogeneous catalysts: $Fe(CN)_5(H_2O)^{3-}$, $[Cr(C_2O_4)_2(H_2O)_2]^-$, $CrCl_5(H_2O)^{2-}$, $FeF_5(H_2O)^{2-}$, $Fe(CN)_5(NH_3)^{3-}$, and 4,5-dihydroxy-1,3-benzenedisulfonatoiron(III). Best current efficiency was 100% for CO and 16% for CO_2 [114]. Controlled potential electrolysis of a DMF solution containing $[Fe_4S_4(SCH_2Ph)_4]^{2-}$ under CO_2 resulted in the formation of formate and phenylacetate. In the presence of excess $PhCH_2SH$ the yield of phenylacetate increased and the cubane structure of the catalyst was preserved during a longer period [115].

The homogeneous photocatalytic reduction of CO_2 to CO was studied with $Rh(bpy)_3Cl_2.5H_2O$ and $Re(CO)_3(bpy)Cl$ as photocatalysts. Maximum activity was achieved with a 1:1 molar ratio of the two complexes [116]. Carbon dioxide could be reduced to methane under irradiation with visible light in an aqueous system composed of $NaHCO_3$, triethanolamine as electron donor, tris(bipyrazine)Ru(II) as senzitier, and a Ru metal colloid as catalyst. The effective electron transfer took place from $(bpz)_3Ru^+$ to colloid-associated CO_2 [117]. Carbon dioxide was electrochemically reduced to formate in aqueous solution using $Rh(bpy)_3Cl_3$ as electron mediator [118]. Cathodic reduction of CO_2 to CO catalyzed by Ni and Co complexes of macrocyclic ligands in MeCN + H_2O was investigated. High turnover numbers were observed [119]. Electropolymerized films of a Ni tetraazaannulene complex catalyze the reduction of CO_2 to formate [120].

Reaction of Et_2NH with CO_2 gives tetraethylurea and diethylformamide selectively with $PdCl_2(MeCN)_2$ as catalyst and PPh_3 or HCOONa as additive already at room temperature and 1 bar:



$$CO_2 + Et_2NH \longrightarrow Et_2N\underset{\underset{O}{\|}}{C}NEt_2 + Et_2NCHO$$

This is a reductive transformation of CO_2 not using H_2 and high pressure [121].

III. Hydrogenation and Reduction

1. H Exchange, D and T Labeling

Catalytic H/D exchange in alcohols is promoted by early-transition-metal (Zr, Nb, Ta) alkoxides at 200°C. Carbonyl compounds are the intermediates of this process [122]. The complex $(\eta^6\text{-}C_6H_6)Re(PPh_3)_2H$ catalyzes if irradiated the H/D exchange between C_6D_6 and aromatic hydrocarbons, and between C_6D_6 and the ortho and meta hydrogens of its PPh_3 ligands. The complex does not exchange its metal-hydride ligand with the D source [123]. Irradiation of the trihydrides $(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)$ ($PR_3 = PPr^i_3$, PPh_3) in C_6D_6 solution with UV light causes H/D exchange between the solvent, the hydride ligands and the coordinated phosphine [124].

The soluble iridium polyhydride $H_5Ir(PPr^i_3)_2$ catalyzes the H/D exchange between C_6D_6 and CH_4 in the presence of neohexene at 80°C. The deuteration of methane needs several days and is preceded by the conversion of all neohexene into neohexane and by H/D exchange between C_6D_6 and both the hydride ligands and all the hydrogens on the phosphine ligands [125].

See also [7].

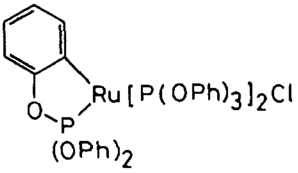
2. Hydrogenation of Olefins

a) Fe, Ru, and Os catalysts

Hydrogenation of cyclohexene is catalyzed by $[CpFe(CO)_2]_2$ at 17°C and 6 bar with a turnover of 16 h^{-1}. No mononuclear intermediates are formed during this reaction because if hydrogenation is performed with a mixture of $[CpFe(CO)_2]_2$ and $[\eta\text{-}C_5Me_5)Fe(CO)_2]_2$ no mixed-ligand dinuclear complex can be found in the product [126]. The PhLi + $Fe_4S_4Cl_4^{2-}$ (6:1) system catalyzes the hydrogenation of terminal double bonds of monoenes and dienes with H_2 [127].

Partial hydrogenation of refined canola oil with $Ru(PPh_3)_3Cl_2$ as catalyst was examined. This complex catalyst was about as effective as heterogeneous Ni catalysts in producing hydrogenated fats with a low trans-fatty acid content [128]. The bis(imido) clusters $Ru_3(NAr)_2(CO)_9$ (Ar = Ph, p-substituted phenyls) catalyze the hydrogenation of olefins under 3 bar H_2 at 98°C. The clusters probably remain intact during the catalytic cycle [129]. The anionic ruthenium cluster $[Ru_3(\mu\text{-NCO})(CO)_{10}]^-$ was shown to catalyze the hydrogenation of terminal, unactivated olefins. The analogous $[HRu_3(CO)_{11}]^-$ cluster was inactive but catalysis could be promoted also by Cl^- or Br^- in place of NCO^- [130]. The tetraruthenium clusters $H_4Ru_4(CO)_{12}$ and $H_4Ru_4(CO)_{10}(PPh_3)_2$ were anchored on polymer supports modified by tertiary phosphine groups and used as catalysts for the hydrogenation of 1-hexene [131]. Three types of Ru carbonyl complexes anchored to SiO_2 via phosphine ligands: $H_4Ru_4(CO)_8(PPh_2C_2H_4\text{-SIL})_4$, $Ru_3(CO)_9(PPh_2C_2H_4\text{-SIL})_3$, and $Ru(CO)_4(PPh_2C_2H_4\text{-SIL})$ were used as catalysts for the hydrogenation of ethene at 70°C. Decarbonylation of the anchored complexes occurred only above 180°C [132].

The orthometalated complexes (19-22) were found to be catalysts for olefin hydrogenation. Activity of (22) was especially high: it was equivalent to that of HRu(PPh$_3$)$_3$Cl and superior to that of Rh(PPh$_3$)$_3$Cl. Small amounts of O$_2$ enhanced its activity by transforming one PPh$_3$ ligand into OPPh$_3$ [133].



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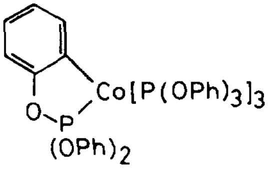

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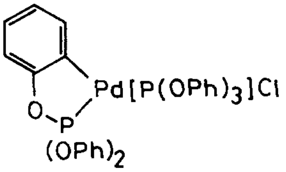

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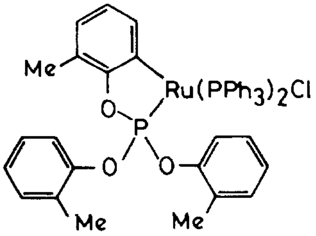

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Hydrogenation of maleic anhydride and 3,3-dimethyl butene is catalyzed by Os$_3$(NCO)(CO)$_{11}$ at 60-80°C and 3 bar with turnover numbers of 3-8/day [134]. Dienes were hydrogenated to monoenes with CpNiOs$_3$(μ-H)$_3$(CO)$_8$L clusters (L = CO, Ph$_2$PH, P(C$_6$H$_4$Me-o)$_3$ as catalysts. An allylic complex derived from the diene was isolated from the reaction mixture [135].

See also [44, 187, 203].

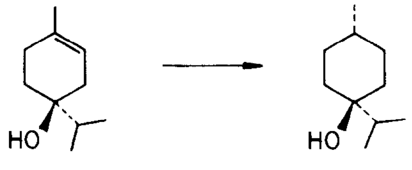
b) Co, Rh, and Ir Catalysts

Selective hydrogenation of citral to citronellal was achieved with cyanoethylenediaminocobalt catalyst in MeOH/H$_2$O at 25°C [136]. Maleic and fumaric acid were reduced to succinic acid, acetylenedicarboxylic acid was first reduced to fumaric acid and then to succinic acid by vitamin B$_{12s}$ (cob(1)alamin) [137]. The corresponding methyl esters of the three acids were also reduced in a similar way to methyl succinate [138].

The complexes $[RhCl(CO)L]_2$ (L = different 2-amino-1,3,2-dioxaphosphorinanes) were used as catalysts for the hydrogenation of olefins [139]. The kinetics of homogeneous hydrogenation of 1-heptene with Rh(DPPA)Cl [DPPA = $HN(CH_2CH_2PPh_2)_2$] as catalyst has been determined and compared with that of the hydrogenation of cyclohexene, determined earlier (see A.S. 1984, ref. 127). Hydrogenation of 1-heptene was faster and this was attributed to the more labile dihydro-olefin complex in this case [140]. Hydrogenation of Me sorbate was studied at 100°C with $Rh(PPh_3)_3Cl$, $[Rh(NBD)Cl]_2$, and $HRh(CO)(PPh_3)_3$ as catalysts. Main product was Me trans-2-hexenoate but significant amounts of Me trans-3-hexenoate and Me hexanoate were also formed. The complexes $Rh(CO)(PPh_3)_2Cl$ and $[Rh(NBD)(dpe)](PF_6)$ which catalyzed the hydrogenation of Me linoleate were inactive for the hydrogenation of Me sorbate [141]. Hydrogenation of highly substituted acrylic acids could be performed by using $RhCl(PPh_3)_2(Ph_2POCOCH{=}CMe_2)$ as catalyst in acetone solution in the presence of a base. The mechanism involves hydrogenation of the mixed anhydride ligand followed by transesterification with the acrylic acid substrate thus liberating the hydrogenated carboxylic acid [142]. The catalytic activity of the $[RhCl(cyclooctene)_2]_2$ + 2-alkylaminopyridine and $RhCl_2$(2-methylallyl) + 2-alkylaminopyridine systems in the homogeneous hydrogenation of different olefins was examined. The allylrhodium complex provided less active catalytic systems than the cyclooctene complex [143]. The solvated ion pair $[(C_8H_{17})_3NMe]^+[RhCl_4]^-$ formed from $RhCl_3.3H_2O$ and methyltrioctylammonium chloride in a two-phase liquid system was shown to catalyze the hydrogenation of α,β-unsaturated ketones and esters selectively at the C=C bonds. The process is both chemically and diffusion controlled [144].

Rhodium(I) polymeric phosphinocarborane complexes were used as catalyst for the hydrogenation of terminal alkenes to alkanes and conjugated dienes to monoenes and alkanes [145]. A polyphenylquinoxaline-Rh complex was prepared and used as catalyst for the hydrogenation of olefins, butyraldehyde and bromopropene [146]. Cationic silica-supported Rh(I) complexes prepared from Rh(COD)(acac) and the phosphines $(EtO)_3Si(CH_2)_nPPh_2$ (n = 1,3) in the presence of p-toluenesulfonic acid were found to be efficient catalysts for hydrogenation of alkenes under mild conditions. Highest activities were attained with P/Rh ratios of 2; such catalysts were more active than their homogeneous analogues [147].

Homogeneous hydrogenation of cyclohexene catalyzed by Rh(I) and Ir(I) complexes of the terdentate ligands $HN(CH_2CH_2EPh_2)_2$ (E = P, As) was investigated. Based on kinetic experiments it was concluded that the enthalpies of formation of the dihydride complexes $H_2M(L)Cl$ (M = Rh, Ir) and the enthalpies of activation of the rate-determining step show an inverse relationship [148]. The presence of a ligating group, e.g. OH or COOMe on an olefinic substrate was shown to direct the addition of H_2 in case of $[Ir(COD)(PCy_3)(py)](PF_6)$ as catalyst and CH_2Cl_2 as solvent onto the face of the molecule containing the directing group. Thus, for example, olefin (23) gave (24) in 99.9% yield. This very pronounced directing effect was characteristic only for the 12-electron "IrL_2" system; 14-electron catalytic species like $Rh(PPh_3)_2Cl$ did not show this selectivity [149].



23 24

See also [133, 216, 217].

c) Ni, Pd, and Pt catalysts

The reaction product of nickelocene and $LiAlH_4$ in THF has been found to be an active homogeneous catalyst for catalytic hydrogenation of alkenes and alkynes. Nitro groups were poisonous to the catalyst; in their presence only stoichiometric reduction took place [150].

The mechanism of formation of hydrogenation catalysts based on $Pd(acac)_2$ was studied [151]. Complexes of Pd(II) with poly(2-vinylpyridine) were reduced by $NaBH_4$ or H_2 and tested as catalysts for the hydrogenation of olefinic and acetylenic alcohols. These complex catalysts were more active than Pd black [152, 153]. Cyclohexene was hydrogenated on a polyaziridine-$PdCl_2$ catalyst at 50°C and 5 bar H_2. Under the same conditions 1,3- and 1,4-cyclohexadienes disproportionated into cyclohexene and benzene [154]. A heterogenized Pd(II) catalyst on phosphinated montmorillonite was prepared and used for hydrogenation of olefins and acetylenes.

The results obtained in various solvents were in accord with the swelling properties of montmorillonite [155].

Polymer-supported Pd(O) and Pt(O) catalysts were prepared by reacting CpPd(η^3-C_3H_5) or Pt(COD)$_2$ with 4,4′-diisocyanobiphenyl and used for the hydrogenation of alkenes and alkynes. The Pd catalysts prepared in this way were found to the about as active as Pd/C or polystyrene-bound Pd [156].

See also [133, 135, 194].

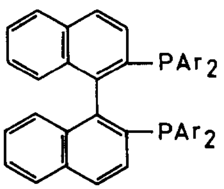
d) Other Metals

Zirconium(III) complexes containing the chelated $\overline{\mathrm{ZrCH_2P}}\mathrm{Ph_2}$ moiety catalyze the hydrogenation of olefins, diolefins and acetylenes. In some cases specific selectivities can be observed: 1,3- and 1,5-cyclooctadienes are transformed into cyclooctene and diphenylacetylene into 1,2,3,4-tetraphenylbutane [157].

3. Asymmetric Hydrogenation of Olefins

The dimeric Rh(II) complex containing bridging mandelate ligands $[Rh(OOCR)_2(H_2O)]_2$ (R =CHOHPh) was tested as catalyst for the asymmetric hydrogenation of prochiral olefinic acids. Practically no enantioselectivity was observed and the reaction mixture was not homogeneous. Addition of PPh_3 or chelating amines significantly decreased the activity but resulted in the formation of a moderately enantioselective homogeneous catalyst (o.y. up to 15%) [158].

A practical synthesis of (R)- or (S)-2,2′-bis(diarylphosphino)-1,1′-binaphthyls (BINAPs, 25; Ar = Ph, p-MeC_6H_4, p-$tBuC_6H_4$) has been developed [159].



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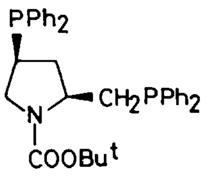
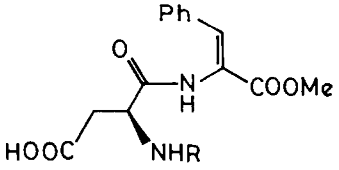
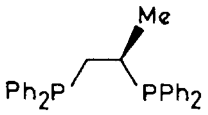


25a

The degree of asymmetric induction in hydrogenation of (+)- and (−)-methyl esters of 3-hydroxy-2-methylenebutyrate catalyzed by [Rh(dipamp)]$^+$ complexes was strongly dependent on the configuration of the menthyl group [160]. The Z- and E-isomers of α-acylamino-2-butenoic acid and its methyl ester were hydrogenated in the presence of *in situ* catalysts formed from [Rh(COD)Cl]$_2$ and several chiral diphosphine ligands. The best results were obtained with the substrate (Z)-α-acetylamino-2-butenoic acid and the ligand (−)-norphos (115) [161]. The dehydroaspartame derivatives (26) were hydrogenated to L,L- and L,D aspartame derivatives using Pd/C and different Rh(I)-chiral phosphine systems as catalysts. Highest yield (90%) of the desired L,L-enantiomer (an artificial sweetener) was obtained with (R)-prophos (27) as ligand [162].



26, R = CHO or COOCH$_2$Ph



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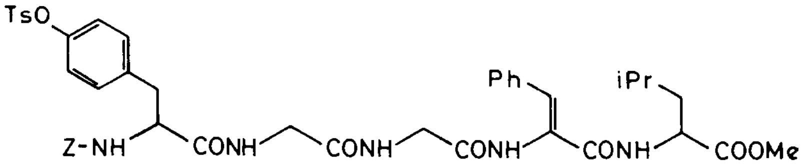
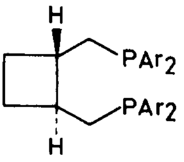
The mono-dehydro Leu-enkephalin (28) was hydrogenated using different chiral Rh(I) complexes as catalysts. Application of [Rh(dipamp)(COD)](BF$_4$) leads to 93% (S)-product while with Rh(BPPM)Cl 68% (R)-product was obtained. This shows that chirality of the product is mainly controled by the catalyst and overcomes asymmetric induction due to the two chiral aminoacids already present in the substrate [163].



28

The water soluble chiral ditertiary phosphines (29) and (30) were prepared from the parent compounds by sulfonation and used in an aqueous-organic two-phase system for the asymmetric hydrogenation of α-acetamido cinnamic acid and some of its derivatives with Rh(I) complexes as catalysts. Optical yields were somewhat lower than those obtained with the unsulfonated phosphines in organic solvents; the best value was 88% [164].



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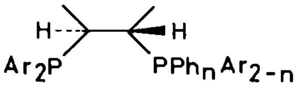

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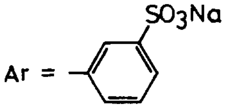
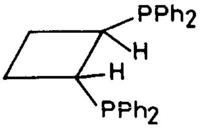
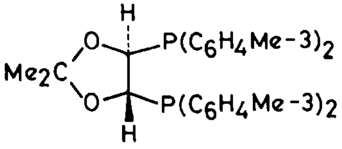


n = 0 or 1

The new chiral biphosphine (31) was prepared and used as ligand in the asymmetric hydrogenation of dehydroamino acids with Rh(I) complexes as catalyst. Best o.y. was 90% [165]. The DIOP analogue (32) was prepared and used as chiral ligand in the asymmetric hydrogenation of dehydro N-acylaminoacids with Rh(I) complexes as catalysts [166].

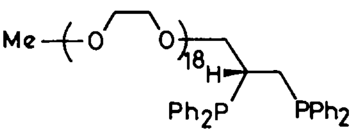


31



32

The water-soluble chiral diphosphines (33) and (34) have been prepared and were used as ligands in the asymmetric hydrogenation of dehydro aminoacids in water or EtOH. Unexpectedly, water strongly decreased the enantioselectivity of these catalysts while no such effect was noted when dipamp or norphos (115) were used as chiral ligands [167].



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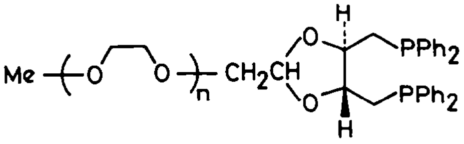
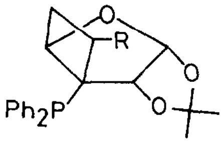


34, n = 16 or 42

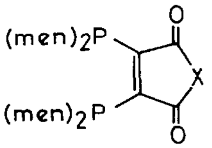
The chiral phosphines (35) and (36) were prepared from D-glucose and used as ligands for the asymmetric hydrogenation of α-acetamidocinnamic acid and itaconic acid with $[Rh(COD)Cl]_2$ as catalyst. Phosphine (35) gave significantly higher optical yields than (36) [168].



35, R = CN

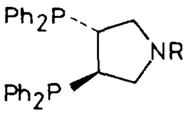
36, $R = CH_2NH_2$

The chiral bis(tertiary phosphines) (37) and (38) were used as ligands in the hydrogenation of unsaturated carboxylic acids with Rh(I)-phosphine complexes prepared <u>in situ</u> from $[Rh(COD)Cl]_2$. The best optical yield (70%) was obtained in the case of α-acetamido cinnamic acid [169]. Several chiral bistertiary phosphines of the type (39) (R = different alkyl and acyl groups) were prepared and used as ligands in the asymmetric hydrogenation of different α-(acylamino)acrylic acid derivatives with $[Rh(COD)(PP)]^+$ complexes as catalysts (PP = 39). In most cases very high optical yields were achieved (up to 99.5%) even under pressure. The substrate:catalyst ratio could be increased up till 50.000 [170].



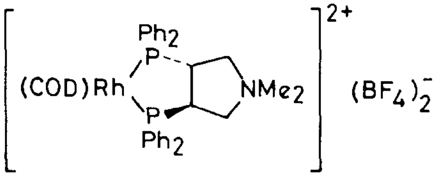
37, X = O

38, X = NPh



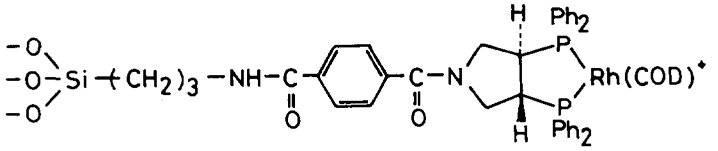
39

The water soluble Rh(I) complex (40) has been prepared and used for the hydrogenation of the sodium salt of α-acetylaminocinnamic acid in water solution. The catalyst was highly active and furnished (S)-N-acetylphenylalanine in 90% o.y. [171].



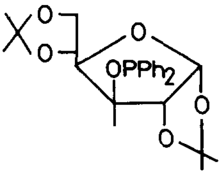
40

Optical yields up to 100% were obtained in the hydrogenation of α-acetylaminocinnamic acid and its methyl ester in the presence of Rh complexes of 3,4-(R,R)-bis(diphenylphosphino)pyrrolidine, bound to silica (41). The catalyst could be reused three times [172].



41

The chiral sugar diphenylphosphinite derivatives (42) and (43) were prepared and used as ligands in the asymmetric hydrogenation of prochiral olefins with $[Rh(COD)Cl]_2$ as catalyst. Complete enantioselectivity was obtained with (43) in the hydrogenation of itaconic acid [173].



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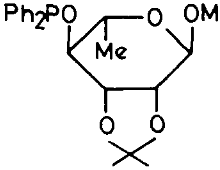
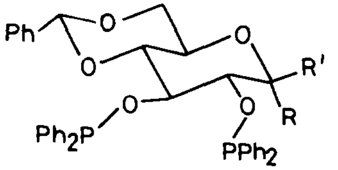


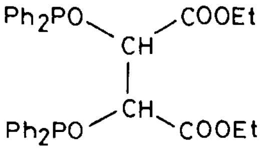
43

The air-stable chiral bisphosphinites (44) were prepared starting from D-glucose and the cationic rhodium complex $Rh(L)(COD)^+$ (L = 44a) was used as catalyst for the asymmetric hydrogenation of N-acyldehydro-α-amino acids. Optical yields of 94-99% were achieved [174]. Immobilizing this complex on an organic cation exchanger resulted in a catalyst which is some cases showed a better enantioselectivity than the homogeneous catalyst. If recycled it slowly lost its activity but not its enantioselectivity [175].



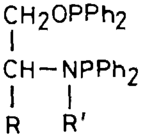
	R	R'
44 a	H	OPh
44 b	OMe	H
44 c	OPh	H

A polymeric phosphine was prepared from diethyl tartrate, tetraethylenepentamine and the chiral bisphosphinite (45). Complexes of this copolymer with $NiCl_2$ and $CoCl_2$ were used as catalysts for the asymmetric hydrogenation of α -acetylaminocinnamic acid [176].



45

The new chiral aminophosphine phosphinites (46-49) were prepared. Cationic Rh complexes of these ligands were used as catalysts for the asymmetric hydrogenation of dehydroamino acids (highest o.y. 92%) [177] or of (50) to pantolactone (51) (best o.y. 53%) [178].



