Journal of Organometallic Chemistry, 432 (1992) 1–214
Elsevier Sequoia S.A., Lausanne
JOM 22594AS

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

ANNUAL SURVEY COVERING THE YEAR 1990*

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(Received November 21, 1991)

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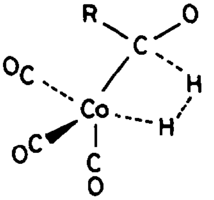
*No reprints available

Previous Annual Survey see J.Organomet.Chem. 404 (1991) 325.

I. THEORETICAL CALCULATIONS

The Bodenstein approximation for trace-level intermediates was used to reduce multistep reaction-kinetic networks of arbitrary topology and size to simpler forms. The method was illustrated with hydroformylation of olefins as model reaction [1]. As part of the hydroformylation catalytic cycle, the oxidative addition of H_2 to $RCOCo(CO)_3$ has been studied theoretically by the ASED-MO method. Two reaction pathways were proposed for the reaction [2]. From the results of approximate density functional calculations, it was concluded that both the oxidative addition/reductive elimination sequence and the process involving the distorted four-center intermediate (1) are likely to be a part of the mechanism of the product forming step in the cobalt-catalyzed olefin hydroformylation. The activation barriers in the case of the acetyl-cobalt tricarbonyl + H_2 reaction were calculated to be 77-85 kJ/mol [3].



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A theoretical study on the insertion of formaldehyde into the cobalt-hydrogen bond of $HCo(CO)_3$ (an important step of CO hydrogenation) revealed that an intermediate trigonal bipyramidal π-complex with CH_2O in equatorial position was favored, and the methoxy insertion product was more stable than the corresponding hydroxymethyl complex [4].

Molecular graphics and van der Waals minimizations were used to analyze the steric interactions of the enantioselective step of asymmetric catalytic hydrogenation of dehydro amino acids using chiral bidentate phosphine Rh(I) complexes [5].

Several INDO/1 calculations on Ru(IV)-oxo complexes with the intent of studying the various pathways and intermediates postulated for transition-metal-catalyzed oxygen atom transfer reactions involving high-valent, metal-oxo complexes have been carried out. Calculations on the epoxidation of olefins with the model compound *cis*-$[Ru(CH-CH{=}NH)_2(NH_3)_2(O)]^{2+}$ showed that in this case the preferred pahtway is a nonconcerted [1 + 2] cycloaddition to yield a bound epoxide [6]. The same molecular orbital model was employed to analyze the reaction between ethene and *cis*- and *trans*-$[Ru(NH{=}CH-CH{=}NH)_2(O)_2]^{2+}$ complexes. In agreement with earlier experimental results calculations did show, that whereas the *trans* isomer is selective for epoxidation, the *cis* isomer furnishes mainly cleavage products [7]. The MO analysis of the interaction between *cis*-$[Ru(HN{=}CH{-}CH{=}NH)_2(NH_3)(O)]^{2+}$ and methanol using the INDO/1 method has shown that a pathway which involves precoordination of the alcohol to the metal is competitive with a pathway which involves C-H activation by the oxo ligand alone [8,9]. For elucidation of the mechanism of oxidative ring cleavage of catechols with O_2 by nonheme iron enzymes, extended-Hückel calculations were performed for mono- and bidentate catecholato-iron complexes and the O_2 adduct of a semiquinonato-iron complex. The results support the direct attack of O_2 on the semiquinonato ligand [10]. By using the frontier orbital approach it was shown that an alkene can add to an osmium tetroxide-nitrogen ligand complex in two ways: to the two equatorial oxygens and to one equatorial and one axial oxygen. The latter was suggested to account for the enantioselective dihydroxylation of alkenes by OsO_4 in the presence of chiral nitrogen ligands [11]. The mechanism of oxidation of ethene to acetaldehyde by the Pd nitrite complex $Pd(NO_2)Cl(CH_3CN)_2$ has been studied with the help of the CNDO-S^2 method [12].

It has been proposed that all oxidations of organic substrates by O_2 are catalyzed by metal ions (sometimes in trace concentrations) and that inhibition is due to the formation of catalytically inactive complexes. Computer-simulated kinetics of such a mechanism accounted for all experimentally observed inhibition effects including those which are considered as proofs of chain mechanisms [13].

II. HYDROFORMYLATION AND RELATED REACTIONS OF CO

1. Hydrogenation (Reduction) of CO to Oxygen-Containing Organic Compounds

Addition of phosphoric acid to the $Ru_3(CO)_{12}$ + PPNCl catalyst system markedly improved the selectivity of EtOH synthesis from synthesis gas at 260 °C and 340 bar. The best result (51%) was achieved in diphenylether as solvent. The favorable effect of phosphoric acid is probably related to its role as a source of H^+ ions. Since the phosphate anion can not coordinate to Ru and thus poison the catalyst it is superior to HX acids which at the same time provide the strongly coordinating halide anions [14].

The electrocatalytic reduction of CO was studied in aqueous solutions with pentacyano complexes of cobalt as catalysts and graphite electrodes. Methanol and formic acid were formed [15].

The hydrogenation of CO was investigated using $Rh_4(CO)_{12}$ catalyst in 1-methylpyrrolidine as solvent at 210-270 °C and 500-1800 bar total pressure ($CO:H_2$ = 1:1). Selectivity for ethylene glycol, 1.2-propanediol and glycerol increased with increasing pressure; increasing the temperature decreased the selectivity to ethylene glycol and increased that to EtOH [16]. See also [76,203,217].

2. Hydroformylation

a) Cobalt Catalysts

Hydroformylation experiments with 1-hexene in MeCN solution at 80 °C and 120 bar CO + H_2 showed that reaction rates and regioselectivities do not depend on whether $Co_2(CO)_8$ or $Co_4(CO)_{12}$ are used as catalyst precursors. It was proposed that in such polar solvents $HCo(CO)_4$ acts mainly as an acid and the first step of the catalytic cycle is the protonation of the olefin [17].

The protioformylation of (E)-1,1,1-d_3-2-butene and the deuterioformylation of (E)-2-butene was investigated using $Co_2(CO)_{12}$, or $Pt(SnCl_3)C[(R,R)\text{-}DIOP]$ as the catalyst precursor. The protium and deuterium contents of the products were discussed according the accepted reaction mechanism of hydroformylation [18].

Carbonyl clusters containing the $Co_3(CO)_9$ entity were investigated as hydroformylation catalysts. Clusters of the type $R_4N[FeCo_3(CO)_{12}]$ were active catalysts for the hydroformylation of both terminal and internal olefins. The activity of $YCCo_3(CO)_{12}$ clusters decreased in the order Y = Pr > H > Ph > EtOOC > Cl [19]. The activity of $Co_2(CO)_8$ - $Ru_3(CO)_{12}$ catalysts for hydroformylation of ethene at 110 °C and 76 bar was higher than that $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ alone. Infrared spectra of the products showed that no mixed-metal carbonyls were formed [20]. Bimetallic systems composed of cobalt carbonyls and lanthanide complexes

(Cp_2Yb, Cp_2YbCl, Cp_2LuCl, and Cp_3Lu) were tested as catalysts for the hydroformylation of 1-octene. No significant influence of the lanthanide component on the activity and regioselectivity of cobalt carbonyl catalysts was observed [21].
See also [61,64,85].

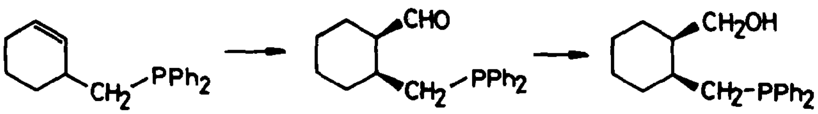
b) Rhodium Catalysts

A kinetic analysis of the $Rh_4(CO)_{12}$-catalyzed hydroformylation of 2-butenes indicated that the mechanism involves fragmentation of the cluster to mono- and binuclear Rh complexes; the mononuclear complexes are the catalytically active species but the larger part of the rhodium is present in the form of the binuclear complexes [22]. The influence of reaction parameters (temperature, total gas pressure, and time) on the chemoselectivity and regioselectivity in rhodium-catalyzed 1-hexene hydroformylation ($Rh_4(CO)_{12}$ as catalyst precursor) has been investigated. It was found that the chemoselectivity to aldehydes was complete at room temperature, it decreased with increasing temperature and decreasing total pressure, but it was independent of the conversion. The regioselectivity increased in favor of the linear isomer when the temperature was raised and was independent of both total pressure and conversion. These observations have been explained by the differing bebaviors of the linear and branched alkyl rhodium intermediates towards β-hydride elimination under the reaction conditions [23]. Excellent regio- and stereoselectivity was observed in the rhodium-catalyzed hydroformylation of the phosphite ester (**2**) at 100 °C and 35 bar CO + H_2 which gave exclusively aldehyde (**3**). Similar regiocontrol was shown in the hydroformylation of (**4**) which gave only the branched-chain aldehyde (**5**). In contrast, the phosphate ester corresponding to (**4**) gave an approximately equimolar mixture of branched-chain and terminal aldehydes [24].

2 **3**

4 5

Similarly, excellent stereo- as well as regio-control was achieved also in the rhodium-catalyzed hydroformylation of substituted alkenylphosphines like (**6**) at 28 bar H_2/CO (1:1) in ethyl acetate solution using $[Rh(OAc)_2]_2$ as a catalyst precursor. At 45-55 °C and 90 °C aldehydes and alcohols, respectively, were formed in good to excellent yield [25].



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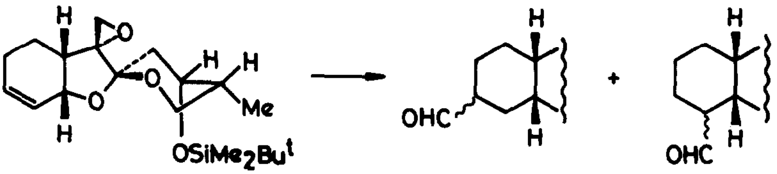
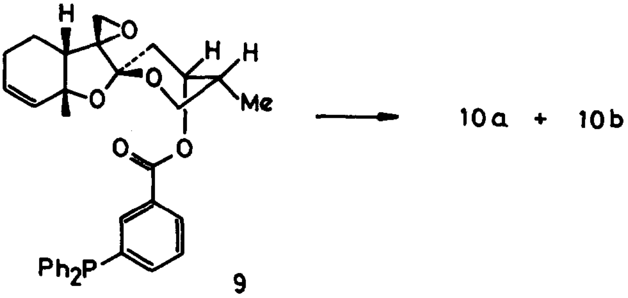
Hydroformylation of the cyclohexene derivative (**7**) with phosphine-free rhodium catalysts resulted in the formation of the two regioisomeric aldehydes (**8a**) and (**8b**) in a 2.3:1 ratio. The addition of different phosphines or phosphites increased the amount of (**8b**). To increase the more valuable isomer (**8a**) the auxiliary *m*-(diphenylphosphino)benzoic acid group was incorporated into the starting olefin (**7**) to give (**9**); this phosphinated olefin gave after hydroformylation with $[(COD)RhOAc]_2$ the two analogous regioisomeric aldehydes (**10a**) and (**10b**) in a 4:1 ratio [26].



7 8a 8b



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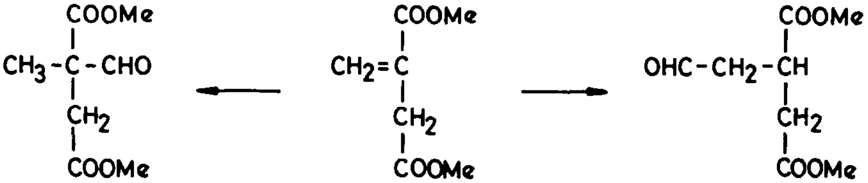
Hydroformylation of olefins was studied under mild conditions (50 °C and 1 bar) using Rh$_4$(CO)$_{12}$ as catalyst precursor. The Rh complex itself was not catalytically active under these conditions but showed high catalytic activity in the presence of phosphines [27]. Hydroformylation of dimethyl itaconate (**11**) with rhodium carbonyl catalyst leads preferentially to (**12**). This regioselectivity is completely reversed by adding phosphines to the catalyst whereupon (**13**) becomes the favored prosuct [28].



13 11 12

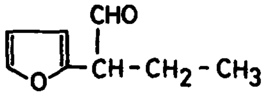
The hydroformylation of *N,N*-diethyl methacrylamide and *N,N,N',N'*-tetraethyl itacondiamide using Rh$_4$(CO)$_{12}$ or Rh$_4$(CO)$_{12}$ and (R,R)-DIOP as the catalyst precursor was studied [29].

The mechanism of propene hydroformylation catalyzed by Rh-phosphine complexes has been studied using IR-spectroscopy. Oxidative addition of H_2 to PrCORh(CO)$_2$(PPh$_3$)$_2$ was found to be the rate-determining step [30]. The effect of different ligands in the catalyst precursor and the effect of excess PR$_3$(R = Ph, OPh, OMe) on catalytic activity and selectivity in the rhodium-catalyzed hexene-1 hydroformylation was studied at 5 bar and 80 °C. Selectivity of n-aldehyde formation increased with increasing P/Rh ratio, this was accompanied in the case of R = OPh, OMe with the decrease of catalytic activity [31]. Hydroformylation of hexene-1 catalyzed by $RhH(PEt_3)_3$ or $Rh_2(OAc)_4/PR_3$, (R = Me, Et or Bu), at 120 °C and 80 bar produces a mixture of aldehydes and alcohols in toluene or THF but exclusively alcohols in ethanol [32]. Aldehydes (n + iso) were obtained in 80-85% yield in hexene-1 hydroformylation at 40 °C under atmospheric pressure of $CO:H_2$ = 1:1 using $Rh(acac)[P(OPh)_3]_2$ as catalyst precursor together with pyridine or other tertiary amines in toluene solution [33]. Terpenes and related molecules were hydroformylated under mild conditions (35 bar, 60-140 °C) using Rh-phosphine catalysts. The selectivity of monohydroformylation of polyunsaturated substrates and the effect of alcohol and ester groups on the reaction was investigated [34].

The liquid-phase hydroformylation of a commercially available low-molecular-weight polybutadiene using $HRh(CO)(PPh_3)_3$ with excess PPh_3 was examined in toluene at 77-114 °C and 22 bar $CO:H_2$ = 1:1. Only negligible olefin hydrogenation was observed. A comparison of the hydroformylation rates of a 1:1 *cis/trans*-3-octene mixture with that of syndiotactic 1,2-polybutadiene and *cis*-1,4-polybutadiene has shown that the influence of molecular weight on rate was not significant under the above reaction conditions [35]. Syndiotactic 1,2-polybutadiene reacted about six times as fast as 1,4-*cis*-polybutadiene and furnished a product containing mainly terminal aldehyde groups [36]. Hydroformylation of a low-molecular-weight polybutadiene composed of 12% 1,2- and 88% 1,4-units with $Rh(PPh_3)_3Cl$ catalyst in the presence of excess PPh_3 was examined. Only negligible hydrogenation was observed and gel permeation chromatograpy showed that aldehyde formation was uniform over the entire range of polymer molecular weight [37,38].

The phosphite $MeC(CH_2O)_3P$ was found to be comparable to PPh_3 as ligand in the hydroformylation of allyl alcohol with $Rh_4(CO)_{12}$ or $Rh(acac)(CO)_2$ catalysts and even gave a more stable catalyst system. The free phosphite was subject to hydrolysis but coordination to Rh suppressed this reaction allowing catalyst recycling after aqueous extraction of the products [39].

Hydroformylation of 2,3-dihydrofuran with $HRh(CO)(PPh_3)_3$ as catalyst gives the regioisomeric aldehydes, tetrahydrofurfural and tetrahydro-3-furancarboxaldehyde. The effect of temperature, pressure, catalyst concentration, and solvent on the isomer ratio was studied [40]. Hydroformylation of 2-vinyl- and 2-propenylfuran was studied with $HRh(CO)(PPh_3)_3$ as catalyst. Vinylfuran gave a mixture of the two isomeric aldehydes whereas propenylfuran underwent a regiospecific reaction to yield aldehyde (**14**) in 89% yield [41].



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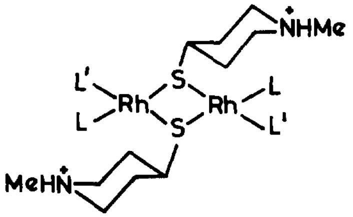
The $[Rh(\mu\text{-}L)(CO)_2]_2/PPh_3$ system (L = thiolato) was used as the catalyst precursor in the hydroformylation of 1-hexene at 5 bar ($CO{:}H_2$ = 1:1) and 80 °C in 1,2-dichloromethane. The best result, 94% conversion and 77% selectivity in linear aldehyde, was obtained with the *p*-SC_6H_4F ligand in the case of a 1:2 = $Rh{:}PPh_3$ ratio [42]. Styrene and 2-vinylfuran can be selectively transformed into the corresponding aldehydes under mild conditions by hydroformylation in the presence of $Rh_2(\mu\text{-}SR)_2(CO)_2L_2$ (R = tBu, Ph; L = PPh_3, $P(OMe)_3$, $P(OPh)_3$) complexes as catalysts. In order to facilitate the recovery of the catalyst two ways to heterogenize the reaction medium were investigated: using the water-soluble trisulfonated triphenylphosphine ligand and immobilizing the complex onto a solid support [43]. Hydroformylation of 2,3-dihydrofuran at 80 °C and 5 bar ($CO{:}H_2$ = 1:1) using $[Rh_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2(COD)_2]$ as catalyst precursor together with $P(O\text{-}2\text{-}tBuC_6H_4)_3$ as auxiliary ligand gave a complete conversion into a 77:23 mixture of tetrahydrofuran-2- and -3-carbaldehyde. The latter was formed selectively from 2,5-dehydrofuran at 30 bar using PPh_3 as auxiliary ligand [44]. The dimeric cationic complexes (**15**) have been prepared and tested in the form of their chloride or tetrafluoroborate salts as hydroformylation or hydrogenation catalysts. The complex (**15a**) $(BF_4)_2$ in the presence of excess PPh_3 was found to be the most active hydroformylation catalyst; all the chlorides were inactive [45].

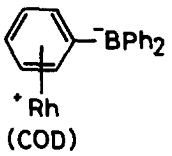


15a; L - L' = COD

15b; L = L' = CO

15c; L = CO, L' = PPh_3

The zwitterionic rhodium complex (16) is a useful catalyst precursor for the regioselective hydroformylation of vinylarenes and vinylethers to branched-chain aldehydes; aliphatic or aromatic, 1,1-disubstituted olefins afford, however, linear aldehydes in a regiospecific process. These reactions occur under remarkably mild conditions: 47 °C, 14 bar $CO:H_2$ = 1:2 in $CHCl_3$ solution [46].



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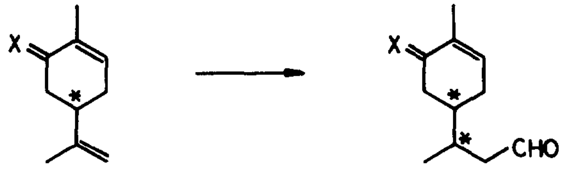
The bimetallic complexes $Cp'_2Zr(CH_2PPh_2)_2[Rh(\mu\text{-}SBu^t)(CO)]_2$ and $Cp'_2Zr(CH_2PPh_2)_2[Rh(COD)]BPh_4$ (Cp'_2 = $\pi\text{-}C_5H_4Bu^t$) were prepared and tested as hydroformylation catalysts [47]. The Keggin-type metal oxide cluster anions $[XM_{12}O_{40}]^{n-}$ (X = Si,P; M = Mo,W; n = 3,4) and $[PVMo_{11}O_{40}]^{4-}$ react with $[(PPh_3)_3Rh(CO)]^+$ in MeCN – EtOH to form $[(PPh_3)_3Rh(CO)(MeCN)]_nXM_{12}O_{40}$ and $[(PPh_3)_3Rh(CO)]_nXM_{12}O_{40}$ complexes. The complexes catalyze the hydroformylation of olefins to aldehydes and the oxidation of aldehydes by O_2 to carboxylic acids. Accordingly, these compounds act as bifunctional catalysts [48].

See also [18,61,64,85,104,141,170,183].

c) Platinum Catalysts

The effect of reaction parameters (temperature, pressure, PPh_3/Pt molar ratio, Sn/Pt molar ratio, catalyst concentration and solvent) in hydroformylation of n-butenes using $PtCl_2(COD)/PPh_3/SnCl_2$ as catalyst precursor was studied. The linearity of the aldehydes was in the range of 40-70%, and in the best case ca. 150 turnovers per hour were obtained [49]. The addition of PPNCl resulted in a more active system with increased stability and decreased isomerizing and hydrogenating behavior [50]. The effect of phosphorus ligands (L) on the activity and selectivity of the catalytic system $PtCl_2(COD)/SnCl_2/L$ in (Z)-2-butene hydroformylation was investigated. Forty ligands were examined at 120 °C and 140 bar CO/H_2 = 1/1 in CH_2Cl_2. With aryl phosphites, selectivities of 65-75% in n-pentanal were achieved, along with a high activity of the catalytic system [51]. The hydroformylation of different olefins using *cis*-$[PtCl_2(PPh_3)_2]/SnCl_2$ as the catalyst at 80-90 °C and 100 bar $CO:H_2$ = 1:1 was studied. The results obtained with allyl benzene (100% conversion, 87% hydroformylation with a selectivity of 80% in γ-aldehyde) are higher than those reported for Co- or Rh-based systems [52]. The complexes *trans*-$[PtCl(COEt)(PMePh_2)_2]$ and *trans*-$[PtCl(COEt)(PMe_2Ph)_2]$ were examined as catalysts in 1-hexene hydroformylation in the presence of an excess of $SnCl_2$ at 80 °C and 100 bar in toluene or CH_2Cl_2 solution [53]. Platinum complexes containing $Ph_2P(O)H$ are active hydroformylation catalysts at 80-100 °C and 30-100 bar; the reaction rates are the same as those obtained with platinum-trichlorostannate catalysts. Both aldehydes and alcohols are formed. Several alkyl and acyl complex intermediates have been identified [54,55]. The effect of chain length of chelating phosphines and the basicity of nitrogen-base additives on hydroformylation of styrene and α-Me-styrene with $PtCl_2$/bisphosphine/$SnCl_2$ catalysts was investigated at 100 °C and 80 bar (CO/H_2 = 1/1) in toluene solution [56].

The hydroformylation of (+)-R-limonene (**17**; X = H_2) and (−)-R-carvone (**17**; X = O) in the presence of $PtCl_2$-bisphosphine-$SnCl_2$ catalytic systems at 40-120 °C and 80 bar resulted in the corresponding linear aldehydes (**18**). The diastereomeric composition of the products upon variation of the chelating phosphine in the catalyst was studied [57].



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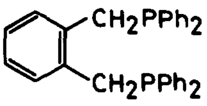
Mixtures of the complexes $[Pt(C_2H_4)((+)\text{-DIOP})]$ and $[PtCl_2((+)\text{-DIOP})]$ were found to be active catalysts for hydroformylation of styrene and 1-hexene at 100 °C and 100 bar. Asymmetry induced in the branched aldehydes was 10 and 27%, respectively [58]. The hydroformylation of methyl methacrylate using $[(R,R)\text{-DIOP}]Pt(SnCl_3)Cl$, $[Rh(CO)_2Cl]_2$ + PPh_3 + Et_3N, $[Rh(CO)_2Cl]_2$ + (S,S)-chiraphos + Et_3N, and $Rh_4(CO)_{12}$ catalyst precursors was reported. In the case of the Pt catalyst, (S)-OHCCH(Me)COOMe was formed with 37% ee [59]. The platinum(0) complexes $Pt(C_2H_4)L$ (L = (+)-DIOP, or **19**), when promoted by $MeSO_3H$, become active catalysts for styrene hydroformylation. No enantioselectivity was observed when using (+)-DIOP as ligand [60].



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See also [18,61,64].

d) Other Metals as Catalysts

Hydroformylation of vinyltrimethylsilane catalyzed by Rh, Pt, Co, and Ru complexes was studied. Rhodium catalysts like $HRh(CO)(PPh_3)_3$ showed high activity but low regioselectivity at 80 °C and 80 bar (CO/H_2 = 1/1). Addition of a large excess of PPh_3, increasing P_{CO}, or lowering temperature improved the regioselectivity to n-aldehyde. With $Co_2(CO)_8$ or with $PtCl_2(PPh_3)_2/SnCl_2$ as catalysts, exclusively n-aldehyde was obtained at 120 °C or at 100 °C, respectively. $Ru_3(CO)_{12}$ gave the n-aldehyde with 86% regioselectivity [61]. A 10:1 ratio of n-butyraldehyde and isobutyraldehyde was obtained in propene hydroformylation at 120 °C and 27 bar CO + H_2 (1:1) using $[Ru^{II}(saloph)CO]$ as the catalyst in aqueous medium. A turnover rate of 17 mol/mol catalyst.hr was reported [62]. The kinetics of 1-hexene hydroformylation in the presence of $K[Ru^{III}(saloph)Cl_2]$ as the catalyst in EtOH at 130 °C and 21 bar CO + H_2 was studied. The conversion of 1-hexene to a mixture of 1-heptaldehyde (75%) and 2-methylhexaldehyde (25%) was found to be first order with respect to the catalyst, substrate, CO, and H_2, concentrations. Based on these results a mechanism was suggested [63].

The regioselectivity of hydroformylation of alkenes can be controlled by the use of bulky silyl groups attached to the alkene. Use of the $tBuPh_2Si$- group leads to almost total regiocontrol (catalyst not given) [64].
See also [19,20,21,47,48,157,170].

e) Heterogeneous Systems (Supported Complexes)

Six kinds of zeolite catalysts containing Rh, Ru, or Co were prepared by cation exchange and tested as catalysts for the hydroformylation of 1-hexene. In general, bimetallic catalysts showed high catalytic activity. Addition of free PPh_3 proved to be advantageous [65]. Ruthenium-loaded NaX zeolite catalysts could be carbonylated to ruthenium carbonyl-loaded zeolite which was used as catalyst for the liquid-phase hydroformylation of 1-hexene. DMF favored normal aldehyde, pyridine favored normal alcohol formation [66].

A novel family of supported aqueous-phase Rh catalysts has been described. These catalysts consist of a water-soluble organometallic complex supported in a thin film of water residing on a high-surface-area hydrophilic solid. The catalytic reaction takes place at the water-organic interface where the organic phase contains the reactants and products. Hydroformylation of oleyl alcohol was accomplished at 100 °C and 51 bar using a Rh catalyst prepared from $Rh(CO)_2(acac)$ [67].

The vapor phase hydroformylation of ethene and propene at 800 torr and 80 °C using cellulose acetate films containing

$HRh(CO)(PPh_3)_3$ and PPh_3 as the catalyst was investigated. The turnover rate with the membrane-supported catalyst (ca. 25 mol propanal/mol Rh.h) was equal to or even slightly higher than that obtained under similar conditions using a homogeneous solution of $HRh(CO)(PPh_3)_3$ in 2-methylnaphthalene solvent [68].

The catalytic activity of $RhCl(CO)(PPh_3)_2$ immobilized to different crosslinked poly(styrene-divinylbenzene) copolymers was evaluated in the hydroformylation of propene. The activity of the catalyst was influenced by the degree of crosslinking, and the n-butyraldehyde/isobutyraldehyde selectivity increased with decreasing crosslink ratio [69]. Rhodium(I) complexes anchored to divinylbenzene crosslinked phosphinated polystyrene were prepared and used as catalysts for hydroformylation of 1-heptene. Catalysts prepared from Rh complexes containing F_5C_6S- ligands were more resistant against deactivation than those prepared from chloride containing precursors [70]. The stability of a polymer-supported rhodium complex has been studied in the hydroformylation of hexene-1, using $[Rh(CO)_2Cl]_2$ as catalyst precursor and poly(vinylbenzyl diethylenetriamine) as the polymeric ligand. Elution of rhodium was strong during hydroformylation experiments but low in certain blank experiments. These results suggest that rhodium elution was probably related to the substitution of the polymeric ligand by a low molecular weight ligand during the catalytic cycle [71].

A new Rh dimer complex, *trans*-$[(RhCp^*Me)_2(\mu\text{-}CH_2)_2]$, bound on the SiO_2 surface, was found to be more active (turnover frequency: 0.0037/min) and more selective (88.9%) than a conventionally prepared Rh/SiO_2 catalyst in ethene hydroformylation at 140 °C and 0.4 bar total pressure of $CH_2{=}CH_2{:}CO{:}H_2$ = 1:1:1. The structural change of the Rh dimer sites in each reaction step of the catalytic hydroformylation was followed by means of *in situ* FT-IR and *in situ* EXAFS techniques. Based on these results a metal-assisted CO insertion mechanism was proposed [72,73].

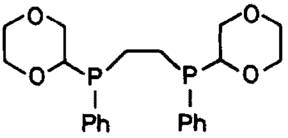
Silica gel-bound RhFe, PtFe and IrFe carbonyl clusters were found to exhibit high activities for C_4 alcohol formation in propene hydroformylation (162 °C, 1 bar total pressure) compared to that observed with $Rh_4(CO)_{12}$ as the precursor [74]. The hydroformylation of 1-hexene with ZSM zeolite-supported Ir catalysts has been investigated. Shape-selective zeolite affected the ratio of straight to branched aldehyde products [75].

Several polymer-supported transition metal catalyst have been prepared and tested for different organic reactions: platinum catalysts supported on polystyrene containing chiral diphosphines for asymmetric hydroformylation, ruthenium catalysts supported on polyquinoline for the oxidation of alcohols to aldehydes, and ruthenium, rhodium, or cobalt catalysts supported on silica containing chelating phosphines for CO reduction, homologation and hydroformylation [76].
See also [43].

3. Hydrocarbonylation (Homologation) of Alcohols and Esters with CO + H_2 ($HSiR_3$)

A new cobalt phosphine carbonyl complex, $Co(CO)_3(PBu_3)PBu_2(O)$, was found to be a very effective catalyst for the homologation of methanol at 230 °C and 200 bar CO + H_2 pressure. At 29% conversion of methanol, 89% selectivity in ethanol formation and 2% selectivity in propanol formation was observed in benzene solution [77]. The kinetics of methanol homologation promoted by a catalyst formed *in situ* from cobalt acetate, PPh_3, and methyl iodide was studied at 185 °C and 190 bar CO/H_2 = 1/1 pressure by operating under batch conditions. Kinetic equations for the formation of acetaldehyde, ethanol, 1,1-dimethoxyethane and methyl acetate were evaluated and used to represent the deactivating effect of reaction product on the catalyst, the positive effect of CO pressure on the homologation reaction rates, and the role of iodine [78]. Testing other metals as cocatalysts, the Ru/Co combination showed a strong synergetic effect and a high selectivity to ethanol [79]. Alcohol homologation catalyzed by cobalt-ruthenium-iodine complexes was studied at 170-200 °C and 450 bar $CO:H_2$ = 1:2 pressure. Primary alcohols were found to be less reactive than secondary ones and much less than tertiary alcohols. The beneficial cocatalytic effect of the ruthenium component was mainly observed with primary low-molecular-weight alcohols. In addition to the expected homologue, also isomeric alcohols were produced in a ratio depending upon the alcohol [80].

The hydrocarbonylation of methanol to acetaldehyde by means of a catalytic system consisting of CoI_2 and the bisphosphine (**20**) with synthesis gas between 130 and 190 $^{\circ}$C has been studied. At 270 bar, MeOH/ligand/CoI$_2$ = 800/1/1 and 190 $^{\circ}$C conversions reached approximately 90% and the total acetaldehyde selectivities were higher than 80% [81].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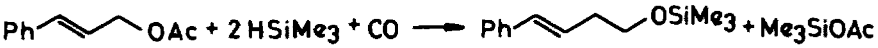
A novel catalytic method for homologation of benzylic or allylic type alcohols has been reported (eqs.1 and 2). The acetates of these alcohols react with excess HSiMe$_3$ under 1 bar CO in the presence of Co$_2$(CO)$_8$ in benzene solution to afford the Me$_3$Si-ether of the homologated alcohol in 70-92% yields. The reaction takes place also with naphthyl-, furanyl-, thiophenyl- and ferrocenyl methyl acetates [82].