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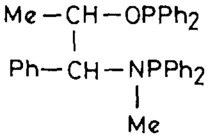

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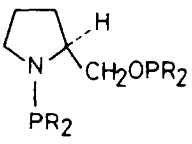

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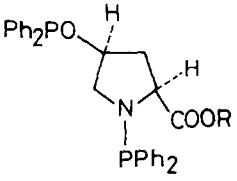
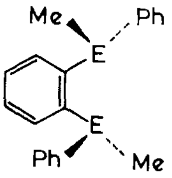


49

50

51

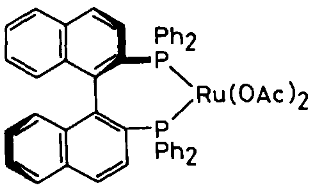
Rh(I) complexes of the chiral phosphines and arsines (52) and (53) were used as catalysts for the enantioselective hydrogenation of dehydro amino acids. Optical yields up to 94% were observed and in some cases the arsine proved to be the more selective ligand [179].



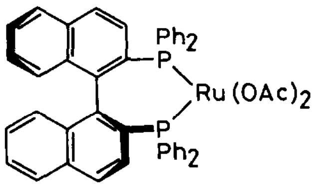
52, E = P

53, E = As

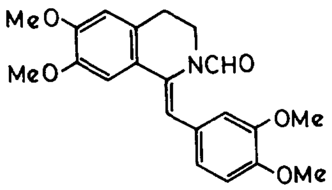
Asymmetric hydrogenation of α,β-unsaturated ketones to saturated ketones was achieved with *trans*-HRuClL$_2$ as catalyst at 50-80°C and 40 bar [L = *trans*-1,2-bis(diphenylphosphinomethyl) cyclobutene). Highest o.y. (62%) was obtained in the case of phorone [180]. The chiral Ru complexes $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ and $Ru_4(CO)_8[OOC(CH_2)_nCOO][(-)\text{-DIOP}]$ (n = 2,3) were used as catalysts for asymmetric hydrogenation of acetylated dehydroamino acids. Highest o.y. was 26% [181]. The hexacoordinate Ru complexes bearing the enantiomers of the chiral ligand BINAP, (54) and (55), were used as catalysts for the asymmetric hydrogenation of enamides like (56) or (57). Although the reaction was rather slow (2-6 days at 23°C) chemical and optical yields were generally excellent (near 100%). This new method is useful for the synthesis of various physiologically important products [182].



Δ - (R) - 54



Λ- (S) - 55



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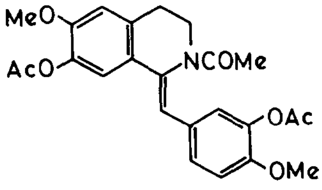
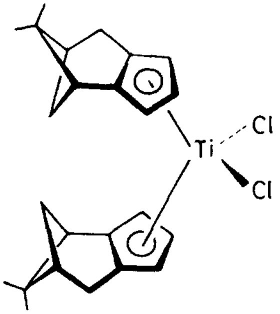
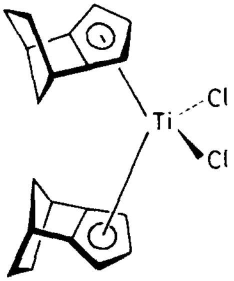


57

The Ti complexes (58) and (59) activated with BuLi were used as catalysts for the asymmetric hydrogenation of 2-ethyl hexene-1 and α-ethyl styrene. Highest o.y. was 34% [183].



58

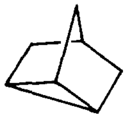


59

4. Hydrogenation of Dienes and Alkynes

Alkynetitanium complexes like $Cp_2Ti(PhCCPh)(PMe_3)$ react with H_2 and are catalyst precursors for the hydrogenation of alkynes. Selective hydrogenation to cis-olefins takes place in the presence of PMe_3 [184]. Homogeneous systems obtained from $(MeC_5H_4)_2TiCl_2$, or $(MeC_5H_4)_2Ti(OPh)_{2-n}Cl_n$ (n = 0,1), BuMgBr and $LiAl(OBu^t)_3H$ catalyze the hydrogenation of cyclopentadiene [185]. The dinuclear Ru carboxylate complex $Ru_2(COD)_2(O_2CCF_3)_4(H_2O)$ catalyzes the selective hydrogenation of COD at 50°C and 1 bar in the presence of cyclooctene and conjugated dienes [186]. Hydrogenation of olefins, dienes, alkynes, aldehydes and ketones, and hydroformylation of olefins is catalyzed by $HOsBr(CO)(PPh_3)_3$. High selectivities were observed in the hydrogenation of dienes to monoenes and of alkynes to alkenes. Unsaturated aldehydes were hydrogenated mainly to unsaturated alcohols, unsaturated ketones to saturated ketones [187].

Hydrogenation of 4-methyl nonatrienes (linear dimers of piperylene) using $K_2[Co(CN)_5]$ or $K_2[Co(CN)_3(ethylene\ diamine)]$ gave 4-methyl-2,6-nonadiene in 90% yield [188]. Norbornadiene was hydrogenated to norbornene and the tricycloheptane (60) by $Co(PPh_3)_3X + BF_3.Et_2O$ catalysts (X = Cl,Br) in 5-19% yield. Main products were different NBD dimers [189]. Tetramethylallene is isomerized to 2,4-dimethyl-1,3-pentadiene and hydrogenated to 2,4-dimethyl-2-pentene by $HCo(CO)_4$ and $HMn(CO)_5$. As supported by CIDNP measurements, both reactions take place over a common radical pair intermediate [190].



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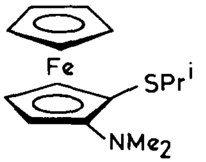


61

Diphosphines of the type $(EtO)_3Si(CH_2)_nP(Ph)CH_2CH_2PPh_2$ (n = 1,3) were used to immobilize Rh complexes on silica. The complexes were effective catalysts for hydrogenation of 1,3-cyclooctadiene [191]. Reaction of $PdCl_2$ with tertiary aliphatic amines gave complexes which were active for the hydrogenation of acetylenes or conjugated dienes to olefins. In some cases the resulting complexes were reduced with $(iBu)_2AlH$ [192]. The complex formed from the ferrocenyl thiother ligand (61) and K_2PdCl_4 was found to be a homogeneous catalyst for the hydrogenation of 1,3-cyclooctadiene to cyclooctene in acetone solution [193].

Several new homogeneous catalyst systems based on linear polymers like poly(vinylpyrrolidinone) or poly(ethyleneimine) as ligands were developed for selective hydrogenations in liquid phase. Depending on the metal, the following hydrogenations could be performed: Rh - aromatics (cyclohexanone from phenol), sugars; Pd - alkenes, nitro groups, C=N bonds, alkynes to *cis* or *trans* alkenes (depending on the ligand); Ni - alkynes to *cis*-alkenes. The catalysts could be separated from the product by ultrafiltration [194].

See also [146, 150, 156, 157, 217].

5. Hydrogenation of Arenes and Heterocyclic Compounds

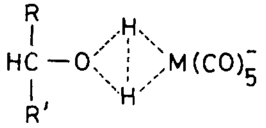
Hydrogenation of benzene is catalyzed by aqueous $Ru(OH)Cl_3$ at 40-80°C and 20-60 bar [195]. Liquid-phase hydrogenation of benzene to cyclohexane was carried out over rhodium trichloride at 20°C [196]. Naphthalene was hydrogenated at 30°C and 1 bar with a $RhCl_3.3H_2O$ + methyltrioctylammonium chloride (Aliquat 336) catalyst in a two-liquid phase system to give decalin-free tetralin. Methyl naphthalenes, naphthols and ethyl naphthoates were hydrogenated mainly at the non-substituted ring. Chlorinated naphthalenes underwent partial hydrogenolysis [197]. Phenol was hydrogenated in the presence of catalysts based on Rh and Pt complexes with water-soluble polymers. Thus, the Rh complex of poly(acrylic acid) activated by $NaBH_4$ gave preferentially cyclohexanone (74%) along with cyclohexanol [198].

Rhodium complexes with polyacrylic acid, styrene-maleic acid copolymer and methyl methacrylate-maleic acid copolimer were used as catalysts for the hydrogenation of furfural. Hydrogenation proceeded over furfuryl alcohol to tetrahydrofurfuryl alcohol [199].

See also [194].

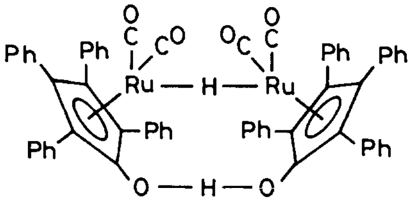
6. Hydrogenation of Carbonyl Compounds

The anionic group 6 carboxylates $M(CO)_5(OAc)^-$ (M = Cr,W,Mo) catalyze the hydrogenation of aldehydes and ketones at 125°C and 50 bar. Activation of dihydrogen was proposed to proceed over the anion-stabilized dihydride or dihydrogen complex (62) [200].



62

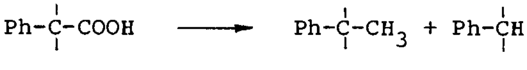
Acetaldehyde was hydrogenated to ethanol with CO + H_2 at 180°C and 445 bar using $[HRu(CO)_4]^-$ as catalyst. The trinuclear hydride $[HRu_3(CO)_{11}]^-$ proved to be much less active as a catalyst for this reaction. A similar activity difference between the two complexes was found in the synthesis of methanol from synthesis gas at 230°C and 500 bar [201]. Hydrogenation of the carbonyl group of citral (3,7-dimethyl-2,6-octadienal) with Ru(II)-PPh_3 complexes as catalysts was investigated. In protic solvents and in the presence of HCl the selectivity for dienol was 99% [202]. The activity of the complexes $RuCl_2[Ph_2P(CH_2)_nPPh_2]$ (n = 1,2,3) as hydrogenation catalysts was tested with different substrates at 65-95°C and 10-17 bar. Linear olefins were easily hydrogenated but cyclic olefins and acetone could be hydrogenated only with the most active catalyst (n=3). Propionaldehyde was hydrogenated to propyl alcohol, and crotonaldehyde or cinnamaldehyde were reduced to the corresponding saturated aldehydes [203]. When trans-4-tert-butylcyclohexanol was subjected to 35 bar H_2 at 145°C in the presence of a catalytic amount of (63) in toluene, a constant-composition mixture of the cis (25.2 mole %) and trans (69.7 mole %) alcohols as well as the corresponding cyclohexanone (5.0 mole %) was formed. This result shows that (63) reversibly catalyzes ketone hydrogenation and alcohol dehydrogenation. Complex (63) was earlier erroneously described as $[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2$ (AS 1985, ref. 97) [204].



63

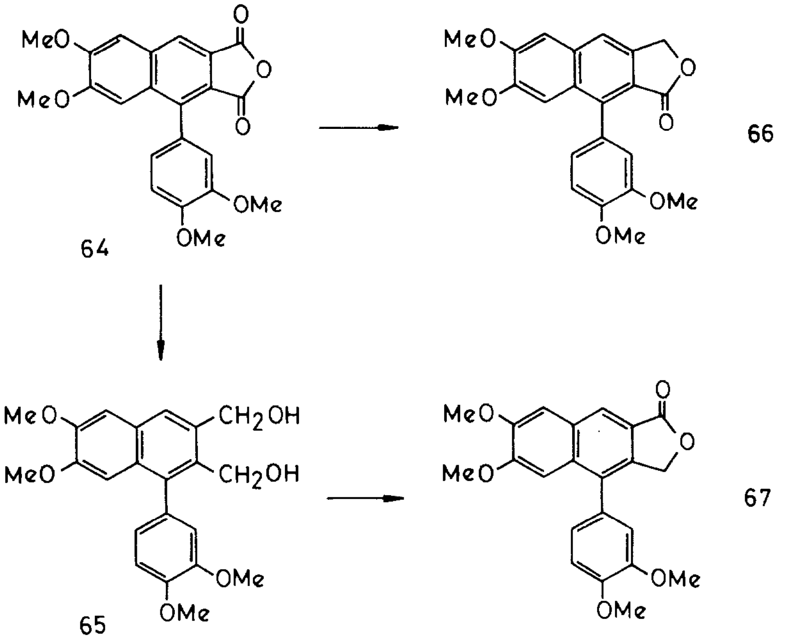
Hydrogenation of aldehydes and ketones was achieved by the use of several Ru and Os complexes of the type $HMX(CO)(PR_3)_3$ or $MX(OCOR')(CO)(PPh_3)_2$ (X = Cl,Br; R = Ph,Cy; R' = Me,Et,Cy,tBu, CH_2Cl, $CHCl_2$, CF_2Cl, CF_3) at 150°C and 30 bar. Mechanisms were proposed involving $HMX(CO)(PR_3)_2$ as catalytically active species or involving a bidentate-monodentate equilibrium for the carboxylate ligand as a key step in the catalysis [205].

Hydrogenation of dimethyl oxalate at 180°C and 130 bar in the presence of $Ru(CO)_2(PBu_3)_2(AcO)_2$ gives methyl glycolate. If the reaction is performed in MeOH as solvent, the glycolate is subsequently partly transformed into ethylene glycol [206]. The ruthenium carbonyl carboxylates $(AcO)_2Ru_2(CO)_4(PBu_3)_2$, $(AcO)_4Ru_4(CO)_8(PBu_3)_2$, and $(AcO)_2Ru(CO)_2(PBu_3)_2$ were identified as intermediates in the homogeneous hydrogenation of AcOH to EtOAc using the catalyst precursor $H_4Ru_4(CO)_8(PBu_3)_4$ [207]. In the presence of Ru + MeI or Rh + MeI catalysts benzylic carboxylic acids undergo reduction, or decarbonylation and reduction by synthesis gas at 220°C and 430 bar:



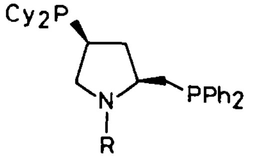
$$Ph\text{-}\overset{|}{\underset{|}{C}}\text{-}COOH \longrightarrow Ph\text{-}\overset{|}{\underset{|}{C}}\text{-}CH_3 + Ph\text{-}\overset{|}{\underset{|}{C}}H$$

The ratio of the two products depends on the structure of the acid on the metal: Ru generally favors reduction and Rh decarbonylation. Benzoic acid is reduced to toluene under such conditions [208]. Hydrogenation of the cyclic anhydride (64) at 160°C with $Ru_2Cl_4(dppb)_3$ as catalyst gave the lactone (66) in 99% yield. On the other hand if (64) was first reduced by $LiAlH_4$ to the diol (65) and the latter compound was dehydrogenated in toluene (reflux) with $H_2Ru(PPh_3)_4$ as catalyst and benzalacetone as H acceptor, the isomeric lactone (67) was obtained in 88% yield [209].



The kinetics of hydrogenation of benzil catalyzed by $Co(dgm)_2$ in py has been determined. The rate was found to be first order in Co and showed a maximum with py concentration [210].

Enantioselectivity and stereoselectivity of Rh-phosphine catalyst systems used for hydrogenation of ketones could be influenced by the addition of suitable bases as additives. These effects were explained by the formation of monohydrido or dihydrido Rh complexes as catalytically active species [211]. Aryl alkyl ketones and aromatic aldehydes react in THF solution with H_2 in the presence of catalytic quantities of $[Rh(HD)Cl]_2$ and β-cyclodextrin to give hydrocarbons in high yields. Yields are much lower in the absence of any cyclodextrin or in the presence of α-cyclodextrin; the favorable effect of β-cyclodextrin is probably due to the fact that it forms a complex with the substrate [212]. D-(−)-Pantolactone (51) was prepared in 92-98% yield by the asymmetric hydrogenation of (50) using the catalyst formed in situ from $[Rh(COD)Cl]_2$ and BPPM [213]. The new chiral pyrrolidinebisphosphines (68) were prepared and used as ligands for the same asymmetric hydrogenation with Rh(I) complexes as catalysts. The most efficient ligand was (68c) with which 92% enantioselectivity could be achieved [214].



68a, $R = MeSO_2-$

68b, $R = -CONHPh$

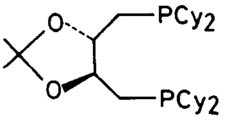
68c, $R = -COOBu^t$

Asymmetric hydrogenation of N-(α-ketoacyl)-α-amino esters (69) with Rh(I) complexes containing the chiral phosphines (71) as ligands produced N-(α-hydroxyacyl)-α-amino esters (70) in 64-72% o.y. The chiral center of the substrate had almost no influence on the diastereoselectivity of the reaction: if an achiral diphosphine $[iPr_2P(CH_2)_4PPr^i_2]$ was used, the o.y. was only 6% [215].

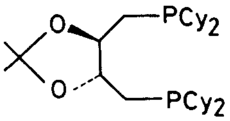
$$\mathrm{RCOCONH\underset{*}{\overset{R'}{C}}HCOOMe} \longrightarrow \mathrm{R\underset{*}{\overset{OH}{C}}HCONH\underset{*}{\overset{R'}{C}}HCOOMe}$$

69 70

$R = Me, Ph$; $R' = Me, PhCH_2$



71 a



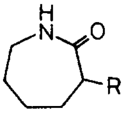
71 b

The selectivity of hydrogenation of α,β-unsaturated carbonyl compounds (benzylideneacetone or cinnamaldehyde) with Ir-phosphine complex catalysts prepared in situ from $[Ir(COD)(OMe)]_2$ and phosphines drastically changed with the P/Ir ratio. When a twofold excess of phosphine was used, the C=C bond was hydrogenated, with a P/Ir ratio of 10 the carbonyl group was reduced with almost 100% selectivity [216]. The Ir(III) complex [Ir(phen)Cl_2]Cl catalyzed the hydrogenation of phenylacetylene to styrene and of cinnamaldehyde to hydrocinnamaldehyde and cinnamyl alcohol at 60°C [217].

See also [19,44,146,178,187,194,199,492].

7. Hydrogenation of Nitro Compounds

Rhenium(V) oxo complexes were used as catalysts for the hydrogenation of nitrobenzene to aniline at elevated pressure. The complex containing benzothiazoline as ligand was found to be the most active [218]. The Rh(I) complex [$Rh_2Cl_2(COD)_2$(phenazine)] was prepared and used as homogeneous catalyst for the hydrogenation of alkenes and aromatic nitro compounds in DMF solution at ambient conditions [219]. Hydrogenation of aromatic nitro compounds by H_2 is catalyzed by trans-$PdCl_2L_2$ (L = quinoline, isoquinoline) complexes in alkaline DMF solution. Formyl, carbonyl and nitrile groups are not hydrogenated under the same conditions [220]. Hydrogenation of p-nitrochlorobenzene was investigated using Pd complexes on polymeric supports as catalysts. Complexing increased the stability, activity, and selectivity for p-$ClC_6H_4NH_2$ of the catalysts; the best support was obtained by photochemical grafting of 4-vinylpyridine onto polyethylene [221]. Asymmetric hydrogenation of 3-nitrocaprolactam (72a) in the presence of $PdCl_2$ + (S)-PhMeCHNH_2 gave after workup with HCl the amine (72b) containing its L-(-)enantiomer in 11% excess. Acidic hydrolysis transformed (72b) into L-lysine [222].



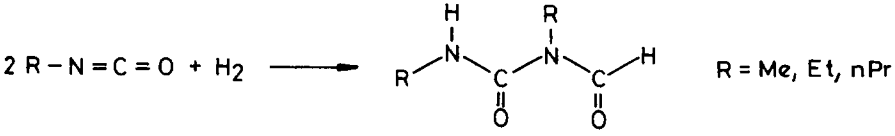
72a, R = NO_2

72b, R = $NH_2 \cdot HCl$

See also [101, 194, 223].

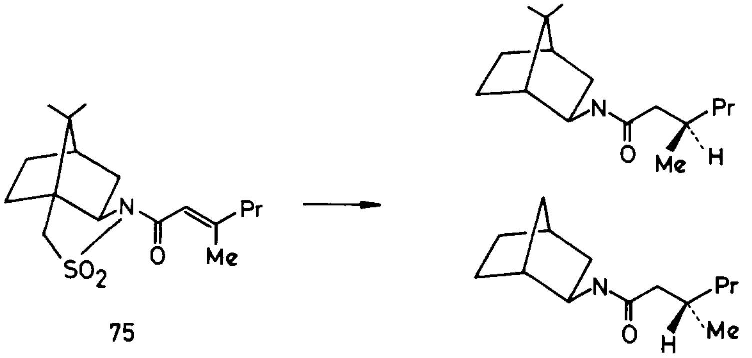
8. Miscellaneous Hydrogenations

The Mo(VI) complexes [(MeCp)Mo(μ-S)$]_2S_2CH_2$ and [(MeCp)Mo(μ-S)(μ-SH)$]_2$ could be used as homogeneous catalysts for the hydrogenation of a series of nitrogen-containing substrates at room temperature and 2-3 bar. Phenyl azide was converted to aniline, azo compounds to hydrazines, nitrobenzenes and phenylhydroxylamines to anilines, azoxybenzene to 1,2-diphenylhydrazine. The C=N double bonds in imines, isothiocyanates and isocyanates were also hydrogenated. The mechanism of the reaction is uncertain [223]. N-Alkylisocyanates (73) could be reductively dimerized to N-formylureas (74) with H_2 in the presence of $[H_3Ru_4(CO)_{12}]^-$ as catalyst precursor at 120°C and 50 bar. The role of the catalyst is probably the hydrogenation of the isocyanates to the corresponding formamides [224].



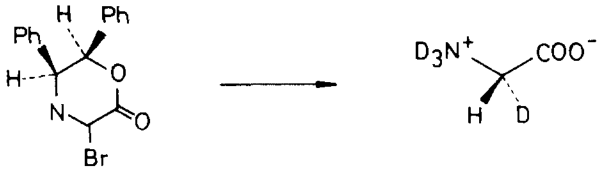
73 74

The olefinic sultam-imide (75) was stoichiometrically ($LiAlH_4$ + $CoCl_2$) and catalytically $[Ir(COD)(PCy_3)]^+PF_6^-$ or Pd/C hydrogenated to give (76) and (77). In all cases diastereoface discrimination favored the formation of (76); highest diastereoselectivity was obtained with the heterogeneous catalytic system [225].



75 76 77

The chiral glycine (79) was prepared by the hydrogenolysis of (78) with D_2 in the presence of catalytic $PdCl_2$ in D_2O/THF at 25°C. Optical purity of the product was about 80% [226].


78

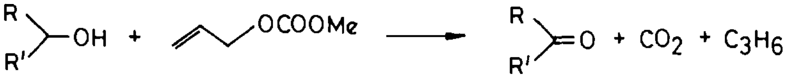
79

Uranium hydride UH_3 reduces PhX (X = Cl,Br,I) to PhH and PhPh, $PhNO_2$ to azoxy- and azobenzene, azoxybenzene to azobenzene, and Ph_3AsO to Ph_3As in boiling THF or at 130-170°C in the absence of added solvent. The low reactivity against organic substrates and the sensitivity towards oxygen do not recommend UH_3 as a synthetic reagent [227].

See also [194, 197].