(eq.1)

79 %


(eq.2)

73 %

The homologation of methyl formate to methyl acetate catalyzed by rhodium complexes in N-methylpyrrolidone was studied. In the presence of I$^-$ as promoter at 10 bar CO pressure and 195 $^{\circ}$C, selectivities above 95% were found [83]. The catalytic hydrocarbonylation of methyl acetate to ethylidenediacetate (eq.3) at 130-190 $^{\circ}$C and CO:H$_2$ = 2:1 pressure was investigated using silica anchored (ether-phosphine)-rhodium and palladium complexes [84].

$$2\,\mathrm{MeOAc} + 2\,\mathrm{CO} + \mathrm{H_2} \longrightarrow \mathrm{MeCH(OAc)_2} + \mathrm{AcOH} \qquad \text{(eq.3)}$$

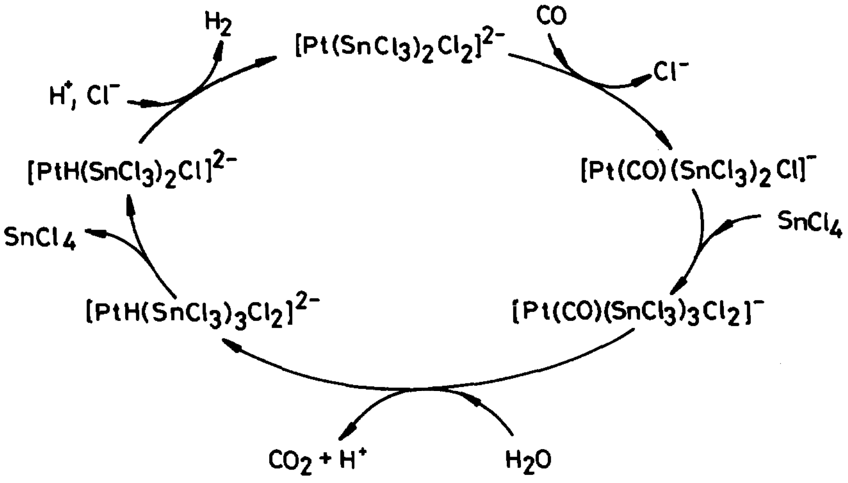
See also [76].

4. Coordination Chemistry Related to Hydroformylation

The reactions of $Rh_4(CO)_{12}$ and $Co_2Rh(CO)_{12}$ were investigated in polar solvents under CO or CO + H_2 pressure by electrochemical and IR spectroscopic methods. Both carbonyls were tested for the hydroformylation of 1-hexene in MeCN [85]. The kinetics of H_2 activation by $CoRh(CO)_7$ were studied by high-pressure *in situ* infrared spectroscopy. The reaction was found to be first order in both $CoRh(CO)_7$ and H_2, and zero order in CO. Based on this result, it was concluded that H_2 reacts with $CoRh(CO)_7$ in a bimolecular reaction without the prior dissociation of a carbonyl ligand [86]. The conversion of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ into the active hydroformylation catalyst by reaction with CO, H_2, and olefin was studied [87]. The acyldihydridoiridium complex $IrH_2(COEt)(CO)$(dppe) has been prepared. This is the first characterized example of that intermediate of the hydroformylation catalytic cycle which preceeds the formation of the aldehyde. The complex eliminates propionaldehyde, a reaction that models the final step of hydroformylation [88].
See also [250].

5. Water Gas Shift Reaction and Reduction with CO, CO + H_2, or CO + H_2O.

The water-gas shift reaction has been observed to take place between 100 and 200 °C with $[HFeM_3(CO)_{13}]^-$ (M = Os or Ru) supported on magnesia as catalyst [89]. A catalyst from $Ru_3(CO)_{12}$ and 2,2'-bipyridine was found to be the most active (4400 turnovers per day at 150 °C and $\leq$ 1 bar CO) in catalyzing the water-gas shift reaction, among other iron group metal homo- and heteronuclear clusters tested [90]. A new cycle for the Pt-Sn-catalyzed water gas shift reaction has been proposed [91]:

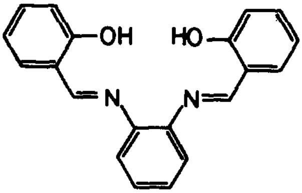


Ketoximes (21; R',R^2=alkyl or aryl) were efficiently reduced to ketimines using catalytic amounts of Ru$_3$(CO)$_{12}$ at 100 °C under 20 bar CO with isolated yields between 70 and 100 [92].

$$R^1R^2C{=}N{-}OH + CO \longrightarrow R^1R^2C{=}NH + CO_2$$

21

Ureas are formed as the main products in the Ru$_3$(CO)$_{12}$-catalyzed reduction of substituted nitroaromatics in cyclooctene or cyclohexene solvent at 170 °C and 60 bar CO pressure [93]. The reductive carbonylation of nitrobenzene to phenylurethane catalyzed by Ru(III)-Schiff base complexes has been studied. Among the complexes tested, K[Ru(saloph)Cl$_2$] showed the highest catalytic activity at 160 °C and 15 bar CO in ethanol (saloph = (22)) [94]. The rate of phenylurethane formation was first-order each in catalyst, CO and nitrobenzone concentrations [95].



22; saloph

A highly selective palladium-catalyzed synthesis of N,N'-diphenylurea from nitrobenzene, aniline and CO was reported. In the most favorable case with a $Ph(OAc)_2$ + NEt_4Cl + PPh_3 catalyst, the conversion of nitrobenzene was 100% at 120 °C and 40 bar CO in toluene solution, and the diphenylurea yield was 98% [96]. Reduction of nitrobenzene with CO in BuOH - H_2O - H_2SO_4 (or $HClO_4$) solutions catalyzed by $Pd-PPh_3$ complexes has been investigated. It was shown, that the reduced forms of the catalyst are $Pd_2(PPh_3)_4(CO).H_2SO_4$ and $Pd_2(PPh_3)_4(CO).HClO_4$ which react with $PhNO_2$ to give PhNO and the oxidized forms of the catalyst, $Pd(PPh_3)_2SO_4$ and $Pd(PPh_3)_2(H_2O)(ClO_4)$ [97].

Reduction and reductive carbonylation of nitrobenzene by CO or CO + H_2 in the presence of $Ru_3(CO)_{12}$ as catalyst has been reinvestigated. Depending on the reaction conditions, aniline, PhNCO, and $(PhNH)_2CO$ were the main products. The mechanism of the reaction was modelled by studying stoichiometric reactions of several triruthenium carbonyl clusters like $[Ru_3(CO)_{10}(\mu_3\text{-NPh})]$ under conditions of the catalytic reaction. Two catalytic cycles were proposed [98].

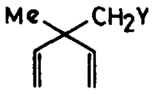
Iron pentacarbonyl showed a high catalytic activity in the liquefaction of soft brown coals with CO + H_2O at 400 °C and 200 bar. This was attributed to its solubility in the coal-oil mixture and the fine dispersion of Fe in the reaction mass [99].
See also [103,136].

6. Hydroformylation-Related Reactions of CO

The extent of ketone formation in the hydroformylation of ethene and propene with cobalt carbonyl catalysts at 120-150 °C has been investigated. At olefin conversions above 90%, 2.5-3.6% of ethene and 0.22-0.42% of propene were transformed into diethyl-

-ketone and C_7-ketones, respectively. The iPrCOPr^i : iPrCOPr : PrCOPr ratio was 0.2:1.2:1 [100].

The effect of functional groups in the Rh- or Co-catalyzed hydrocarbonylating cyclization of 1.4-dienes (**23**) or (**24**) on the yield of substituted cyclopentanones (**25**) was investigated. Dienes (**23**) with Y = COOR, OH, OR, and OAc result in the corresponding cyclopentanones (**25**) in moderate to good yields [101] whereas dienes (**24**) with Z = OH, OMe, OAc, and $OSiR_3$ loose the original functional group Z during cyclization [102].



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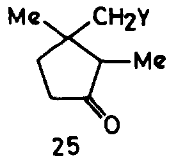
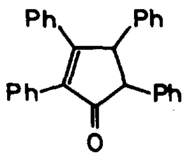


25

Carbonylation of cyclohexene in an alcohol/water (80/20) mixture catalyzed by [Ru^{II}(EDTA-H)(CO)] at 120 °C and 20 bar CO yields cyclohexene-1-carboxaldehyde (20%), cyclohexene-3-carboxaldehyde (20%) and cyclohexane carboxaldehyde (60%). The cyclohexane derivative is formed via hydrogenation of the unsaturated aldehydes by H_2 formed in a water-gas-shift reaction [103]. Hexene-1 could be hydroformylated to n-heptanol and 2-methylhexanol with CO in the presence of $HRh(PEt_3)_3$ as catalyst using alcohols as hydrogen source [104]. Diphenylacetylene was hydrocarbonylated at 220 °C under 30 bar CO pressure in iPrOH in the presence of $M_4(CO)_{12}$ (M = Co,Rh,Ir) catalysts. The cyclic ketone (**26**) was formed in 42% yield together with carbonylated, hydrogenated and oligomerized products. In the presence of $M_3(CO)_{12}$ (M = Fe,Ru,Os), no hydrocarbonylation but selective hydrogenation to stilbene occurred. $Ru_3(CO)_{12}$ showed the highest catalytic activity and gave 99% yield of stilbene (E/Z = 84/16) at 100% conversion [105].



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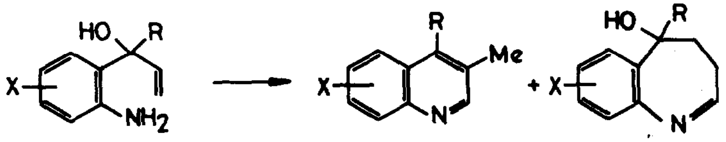
In connection with intermolecular hydroacylation of olefins with aldehydes it was found that a mixture of n-heptanol and cyclohexene at 200 °C and 20 bar CO pressure in the presence of catalytic amounts of $Ru_3(CO)_{12}$ gave cyclohexane carbaldehyde as transhydroformylated product in 29% yield [106].

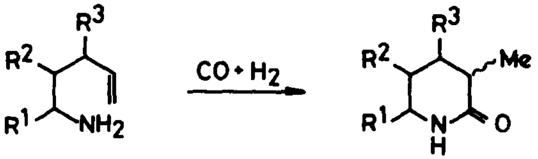
ortho-Propenylanilines (**27** and **28**; R = H, Me, Ph, *p*-tolyl; X = H, Me, Cl) were hydroformylated with $Rh-PPh_3$ catalysts at 60 °C and 28 bar. The parent compound (**27**) gave exclusively the dihydroquinoline (**29**) but the alcohols (**28**) were transformed into a mixture of quinoline (**30**) and dihydrobenzazepin (**31**) derivatives. With larger R substituents the selectivity of dihydrobenzazepin formation was 83-91% [107].

27 29



28 30 31

Piperidones (**32**; R^1 = H, Me, Ph, 2-MeCy; R^2 = H, 2-MeCy; R^3 = H, Me) were prepared in high yields from 5-aminopent-1-enes and syn gas at 30 bar and 50 °C using $[Rh(OAc)_2]_2$ and PPh_3 as catalyst precursors [108].



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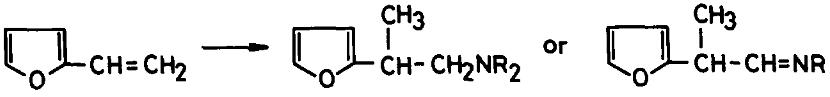
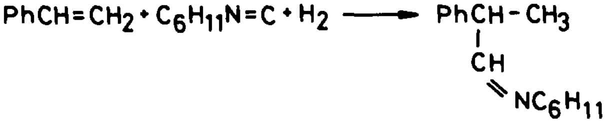
Hydroformamination (hydroformylation followed by reductive amination of the aldehydes with secondary or primary amines in one step) of 2-vinylfuran (**33**) using $HRh(CO)(PPh_3)_3$ as catalyst gave tertiary amines (**34**) or imines (**35**), respectively, with 42-85% yield [109].



33 34 35

Styrene was hydroiminoformylated with cyclohexylisocyanide and H_2 at 150 °C and 50 bar in the presence of catalytic amounts of $Ru_3(CO)_{12}$ [110] (eq.4):



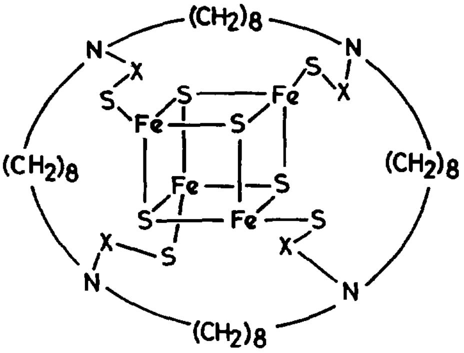
$$PhCH{=}CH_2 + C_6H_{11}N{=}C + H_2 \longrightarrow PhCH(CH_3)CH{=}NC_6H_{11} \quad 30\% \qquad \text{(eq.4)}$$

The mechanism of $Co_2(CO)_8$-catalyzed amidocarbonylation of aldehydes was studied on the basis of a stereochemical approach. The results of experiments and molecular mechanics energy calculations indicate that the direct hydrolysis (or alcoholysis) of acylcobalt species is the actual pathway of amidocarbonylation. It was concluded that the coordination of the amide carbonyl to the cobalt metal center bearing a water (or alcohol) as a ligand is crucial for the suppression of hydrogenolysis (the formation of an aldehyde) and promotes hydrolysis (or alcoholysis) even under high pressure of H_2 [111].
See also [157,213].

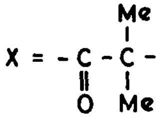
7. **Reduction of CO_2**

Dititanodecatungstophosphate, $[PTi_2W_{10}O_{40}]^{7-}$ was found to act as a multielectron transfer catalyst for the photochemical reduction of CO_2 to CH_4 in aqueous solutions containing methanol as the electron donor [112].

Electrochemical reduction of CO_2 into formate was carried out by using Fe_4S_4 cubane clusters (**36**) in DMF with initial current efficiencies of 40% (**36a**) and 23% (**36b**) [113].

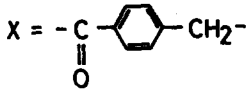


36 a;



$X = -C(=O)-C(Me)_2-$

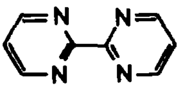
36 b;



$X = -C(=O)-C_6H_4-CH_2-$

The electrochemical reduction of CO_2 to CH_4 was studied on Nafion polymer electrolytes with chemically deposited transition metals (Re,Ru,Os,Rh,Ir,Ni,Pd,Pt,Ag, and Au). Rate of CO_2 reduction increased with increasing heat of formation of the corresponding metal formates; this correlation suggests that formic acid (or formate) is the intermediate of the reduction [114]. Formate is photogenerated by visible light irradiation from CO_2 in DMF solution containing triethanolamine as electron donor in the presence of Ru complexes. Two catalytic systems have been investigated in detail: the first is composed only of $[Ru(bpy)_3]^{2+}$ and prodeuces the active catalytic species by photolabilisation of a bipyridine ligand, the second consists of $[RuL_3]^{2+}$ (L = bipyridine derivatives or 1,10-phenanthroline) as photosensitizer and a Ru-bpy-CO complex as homogeneous catalyst [115]. Irradiation with visible light of a CO_2-saturated triethanol- amine/DMF solution containing $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ selectively produces $HCOO^-$ with a maximum quantum yield of 14%. Also 1-benzyl-1,4-dihydronicotinamide be used instead of triethanolamine as electron donor, in this case along with some $HCOO^-$ mainly CO was the reduction product [116].

Carbon dioxide has been reduced catalytically to methanol with an electrode mediator and 1-nitroso-2-naphthol-3,6--disulphonatocobalt(II) and aquapentacyanoferrate(II) complexes in 0.1 M KCl solutions. A hydrogen fuel cell was used as an energy source to regenerate the active mediator [117]. The polypyridyl bridging ligand complexes $[Rh(L)_2Br_2]^+$ and $[Ir(L)_2Cl_2]^+$ (L = 37–40) catalyze the electrochemical reduction of CO_2 to formate. The substitution of these bridging ligands for 2,2'-bipyridine produces complexes which require lower potentials for this reduction [118].



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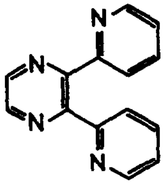

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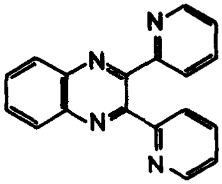

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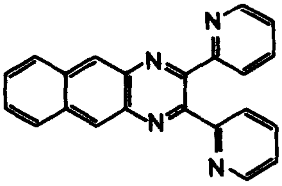

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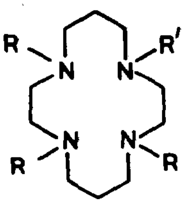
Nickel(II) complexes of the long-alkyl-substituted cyclam derivatives (**41b,c**) were prepared and immobilized as monolayers onto glassy carbon disc electrodes. These electrodes were found to be active for the electrocatalytic reduction of CO_2 despite the small amounts of catalysts when compared to the analogous homogeneous system [119].



41a; R,R' = H (cyclam)

41b; $R = nC_{16}H_{33}$, R' = H

41c; $R,R' = nC_{16}H_{33}$

The homogeneous catalytic reduction of CO_2 by a Pt cluster complex was reported [120]. The platinum cluster complex $[Pt_2(\mu\text{-dppm})_3]$ catalyzes the reversible reaction

$$CO_2 + H_2 + Me_2NH \;\text{———}\; HCONMe_2 + H\ O_2$$

The hydrogen producing reaction of DMF with water has been studied now at 100 °C in some detail. The activity of the catalyst gradually diminishes because some CO is formed as byproduct which poisons the catalyst [121].

The electrochemical reduction of CO_2 at various metal electrodes in aqueous $KHCO_3$ solution was studied. Copper showed the highest electrocatalytic activity in formation of hydrocarbons, aldehydes, and alcohols [122].
See also [213].

III. HYDROGENATION AND REDUCTION

1. Deuteration and H/D or H/T exchange

From the stereochemical course and pattern of D-incorporation during hydrogenation of unsaturated carboxylic acids catalyzed by $Ru(OAc)_2(BINAP)$ it was concluded that a mechanism involving Ru monohydride complexes is operating [123]. Tripalmitolein, triolein, trilinolein and trilinolenin were deuterated with D_2 using $Rh(PPh_3)_3Cl$ as catalyst. The deuterated triglicerides were transformed into methyl esters and analyzed for isotopic purity in this form. The d_2 products were 93-97%, the d_4 product 74%, and the d_6 product 58% pure [124]. Selective hydrogenation of the prostaglandin derivatives $PGF_{2\alpha}$ and PGE_2 with deuterium in the presence of $Rh(PPh_3)_3Cl$ in dioxane gave 5,6-deuterated analogs with 60-80% yields and isotopic purities of 85-99% [125]. The mechanism of alkene hydrogenation with colloidal rhodium species stabilized by polysulfonated phosphines and phosphine oxides (AS 1988, ref.116) was investigated using D_2 in D_2O or H_2O and alternatively H_2 in D_2O. The results show that H(D) both from $H_2(D_2)$ and $H_2O(D_2O)$ are incorporated into the product, the activation of $H_2(D_2)$ being predominant [126].

Hydrogen-deuterium exchange between H_2 and C_6D_6 or $C_6D_5CD_3$ is catalyzed by $L_2Rh(H)Cl_2$ ($L = PPr^i_3$ or PCy_3) in the presence of solid KOH and by $(PPr^i_3)_2Ru(H)Cl(CO)$ in the presence of 50% aqueous NaOH and $(PhCH_2NEt_3)Cl$ [127]. A new mechanism was proposed for the multiple H/D exchange in alkanes in the presence of Pt(II) complexes [128].

Hydrogen isotope exchange of nitrobenzene with tritium gas and with tritiated water was studied over heterogeneous and homogeneous forms of Ni, Pd, and Pt. It was found that the exchange with tritiated water is characteristic for homogeneously catalyzed isotope exchange [129].
See also [171].

2. Hydrogenation of Olefins

a) Fe and Ru Catalysts

Hydrogenation of cyclohexene and phenylacetylene with the $Fe(St)_3 + Et_3Al$ catalyst system was studied. The composition of the system varied during the course of hydrogenation [130]. The catalytic activity of the complexes formed *in situ* from Et_3Al and $[Fe_nCr_{3-n}O(OOCR)_6(H_2O)_3]NO_3$ (n = 0–3; R = C_{14}, C_{15}, C_{17} linear alkyl) exceeds that formed from $Et_3Al + Fe(St)_3$. This supports the determining role of polynuclear complexes in Ziegler hydrogenation catalysts [131]. Kinetic and mechanistic experiments have shown that hydrogenation of α-cyclopropylstyrene by a series of metal carbonyl hydrides ($HCr(CO)_3Cp$, $HFe(CO)_2Cp$, $HMn(CO)_5$, $HFe(CO)_2Cp^*$, $HMo(CO)_3Cp^*$, $HMn(CO)_4PPh_3$, $HMo(CO)_3Cp$, $HMo(CO)_2(PMe_3)Cp$, $HW(CO)_3Cp$) occured by a radical pathway. Rate-determining is the first hydrogen atom transfer in which a carbon-centered radical is formed, followed by a faster second hyrogen atom transfer from the metal hydride to this carbon-centered radical. The rate of the first hydrogen atom transfer is largely influenced by the strength of the M-H bond [132].

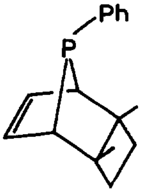
A slow hydrogenation of 2-norbornene-5-carboxaldehyde to the norbornane aldehyde at 1 bar H_2 and 65 °C in the presence of $RuHCl(CO)_2(PPh_3)_2$ was observed [133]. The molecular hydrogen complex $[(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$ catalyzes the hydrogenation of alkenes in *N,N*-dimethylacetamide solution at 30 °C and the transfer hydrogenation of acetophenone by iPrOH at 50 °C in the presence of KOH [134]. Divinylbenzene-styrene copolymer-supported ruthenium-(trimethylenediamine) complexes were found to be active for cyclohexene hydrogenation in methanol at 35–50 °C and 1 bar H_2 [135].

Reductive alkylation of active methylene compounds was observed when heated with aldehydes at 135–230 °C under 100 bar synthesis gas in the presence of ruthenium carbonyl. E.g. from $PhCH_2CN$ and HCHO 86% isolated yield of $PhCH(CH_3)CN$ was obtained. The reaction pathway presumably involves aldol type condensation between the substrate and aldehyde, dehydration, and hydrogenation of the resulting olefinic bond [136].
See also [103].

b) Co, Rh, and Ir Catalysts

The relationship between hydrogenation catalytic activity of $[Co(dpnH)]^+X$ complexes (dpnH = trimethylenedinitrilodibutanone; X = I^-, Br^-, SCN^-, H_2O, PPh_3, pyridine), the ligand field parameters of the various X ligands and the ligand donor strength of the solvents used was studied [137]. The near IR spectra of $Co(dmgH)_2$ and related complexes have been discussed with respect to the activity of these complexes as hydrogenation catalysts [138]. The β-cyclodextrin-$HCo(CN)_5^{3-}$ system has been found to be active in catalytic hydrogenation of α,β-unsaturated acids and their derivatives under 1 bar H_2 at 70 °C [139]. The $Co(acac)_2$ + Et_3Al catalytic system looses its hydrogenating activity in the presence of CO; $Co_2(CO)_8$ is being formed. The same deactivation was observed with the phosphine-containing catalytic systems $Co(acac)_2$ + PR_3 + R'M (R'M = BuLi, PhMgBr) [140].

A detailed study on the hydrogenation of various alkenes and alkynes and of the hydroformylation of alkenes has been carried out using organorhodium complexes containing $MeC(CH_2PPh_2)_3$ [141]. The activity for hydrogenation of olefins of the catalytic systems composed of $[Rh(OAc)_2]_2$ and 1,10-phenathroline, 2,2'-dipyridyl, or some of their derivatives has been investigated in methanolic NaOH solutions [142]. The binuclear Rh complexes $[Rh_2(hfacac)_4L_2]$ (hfacac = hexafluoro acetylacetonato; L = axial pyridine or H_2O ligand) are effective catalysts for the hydrogenation of allylbenzene. Addition of PPh_3 greatly increases the activity [143]. The tridentate rhodium(I) chelate complexes (PBA)RhCl and (PPA)RhCl (PBA = bis(4-(diphenylphosphinobutyl)benzyl)amine; PPA = bis(3-diphenylphosphino)propyl)amine) were compared in catalytic cyclohexene hydrogenation. The rate-determining step is for both catalysts dependent on chloride dissociation; accordingly the rate of hydrogenation increases in polar solvents [144]. The hydrogenation products of 2,5-norbornadiene, 2,5-dihydrofuran and 2,3-dihydrofuran using parahydrogen and $[Rh(NBD)_2(PPh_3)_2]^+PF_6^-$ or $RhCl(PPh_3)_3$ as catalyst precursors in C_6D_6 show nuclear spin polarization in their H-NMR spectra [145]. A kinetic study of the hydrogenation of *cis*-1,4-polybutadiene in *o*-dichlorobenzene at 65 °C and <1 bar H_2 in the presence of $RhCl(PPh_3)_3$ as the catalyst was performed [146]. Rhodium(III) complexes of organic sulfides, $RhCl_3L_3$ (L = different dialkyl sulfides), were tested as catalysts for the hydrogenation of maleic acid. A relation was found between the extent of dissociation of these complexes in solution and their catalytic activity [147]. The relative initial rates of 1-hexene hydrogenation in acetone catalyzed by $Rh(COD)L_2^+$ complexes were found to be 1:7.5:13 for L = PPh_3; (**42**), and (**43**), respectively [148].



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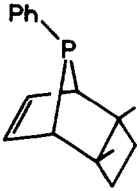
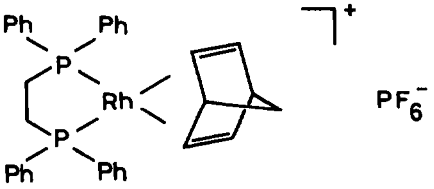


43

Rhodium-phyllosilicate catalyst precursors were prepared by supporting $[Rh(NBD)(Me_2CO)_x]ClO_4$ on polygorskite or montmorillonite. These catalyst precursors became active for 1-hexene hydrogenation in the liquid phase only after keeping them for some time under the reaction conditions [149]. The activity of the catalysts remained constant over several runs and no leaching was observed [150]. A polymer-anchored Rh catalyst has been prepared by sequential attachment of ethylenediamine to chloromethylated styrene-divinylbenzene and treating the functionalized polymer with $RhCl_3.3H_2O$. This catalyst has been used for the hydrogenation of 1-octene [151]. The physically entrapped complex (**44**) inside of cross-linked polystyrene was found to be an active catalyst for 1-hexene hydrogenation in methanol at 3 bar H_2 pressure [152].



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A catalytic cycle for ethene hydrogenation using $[IrH_4(PMe_2Ph)_3]^+$ as precursor has been established. One of the intermediates contains both an ethene ligand and an ethyl group [153]. The catalytic activity of cationic complexes of Ir(I) and Ir(III) containing thioether and dithioether ligands was studied in hydrogenation of 1-heptene and cyclohexene at 25 °C and 1 bar H_2 in CH_2Cl_2 [154].
See also [105,156,164,335].

c) Ni, Pd, and Pt Catalysts

Ziegler-type homogeneous catalysts containing Et_3Al and Ni, Co, or Pd salts were used to hyrogenate methyl linoleate under very mild conditions selectively to monounsaturated products. Model experiments showed that this selectivity was mainly due to the 1,4-position of the double bonds; dienes with greater distance between the double bonds were hydrogenated with less selectivity [155].

Unsaturated substrates were hydrogenated with $PdCl_2$ or $RhCl_3$ as catalysts in the presence of $(MeOCH_2CH_2OCH_2CH_2)_3N$ [156]. The palladium carbonyl hydrido complexes $[Pd_4(phen)_4(CO)_2H_2](OAc)_2.2AcOH$ and $[Pd_4(phen)_3(CO)_3H_2](OAc)_2.2AcOH$ catalyze the hydrogenation of olefins and the hydrocarbonylation of ethene to propanol and diethyl ketone [157]. Catalytic hydrogenation of alkenes, alkynes, organic nitro compounds, and compounds containing C=O, C=N, N=N, and C≡N bonds has been carried out using *ortho*-palladated complexes of the types *trans*-PdL_2X_2 and $PdLL'Cl_2$ (L = 2-benzoylpyridine, 2-benzylpyridine, N,N-dimethylbenzylamine; L' = pyridine, PPh_3; X = OAc, Cl) in DMF. The actual catalytic species are Pd(L)(H)DMF complexes which have been isolated [158]. Hydrogenation of the unsaturated fatty acids of living *Tetrahymena* *mimbres* cells was attempted using palladium di-(sodium alizarine monosulfonate) as homogeneous catalyst. Chemical conversions were small and some enzymic retroconversion of saturated lipids to unsaturated lipids seemed to take place [159].

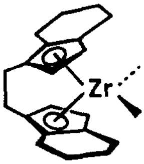
4-Vinylpyridine was copolymerized with divinylbenzene in the presence of silica gel to provide supports for $PdCl_2$ and $Pd(OAc)_2$ hydrogenation catalysts. Kinetic results were given for the hydrogenation of cyclohexene at 30 °C and 1 bar [160]. $(PhCN)_2PdCl_2$ was supported on two copolymers containing carboxyl and pyridyl groups and employed as a catalyst for the hydrogenation of olefins under mild conditions. It was proposed that the Cl atom bridges present in the original Pd-polymer complexes were broken during activation [161]. Polymer-supported Pd catalysts for hydrogenation of cottonseed oil were prepared starting from different ion exchange resins. Catalysts with large pore diameters and surface showed the highest catalytic activity [162]. Palladium-lanthanoid bimetallic complex catalysts supported on chloromethylated beads derivatized with anthranilic acid have been synthesized and used for the hydrogenation of olefins. The promotion effect of the anchored Ln ions varied with their atomic number; the catalysts possessed the highest activity when the f electron number was 0, 7, or 14 [163]. Supported Pd and Rh hydrogenation catalysts were made by anchoring Pd(II) or Rh(III) salts on hydrogel polymers based on 2-hyroxyethyl methacrylate and other functional monomers. These catalysts were found to be effective for the hydrogenation of alkenes, alkynes and dienes in methanol and water under mild conditions (33 °C, 1 bar H_2 [164].

Reacting $Pt(OAc)_4$ with octyl-, dioctyl-, or trinonylamine in toluene at RT gave products exhibiting catalytic activity for the hydrogenation of alkenes. Activity of the complexes was increased by supporting on Al_2O_3 [165].

d) *Other Metals as Catalysts*

An active hydrogenation catalytic system could be generated *in situ* by stirring a solution of Cp_2TiCl_2 in THF with activated magnesium (metallic Mg either recovered from a Grignard reaction or activated by the addition of a small amount of 1,2-dibromoethane). The stable solution obtained in this way effectively hydrogenated various types of olefins and acetylenes under ambient conditions [166]. Hydrogenation of 1-hexene is catalyzed by Ti hydride complexes formed *in situ* from Cp_2TiCl_2 (or its derivatives containing substituted cyclopentadienyl ligands) and NaH or KH in toluene. Most of these catalysts exhibit high initial rates but then lose much of their activity within a few minutes [167]. Hydrogenation of alkenes and cycloalkenes catalyzed by reduced Cp_2TiCl_2 and by its immobilized analogue coordinatively bound to silica has been studied. The immobilized catalyst remained bound to the support and thus could be reused [168]. The trinuclear complexes $(Cp'Ti)_2AlH_4R$ (Cp' = C_5H_5, C_5H_4Me, C_5Me_5, $C_5H_4Bu^t$; R = Me, Bu, Ph, NEt_2, BH_4, OBu, OPr^i) were prepared and tested as catalysts for the hydrogenation of hexene-1. Highest catalytic activities were observed for the complexes with R = OBu and OPr^i [169].