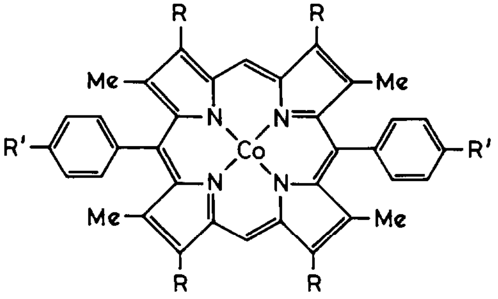
9. Dehydrogenation

Cycloalkanes were dehydrogenated to cycloalkenes and arenes stoichiometrically and in some cases catalytically by $[H_2Ir(Me_2CO)_2(PPh_3)_2](SbF_6)$. Multiple coordinative unsaturation was necessary for these reactions [228]. Dehydrogenation of secondary or allylic alcohols to ketones or α, β-unsaturated aldehydes was achieved with $H_2Ru(PPh_3)_4$ as catalyst and allyl methyl carbonate as hydrogen acceptor:



Ruthenium allyl complexes were proposed as intermediates of the catalytic cycle [229]. Dehydrogenation of iPrOH to acetone was investigated with Ir, Rh, Pt, and Ru complexes combined with $SnCl_2.2H_2O$ as catalyst under photoirratiation. Quantum efficiency was higher than unit in all cases; in one case (iridium) even the "photo-thermal energy conversion efficiency" was larger than one [230].

Dehydrogenation of tetralin to naphthalene is catalyzed at 200°C by the black solid formed from $CoCO_3$ (suspended in tetralin) and $AlEt_3$. The catalyst contains tetraline and naphthalene which can be extracted from it with Et_2O; the residue of this extraction is catalytically inactive. The activity of the system can be enhanced by adding $Rh(PPh_3)_3Cl$ which, however, is inactive with $AlEt_3$ alone [231]. The Co porphyrins (80) were tested as catalysts for the dehydrogenation of hydroquinone [233].



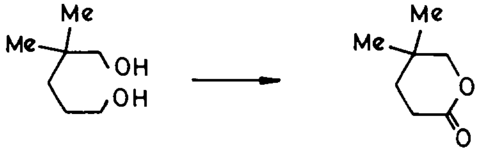
80

R = Me, Et

R'= H, Me, OMe, NO_2, NMe_2

Dehydrogenation of unsymmetrically substituted 1,4- and 1,5-diols is catalyzed by Ru- or Rh-phosphine complexes in the presence of H-acceptors like α, β-unsaturated ketones. The predominant products are β-substituted γ-lactones (81) and γ-substituted δ-lactones (82), respectively. $H_2Ru(PPh_3)_4$ [234] and $HRh(PPh_3)_4$ [235] were found to be the most active and selective catalysts. Using the corresponding complexes of DIOP some optical induction could be achieved [234-236].

81



82

Primary and secondary amines react with Fe(III) porphyrins by simultaneous ligation and dehydrogenation (P = porphyrin ligand):

$$2\ (P)Fe(III)Cl + 5\ RNH_2 \longrightarrow 2\ (P)Fe(II)(H_2NR)_2 + R'CH{=}NH + 2\ RNH_3^+Cl^-$$

Dehydrogenation starts by reversible outer-sphere electron transfer from amine nitrogen to the porphyrin ring. The reaction models the monoamine oxidase function of cytochrome P-450 [237]. See also [209, 239, 243].

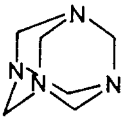
10. Hydrogen Transfer Reactions

a) Hydrogenation of C=C or C≡C bonds

Irradiation of $(Bu_4N)_4[Pt_2(P_2O_5H_2)_4]$ with light in a cyclohexene + iPrOH mixture resulted in the formation of cyclohexane and acetone. No photoreaction was observed with hexene-1 or hexene-2 [238]. Transfer hydrogenation of methyl linoleate to methyl oleate by iPrOH is catalyzed by $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$. Some transfer hydrogenation takes place also in n-octane as solvent, in this case the H-donor is methyl linoleate which is transformed into a conjugated triene [239]. Intramolecular H-transfer of 2-cyclohexene-1-ol to give cyclohexanone is catalyzed by $HCo[PPh(OEt)_2]_4$ under irradiation. The active catalyst is $HCo[PPh(OEt)_2]_3$. Addition of free phosphonite decreases conversion [240].

Hydrogen-transfer from methanol to diphenyl-acetylene was achieved with Ru-phosphine complexes as catalysts in toluene solution at 130°C. Methyl formate, trans-stilbene and bibenzyl were the products. If the reaction was carried out in the presence of ammonium acetate, hexamethylenetetramine was formed in quantitative yield according to the following equation:

$3\ PhC_2Ph + 6\ MeOH + 4\ MeCOONH_4 \longrightarrow$



$+\ 3\ PhCH_2CH_2Ph$

$+\ 6\ H_2O$

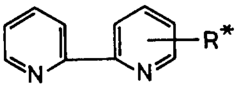
$+\ 4\ MeCOOH$

The formation of hexamethylenetetramine was obviously the result of trapping of formaldehyde formed as the primary product of methanol dehydrogenation [241].

b) Hydrogenation of C=O bonds

Various *p*-benzoquinones and 1,4-naphthoquinones were reduced to the corresponding hydroquinones by iPrOH with $Zr(OH)_2O$ as catalyst in very good yields [242]. Transfer hydrogenation of ketones by iPrOH and dehydrogenation of alcohols by benzaldehyde or benzophenone is catalyzed by Cp_2ZrH_2 at 130°C. The method is especially suitable for the dehydrogenation of primary alcohols to aldehydes [243].

Alkyl aryl ketones were hydrogenated to benzylic alcohols using iPrOH as hydrogen source and an *in situ* Rh catalyst formed from $[Rh(1,5\text{-hexadiene})Cl]_2$, methionine sulfoxide, and KOH. Reaction rates were low but optical yields up to 75% were achieved [244]. Transfer hydrogenation of aldehydes and ketones with iPrOH as H donor and $[Rh(NBD)L_2]^+$ complexes as catalysts (L = *p*-substituted triphenylphosphines) in the presence of iPrONa was investigated. The rate increased with increasing electron-donating property of the substituents [245]. The new chiral 2,2'-bipyridines (83) were synthesized and used as ligands in the transfer hydrogenation of acetophenone by iPrOH in the presence of $[Rh(COD)Cl]_2$ as catalyst. Optical yield was 15% in the best case [246].



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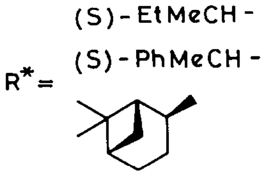


Asymmetric hydrogen transfer from iPrOH to prochiral ketones is catalyzed by Rh and Ir complexes of the chiral diphosphines DIOP, prophos (27), and chiraphos. The catalysts have to be activated by first treating them with KOH; catalytic activity and especially optical yield depend on activation time. Highest o.y. (58%) was achieved with an Ir/prophos catalyst and acetophenone [247]. The complexes formed *in situ* from Ir(COD)(acac) and the phosphines $P(men)Ph_2$, $P(men)_2Ph$ and $P(nmen)Ph_2$ proved to be active catalysts in the hydrogen transfer reaction from iPrOH to prochiral ketones. When acetophenone was used, optical yields up to 42% were achieved [248]. The complexes $HIr(COD)L_2$ (L = PPh_3, $AsPh_3$; L_2 = dppe, dppp) were used as catalysts for the transfer hydrogenation of cyclohexanone using iPrOH, EtOH or MeOH as H-donors. Cocatalysts like KOH were not necessary for catalytic activity [249].

c) Hydrogenolysis by Hydrogen Transfer

See [229].

11. Reduction without Molecular Hydrogen

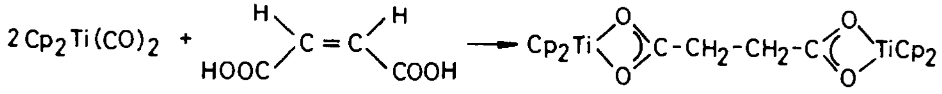
a) Transition Metal Hydrides

The binuclear rhodium hydride (84) hydrogenates phenylacetylene to styrene. This reactions shows CIDNP which was explained by the reversible formation of the metal-centered biradical isomer (85) which is the active hydrogenating agent [250].

84 85

b) Low Valent Transition Metal Complexes

Unsaturated dicarboxylic acids (e.g. maleic acid) react with $Cp_2Ti(CO)_2$ to give Ti(III) carboxylato complexes (86) containing the saturated carboxylic acid. Experiments with deuterium-labeled substrates proved that the hydrogen source is the carboxylic acid -OH group [251].



86

Reduction of α,β-epoxy ketones (e.g. 87) with SmI_2 yields β-hydroxy ketones in good yields. Stereochemistry is retained β to the carbonyl group but is lost at the α-position. The mechanism of reduction probably resembles that of dissolving metal reductions of ketones [252].

87

Functionalized vinyloxiranes like (88) have been found to undergo facile reductive epoxide ring opening with SmI_2 in THF in the presence of a proton source to provide (E)-allylic alcohols (89). The reactions take place already at -90°C and yields above 70% can be achieved in most cases [253].

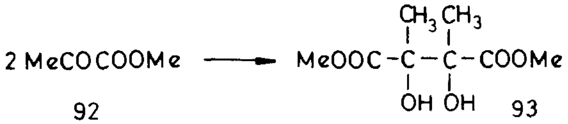
R=COOEt, CN, COMe

88 89

Several α-ketocarboxylic acids and α-dicarbonyl compounds were reduced by $TiCl_3$ to the corresponding α-hydroxycarboxylic acids and α-hydroxyketones, respectively [254]. Tricyclic epoxides like (90) were successfully deoxygenated to the corresponding olefins (91) in a one-step procedure using 2 equivalents of WCl_6 in refluxing THF [255].

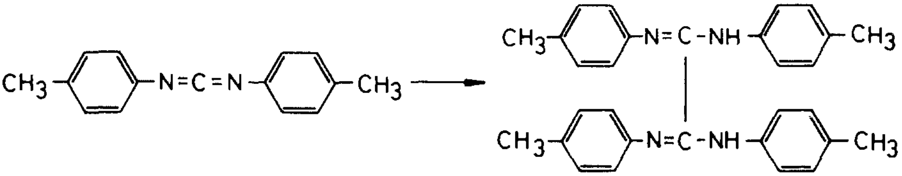
90 91

The bifunctional complex [Co(salen)Na(THF)] promotes the reductive coupling of methyl pyruvate (92) to dimethyl dimethyltartrate (93) and of p-tolylcarbodiimide (94) to tetra-p-tolyloxalamide (95); the reductant is transformed into Co(salen) [256].



$$2\,\mathrm{MeCOCOOMe} \longrightarrow \mathrm{MeOOC{-}\overset{CH_3}{\underset{OH}{C}}{-}\overset{CH_3}{\underset{OH}{C}}{-}COOMe}$$

92 93

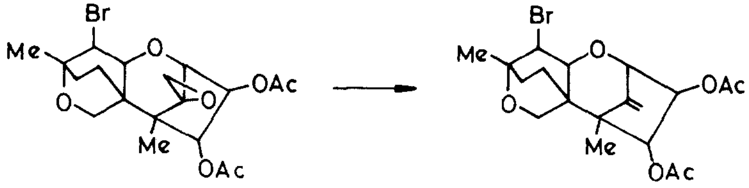


94 95

Reduction of substituted nitrostyrenes with aqueous $TiCl_3$ gave pyrroles, oximes, and in some cases divinylamines. Thus $PhCH{=}CHNO_2$ could be reduced in aqueous THF to 3,4-diphenylpyrrole [257]. Arylnitroalkenes $ArCH{=}CRNO_2$ were reduced to the corresponding oximes $ArCH_2CR{=}NOH$ by $CrCl_2$ with 15-17% yields [258]. The kinetics of the reduction of bromamine-T by $[Fe(CN)_6]^{4-}$ was determined [259]. The biphasic reduction of benzylic thiols with $Fe_3(CO)_{12}$ and HBF_4 in benzene afforded desulfurized products in good yields [260].

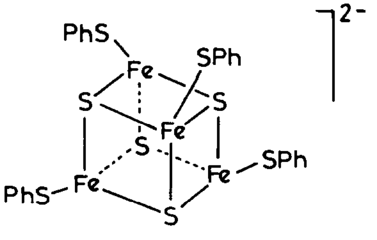
c) Inorganic Reductants in the Presence of Transition Metal Complexes

The epoxide (96) was deoxygenated to the corresponding alkene (97) by WCl_6 + BuLi in refluxing THF with 98% yield [261].



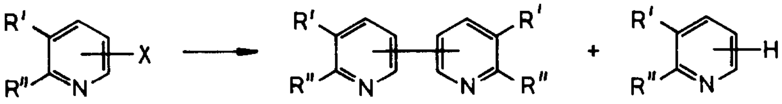
96 97

The Fe-S cluster (98) acts as an electron transfer agent in the reduction of S-phenyl thiobenzoate and phenyl benzoate with nBuLi and PhLi to give benzil and benzoin along with coupling products formed from the substrates and the reductants. If $FeCl_3$ was used instead of the cluster, practically only these coupling products were formed [262].



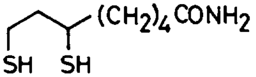
98

The activity of the complex reducing agent obtained from tBuOH, NaH and Ni acetate could be significantly increased for the reduction of olefinic double bonds by the addition of Me_3SiCl [263]. The reagent prepared from tBuOH, NaH, PPh_3, and Ni acetate in an etheral solvent was found to be very effective for the reductive coupling of heteroaromatic halides (99, R′ and R″ = = H, Me, MeO, C_4H_4). Chlorides or bromides were better than iodides which often led to significant amounts of reduced byproducts (100) [264].



99 100

Reduction of alkyl and aryl halides by iPrMgBr, KBH_4 or $LiAlH_4$ is catalyzed by Ti complexes. A catalyst system containing Cp_2TiCl_2 and iPrMgBr was found to be the most effective [265]. The nitrogenase iron center model compound $(Et_4N)_4[Fe_6S_9(SCH_2CH_2OH)Cl]$ was prepared and its catalytic activity for the reduction of acetylene to ethene by KBH_4 determined [266]. Reduction of acetylenes to olefins was performed by $NaBH_4$ in the presence of $FeCl_2$ and dihydrolipoamide (101) or a similar dithiol as catalyst systems. Best results were obtained with a catalyst containing equimolar amounts of Fe(II) and dithiol. Hydrogen transfer probably took place within an iron-dithiol-acetylene complex and $NaBH_4$ served to regenerate the starting complex [267].

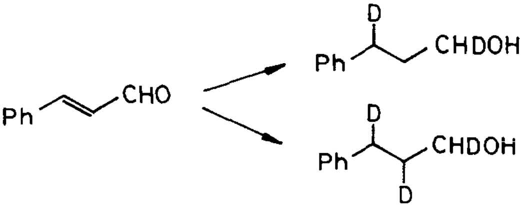


101

The mechanism of reductions performed with $NaBH_4$ or $LiAlH_4$ and assisted by $CoCl_2$ was investigated. In the three cases examined (reduction of nitriles, alkenes or alkyl halides) it was found that the cobalt boride (or aluminide) formed as a black precipitate acted as a heterogeneous catalyst [268]. Aerobic reduction of ketones with $NaBH_4$ in THF is catalyzed by Rh(TPP)Cl or Rh(OEP)Cl according to the following stoichiometry:

$$2\ R_2C{=}O + [BH_4]^- + O_2 \longrightarrow 2\ R_2CH\text{-}OH + [BO_2]^-$$

A rhodium hydride is an intermediate of the catalytic cycle, the actual reductant is borane [269]. Copper(II) and $NaBH_4$ in MeOH solution was found to be an efficient, mild reagent for the reduction of aryl and tertiary aliphatic nitro groups in the presence of other functionalities. If the $Cu^{2+}/NaBD_4$ system was used for the reduction of cinnamaldehyde, the deuterated alcohol (102) was produced. The analogous reductants $Ni^{2+}/[BD_4]^-$ and $Co^{2+}/[BD_4]^-$ furnished the deuterated akcohol (103) under such conditions [270].



102

103

Diisobutylaluminium hydride reduces α,β-unsaturated carbonyl compounds to saturated carbonyl compounds if HMPA is present. It has now been found that the addition of MeCu (prepared in situ from MeLi and CuI) dramatically increases the activity and selectivity of this reagent. The new reducing system transformes doubly unsaturated carbonyl compounds [104] to β,γ-unsaturated carbonyl compounds (105) [271].

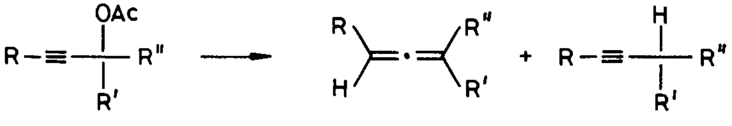
104

105

Reduction of (E)-1,3-dichloropropene by Bu_3SnH is catalyzed by $Pd(PPh_3)_4$ and yields only two of the three possible 1-chloropropenes (the Z and E isomers of 1-chloropropene-1). The results support an allylpalladium complex as intermediate [272]. Applying the same method for the reduction of 1,1,1,4-tetrachlorobut-2-ene, 1,1-dichlorobutadiene was observed as the only product. In this case an oxidative addition- β-elimination process leading to the product and a Pd(II) species was proposed as the probable pathway for the reaction. Reduction of Pd(II) to Pd(0) by Bu_3SnH completes the catalytic cycle [273]. Reduction of methylene blue by $SnCl_2$ in acid media is catalyzed by NH_4TcO_4. The catalytically active form of technetium is probably Tc(V) [274].

Octene-1 is transformed into octane in MeOH containing aqueous KOH and $Ru(PPh_3)_3Cl_2$ or $Rh(PPh_3)_3Cl$ if KH_2PO_2 is present. No hydrogenation takes place in the absence of hypophosphite which apparently serves as the H donor [275].

Propargylic acetates (106) were reduced to allenes and alkynes by SmI_2 in the presence of $Pd(PPh_3)_4$ as catalyst. tert-Acetates yielded allenes exclusively; allene-selectivity was decreased in cases of sec-acetates and from primary acetates mainly alkynes were formed [276].

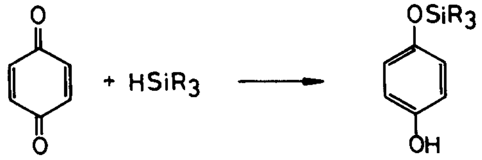


106

See also [225].

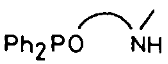
d) Reduction via Silylation

The homogeneous reductive silylation of quinones to hydroquinone monosilyl ethers (107) was found to be catalyzed by $Rh(PPh_3)_3Cl$ in refluxing benzene [277].



107

α,β-Unsaturated ketones and aldehydes were selectively reduced at the olefinic double bond using a three-component system comprised of $Pd(PPh_3)_4$, Ph_2SiH_2 and $ZnCl_2$. The reduction of α,β-unsaturated carboxylic acid derivatives was very sluggish under the same conditions [278]. Several chiral aminophosphinites (108) and aminophosphine-phosphinites (109) were tested as ligands in the asymmetric hydrosilylation of acetophenone catalyzed by Rh complexes. Enantioselectivity of the catalyst was determined after hydrolyzing the product and measuring the optical purity of α-phenyl ethanol. Highest o.y. (43%) was obtained with the ligand (110) and (α-naphthyl)$PhSiH_2$ [279].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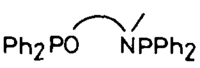
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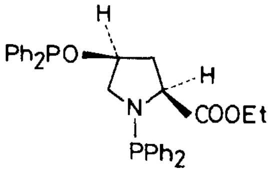
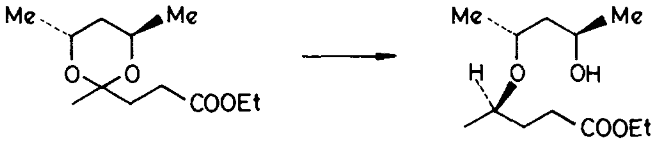
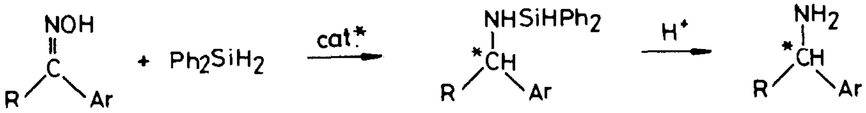

110

Reductive cleavage of acetals to ethers was performed with $TiCl_4$ + Et_3SiH. The reaction is highly chemoselective: for example, the acetal (111) could be transformed into the ether (112) without reduction of the ester group [280].


111 112

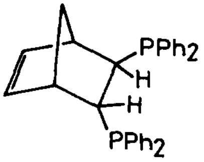
Alkyl aryl ketoximes (113) were shown to undergo hydrosilylation with Ph_2SiH_2 in the presence of Rh(I)-phosphine catalysts. The resulting silylamines (114) yielded amines on hydrolysis and accordinly this method could be used for the reduction of oximes to amines. Using prochiral ketoximes and <u>in situ</u> catalyst systems composed of $[Rh(NBD)Cl]_2$ and a chiral phosphine like (-)-DIOP or (-)-norphos (115), optical inductions up to 36% were achieved [281].



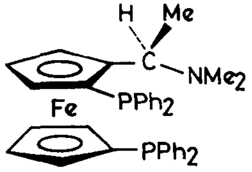
113 114

e) Organic Reductants in the Presence of Transition Metals

The use of 80% aqueous formic acid for enantioselective transfer hydrogenation of N-acyl dehydroaminoacids using Rh(I) complexes of the ligands norphos (115), prophos (27), DIOP, and (116) was described. Addition of HCOONa increased the optical induction which in some cases exceeded the values obtainable with H_2 [282].

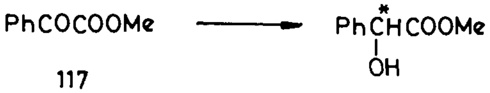


115 ; (-)-norphos



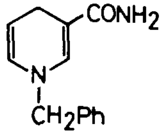
116 (-)-BPPFA

The reduction of phenylglyoxalate (117) to give methyl mandelate by the NADH model compounds (118) or (119) is catalyzed by Lewis acids. Using chiral europium β-diketonates (shift reagents) as Lewis acids optical yields up to 55% were achieved [283].

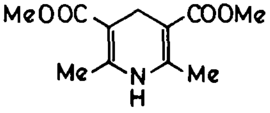


$$\text{PhCOCOOMe} \longrightarrow \text{Ph}\underset{\substack{|\\ \text{OH}}}{\overset{*}{\text{C}}}\text{HCOOMe}$$

117

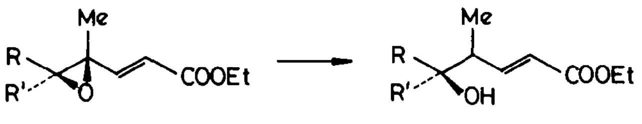


118



119

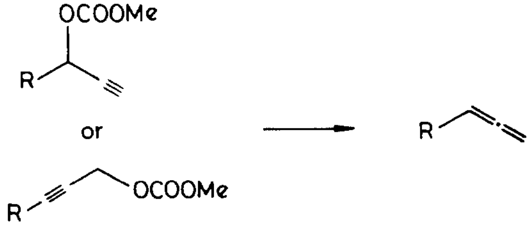
The epoxides (120) were transformed into the hydroxy alkenoates (121) by stereospecific hydrogenolysis with ammonium formate catalyzed by Pd(0)-phosphine complexes. Yields were around 80% [284].



120 121

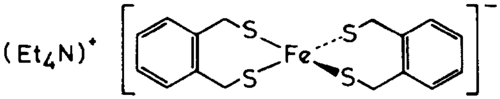
R	R'
Ph	H
Et	H
H	Et

1,2-Dienes (123) were prepared by the selective hydrogenolysis of alkynyl carbonates (122) with ammonium formate catalyzed by $Pd_2L_3.CHCl_3$ + PBu_3 (L = dibenzylideneacetone) at 30°C. At 65°C the dienes were reduced to alkanes [285].