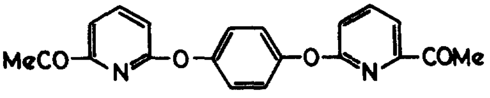
The hydrozirconium complex $(\eta^5\text{-tBuC}_5H_4)ZrH(CH_2PPh_2)$ catalyzes the hydrogenation of olefins and diolefins at 80 °C and 40 bar in THF solvent. The related bimetallic Zr–Rh complexes $[(\eta^5\text{-tBuC}_5H_4)_2Zr(CH_2PPh_2)_2Rh(COD)]BPh_4$ and $(\eta^5\text{-tBuC}_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-SBu}^t)_2(CO)_2]$ act as hydroformylation catalysts at 80 °C and 20 bar CO + H_2. The latter complex is significantly more active than $Rh_2(\mu\text{-SBu}^t)_2(CO)_2(dppb)$ [170]. Styrene was hydrogenated at 12 turnovers/min with 20 bar H_2 at 25 °C using (**45**) and methylaluminoxane as catalyst. The catalytic deuteration using (–)-(**46**) and methylaluminoxane gave (–)-(R)-1,2-dideuteroethyl-benzene in 93% yield and 65% ee [171].



45; R = Me

46; R= (R)-binaphtholate

The lutetium complex $[(1,3\text{-tBuC}_5H_3Bu^t)_2Lu(\mu_2\text{-H})]_2$ catalyzes the slow hydrogenation of 1-hexene [172]. Catalyst systems composed of $(C_5Me_5R_5)_2LnCl_2Li(THF)_2$ + MH (Ln = Nd, Yb, Gd; R = Me, Pr; M = Na, K) exhibit good activity for the hydrogenation of α-olefins. Removal of THF increased their catalytic activity but decreased their solubility in toluene. The activity of the catalysts decayed rapidly in the presence of olefins [173]. Tridentate and bidentate polyquinolines were prepared by copolymerization of the three monomers (47), (48), and (49). Complexes of these polymers were used as catalysts for hydrogenation of 1-hexene and hydroformylation of 1-pentene (metal not given) [174].



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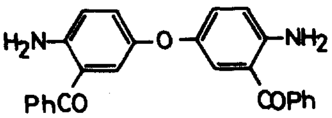

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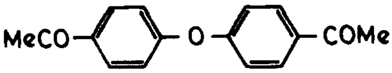

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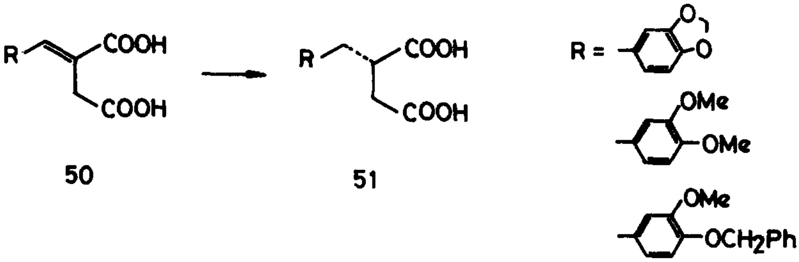
See also [131,132,163].

3. Asymmetric Hydrogenation of Olefins

The application of the complexes Ru(OOCR)$_2$(BINAP) (R = Me, tBu) and [RuX(BINAP)(arene)]Y (X,Y = halide) for asymmetric hydrogenation of enamides, substituted acrylic acids, unsaturated carboxylic acids, allylic and homoallylic alcohols, β-keto esters and α-amino ketones has been briefly summarized [175]. The substituted benzylidene succinic acids (50) were hydrogenated at room temperature and 3 bar with Ru$_2$Cl$_4$[(R)-(+)- or (S)-(-)-BINAP]$_2$ as catalyst to give the (S)- and (R)-products (51), respectively, in over 90% optical yields. The corresponding alkylidene succinic acids (50; R = Me, iPr) gave only significantly lower enantioselectivities (65-75% ee) [176].



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51

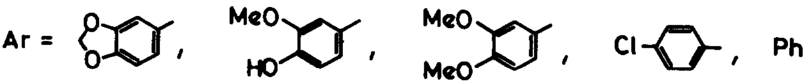
The structure of the 1:1 adduct formed from the asymmetric hydrogenation catalyst $[Rh(DIPAMP)(MeOH)_2]^+$ and methyl(Z)-β-propyl-α-acetamidoacrylate (an intermediate of the catalytic cycle) was determined. Also in this case the face of the C=C bond that is coordinated to the Rh atom is opposite to that to which H_2 adds to form the predominant enantiomer of the hydrogenated product. Accordingly, the origin of enantioselection in hydrogenation is not the preferred mode of binding of the substrate but the higher reactivity of the minor diastereomer of the intermediate complex [177].

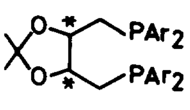
The catalytic asymmetric reduction of (1-naphthylmethylene)-succinic acid (52) with $[(+)\text{-BPPM-RhCl}]/Et_3N/H_2$ (1 bar) in methanol or with $[(+)\text{-BPPM-RhClO}_4]/H_2$ (5 bar) in PhH-EtOH gave (R)-(1-naphthylmethyl)succinic acid (53) in 85% and 87% ee, respectively [178].

52 53

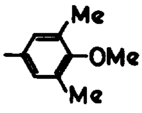
The hydrogenation of arylidene succinic acid half methylester (54) catalyzed by a rhodium(I) complex of the modified DIOP (56) in the presence of Et_3N gave optically active succinic acid derivatives (55) in 90-96% optical yield [179].

54 55

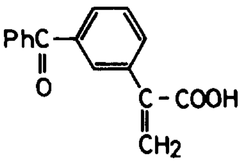




56; Ar =



The prochiral unsaturated carboxylic acids (**57**) and (**58**) were hydrogenated in the presence of Rh(I) complexes containing chiral diphenylphosphines and diphenylphosphinites. Optical yields varied between 10-15%, indicating that the two substrates did not behave as bidentate ligands. Highest enantioselectivity (45% ee) with (**58**) was obtained using the chiral phosphine (**59**) [180].



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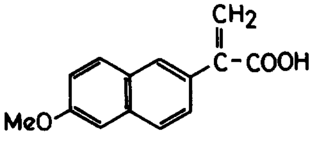

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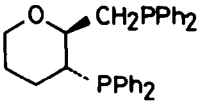
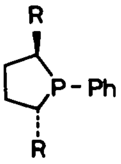


59

Rhodium complexes $[COD)Rh(PR_3)_2]^+PF_6^-$ (or SbF_6^-) with new chiral electron-rich phospholanes (**60**,**61**, or **62**; R = Me, Et, iPr) were found to be efficient precursors for the enantioselective hydrogenation of methyl acetamidocinnamate and dimethyl itaconate to the corresponding phenylalanine and succinate derivatives. Quantitative yields and up to 91% ee were achieved at 1 bar H_2 and 25 °C [181].



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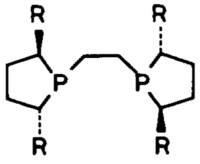

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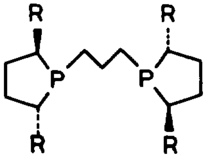
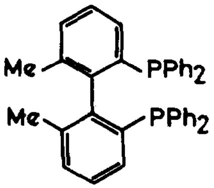


62

The chiral bisphosphine ligand (**63**) was prepared and tested for the asymmetric hydrogenation of methyl (Z)-α-benzamido-cinnamate catalyzed by Rh(I) complexes. It was found that (**63**) gave a lower ee than the related well-known BINAP (**64**) [182].



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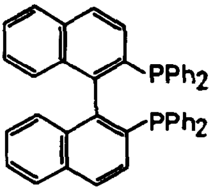
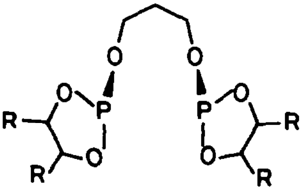


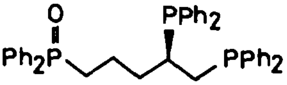
64

The complexes $[(P-P)Rh(COD)]^+$ formed from $[Rh(COD)_2](BF_4)$ and the chiral chelating bis(dioxaphospholane) ligands (P–P) = (**65**; R = COOEt, COOPr^i, Ph) were tested as catalysts for asymmetric hydrogenation of enamides and asymmetric hydroformylation of styrene. Optical yields, however, were very low. Interestingly, the COD ligand was hydrogenated only after complete hydrogenation of the enamides [183].



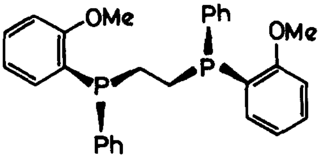
65

Twenty-one optically active phosphines were tested as ligands in the Rh-catalyzed hydrogenation of (Z)-α-acetamidocinnamic acid (AAC) and of itaconic acid. Ligand (**66**) gave the best result. Thus hydrogenation of AAC at 1.1 bar H_2 at 30 °C with an *in situ* catalyst from $[Rh(COD)Cl]_2$ and (**66**) in methanol led to (S)-N-acetylphenylalanine with 85-89 ee [184].



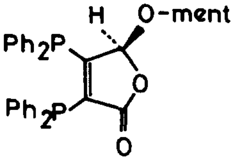
66

Based on the crystal and molecular structure of the predominant diastereomer adduct of $[Rh(R,R-DIPAMP)(MeOH)_2]^+$ (DIPAMP = **67**) and (Z)-β-propyl-α-acetamidoacrylate (MPAA), it was concluded that the origin of enantioselection in the $[Rh(R,R-DIPAMP)]^+$-catalyzed hydrogenation of MPAA is not the preferred mode of binding of the prochiral substrate but, rather, the higher reactivity toward H_2 of the minor, less stable, diastereomer [185].



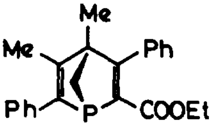
67

The aminophosphine phosphinite ligands (R)- and (S)-1-$C_{10}H_7O$ $CH(OR)CH_2NRCHMe_2$ ($R = PPh_2$) were prepared from the propranolol derivative R = H. Their neutral and cationic Rh complexes gave 80-90% ee in the asymmetric hydrogenation of dehydroaminoacids [186]. Asymmetric hydrogenation of methyl-α-acetamidocinnamate with [RhCOD)(L)]PF_6 as catalyst (L = 68) gave the corresponding (R)-phenylalanine derivative with 33% optical yield [187].



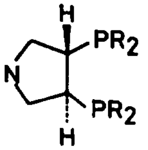
68

Chiral 1-phosphanorbornadienes like (69) were used as ligands in the asymmetric hydrogenation of Z-α-acetamidocinnamic acid with $[Rh(COD)_2](PF_6)$ as catalyst. Optical yields up to 50% were achieved. Phosphines of this type are not susceptible to racemization [188].



69

The diphosphines (**70a-c**) have been prepared and their cationic Rh(I) complexes used as chiral catalysts for asymmetric hydrogenation of (Z)-α-acetamido cinnamic acid. Ligands (**70b**) and (**70c**) were more efficient than (**70a**) [189].



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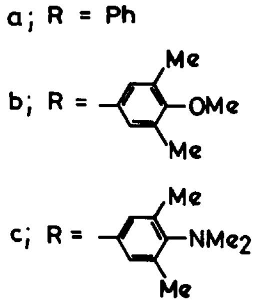
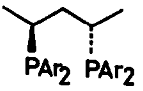


Enantiomeric excesses of 67 to 97% were obtained in the enantioselective hydrogenation of Z-(4-MeO, 3-AcOC$_6$H$_3$CH=C(NHCOMe)COOH using the cationic complex [L$_2$Rh(NBD)]$^{3+}$ (L$_2$ = the BDPP- derived water soluble phosphine 71) as catalyst in aqueous HBF$_4$ at 20 °C and 14 bar H$_2$ [190].



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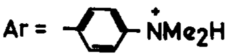
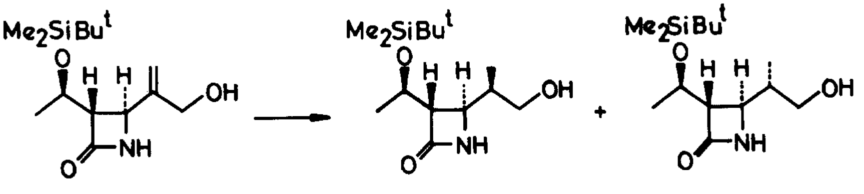


The relationship between product configuration and complex conformation of the catalyst in asymmetric hydrosilylation of acetophenone, ethyl acetoacetate and acetophenoxime, and in asymmetric hydrogenation of α-acetylaminocinnamic acid was studied using [Rh(COD)Cl]$_2$ and chiral chelating phosphine ligands. A simple rule was deduced: δ and chair δ conformation of the catalyst results in R-products, and λ and chair λ conformation results in S-products [191]. With (−)-1,2-bis(dimenthylphosphino)ethane as the ligand in the Rh-catalyzed hydrogenation of α-acetamino cinnamic acid to N-acetylphenylalanine, 20% ee was reported. The same catalyst led to 49% ee of 1-phenylethanol in the hydrosilylation of acetophenone after hydrolytic workup [192]. Dehydrodipeptides having the general formula RCONHC(=CHR')CONHCHR"COOH with a polycondensed aromatic ring (R' = 1-naphthyl, 1-pyrenyl, 9-anthryl) were hydrogenated using a chiral Rh-phosphine catalyst. Dipeptides with a diastereoselective excess of 74–91% were obtained [193]. Prochiral allylic amines were hydrogenated in the form of their hydrochlorides using Rh complexes of various chiral 1,2-, 1,3-, and 1,4-diphosphines. Up to 60% ee-s were achieved [194]. Hydrogenation of alkene (**72**) in the presence of Ru(OAc)$_2$-(R)-tolBINAP gave a quantitative yield of (**73**+**74**) with a **73**:**74** ratio of 99.9:0.1. The (S)-tolBINAP ligand afforded a **73**:**74** ratio of 22:78 [195].



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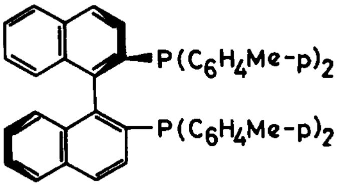
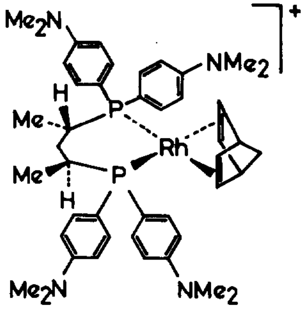


(R) - tol BINAP

Highly active and enantioselective heterogenized catalysts for the asymmetric hydrogenation of N-acylated dehydroamino acid esters were obtained by immobilizing chiral cationic rhodium(I) complexes with bisphosphinite ligands on sulphonated ion exchangers [196]. The catalytic asymmetric hydrogenation of prochiral unsaturated acids and esters using homogeneous and silica-immobilized μ-thiolato-μ-chlorodicarbonyl bis(neomenthyl-diphenylphosphine)dirhodium complexes were studied [197]. Catalysts obtained by impregnating BaSO$_4$, cellulose, silica gel, aluminium oxide, AgCl, and charcoal with the complexes [Rh(COD)(-)-DIOP]PF$_6$, [Rh(COD)(-)-norphos]PF$_6$ and [Rh(COD)(+)-norphos]PF$_6$ catalyze the enantioselective hydrogenation of (Z)-α-N-acetamidocinnamic acid in aqueous NaOH with up to 79% ee. If the cations of the mentioned complexes were bound to different acidic ion exchangers, even higher optical yields (87%) were achieved in ethanol solution [198]. The immobilized rhodium complexes (**75**), (**76**) and (**77**) on cation exchange resins catalyze the asymmetric hydrogenation of dehydroaminoacid derivatives with no detectable loss of rhodium into the substrate phase. The observed rates are much slower but the enantioselectivities are comparable to those obtained with the non-supported complexes in homogeneous solution [199].



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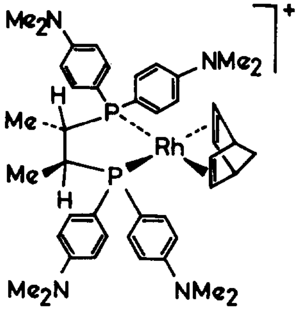

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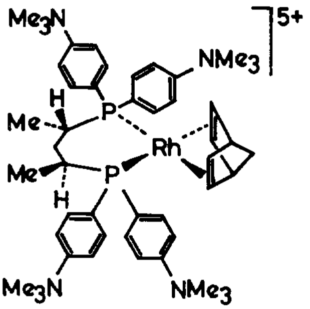
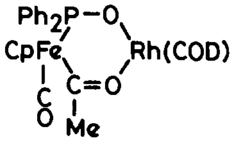


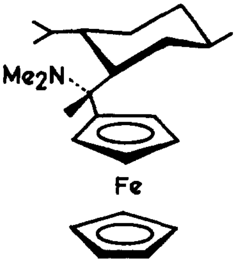
77

The binuclear complexes (+)- and (−)- (78) and the *in situ* catalysts formed from $[Rh(COD)Cl]_2$ and (+)- and (−)-CpFe(CO)(COMe)(DIOP), were used in the enantioselective hydrogenation of Z-α-N-acetamidocinnamic acid. Optical inductions of up to 76% were obtained at RT and 1.1 bar H_2. Using the same catalysts in the hydrosylylation of acetophenone with Ph_2SiH_2 gave very low (<6.1%) optical yields [200].



78

Chiral phosphines were prepared from the ferrocenylalkylamines (79) and (80) by lithiation and reaction with Ph_2PCl. Only oily mixtures with an ill-defined distribution of phosphine substituents on the ferrocenyl ring were obtained which could not be separated satisfactorily. Use of this mixture in hydrogenation of N-acetyl-α-amino cinnamic acid with *in situ* Rh(I) catalysts gave N-acetylphenylalanine with 84% ee [201].



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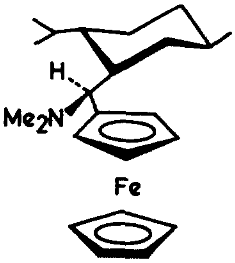
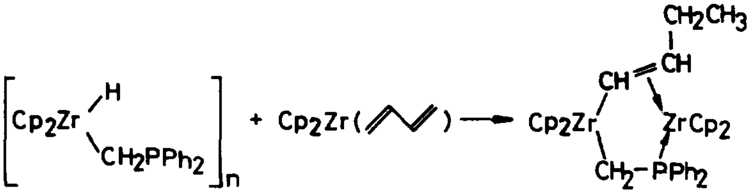


80

4. Hydrogenation of Dienes and Alkynes

A binuclear alkenyl-bridged Zr complex (83), obtained from the reaction of (81) and (82) catalyzes the selective hydrogenation of 1,3-cyclooctadiene to cyclooctene at 80 °C and 40 bar H_2 in toluene solution [202].



81 82 83

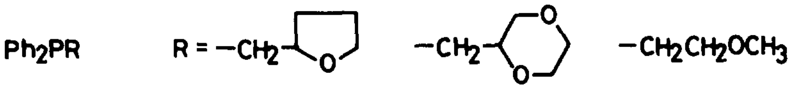
Using spectroscopic techniques it has been shown that d^6 metal carbonyls (Cr, Mo, and W) form nonclassical dihydrogen complexes rather than dihydrides under the conditions of photocatalytic hydrogenation of dienes. A new mechanism for the hydrogenation (deuteration) of norbornadiene was proposed in which all species have been identified by IR spectroscopy [203,204]. Highly stereoselective hydrogenation of *trans*-1,3-pentadiene to *cis*-2-pentene was found to be catalyzed at 150 °C by $Mo(CO)_6$ encaged in a NaY zeolite [205].

Regioselective catalytic hydrogenation of conjugated dienes has been reported using hydridopentacyanocobaltate anion together with lanthanum or cerium chloride promoter and β-cyclodextrin as phase-transfer agent [206]. Photoreduction of Ni(acac)$_2$ by H$_2$ in benzene sensitized by acetone yields transient Ni-hydride species. If the reaction is performed in the presence of excess COD, the diolefin is hydrogenated [207]. Amine-containing Pd complexes supported on Al$_2$O$_3$ used as catalysts for the selective hydrogenation of dienes and acetylenes were found to be relatively stable against different catalyst poisons such as organic sulfur compounds, PPh$_3$, and CO [208].

Hydrogenation of diphenyl acetylene was studied using $Mn_2(CO)_{10}$, $Mn_2(CO)_9(PPh_2H)$, $Mn_2(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_8$, $Mn_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8$, and $Mn_2(\mu\text{-}PPh_2)_2(CO)_8$ as catalysts [209].

A comprehensive investigation of the alkyne/alkene hydrogenation reaction in the presence of a range of *in situ* prepared $[RuHL'_5]^+$ and $[RuHL'_2L''_2]^+$ (L' = group 15 donor ligand; L" = PMe$_3$, PMe$_2$Ph) complexes was made. It was found that the course of the reaction depends on the size of the ligand L'. In the case of $[RuHL'_5]^+$ complexes a maximum rate of alkyne hydrogenation was observed at ca. 120° cone angle. The $[RuHL'_2L''_2]^+$ complexes catalyze the hydrogenation of alkynes exclusively when the sum of the cone angles for the L' and L" ligands is 610 ± 20°. No correlation was found between electronic parameters and the reaction rates or product selectivities [210]. The activation by hydrogen of RhCl$_3$-polyethyleneimine catalysts for hydrogenation of alkynes has been studied. Depending upon the extent of H$_2$ treatment, the Rh(III) centers were reduced to Rh(I) and Rh(0); the Rh(I) centers were the catalytically active ones. Formation of rhodium hydrides could not be observed [211].

The Pd-phosphine complexes $[\mu\text{-}ClPdCl(L)]_2$ and *trans*-Cl$_2$PdL$_2$ (L = **84a**, b, or c) were tested as catalysts for the hydrogenation of hexyne-1 to hexene-1. Selectivities between 91 and 99% were achieved at 60 °C and 5 bar [212].

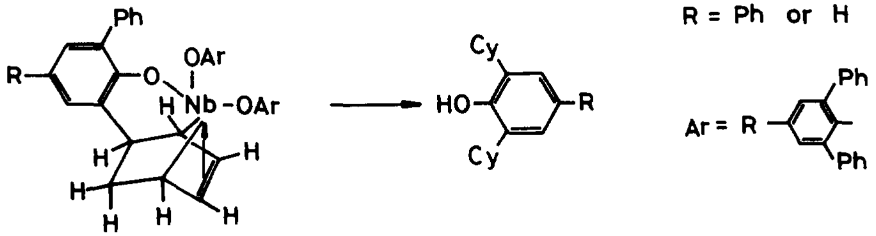


84 a b c

A new oligomeric heterogeneous salicylidene-ethylenediaminepalladium(II) complex was described. This green complex was a selective catalyst for the hydrogenation of alkynes and reduced only few other functional groups (aromatic nitro compounds and aromatic aldehydes) [213]. Radiation-induced copolymerization of *cis*-$PdCl_2[CNMe_2OC(O)CH{=}CH_2]_2$ with dimethylacrylamide and methylenebisacrylamide furnished a terpolymer which was catalytically active for the hydrogenation of PhC≡CH, styrene, and $PhNO_2$ in MeOH at RT and 1 bar [214]. Hectorite-intercalated Pd(II) complex catalysts were prepared from $[Pd(NH_3)_4]^{2+}$ or a Pd(II)-triazine complex and used for the hydrogenation of terminal alkynes in DMSO [215].
See also [130,164].

5. Hydrogenation of Arenes and Heterocyclic Compounds

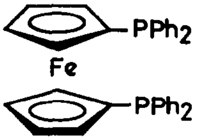
The use of 2,6-diphenylphenoxide or 2,4,6-triphenylphenoxide ligation in the synthesis of the niobium complex (**85**) followed by hydrogenation (25 °C, 70 bar, 6 days) and hydrolysis gave 2,6-dicyclohexylphenol or 2,6-dicyclohexyl-4-phenylphenol as the final product, respectively [216].



85

Simple and polycyclic aromatic hydrocarbons are partially or completely hydrogenated with a large excess of $LiAlH_4$ at 100 bar H_2 and 200 °C in the presence of small amounts of $TiCl_4$ or $TiCl_3$. Experiments with D_2 gas prove that the H_2 molecule is also incorporated into the products [217]. Arenes (benzene, toluene, naphthaline) can be hydrogenated at RT and 1 bar using $[R_2P(CH)_3PR_2]Co$(allyl or cyclohexadienyl) (R = iPr, Cy) complexes as catalysts [218]. Cyclohexanecarboxylic acids were prepared by the hydrogenation of aromatic carboxylic acids using polycarboxylic acid-bound Pt or Rh catalysts. Polyacrylic acid-Rh displayed the highest catalytic activity [219].

The two Rh(I) complexes $[Rh(L)(NBD)]ClO_4$ and $Rh(L)Cl_2$ (L = **86**) were found to be efficient catalysts for the regioselective hydrogenation of N- or S-containing polynuclear heteroaromatic compounds. Ring saturation took place in all cases in the heterocyclic ring of the molecule. Both catalysts were inactive for the hydrogenation of pyridine and thiophene [220].

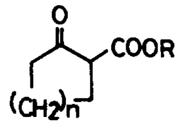


86

The ruthenium monohydride K[Ru(OEP)(H)] has been found to catalyze H/D exchange at 50 °C between D_2O and H_2 in THF. Under similar conditions the monohydride complex reduces the NAD^+ analogue (1-benzyl-*N*,*N*-diethylnicotinamide)PF_6 to 1-benzyl-*N*,*N*-diethyl-1,6-dihydronicotinamide [221].

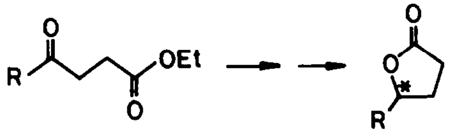
6. Hydrogenation of Carbonyl Compounds

Extremely high (97-99%) selectivities at complete conversion of α,β-unsaturated aldehydes (cinnamaldehyde, crotonaldehyde, methyl-3-buten-2-al and citral) in hydrogenations to the corresponding unsaturated alcohols using an *in situ* $RuCl_3$/TPPTS catalyst system in toluene/water = 1/1 at 35 °C and 20 bar H_2 were reported [222]. The combination of chiral carboxylato bridges with a chiral diphosphine bridge in diruthenium carbonyl complex catalysts resulted in satisfying catalytic turnovers, but very low enantioselectivity in the hydrogenation of hydroxyacetone to 1,2-propanediol [223]. Hydrogenation of cyclic oxo esters (**87**; R = Me, Et; n = 1-3) using $[(BINAP)Ru(C_6H_6)Cl]^+Cl$ as catalyst gave the corresponding hyroxy esters in high enantiomeric and diastereomeric excesses [224].



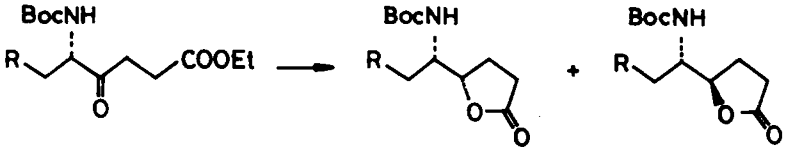
87

Hydrogenation of the prochiral 4-oxo carboxylates (88; R = Me, Et, nC_8H_{17}) at 100 bar and 25–35 °C in ethanol solution containing 0.1–0.3 mol% of a BINAP-Ru(II) catalyst, followed by heating the product mixture of the corresponding 4-butanolide and 4-hydroxy carboxylic ester with AcOH in PhMe gave optically active 4-substituted 4-butanolides (89) in high yield. Hydrogenation with the (S)-BINAP catalyst affords (S)-(89), whereas the (R) catalyst produces the (R) enantiomer in more than 98% ee [225].



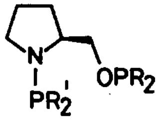
88 89

Asymmetric hydrogenation of the keto esters (90; R = Cy, iPr) with $RuBr_2$[(R)-BINAP] catalyst at 100 bar and 100 °C in EtOH solvent and lactonizing the obtained hydroxy esters in refluxing toluene containing acetic acid gave (91) and (92) in 97–98% yield in an approximately 6:1 ratio [226].



90 91 92

Isomerization of unsaturated alcohols to the corresponding saturated carbonyl compounds by $Rh(CO)(PPh_3)_2(ClO_4)$ or $[Rh(CO)(PPh_3)_3](ClO_4)$ is accompanied by hydrogenation to saturated alcohols if the reaction is performed under H_2 [227]. Ketocarboxylicacid derivatives were hydrogenated to the corresponding alcohols with excellent ee at room temperature and 1 bar H_2 using $[Rh(COD)Cl]_2$ and the aminophosphinephospinites (93) or (94) (R,R' = Cy or cyclopentyl) as catalyst [228].



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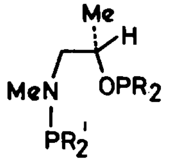
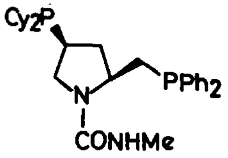


94

Asymmetric hydrogenation of amino ketone derivatives (95) gave quantitative chemical yields and 86–97% ee of the corresponding (S)-alcohols (96) in methanol at 50 °C and 20 bar H_2 pressure using ligand (97) with 0.01 mol% $[Rh(COD)Cl]_2$ as catalyst [229].

95 96

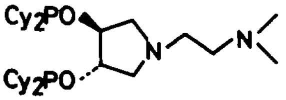


97

Asymmetric hydrogenation of N-(benzoylformyl) amino acids (98; R = Me, $PhCH_2$) has been studied under ambient conditions in the presence of Rh(I) catalysts with (99) as chiral ligand. The neutral rhodium(I) precursor gave double asymmetric induction in methanol, while the cationic precursor caused an asymmetric induction controlled mainly by the substrate chirality [230].

$$\mathrm{PhCOCONH}\underset{\mathrm{R}}{\overset{*}{\mathrm{C}}}\mathrm{HCOOH} \longrightarrow \mathrm{Ph}\underset{\mathrm{OH}}{\overset{*}{\mathrm{C}}}\mathrm{HCONH}\underset{\mathrm{R}}{\overset{*}{\mathrm{C}}}\mathrm{HCOOH}$$

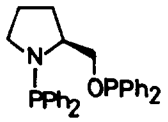
98



99

The complex $IrH_5(PPr^i_3)_2$ catalyzes the hydrogenation of cyclohexanone to cyclohexanol at 80 °C and 1 bar H_2, and the transfer hydrogenation of 3,3-dimethylbutene by isopropanol at 30 °C [231]. Selective hydrogenation of PhCH=CHCHO, PhCH=C(Me)CHO, and PhCH=C(Cl)CHO to the corresponding unsaturated alcohols was reported by using $Ir(ClO_4)(CO)(PPh_3)_2$, $IrCl(PPh_3)_3$, $IrCl(CO)(PPh_3)_2$, or $[Ir(CO)(PPh_3)_3]ClO_4$ as catalyst precursors at 50 °C and 9 bar of H_2 in $CDCl_3$ solution [232]. The asymmetric catalytic hydrogenation of α-aminoketones (**100**; R = R' = CH_2Ph; R-R' = $(CH_2)_5$; R = Me, R' = CH_2Ph) at 60 °C and 70 bar using the cationic iridium complex $[Ir(prolophos)(COD)][BPh_4]$ (prolophos = **102**) resulted in (R)-(+)-(**101**) with 20-30% ee [233].

100 101



102; prolophos

See also [136,158,175].

7. Hydrogenation of Nitro Compounds

The complex $Re_2S_6(L)_3Cl_2$ (L = thiourea) was prepared from thiourea, ReO_4, and HCl at 95 °C. This complex was found to be an active catalyst for the hydrogenation of aromatic nitro compounds. Its activity increased in the presence of added ligands like thiourea, PPh_3, or 2-mercaptobenzthiazole [234]. Rhenium(V) oxohalide complexes $ReOX_3L_2$ (X = Cl,Br; L = $(H_2N)_2CS$, PPh_3, and their derivatives) have been tested as hydrogenation catalysts. Complexes containing a Re-S bond were found to catalyze the reduction of the nitro group in nitrobenzene and p-nitrotoluene at 70-95 °C and 1-100 bar H_2 in DMF. Complexes with a Re-P bond selectively catalyzed the reduction of linear C_6-C_{10} α-olefins [235].