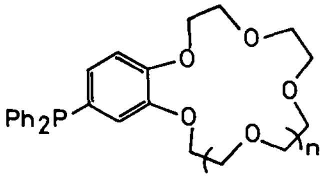
122 123

The hydrogenating activity of the $HCOOH/Et_3N/Ru(PPh_3)_3Cl_2$ system (AS 1985, ref. 274) could be increased by the addition of Pd on carbon. This new combined reagent enabled the selective reduction of nitro groups in the presence of many functional groups (olefins, ketones and aromatic halides) [286]. Complex (124), an analog of rubredoxin active sites, catalyzes the reduction of aromatic nitro compounds to N-aryl hydroxylamines and anilines by o-xylene- α,α -dithiol. The reduction can also be achieved by using $FeCl_2$ and Et_4NCl as catalyst since under such conditions complex (124) is formed in situ [287].



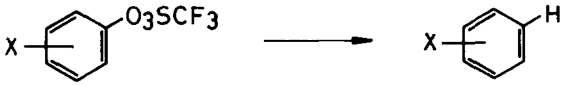
124

The ion pair formed from $RhCl_3.3H_2O$ and methyltrioctylammonium chloride was shown to catalyze the hydrogen transfer from polymethylhydrosiloxane to acetylenes, olefins and acid chlorides. The catalyst could be recovered in the form of $NaRhCl_4$ by addition of $NaClO_4$ and after addition of the quaternary ammonium salt could be again transformed into the catalytically active species [288]. Allyl chlorides and allyl acetates could be reduced by aqueous HCOONa to the corresponding olefins by using water-soluble Pd phosphine complexes as chemical and phase-transfer catalysts in a heptane-water two-phase system. The reaction took place in the aqueous phase [289]. In a similar system, crown-functionalized triarylphosphines (125) were used as ligands in the reduction of 1-chloromethylnaphthalene to 1-methylnaphthalene with formate salts, catalyzed by Pd complexes. In this case the reaction was taking place in the organic phase [290].



125; n = 1, 2

Reductive dehalogenation (hydrogenolysis) of organic halides was achieved by $Pd(PPh_3)_4$ as catalyst and polymethylhydrosiloxane or sodium formate as hydrogen donor in $MeCN/Me_2SO$ solvent. Unsaturated functional groups like nitro, aldehydes, olefins, and ketones were found to tolerate these reaction conditions [291]. Phenol could be selectively deoxygenated by reduction of the corresponding aryl triflates (126) with formic acid and Et_3N in the presence of $Pd(OAc)_2$ and a tertiary aromatic phosphine. Unsaturated functional groups (X) like nitro, ketones, esters, and olefins were found to tolerate the reaction conditions well [292].



126

f) Electroreduction and Photoreduction

Electrochemical reduction of $HOCH_2CH_2N_3$ and MeN_3 was performed with a $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$-modified glassy-carbon electrode in water or with the same complex in MeOH/THF with a Hg electrode. Ammonia, hydrazine, N_2, and the corresponding primary amines were formed. The system based on the glassy-carbon electrode was far more efficient [293]. Heat-treated Co(TPP-OMe-p) showed a significant catalytic effect on the electroreduction of cystine and improved current efficiency [294]. Functionalized or non-functionalized aliphatic halides were electrochemically reduced in DMF or N-methylpyrrolidone and with $Ni(bpy)Br_2$ as catalyst. In the case of secondary or tertiary halides, alkanes and alkenes were the main products; primary halides were transformed mainly into dimeric products [295].

Water-soluble polymer-supported metal phthalocyanines were used to catalyze the photoreduction of methyl viologen by visible light in aqueous solution. The Ni and Cu complexes showed catalytic activity [296]. The Ru(II)-tris(1,4,5,8-tetraazophenanthrene) dication proved to be a better photocatalyst for the reduction of methylviologen (MV^{2+}) to $MV^{\cdot +}$ than $Ru(bpy)_3^{2+}$ [297]. Bis(phthalocyaninato) complexes of several lanthanoid(III) ions (Lu, Er, Y, Gd, Eu, Sm, Nd, and La) catalyze the photoreduction of methylviologen in methanol. Relative quantum yields decrease in the stated order [298].

IV. Oxidation

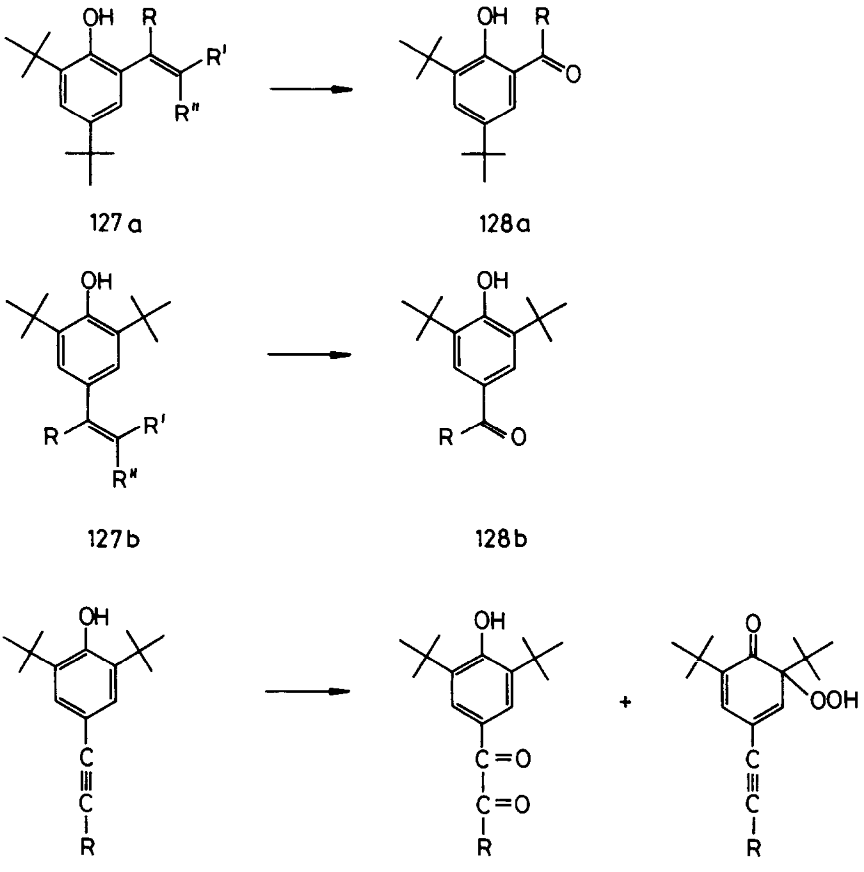
1. Catalytic Oxidation of Hydrocarbons or Hydrocarbon Groups with O_2

a) Oxidation of Alkanes

The effect of individual and polymetal salts of Co, Cr, and Mn on oxidation of paraffins was examined [299]. Oxidation of cyclohexane by ozone-air in the presence of $Cr(CO)_6$ gave cyclohexanone with 84-89% selectivity at low conversions. Cr(III), Cr(IV), and Cr(VI) were present in the system [300]. Hydroxylation of cycloalkanes was carried out with oxygen in CF_3COOH + py as solvent using $Fe_3O(OAc)_6py_{3.5}$ as catalyst and a cathode as reductant. The active form of reduced oxygen in this electrochemical system is probably superoxide. Ketones were the main products and coulombic yields as high as 49% were attained [301,302]. Oxidation of alkanes in the presence of $Ni(st)_2$ resulted in high selectivities for hydroperoxides and carbonyl compounds and a higher content of carboxylic acid in the product [303].

b) Oxidation of Olefins or Alkynes

Oxidation of 2-alkenyl and 4-alkenyl-di-*tert*-butylphenols (127) promoted by Co(salpr) leads selectively to the incorporation of oxygen into the side chain and thus to the formation of the corresponding carbonyl compounds (128). In the case of the alkynyl derivative (129), oxygen is incorporated both into the side chain (product 130) and into the ortho position (product 131) [304].



127a 128a

127b 128b

129 130 131

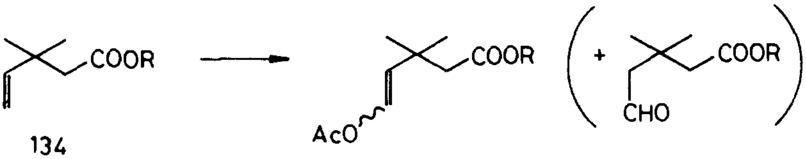
The cleavage of olefins at the double bond by O_2 to give carbonyl compounds is catalyzed by several Rh complexes, e.g. $Rh(PPh_3)_3Cl$. The reaction requires enhanced concentrations of O_2 in solution [305]. Homocooxygenation of COD by O_2 to give cyclooctadiene-1,4-dione occurs in the presence of $RhCl(PPh_3)_3O_2$ as catalyst. Some Ph_3PO is also formed. Isotopic labeling experiments showed that both O atoms in the complex are transferred to the same diene molecule [306]. Cationic Rh complexes containing bidentate ligands $[Rh(LL)]BF_4$ (LL = dppe or $Ph_2P(CH_2)_2SPh$) were used to catalyze the air oxidation of olefins. Formation of ketones was the predominant reaction in the case of terminal linear alkenes while cycloolefins and branched terminal olefins mainly yielded products of allylic oxidation. Some epoxidation occurred in all cases [307]. Homogeneous oxidation of octene-1 by O_2 or tBuOOH catalyzed by Rh(III) or Pd(II) species was studied using isotopically labeled O_2 and octene-1. Oxidation of olefin became catalytic only in the presence of oxidizable alcohols. Hydrido complexes were supposed as intermediates [308].

Oxidation of cyclopentene to cyclopentanone is catalyzed in ethanol solvent by $PdCl_2$ or, more effectively, by $[PdCl_2(N,N\text{-diethylacetamide})_2]$. One mole ketone is produced by one mole O_2; the active species is probably a palladium hydroperoxide which may be formed from a palladium hydride which, in turn, derives its H from ethanol [309]. The giant cluster $[Pd_{561}(phen)_{80}](PF_6)_{60}$ was prepared and found to be more active as a catalyst in the oxidation of ethene to vinyl acetate than the analogous $[Pd_{561}(phen)_{60}](OAc)_{180}$ [310].

Aldehydes were the major products of the catalytic oxidation of 1-alkenes with air using a catalyst that comprises $(MeCN)_2PdClNO_2$, $CuCl_2$, and a tertiary alcohol. No aldehydes were formed when either $CuCl_2$ or the tertiary alcohol were omitted from the catalyst system [311]. Wacker-oxidation ($PdCl_2$, CuCl, O_2, H_2O) of the two diastereomers of alkene (132) yielded the corresponding benzoyl derivatives (133) in about 40% yield. The isomeric phenylacetyl derivatives were not formed [312].

132 133

Selective terminal oxidation of 3,3-dimethyl-4-pentenoates (134, R = Me,Et) was achieved under Wacker-conditions in AcOH if no chloride was present in the reaction mixture. In the presence of chloride, the corresponding methyl ketones were obtained [313].



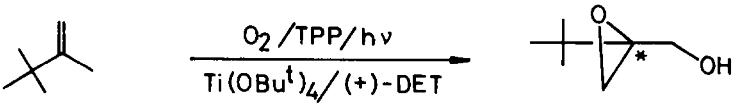
134

Olefins were oxidized to ketones by O_2, $PdCl_2$, $CuCl_2$, and water using a cyclodextrin to transfer the organic molecules into the aqueous phase. The relative reactivity of cyclodextrins as phase transfer agents for the oxidation of 1-decene to 2-decanone was $\beta > \alpha > \gamma$ [314]. Based on the unexpectedly high trans influence of the OH^- ligand it was proposed that the rate-determining step of the Wacker-oxidation of ethene is the attack of H_2O on $PdCl_2(OH)(C_2H_4)^-$ [315].

See also [364].

c) Epoxidation of Olefins

The reaction of singlet oxygen with alkenes in the presence of Ti alkoxides was employed to prepare epoxy alcohols. If diethyl tartrate was used as chiral auxiliary the reaction could be performed with high enantioselectivity; e.g. in the case of (135) the (S)-enantiomer of (136) was formed in 72% o.y. [316].



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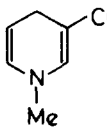
136

Olefins could be epoxidized by O_2 in the presence of Mn(TPP)Cl, 1-Me-imidazole (as axial base), and benzoic anhydride if electrolytic reduction was applied. Faradaic efficiency of the system was 56% which is high if compared to analogous systems using chemical reductants [317]. The catalytic system composed of the NADH analogue (137), flavin mononucleotide (138), N-methylimidazole, Mn(tetraphenylporphyrintetrasulfonate) and benzoic anhydride (or benzoic acid) was found to be a highly efficient catalyst for the epoxidation of olefins with O_2. Any system lacking one of the components did not show activity; if Mn was replaced by Fe the activity was much lower. Significantly, the structure of each component is very close to that of the native P-450 system [318].



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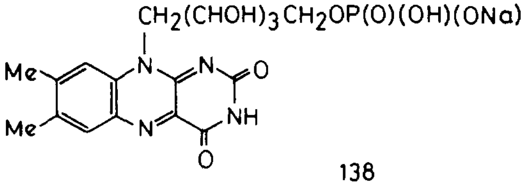

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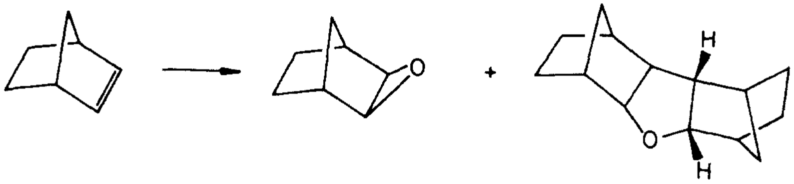
Air oxidation of norbornene catalyzed by $(MeCN)_2PdCl(NO)_2$ furnished as the main product exo-epoxynorbornene (139) at low concentrations and a tetrahydrofuran derivative (140) at high concentrations [319].



139 140

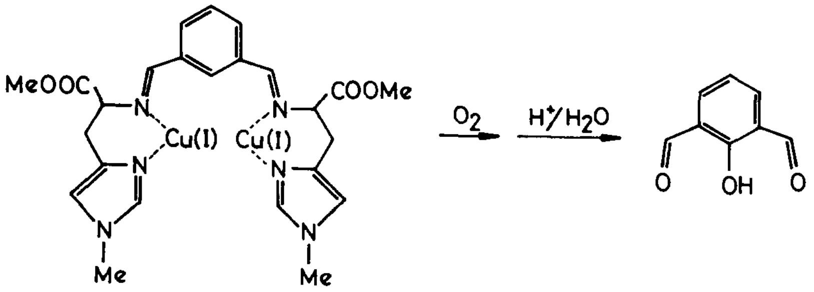
See also [307, 346].

d) Oxidation of Aromatics

Aromatic hydrocarbons were effectively hydroxylated by the artificial P-450 type catalytic system consisting of (TPP)MnCl, N-methylimidazole, colloidal Pt, O_2 and H_2. Addition of HCl increased the overall turnover number [320]. The kinetics of oxidation of m-diisopropylbenzene with O_2 in the presence of $Mn(st)_2$ as catalyst was determined and the reaction conditions were optimized for the formation of the dihydroperoxide [321].

The formation of volatile (C_2-C_6) monocarboxylic acids from coal during oxidation in the presence of RuO_4 as catalyst was studied. The results provided information concerning the distribution of alkyl groups within the coal sample [322].

The reduction of $Co(OAc)_3$ by xylene was studied as part of the catalytic oxidation of xylene with O_2 in the presence of a $Co(OAc)_2$ + NaBr catalyst [334]. The complex formation between $CoBr_2$ and chloro-substituted alkylaromatic compounds has been studied by NMR. It could be shown that the catalytic activity of $CoBr_2$ in the oxidation of these alkylaromatic compounds with O_2 increases with decreasing stability of the complexes [335]. Oxidation of ethyl-



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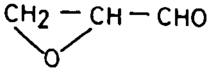


143

A heterogeneous-homogeneous mechanism was demonstrated for the oxidation of anthracene to anthraquinone by O_2 in the presence of Ag ketenide [342].

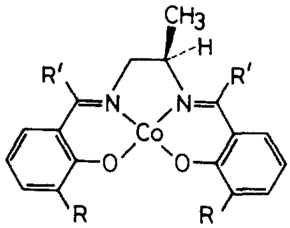
See also [304].

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

a) Oxidation of Alcohols

The heteropolyacids $H_6[CoW_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, and $H_3[PMo_{12}O_{40}]$ anchored to poly(4-vinylpyridine) were used as catalysts for the oxidation of primary diols [343]. Photocatalytic oxidation of iPrOH by O_2 catalyzed by $(Bu_4N)_4(W_{10}O_{32})$ in acetonitrile was studied. A mechanism was suggested which involves oxidation of the substrate by the decatungstate and reoxidation of the 2e-reduced species by O_2 [344]. The kinetics of cyclohexanol oxidation by O_2 catalyzed by Ru(III) and Ru(III)-EDTA complexes was studied at 30°C. The reactions were first order each in substrate and catalyst. EtOH was not oxidized under the reaction conditions [345]. Oxidation of allyl alcohol by O_2 catalyzed by Ru(III) chloride was investigated in the pH range 1-3. Different reaction kinetics were found below and above pH 2.0. The product of oxidation was acrolein at pH 1.5 and glycidaldehyde (143) at pH 2.5 [346].

The reactivity of coordinated dioxygen in $CoL_4(B)(O_2)$ complexes toward H abstraction is controlled by electron transfer from Co to O_2. Low electron transfer enhances reactivity but is at the same time associated with low affinity toward O_2. These two effects determine the catalytic activity of such complexes for the oxidation of secondary alcohols [347]. The rate of oxidation of 2-ethylhexanol by O_2 in the presence of Co 2-ethylhexanoate is mainly determined by the reactions of Co(III) with the substrate and the 2-ethylhexanal intermediate [348]. Oxidation of α -phenylethanol by O_2 to acetophenone (and H_2O_2 as byproduct) is catalyzed by Co(salen) in the presence of PPh_3. The rate-determining step is the abstraction of the α -hydrogen atom by the O_2 coordinated to Co. In a side reaction PPh_3 is oxidized by H_2O_2 to $OPPh_3$ which leads to the deactivation of the catalyst [349]. The chiral Co(II) Schiff-base complexes (144) were used as catalysts for the oxidation of racemic 1-phenylethanol by O_2 to acetophenone; PPh_3 or $P(OMe)_3$ were used as axial ligands. The two enantiomers of the substrate were oxidized at different rates leading to partial kinetic resolution of the unconverted alcohol. Best enantioselectivity was obtained with PPh_3 and (144c) [350].



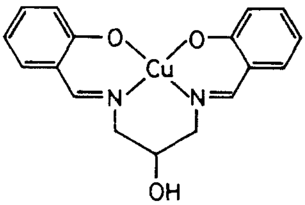
144a ; R, R' = H

144b ; R = OMe, R' = H

144c ; R = H, R' = Me

The giant Pd cluster $Pd_{561}phen_{60}(OAc)_{180}$ catalyzes the oxidation of alcohols by O_2 to aldehydes or ketones; the aldehydes are subsequently transformed into esters [351].

Oxidation of alcohols to aldehydes or ketones with O_2 and catalyzed by Cu(I) complexes was investigated using different ligands and counteranions. Effectivity of the complexes decreased in the order 4,4'-Me_2bpy > bpy > phen and Cl^- > Br^- > I^-. No detectable product was found with imidazole or py as ligand [352]. The Cu(II) complex (145) was shown to catalyze the oxidation of aliphatic alcohols to aldehydes by O_2 in the presence of KOH [353].



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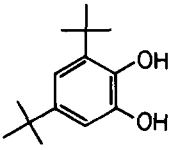
b) Oxidation of Phenols

The reaction of Mo(3,5-tBu$_2$-catecholato)$_3$ with O$_2$ gives 3,5-di-tBu-1,2-benzoquinone and Mo$_2$O$_2$(3,5-tBu$_2$-catecholato)$_4$. This reaction constitutes one step of the reaction scheme describing the oxidation of catechol with O$_2$ to benzoquinone through a series of well-characterized Mo complexes [354].

According to NMR and Moessbauer spectra of the reaction mixtures, the oxidation of catechols with O$_2$ in the presence of pyridineiron(III) complexes probably proceeds via semiquinonato-Fe(II) complexes as intermediates [355]. Oxygenation of (146) by O$_2$ in the presence of an Fe(III)-bpy-py complex formed in situ from FeCl$_3$ (dissolved in THF) and the ligands was studied. The reaction proceeded by the formation of a catecholate complex, reaction with O$_2$ to form peroxide intermediates and incorporation of one of the oxygen atoms accompanied by ring opening. Final products of this process were (147), (148), and (149) [356].



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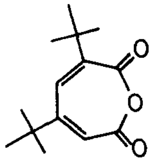

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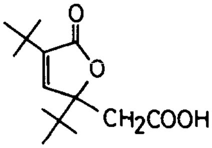

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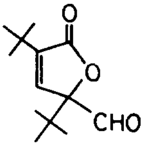

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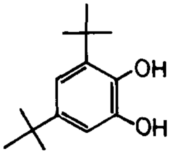

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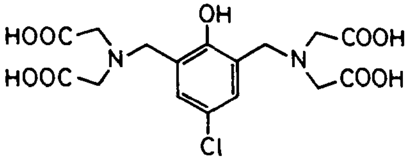

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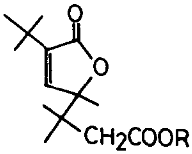
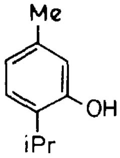


152

Oxidation of (150) with O$_2$ was studied in the presence of various catalyst systems. Thus the binuclear complexes of Fe,Cu, Co, and Mn with the multidentate ligand (151) were tested as catalysts. The Cu,Co, and Mn complexes promoted the selective formation of the corresponding benzoquinone but with the iron complex also the lactone (152) was formed [357]. Oxidation to the corresponding quinone in a nonaqueous phase has been investigated using $Co(acac)_2$ [358] and $[CuCl(py)]_n$ [359] as catalysts. In the case of the Co catalyst the byproduct of the oxidation was found to be water and no H_2O_2 could be detected. The decomposition of a catechol-$Co(acac)_2$-O_2 complex was assumed to be the rate-determining step. With the Cu catalyst no ring cleavage could be observed and the reaction could be used for the preparation of the o-quinone. The formation of a dinuclear peroxo complex was proposed as the rate-determining step.

Oxidation of phenols to quinones by O_2 catalyzed by Co-Schiff base complexes was investigated in different solvents [360]. Oxidation of di-, tri-, and tetramethylphenols to p-quinones by O_2 was studied in the presence of Co(salen) and other Co(II) Schiff base complexes as catalysts. No reaction was observed under the conditions used in the case of o-cresol [361]. Thymol (153), carvacrol (154) and o- and m-cresol were oxidized with O_2 and Co salen as catalyst to the corresponding p-benzoquinones with high yields [362].



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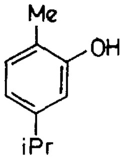
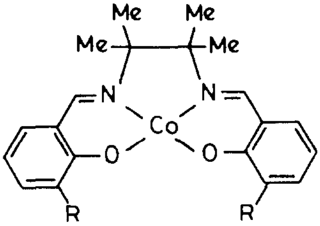


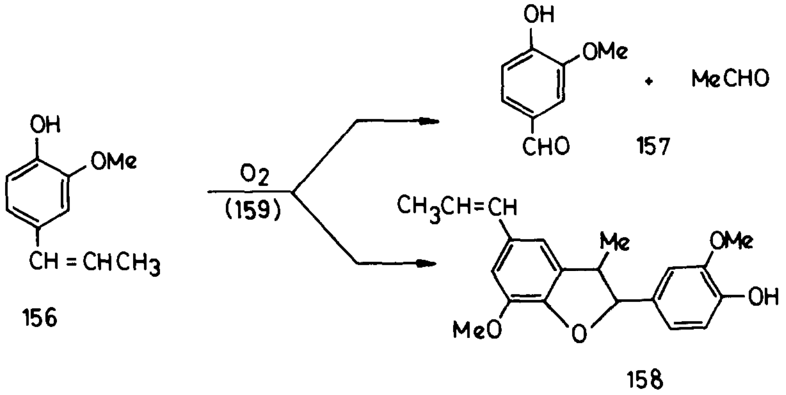
154

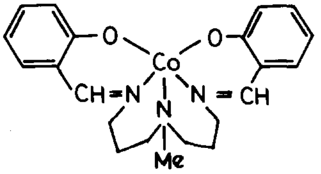
The Co(II) Schiff base complexes (155) were found to be useful catalysts for the oxidation of 2,6-dimethylphenol by O_2 to the corresponding p-benzoquinone. Although their activity was lower than that of the analogous ethylenediamine-derived Schiff base complexes their stability against oxidative decomposition was better [363].