Rate constants were determined for the hydrogenation of aromatic nitro compounds in alcohols on a palladium-containing anion exchanger composed of an aminated chloromethylated styrene-divinylbenzene copolymer. Swelling of the anion exchanger in alcohol increased the rates of hydrogenation [236]. Catalytic activities in hydrogenation of nitrobenzene were determined for $PdCl_2$ catalysts supported on different ion exchangers containing NH_2 or NH functional groups. The activities differed due to the differences in $PdCl_4^{2-}$ or polynuclear Pd chloro complex structures in the polymer matrixes [237]. Three types of bipolymer-supported $PdCl_2$ catalysts were prepared by combining linear polymers having strong or weak acidic oxy groups into strong-strong, strong-weak, and weak-weak polymer pairs. The activity of these catalysts for hydrogenation of nitrobenzene was about 4 times higher than that of a catalyst supported by a single polymer [238]. The hydrogenation of (**103**) at 20-25 °C and 0.3-3 bar H_2 pressure in the presence of catalytic amounts of $PdCl_2$ and iron powder in an EtOH/AcOH solvent mixture gave (**104**) in 87% isolated yield. When iron powder was replaced with $Fe(OAc)_2$, comparable results were obtained. The high selectivity was attributed to the intermediate formation of an iron-dinitroaromatic compound [239].

103 104

N-Arylhydroxylamines were prepared by hydrogenating aromatic nitro compounds in the presence of Pt(II)-polyethyleneimine complexes reduced by $NaBH_4$. Yields up to 98% were obtained when the hydrogenation was conducted in the presence of excess polyethyleneimine [240].

8. Miscellaneous Hydrogenations

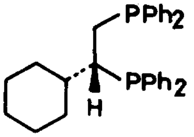
Hydrogenolysis of allylic alcohols like (**105**) using *in situ* generated $HCo(CN)_5^{3-}$ and β-cyclodextrin gave the corresponding *trans*-olefins in good yield at room temperature [241].

105 91% 4%

Ruthenium carbonyl complexes were found to be active catalysts for the selective reduction of Schiff bases between 70 and 130 °C under 100 bar CO/H_2 = 1/1 pressure. In *N*-isopropylpyrrolidinone as solvent and $Ru_3(CO)_{12}$ as catalyst precursor a complete conversion of *N*-benzylideneaniline to benzylaniline was achieved at 100 °C [242]. Asymmetric hydrogenation of imine (**106**), catalyzed by $Ru_2Cl_4[(R)-(+)-BINAP]_2(NEt_3)$ furnished, after crystallization, the enantiomerically pure sultam (R)-(**107**) in 72% yield. Analogous (S)-BINAP-directed hydrogenation of (**106**) gave pure crystalline (S)-(**107**) in 71% yield [243].

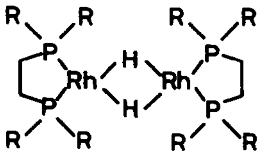
106 (R)-107

Catalytic asymmetric hydrogenation of the imine, ArN=C(CH_2OMe)Me (Ar = 2,6-dimethylphenyl or 2-methyl-6-ethylphenyl), using *in situ*-prepared rhodium-phosphine catalyst systems was studied. Optical yields up to 69% ee were achieved by using low temperatures (-25 °C) and 100 bar H_2 pressure in a methanol-toluene solvent mixture and cycphos (**108**) as the phosphine component of the catalyst [244].



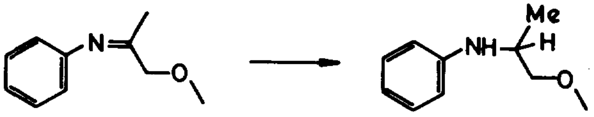
108; cycphos

An attempt to model the catalytic hydrogenation of the carbon-nitrogen double bond, reactions of binuclear rhodium hydrides (**109**) with *N*-benzylideneaniline, benzophenone imine, and isoquinoline have been studied. Amido-hydride products of the general formula $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}NR'CH_2R)(\mu\text{-}H)$ were prepared. Mechanistic studies of these reactions revealed that both metal centers are involved in the reduction of the C=N bond. The use of (109) as catalyst precursor in imine hydrogenation resulted in seven turnovers at 25 °C, 1 bar H_2 in 16 hours [245].



109; R = iPr, OPr^i

Imines of type (**110**; R = Me, Et) were hydrogenated to the corresponting amines (**111**) at RT and 20 bar with catalysts obtained *in situ* from $[Ir(COD)Cl]_2$ and the chiral diphosphines (**112**–**116**). The 1,2-diphosphines (S,S)-chiraphos (**112**) and (R,R)-norphos (**113**) formed catalysts with low activity and enantioselectivity; among the 1,3- and 1,4-diphosphines (S,S)-BDPP (**114**), (S,S)-BPPM (**115**), and (S,S)-DIOP (**116**), BDPP proved to be the most efficient (98% yield and 84% ee) [246].



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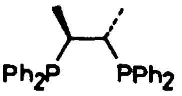

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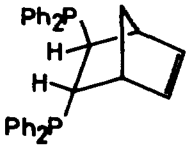

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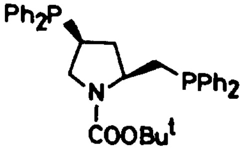

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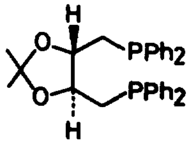
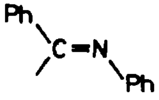


116

Catalytic asymmetric hydrogenation of the imines (**117**-**119**) was studied in the presence of $[Ir(P\text{-}P)HI_2]_2$ type complexes (P-P = DIOP, BDPP, norphos, and BINAP). The highest ee (80%) was obtained in the hydrogenation of (**118**) using (-)-BDPP as ligand in the catalyst precursor at 30 °C and 40 bar H_2 pressure [247].



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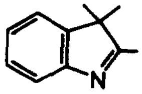

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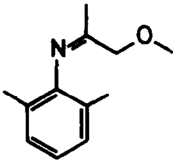
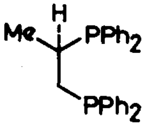


119

The new anionic iridium(III)-tetraiododiphosphine complexes $Li[Ir(P\text{-}P)I_4]$ (P-P = dppe, dpe, (R)-prophos (**120**)) were found to be active catalysts for the hydrogenation of imines under 25 bar H_2 at 20 °C [248].



120 ; (R)-prophos

A series of silica-supported amino-containing polysiloxane-Pd complexes with N-donor ligands were prepared and used as catalysts for hydrogenation of imines. The hydrogenation of N-benzylideneaniline was studied in detail [249].

The agglomerate $\{(Ph_4P)_2[Fe_4S_4(tmbdt)_2(Mo^VO)_{0.76}]\}_n$ exhibits catalytic activity for the reduction of azobenzene and phenylacetylene to hydrazobenzene and styrene, respectively, by Et_4NBH_4 in DMF-EtOH solution [250].
See also [158,175].

9. Dehydrogenation

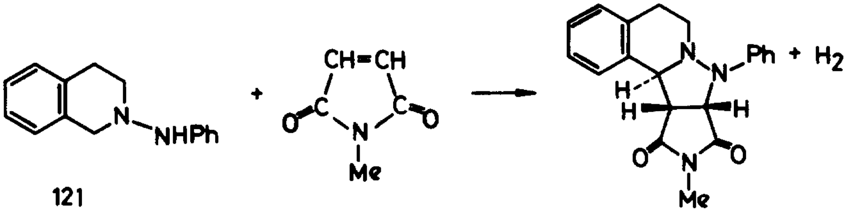
$(Bu_4N)_4W_{10}O_{32}$ catalyzes the photocatalytic dehydrogenation of saturated hydrocarbons in the presence of alcohol, ester, and ketone functional groups. Thus, a 1:1 mixture of cyclooctane and 2-butanol gave 75% cyclooctene and <2% 2-butanone [251].

Polyoxotungstates with formal redox potentials more negative than −1.0 V (vs. $Ag/AgNO_3$ in MeCN), such as $[W_{10}O_{32}]^{4-}$ and $[W_6O_{19}]^{2-}$, photochemically dehydrogenate branched acyclic alkanes (2,3-dimethylbutane or 2,3-dimethylpentane) in high selectivity to α-olefins and the least substituted alkenes. Polyoxotungstates with ground-state formal redox potentials less negative than −1.0 V, such as $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ and $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, photodehydrogenate the above alkanes in high selectivity to the thermodynamically most stable (i.e. the most substituted) alkenes. The intermediacy of organic radicals in these reactions was deduced from product distribution and kinetic data [252].

Catalytic cyclooctane dehydrogenation, yielding cyclooctene and dihydrogen, was observed under thermal reaction conditions using $RhClL_3$ or $[RhClL_2]_2$ (L = PPh_3 and $P(p\text{-tolyl})_3$) complexes. The best initial turnover frequency reported was 1.24 at 151 °C [253]. Bulky hydrocarbons like 2,2,5,5-tetramethylhexane and 1,3,5-tri-*tert*-butylbenzene proved to be inert solvents in the photo-assisted dehydrogenation of cyclooctane to cyclooctene catalyzed by $RhCl(CO)(PMe_3)_2$ at 100 °C. The main byproduct at high conversion was 1,3-cyclooctadiene [254]. The wavelength dependence in excimer laser-induced cyclooctane dehydrogenation catalyzed by $RhCl(CO)(PMe_3)_2$ was studied and compared with benzene carbonylation to benzaldehyde. From the observed differences it was concluded that photoexcitation is necessary not only for the dissociation of CO from $RhCl(CO)(PMe_3)_2$ but also for other steps in the carbonylation reaction [255].

The dehydrogenation of methanol to methyl formate and the isomerization of the latter to acetic acid (followed by esterification to methyl acetate) were achieved in a single step between 40 and 65 °C in $MeNO_2$ or MeCN using $[Ru(SnCl_3)_5L]^{3-}$ (L = MeCN, PPh_3) as catalyst [256]. In the presence of $Pt(PPh_3)_4$, 4,4-dimethoxybenzoin is transformed (dehydrogenated?) in benzene solution under N_2 to 4,4'-dimethoxybenzil. The Pt complex formed in the reaction could be isolated after exposure to air in the form of $PtO_2(PPh_3)_2$ [257]. Copper(II) chloride dissolved in hydrochloric acid photocatalyzes the evolution of hydrogen at 26 °C from aqueous solutions of ethanol [258].

Catalytic dehydrogenation of the hydrazine (**121**) with $RhCl(PPh_3)_3$ in hot DMF in the presence of N-methylmaleimide leads to cycloadduct (**122**) in 77% yield [259].



121

122

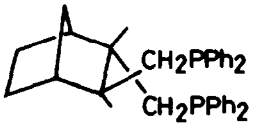
See also [121,263,264].

10. Hydrogen Transfer Reactions (Organic Compounds as Reductants)

a) Transfer Hydrogenation of C=C and C≡C Bonds

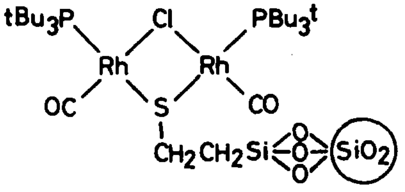
The complexes $HMCl(CO)(PPr^{i}_{3})_{2}$ (M = Ru,Os) catalyze in the presence of $NaBH_4$ the transfer hydrogenation of phenyl acetylene to styrene by iPrOH. The reaction rate decreases significantly with time; this can be explained by a change in the active catalyst which is present in the reaction mixture. In the initial phase of the reaction the active complex is $H_4M(CO)(PPr^{i}_{3})_{2}$ which is transformed during the reaction gradually into $M(C{\equiv}CPh)_2(CO)(PPr^{i}_{3})_{2}$ [260].

Transfer hydrogenation of itaconic acid with a mixture of formic acid and an amine (5:2) using a BPPM complex of rhodium as catalyst gave optically pure (S)-methylsuccinic acid [261]. The asymmetric transfer hydrogenation of α,β-unsaturated carboxylic acids, esters and ketones using *in situ* catalysts formed from $[Rh(COD)Cl]_2$ and chiral phosphines ((−)-DIOP, BPPM, or **123**) with a mixture of formic acid and Et_3N as the hydrogen source was investigated. The best enantioselectivities were achieved in the case of α,β-unsaturated carboxylic acids. In the case of 3-methyl-2-cyclopentenone the carbon-carbon double bond was selectively reduced in the presence of BPPM and resulted in 30% ee of the (R)-product [262].



123

The silica-bound rhodium carbonyl phosphine complex (**124**) was shown to catalyze the disproportionation of 1.3-cyclohexadiene to cyclohexene and benzene at 60 °C and of dihydronaphthalene to tetralin and naphthalene at 90 °C in toluene or CD$_3$OD solution. The accompanying dehydrogenation was less than 10% [263].

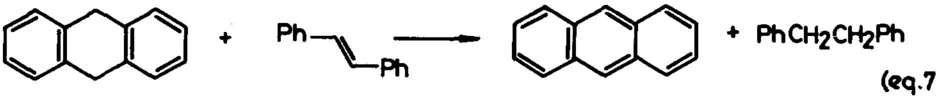


124

Disproportionation of cyclohexadienes or dihydronaphthalenes and the dehydrogenation of dihydroanthracene by stilbene are catalyzed by Ni(COD)$_2$. Alkyl aluminum compounds increase the rates of these H-transfer reactions (eqs.5-7) [264]:

(eq.5)

(eq.6)



(eq.7)

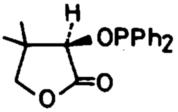
See also [231].

b) Transfer Hydrogenation of Ketones and Aldehydes

The ruthenium hydrides RuH$_4$(PPh$_3$)$_3$ and RuH$_2$(PPh$_3$)$_4$ were found to be effective catalysts for the reduction of cyclohexanones by hydrogen transfer from 2-propanol at room temperature [265]. The reduction of cyclohexanone by hydrogen transfer from isopropanol catalyzed by $[H(CO)(PPh_3)_2Ru(\mu\text{-}Cl)(\mu\text{-}pyrazolo)M(diolefin)]$ (M = Ir,Rh; diolefin = COD, tetrafluorobenzobarrelene) at 83 °C was reported [266]. A radical mechanism was suggested for the $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$-catalyzed disproportionation and transfer hydrogenation (by iPrOH) of cyclohex-2-ene-1-one to cyclohexanone and cyclohexanol. The mechanism was based on the observed ESR signal and on the inhibiting effect of radical scavengers [267]. Transfer hydrogenations of cyclohex-2-en-1-one, benzylidene aniline, and carbon tetrahalides by iPrOH and using $Ru_3(CO)_{12}$ as precatalyst have been studied. Hydrogenation of cyclohex-2-en-1-one into cyclohexanol was found to proceed over cyclohexanone; two catalytically active Ru cluster intermediates have been isolated from this reaction [268]. Aromatic and aliphatic aldehydes were reduced selectively to the corresponding alcohols with good to excellent yields at 80 °C by hydrogen transfer from formate using water-soluble complexes of Ru(II), Rh(I) and Ir(I) with monosulphonated triphenylphosphine ($mSPPh_2$), as the catalyst in an aqueous/organic biphasic system, according to eq.8

$$RCHO_{(org)} + HCOO^-_{(aq)} + H_2O \longrightarrow RCH_2OH_{(org)} + HCO_3^-{}_{(aq)} \qquad (eq.8)$$

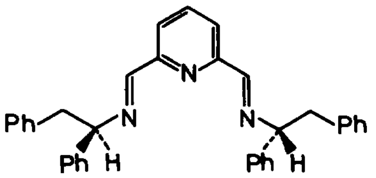
$RuCl_2(mSPPh_2)_2$ was found to be the most useful catalyst and $HRu(OOCH)(mSPPh_2)_3$ was identified as the key intermediate in the catalytic cycle [269]. Asymmetric transfer hydrogenation of acetophenone with 2-propanol at 60-80 °C using chiral ruthenium complexes of (+)-diphenylphosphinite-pantolactone (**125**) or (+)-DIOP was studied. In the best case, 12% ee of the (+) phenyl ethyl alcohol was obtained. In the presence of asbestos, however, the (+) DIOP-based catalyst resulted in the (−) alcohol in 19% ee [270].



125

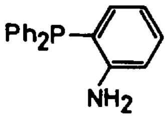
Hydrogenation of carbonyl compounds to alcohols was investigated using cyclooctane as a hydrogen donor in the presence of $RhCl(CO)(PMe_3)_2$ and irradiation at 325 nm. Cyclohexane-carbaldehyde is reduced to cyclohexanemethanol in 87% at room temperature. In 48 h, 359 turnovers were achieved [271].

The Ir complexes (PNP)Ir(σ,η^2-cyclooctenyl) and (P_2N_2)Ir(σ,η^2-cyclooctenyl) (PNP = $PrN(CH_2CH_2PPh_2)_2$, P_2N_2 = $Et_2NCH_2CH_2N(CH_2CH_2PPh_2)_2$ were found to be good catalyst precursors for the chemoselective hydrogen-transfer reduction of α,β-unsaturated ketones (such as benzylidene acetone) to allylic alcohols in refluxing iPrOH or cyclopentanol. The *in situ* prepared catalysts from $[Ir(COD)OMe]_2$ and PNP or P_2N_2 showed practically the same selectivities (70-80%) as the isolated catalyst precursor complexes, but they were found to be more active [272]. The *in situ* system $[Ir(COT)_2Cl]_2$ + (R,R)-(**126**) was found to be a very effective catalyst in the asymmetric hydrogen transfer reaction from isopropanol to acetophenone and to unsaturated ketones in the presence of KOH as cocatalyst at 83 °C. Good to excellent conversions and ee-s between 13 and 82% were reported [273].



126

Benzylideneacetone and other α,β-unsaturated ketones were selectively reduced (up to 95%) to the corresponding allylic alcohols by hydrogen transfer from iPrOH at 83 °C catalyzed by $[Ir(COD)X]_2$ (X = Cl or MeO) in the presence of aminophosphines (**127**) and (**128**) or using the Ir complex (**129**) [274,275].



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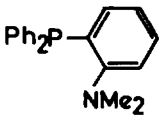

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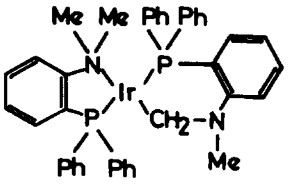
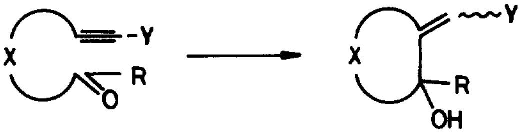


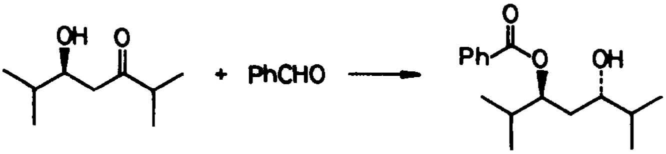
129

Cyclic functionalized products (**130**; X = $(CH_2)_n$, $O(CH_2)_n$, Boc-$N(CH_2)_n$, n = 1,2; Y = H, $SiMe_3$, Ph, COOMe, COOEt; R = H, Me) were prepared in 30-75% yield by an intramolecular reductive cyclization of aldehydes and ketones with alkynes promoted by SmI_2 at 0 °C in THF/HMPA containing stoichiometric amounts of tBuOH [276].



130

The SmI_2-catalyzed Tishchenko reduction of β-hydroxy ketones (for example, **131**) has been reported; this reaction affords the corresponding *anti* diol monoesters (**132**) in high yield and with excellent levels of stereochemical control. By using CD_3CDO it could be demonstrated that the aldehyde is the exclusive source of hydride [277].



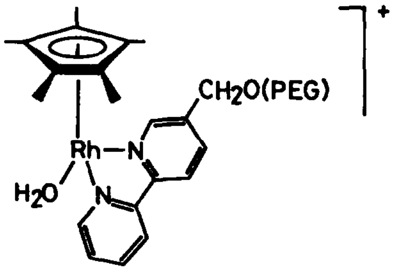
131

132

The reduction of ethylbenzoylformate with 1,5-dihydro-5-deazaflavin in the presence of the chiral NMR shift reagent tris-[3-(heptafluoropropylhydroxymethylene)(+)-camphorato] europium gave (S)-ethyl mandelate with 24-36% ee [278].
See also [134].

c) Transfer Hydrogenation of Miscellaneous Organic Compounds

Reduction of NAD^+ to NADH by formate in aqueous solution is catalyzed by the high-molecular weight Rh complex (**133**; PEG = polyethyleneglycol with molecular mass 20,000). The use of this catalyst enables the continuous reduction of NAD^+ in a membrane reactor without the need of catalyst recycling [279].



133

The catalytic activity of polymer-supported $RhCl_3$ catalysts modified by 3-methylpyrazole, imidazole, or benzimidazole in the reduction of nitrobenzene by $NaBH_4$ or iPrOH was determined. Reductions with iPrOH were more effective [280]. Highly hindered phenols could be efficiently deoxygenated by first transforming them into the corresponding triflates and treating the latter with HCOOH + Bu_3N in the presence of $(PPh_3)_2PdCl_2$ and dppp in DMF solution at 100 °C [281]. Aryl sulfonates (**134**; Ar = 1-naphthyl, 4-CNPh, 4-AcPh, 1-(9,10-anthraquinoyl); R = CF_3, 4-FPh, Ph, *p*-tolyl, 4-MeOPh, Me) were reduced to the corresponding arenes by triethylammonium formate in the presence of $Pd(OAc)_2$ + phosphine catalysts in DMF solution at 90 °C. With dppp as ligand arene yields were around 90% and no hydrolysis to phenols was observed [282].

$$ArOSO_2R \longrightarrow ArH$$

134

Reduction of methylene blue to leuco methylene blue by thioglycolic acid is catalyzed by Cu(II); this redox reaction was carried out also across a keratine-immobilized membrane containing Cu(II) ions [283].

See also [268].

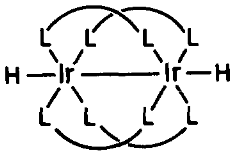
11. Reduction Without Molecular Hydrogen

a) Stoichiometric Reduction with Low-Valent Transition Metal Complexes

Steroidal 3-oxo-1,4-dienes (for example **135**) could be reduced by $Fe(CO)_5$-$NaOH$-H_2O in MeOH solution at 50–60 °C to the corresponding cyclohexenones (**136**). The regio- and stereoselectivity of the reaction depends on the substitution pattern of ring A: C(1) and C(2) methylated products furnish Δ^1 products with 5β-stereochemistry, whereas C(4) methylated and unsubstituted steroids (like **135**) afford Δ^4 derivatives [284].

135 136

The dinuclear Ir(II) complex $[Ir_2(L\text{–}L)_4H_2]^{2+}$ (**137**) (L–L = **138**) reacts with styrene to give ethylbenzene and $[Ir_2(L\text{–}L)_4]^{2+}$ [285].



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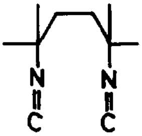


138

Selective reduction of terminal or internal alkynes to *cis*-alkenes in good yields was brought about by hydrometallation using $[(Ph_3P)CuH]_6$ in benzene at RT or at reflux temperature. In the case of the acetylated tertiary propargyl alcohol (**139**), reduction to a 1,1-disubstituted allene was observed [286].

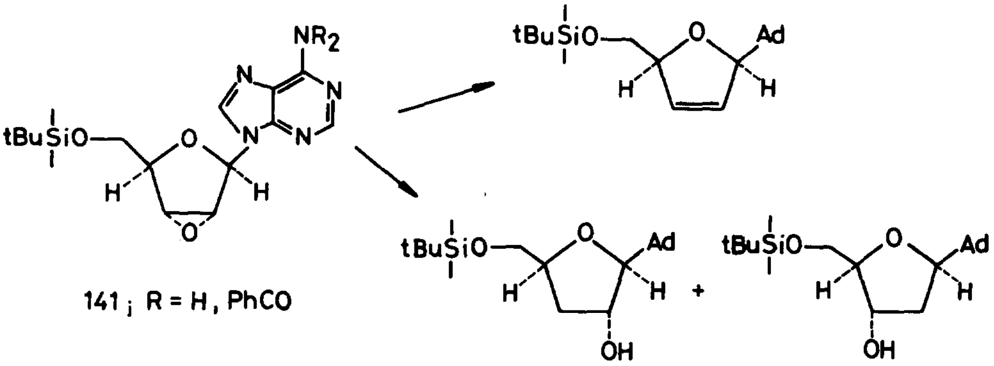
$$Ph\text{-}\underset{OAc}{\overset{Me}{C}}\text{-}C{\equiv}CH \longrightarrow (Me)(Ph)C{=}C{=}CH_2$$

139

Rapid deoxygenation of alcohols and desulfurization of thiols was observed at room temperature by $WCl_2(PMePh_2)_4$ (**140**) in stoichiometric reactions (eqs.8 and 9) [287].

$$\mathrm{EtSH} + 140 \longrightarrow \mathrm{EtH} + W(S)Cl_2(PMePh_2)_3 + PMePh_2 \quad \text{(eq.9)}$$

Epoxides can be deoxygenated to olefins by Cp_2TiCl_2 in THF solution. If the reaction is performed in the presence of a H atom donor such as 1,4-cyclohexadiene, the intermediate radical can be trapped in the form of an alcohol. Both methods were successfully used for a variety of epoxides including the adenosine epoxides (**141**) [288].



141 ; R = H, PhCO

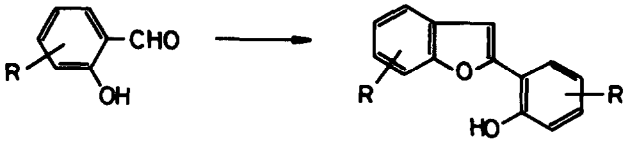
The reduction of 2,3-epoxy alcohols (like **142**) with Cp_2TiCl in THF at room temperature gave alk-1-ene-3-ols in 80-91% yields [289].

142

Acetone has been reduced to isopropyl alcohol in >80% yield by $[Os(NH_3)_5(H_2)]^{3+}$ in CH_3CN solution [290]. Organic carbonyl compounds such as acetaldehyde and acetone were reduced to the corresponding alcohol with Cp_2MoH_2 and a protonic acid (e.g. AcOH) at room temperature. The reduction of *4-tert*-butylcyclohexanone afforded *cis-4-tert*-butylcyclohexanol [291]. The asymmetric reduction of ethyl phenyl pyruvate with the homochiral iron complex (R)-(-)-[CpFe(CO)(PPh$_2$(O-1-menthyl))]-1-methyl-1,4-dihydronicotinoyl in the presence of magnesium perchlorate gave (R)-(-)-ethyl mandelate in 71% isolated yield and 52% ee [292]. The stable copper(I) hydride cluster $[(PPh_3)CuH]_6$ allows chemoselective conjugate reduction of α,β-unsaturated carbonyl compounds substituted at the γ-position with methoxy, acetoxy or thiophenoxy groups at RT in excellent yield. Similarly, good results were obtained in the case of iodo, bromo or tosylato substituents in ω-position. In the presence of Me_3SiCl, the iodoalkyl enol ether (**143**) resulted quantitatively [293].

143

The reduction of o-hydroxybenzaldehydes (**144**; R = H, 3-OMe, 4-OMe, 5-OMe, 3-OH, 5-OH, 5-Br, 5-Cl) by aqueous $TiCl_3$ at 50-80 °C is a new simple way to the synthesis of 2-(benzofuran-2-yl)phenols (**145**). When the reduction is performed at 0 °C in the presence of acetaldehyde, stereoselective formation of 1,3-dioxolanes (**146**) occurs, due to *in situ* condensation with the intermediate diols [294].



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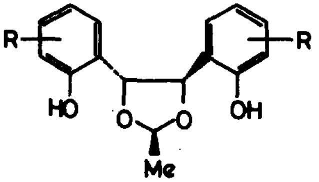
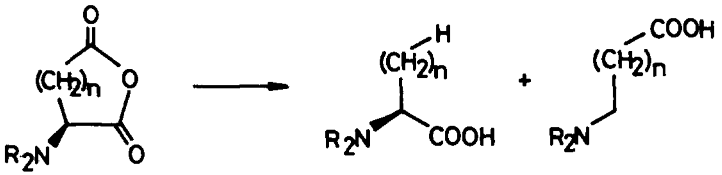
145



146

N-protected aspartic and glutamic anhydrides (**147**; n = 1,2) were reduced and decarbonylated to amino acids by refluxing with stoichiometric amounts of Ni(COD)L_2-type complexes followed by acidic workup of the reaction mixture. The correlation of the product ratio **148**:**149** with the substituents R_2 (H, Z; phthaloyl; H, CF_3COO) and ligands L (bpy, PCy_3 PPh_3, $Me_2NCH_2CH_2NMe_2$, 4,4-Me_2phen) was studied [295].



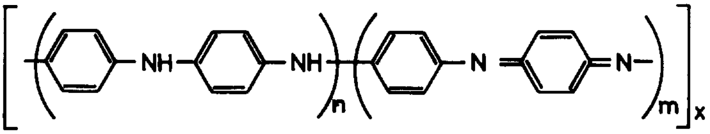
147 148 149

Ketimines were readily reduced at RT to the corresponding amines by treatment with ytterbium metal followed by quenching with water [296]. Primary amines like aniline, benzylamine, 2-phenylethylamine, and cyclohexylamine gave selectively N-(cyclohexylmethyl)- or N-(cycloheptylmethyl-N-alkyl(aryl)amines (**150**) with pimelaldehyde or suberaldehyde, respectively, in 42-63% isolated yield using $KHFe(CO)_4$ as a reducing agent under CO in EtOH solution [297].

n = 5, 6

150

Aromatic aldimines were reductively coupled to 1,2-diamines with good yields by treatment with SmI_2 in refluxing THF solution. Cross-coupling of aromatic ketimines with ketones to 2-aminoalcohols was achieved by the same reagent in 44-73% yields [298]. Reduction of the substituted nitrosobenzenes RC_6H_4NO (R = 3-Me, 4-OH, 4-NMe_2) with $TiCl_3$ in dioxane/H_2O gave the corresponding aniline derivatives. In the case of R = 4-NHPh, however, the product was oligomeric emeraldine (**151**) [299].

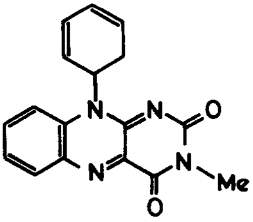


151

Dihydro-1,2-oxazines (**152**; R' = Ph, EtOOC; R^2,R^3 = H, R, Ph; X = morpholino, BuO, PhO, Me_3SiO) were converted into pyrrole derivatives (**153**) via reductive deoxygenation by treating with $Fe_3(CO)_{12}$ in $ClCH_2CH_2Cl$, THF, or toluene at 90 °C. Yields between 16 and 99% were reported [300].

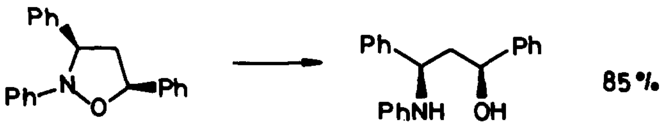
The flavin analogue (**154**) is reduced by the *cis*-dialkylcobalt(III) complexes $[R_2Co(bpy)_2]^+$ (R = Me, Et) in the presence of $HClO_4$ to the corresponding dihydroflavin radical cation (eq.10) [301].

$$[R_2Co(bpy)_2]^+ + (\mathbf{154}) + 2\,H^+ \longrightarrow R\text{–}R + [Co(bpy)_2]^{2+} + (\mathbf{154})H_2^+ \qquad \text{(eq.10)}$$



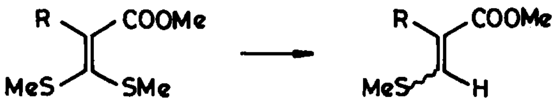
154

Isoxazolidines like (**155**) were reduced to 1,3-aminoalcohols with $Mo(CO)_6$ in refluxing wet acetonitrile [302].



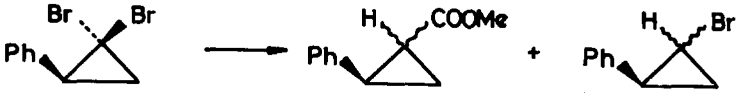
155

α-Alkoxycarbonylketene dithioacetals (**156**; R = H, Et, Ph, allyl) were smoothly reduced by the cyanocuprate $Me_2Cu(CN)Li_2$ at -20 °C to the corresponding vinyl sulfides (**157**) in high yields. Mainly the (E)-isomers were formed with about 90% stereoselectivity [303].



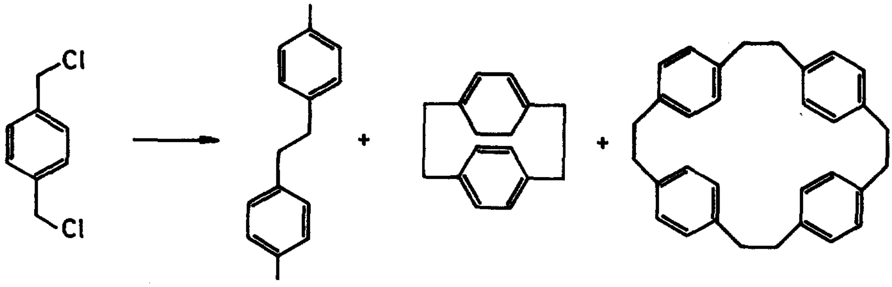
156 157

The gem-dibromocyclopropane (**158**) reacts with $Fe(CO)_5$ in presence of MeONa to yield the cyclopropane methyl esters (**159**) along with monobromocyclopropanes (**160**). Neither reduction nor reductive carbonylation take place in the absence of a nucleophile (MeONa), this suggests that the active species of the reactions is $[Fe(CO)_4(COOMe)]^-$ [304].



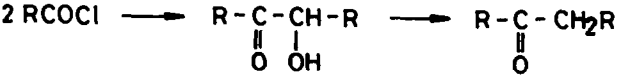
158 159 160

Reductive coupling of aromatic geminal dichlorides by Fe(II) oxalate dihydrate in DMF gave (E)-olefins. Thus, coupling of $PhCHCl_2$ gave 60% (E)-stilbene [305]. Reaction of $Cr(CO)_3(NH_3)_3$ with benzylic mono-, di-, and trihalides leads to the formation of 1,2-diarylethanes, -ethenes, and diphenylethyne in satisfactory yields. Di(halomethyl)benzene derivatives yield product mixtures containing both reduction products and coupling products: (**161**) is transformed into a mixture of (**162**), (**163**), and (**164**) [306].



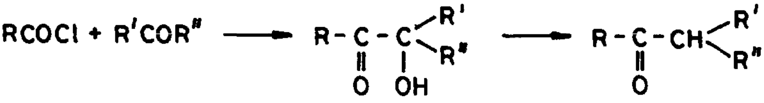
161 162 163 164

Aliphatic acid chlorides are reductively coupled by excess SmI_2 to ketones (**166**). Under the same conditions, acid chlorides reductively couple with ketones to form the higher molecular weight ketones (**168**). Ketols (**165**) and (**167**) are the intermediates of these reactions [307].



$$2\,RCOCl \longrightarrow R-\underset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle OH}{\overset{|}{C}H}-R \longrightarrow R-\underset{\displaystyle O}{\overset{\|}{C}}-CH_2R$$

165 166

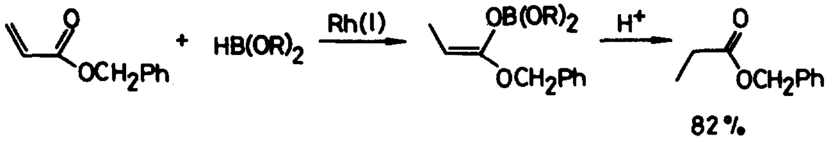


$$RCOCl + R'COR'' \longrightarrow R-\underset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle OH}{\overset{|}{C}}(R')(R'') \longrightarrow R-\underset{\displaystyle O}{\overset{\|}{C}}-CH(R')(R'')$$

167 168

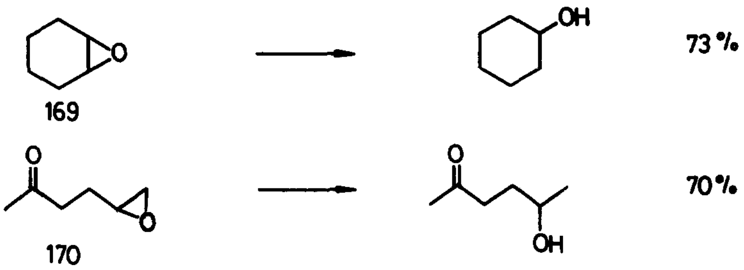
b) *Inorganic Reductants in the Presence of Transition Metal Complexes*

The reaction of the yttrocene chloride derivative $(C_5H_4CH_2OCH_2CH_2C_5H_4)YCl$ and NaH with 1-hexene in THF at 45 °C afforded hexane [308]. Partial reduction of internal alkynes to (Z)-alkenes with up to 99/1 = Z/E ratios has been achieved with reagents prepared from $NbCl_5$ or $TaCl_5$ and zinc, in polar solvents [309]. The conjugate reduction of α,β-unsaturated carbonyl compounds by catecholborane was found to be greatly accelerated by the addition of 2 mol% $Rh(PPh_3)_3Cl$ at −20 °C (eq.11) [310].



(eq.11)

Chemoselective reduction of oxiranes (169,170) to secondary alcohols by MeLi or MeMgI in the presence of $CuBr(PBu_3)_2$ was observed after work up with aqueous NH_4Cl [311].



169

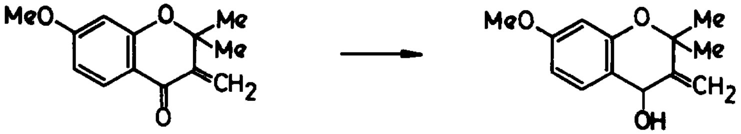
170

The reduction of ketones and aldehydes with MgH_2 as a reducing agent in the presence of a catalytic amount of first row transition metal halides was studied. The best conversions of cyclohexanone to cyclohexanol, 98% and 74%, were obtained at 25 °C in THF with $FeCl_3$ and $CoCl_2$, respectively. Cyclohexanecarboxaldehyde and benzaldehyde were also reduced with high yields (60-90%) to the corresponding alcohols in the presence of either $CoCl_2$ or $FeCl_3$ [312]. Aliphatic, aromatic, and α,β-unsaturated ketones were reduced to the corresponding secondary alcohols by iPrMgBr in the presence of bis(neomenthylcyclopentadienyl)titanium dichloride as catalyst. Diaryl ketones afforded reductive coupling products (pinacols) under these conditions. Esters were reduced to the corresponding primary alcohols [313]. The reduction of alkylcyclohexanones and rigid bicyclic ketones to the corresponding cyclic secondary alcohols with NaH containing transition metal (Zn, Cd, Mn, Co, and Ni) complex reducing agents was studied. Steric hindrance plays an important role in determining the structure of the alcohol; the apparent size of the reagents follows the trend Mn>Zu,Cd>Ni,Co [314]. Reduction of acyclic β-hydroxy ketones mainly to *syn* 1,3-diols has been achieved with catecholborane; the stereoselectivity of the reaction could be increased in some cases by the addition of Rh(PPh$_3$)$_3$Cl. If reducing for example (**171**) to (**172**), the *syn:anti* ratio could be increased in this way from 3:1 to 10:1 [315].


171

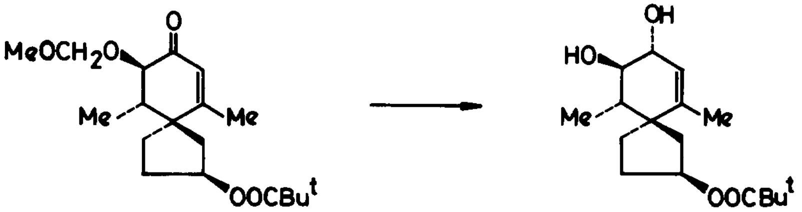
172

Reduction of the alkylidenechromanone (**173**) with NaBH$_4$ in the presence of CeCl$_3$ gave the allylic chromanol (**174**) [316].


173

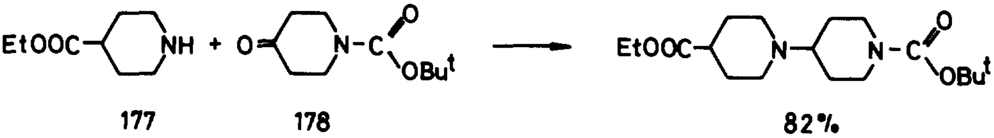
174

The bicyclic ketoether (**175**) was reduced with NaBH$_4$ and CeCl$_3$.7H$_2$O predominantly to the diol (**176**) [317].

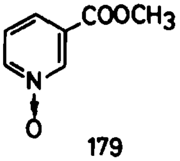

175

176

The reduction of alkyl azides to NH$_3$ by Na$_2$S$_2$O$_4$ catalyzed by [MoFe$_3$S$_4$(SAr)$_3$]$^{2-}$ or [Fe$_4$S$_4$(SAr$_4$]$^{2-}$ clusters or on a glassy carbon electrode modified with (Bu$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$(SPh)$_9$] has been reviewed [318]. A one-pot reductive alkylation procedure to aromatic amines, hindered amines, and α-trifluoromethylamines from ketones and one equivalent of the corresponding starting amine was developed using $TiCl_4$ and $NaCNBH_3$ [319]. An improved method for reductive alkylation of amines with aldehydes and ketones using $Ti(OPr^i)_4$ and sodium cyanoborohydride at room temperature was reported. Good yields (above 80%) were achieved even in the presence of acid-sensitive functional groups, for example in the reaction between (177) and (178) [320].



Heteroaromatic N-oxides and nitrones (for example 179 and 180) were readily and selectively deoxygenated to the corresponding bases or imines in excellent yields with a $TiCl_4$ + NaI reagent system. The actual reducing agent is probably a low-valent Ti complex which is formed by the reduction of $TiCl_4$ with iodide [321].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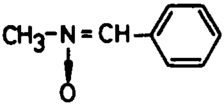
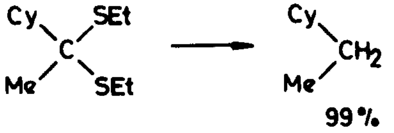

180

The $TiCl_4/SnCl_2$ reagent system was used for the reductive deoximation of various aldoximes and ketoximes under mild conditions; the corresponding carbonyl compounds were obtained in high yields [322]. Reducing agents prepared from $NaBH_4$, $ZrCl_4$, and chiral amino alcohols were applied to the enantioselective reduction of oxime ethers to primary amines. High optical yields (up to 95%) were achieved by proper combination of solvent, temperature, the structure of the amino alcohol, and the ratio of reagents [323]. Amine (182) is readily available in good yields by the reduction of oxime (181) with $TiCl_4$ + $NaBH_4$ [324].

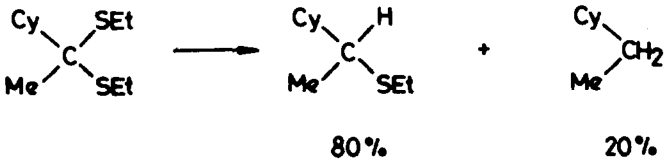
181 182

Aromatic nitro compounds were cleanly reduced to the corresponding primary amines by KBH_4-CuCl. Nitroso-, azoxy-, and azobenzene were also reduced to aniline by the same reagent system [325]. Aromatic nitro compounds were reduced to the corresponding amines in 80-95% yield using a freshly prepared solid mixture of aluminium powder and $NiCl_2.6H_2O$ in THF [326]. Molybdophosphoric acid, $H_3PMo_{12}O_{40}.XH_2O$ catalyzes the selective reduction of nitro compounds to anilines in the presence of aldehydes by $NaBH_4$ at room temperature in MeOH solution. Tungstosilicic acid, $H_4SiW_{12}O_{40}.XH_2O$ is, under the same conditions, a selective catalyst for the reduction of cyclic ketones to cycloalkanols by $NaBH_4$ in the presence of aldehydes [327]. Reduction of substituted nitrobenzenes with NaH + $Ni(OAc)_2$ gave the corresponding aniline derivatives [328].

Reductive cleavage of S-O and S-C bonds in aromatic sulfoxides and of S-N bonds in aromatic sulfilimines by 1-benzyl-1,4-dihydronicotinamide or $NaBH_4$ is catalyzed by (TPP)FeCl [329]. Complex reducing agents prepared from NaH, *tert*-pentylONa, and $Ni(OAc)_2$ were found to be active in hydrodesulfurization of dithioketols at 65 °C in THF solution (eq.12). Partial desulfurization was achieved by modifying the complex reducing agent with 2,2'-dipyridine (eq.13) [330].



(eq.12)



(eq.13)

The catalytic activities of ammonium pertechnetate and sodium molybdate in the reduction of methylene blue by $SnCl_2$ in acidic media at 25 °C were compared [331]. Selective reduction of the substituted 4H-1,3-thiazine-4-one (**183**; R = Ph, OEt) using $NaBH_4$ and $CeCl_3$ in methanolic solution at 10 °C gave (**184**) in 50-57% yield [332].

183 184

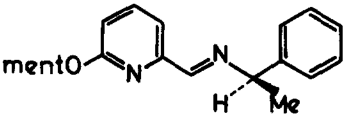
Organic halides can be reduced to the corresponding hydrocarbons by $NaBH_4$ in the presence of Cp_2MoH_2 or Cp_2MoCl_2 as catalysts. The reaction takes place at 50-75 °C in THF or iPrOH. Alkoxycarbonyl and cyano groups are unaffected [333]. Primary alkyl halides were reduced to the corresponding hydrocarbons with Grignard reagents in the presence of $(dppf)PdCl_2$ or (dppf)Pd(0) (dppf = dichloro[1,1'-bis(diphenylphosphino)ferrocene) at subambient temperatures [334].
See also [217,281].

c) Reduction via Hydrosilylation

Rhodium(II) perfluorobutyrate was found to be an effective catalyst for the reaction of alcohols with trialkylsilanes to yield trialkylsilyl ethers and H_2. If this reaction between Et_3SiH and cinnamyl alcohol was performed in a closed vessel to contain the liberated H_2, reduction of the C=C double bond occured along with silane alcoholysis to give the saturated ether (**185**) [335].

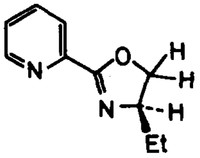
$$PhCH{=}CHCH_2OH + Et_3SiH \longrightarrow \underset{\textbf{185}}{PhCH_2CH_2CH_2OSiEt_3}$$

The reduction of acetophenone through catalytic hydrosilation at 0 °C in CH_2Cl_2 with H_2SiPh_2 and a rhodium-imine catalyst, prepared *in situ* from $[(COD)RhCl]_2$ and ligand (**186**), led to 1-phenylethanol with 80-84% yield and low asymmetric induction [336].



186

The Rh-catalyzed asymmetric reduction of acetophenone with H_2SiPh_2 in the presence of pyridineoxazoline (187) and picolineoxazoline (188) cocatalysts was studied. It was found that the direction of optical induction was inverted in going from (187) to (188) and in the case of (188) a 1.2-fold excess of the ligand was sufficient to achieve the highest ee (47%) [337].



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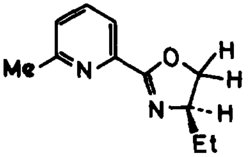
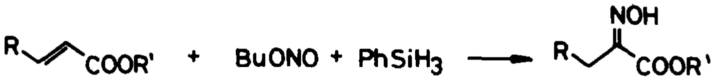


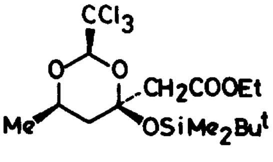
188

Various α,β-unsaturated esters were directly converted to the corresponding 2-hydroxyiminocarboxylic acid esters (189; R = H, Me, Pr, iPr, COOEt; R' = alkyl, Bn, Ar) at room temperature with butyl nitrite and $PhSiH_3$ in 78-98% isolated yields by using *N,N'*-bis(2-ethoxycarbonyl-3-oxobutylidene)ethylenediaminato cobalt(II) as the catalyst in THF solution [338].



189

Compound (190) was stereoselectively reduced in the presence of $TiCl_4$ by Et_3SiH to (191) [339].



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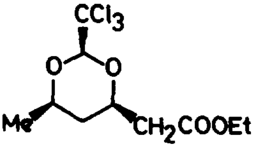


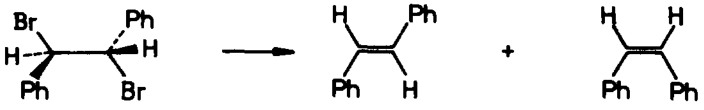
191

See also [191,192].

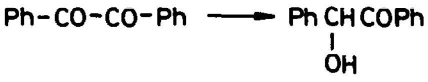
d) *Electroreduction and Photoreduction*

The photoreduction of methylviologen in MeOH solution with triethanolamine as electron donor and catalyzed by phtalocyanine complexes of Y(III), Sm(III), Gd(III), Yb(III), and Lu(III) has been reported [340]. The electrocatalytic reduction of cystine is catalyzed by the water-soluble Co(II) porphyrin complexes Co(TTAPP) and Co(TSPP) (TTAPP = tetrakis (4-trimethylammoniumphenyl)porphyrin; TSPP = tetrakis (4-sulfophenyl)porphyrin) in aqueous sulfuric acid solution [341]. Oligomers of poly[4,4'-(*p*-biphenylene)amide] were synthesized by electrochemical reduction of *p*-$BrC_6H_4CONHC_6H_4Br$-*p* in the presence of a catalytic amount of $(bpy)NiBr_2$ [342].

Photocatalytic hydrogenation of cyclohexene with H_2O as a source of H_2 by a $Pt/CdS/RuO_2$ semiconductor particulate system catalyzed by $K[Ru(H\text{-}EDTA)Cl].2H_2O$ under ambient conditions in aqueous ethanolic solution was observed [343]. Photoinduced hydrometalation and hydrogenation of activated olefins with $C_5H_5MoH_2$ and $C_5H_5WH_2$ was investigated. Irradiation of a mixture of $C_5H_5MoH_2$ and excess fumaronitrile at 25 °C with 550 nm light gave $C_5H_5Mo(CH(CN)CH_2CN)H$ in 95% isolated yield. Prolonged irradiation gave $C_5H_5Mo(NCCH{=}CHCN)$ and $NCCH_2CH_2CN$. The reductive elimination of succinonitrile from the hydridoalkylmolybdenum complex could be achieved thermally at 95 °C as well [344]. Photocatalytic asymmetric reduction of 3-methyl-2-oxo-butanoic acid to 2-hydroxy-3-methylbutanoic acid was carried out in up to 60% ee in aqueous methanol with chiral BINAP-Rh(I) complexes and the semiconductor photocatalysts TiO_2 or CdS [345]. $Rh(terpy)_2^{3+}$ and $Rh(bpy)_3^{3+}$ catalyze the photochemical reduction of NAD^+ into 1,4-NADH; triethanolamine acts as an electron donor [346]. Photosensitized reduction of *vic*-dibromo and keto compounds occurs in MeCN solution containing $[Ru(bpy)_3]^{2+}$ as photosensitizer and Et_3N as electron donor. For example, dibromide (**192**) is reduced to olefins (**193a**) and (**193b**), and diketone (**194**) is reduced to hydroxyketone (**195**). Cyclic voltammetry measurements reveal that $[Ru(bpy)_3]^+$ acts as the catalyst [347].



192 193a 193b

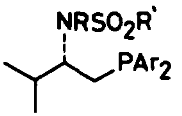


$Ph{-}CO{-}CO{-}Ph \longrightarrow Ph\underset{OH}{CH}COPh$

194 195

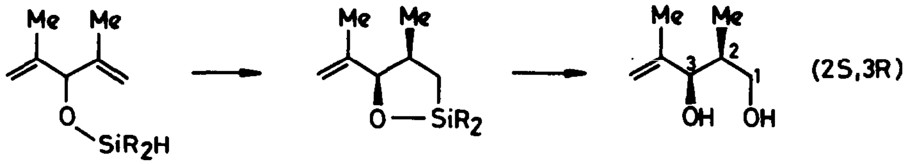
12. Hydrosilylation

The kinetics of 1-hexene hydrosilylation by triethoxysilane catalyzed by [RhCl(COD)L] (L = PPh_3 or 0.5 bis(diphenylphosphinoethyl)tetramethyldisiloxane was investigated using spectrophotometric and gas-chromatographie methods. It was concluded that hydrosilylation consists of two stages: the activation of the catalyst precursor, and a much faster catalytic cycle of hydrosilylation [348]. Hydrosilylation of 1-vinylcycloalkenes with $HSiMeCl_2$ in the presence of 0.5 mol% $PdCl_2(PPh_3)_2$ gave (Z)-1-ethylidene-2-silylcycloalkanes in good yields at 80 °C [349]. Palladium complexes with chiral (β-aminoalkyl)phosphine ligands (196; R = H, Me; R' = Me, Ph; Ar = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4) were found to be efficient catalysts for asymmetric hydrosilylation of cyclopentadiene and styrene with chlorosilanes at room temperature [350].



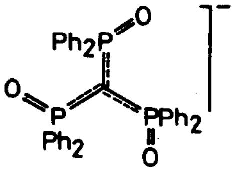
196

Catalytic asymmetric hydrosylation of (197) in the presence of $RhCl(C_2H_4)_2$ and (R,R)-DIOP or (R)-BINAP in $ClCH_2CH_2Cl$ at 30-50 °C, followed by H_2O_2 oxidation of the intermediate (198), afforded (199) with up to 93% ee [351].



197 198 199

The factors influencing the product composition in the hydrosilylation of 1-hexyne catalyzed by Rh and CoRh mixed-metal complexes were studied. Under optimum conditions (1-hexyne: $Co_3Rh(CO)_{12}$ = 1000, 1-hexyne : Et_3SiH = 1.5, 20 °C, 72 h in toluene) 96% yield of *cis*-1-(triethylsilyl)-1-hexene was achieved [352]. The effect of O_2 on the products of the Pt-catalyzed addition of $(nC_6H_{13})Me_2SiH$ or $BuMe_2SiOSiMe_2H$ to $Me_3SiC{\equiv}CSiMe_3$ was investigated. With both hydrides, higher yields of the expected *cis*-adducts were obtained at 130 °C under N_2 containing traces of O_2 than under dry air [353]. The iridium complexes $(triso)Ir(C_2H_4)_2$, $(triso)Ir(coe)_2$, and (indenyl)Ir(coe) were found to be highly active hydrosilylation catalysts even at room temperature (triso = tris(diphenyloxophosphoranyl)methanide, **200**; coe = cyclooctene). The reaction is selective for 1-alkyne and regioselective for β-products. From phenylacetylene and Et_3SiH in the presence of 0.1 mol% catalyst (Z)-β-(triethylsilyl)-styrene was obtained in 80% isolated yield [354].



200

Hydrosilylation of a wide variety of nitriles with $HSiMe_3$ at 60 °C in the presence of $Co_2(CO)_8$ under an atmosphere of CO to give N,N-disilylamines in good yields (eq.14) has been examined [355].

(eq.14)

91 %

IV. OXIDATION

1. Catalytic Oxidation of Hydrocarbons and Hydrocarbon Groups with O_2

a) *Oxidation of Saturated Hydrocarbons*

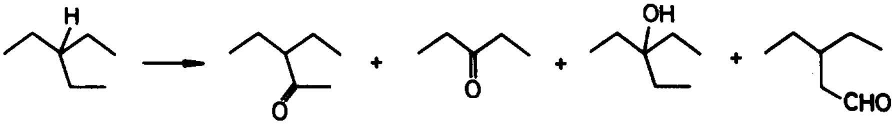
The role of Ce(III) stearate in the oxidation of pentadecane by O_2 has been studied. The Ce salt participated only in the chain termination step [356].

$CrSt_3$ and $Cr(acac)_3$ are very active catalysts for the oxidation of hydrocarbons by O_2. The hydroperoxides formed under such conditions oxidize these Cr(III) compounds to Cr(VI) compounds and the latter catalyze the oxidation of secondary alcohols to ketones by hydroperoxides [357].

The contribution of monohydroperoxides to chain branching in liquid-phase oxidation of n-decane catalyzed by KSt + $MnSt_2$ was determined [358].

$Fe(DPAH)_2$ [DPAH = (2-carboxy-6-carboxylato)pyridine] activates O_2 for the ketonization of methylenic carbons and the dioxygenation of acetylenes, aryl olefins and catechols at room temperature. The reaction of cyclohexane and H_2S with the iron complex and O_2 in 1.8:1 = py:HOAc yielded cyclohexanone and S_8 [359]. Saturated hydrocarbons may be oxidized at room temperature to alcohols and ketones by O_2 and the same catalyst also with hydrazobenzene as reducing agent. In the absence of hydrazobenzene only the catalyst is oxidized to $(DPAH)_2FeOFe(DPAH)_2$. This catalyst system mimics the chemistry of the methane monooxygenase proteins [360]. Isobutane and propane were oxidized by air in the presence of halogenated porphyrinatoiron(III) complexes to give tBuOOH and iPrOH + acetone, respectively. Increasing the halogen content of the ring increased the life and activity of the catalysts [361]. Oxidation of isobutane with O_2 is catalyzed by $(F_{20}TPP)FeX$ (X = N_3, OH, Cl, Br, I) complexes. With $(F_{20}TPP)FeOH$ as catalyst 95% yield of tBuOH was achieved [362]. In the presence of catalytic amounts of $FeCl_3.6H_2O$, alkanes (cyclohexane, n-hexane), toluene and ethylbenzene were oxidized by air under visible light irradiation to ketones, aldehydes, and alcohols. MeCN, acetone, or CH_2Cl_2 were used as solvents; in the latter case $(Et_3NCH_2Ph)Cl$ was added to aid the dissolution of the iron complex

[363]. Evidence for a second intermediate, probably an Fe(III) alkoxide, has been found in a study of the Gif-type oxidation system (pyridine, $FeCl_2.4H_2O$, Zn-powder, AcOH) converting adamantane into adamantanone [364]. The oxidation of 3-ethylpentane at room temperature under Gif^{IV} (Fe^{2+}, Zn, py-AcOH, O_2) or GoAg^{II} (Fe^{3+}, H_2O_2, py-AcOH) conditions gave 3-acetylpentane (**201**) as major product (30-50% selectivity) [365].

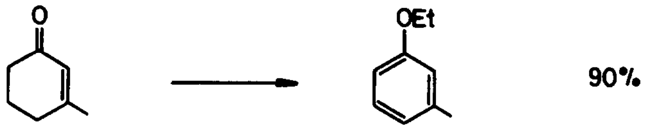


201

The liquid-phase oxidation of n-octane with oxygen-nitrogen mixtures p(O_2) = 0.4 bar) catalyzed by cobalt palmitate at 145 °C was studied. Detected products were: hydroperoxides, 2-, 3-, and 4-octanone, 2-, 3-, and 4-octanol, acetic, propionic, butyric, valeric, and caproic acids. Kinetic models were formulated [366]. The effects of formic and acetic acids on the $CoSt_2$-catalyzed oxidation of cyclohexane by O_2 have been studied. Formic acid retarded whereas acetic acid accelerated oxidation. Formic acid exerts its inhibiting influence by competing with cyclohexyl hydroperoxide for Co(III) and by enhancing chain-terminating processes [367]. Acetic acid enhances both the rate and selectivity of the oxidation of cyclohexane by O_2 catalyzed by $CoSt_2$. This effect was attributed to the formation and rapid decay of the ternary complexes [cyclohexane hydroperoxide.$CoSt_2$.AcOH] to radicals [368].

b) Oxidation of Olefins

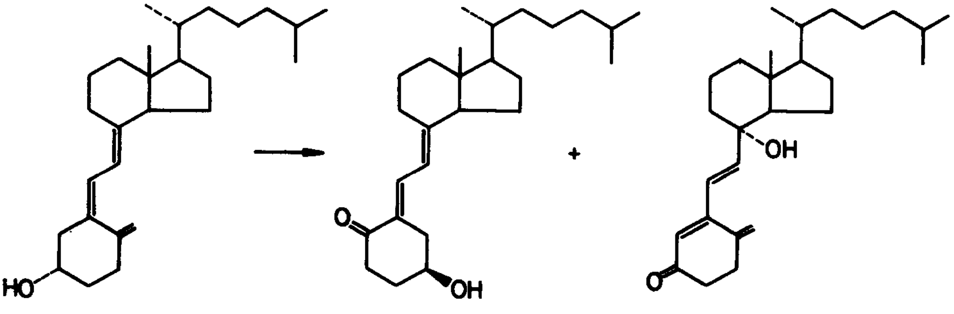
Alkane oxidation by air at 75 °C and 3 bar is catalyzed by $[Ru_3O(C_3F_7COO)_6(Et_2O)_3]^+$. Cyclohexane is oxidized to a 5:1 mixture of cyclohexanol and cyclohexanone. The turnovers are enhanced by the addition of Mn^{2+}, Fe^{3+} or Cr^{3+}. From n-hexene a 1:1 mixture of hexanol-2 and hexanone-2 was obtained [369]. The $VO(OR)Cl_2$-induced oxidative aromatization of α,β-unsaturated cyclohexanones (for example (**202**)) with O_2 at 80 °C and 1 bar in EtOH solution has been reported [370].



202

Piperylene oligomers and cooligomers of piperylene with styrene, α-methylstyrene, isobutene or butadiene were oxidized in hydrocarbon solution with air in the presence of Mn or Co salts as catalysts and the oxidized oligodienes reacted with $MnSO_4$ and $Co(NO_3)_2$. The oxidized oligodiene Mn or Co salts prepared in this way were used as catalysts for the oxidation of diene oligomers [371]. Studies on cyclohexene oxygenation (20 °C, 1 bar O_2, benzene solvent) with metalloporphyrin-sodium borohydride-microcrystalline cellulose catalysts showed that the (TPP)Mn(III)/$NaBH_4$/Avicel®/O_2 system is a good model of cytochrome P-450 monooxygenases [372].

Linoleic acid under oxygen atmosphere at room temperature in a phosphate buffer (pH 8) was rapidly converted into a mixture of hydroperoxides in the presence of a catalytic amount of the iron(III) complex of peplomycin [373]. Oxidation of vitamin D_3 (**203**) with O_2 at room temperature or at 50 °C in MeCN in the presence of $(n\text{-}Bu_4N_2)[Fe_4S_4(SPh)_4]$ produced (5E)-10-oxo-19-norvitamin D_3 (**204**) and 8-α-hydroxy-9,10-seco-4,6,10(19)-cholestatriene-3-one (**205**) mimicking biological oxidation [374].



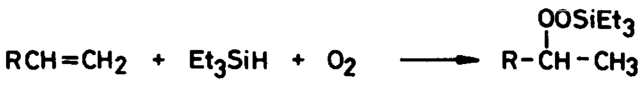
203 204 205

The ruthenium-catalyzed oxidative cleavage reaction of carbon-carbon double bonds using molecular oxygen resulted in the corresponding carbonyl compounds. E.g.: from 1-dodecene 90% undecanoic acid, from 2-ethyl-1-hexene 88% 3-heptanone, and from methyl methacrylate 85% methyl pyruvate was obtained at atmospheric pressure and 40 °C in acetone solution using RuO_2 or $RuCl_3.nH_2O$ as the catalyst precursor. Internal and methyl-substituted alkenes gave 20-25% epoxide besides the carbonyl product [375].

The activities of Co-containing polymeric catalysts for liquid-phase oxidation of cyclohexene have been determined. Catalysts with larger Co-Co distances were found to be more active [376]. The catalyst system $CoBr_2(py)_2$ + AIBN + AcOH was found to be the best for the oxidation of (−)-α-pinene to verbenone by O_2 (24% selectivity and 76% conversion at 60 °C) [377]. Various 5-hydroxy-1-alkenes (**206**; R = Ph, *p*-$MeOC_6H_4$, p-ClC_6H_4, Me, tBu, $PhCH_2$) were converted to the corresponding 2-hydroxymethyl tetrahydrofurans in good yield with extremely high *trans* selectivities by oxidative cyclization with molecular oxygen in the presence of a catalytic amount of bis(1-morpholino-carbamoyl-4,4-dimethyl-1,3-pentadionato)cobalt(II) [378].

206

A method for the direct peroxygenation of 4-phenyl-1-butene, styrene, and ethyl acrylate with O_2 and Et_3SiH in the presence of catalytic amounts of bis(1,3-diketonato)cobalt(II) complexes was developed (eq.15). Up to 96% yields were observed in 1,2-dichloroethane at 20 °C [379].