155 R = H, OMe

Oxidation of isoeugenol (156) to vanillin (157) was performed with O_2 and the Co(II) complex (159) as catalyst. Selectivity of the reaction was about 75% and dehydroisoeugenol (158) was formed as byproduct [364].





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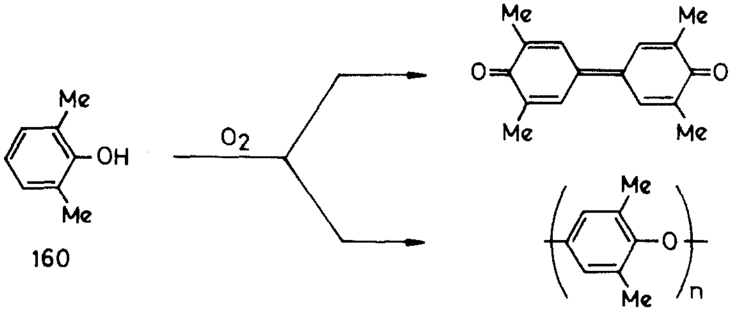
The direct air oxidation of phenol to p-benzoquinone is catalyzed by Cu(I) and Cu(II) complexes in polar aprotic solvents; some of the catalyst systems achieve > 90% selectivity. Binucleating ligands enhance o-quinone formation. The Cu catalysts used for oxidation also catalyse the hydrogenation of benzoquinone to hydroquinone thus affording a convenient one-pot preparation of the latter [365]. Mononuclear and dinuclear Cu(II) Schiff base complexes were tested as catalysts for the air oxidation of (150) and 4-methylcatechol. In general, complexes containing pyrrolic residue exhibited the highest reactivity. Mononuclear complexes were found to be more active for the oxidation of (150) and dinuclear complexes were more active in the oxidation of 4-methylcatechol [366]. The catalytic activity of the Cu(II) complex of partially N-ethylated poly(4-vinylpyridine) in the oxidation of hydroquinone was studied [367]. Catalytic oxidation of hydroquinone was performed in the presence of alginate-Cu(II) membranes prepared from Na-alginate membranes and aqueous solutions of $CuCl_2$. Oxidations followed a Michaelis-Menten type kinetics [368]. Oxidation of (160) to (161) and (162, polyphenylene oxide) by O_2 and catalyzed by Cu(II) complexes of 4-(N,N-dimethylamino)pyridine (DMAP) has been studied. It was concluded that both mono- and dinuclear complexes were active, the most active species being Cu(DMAP)$_4$Cl(OH). Using a DMAP:Cu ratio of 4:1, Cl^- as the counter-ion and adding OH^- to the reaction mixture increased the yield of the desired product (162) above 95% [369].



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162

c) Oxidation of Aldehydes and Ketones

Oxidation of propionaldehyde into perpropionic acid by O_2 with Co acetate as catalyst in acetone + EtOAc as solvent was found to be 1.5 order in aldehyde and 0.5 order each in O_2 and catalyst [370]. The redox properties of 12-molybdophosphates $M_xH_{3-x}PMo_{12}O_{40}$ were studied in connection with their role in catalyzing the oxidation of organic compounds like isobutyric acid or methacrolein [371]. Oxidation of cyclohexanone with O_2 in the presence of Cr(III) or Co(II) naphthenate gave successively 2-hydroxycyclohexanone, 1,2-cyclohexanedione, ε-caprolactone, adipic acid, and adipic acid anhydride [372].

See also [330, 331, 332].

d) Miscellaneous Oxidations

The catalytic activity of Fe^{2+} phthalocyanine derivatives for the oxidation of oxalic acid was studied. The highest oxidation rate was observed in the case of Fe-phthalocyanine treated with HCl [373].

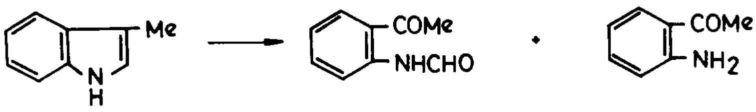
The kinetics of oxidation of ascorbic acid by O_2 catalyzed by $RuCl_3.nH_2O$ or different Ru(III)-aminopolycarboxylic acid complexes has been studied. An inverse relationship was found between the stability and catalytic activity of the Ru(III) chelates [374]. The rate of oxidation did not depend on O_2 concentration with these latter catalysts which act as oxidase models in this reaction [375].

Oxidation of sodium oxalate with O_2 was studied using a(Co phthalocyanine.2py)adduct as catalyst [376]. The catalytic activity of a histamine-containing polymer latex-Cu(II) complex in the oxidation of ascorbic acid was examined. The catalyst showed a Michaelis-Menten type saturation behavior [377]. Oxidation of ascorbic acid by O_2 in the presence of the Cu complex of tetrabenzo[1,5,9,13][b,f,j,n] tetraazacyclohexadecine was shown to exhibit oscillatory character. The conditions of the oscillatory regime were specified [378, 379]. The activity of $Cu(OAc)_2$ in the liquid-phase oxidation of Me isobutyrate by O_2 is decreased by even small amounts of water [380]. The dicumyl peroxide-initiated oxidation of pentaerythritol esters was studied in the presence of copper using different aromatic amines as inhibitors. Diisooctyldiphenyl amine was an efficient inhibitor [381].

See also [371].

3. Catalytic Oxidation of N-containing Organic Compounds

The amount of polymeric byproducts in the oxidation of N-methylpyrrolidone to N-methylsuccinimide by O_2 in the presence of $KMnO_4$ sharply increased on the addition of Na_2CO_3 [382]. The oxygenolysis of 3-methylindole (163) to (164) and (165) is catalyzed by Fe, Co, Cu or Mn phthalocyanines. Addition of py or imidazole inhibits the reaction [383].

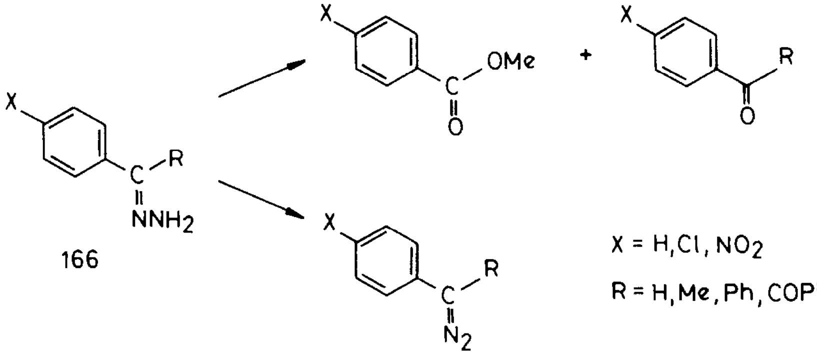


163 164 165

The oxidation of Et_3N by O_2 to Et_2NH and MeCHO is catalyzed by a Ru(III)-EDTA complex prepared *in situ*. The kinetics of the reaction was studied [384].

Anilines are oxidized by O_2 and Co(salen) as catalyst to azo derivatives in MeOH at reflux temperature. In the presence of carbon monoxide, isocyanates or urethanes and ureas are formed too [385, 386].

Oxygenation of aromatic ketone hydrazones (166) using Co(salen) as catalyst in MeOH resulted in the formation of methyl benzoate derivatives and aromatic ketones [387]. In the presence of methylimidazole as additive diazo compounds (167) were formed [388].



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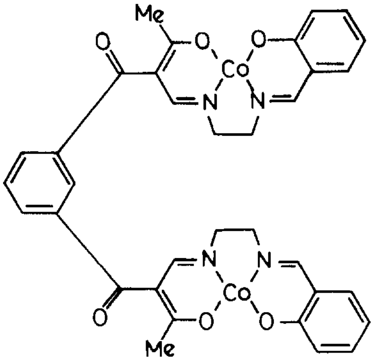
167

X = H,Cl, NO_2

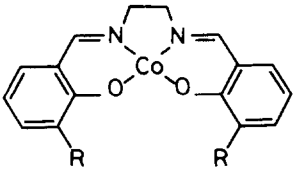
R = H,Me,Ph,COPh

The binuclear Co(II)-Schiff base complex (168) was used as catalyst for the oxidation of N,N,N',N',-tetramethyl-*p*-phenylenediamine with O_2. The analogous mononuclear complex was practically inactive [389].



168

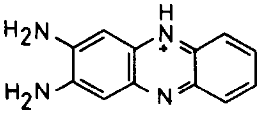
Hydrazobenzene was oxidized by O_2 into azobenzene using Co(salen) (169) or its bis(3-methoxy) derivative (170) as catalyst. A mechanism involving a complex of substrate, catalyst, and O_2 was proposed [390].



169 R = H

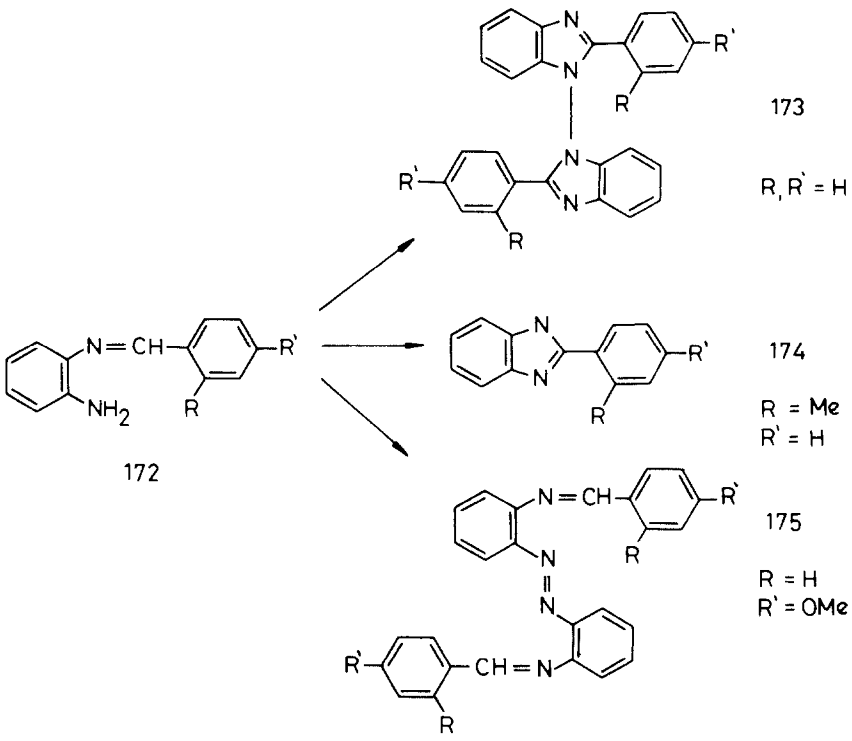
170 R = OMe

The Cu(II) complexes of 1-methyl-3,5-diphenylpyrazole or 3,5-diphenylpyrazole could be used as catalysts for the dehydrogenation of 1-methyl-3,5-diphenylpyrazoline in the presence of O_2 [391]. Oxidation of o-phenylene diamine with air in the presence of Cu^{2+} in MeCN solution yielded the protonated 2,3-diaminophenazine cation (171) [392].



171

Oxidation of N-benzylidine-o-phenylenediamines (172) with O_2 catalyzed by CuCl in pyridine furnished different products depending on the substituents of the benzene ring in the benzylidene group. In most cases 2,2'-diaryl-1,1'-bibenzimidazoles (173) were obtained but ortho substitution caused cyclization to 2-arylbenzimidazoles (174) and with the p-methoxy derivative only oxidative coupling of the amino groups to the diazo compound (175) was found [393].



Indolines (176) were oxidized to indoles (177) with O_2 using $[CuCl(py)]_n$ as catalyst in CH_2Cl_2 solution. The reaction was rather selective (up to 92%) and no ring cleavage was observed [394].

Autoxidation of diaminouracils (178) is strongly catalyzed by Cu(II). Reaction products are H_2O_2 and imines (179). Probably a ternary complex between diaminouracil, Cu(II) and O_2 is the intermediate which reacts with an ionic two-electron mechanism to give the products [395].

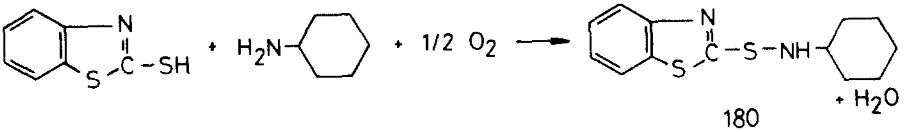
178 179

See also [402].

4. Catalytic Oxidation of P- or S- Containing Organic Compounds

The Fe(II) complex $Fe(OPPh_3)_4(I_3)_2$ was found to act as a catalyst for the oxidation of Ph_3P to Ph_3PO by O_2 in MeCN [396]. In the oxidation of PPh_3 by O_2 and Ru(III)-EDTA as catalyst the μ -peroxo complex $[Ru(EDTA)(PPh_3)]_2O_2$ was identified as an intermediate. The rate-determining step is the formation of the ruthenyl complex Ru=O(EDTA)(PPh_3) [397]. Catalytic activity of (TPP)Co(NO_2)(L) complexes in the oxidation of Ph_3P to Ph_3PO by O_2 was studied as a function of L. Best yields were achieved with L = 4-cyanopyridine as axial ligand [398].

The complexes $RuX_2(Me_2SO)_4$ (X = Cl,Br,$SnCl_3$,SCN) were excellent catalysts for the oxidation of thioethers to sulfoxides with O_2 at 105°C and 7 bar in MeOH solution. The all-trans-$RuX_2(SR_2)_2(Me_2SO)_2$ complexes (which were separately synthesized) were regarded as key-intermediates in the catalytic process [399]. Autoxidation of sulfides to sulfoxides is strongly accelerated by the addition of a catalytic amount of Ce(IV) salts. Oxidation proceeds under 13 bar O_2 at 100°C and is a synthetically useful reaction [400]. Oxidation of EtSH to Et_2S_2 at 25°C is catalyzed by Co(II) complexes anchored to amorphous silica via a bond with py. The Co(II) complex of bis(salicylal-*o*-phenylenediamine) was found to be the most active [401]. The kinetics, selectivity and yields of the oxidative condensation of 2-mercaptobenzthiazole with cyclohexylamine in the presence of O_2 and $Cu(OAc)_2.4H_2O$ as catalyst to give N-cyclohexylbenzothiazole-2-sulphenamide (180) were investigated. The catalytically active species were probably Cu-cyclohexylamine complexes with coordinated thiolate ligands and the overall rate was controlled by the reoxidation of Cu(I) to Cu(II) [402].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The kinetics of oxidation of cysteine with O_2 in the presence of Mn(II) iminodiacetate immobilized on Silochrome [403], and in the presence of iron phosphate complexes [404] was studied.

See also [306].

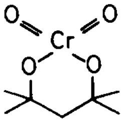
5. Catalytic Oxidation of Organic Compounds with Organic or Inorganic Oxidants

a) General

The high valent Mn complexes (TMP)Mn(O)Cl and (TMP)Mn(O)Br were prepared by oxidizing (TMP)MnCl with NaOCl or NaOBr. These active species are able to transfer one O atom to any good oxygen acceptor and act as catalysts in the (TMP)MnX/NaOCl system [405]. Oxygenation and dehydrogenation of different organic compounds by H_2O_2 in the presence of $Fe(MeCN)_4(ClO_4)_2$ and $FeCl_3$ in dry acetonitrile were investigated as models for peroxidases, catalases and monooxygenases [406]. Spectral evidence was obtained for the formation of active intermediates (metal oxo species) from $RuCl_3$ and $Ru(PPh_3)_3Cl_2$ with N-methylmorpholine N-oxide and phenyliodosoacetate. These systems may be used for the oxidation of a vide variety of organic substrates [407].

b) Oxidation of Hydrocarbons or Hydrocarbon Groups

Oxidation of anthracene with tBuOOH in the presence of Mo(VI) acetylacetonate gave anthraquinone in 97-100% yield at 40°C [408]. Benzylic methylene groups could be oxidized into carbonyl functions by tBuOOH in dichloromethane solution if small amounts of the cyclic chromate (181) were used as catalyst. tert-Butylperoxy compounds (182) were proposed as intermediates [409].



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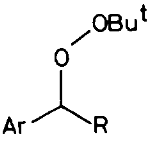
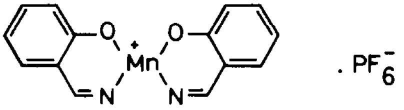


182

Oxidation of styrene to phenylacetaldehyde and epoxide has been investigated by two cytochrome P-450 model systems: Mn(TPP)Cl catalyst with NaOCl as oxidant and Fe(PFP)Cl + C_6F_5IO [PFP = tetrakis(pentafluorophenyl)porphyrinato]. It was shown that the aldehyde is a primary product and does not result from isomerization of styrene oxide [410]. High conversions of alkanes into alcohols and ketones were obtained by using H_2O_2 as an oxidizing agent and Mn(TDCPP)Cl as the catalyst in the presence of imidazole and in MeCN as solvent. No significant degradation of the catalyst was observed [411]. Shape selectivity for the hydroxylation of alkanes has been demonstrated by using very sterically hindered metalloporphyrins as catalysts. With iodosobenzene as oxidant good regioselectivity was observed for hydroxylation at the least hindered methyl group with [5,10,15,20-tetrakis(2',4',6'-triphenylphenyl) porphyrinato)-Mn(III) acetate as catalyst. The corresponding iron complexes also showed good primary selectivity, although to a lesser degree. The regioselectivities were comparable to or better than those found for some ω-hydroxylase enzymes [412]. Oxidation of various olefins with tBuOOH, the Mn(III) complex (183) as catalyst and py or imidazole as cocatalyst was studied. With cyclohexene as substrate cyclohexene oxide and cyclohexenyl t-butyl peroxide were the two products. The formation of peroxide involved a free radical chain mechanism which could be completely inhibited by the hindered phenol ionol [413].



183

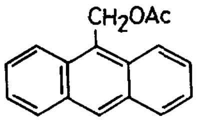
Oxidation of benzene to phenol and benzoquinone with H_2O_2+Fe^{2+} under air has been investigated using isotopic tracer techniques. It was concluded, that oxygen is included from both sources into the reaction products and that H_2O_2 is in part regenerated during the process [413a]. Oxidation of cis-stilbene by different oxidants (H_2O_2, $NaIO_4$, PhIO, and cumene hydroperoxide) in the presence Fe(III)-bleomycin leads to benzaldehyde, cis-stilbene oxide and under anaerobic conditions to trans-stilbene. The results could be explained by assuming two parallel oxidative mechanisms [414]. The hydroxylation of anisole by H_2O_2 was investigated in the presence of the Fe(III) complex of N-dodecyl-3,4-dihydroxybenzamide. No deactivation of the catalyst was observed [415]. Cobalt and Fe phthalocyanines and tetraazaporphines were tested as catalysts in the oxidation of cyclohexene with cumene hydroperoxide. The best catalyst was an iron tetraataporphirin μ -oxo dimer [416]. Iron phthalocyanine was encapsulated inside large pore zeolites and used is this form as catalyst for the oxidation of alkanes by iodosobenzene. Two types of shape selectivity were observed: cyclohexane was preferentially oxidized in competition with cyclododecane and in the oxidation of n-octane the extent of oxidation at position 2 increased with respect to that at positions 3 and 4 [417]. Oxidation of crotonic acid by H_2O_2 in the presence of $Fe(SO_4)_2$ as catalyst was first order in substrate and catalyst but zero order in oxidant [418]. Hydrocarbons were oxidized to the corresponding acetamides by $NaIO_4$ in $MeCN/Ac_2O$ in the presence of $Fe(ClO_4)_3$ [419].

Cycloolefins were oxidized to dicarboxylic acids with NaOCl and $RuCl_3.xH_2O$ as catalyst in a two-phase system. Best results were obtained with cyclopentene in which case the yield of glutaric acid was 82% [420]. Methyl-substituted benzene derivatives were oxidized to the corresponding carboxylic acids in > 90% yield in a two-phase system with NaOCl as oxidant and both Ru salts and quaternary ammonium salts as catalysts. Initial step of the reaction was hydride abstraction by RuO_4 from the methyl group [421]. The kinetics of the Ru(III)-catalyzed oxidation of phenylacetic acid by phenyliodosoacetate or $Pb(OAc)_4$ were studied. The reaction was zero order with respect to both oxidant and first order in Ru and substrate [422].

Oxidation of C_2-C_4 olefins with HIO_4 in AcOH solution and in the presence of $Pd(OAc)_2$ yields glycol acetates with high selectivity. From ethene mainly ethylene glycol diacetate is being formed, higher olefins yield glycol monoacetates as principal products [423]. Methylbenzenes and methylnaphthalenes were oxidized to quinones with aqueous H_2O_2 in AcOH in the presence of a Pd(II)-

sulfonated polystyrene type resin at 20-80°C. Selectivities to 1,4-napthoquinones were 50 to 70% but 1,4-benzoquinone selectivities were rather low. The catalyst could be recovered by filtration and reused [424, 425].

The Cu(II) + $S_2O_8^{2-}$ oxidation of 9-methylanthracene was studied in refluxing MeCN/AcOH and aqueous MeCN. Side-chain oxidation products (184)-(186) and the dimeric compound (187) were the main products [426].



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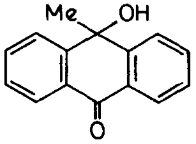

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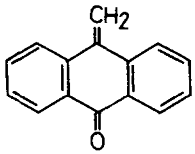

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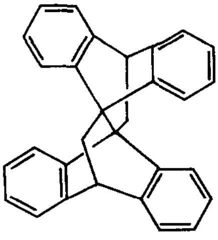


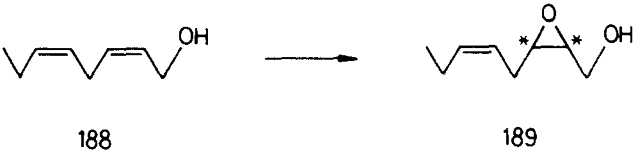
187

Allylic oxidation of butenes with tBu peroxyacetate and Cu(I) or Cu(II) salts gave 3-acetoxybut-1-ene and trans-acetoxybut-2-ene. An allylic radical and a Cu(III) complex were supposed as intermediates [427]. Polynuclear aromatic hydrocarbons were oxidized by $S_2O_8^{2-}$ with catalytic amounts of Ce(IV) and Ag^+ in a two-phase system using $(Bu_4N)(HSO_4)$ as phase-transfer catalyst. Naphthalene could be transformed into o-naphthoquinone with 70% yield in this way [428].