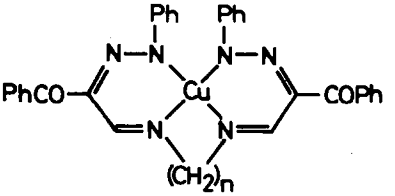


$$RCH{=}CH_2 + Et_3SiH + O_2 \longrightarrow R{-}\overset{\displaystyle OOSiEt_3}{\overset{|}{C}H}{-}CH_3 \qquad \text{(eq.15)}$$

Wacker-oxidation of various olefins catalyzed by $PdCl_2$ and conducted in a microemulsion containing formamide, H_2O, iPrOH, and *p*-$Me(CH_2)_8C_6H_4(OCH_2CH_2)_8OH$ gave faster oxidation rates and better yields of ketones than did classical (aqueous) media [380]. A method for the prediction of critical oxygen concentration has been demonstrated for the Wacker process [381]. New aspects of the oxypalladation of alkenes have been described. It was shown that in the Wacker-type oxidation the formal oxidation state of palladium(II) remains constant throughout the reaction and that the Pd-OOH species derived from the oxygenation of the Pd-H species by O_2 is the active catalyst [382]. Oxidation of 1-butene to 2-butanone with O_2 using a heterogenized Wacker catalyst ($PdCl_2$, NaCl, and V_2O_5 on Al_2O_3) was studied at 90-120 °C. Butanone selectivity was 80-95%, crotonaldehyde, acetone, acrolein, acetaldehyde and acetic acid were formed as byproducts. The activity of the catalyst gradually decreased due to chlorine loss [383]. The formation of π-olefin-palladium-cuprate complexes as intermediates was demonstrated by kinetic and spectroscopic methods in the formation of propylene glycol monoacetate in oxidation of propene by O_2 in a $PdCl_2$ + $CuCl_2$ + AcOH system [384]. The following reactions, catalyzed by $Pd(OAc)_2$ have been examined: acetoxylation of propene and butene-2, and the oxidative coupling of PhOAc in AcOH to give acetylated and acetoxylated PhOAc and biphenyl derivatives [385]. A palladium-catalyzed acetoxylation of cyclohexene to cyclohexenyl acetate in >85% yield was achieved using O_2 as oxidant and a mixture of hydroquinone or benzoquinone and $Cu(OAc)_2$ as cooxidant at 50 °C and 1 bar in AcOH. $Mn(OAc)_3$ or $Co(OAc)_2$ in place of $Cu(OAc)_2$ were found to be less efficient [386].

Oxidation of cyclohexene with O_2 in the presence of Cu(II) complexes of enaminoketone hydrazones derived from benzoylacetaldehyde was studied. Oxidation rate increased with increasing tetrahedral distortion of Cu(II) coordination [387]. In the presence of a μ-peroxo copper(II) complex, $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(O_2)$ (pz = 1-pyrazolyl), cyclohexene was oxidized by O_2 at 25 °C to oxygenated products such as 2-cyclohexen-1-ol and 2-cyclohexen-1-one. Phenols and a catechol were both oxidatively coupled and oxygenated to give benzoquinones. Based on kinetic results, a mechanism was proposed for the oxygenation reactions in which homolytic cleavage of the O-O bond in the μ-peroxo complex is followed by free radical chain reactions with O_2 [388]. The kinetics of oxidation of cyclohexene by O_2 in the presence of the Cu(II) chelates (**207**; n = 2,6) has

has been studied. The kinetic parameters changed with time in the case of (**207**; n = 6) but remained constant with the other catalyst. This was explained by assuming that the tetrahedrally distorted complex went through a configurational isomerization during the catalytic process [389].



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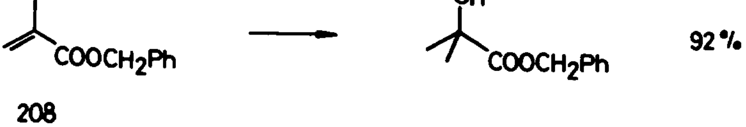
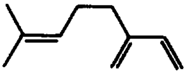
In the presence of bis (1,3-diketonato)cobalt(II) complexes, olefins (e.g. 1-decene, 2-methyl-1-decene, styrene, 3-methyl-3-butenyl benzoate) were converted to the corresponding hydrated products according to the Markownikov rule and to alkanes on treatment with molecular oxygen at 75 °C in a secondary alcohol as solvent. The formation of alkanes in this "oxidation-reduction hydration" was suppressed by using bis(trifluoroacetylacetonato) cobalt(II) or bis(2-ethoxycarbonyl-3-oxobutanolato)cobalt(II) as catalyst and the alcohol products were obtained selectively from the olefinic compounds in good yields [390]. It was found that the oxygenation of α,β-unsaturated carboxylic acid esters like (**208**) with O_2 proceads smoothly in the presence of $PhSiH_3$ and catalytic amounts of bis(dipivaloylmethanato)manganese(II) to afford the corresponding α-hydroxycarboxylic acid esters in 76-94% isolated yields under mild conditions (0 °C, 1 bar) [391].



Regioselective (1,4)-hydrocobaltation of myrcene (**209**) with $Co(dmg)_2$ and H_2 leads to a mixture of (E)- and (Z)-allylcobaloximes (**210**). These can be converted via oxidation by tetramethylpiperidine oxide followed by reduction with Zn dust into geraniol and nerol (Z- and E-isomers of (**211**)), or via oxidation by O_2 followed by reduction with $NaBH_4$ to racemic linalool (**212**) [392].



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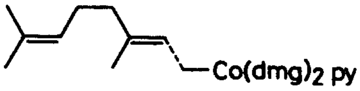

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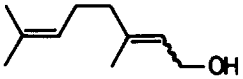

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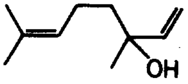


212

See also [359].

c) Epoxidation of Olefins

Epoxidation of styrene, 2-norbornene and several norbornene analogues at 75 °C by molecular oxygen (1-3 bar) catalyzed by bis(2-alkyl-1,3-diketonato)oxovanadium(IV) complexes in the presence of 2-propanol and 4A molecular sieves was reported [393]. New catalysts consisting of a carbon fiber support loaded with vanadyl meso-tetra(3-acetaminophenyl)porphyrin (A) through covalent bonding or vanadyl meso-tetra(4-pyridyl)porphyrin (B) through ionic bonding were prepared and their catalytic activity for olefin epoxidation investigated. Catalyst A gave higher yields and showed improved durabilty over a carbon fiber catalyst loaded with with mono- or bidentate vanadium complexes [394].

1,4-Diacryloylpiperazine-*N*,*N*-ethylenediaminediacetic acid Michael addition copolymers crosslinked with N-vinylpyrrolidone were grafted with Mo(VI) to provide a catalyst for epoxidation of cyclohexene [395].

The epoxidation of alkenes with O_2 using (TPP)MnCl as catalyst and *N*-hydroxyphthalimide, styrene, 2-norbornene, or indene as activators was reported. Alkyl hydroperoxides which are formed by autoxidation of these activators are the oxygen sources which transfer monooxygen to the catalyst [396].

Catalytic epoxidation of cyclooctene with O_2 using electrochemically reduced $(F_{20}TPP)FeCl$ or [5,10,15,20-tetrakis(1-naphthyl)porphinato]manganese(III) chloride was achieved in DMF containing Ac_2O as the electrophile [397]. The kinetics of the epoxidation of cyclohexene, methylcyclohexene and *cis*-cyclooctene by O_2 catalyzed by $[RuCl_2(H_2O)_4]^+$ at pH 2.0 in water-dioxane were reported. The rate of the selective epoxidation was found to be first order with respect to catalyst and substrate concentrations and 1.5 order with respect to O_2 concentration. Based on the kinetics, a mechanism involving homolytic cleavage of the O-O bond with concerted transfer of the oxygen atom to the substrate was suggested [398].

Olefins were epoxidized at 100 °C with molecular oxygen (4 bar) in the presence of a primary alcohol, 4A molecular sieves and bis(2-alkyl-1,3-diketonato)nickel complexes as catalysts. For example see (eq.16; 86% yield) [399].

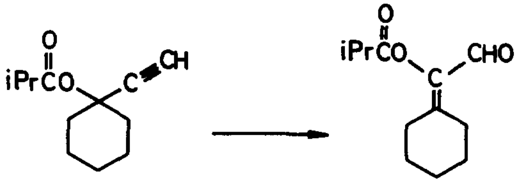
$$(p\text{-}ClC_6H_4)_2C=CHCH_2CH_2CH_3 \longrightarrow (p\text{-}ClC_6H_4)_2\overset{O}{\overbrace{C-C}}HCH_2CH_2CH_3$$

(eq.16)

See also [375, 454].

d) Oxidation of Alkynes

Alkynes (6-dodecyne, phenylacetylene, diphenylacetylene) were selectively (>90%) oxygenated at 70-100 °C and 7 bar O_2 to the corresponding carboxylic acids in the presence of ceric ammonium nitrate in CH_3CN and H_2O [400]. Oxygenation of 4-substituted phenylacetylenes catalyzed by Co(salen) in alcohol at 60 °C resulted in highly selective incorporation of oxygen into the triple bond to give the corresponding acetophenones, and mandelic and phenylglyoxylic esters [401]. Propargyl esters like (213) were converted to α-acyloxy-α,β-unsaturated aldehydes in good to excellent yields by $PdBr_2$ in THF under O_2 at 65 °C [402].



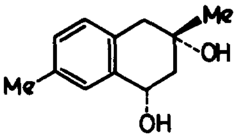
213

See also [359].

e) Oxidation of Aromatics

Ethylbenzene was oxidized to acetophenone with air in the presence of CrO_3. The same reaction was faster if PhIO was used as oxidant and CrO_3 with α-picolinic acid as catalyst [403]. Supported reagents prepared by adsorption of dichromate or permanganate on alumina catalyze the oxidation diphenylmethane to benzophenone in the liquid phase by air at 150 °C. The reaction starts as a rapid stoichiometric oxidation and after some time goes over into a truly catalytic (but significantly slower) process [404]. The effect of free radical initiators like 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide on the oxidation of tetralin by O_2 catalyzed by Cr(III), Mn(III), Fe(III), Co(II), Co(III), and Cu(II) acetylacetonates has been investigated. Both increase and decrease of rate were observed. The results indicate that the free radical initiators act by affecting catalyst activity [405].

The addition of p-$O_2NC_6H_4C(OOH)HMe$ had no effect on the rate of oxidation of p-$O_2NC_6H_4Et$ by O_2 in the presence of $Mn(OAc)_2$ as catalyst. This was attributed to the inhibition of the non-catalyzed radical chain oxidation process by the catalyst [406]. Porphyrin complexes of Mn in the presence of $NaBH_4$ catalyze the oxidation of 2,6-dimethylnaphthalene by O_2 to a mixture of tetralin derivatives containing 1,3-diol, epoxy alcohol, and β-hydroxy ketone groups. Thus, the two main products of oxidation were (**214**) and (**215**) if meso-p-methoxyphenylporphinatomanganese chloride was used as catalyst [407,408].



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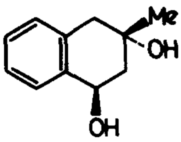

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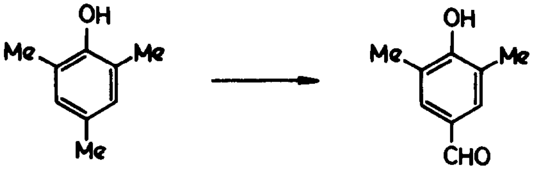
The hydroxylation of benzene, toluene and anisole with 1 bar O_2 at 25 °C using the oxygenase model $FeCl_3$/pyrocatechol/pyridine in the presence of excess hydroquinones as reductants was studied in MeCN solution. Probably an iron-oxygen species is the active species and not the OH radical [409]. The relatively weak catalytic activity of (TPP)FeCl for the oxidation of cholesterol and anthracene in the presence of $NaBH_4$ was attributed to the formation of a catalytically inactive *μ*-oxo dimer [410].

Mild benzylic oxidation with O_2 (1 bar) was reported using catalytic amounts of cobalt(II) chloride in diglyme or diglyme-methylethylketone. From *p*-methylanisole 50% yield of p-anisaldehyde and 19% yield of *p*-anisic acid was obtained in 5 h at 90 °C. The selectivity for *p*-anisaldehyde could be increased dramatically either by lowering the temperature (60 °C) or by using $CrCl_3$ as a cocatalyst. Tetraline and indane were oxidized selectively to 1-tetralone (71% yield) and 1-indanone (72% yield), respectively [411]. Oxidation of *p*-toluic acid methyl ester by O_2 in the presence of $CoSt_2$ was studied. Addition of $MnSt_2$ suppressed the formation of CO_2 and thus increased selectivity [412]. A heterogenized complex of Co(II) was synthesized using chromatographic grade silica as support. It has been used as catalyst for the oxidation of cumene by O_2 in the liquid phase. High cumyl hydroperoxide concentrations were attained (up to 29%) [413]. Oxidation of cumene and cyclohexene at 65-95° in the presence of $CoCl_2$, $MnCl_2$, $CuCl_2$, or $NiCl_2$ on Li-modified silica supports was studied. In the presence of the Co-, Mn-, and Ni-containing catalysts oxidation ocurred by a heterogeneous-homogeneous radical-chain mechanism, whereas in the case of the Cu-containing catalyst the reaction proceeded at the surface of the heterogeneous catalyst [414].

A new phenol synthesis from benzene and O_2 via direct activation of a C-H aromatic bond by the $Pd(OAc)_2$/phenanthroline catalyst system has been reported. Up to 13 turnovers were achieved in 1 hour at 180 °C, 15 bar O_2 and 15 bar CO [415]. An increase of the turnover number up to 100 and of the yield of phenol from 6% to 25% was achieved by reducing the catalyst concentration to 20 mmol% [416].

Oxidative carbonylation of benzene derivatives to benzoic acids with O_2 + CO was accomplished with the catalytic system consisting of Rh or Pd complex + Cu salt + CF_3COOH + $(CF_3CO)_2O$. The predominant formation of *ortho*- and *para*-toluic acids in the carbonylation of toluene suggests an electrophilic substitution mechanism [417]. A novel oxygenation of (**216**) to (**217**) by O_2 with a $CuCl_2.2H_2O$-diethylamine complex catalyst was reported. At 60 °C and under O_2 at atmospheric pressure, 97.6% conversion and 77.7% yield was achieved in 4 h. As a byproduct of the oxygenation 3.7% 2,6-dimethyl-*p*-benzoquinone was also formed [418].



216 217

See also [363, 385].

2. Catalytic Oxidation of O-Containing Compounds with O_2

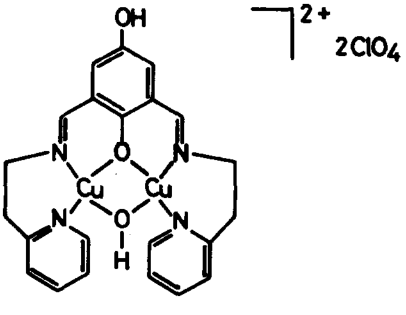
a) Oxidation of Alcohols

Oxidation of EtOH by CrO_3 on SiO_2 and the reoxidation of chromium by O_2 was studied [419]. The catalytic oxidation of benzoin and *para*-sustituted benzoins by O_2 or pyridine-N-oxide, in the presence of $[MoO_2L_2]$ complexes (L = S-deprotonated cysteine methyl ester or diethyl dithiocarbamate) was studied kinetically [420].

Manganese thiophenolate and selenophenolate complexes $[Mn(EPh)_4]^{2-}$ (E = S,Se) catalyze the air oxidation of benzoin to benzil, benzaldehydes to benzoic acids, benzhydrols to benzophenones, and hydrazobenzene to azobenzene in DMF. ESR measurements indicate that the catalytically active species are diamagnetic [421]. The tetranuclear Mn(IV) complex $[TACN)_4Mn_4O_6]Br_4$ catalyzes the air oxidation of secondary alcohols into ketones and of PPh_3 into $OPPh_3$ [422].

The ruthenium cluster $[(EtCOO)_6Ru_3O(H_2O)_3]^+(EtCOO)^-$ used as catalyst for oxidation of alcohols with O_2 could be quantitatively recovered and reused by adding to the solution polyethylene oligomers containing a terminal carboxylic acid group [423].

Copper and nickel chelates with O- and N-containing ligands catalyze the autoxidation of polyethylene glycol. Their effect is due to the additional initiation of chains [424]. Oxidation of alcohols with O_2 and using a Cu^{2+} – *N,N*-disalicylidene-ethylene-diamine system has been investigated. Primary alcohols were oxidized faster than secondary alcohols. Oxidation was promoted by the addition of NaOH but at the same time the selectivity of the reaction decreased [425]. The binuclear copper(II) complex (**218**) was found to catalyze the selective oxidation of benzoin to benzil and the oxidation of hydroquinone to *para*-quinone by O_2 under ambient conditions in methanol solution [426].



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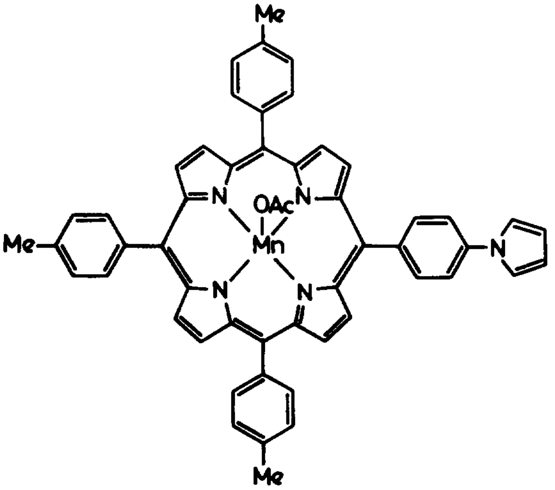
See also [76].

b) Oxidation of Phenols

The possibility of phenol hydroxylation during oxidation by O_2 in presence of metal ions in acidic solutions was studied. Hydroxylation products (pyrocatechol and hydroquinone) were found in the case of V(II) and Cr(II) [427].

The Mn(II)-containing polytungstates $[W_{11}O_{39}Mn(OH)_2]^{n-}$ (X = Si,Ge) and α_2-$[P_2W_{17}O_{61}Mn(OH)_2]^{8-}$ are soluble in non-polar solvents such as benzene or toluene in the presence of tetraheptylammonium bromide or other phase transfer agents. These solutions catalyze the oxidation of 2,6- or 2,4,6-substituted phenols by O_2 to the corresponding benzoquinones or polyphenyl ethers [428]. The epoxidation of *cis*-cyclooctene and the oxidation of 2,6-di-*tert*-butylphenol with molecular oxygen under atmospheric pressure in acetonitrile and dichloromethane solutions has been described using a poly(pyrrole manganese porphyrin) film electrode as a catalyst, which was propared by electrochemical polymerization of Mn(*p*-pyr)TPP (**219**) [429].



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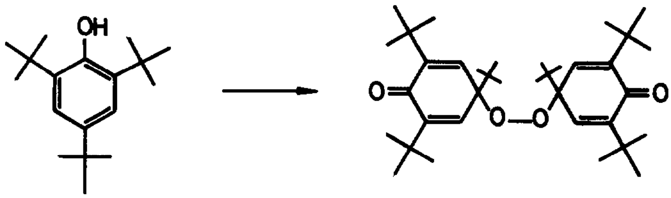
Oxygenation of 3,5-di-*tert*-butylcatechol in THF by $FeCl_2$/pyridine/2,2'bipyridine/O_2 (1 bar) at 25 °C results in 3,5-di-*tert*-butyl-5-(carboxymethyl)-2-furanone and 3,5-di-*tert*-butyl-1,2-benzoquinone. The ESR spectra revealed that the systems with the highest g values were the most active [430]. The kinetics of tri-t-butylphenol (TBP) oxygenation to the peroxide (**220**) in the presence of $[Fe(L)(MeCN)_2][PF_6]_2$ (L = **221**) as catalyst have been described by the following expression: $-d[O_2]/dt = k[catalyst][TBP]^2[O_2]$.The reaction is inhibited by methane sulfonic acid and pyridine [431].



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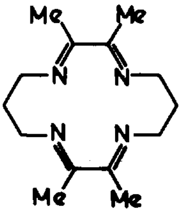

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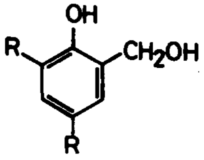
New catalytic systems composed of iron or copper, and CuCl or $FeCl_2$ were described for the oxidation of 2-(hydroxymethyl)phenols (**222**; R = H, Me, tBu) to the corresponding salicylaldehydes (**223**). One of the most active systems was $Fe/FeCl_2/O_2/MeOH$ [432].



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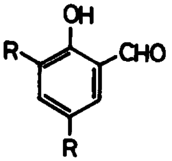
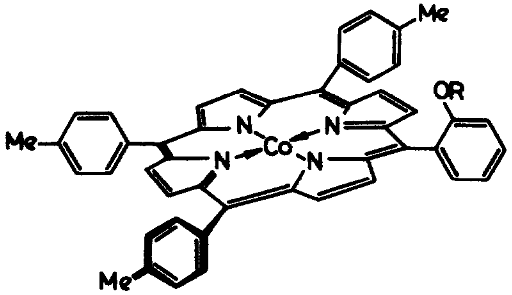


223

Three groups of Co(II) Schiff base complexes with different coordination core geometries and metal ion spin states were tested in MeCN solution as catalysts for oxygenation of 2,6-di-*tert*-butylphenol. The reactions proved to be very selective leading in most cases only to the corresponding *para*-benzoquinone. The results were interpreted in terms of electronic, structural, and steric factors [433]. Complexes of cobalt with 2,2'-bipyridyl or imidazole and of manganese with PPr_3, capable of binding O_2, were tested as catalysts for the oxidation of organic substrates with O_2. Oxidation of hydroquinone with Co complexes as catalysts and of acrolein with the Mn complexes as catalyst were investigated in detail [434]. The liquid-phase oxidation of *p*-cresol and substituted *p*-cresols by air under alkaline conditions using $CoCl_2$ as catalyst and MeOH as solvent was investigated and the reaction conditions optimized in order to obtain the corresponding aldehydes with high selectivities. Based on the experimental results a potentially useful procedure was developed for the production of 4-hydroxybenzaldehyde from *p*-cresol [435]. Cresols were oxidized by O_2 in Ac_2O solution in the presence of transition metal acetates and different bromides as catalysts. The most active system was that which contained Co(II), Ce(III), and NH_4Br. Using this catalyst system, *p*-cresol was transformed at 120 °C into *p*-acetoxybenzoic acid derivatives in about 90% yield [436]. The oxidation of 2,6-di-*tert*-butylphenol by O_2 was used to test the catalytic efficiency of "looping-over" cobalt tetraarylporphyrins (**224**). The most active systems at 23 °C and 1.1 bar O_2 in toluene solution were those with R = $(CH_2)_4$-imidazol and R = $(CH_2)_4NH_2$ in the presence of NEt_3. In both cases 100% yield of 2,6-di-*tert*-butylbenzoquinone was achieved [437].



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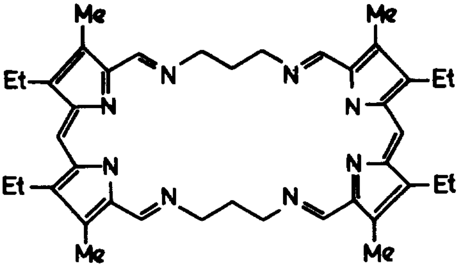
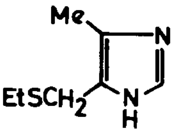
Dinuclear complexes of Cu(II) and Co(II) of ligand (**225**) catalyze the oxidation of 3,5-di-*tert*-butylcatechol and 2,6-di-*tert*-butylphenol by O_2. The catalytic activity of the Cu(II) complex with N_3^- as anion was found to be the highest [438].



225

A kinetic study of the oxidative coupling polymerization of 2,6-dimethylphenol by O_2 catalyzed by Cu(II)-tmen complexes was described. Addition of OH^- significantly increased the rate of the reaction [439]. The kinetics of the oxidation of pyrocatechol by O_2 in the presence of catalytic amounts of Cu(II) have been determined. The complicated rate law is explicable in terms of a chain mechanism in which the Cu(I)-dioxygen adduct CuO_2^+ is the active oxidizing agent [440]. Six different types of Cu(II) complexes have been observed in the oxidative coupling of 2,6-dimethylphenol by O_2 to poly[oxy-(2,6-dimethyl)-1,4-phenylene] and their roles in the catalytic process have been identified. The rate-determining step of oxidative coupling seems to be electron transfer from phenolate ions to Cu(II) in these complexes [441]. The activities of the complexes $(CuL_2)(BF_4)_2$ and $[CuL_2(H_2O)_2](NO_3)_2$ (**226** = 1) as catalysts for the oxidation of 2,6-dimethylphenol with O_2 to give poly(phenylene oxide) and the diphenoquinone (**227**) have been determined. Et_3N increased the activity of these catalysts [442].



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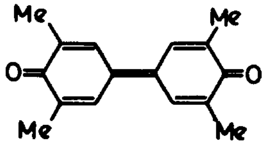
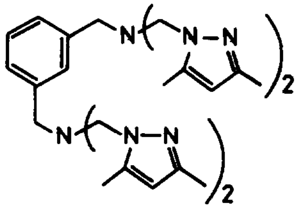


227

The mono- and binuclear Cu(II) complexes $[Cu_2(L)(OMe)_2](BF_4)_2$, $[Cu_2(L)Cl_2]Cl_2$, $[Cu_2(L')_2(OMe)_2](BF_4)_2$, and $Cu(L')Cl_2$ (L = **228**; L' = **229**) catalyze the oxidation of catechol by O_2 to *o*-quinone. The mononuclear complex was found to be the least active. This supports the conclusion that two coppers need to be proximate for the binding of the two phenolic oxygens of the catechol for the two-electron redox reaction to occur [443].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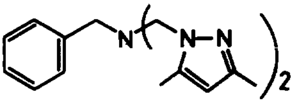

229

See also [359, 426].

c) *Oxidation of Aldehydes and Ketones*

In the presence of O_2, the heteropolyacids $H_{3+n}[PMo_{12-n}V_nO_{40}]$ (n = 1–3), or their Na acid salts react with benzylic ketones at room temperature in MeCN to afford the corresponding carboxylic acids and benzaldehyde in high yields [444]. Aldoses, e.g. xylose and glucose are oxidized at 30–80 °C by O_2 in the presence of porphyrin complexes of Mn(II) or Mo(VI) immobilized on polyacrylamide containing gels to HCOOH, CH_2O, and xylonic and gluconic acids, respectively. The kinetics of the reaction were determined [445]. Oxidation of acetophenone by O_2 in the presence of Mn(II) salts gave mainly benzoic acid, with formaldehyde, formic acid, CO_2, and CO detected in the gaseous product. Based on kinetic measurements a nonchain radical mechanism was proposed [446].

(TPP)Fe(III) complexes as the chloride, fluoride, or oxo-bridged dimer, were shown to catalyze the aerobic oxidation of propanal to propionic acid at ambient conditions in benzene solution [447].

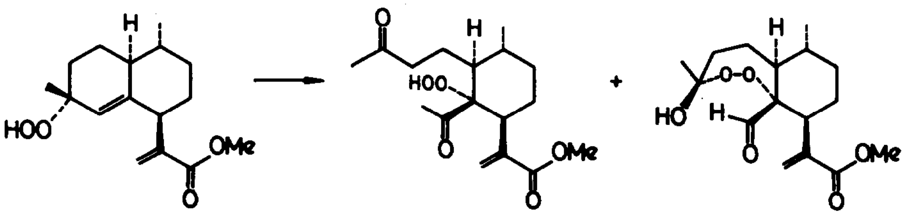
A detailed molecular mechanism for the oscillation of the Co^{3+} concentration during the Co^{2+}– and Br^-–catalyzed air-oxidation of benzaldehyde to benzoic acid in 90% aqueous AcOH was proposed [448]. The first report on the phenomenon of propagating reaction fronts in the autoxidation process dissolved oxygen-Co(Ac)$_2$-benzaldehyde in glacial acetic acid has appeared. The effect of concentration on the velocity of the propagating front was studied [449].

Liquid-phase oxidation of crotonaldehyde by O$_2$ to crotonic acid with a CuSt$_2$-aniline catalyst system was optimized [450]. The products formed in the copper-mediated oxygenation of phenylacetaldehyde and 3-phenyl propionaldehyde at 25 °C using the Cu(II)-py-Et$_3$N-MeOH system have been identified [451]. The product profiles of the liquid-phase air oxidation of 2-methylpropanal to 2-methylpropionic acid revealed that copper ion is an effective reaction moderator for the Co or Mn ion catalyzed reaction [452]. See also [434].

d) Miscellaneous Oxidations

The oxidation of cyclohexenyl hydroperoxide with O$_2$ was studied in the presence of different vanadyl complexes. A high rate of radical formation was observed [453]. The simultaneous oxidation of α-cyclohexenyl hydroperoxide and 2-cyclohexen-1-ol with O$_2$ in the presence of VO(DMSO)$_5$(ClO$_4$)$_2$ has been investigated. Epoxidation of 2-cyclohexen-1-ol by the hydroperoxide was observed [454].

Fe^{II}OEP-O$_2$ was reduced with ascorbic acid sodium salt in the presence of water to Fe^{II}OEP-OOH [455]. Oxygenation of the hydroperoxyde (**230**) in acetonitrile at 0 °C in the presence of Fe(phen)$_3$(PF$_6$)$_3$ and Cu(OSO$_2$CF$_3$)$_2$ gave the equilibratig mixture of the dicarbonyl hydroperoxyde (**231**) and the peroxy hemiacetal (**232**). The iron catalyst alone was ineffective and converted (**230**) only into cleavage products [456].



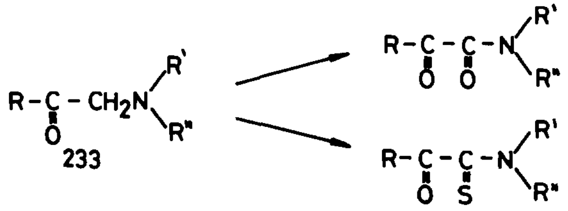
230 **231** **232**

Liquid-phase oxidation of formic acid in MeCN by O_2 is catalyzed by the giant Pd clusters $Pd_{561}(phen)_{60}(OAc)_{180}$ and $Pd_{561}(phen)_{60}O_{60}(PF_6)$ at 20-70 °C. The reaction is first order in the cluster and formic acid and the dependence on O_2 concentration is described by a Michaelis-type equation [457].

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

Treatment of 2-phenylglycine with a stoichiometric amount of $VO(OEt)Cl_2$ in ethanol under oxygen gave a mixture of ethyl benzoate and ethyl phenylglyoxylate [458].

Air oxidation of *N,N*-(dialkyl)acylmethylamines (**233**) using a catalytic amount of $[Fe(salen)]_2O$ in the presence of 2-mercaptoethanol gave the corresponding α-oxo amides (**234**) (R,R',R" = alkyl, phenyl, substituted phenyl). If Na_2S was used instead of the thiol, α-oxo thioamides (**235**) were obtained as the predominant products [459].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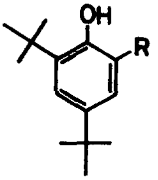
235

Aminomethylphenols (**236**; R = CH_2NHMe or CH_2NMe_2) oxidized by O_2 in the presence of Fe and $FeCl_2$ give aldehyde (**236**; R = CHO), formamide (**236**; R = $CH_2NMeCHO$), and oxazine (**237**) [460].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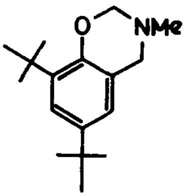
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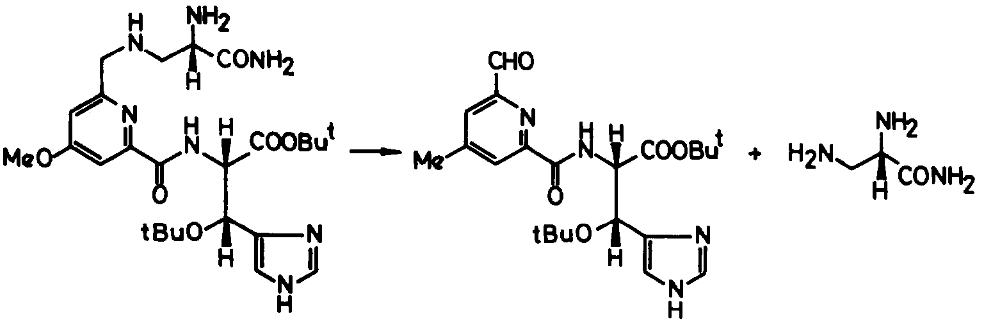
The breakdown at the amino acid side chain of the metal binding site in the bleomycin model compound (**238**) was observed in the reaction with Fe(III) + H_2O_2 or with Fe(II) + O_2 at room temperature [461].



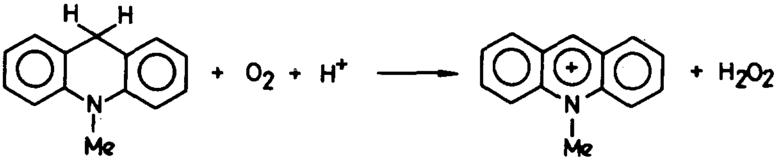
238

Low yields of lactams (0.5–4%) have been achieved in the Gif oxidation of quinine O-acetate, quinuclidine, N-methylmorpholine, codeine 6-acetate, and mesemrane using $Fe_3O(OAc)_6Py_{3-5}$ catalyst, zinc powder, acetic acid, and pyridine in air [462]. The mechanism of the dioxygenation of 3-methyl-indole to *o*-formamidoacetophenone by atmospheric O_2 in the presence of (TPP)FeCl and alkaline reagents was studied [463]. Oxygenation of *N-tert*-butoxycarbonyl-L-tryptophan mediated by Fe(II)-EDTA and L-ascorbate resulted mainly in the oxidation of the indole moiety. Hydroxylation at C-3, C-5, and C-6 as well as ring opening between C-2 and C-3 have been observed [464]. An iron-catalyzed oxidation of bis(imidazol-2-yl)methane (**239**) into bis(imidazol-2-yl)ketone (**240**) using $FeCl_3$ or $Fe(ClO_4)_3$ in ethanol at 50 °C and air has been reported [465].

239 240

Cyclohexylamine in ethanol medium was selectively converted to cyclohexylurethane by catalytic oxidative carbonylation at 160 °C and 21 bar CO + O_2 (1:0.5) in the presence of Ru(saloph)Cl_2 [466].

The oxidation of 4-substituted N,N-dialkylanilines with O_2 using a catalytic amount of $CoCl_2$ in MeCN in the presence of acetic anhydride resulted in N-alkylacetanilides in up to 81% yield [467]. $[(TPP)Co]^+$ was found to be an efficient electron-transfer catalyst for both the two-electron (eq.**17**) and overall four-electron (eq.**18**) reduction of dioxygen by the NADH model compound 10-methylacridan at 25 °C in acetonitrile in the presence of perchloric acid [468].

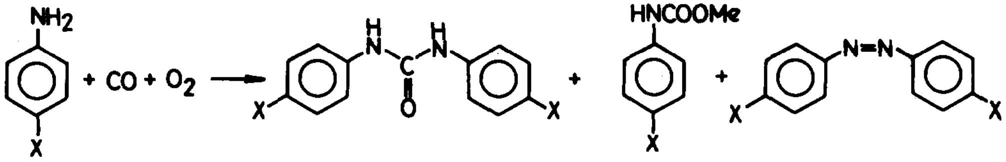


(eq.17)

($AcrH_2$) ($AcrH^+$)

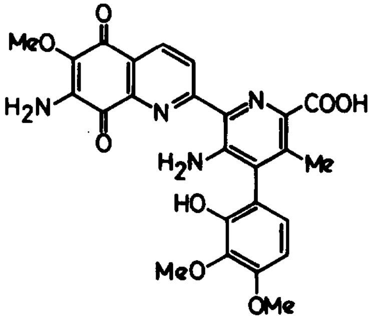
$$2\ AcrH_2 + O_2 + 2H^+ \longrightarrow 2\ AcrH^+ + H_2O \qquad (eq.18)$$

The oxidative carbonylation of aromatic primary amines (**241**; X = H, Me, F, Cl, Br) in methanol using CO and O_2 with catalytic amounts of Co(salen) was investigated. At 60 °C, 10 bar CO and 2 bar O_2 ureas (**242**) were the main products; at 100 °C more carbamates (**243**) were formed and azoderivatives (**244**) were usually minor side products. Starting from *o*-aminophenol, however, the corresponding azoderivative was the main product even at 25 °C [469].



241 242 243 244

The 1:1 Pd(II) complex of streptonigrin (**245**) catalyzes the oxidation of NADH by O_2 to NAD^+ in a HEPES-buffered aqueous solution at pH 7.2 [470].



245

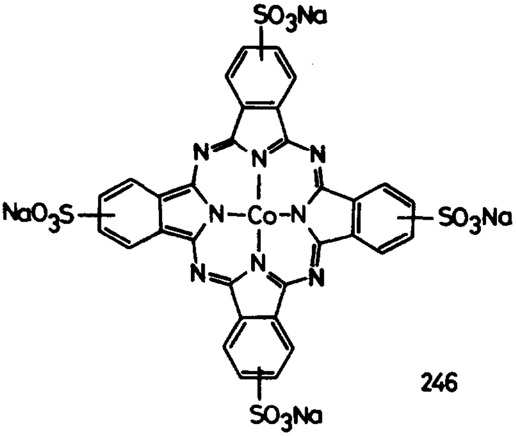
An improved methodology for the oxidation of primary amines to nitriles by the CuCl – O_2 – pyridine system was reported. Almost quantitative yields of aliphatic or aromatic nitriles were achieved [471]. The kinetics of this reaction have been determined and electron transfer from the amine to an oxocopper(II) complex was proposed as the possible rate determining step [472]. The products and the kinetics of the copper(II)-catalyzed autoxydation of carbohydrazyde, $H_2NNHC(=O)NHNH_2$, with dissolved oxygen in water at pH 7.9 and 32 °C were studied. It was found that carbohydrazide reduces dissolved oxygen to H_2O_2 and probably H_2O in the presence of $CuCl_2$ or $CuSO_4$, and is transformed into hydrazine. The reaction is first order in O_2 concentration [473]. Air oxidation of *N*,*N*,-dimethylaniline in MeCN is catalyzed by Cu(II); the products are $[Me_2NC_6H_4C_6H_4NMe_2]^{2+}$ and crystal violet. The reaction starts with a rapid electron transfer within a complex formed from the reactants, the rate-determining step is the decomposition of this complex [474]. The rate of this oxidation increased with increasing donor properties of the solvent. $Cu(NO_3)_2$ was more efficient than $CuCl_2$, and no reaction was observed with $Cu(OAc)_2$ or $CuBr_2$ [475]. In the presence of catalytic amounts of Cu^{2+}, N-benzoylhistidine is completely oxidized under physiological conditions by O_2 and ascorbate to a mixture of at least eight products [476]. 1-Methylimidazole and its analogs, including for example L-1-methylhistidine are oxidized by air in the presence of

Cu(II) and ascorbate to the corresponding 1-methyl-2-imidazolones [477]. Irregular oscillation (chaotic behavior) was observed in the oxidation of NADH by air in the presence of some Cu(II) complexes. The demonstration of chaotic oscillation depended on the CuL^{2+}/CuL^{+} redox potential (L = e.g. 1,4,7,10-tetrathiacyclododecane) [478].
See also [421].

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

Triphenylphosphine was catalytically oxidized in refluxing methanol by air in the presence of $[NH_4]_2[MoO_2\{OOCC(S)Ph\}_2].2H_2O$ [479]. Oxidation of PPh_3 by O_2 in MeCN solution was studied in the presence of $Fe(ClO_4)_3$. In the course of the reaction Fe(III) is reduced to Fe(II) and stable $(Ph_3PO)_4Fe(ClO_4)_2$ is formed. Oxidation of PPh_3 is therefore not catalytic but stoichiometric in iron [480]. Epoxidation of cyclohexene and oxidation of PPh_3 to $OPPh_3$ with O_2 or NaOCl as oxidants is catalyzed by $Ru(HL)(H_2O)$ (H_4L = EDTA). In both cases, the active catalytic species has been characterized as $Ru(=O)L^-$. The transfer of oxygen to the substrate is a concerted reaction [481]. The superoxo complex $[(triphos)Rh(\eta^1-O_2)(\eta^2-3,5-DBSQ)]^+$ catalyzes the oxygenation of PPh_3 to $OPPh_3$ and of 3,5-di-*tert*-butylcatechol to the corresponding *o*-quinone, muconic acid anhydride, and 2*H*-pyran-2-one under a dioxygen atmosphere at −15 °C in CH_2Cl_2 (triphos = $MeC(CH_2PPh_2)_3$; 3,5-DBSQ = 3,5-di-*tert*-butylsemiquinonate) [482].

Enzyme-like behavior was observed for the autoxidation of 2-mercaptoethanol with O_2 (1 bar) using polypeptide-wrapped unsubstituted Co or Fe phthalocyanine as a polymer catalyst. The polypeptide consisted of L-lysine, L-glutamic acid and β-alanine [483]. Tetrasodium phthalocyaninatocobalt was used as a catalyst for the oxidation of thiols by O_2 [484]. The kinetics of O_2 uptake in the catalytic oxidation of 2-mercaptoethanol to the corresponding disulfide in aqueous solution at 25 °C in the presence of $CoPc(SO_3Na)_4$ (**246**) and 2,4-ionene (**247**) was best described by including the intermediate H_2O_2 accumulation process into the kinetic equations [485]. The effect of pH and the type of ionene polymer on the observed kinetics of the oxidation reaction were studied in the case of 2-mercaptoethanol, aminoethanethiol and mercaptoacetic acid [486].



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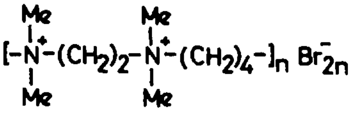


$$[-\underset{Me}{\overset{Me}{N^{+}}}-(CH_2)_2-\underset{Me}{\overset{Me}{N^{+}}}-(CH_2)_4-]_n\ Br^{-}_{2n}$$

n = 8600

247

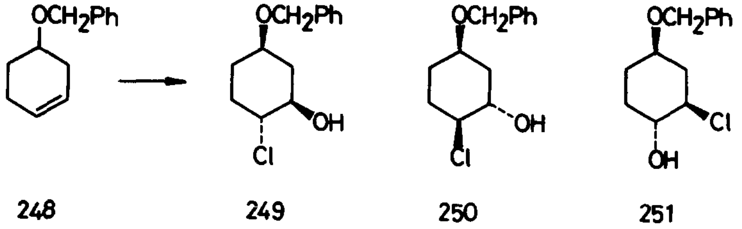
Oxidation of cysteine by O_2 proceeds in two steps. The first step is catalyzed by Cu(II) and yields H_2O_2. The second step is the reaction between cysteine and H_2O_2 which is spontaneous (not catalyzed by Cu(II)) but can be catalyzed by Fe(II) or Fe(III). The Cu- and Fe-catalyzed rates are not additive and the mechanisms of the two catalyzed reactions are not clear yet [487].

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

a) Oxidation of Hydrocarbons and Hydrocarbon Groups

Titanosilicates with Si/Ti = 60 were prepared from $Ti(OEt)_4$, $Si(OEt)_4$ and Pr_4NOH and tested as catalysts for the oxidation of alkanes with H_2O_2 at 50 °C. Ketones and secondary alcohols were formed and a high shape-selectivity was observed; competitive oxidation of hexane and cyclohexane led to a substrate selectivity of hexane/cyclohexane = 41. Oxidation rates of branched alkanes were negligible [488]. Chlorohydroxylation of olefin (**248**) with $TiCl_4$ in the presence of tBuOOH in CH_2Cl_2 at −78 ^{P}C yielded

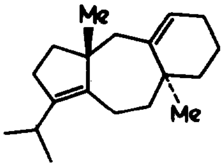
(**249**,**250**) and (**251**) in a 96:2 ratio. Recrystallization of the crude product gave (**249**) in 76% isolated yield [489].



248 249 250 251

Oxidation of methane by H_2O_2 is catalyzed by KVO_3 and $VO(acac)_2$ in CF_3COOH at 20 °C and 30-35 bar. The main product is CO_2; small amounts of MeOH and CF_3COOMe are also formed [490]. Oxidation of cyclohexane by H_2O_2 is catalyzed by vanadium compounds in AcOH and CF_3COOH solutions. In AcOH, the only products are cyclohexanol and cyclohexanone; the ratio of the two products does not depend on conversion, and inhibitors of radical chain oxidations do not influence the reaction rate. The rate of oxidation is considerably higher in CF_3COOH and the only product is the trifluoroacetate ester of cyclohexanol [491].

Oxidation of cyclohexene with CrO_3 + tBuOOH gave cyclohexene oxide, cyclohexenol and cyclohexenone in the ratio 3:1:40. Addition of $NaHCO_3$ increased the yield of epoxide [492]. Chromium(VI) oxo compounds like CrO_3 or $(Bu_4N)_2Cr_2O_7$ catalyze the oxidation of cyclohexane, PhEt, and styrene by H_2O_2 in MeCN solution [493]. Oxidation of benzylic alcohols, methylene groups in α-position to aryl, ethylenic or acetylenic groups into ketones, anthracene into anthraquinone and adamantane into adamantan-1-ol and adamantan-2-one by tBuOOH is efficiently catalyzed by $(Bu_3SnO)_2CrO_2$ at 40-80 °C. Yields are generally superior to those achieved in the presence of CrO_3 [494]. The allylic oxidation of (**252**) using $Cr(CO)_6$ and tBuOOH to give enone (**253**) (47%) and bis enone (**254**) (10%) has been reported [495].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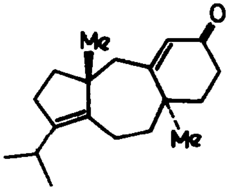
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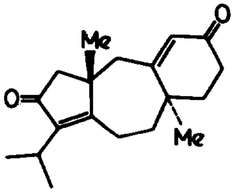
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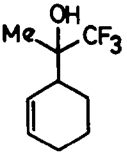
Oxidation of (255) with tBuOOH in the presence of CrO_3 or $Cr(CO)_6$ gave (256) and (257). Addition of pyridine or AcOH influenced the relative amounts of the two products [496].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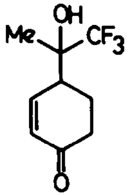
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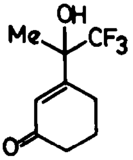
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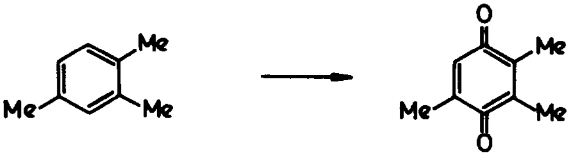
Oxidation of (258) by AcOOH in AcOH to give (259) is catalyzed by the heteropoly acids $H_2V_{12-x}Mo_xO_{31}$ (x = 0–4). Selectivity of the formation of (259) increases with increasing proportion of Mo in the catalyst [497].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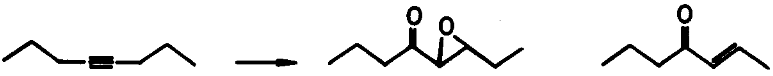
259

Internal alkynes (for example 260) were oxidized with aqueous H_2O_2 catalyzed by peroxotungstophosphate under two-phase conditions using $CHCl_3$ as the solvent, giving α,β-epoxy ketones and α,β-unsaturated ketones as major products [498].


260

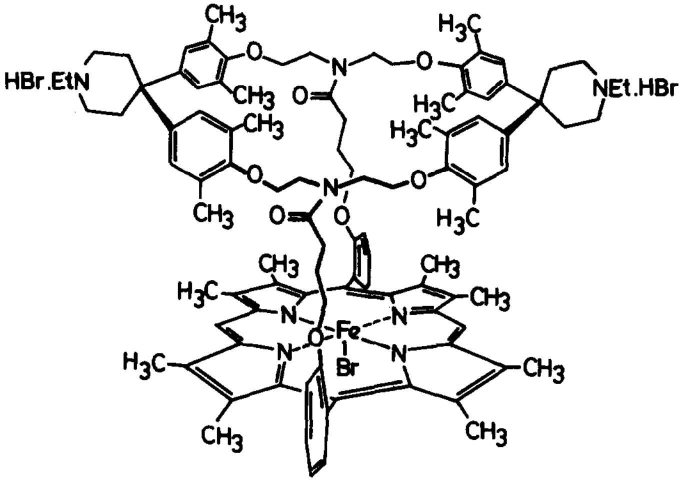
62 %

15 %

Cyclohexane, ethylbenzene or adamantane were oxidized with 40-65% yield to alcohols and ketones at 20 °C with turnover rates up to 80 cycles/min with magnesium monoperoxyphtalate in the presence of $(Cl_8TPP)MnOAc$ as catalyst [499]. In the manganese porphyrin (TPP, TMP, $F_{20}TPP$ and Cl_8TPP) catalyzed oxidation of cyclohexane by sodium chlorite, cyclohexanol and cyclohexanone are formed in CH_2Cl_2 solution at 23 °C with high turnovers in parallel 2e and 4e reactions, respectively [500]. Hydroxylation of ethane, propane, and cyclohexane by PhIO or tBuOOH using the following biomimetic Mn catalysts were described: Mn supramolecular porphyrins and open-face porphyrins, Mn nonporphyrin tri- and tetranuclear clusters, and a mononuclear Mn-substituted Keggin ion [501]. Mn(III) *meso*-tetraarylporphyrins bearing halogen substituents on their *meso*-aryl and pyrrole groups gave up to 70% yields for the parahydroxylation of anisole with H_2O_2 as the oxidant in the presence of imidazole at 20 °C in CH_2Cl_2-MeCN solution. Under the same conditions, phenanthrene was quantitatively oxidized to its 9,10-epoxide, and naphthalene was mainly oxidized to 1-naphthol (40% yield) [502]. Manganese(III) 5-(*m*-(carboxyl)phenyl)-10,15,20-triphenylporphyrin, attached to steroidal substrates (17β-methyl- or 17β-vinyl-5α-androstan-3α-ol) by an ester linkage, catalyzes the hydroxylation of these substrates at the C(17) position with iodosylbenzene as the source of oxygen at ambient temperature in dry CH_2Cl_2 under argon. Isolated yields of 80%, 90%, and 76% were obtained, respectively, based on recovered starting material. By altering the length of the tether linking of the steroid to the template, the hydroxylation could be directed to replace a hidrogen atom at the C(12) or C(14) position [503].

Cyclo-octane, cyclohexane, adamantane, heptane and pentane were oxidized to a mixture of alcohols and ketones by PhIO in MeCN-CH_2Cl_2 solvent at 20 °C in the presence of catalytic amounts of Mn[meso-tetra(4-*N*-methylpyridiniumyl)porphyrin]Cl^{4+} supported on montmorillonite. Yields up to 65%, based on PhIO were achieved. Under the same conditions cyclo-octene was almost completely epoxidized. In these oxidations, the montmorillonite-supported catalyst was more efficient than the corresponding homogeneous or silica-supported Mn-porphyrin catalyst [504]. Manganese tetraphenylporphyrin fixed on imidazole modified silica was used as a catalyst for the oxidation and hydroxylation of cyclohexane with H_2O_2. A rather high loading of imidazolyl groups was necessary to ensure the permanent ligation of Mn to the surface [505]. Zeolite-encapsulated iron and manganese tetramethylporphyrin complexes were found to catalyze the oxidation of cyclohexane with hydrogen peroxide at 50 °C to cyclohexanone [506].

Cyclohexane has been oxidized to cyclohexanone with up to 83 turnover at 20 °C under argon by 30% aqueous H_2O_2 in pyridine in the presence of iron(II)-picolinate or iron(II)-1,10-phenanthroline-2-carboxylate [507]. Unusually high values of kinetic isotope effect, up to 21.9 ± 1.9 at 20 °C, were observed in cyclohexane oxidation by an iron tetramesitylporphyrin-hypochlorite system. Based on the very sharp temperature dependence of the effect, a tunnelling contribution to the C-H bond cleavage step has been suggested [508]. A new type of metal-induced activation of hydrogen peroxide by iron-picolinate complexes in pyridine/acetic acid solvent at room temperature for the efficient and selective transformation of methylenic carbons to ketones and the dioxygenation of acetylenes and aryl olefins has been investigated. Thus bis(picolinato)iron(II) catalyzes the near stoichiometric (72%) transformation of cyclohexane and H_2O_2 to cyclohexanone (95%) and cyclohexanol (5%). Similarly n-hexane gives with 52% conversion 3-hexanone (53%), 2-hexanone (46%), and <2% 1-hexanol. From ethyl benzene the only detectable product acetophenone forms in 51% yield [509]. Cyclohexane was oxidized at 25 °C under Ar in MeCN solution with tBuOOH in the presence of catalytic amounts of $[Fe(tris(2\text{-}pyridylmethyl)amine)Cl_2](ClO_4)$ to cyclohexanol, cyclohexanone, *t*-butylperoxy-cyclohexane and chlorocyclohexane with 37% total yield [510]. Yields approaching 10% based on H_2O_2 and turnover numbers of about 10 were observed in catalytic alkane (cyclooctane, *cis*-dekalin, *trans*-dekalin and tetralin) oxidations at room temperature in reverse microemulsions containing iron salts like $FeSO_4$. Mixtures of ketones and alcohols were formed [511]. The $FeCl_3$-H_2O_2-pyridine-acetic acid system showed up to fiftyfold higher rates in oxidation of cyclododecane to cyclododecanone at room temperature in the presence of picolinic acid or its congeners [512]. Hydroxylation of aliphatic hydrocarbons by H_2O_2 catalyzed by iron complexes in the presence of Zn powder, AcOH, and 2,2'-bipyridine was studied. Major products were secondary alcohols [513]. Benzylic oxidations promoted by iodosylbenzene in the presence of $(F_{20}TPP)FeCl$ have been reported. The scope of hydrogen atom transfer and electron transfer mechanisms in these oxidations has been established [514]. Oxidation of ethylbenzene with H_2O_2 in the presence of $Fe(NO_3)_3$ in homogeneous medium (H_2O-MeCN) afforded PhCOMe. Catalytic activity could be increased by the addition of polyethylene glycol. Oxidation under heterogeneous phase-transfer conditions resulted in lower product yields [515]. The oxidation of n-butane and propane in a H_2O_2-Fe^{3+}-pyridine-acetic acid-picolinic acid system gave 25% yield of 2-butanone and 13% yield of acetone, respectively based on H_2O_2 [516]. The Fe(III) porphyrinato complex (**261**) catalyzes the oxidation of acenaphthylene to acenaphthen-1-one by iodosobenzene with 65% yield in CF_3CH_2OH as solvent. The special structure of the porphyrin ligand helps the binding of aromatic substrates in the vicinity of the iron center [517].



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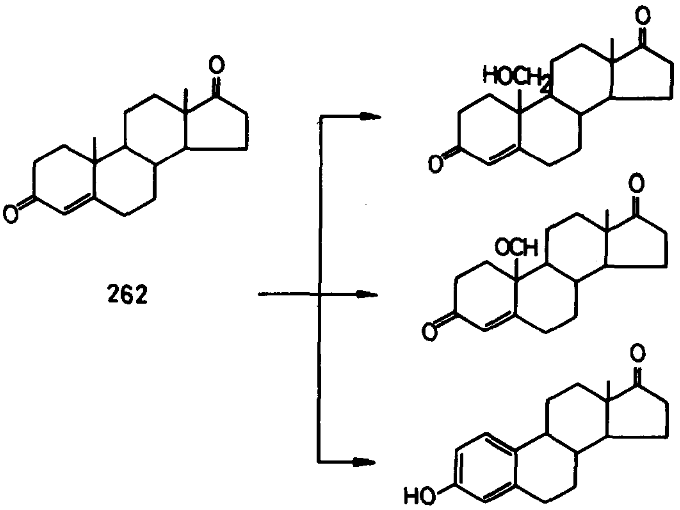
The oxidation of (**262**) with cumene hydroperoxide catalyzed by chloroiron(III)-5,10,15,20-tetraarylporphinate/*N*-methylimidazole systems gave (**263**), (**264**), and (**265**) in various proportions. The $(Cl_8TPP)FeCl$/*N*-methylimidazole system in CH_2Cl_2 at 25 °C was found to be the most effective for the aromatization of the ring *A* of (**262**) [518].



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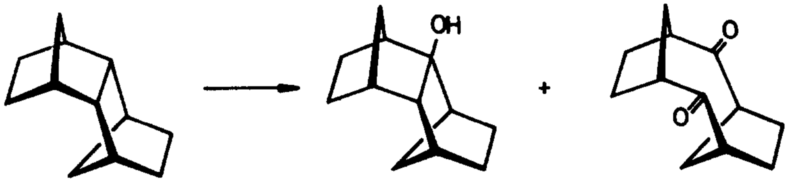
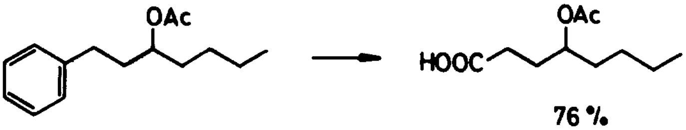
Oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone by $(Bu_4N)_2Cr_2O_7$ or $(NH_4)_2Cr_2O_7$ in acidic aqueous MeCN is catalyzed by $RuCl_3$ [519]. The kinetics and mechanism of oxidation of alkylbenzenes by Cr(VI) catalyzed by Ru(IV) has been studied. The results suggest that – among others – binuclear Cr(VI)-O-Ru(IV) species are responsible for the attack of the C-H bonds [520]. Ruthenium complexes containing aromatic diimines, macrocyclic tertiary amines, and porphyrins as ligands were used as catalysts for the oxidation of adamantane, cyclohexane, 2,3-dimethylbutane, and methylcyclohexane with tBuOOH or PhIO [521]. The new ruthenium porphyrin, [tetrakis(2,6-difluorophenyl) porphinato]Ru(CO)(*N*-methylimidazole) was prepared and used as catalyst for the oxidation of hydrocarbons with NaOCl or tBuOOH. Styrene and α-methylstyrene underwent mainly double bond cleavage to give benzaldehyde and acetophenone, respectively; epoxidation was the principal reaction with cyclooctene, and cyclohexane was oxidized to cyclohexanol and cyclohexanone [522]. A ruthenium-substituted heteropolyanion with a hydrophobic counter cation, $((C_6H_{13})_4N)_5SiRu(H_2O)W_{11}O_{39}$, catalyzes the oxidation of cyclohexene, styrene and 1-octene by tBuOOH, K_2SO_5, PhIO, and $NaIO_4$ at 60 °C in a 1,2-dichloroethane-water mixture. Selective bond cleavage to aldehydes was found with $NaIO_4$ [523]. Oxidation of the bridged polycyclic alkane (**266**) with stoichiometric quantities of $NaIO_4$ in the presence of catalytic amounts of $RuCl_3$

in a CCl_4-MeCN-H_2O solvent mixture resulted in 73% (**267**) and 13% (**268**) at 70 °C. The results were explained by assuming a concerted oxidation mechanism involving the interaction of a tertiary C-H bond with *in situ* generated RuO_4 [524].



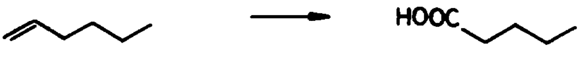
266 267 268

The oxidation of aromatic rings (eq.19), primary alcohols, alkenes (**269**), and diols to carboxylic acids with RuO_4 in the temperature range of 25-40 °C has been shown to be a very efficient and simple reaction using periodic acid as the stoichiometric oxidant in a two-phase solvent system. The oxidation of an alcohol to the corresponding aldehyde by pyridinium chlorochromate, the Sharpless asymmetric epoxidation of an allyl alcohol using Ti(O-i-Pr)$_4$, tBuOOH, and L-(+)-diethyl tartarate, and the RuO_4-HIO_4 oxidation of a phenyl ring to carboxylic acid have been used in the total synthesis of (R)-γ-caprolactone (**270**) [525].



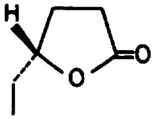
(eq.19)

76 %



269

80 %



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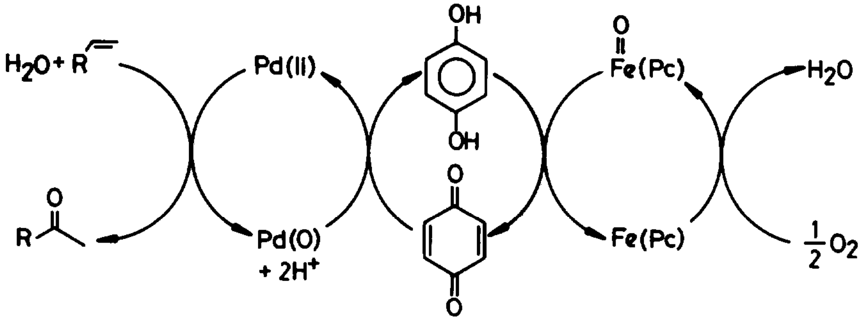
The $RuCl_3$-catalyzed oxidation of (**271**) by $NaIO_4$ gave (**272**) in 94% yield [526].

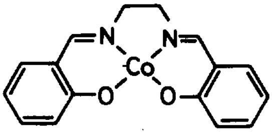
271 **272**

$Co(bpy)_2^{2+}$ catalyzes several oxidations by H_2O_2 in MeCN or MeCN/py = 4/1 solvent at room temperature. Aliphatic hydrocarbons are oxidized to alcohols and ketones, toluene to benzaldehyde and benzyl alcohol, benzene to phenol, benzaldehyde to benzoic acid, stilbene to benzaldehyde, and diphenyl acetylene to benzil [527].

Saturated hydrocarbons were oxidized and oxidatively chlorinated under ambient conditions with aqueous solutions of NaOCl in the presence of Ni(salen) as the catalyst. E.g. using 2.5 mol% catalyst, cyclohexane gave in 2 hr 51% yield of cyclohexyl chloride and 5% yield of cyclohexanone [528].

Ethene, propene, 1-butene, and 1-hexene were selectively oxidized to acetaldehyde, acetone, 2-butanone, and 2-hexanone, respectively, by NO using a $PdCl_2$-$CuCl_2$-H_2O catalytic system under ambient conditions [529]. The pentacoordinated tetravalent Pd complex $PdCl_2(COOBu)NO(PPh_3)$ has been found to be an intermediate in the Pd-catalyzed oxidative carbonylation of ethene and propene to acrylates and succinates by butyl nitrite and CO. A catalytic cycle involving the redox transition Pd(II)/Pd(0) has been suggested [530]. A general laboratory-scale method for the rapid, quantitative conversion of olefins (1-octene, *trans*-2-octene, cyclohexene, cycloheptene and styrene) to ketones between 23 and 60 °C by a chloride-free Pd(II)/benzoquinone/HX system (X = ClO_4, NO_3, HSO_4, BF_4) has been reported [531]. Pseudocumene was oxidized to a mixture of trimethylphenol isomers by $Na_2S_2O_8$ or H_2O_2 in the presence of $Pd(OAc)_2$ as catalyst [532]. A triple catalytic system, consisting of $Pd(OAc)_2$, hydroquinone, and a metal macrocycle [Fe(Pc), Co(salen) (**273**), Co(saloph), Co(TPP) or Mn(TPP)] was applied under mild aerobic conditions in selective oxidation of 1,3-dienes to 1,4-diol derivatives, in oxidation of terminal olefins to methyl ketones, and in allylic oxidation of cyclic olefins. For example, air oxidation of 1,3-cyclohexadiene in AcOH at 25 °C gave up to 89% isolated yield of *trans*-1,4-diacetoxy-2-cyclohexene. The interaction of the three catalytic cycles necessary for the functioning of this system is shown below [533].





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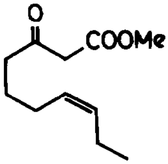
Oxidation of 2-alkylcyclohexanones by $Cu(OAc)_2$ + I_2 in aqueous acetic acid gave the corresponding 3-alkyl-1,2-cyclohexanediones in the form of their enol tautomers [534]. Oxidative free-radical cyclizations of unsaturated *β*-keto esters, 1,3-diketones, and malonate diesters with 2 equiv of $Mn(OAc)_3.2H_2O$ and 1 equiv of $Cu(OAc)_2.H_2O$ were described. For example, (**274**) was transformed into (**275**) in acetic acid solution between 20 and 50 °C with 71% yield [535].