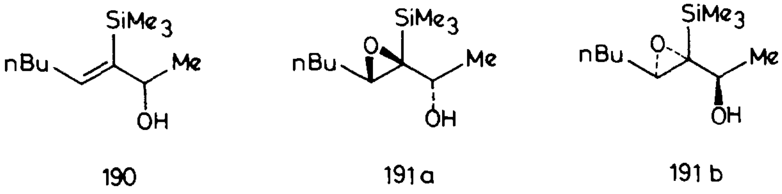
See also [308, 332, 440, 469, 508].

c) Epoxidation of Olefins

Asymmetric epoxidation of allyl alcohol using the $tBuOOH/Ti(OPr^i)_4$/diisopropyltartrate system has now been developed into a practically useful procedure. The strategy employed consists in the *in situ* derivation of the very reactive epoxide thus preventing its decomposition [429]. Asymmetric epoxidation of allylic alcohols employing tBuOOH could be successfully carried out with only catalytic amounts of $Ti(OPr^i)_4$ (5-10 mole %) and tartrate ester (6-13 mole %) if 3A or 4A molecular sieves (zeolites) were present [430]. Allylic alcohol (188) was subjected to asymmetric epoxidation with tBuOOH and $Ti(OPr^i)_4$, using (+)- or (-)-diisopropyl tartarate giving both enantiomers of (189) with 75-77% chemical and at least 88% optical yield [431].



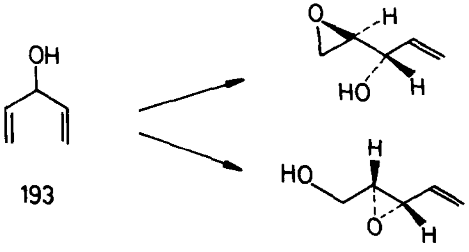
Asymmetric epoxidation of E-2-hexen-1-ol with tBuOOH in the presence of $Ti(OPr^i)_4$ and diethyl- 2R,3R -tartrate gave (2S,3S)-3-propyloxiranemethanol in 80% yield and 96,8% enantiomeric purity [432]. A practical and efficient method for the preparation of both enantiomers of the *erythro*-epoxy secondary alcohol (191) from the racemic allylic alcohol (190), based on the Sharpless kinetic resolution process has been developed. First, (191a) was prepared by epoxidation of (190) with tBuOOH, $Ti(OPr^i)_4$, and (+)-diisopropyl-tartrate. The unreacted enantiomer of (190) was then transformed into (191b) by epoxidation with tBuOOH and $VO(acac)_2$ [433].



Asymmetric oxidation of methyl p-tolyl sulfide to the corresponding sulfoxide by tBuOOH in the presence of Ti(OPr^i)$_4$, diethyl tartrate, and water and asymmetric oxidation of (E)-geraniol (192) with the classical Sharpless reagent was investigated using (+)-diethyl tartrate of varying enantiomeric purity. It was found that the correlation between the enantiomeric purity of the chiral auxiliary and the optical yield of the asymmetric synthesis strongly departs from linearity [434].

192

Asymmetric epoxidation of the divinylcarbinol (193) with tBuOOH and Ti(OPr^i)$_4$ in the presence of L(+)-diethyl tartrate gave the epoxides (194) or (195) depending on the workup procedure [435]. Epoxidation of (193) according to the above method in the presence of 4A molecular sieve gave the epoxide (194) in 60% yield [436].



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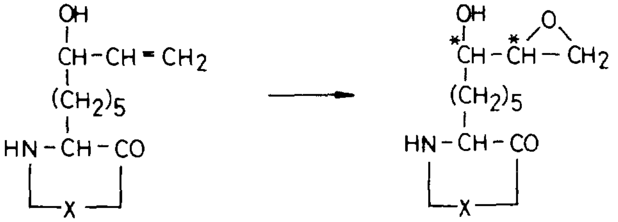
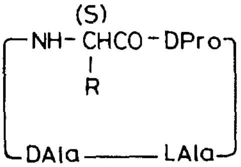
195

Epoxidation of the racemic allylic alcohol derivative of the cyclic peptide (196) with tBuOOH in the presence of (-)-(D)-diisopropyl tartrate and $Ti(OPr^i)_4$ in CH_2Cl_2 gave the epoxide (197) in 27% yield (-X- = α-aminoisobutyric acid-L-Phe-D-Pro) [437]. The analogous cyclopeptide (198) bearing a side chain with a racemic allylic alcohol structure was also epoxidized with the same procedure. First, (-)-(D)-diisopropyltartrate was used as chiral reagent and the epoxy alcohol (199a) was obtained with 20% yield. The unconverted allylic alcohol was then epoxidized in the presence of (+)-(L)-diisopropyltartrate to yield the epimeric epoxy alcohol (199b) [438].



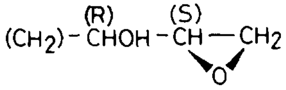
196

197 8R, 9S

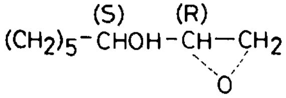


R

198 $(CH_2)_5-CHOH-CH=CH_2$



199 a $\overset{(R)}{(CH_2)-CHOH}-\overset{(S)}{CH}-CH_2$ (epoxide O)



199 b $(CH_2)_5-\overset{(S)}{CHOH}-\overset{(R)}{CH}-CH_2$ (epoxide O)

Chiral 2-methyl-3,4-unsaturated aldehyde acetals (200) were epoxidized with tBuOOH and $TiCl_3OPr^i$ to give the anti-epoxides (201) in 60-80% yield (R = aralkyl group) [439].

200

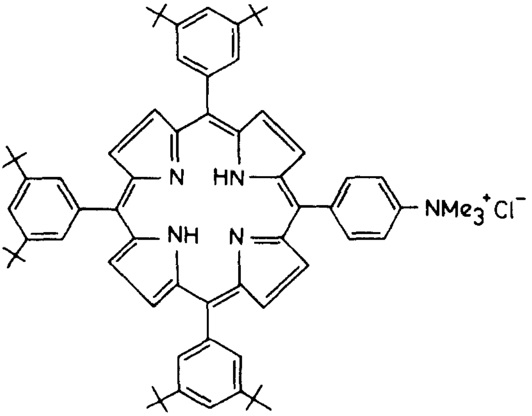
201

Cyclohexene and different methylcyclohexenes were oxidized with PhIO or m-MeC_6H_4IO in the presence of $VO(acac)_2$. Epoxides and allylic oxidation products were formed; the results were in accord with a free radical mechanism [440]. The dienes (202; R = Et,CoOMe) were epoxidized by tBuOOH in the presence of $VO(acac)_2$ with high regio- and diastereoselectivity to epoxides (203) [441].

The stepwise epoxidation of COD with tBuOOH in the presence of Mo complexes was studied. The second epoxidation was at least five times slower than the first one [442]. Epoxidation of refined soybean oil using $MoO_2(acac)_2$ as catalyst [443] and that of sardine oil using $Mo(CO)_6$ as catalyst [444], in both cases with cumene hydroperoxide, was studied. Empirical kinetic equations were determined in order to optimize operating variables. Epoxidation of cyclohexene by tBuOOH catalyzed by Mo complexes was investigated by IR and UV spectroscopy. The results suggested on initial rapid reaction of the catalyst with tBuOOH to give a Mo peroxo complex which then epoxidized the alkene [445]. Molybdenum peroxide immobilized on a chelating polymer was used as catalyst for the epoxidation of olefins with tBuOOH. Isolated product yields ranged between 38-89% and the catalyst could be reused several times, preferably after reactivation by H_2O_2 [446].

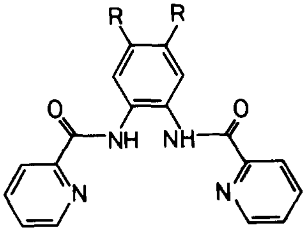
Simple monoolefins were effectively epoxidized with H_2O_2 and a catalytic amount of a quaternary phosphonium or ammonium pertungstate at 40-50°C. The catalyst could be prepared also in situ by the addition of tungstic acid and $Ph_3PCH_2Ph^+Cl^-$ to 30% H_2O_2 [447]. The scope of the tungstic acid catalyzed epoxidation of olefinic alcohols by H_2O_2 has been examined. Epoxidation occurred with complete retention of configuration for both cis and trans alkenes and no isomerisation or cleavage of the olefinic bond was observed [448]. This epoxidation afforded in the case of allylic alcohols the same diastereoisomer as the $VO(acac)_2$ + tBuOOH system. Epoxidation of homoallylic alcohols appeared to be much less stereoselective [449]. The transition metal substituted heteropolytungstates $(Bu_4N)_4[H(M)PW_{11}O_{39}]$ (M = Mn, Co) are remarkably effective catalysts for the epoxidation of olefins using PhIO or C_6F_5IO as oxygen donors. Product selectivities (> 90%), reaction rates, and stabilities (10000 equiv. of C_6F_5IO per equiv. of catalyst) compare favorably with those for metalloporphyrins and related systems [450].

The kinetics of olefin epoxidation by NaOCl and Mn(TPP)OAc has been studied. It could be shown that the rate limiting step is the formation of the oxomanganese complex $[(TPP)Mn{=}O]^+$ which either reacts with the olefin or is transformed in an equilibrium reaction into the unreactive dimer $[(TPP)Mn{-}O{-}Mn(TPP)]^+$ [451]. Substitution of (TPP)Mn(III) complexes on the peripheral Ph groups makes these compounds suitable as catalysts for the epoxidation of terminal olefins with NaOCl, LiOCl and $KHSO_5$ in a biphasic system [452]. Epoxidation of alkenes with NaOCl in the presence of Mn(TPP-Me-p)OAc as catalyst was investigated. Methanol changed the kinetics of the reaction and styrene had a synergistic effect. This latter was attributed to phenylacetaldehyde (a byproduct of the epoxidation of styrene) which transfers a H atom onto an oxo manganese species and thereby changes the mechanism of the reaction [453]. The new porphyrin (204) was synthesized and its Mn(III) complex used as a catalyst for the epoxidation of olefins with NaOCl in a two-phase (CH_2Cl_2 + H_2O) system. No phase-transfer agent was necessary [454].



204

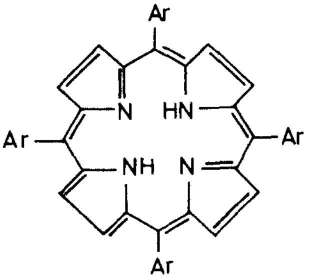
The Mn(III) complexes $[Mn(\text{substituted salen})]^+$ were found to be effective catalysts for the epoxidation of olefins with iodosylbenzene. Electron-withdrawing groups enhanced the activity of the catalyst; the relative reactivity of olefins depended only slightly on the structure of the substrate. Epoxidation was stereospecific and only minor competition from allylic oxidation was observed [455]. The Mn(III) complexes Mn(L)Cl, Mn(L')Cl and Mn(L)(N_3) (H_2L = 205a, H_2L' = 205b) have been found to catalyze the epoxidation of alkenes with PhIO. These new catalysts show high chemoselectivity: cyclohexene oxide was the only product in the oxidation of cyclohexene [456].



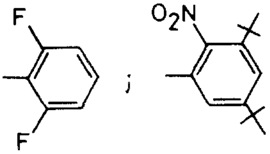
205a R = H

205b R = Cl

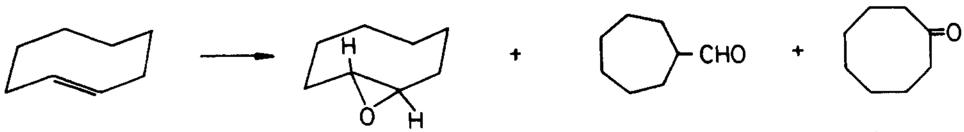
Epoxidation of cyclohexene with PhIO was investigated under identical conditions using different metalloporphyrins (PMX) as catalysts. Using TPP complexes, Mn and Fe were found to be the most selective metals (M), with Fe as metal meso-tetramesitylporphyrin was the best porphyrin ligand (P) and among (TPP)FeX catalysts ClO_4 was most effective as axial ligand (X) [457]. Six different alkenes were epoxidized with p-cyano-N,N-dimethylaniline using (TPP)FeCl, (TDCPP)FeCl, or (TDMPP)FeCl as catalyst. Best yields (80-100%) were obtained with (TDMPP)FeCl. The rate determining step of the catalytic reaction was the transfer of oxygen from the oxidant onto the iron complex [458]. Along with the epoxidation of alkanes with PhIO catalyzed by Fe tetraarylporphyrin chloride complexes, three important side reactions were observed: formation of $PhIO_2$, destruction of the porphyrin ring, and N-alkylation of the porphyrin ligand. The latter reaction was only observed in the case of monosubstituted olefins not hindered in the vicinity of the double bond. The same alkenes act as suicide substrates of cytochrome P 450 [459]. Using Fe(TDCPP)Cl as catalyst for the epoxidation of olefins with C_6F_5IO it was observed that N-alkylation of the porphyrine ligand takes place. Depending on olefin structure 100 to 10000 moles of epoxide were formed per mole of N-alkylated catalyst. This side reaction significantly decreased the activity of the catalyst but did not lead to complete deactivation [460]. Oxidation of 2,4,6-tri-tert-butylphenol to the 2,4,6-tri-tert-butylphenol radical and epoxidation of different olefins by p-cyano-N,N-dimethylaniline N-oxide in the presence of (TDCPP)FeCl as catalyst has been investigated. Rates and equilibria leading to the formation of the iron(IV)-oxo porphyrin π-cation radical species and minimal rate constants for the oxidations could be determined [461]. Oxidation of Fe(TMP)Cl or Fe(TMP)OH with m-chloroperoxybenzoic acid gives an oxo-Fe(IV) porphyrin radical species which reacts with olefins to give epoxides. In the case of substituted styrenes the rate of reaction correlates with the Hammett σ^+. The formation of an intermediate was observed by UV spectroscopy [462]. Iron(III)-porphyrin + NaOCl two-phase (CH_2Cl_2/H_2O) systems were developed for the epoxidation of olefins. The protected porphyrins (206) were found to give more stable and active catalyst than TPP [463].



206, Ar =

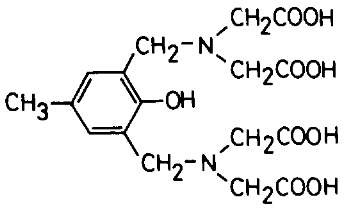


The ratio of exo- to endo-epoxy product obtained from the epoxidation of norbornene by C_6F_5IO or iodosylxylene and using different substituted [(tetraarylporphinato)Fe(III)] complexes as catalyst has been determined. The results suggest that the mechanism involves electron transfer from the alkene to the iron(IV) porphyrin radical cation $(Fe{=}O)^+$ followed by radical collapse to give a carbocation [464]. Epoxidation of cis-cyclooctene with iodosylxylene and Fe(TPP)Cl as catalyst gave the cis-epoxide practically exclusively. If trans-cyclooctene was epoxidized in this way skeletal rearrangement also took place and the carbonyl compounds (207a) and (207b) were formed as byproducts. A carbocationic mechanism was proposed [465].



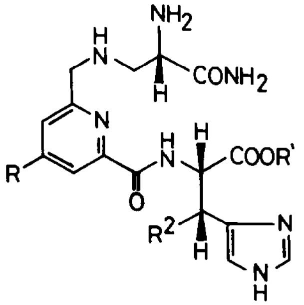
207a 207b

Epoxidation of cholesteryl acetate by nonradical reagent systems as $Mo(CO)_6$ + tBuOOH or $Fe(ClO_4)_3$ + H_2O_2 was highly α-stereoselective while a radical reagent system like $Fe(acac)_3$ + tBuOOH showed high β-stereoselectivity. Based on this observation it was concluded that epoxidation with the (TPP)FeCl + PhIO system is a radical process [466]. The binuclear iron complex $(Me_4N)[Fe_2L(OAc)_2]$ (LH_5 = 208) catalyzes the epoxidation of olefins with H_2O_2, although with low yields (1-3%) [467].



208

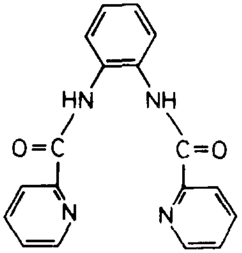
The synthetic analogues (209) of bleomycin have been prepared and their Fe(III) complexes used as catalysts for the epoxidation of cis- and trans-stilbene with H_2O_2. The epoxidation of trans-stilbene was highly suppressed if the tBu-substituted derivatives (209b-d) were used suggesting a highly crowded environment of the iron complex in these cases [468].



209

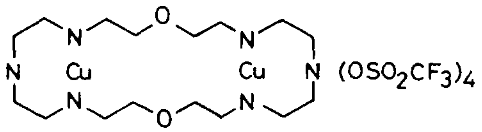
	R	R'	R^2
a	H	H	H
b	H	Bu^t	OBu^t
c	OMe	Bu^t	OBu^t
d	Cl	Bu^t	OBu^t

The Ru(IV) oxo complex $[(bpy)_2(py)RuO]^{2+}$ epoxidizes styrene stilbene in acetonitrile solution in high yield. The oxidation can be performed also in a catalytic way by using $[(trpy)(py)Ru(OH_2)]^{2+}$ as catalyst and NaOCl as oxidant in a two-phase system with benzyldimethyltetradecylammonium chloride as phase-transfer agent. In this case, however, significant amounts of benzaldehyde are formed due to the oxidative fission of the C=C bond [469]. The Os(III)-porphyrin complexes $(OEP)Os(PBu_3)Br$ and $(TPP)Os(PBu_3)Br$ were used as catalysts for the epoxidation of cyclohexene and styrene with PhIO. Turnover numbers around 100 were obtained. The byproduct in the case of cyclohexene was cyclohexanone. If tBuOOH was used as oxidant, cyclohexanol was the only product [470]. The Os(VI) dioxo complex $[Os(LH_2)O_2]^{2+}$ reacts with PPh_3 to form $OPPh_3$ and the Os(III) complex $Os(L)(PPh_3)Cl$ (LH_2 = 210). This latter complex catalyzes the epoxidation of cyclohexene with PhIO. A highly colored intermediate was observed during epoxidation [471].



210

Several dinuclear copper complexes have been tested as catalysts for the epoxidation of olefins with iodosylbenzene in acetonitrile solution. These proved to be much more effective than analogous mononuclear complexes. With complex (211) 70% yield could be achieved in the case of cyclohexene as substrate [472].



211

See also [410, 413, 414].

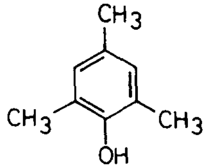
d) Oxidation of O-containing Functional Groups

Di- and trimethylphenols were oxidized to the corresponding quinones by H_2O_2 and alkali metal polyvanadatomolybdate or alkali metal polyvanadatotungstate hydrates as catalysts. The phenols were actually oxidized by $[VO(O_2)_2]^+$ which was formed from H_2O_2 and the vanadate [473]. Oxidation of cyclohexanol to adipic acid by HNO_3 occurs via 2 routes. One of these, involving 1,2-cyclohexanedione as intermediate, gives a significant yield of adipic acid only in the presence of V^{5+} [474].

Primary and secondary alcohols could be oxidized to the corresponding carbonyl compounds with dilute H_2O_2 using $Na_2WO_4.2H_2O$ or $Na_2MoO_4.2H_2O$ as catalyst under phase-transfer conditions [475]. Oxidation of furfural, thymine, and EtOH by H_2O_2 was studied with Mo or W compounds as catalysts [476]. Aqueous H_2O_2 in conjunction with catalytic amounts of WO_4^{2-} and PO_4^{3-}, under acidic conditions, provides a synthetically useful procedure for the selective oxidative cleavage of water-soluble 1,2-diols to carboxylic acids. The use of tungstate alone leads to a significant decrease of the yields [477].

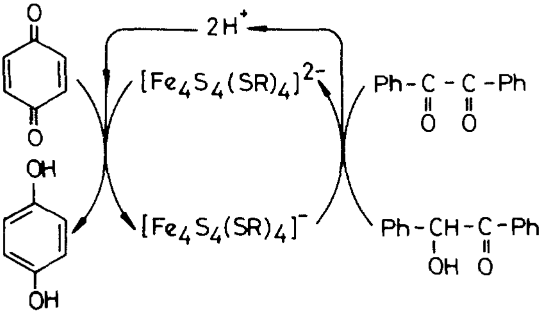
Primary alcohols were oxidized to aldehydes in good yields using lead tetraacetate in combination with $Mn(OAc)_2$ (molar ratio 1 : 0.1-0.5). The new method was suitable for the oxidation of olefinic alcohols and of secondary alcohols too [478].

Phenol was oxidized by aqueous H_2O_2 in the presence of different transition metal ions to yield catechol and hydroquinone. Detailed investigations were performed with Fe^{3+}. Optimized conditions gave dihydroxybenzene yields of 84% and catechol:hydroquinone ratios between 1.5:1 - 2:1 [479]. The efficiency of Fe^{2+} in the catalytic oxidation of phenol by H_2O_2 in aqueous solution is higher than that of Fe^{3+} [480]. Oxygen transfer from percarboxylic acids to (EDTA)Fe(III) has been investigated in methanol solvent, using (212) as a trapping reagent for the reactive iron-oxo intermediate. Phenoxyl radical, formaldehyde and a peroxidic component formed from the peracid and (212) were identified as organic products [481].



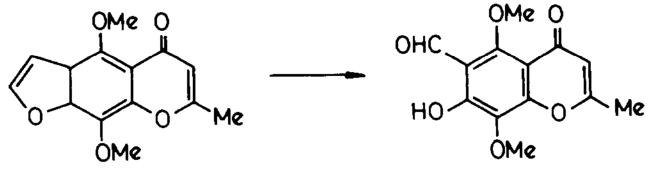
212

Oxidation of benzoin to benzil by p-benzoquinone could be catalyzed by $[Fe_4S_4(SR)_4]^{2-}$ complexes containing cysteine-containing peptides or bulky thiolates as RS groups. The catalytic cycle of this reaction is shown below [482]:



Sodium bromate was found to be an effective oxidant for the conversion of alcohols into carbonyl compounds in the presence of Ce or Ru compounds in an organic-water two-phase reaction. Quaternary ammonium salts as phase-transfer catalysts accelerated the reaction. The cerium-catalyzed oxidation was selective for the transformation of primary alcohols into aldehydes in the presence of secondary alcohols [483]. The kinetics of the Ru(III)-catalyzed oxidation of lactic acid by peroxodiphosphate has been studied. The effect of Ru(III) was explained by the formation of a 1:1 complex between Ru(III) and lactic acid [484]. Secondary alcohols were oxidized by N-methylmorpholine N-oxide in the presence of $Ru(PPh_3)_3Cl_2$ in DMF to give ketones in 80% yield [485]. Rate constans were determined for the oxidation of mandelic acid, lactic acid, and glycolic acid by IO_4^- catalyzed by Ru(III) chloride [486].

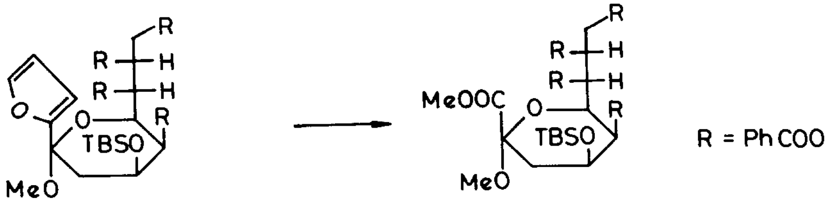
Oxidation of aldehydes to carboxylic acids with water according the equation $RCHO + H_2O \rightleftharpoons RCOOH + H_2$ is catalyzed by $[(\eta^6\text{-p-cymene})_2Os_2(\mu\text{-OH})_3](PF_6)$. Raising the temperature to 60°C and adding a base (Na_2CO_3) enhances the rate of the reaction; turnover numbers of up to 100 were achieved [487]. Oxidation of glycolic acid and lactic acid by chloramine-T catalyzed by Os(VIII) is first order in oxidant [488]. The furan ring of khellin (213) could be oxidized with $NaIO_4$ and OsO_4 in THF to give the aldehyde (214) in 73% yield. Isolation of the intermediate diol was not necessary [489].



213 214

Hydroxylation of the <u>cis</u>-enoate (215) with OsO_4 afforded the diol (216) in 87% yield. After transforming this compound into the tetrabenzoate (217) the furan ring could be degraded by $NaIO_4$ in the presence of RuO_2 to give (218) [490].

215 216



217 218

Palladium salts catalyze the oxidation of primary and secondary alcohols into esters and ketones, respectively, by CCl_4 in the presence of K_2CO_3. Allylic alcohols give addition products with halohydrin structures which, however, are transformed into the corresponding ketones at higher temperatures [491]. Steroidal alcohols were successfully transformed into ketones using polymer-anchored $PdCl_2$ or homogeneous $Pd(PPh_3)_4$ as catalyst and bromobenzene as oxidant in the presence of K_2CO_3. The method was especially useful for the conversion of Δ^5-sterols (219) into $\Delta^{4,6}$-dien-3-ones (220) [492].

219 220

A first-order rate constant was determined for the oxidation of formic acid by $S_2O_8^{2-}$ catalyzed by Cu(II) [493].

See also [461, 569, 573, 578].

e) Oxidation of N-containing Organic Compounds

The $PhNHNH_2$ radical was observed by EPR spectroscopy during the oxidation of phenylhydrazine by $H_2O_2/TiCl_3$ [494]. Oxidation of amines by $PhIO_2$ catalyzed by $VO(acac)_2$ was studied. Oxidative dealkylation was observed: for example $PhNMe_2$ gave PhNHMe and azobenzene [495].

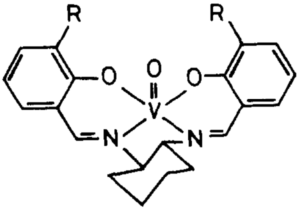
Oxidation of different dyes with H_2O_2 using complexes of Mn(II) with triethylenetetramine was studied [496]. The oxidation of indigo dyes, murexide, carmin, lumomagneson, and lumogallion by H_2O_2 was studied with Mn(II) complexes of ethylenediamine or polyamines as catalysts. Mechanisms were proposed [497].

The chiral polymer-supported catalysts prepared from $[Fe(tetpy)(OH)_2]^+$ and Na poly(L-glutamate) or Na poly(D-glutamate) were applied for the stereoselective oxidation of L-DOPA by H_2O_2 [498]. The unsaturated tertiary amine $CH_2{=}CH(CH_2)_3CH{=}CHCH_2NEt_2$ was selectively oxidized by H_2O_2 or p-benzoquinone in the presence of Na_2PdCl_4 into $MeCO(CH_2)_3CH{=}CHCH_2NEt_2$ [499]. The oxidation of o-dianisidine by Tc(VII) in acid media is catalyzed by Cu(II). A mechanism was proposed for this reaction [500].

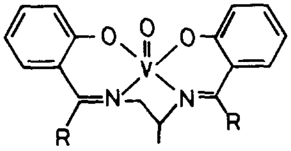
See also [419, 459, 476, 597].

f) Oxidation of P- or S- Containing Organic Compounds

The asymmetric oxidation of sulfides into the corresponding sulfoxides was achieved with cumene hydroperoxide in the presence of catalytic amounts of optically active Schiff base-oxovanadium(IV) complexes (221,222). Optical yields ranged between 20-40% [501].

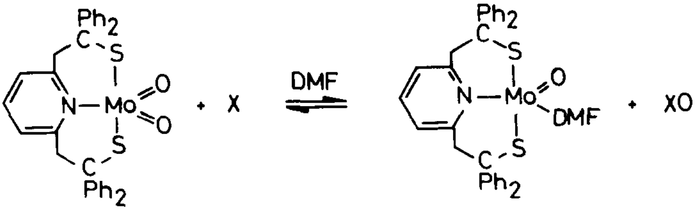


221; R = H, OMe, OEt, tBu



222; R = H, Me

It was shown that the Mo(VI) complex (223) oxidizes and the Mo(IV) complex [224] reduces several organic compounds by oxygen transfer in DMF solution. Thiols and PPh_3 were oxidized while sulfoxides, N-oxides and Ph_3AsO were reduced by this "oxo transferase" system [502].



223

224

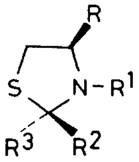
Accordingly, complexes (223) and (224) acted as catalysts for the reduction of sulfoxides by thiols [503]:

$$R_2SO + 2\ R'SH \longrightarrow RSR + R'SSR' + H_2O$$

Asymmetric oxidation of dithiolanes (225; n = 2) with tBuOOH, $Ti(OPr^i)_4$, and diethyltartrate gave the corresponding sulfoxides (226) with high chemical and optical yields. By contrast, the analogous dithianes (225; n = 3) gave much lower optical yields [504].

225 226

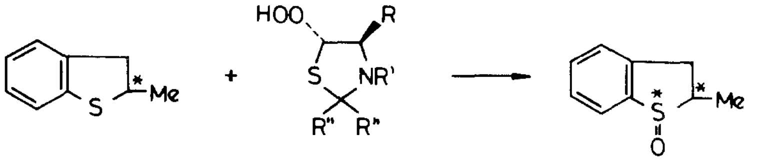
Asymmetric S-oxidation of the chiral thiazolidines (227) has been investigated using different oxidants. The tBuOOH + $Ti(OPr^i)_4$ system furnished predominantly the <u>cis</u> sulfoxide in the case of (227a) and (227b), the <u>trans</u> isomer from (227c) and a mixture of the two stereoisomers from (227d) [505].



227

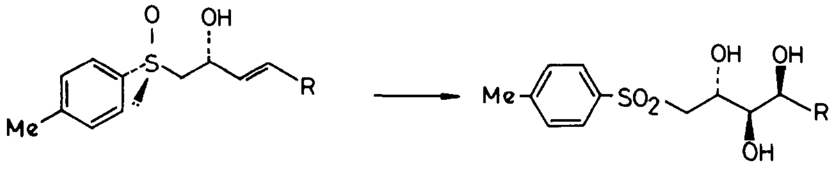
	R	R′	R^2	R^3
a	CH_2OH	CH_2Ph	Me	Me
b	CH_2OH	CH_2Ph	nPr	H
c	COOMe	CHO	tBu	H
d	COOMe	CH_2Ph	Me	Me

Oxidation of (228) with optically active hydroperoxides of type (229) was studied in the absence and in the presence of $Ti(OPr^i)_4$. The relative yields of the <u>cis</u> and <u>trans</u> isomers of (230) and the enantiomeric composition of these strongly depended on the Ti compound [506].



228 (racemic) 229 230 (four enantiomers)

Thiophenol was oxidized to diphenyldisulfide by N,N-dimethylaniline N-oxide in the presence of Fe(TPP)Cl as catalyst [507]. Optically active triols (232) could be prepared by the hydroxylation of chiral allylic β-hydroxysulfoxides (231) by Me_3NO and OsO_4 as catalyst. The diastereoselectivity of the reaction ranged between 72-95%; if the sulfoxide was previously oxidized to the sulfone it dropped to 30%, however [508].



231 232

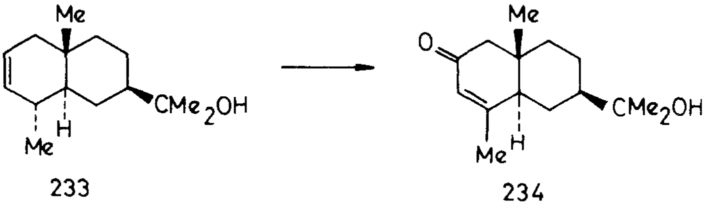
Thioethers were oxidized into sulfoxides by $NaIO_4$ under phase-transfer catalysis conditions in the presence of $Bu_3(hexadecyl)P^+$ and $Cu(OAc)_2$ [509].

See also [434, 614].

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

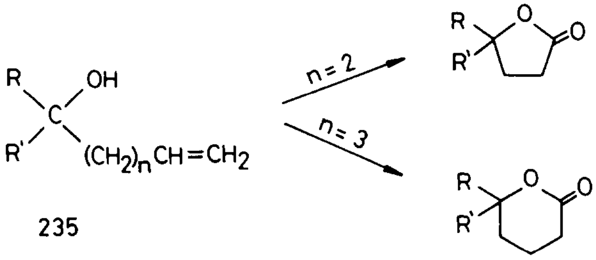
a) Oxidation of Hydrocarbons or Hydrocarbon Groups

Reactions of CrO^+ with alkenes in the gas phase model hydrocarbon oxidation processes. In the first step allylic hydrogen is abstracted to form CrOH which then adds to the double bond to form aldehydes and other products. In these latter reactions metallocycles can be supposed as intermediates [510]. Second-order rate constants were determined for the oxidation of substituted cinnamic acids by chromic acid. Electron releasing substituents favored an ionic, electron withdrawing substituents a radical pathway [511]. Chromyl trifluoroacetate, $CrO_2(OOCCF_3)_2$, oxidized hydrocarbons to give predominantly alcohols and ketones. The reaction was extremely rapid: a solution of n-hexane in CCl_4 was oxidized upon mixing at -50°C [512]. The kinetics of oxidation of substituted toluenes to the corresponding aldehydes by pyridinium fluorochromate has been studied. The data suggest that the initial step involves hydrogen atom abstraction [513]. Oxidation of eudesmol (233) with dipyridylchromium trioxide gave (234) and two isomeric ketones [514].



Alkynes were oxidized to the corresponding α-dicarbonyl compounds by $(HMPA)MoO(O_2)_2$ in the presence of mercuric acetate. The role of mercuric acetate is probably to form a π-complex with the alkyne thus favoring oxidative attack by the metalperoxide [515].

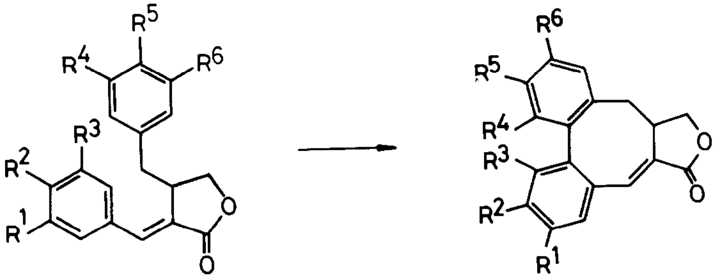
The kinetics of permanganate ion oxidation of substituted α,β-unsaturated carboxylate ions were investigated in phosphate buffered solutions (pH 6.8). The rate was found to be not very sensitive to electronic effects but steric factors appeared to be important. These results support the accepted mechanism according to which the MnO_4^- ion undergoes cycloaddition with the C=C bond to yield a metallacyclooxetane intermediate [516]. In the oxidation of solid paraffin by $KMnO_4$, addition of n-hexadecane improved the carboxylic acid selectivity [517]. Olefins were cleaved at the C=C bond to yield aldehydes as main products with $KMnO_4$ in a dilute THF solution. Conjugation increased and bulky substituents decreased the yield [518]. Oxidation of ethylbenzene by MnO_4^- in benzoic acid was catalyzed by Bu_4NOH [519]. Oxidation of dicyclopentadiene with $KMnO_4$ in CH_2Cl_2 solution in the presence of quaternary ammonium salts has been investigated. It was shown that the rate of reaction was determined by the rate of decomposition of a spectrophotometrically detectable intermediate. The rate increased with increasing size of the ammonium cation [520]. Oxidation of alkenes by $Bu_3MeN^+MnO_4^-$ is accompanied by the formation of colloidal MnO_2. This product is stabilized by adsorption of the alkane [521]. Oxidation of styrene derivatives by quaternary ammonium and phosphonium permanganates has been studied in different solvents. In polar organic solvents such as acetone the structures of the cations had little effect on the rates of reaction; significant differences were found, however, in less polar organic solvents such as CH_2Cl_2 or toluene [522]. Oxidation of γ- and δ -hydroxyolefins (235) with cetyltrimethylammonium permanganate leads to γ - and δ -lactones (236) with good yield. One carbon atom is lost in this oxidative cyclization [523].



235

236

The ethylenic lactones (237, R^1-R^6 = H,MeO,OCH_2O) [524] and the dibenzobutanolides (239) [525] were oxidized into the tetracyclic compounds (238) and (240) by Ru(IV) tetrakis(trifluoroacetate) formed in situ from RuO_2, trifluoroacetic acid, Tl(III) tris(trifluoroacetate), and BF_3OEt_2 in CH_2Cl_2.



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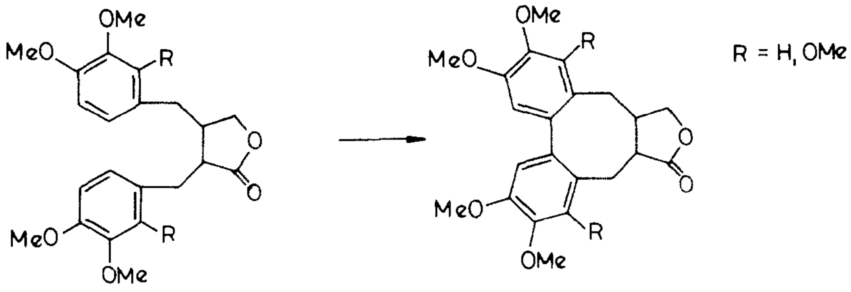
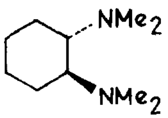


239 240

Transformation of allylic groups into vicinal diols by OsO_4 was investigated using chiral silanes, sulfones, sulfides, siloxanes, and acetates as substrates. The observed diastereoselectivities were opposite to those achieved in epoxidation with m-chloro perbenzoic acid and did not support a hyperconjugative model for osmylation [526]. Hydroxylation of olefins to vicinal diols by OsO_4 could be performed enantioselectively in the presence of chiral diamines. Optical yields up to 86% were achieved with diamine (241) [527]. Chiral diamines derived from L-tartaric acid have also been used for this purpose. Optical yields up to 90% were achieved for example with (242) in the case of trans-stilbene [528].



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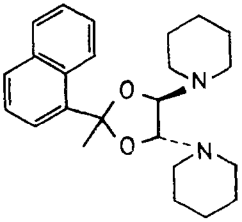
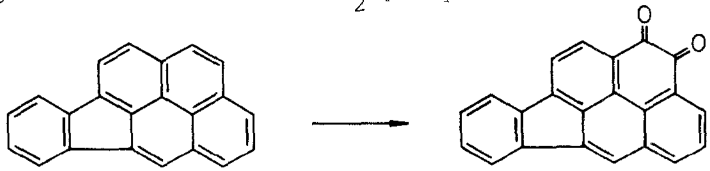


242

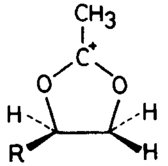
The indenopyrene (243) was transformed into the quinone (244) by first treating it with OsO_4 in py and then oxidizing the resulting diol with activated MnO_2 [529].



243 244

Oxidation of p-xylene in acetic acid by Co(III)-acetate and the effect of Br_2 and py on this reaction has been studied. 4-Methylbenzaldehyde, 4-methylbenzyl alcohol and 4-methylbenzyl acetate were the organic oxidation products. The reaction is probably initiated by bromine anion radicals Br_2^- [530]. Side-chain oxidation of 5-substituted-1,2,3-trimethylbenzenes by Ce(IV) ammonium nitrate and Co(III) acetate has been investigated. The regioselectivity of the reactions suggests that the two oxidants operate with different reaction mechanisms: in the Ce-containing system electron transfer is the first step while in the Co-containing system H atom abstraction seems to be more plausible [531]. Oxidation of olefins by $Co(OAc)_3$ in AcOH gave allylic acetates and glycol monoacetates. In the case of disubstituted olefins allylic acetates were the main products, in the oxidation of tri- and tetrasubstituted olefins the yield of glycol monoacetates was highher. Both products were formed from aromatic olefins [532].

Oxidation of xylenes by Pd(II) complexes in acidic media was found to proceed by two different mechanisms: one involving an organometallic intermediate and an other with a cation radical as intermediate [533]. The liquid-phase oxidation of α -pinene with $PdCl_2$ in aqueous acidic solutions and in different organic solvents was investigated. The allylic oxidation products verbenol and verbenone were predominant [534]. Oxidation of ethene to acetaldehyde by $Pd(ONO)Cl(MeCN)_2$ in CH_3Cl solution was studied. The nitrito complex was transformed into a nitrosyl complex during the reaction. Several intermediates of the process were identified by spectroscopic methods [535]. Olefins were oxidized by $PdCl(NO_2)(MeCN)_2$ in AcOH solution to glycol monoacetates (AS 1985, ref. 515). A mechanism involving the acetoxonium intermediate (245) was now proposed for this reaction [536].



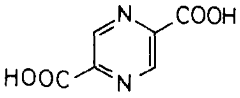
245

Oxidation of toluene derivatives into the corresponding benzaldehydes by $(NH_4)_2Ce(NO_3)_6$ in a two-phase reaction system could be catalyzed by anionic surfactants like $Me(CH_2)_{11}OSO_3Na$. The observed rate enhancements were interpreted in terms of a micelle-substrate interaction [537].

See also [334, 564].

b) Epoxidation of Olefins

The polymeric peroxo titanium derivatives $TiO_2(L)(HMPA).H_2O$ (L = 246 or 247) were found to epoxidize tetramethylethylene with 5-15% yield [538].



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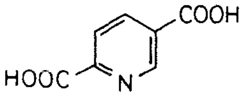
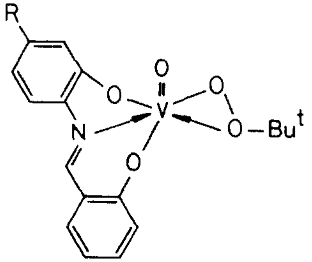


247

The novel vanadium(V) alkylperoxy complexes (248) were prepared and used for stoichiometric epoxidation of olefins. Kinetic studies showed that the olefin coordinates to the metal prior to the rate-determining step. The features of these epoxidations are in agreement with the general characteristics of the Halcon epoxidation process [539].



248

R = H,Me,Cl,NO_2

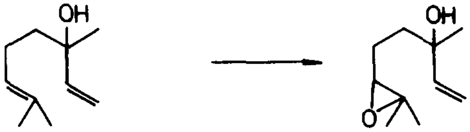
Epoxidation of cis-2-butene-1,4-diones (249) by $MoO_5.H_2O.HMPA$ occured stereospecifically to give the cis-epoxides (250)[540].

R = Ph,Me,OMe

249 250

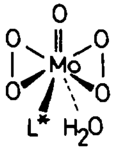
Stoichiometric epoxidation of olefins with $MO(O_2)_2(HMPA)$ (M = W,Mo) complexes has been studied in CH_2Cl_2 at 40°C. The tungsten complex was more active and it could be shown that the two peroxo groups react at different rates [541]. Epoxidation of geraniol (251) and linalool (252) with the same complexes in dichloroethane gave the epoxides (253) and (254), respectively. This change in regioselectivity suggests that epoxidation with these Mo and W complexes does not involve a coordinated substrate [542].

251 253

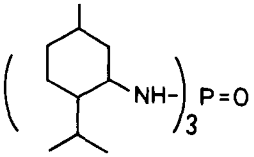


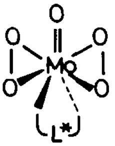
252 254

Peroxomolybdenum complexes (255, 256) containing chiral ligands were found to exhibit asymmetric induction in the epoxidation of trans-2-octene. Optical yields were about the same (highest value 11%) whether monodentate or bidentate chiral ligands were used [543].

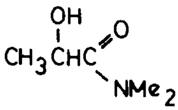


255; L* = e.g.





256; L* = e.g.



$CH_3CH(OH)C(=O)NMe_2$

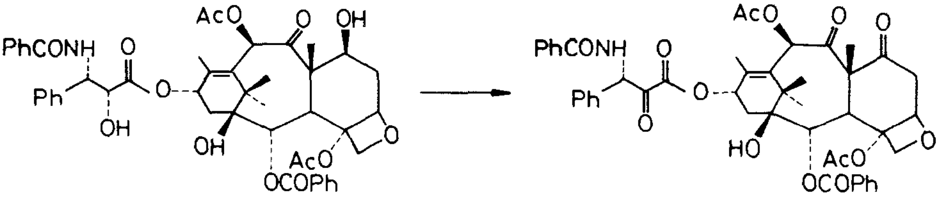
See also [526].

c) Oxidation of O-containing Functional Groups

Oxidation of benzaldehyde and its substituted derivatives by V^{5+} in $HClO_4$ was found to be first order in oxidant and less than first order in substrate. Kinetic and spectrophotometric results indicated the formation of a complex between V^{5+} and hydrated benzaldehyde [544]. The rate of oxidation of 20 heterocyclic alcohols by vanadium(V) in aqueous AcOH were measured [545].

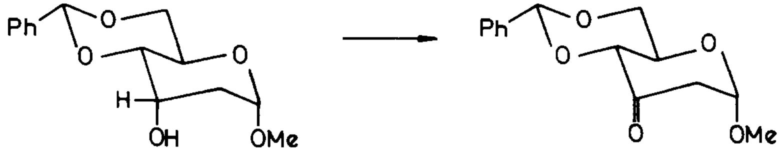
The kinetics of oxidation of butene-1,4- and pentane-1,5-diol by the 12-tungstatocobaltate(III) anion were investigated in aqueous perchloric acid [546].

The kinetics of oxidation of glycerol with Cr(VI) in strong acid media was studied [547]. The rate of iPrOH oxidation by chromic acid increased considerably in the presence of lactic acid. The formation of a termolecular complex was suggested [548]. Oxidation of oxalic acid and tartaric acid with $(tBuO)_2CrO_2$ was studied using IR spectroscopic methods [549]. The two secondary OH groups of taxol (257) could be oxidized with Jones's reagent (CrO_3 in aq. H_2SO_4) selectively to yield compound (258) [550].



257 258

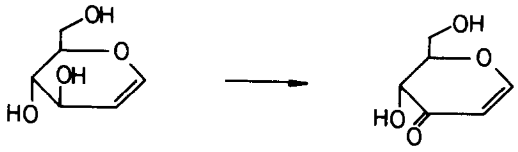
In the presence of quaternary ammonium species, CrO_3 gave complex chromate salts which could be used as homogeneous oxidants in CH_2Cl_2 solution for the conversion of alcohols into aldehydes or ketones. Oxidation was even more efficient if the quaternary ammonium species were applied in only catalytic amounts and the reaction was performed with solid CrO_3 under solid-liquid phase-transfer catalytic conditions. These complex chromates could also be fixed onto pyridinium or quaternary ammonium resins and used in this form [551]. Two new mild, Cr(VI) oxidation reagents based on nicotinic acid and isonicotinic acid were developed. Nicotinium dichromate and isonicotinium dichromate were suitable for the oxidation of alcohols into carbonyl compounds, hydroquinones into quinones and thiols into disulfides [552]. Oxidation of 2-octanol with CrO_3 and different quaternary ammonium salts gave 2-octanone in 60-80% yield. Thiols were oxidized into disulfides with pyridinium oxychromate or pyridinium oxydichromate [553]. Imidazolium dichromate was found to be a mild selective reagent for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds in DMF at 25°C [554]. The deoxyhexapyranoside (259) was oxidized to the corresponding ketone (260) by pyridinium dichromate in CH_2Cl_2 in the presence of 3A molecular sieve [555].



259

260

Allylic alcohols derived from carbohydrates (e.g. 261) could be oxidized to the corresponding enones with pyridinium dichromate with reasonable (40-80%) yields [556].



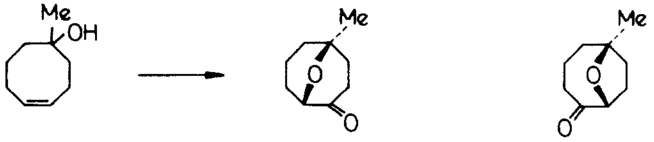
261

The bisphosphonium bichromate $(Ph_3PCH_2PPh_3)^{2+}(Cr_2O_7)^{2-}$ was found to be a selective agent for the oxidation of allylic or benzylic primary alcohols to the corresponding aldehydes. Saturated aliphatic alcohols were not affected [557].

Oxidation of D-glucose by pyridinium fluorochromate is first order each in oxidant and substrate. Reaction products are arabinose and formic acid [558]. Oxidation of allenic secondary alcohols like $CH_2{=}C{=}CMeCH_2CH(OH)Ph$ with pyridinium chlorochromate in CH_2Cl_2 gave the corresponding ketones in 71-87% yield [559]. Tetrasubstituted furans (262) (R = COOMe, COMe; R′ = substituted phenyl) were oxidized by pyridinium chlorochromate to give (Z)-MeCOCR=CR′OAc [560].

262

Treatment of the tertiary cyclooctenol (263) with Cr(VI) reagents results in transannular oxidative cyclization to the bicyclic ethers (264) and (265). The ratio of the two products strongly depends on the nature of the Cr(VI) reagent (CrO_3, pyridinium chlorochromate, Na_2CrO_4, etc.) [561].



263 264 265

Kinetic studies of the oxidation of C_1-C_3 alcohols by Mn(III) in acid media showed, that the reaction is first order with respect to alcohol and second order with respect to Mn(III) [562]. Oxidation of phenoxyacetic acid with permanganate in aqueous AcOH is first order each in oxidant and substrate [563]. Oxidation of citric, tartaric, or adipic acids, and sugars by MnO_4^- was studied in the presence of Fe(II), As(III) or Sb(III). The effect of these additives varied videly and depended on the organic substrate [564]. The unsaturated aldehyde (267) was prepared by the MnO_2 oxidation of the allyl alcohol (266) in 72% yield [565].

266 267

Aldehydes with protected hydroxyl groups (e.g. 268) were oxidized with $KMnO_4$ to the corresponding carboxylic acids in 95-98% yield using a mixture of tBuOH and aqueous NaH_2PO_4 as reaction medium [566].

268

Oxidation of simple aldehydes to carboxylic acids by K_2FeO_4 was shown to follow a mixed order rate equation containing three terms; only one of these was substrate dependent [567]. A solid mixture of $K_2FeO_4.Al_2O_3$, and $CuSO_4.5H_2O$ efficiently oxidized allylic, benzylic, and saturated secondary alcohols to the corresponding aldehydes or ketones. Since this solid mixture was practically inactive for the oxidation of primary alcohols it could be used for selective oxidations like that of (269) into (270) [568].

269 270

The kinetics of the oxidation of ethylene glycol, diethylene glycol, and tetraethylene glycol by $[Fe(CN)_6]^{3-}$ and using $RuCl_3.nH_2O$ as homogeneous catalyst has been determined. The proposed mechanism involves the formation of a complex between the glycol anion and a Ru(III) species; this complex slowly breaks up into the intermediate products and a Ru hydride which is then oxidized by $[Fe(CN)_6]^{3-}$ [569]. The Ru(IV)-oxo complex $[(bpy)_2Ru(O)(PEt_3)]^{3-}$ oxidizes iPrOH to acetone, propionaldehyde to propionic acid and Ph_3P to Ph_3PO. Analogous complexes containing other tertiary phosphines also oxidize organic substrates, their activity strongly depends on the nature of the phosphine ligand [570]. The kinetics of oxidation of formic acid (formate ion) by $[Ru(bpy)_2(py)(O)]^{2+}$ has been studied. The results suggest that oxidation occurs by a two-electron hydride transfer [571]. Oxidation of Na salts of lactic, tartaric, and glycolic acid by $[Fe(CN)_6]^{3-}$ catalyzed by

Ru(VI) in aqueous alkaline solution is first order in Ru(VI) and independent of $[Fe(CN)_6]^{3-}$ [572]. Oxidation of 2-methyl cyclohexanol by $Ce(SO_4)_2$ was investigated with $RuCl_3.nH_2O$ and RuO_4 as catalysts. The kinetics of the two reactions were different: the rate of oxidation was first order in Ru-trichloride but with RuO_4 the catalytic effect decreased at high concentrations [573]. Oxidation of butanol by OsO_4 was found to be first order in oxidant and substrate [574].

A system composed of (TPP)CoCl and its π cation radical $[(TPP)Co^{+\cdot}]Cl_2$ oxidized phenols to phenoxy radicals [575]. Oxidation of carboxymethylcellulose by Co(III) ions has been investigated in aqueous sulfuric acid and acetic acid solutions. The reaction was faster in AcOH [576]. The kinetics of oxidation of different substituted 1,2- and 1,4-dihydroxybenzenes by $[Rh_2(OAc)_4(H_2O)_2]^+$ was investigated. The rate was determined by the one-electron oxidation of the hydroquinone to a semiquinone radical intermediate [577]. A rate expression was derived for the oxidation of propanone-2 by $[Fe(CN)_6]^{3-}$ catalyzed by Ir(III) [578].

The oxidation of lactic acid and mandelic acid by Ni^{3+} has been studied. The reaction proceeded via C-C bond leavage; acetaldehyde, benzaldehyde, and CO_2 were detected as products [579]. The rate of oxidation of aliphatic primary alcohols by Ni^{3+} is both first order in oxidant and substrate; on outer sphere electron transfer from alcohol to Ni^{3+} was proposed as the rate-determining step [580].

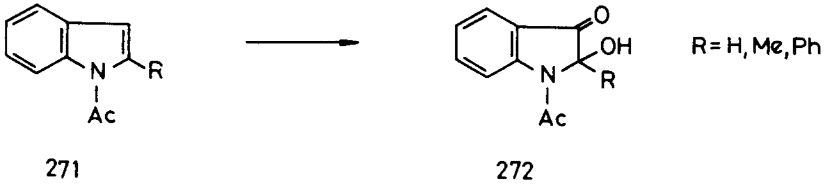
The dimeric Cu(II) complex of 3,5-di-tert-butyl-o-semiquinone has been synthesized. The existence of this complex proves that the (stoichiometric or catalytic) oxidation of catechols by Cu(II) complexes proceeds in two, one-electron steps [581].

The oxidation of dihydroresorcin, dimedone, and 3,5-dimethyl-2-cyclohexene-1-one with Ce(IV) was studied [582]. The kinetics and mechanism of Ce(IV) oxidation of glyoxylic acid and pentamminegly-oxalatocobalt(III) perchlorate were investigated in acidic sulfate media. Both $Ce(SO_4)_2$ and $[Ce(SO_4)_3]^{2-}$ appeared to be the oxidant species for coordinated glyoxalate while for free glyoxylic acid $Ce(SO_4)_2$ seemed to be the only oxidant [583]. 1,4-Dimethoxynaphthalenes were oxidized with high para regioselectivity to 1,4-naphthoquinones by $(NH_4)_2Ce(NO_3)_6$ under mild conditions [584]. Kinetics of the oxidation of D-altrose by $Ce(ClO_4)_4$ was studied in aqueous $HClO_4$. No evidence for initial complexation was obtained [585].

See also [587, 596].

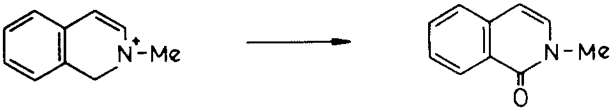
d) Oxidation of N-containing Organic Compounds

Oxidation of $H_2NCOCOOH$ (oxamic acid) by $K_2Cr_2O_7$ showed that the unprotonated substrate reacted faster than the protonated substrate [586]. Second-order rate constants for the cooxidation of various 2,6-diphenylpiperidin-4-ols and oxalic acid with Cr(VI) were determined [587]. Nitroketones were produced by oxidation of nitroalkanols dissolved in dichloromethane with montmorillonite-supported CrO_3. Irradiation by ultrasound improved the yield [588]. Oxidation of acetylindoles (271) with $MoO_5.OP(NMe_2)_3$ gave indolones (272) [589].



The kinetics of oxidation of aniline and substituted anilines by Mn(IV) have been studied. Reactions were first order both in oxidant and substrate; hydride transfer was proposed as the rate-determining step [590]. Stilbazoles were oxidized by $KMnO_4$. The 2- and 4- isomers underwent oxidative cleavage to yield PhCHO and the corresponding pyridinecarboxylic acid; the 3-isomer was unreactive under the same conditions [591]. Colloidal MnO_2 was found to act as an autocatalyst in the oxidation of aliphatic amines by MnO_4^- in phosphate buffered solutions [592]. The soluble Mn(IV) species formed in the oxidation of amines by MnO_4^- in phosphate buffered solutions were shown to consist of colloidal particles of MnO_2 with HPO_4^{2-} and $H_2MnO_4^-$ ions bound to the surface [593].

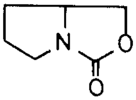
1-Phenylsemicarbazide is oxidized by ferricinium ion to $PhN{=}NCONH_2$. The equilibrium and the kinetics of this reaction were studied [594]. The effect of substituents on the rate constants and activation energies in the oxidation of substituted anilines by $[Fe(bpy)_3]^{3+}$ was studied. The data correlate with the pK values of the anilinium ions [595]. Oxidation of benzyl alcohol or benzyl-amine by $[Fe(CN)_6]^{3-}$ in presence of Os(VIII) as catalyst is first order both in oxidant and substrate [596]. The kinetics of the Ru(III)-catalyzed oxidation of triethanolamine by $[Fe(CN)_6]^{3-}$ has been determined. The reaction was second order in oxidant and both first order in the substrate and the catalyst [597]. The 2-methylisoquinolinium cation and the 1-methylquinolinium cation are rapidly oxidized by $[Fe(CN)_6]^{3-}$ to 2-methyl-1-isoquinolinone (273) and 1-methyl-2-quinolinone (274), respectively. Both oxidations are inhibited by the ferrocyanide ion reaction product. Other heteroaromatic cations with related structures behave similarly [598, 599].



273

274

1-Azabicycloalkan-2-ones like (275) were oxidized with RuO_4. Oxidation occured regioselectively at the bridgehead carbon atom and afforded either the corresponding hydroxy compounds or carboxylic acid derivatives like (276) [600].



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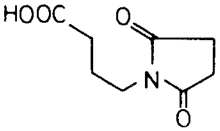
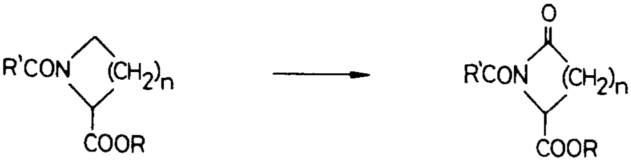


276

Cyclic amino acids (277) (R = Me,Et; R′ = Me,Et,Cy,OEt; n = 1,2,3) were oxidized by RuO_4 to give lactams (278). Oxidation was performed in a two-phase system; EtOAc/H_2O was the best solvent combination [601].



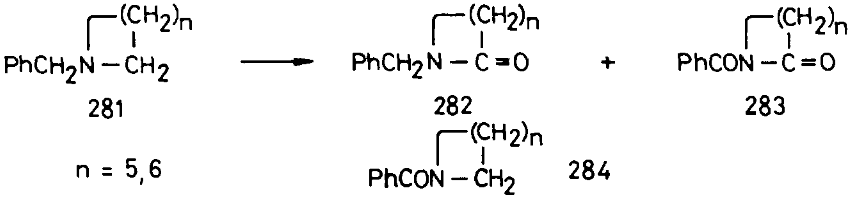
277

278

Oxidation of cyclic amides (279) with RuO_4 gave cyclic lactams (280). Under the same conditions cyclic benzylamines (281) gave lactams (282) and (283), and benzamides (284) [602].

279 280

R = H,Me,Ph
n = 5,6



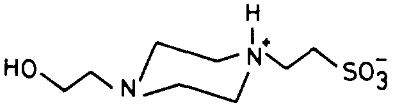
281 282 283

n = 5,6

284

Kinetic data for the oxidation of p-$H_2NC_6H_4N(Et)CH_2CH_2OH$ to benzoquinone by the Co(III) complex $[Co(NH_3)_3Cl]Cl_2$ indicated that the rate-determining step was the conversion of the substrate to the semiquinone [603].

The widely used buffer HEPES (285) and N,N-dimethylethanolamine are oxidized by Cu(I). Probably the alcoholic OH is oxidized but simple alcohols like EtOH do not react under the same conditions [604].

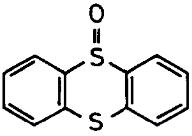


285

Oxidation of hydroxypyridines with Ce perchlorate in perchloric acid medium was studied [605].

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

Oxidation of thianthrene-5-oxide (286) with $(HMPA)MO_5$ (M = Cr, Mo,W) leads to about equal amounts of (287) and (288) [606].



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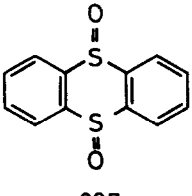

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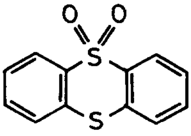
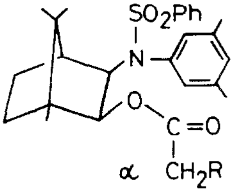


288

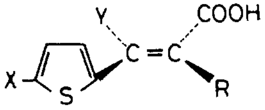
Diastereoselective α-hydroxylation of the chiral carboxylic esters (289) was achieved with MoO_5.py.HMPA in the presence of

$KN(SiMe_3)_2$ and K(sec-BuO). Hydroxylation proceeded over the enolate form of the esters and was practically restricted to esters having no substituents at the α carbon atom [607].



289

Oxidation of thiocaprolactam by $KMnO_4$ was investigated. Reaction products were identified [608]. The kinetics and mechanism of the permanganate ion oxidation of thienyl propionates (290, 291) has been studied. A rate-determining step leading to the formation of a metallacyclooxetane (292) or a cyclic Mn(V) diester (293) was proposed [609].



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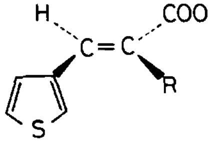

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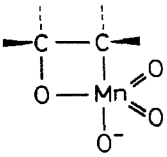
X = H, Br, Me
Y = H, D, Me
R = H, Me, Ph, CN



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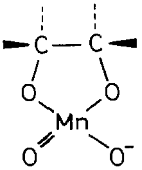
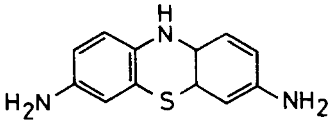


293

The pertechnate ion oxidizes L-cysteine in strong acids to form Tc(V)-cystine and Tc(V)-cysteine complexes [610].

Oxidation of methionine by alkaline $[Fe(CN)_6]^{3-}$ is first order in substrate, oxidant and alkali [611]. Potassium ferrate (K_2FeO_4) was found to be a strong oxidizing agent for the transformation of aliphatic sulfides to sulfoxides and sulfones. Iron(VI) was reduced during the reaction to iron(III) [612]. The kinetics of the oxidation of disulfonated leucothionines (parent compound see 294) by Fe^{3+} has been examined. Since the formation of the thionine skeleton (295) involves flattening of the phenothiazine moiety, the necessary electron transfer is much more difficult if the organic molecule is a ligand within a metal complex than if it is the anion of an ion pair [613].



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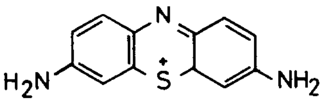

295

Complete oxidation of $(H_2NCH_2CH_2S)_2$ to NH_3, carbonate and sulfate by ditelluratocuprate(III) in aqueous KOH is catalyzed by OsO_4 [614]. Cysteine is quantitatively oxidized to cystine by an excess of the Cu(II) complex of tris[2-(2-pyridyl)ethyl]amine [615].

Triphenyl phosphine was oxidized by $[Bu_4N][PMo_{12}O_{40}]$ to Ph_3PO; the molybdophosphate anion was reduced to $[Bu_4N]_3[PMo_{12}O_{39}]$ [616].

2-Bromo-m-xylene could be oxidized to 2-bromoisophthalic acid by $Na_2Cr_2O_7$ at 230°C under 20 bar CO_2 pressure [617]. Polymer-supported H_2CrO_4 was applied for the oxidation of p-$C_6H_4(CH_2X)_2$ (X = Br,Cl,H) to p-$C_6H_4(CHO)_2$ [618].

See also [349, 471, 526, 552, 553, 570].

7. Electrooxidation and Photooxidation

β -Cyclodextrin accelerates the electrocatalytic oxidation of NADH by ferrocenecarboxylic acid (Fca). Probably a cyclodextrin-Fca^+ complex acts as the effective oxidant [619]. Constant-potential electrolysis of a solution of (TMP)FeOH in the presence of olefins was found to produce epoxides as major products [620]. A system consisting of RuO_4/RuO_2 and Cl^+/Cl^- redox couples has been developed for the indirect electrooxidation of secondary alcohols to ketones, of primary alcohols and aldehydes to carboxylic acids and of diols to lactones and keto acids. Oxidation proceeds in an aqueous-organic two-phase reaction mixture; RuO_4 is the actual oxidant of the organic substrate [621]. The oxo-bridged Ru(III)-

dimer $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ was used as a catalyst for the electrooxidation of alcohols, sugars, and amino acids in basic solutions. Actual oxidant was the Ru(IV)Ru(V) dimer generated in situ [622]. A series of Ru complexes containing bpy and phen ligands were tested as electron transfer mediators in the electrocatalytic oxidation of 1,2,4,5-tetramethylbenzene and pentamethylbenzene [623].

D-Fructose was oxidized to D-erythrose by Fe(III) or Mn(III) ions under photochemical conditions. Since Fe(II) and Mn(II) thus formed were reoxidized by atmospheric oxygen, the photochemical oxidation of D-fructuse could be performed catalytically. No metal hydroxide was precipitated from the solutions [624].

V. Reviews

Homogeneous catalysis by transition-metal complexes. 330 refs. [625].

Catalysis by zeolite inclusion compounds. 15 refs. [626].

Recent developments in homogeneous catalysis [627].

Industrial applications of homogeneous catalysis. 50 refs. [628].

Homogeneous metal complex catalyst design. 7 refs. [629].

Organometallic chemistry and catalysis in industry. [630].

Hydroformylation. An old yet new industrial route to alcohols. 11 refs. [631].

Asymmetric hydrosilylation and hydrocarbonylation. 112 refs. [632].

Homogeneous mixed-metal catalyst systems: new and effective routes to N-acyl-α-amino acids via carbonylations. 21 refs. [633].

Homogeneous catalytic reaction of CO, H_2 and methyl acetate: a new process for acetic anhydride/vinyl acetate. 12 refs. [634].

Convert methanol to ethanol [635].

Direct route from synthesis gas to ethylene glycol. 23 refs. [636].

Syntheses of oxygen-containing organic compounds from synthesis gas in the presence of Rh catalysts. 77 refs. [637].

Metal carbonyls in phase transfer catalysis. 102 refs. [638].

Homogeneous and phase transfer catalyzed carbonylation reactions. 27 refs. [639].

Reactivity of CO in transition metal complexes. 147 refs. [640].

Catalytic fixation of carbon dioxide by metal complexes. 274 refs. [641].

Reversible binding of H_2, O_2, and CO, and catalysis by cationic complexes containing bis ditertiaryphosphine complexes of Rh(I). 33 refs. [642].

Carbonyls of transition metals in conjugation with hydrogen donors - initiators of radical reduction of trichloromethyl compounds. 78 refs. [634].

Syntheses and catalytic actions of organosilicon polymer-supported metal complexes. 25 refs. [644].

Supported metal complexes as hydrogenation catalysts. 206 refs. [645].

Mechanism and stereochemistry of asymmetric catalytic hydrogenations. [646].

Asymmetric catalytic hydrogenation: mechanism and origin of enantioselection. 40 refs. [647].

The applicability of asymmetric homogeneous catalytic hydrogenation. 112 refs. [648].

Enantioselective catalysis with transition metal complexes. 73 refs. [649].

Chiral ligands for asymmetric catalysis. 163 refs. [650].

Application of organometallic catalysis to the commercial production of L-DOPA. 13 refs. [651].

Complex reducing agents: their applications and their outcome in the field of carbonylations. 19 refs. [652].

Selective reduction of aldimines by formic acid in the presence of $HRh(PPh_3)_4$. 9 refs. [653].

Electrochemistry of Ni compounds and their applications in electrocatalyzed organic synthesis. 64 refs. [654].

Indirect electro-organic syntheses - a modern chapter of organic electrochemistry. 201 refs. [655].

Catalyzed liquid-phase oxidation of olefinic hydrocarbons. II. Effect of catalyst type, reaction conditions and other oxidizable organic compounds on epoxide yield. 53 refs. [656].

Activation of molecular oxygen by metal complexes and its role in the mechanism of liquid-phase oxidation. 119 refs. [657].

Metalloporphyrins as catalysts in autoxidation processes. 170 refs. [658].

Metalloporphyrin-catalyzed oxygenation of hydrocarbons. 184 refs. [659].

Dependence of activity and selectivity of immobilized catalysts for hydroperoxide epoxidation of olefins on the structure of the carrier. 8 refs. [660].

The discovery of the asymmetric epoxidation. 22 refs. [661].

The discovery of titanium-catalyzed asymmetric epoxidation. 26 refs. [662].

On the mechanism of asymmetric epoxidation with titanium-tartrate catalysts. 104 refs. [663].

Asymmetric epoxidation of allylic alcohols: the Sharpless epoxidation. 105 refs. [664].

Synthetic aspects and applications of asymmetric epoxidation. 69 refs. [665].

A short route to chiral sulfoxides using titanium-mediated asymmetric oxidation. 25 refs. [666].

25 Years in the organic chemistry of palladium. 83 refs. [667].

The chemistry of activated bleomycin. 58 refs. [668].

Toward functional models of metalloenzyme active sites: analogue reaction systems of Mo oxo transferases. 50 refs. [669].

Biomimetic oxidations catalyzed by copper. 49 refs. [670].

Biomimetic oxidation of hydrocarbons and drugs by metalloporphyrinic systems. 41 refs. [671].

Biological strategies for the manipulation of dioxygen. The chemistry of cytochrome P-450. 34 refs. [672].

List of Abbreviations

acac = acetylacetonate
AS = Annual Survey on Hydroformylation, Reduction, and Oxidation
BPPM = see Fig. (25a)
bpy = 2,2'-bipyridine
chiraphos = see AS 1985, Fig.(9)
COD = 1,5-cyclooctadiene
Co(salen) = see Fig. (169)
Co(salpr) = see AS 1985, Fig. (109)
Cp = cyclopentadienyl
Cy = cyclohexyl
DET = diethyl tartrate
DIOP = see AS 1985, Fig. (31)
dipamp = see AS 1985, Fig. (34)
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 $Ph_2P(CH_2)_3PPh_2$
HD = 1,5-hexadiene
HMPA = hexamethylphosphoric triamide
men = menthyl
NBD = norbornadiene
nmen = neomenthyl

OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato
o.y. = optical yield
phen = 1,10-phenanthroline
py = pyridine
salen = N,N'-bis(salicylidene)-ethylenediamino
SIL = silica
st = stearate, $nC_{17}H_{35}COO$
TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato
TDMPP = 5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrinato
tetpy = 2,2':6',2":6",2‴ -tetrapyridine
TMP = 5,10,15,20-tetramesitylporphyrinato
TPP = 5,10,15,20-tetraphenylporphyrinato
TPP-Me-*p* = 5,10,15,20-tetrakis(*p*-tolyl)porphyrinato
TPP-OMe-*p* = 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrinato
trpy = 2,2':6'2"-terpyridine
Ts = *p*-toluenesulfonyl (tosyl) *p*-$CH_3C_6H_4SO_2$-
Z = benzyloxycarbonyl, $PhCH_2OOC$-

Metal index

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