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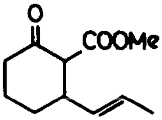


275

See also [403, 569, 572, 620, 655, 657, 663, 687, 688, 693].

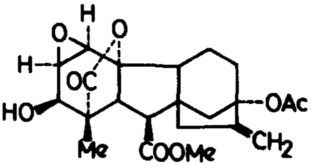
b) Epoxidation of Olefins

A mechanistic explanation for the stereoselectivity of the Katsuki-Sharpless epoxidation of allylic alcohols by diesters of (R,R)-(+)-tartaric acid, $Ti(Oi\text{-}Pr)_4$, and tBuOOH has been proposed [536].

The Sharpless epoxidation procedure [tBuOOH, $Ti(OPr^i)_4$ and diisopropyl or dietyl tartrate] was used in the following cases:

- (276) gave (277) in 90% yield and 90% ee [537];

- (278) and (279) were prepared from methyl gibberellate [538];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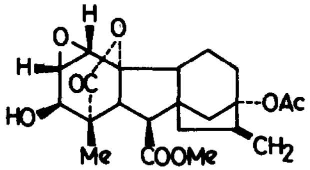
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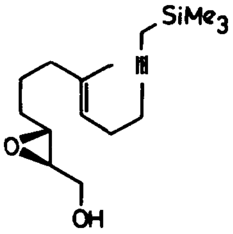
- (280) and were (281) prepared with ≃100 and ≥90% ee, respectively, from the corresponding alkene precursors [539];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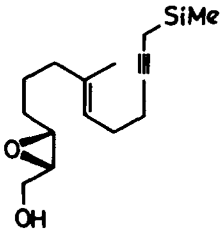
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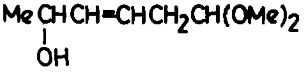
- (**282**) was transformed into (**283**; PMB = *p*-methoxybenzyl) [540];

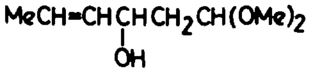
282 283

- epoxidation of the (Z) and (E) racemic allyl alcohols (**284**) and (**285**) [541];



$\underset{\displaystyle OH}{MeCH}CH{=}CHCH_2CH(OMe)_2$

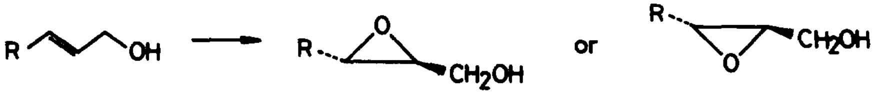
284



$MeCH{=}CH\underset{\displaystyle OH}{CH}CH_2CH(OMe)_2$

285

- with cumene hydroperoxide instead of tBuOOH to prepare the epoxyalcohols (**286**) and (**287**) in 86 and 45% yield, respectively. Further catalytic oxidation of (**286**) and (**287**) in MeCN at 25 °C using $NaIO_4$ and $RuCl_3.3H_2O$ gave the corresponding epoxyacids in 65-86% yield (R = Me, H) [542];



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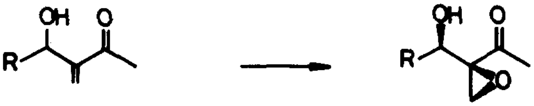
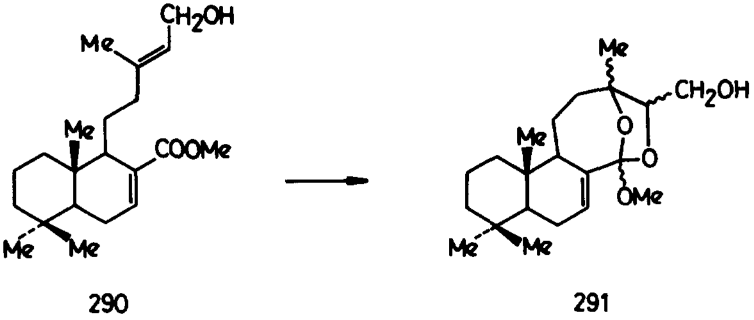
- diastereospecific formation of *syn*-epoxides (**289**; R = Cy, Me, Et, iPr) in good yields from α,β-unsaturated ketones (**288**) [543];



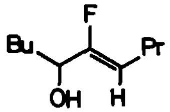
288 289

- (**290**) gave the orthoester (**291**) [544].



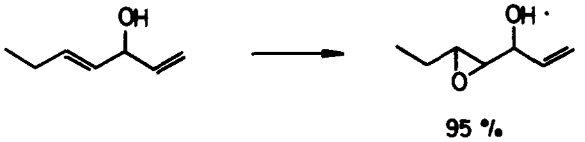
An improved asymmetric epoxydation of allyl alcohols using dialkyl tartarate/titanium-pillared montmorillonite as a heterogeneous catalyst and H_2O_2 as oxygen source was reported. In a CH_2Cl_2/PhMe solvent mixture at −15 °C under N_2 68−91% isolated yields and 90−98% ee were achieved [545]. Epoxidation of 1- and 2-hexenes with H_2O_2 is catalyzed by titanosilicate at 50 °C [546].

Various fluoroallylic alcohols like (**292**) were oxidized to the corresponding epoxides by tBuOOH in the presence of $VO(acac)_2$ or $Ti(OPr^i)_4$ with 90−95% diastereoselectivity to the erythro epoxy alcohols [547].



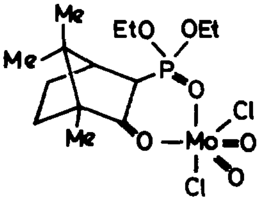
292

Appropriately pretreated and modified carbon fibers were loaded with $VO(acac)_2$ or $VOSO_4.2H_2O$ and used as catalysts for the epoxidation of cyclohexene with tBuOOH. The activity of these new catalysts was comparable to that of homogeneous vanadium catalysts [548]. Oxidation of 1,3-diphenylisobenzofuran by tBuOOH or cumyl hydroperoxide is catalyzed by vanadium(V) complexes. The results suggest that alkylhydroperoxides are activated by such vanadium complexes in a manner which gives them some singlet oxygen character. This could also explain the mechanism of olefin epoxidation with these catalytic systems [549]. A $VOCl_3$ based new vanadium-pillared montmorillonite catalyst showed unusual regioselectivity towards internal allylic double bonds in preference to terminal allylic double bonds in epoxidation with H_2O_2. For example (eq.20) [550]:



(eq.20)

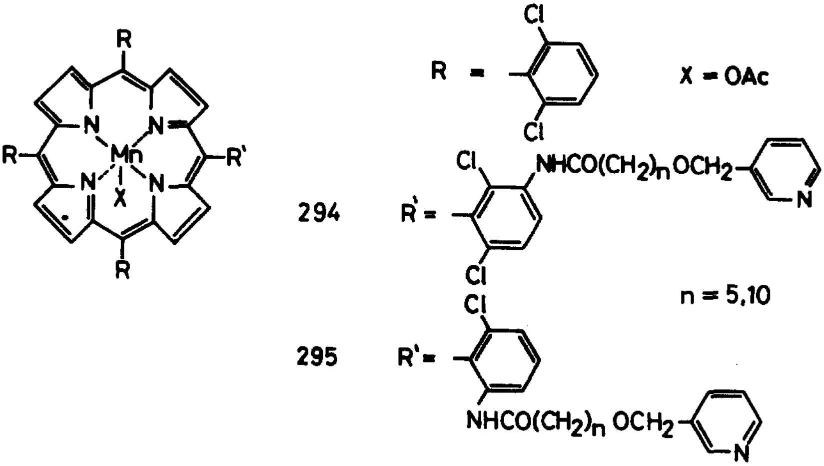
The epoxydation of cyclohexene with t-butyl hydroperoxide catalyzed by molybdenum complexes showed a second order kinetics between 50 and 70 °C [551]. (TPP)MoO was used as catalyst in the epoxidation of alkenes by H_2O_2 at 60 °C in n-propyl acetate. 1,5-Cyclooctadiene, cyclooctene and styrene transformed selectively into the corresponding epoxides with yields up to 96%. In the case of 2-methyl-2-butene and cyclohexene, both epoxides and 1,2-diols were formed [552]. The epoxidation of C_5–C_{10} alkenes with aqueous 60% hydrogen peroxide in the presence of molybdenum blue and $Bu_3SnOSnBu_3$ was studied. In the two-phase solvent $CHCl_3$–H_2O at 25 °C 48–98% yields were obtained [553]. The epoxidation of sunflower oil by cumyl hydroperoxide using $Mo(acac)_2$ as catalyst was optimized to a maximum yield of 81% [554]. Rapeseed, soybean and sunflower oils were epoxidized by tBuOOH or cumyl hydroperoxide using $Mo(CO)_6$ as catalyst. Epoxide yields up to 98% were achieved. This catalyst was more efficient than supported MoO_3 [555]. The Mo complex (**293**) is a highly selective catalyst for the epoxidation of alkenes by tBuOOH. With polybutadiene containing *cis*-1,4-, *trans*-1,4-, and 1,2-polymer units a very high selectivity for epoxidation of the backbone double bonds was observed [556].



293

Octene-1 was epoxidized with H_2O_2 and W_2B_5 as catalyst. Water inhibited the reaction [557].

Propene was epoxidized with EtCOOOH (generated *in situ* by O_2 oxidation of MeCHO) using (TTP)MnCl as catalyst. This catalyst system was more active than that formed from (TTP)Co and PhCHO [558]. Factors ruling the epoxidation of internal and α-olefins by HOCl and/or ClO^- or H_2O_2 and catalyzed by Mn(III) tetraarylporphyrins were investigated in detail to find conditions for large scale practical application. The reactions were carried out in a CH_2Cl_2-H_2O two-phase system at 0 °C [559]. Olefins (both cyclic and terminal) can be easily epoxidized with 30% H_2O_2 under H_2O-CH_2Cl_2 two-phase conditions in the presence of $(Cl_8TPP)MnCl$ as catalyst. The reaction is strongly accelerated by catalytic amounts of carboxylic acids (especially benzoic acid) and a lipophilic imidazole or pyridine (e.g. n-hexylimidazole or 4-tBu-pyridine) which acts as an axial ligand. Several other phenyl-substituted TPP ligands were also tested but found to furnish less active or less stable catalysts. Kinetic data fit a Michaelis-Menten equation well [560]. Dibenzo-18-crown-6 acts both as a phase-transfer catalyst and as an axial ligand in the epoxidation of olefins by NaOCl in the presence of Mn(III) porphyrins [561]. The catalytic activity of (TAP)MnCl catalysts (TAP = tetrakis (aryl)porphyrin; aryl = 2,4,6-trimethyl-3,5-dihalophenyl; halo = chloro, bromo, iodo) has been tested in $HOCl/ClO^-$ alkene epoxidations. The stability towards oxidative degradation of these catalysts is similar to that of $(Cl_8TPP)MnCl$ but they are optimized under quite different reaction conditions [562]. The new Mn(III)-tetraarylporphyrins (**294**) and (**295**), which contain a pyridine axial ligand connected through a flexible chain of 9 or 14 atoms connected to the Cl_8TPP structure, have been prepared and used as catalysts for the epoxidation of alkenes with HOCl and H_2O_2. In some cases these catalysts proved to be as active and resistant to oxidative degradation as $(Cl_8TPP)Mn(III)$ in the presence of an excess of pyridine, but generally their activity was inferior compared to that of this well-established catalytic system [563].



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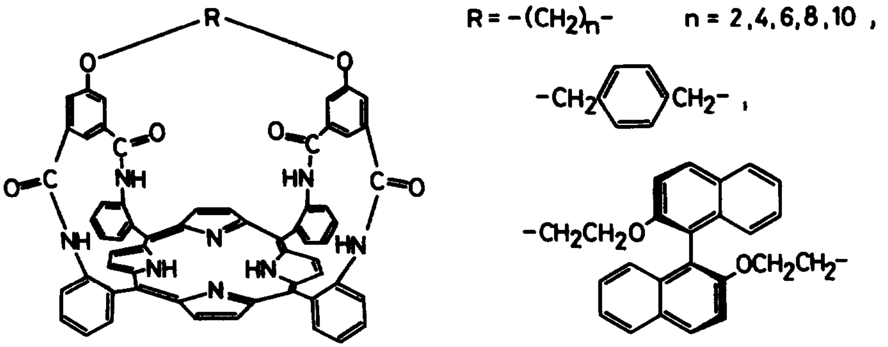
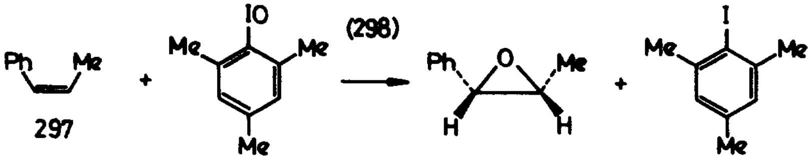
295

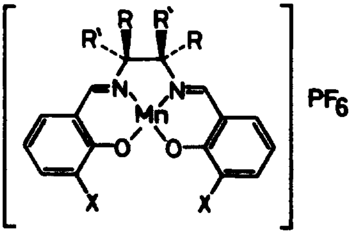
A comparison of Mn(Br$_8$TMP)Cl with Mn(TMP)Cl as catalyst in the KHSO$_5$ or magnesium monoperoxyphtalate epoxidation of olefins (cyclohexene, cyclooctene, styrene, and 1-octene) in air at room temperature showed higher reactivity and enhanced stability of the perbrominated derivative (Br$_8$TMP = *meso*-tetramesityl-*β*-octabromoporphyrinato) [564]. Enhanced yields of styrene oxide (59%), stilbene oxide (53%) and cyclohexene oxide (49%) were obtained in the (TPP)MnCl-catalyzed oxidation of styrene, *cis*-stilbene, and cyclohexene by H$_2$O$_2$ in the presence of catalytic amounts of phenanthrenequinone [565]. The catalytic epoxidation of indene, styrene and 1-methyl-indene with (TMP)MnCl and hypochlorite was investigated. High yields of epoxide and good material balances were found in experiments at relatively high olefin concentrations [566]. Shape-selective catalytic epoxidation within the cavities of a series of manganese picnic basket porphyrins, Mn(PBP)X (**296**) was achieved by using a bulky, anionic axial ligand X (3,5-di-*tert*-butylphenoxide) and MeCN as solvent with iodosylbenzene as the oxidant at room temperature. The flat rigid *p*-xylyl basket (R = $-CH_2C_6H_4CH_2-$) showed a dramatic shape selectivity for *cis*-2-octene versus *cis*-cyclooctene (>1000:1) in competitive epoxidation [567].



296

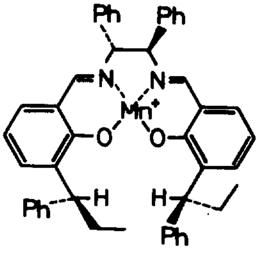
Mn(II)-salicylidene-aminoacid complexes are efficient catalysts for the epoxidation of olefins with PhIO. Oxygen transfer is not stereoselective since the E/Z epoxide ratio does not change significantly by changing the amino acid in the ligand [568]. Epoxidation of cyclohexene using various Mn(III) Schiff base complexes as catalysts and PHIO as oxidant gave cyclohexene oxide, cyclohexenol, and cyclohexenone. The effect of various additives like pyridine, imidazole, etc. showed, that axial ligation increases the yield of epoxide [569]. Manganese complexes of chiral Schiff bases have been found to catalyze epoxidation of alkyl- and aryl-substituted olefins (e.g.**297**) with enantioselectivities higher than obtained with other nonenzymatic catalysts. Thus in the presence of catalysts of type (**298**) (R,R' = H, Ph or tBu) and iodosomesitylene as the oxygen atom source in CH_3CN or CH_2Cl_2 at 25 °C, 20-93% ee and good isolated yields were reported [570].





298

The catalytic asymmetric epoxidation of 1-phenyl-1-propene and dihydronaphthalene with PhIO in MeCN at 25 °C was studied using the optically active salen-Mn complexes (**299**) and (**300**) as catalysts. The highest enantioselectivity (50% ee) was obtained for (E)-1-phenyl-1-propene [571].



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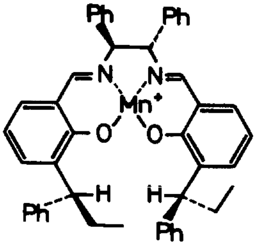
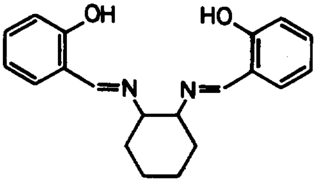


300

Manganese(III) complexes of the tetradentate Schiff bases (**301**) and (**302**) catalyze the oxidation of cyclohexene by PhIO. With catalysts (**301**) and (**302**; R = Ph) epoxide is the main product, catalyst (**302**; R = Me) yields both cyclohexene epoxide and cyclohexenol [572].



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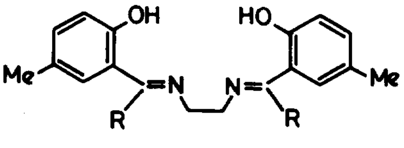
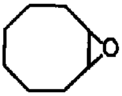


302

Treatment of cyclooctene with H_2O_2 in $CHCl_3$ in the presence of (TPP)[Re(CO)$_3$]$_2$ as catalyst at 70 °C gave epoxide (**303**) in 90% yield. If the reaction was performed in dichlorethane in the presence of acetone, (**304**) and (**305**) were also formed [573].



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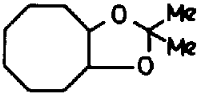

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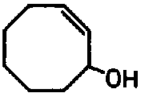
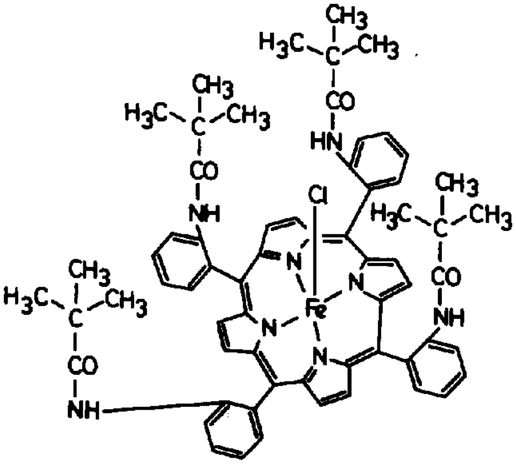


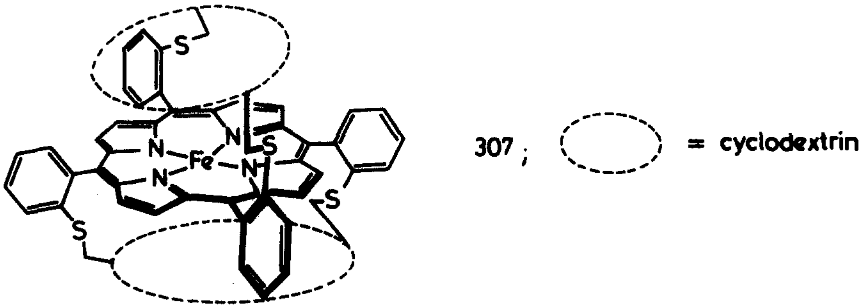
305

The epoxidation of steroids with magnesium monoperoxyphthalate or with PhIO in the presence of Mn and Fe porphyrins was investigated. Nearly complete *β*-stereoselectivity (97-99%) and 58% yield was observed in the epoxidation of cholesteryl acetate using PhIO as the oxidant and (TMP)FeCl as the catalyst [574]. The oxidation of *trans*-hexene-2 by PhIO catalyzed by (Cl_4TPP)FeCl is accompanied by the irreversible transformation of the catalyst. After acidic demetallation, two isomeric N-alkylporphyrins were obtained which were formed by the two possible *syn* additions of an O atom and a pyrrole N to the alkene double bond [575]. Cyclohexene is epoxidized quantitatively by *m*-chloroperbenzoic acid in the presence of (L)FeCl (L = **306**) already at 220-230 K [576].



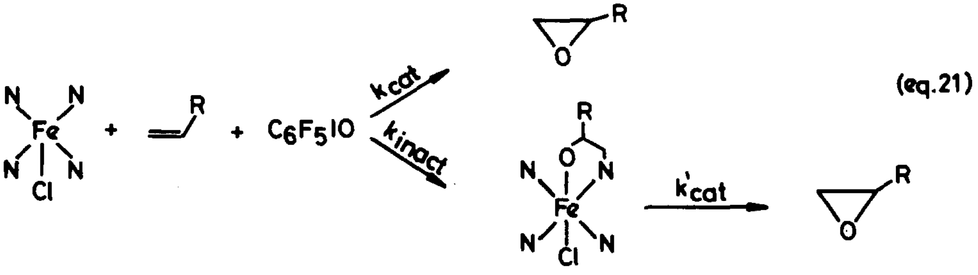
306

Catalytic epoxidation of cyclohexene, 2,3-dimethyl-2-butene, and styrene with iodosobenzene at 0 °C using a cyclodextrin sandwiched Fe^{II} porphyrin (**307**) was reported [577].



307 ;

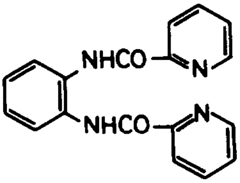
A detailed study of olefin epoxydation (1-decene, vinylcyclohexane, styrene and cyclooctene) by the (Cl$_8$TPP)FeCl + C$_6$F$_5$IO system has been carried out mainly with the intention to determine the significance of catalyst deactivation by alkylation (see eq.21) of the porphyrin ring. From computer fitting of experimental data, partition numbers PN (PN = k_{cat}/k_{inact}) were obtained which were found to be highly sensitive to the structure of the olefin [578]. The effects of electronic and steric properties of different synthetic hemin catalysts and olefin substrates on partition numbers were reported [579].



(eq.21)

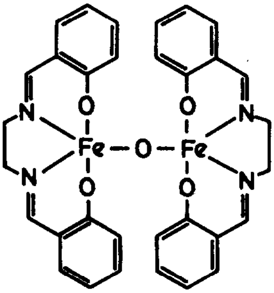
The epoxidation of alkenes catalyzed by Mn(II), Fe(II), Fe(III), Co(II), and Ni(II) phthalocyanines has been studied. Mn and Fe phthalocyanines were most effective with PhIO as oxygen donor, whereas Co and Ni phthalocyanines were best under phase-transfer catalysis conditions with NaOCl as oxidizing agent.

In the presence of 2,6-di-*tert*-butyl-*p*-cresol the Fe catalyzed reaction leads to a highly stereospecific epoxidation of *cis*-alkenes [580]. The epoxidation of cyclohexene with PhIO in the presence of Fe(III) Schiff base complexes in MeCN at 25 °C was studied [581]. Epoxidation of cyclohexene with iodosobenzene in the presence of $Fe(OTf)_3$, $(Et_3NH)Fe(bpb)(OTf)_2$ (H_2bpb = 308) and $Al(OTf)_3$ was studied. Since no significant difference was found between the reactivity of the iron an aluminum complexes it was concluded that high-valent metal oxo species are not involved in the reaction. The byproducts formed suggest a mechanism that involves electrophilic attack of I(III) on the olefin [582].



308

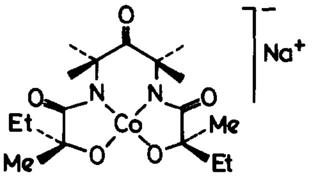
Epoxidation of chalcone and several substituted chalcones was carried out with tBuOOH using the Fe(III) complex (309) as catalyst. A free radical mechanism was proposed [583].



309

The kinetics of catalytic cyclohexene epoxidation with the Ru(III) + EDTA + ascorbate + H_2O_2 system between 15 and 45 °C were studied. First order dependence of the reaction was observed with respect to Ru(III)-EDTA, ascorbic acid, H_2O_2 and cyclohexene. A negative first order dependence was found with respect to hydrogen ion concentration [584]. The kinetics of epoxidation of cyclohexene and cyclooctene with $KHSO_5$ catalyzed by $[(EDTA)Ru^{III}(H_2O)]^-$ at pH 6 between 30 and 50 °C was determined [585].

Epoxidation of several chalcones with substituents on the phenyl rings was carried out with tBuOOH and a Co(II) Schiff base complex as catalyst. The effect of reaction conditions on yield was studied [586]. Several chiral square planar Co(III) complexes like (**310**) or (**311**) have been prepared and used as catalysts in the epoxidation of styrene or substituted styrenes with iodosylbenzene. Chemical yields of 25-86% and enantiomeric excesses between 0 and 17% were achieved [587].



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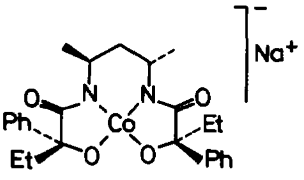


311

Up to 640 turnovers per minute were found in the epoxidation of *trans*-β-methylstyrene at room temperature using NaOCl and Ni^{II}(salen) catalyst at pH 9.3. The best turnover rate is comparable to that observed in the presence of (Cl_8TPP)Fe(III) as catalyst [588].

Inorganic oxides promote the epoxidation of 1-octene by H_2O_2 catalyzed by (*cis*-$Ph_2PCH{=}CHPPh_2$)Pt(CF_3)OH in the liquid phase. The significant increase of catalytic activity observed under certain conditions was interpreted as a cooperation effect taking place at the interface between solid oxide support and solution [589].

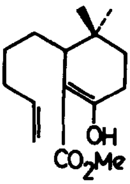
It has been shown that in the presence of tertiary amines (e.g.) pyridine) Ag_2O and $AgNO_3$ catalyze the oxidation of alkenes to epoxides with iodosobenzene. The reaction is not stereoselective: *cis*-alkenes yield mainly *trans*-epoxides. Epoxidation can also be achieved with Ag_2O_2 alone; the yields and stereoselectivities are the same as in the case of Ag_2O and PhIO, indicating identical reaction paths [590].

See also [492, 502, 504, 522, 525, 592, 663, 664, 789].

c) Dihydroxylation of Olefins

A rate equation for the consumption of H_2O_2 in the Na_2WO_4-catalyzed hydroxylation of maleic acid by H_2O_2 was determined [591].

In a multistep synthesis of a *trans*-decalin epoxy-diacetate compound, dihydroxylation of (**312**) with OsO_4 and *N*-methylmorpholine-*N*-oxide, and epoxidation of (**313**) with $VO(acac)_2$ and tBuOOH was used [592].



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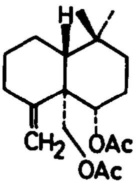
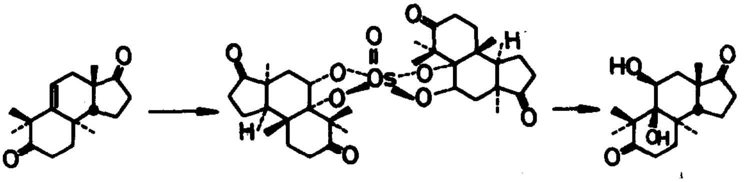


313

The sterically hindered chiral alkene (**314**) was cis-hydroxylated to (**316**) in 70% isolated yield by OsO_4· + *N*-methylmorpholine-*N*-oxide. An Os(VI) intermediate (**315**) which acts as a catalyst in the oxidation, has been isolated and characterized [593].

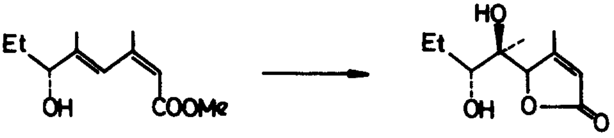


314 315 316

A modification of the catalytic vicinal hydroxylation of higher olefins by using hexacyanoferrate(III) ion as a cheap and convenient oxidant and OsO_4 as catalyst has been reported (for example eq.**22**) [594].

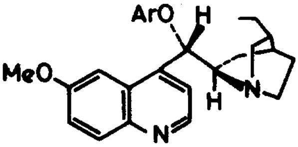
(eq. 22)

The OsO_4-catalyzed hydroxylation of the diene (**317**) with *N*-morpholine-*N*-oxide at room temperature provided butenolide (**318**) in 53% yield [595].

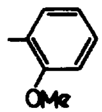


317 318

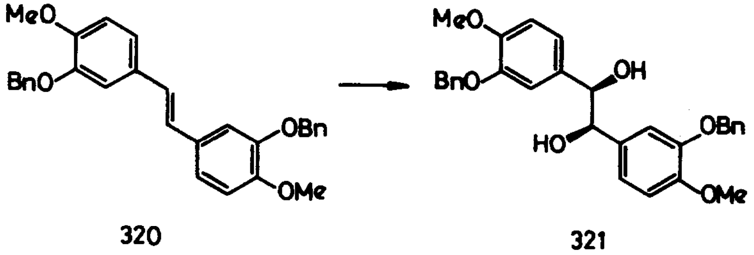
The highest enantioselectivities yet obtained in catalytic asymmetric dihydroxylation of olefins by OsO_4 have been realized using $K_3[Fe(CN)_6]$ as the reoxidant. Isolated yields of 85-95% and up to 99% ee at room temperature were reported in the case of styrene, *trans*-stilbene, *trans*-propenylbenzene, methyl cinnamate, cinnamyl acetate and *trans*-decene using dihydroquinidine *p*-chlorobenzoate as the chiral ligand [596]. Aryl ethers of dihydroquinidine (**319**) were found to be excellent ligands for both stoichiometric and catalytic asymmetric dihydroxylation of dialkyl substituted olefins such as (E)-3-hexene. The catalytic asymmetric dihydroxylation reactions were carried out by using 0.004 equiv of OsO_4 and *N*-methylmorpholine-*N*-oxide or $K_3Fe(CN)_6$ as the secondary oxidant at 0 °C or at RT, respectively. The (R,R)-diol was obtained in 85-90% yield with up to 95% in both the stoichiometric and catalytic processes [597].



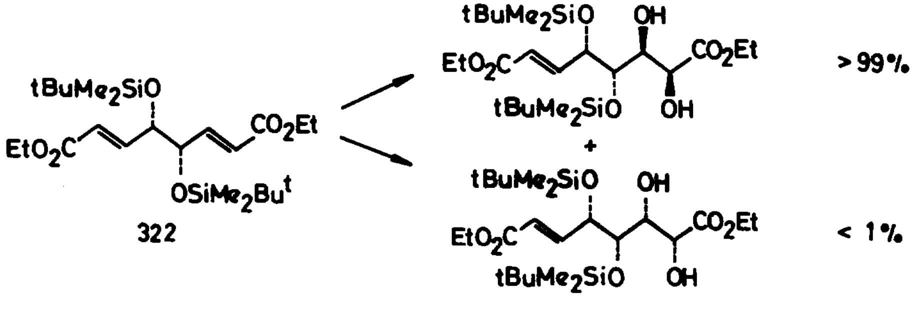
319 ; Ar = Ph,



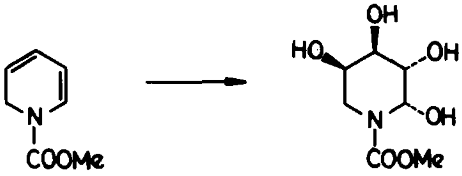
Good to excellent asymmetric induction and reasonable reaction rates were observed in heterogeneous catalytic dihydroxylation of *trans*-stilbene by using a polymer-bound alkaloid-OsO_4 complex and *N*-methylmorpholine-*N*-oxide or $K_3Fe(CN)_6$ as the secondary oxidant [598]. The catalytic enantioselective Sharpless dihydroxylation (2 mol% $OsCl_3$, 10% dihydroquinidine-4-chlorobenzoate, *N*-methylmorpholine-*N*-oxide, acetone/H_2O = 9/1, RT) was applied to obtain (**321**) in 88% yield and 82% ee from (**320**) [599].



High diastereofacial differentiation in OsO_4-catalyzed dihydroxylation (5 mol% OsO_4, 2 equiv *N*-methylmorpholine-*N*-oxide, acetone:H_2O = 5:1, 25 °C) of acyclic bis-allylic compounds (such as **322**) was found [600].



Stereospecific double glycolization of the 1,2-dihydropyridine derivative (**323**) in the presence of an excess of *N*-methylmorpholine-*N*-oxide and catalytic amounts of OsO_4 at RT leads to the tetrol (**324**) in 85% yield [601].



323 324

See also [653, 658].

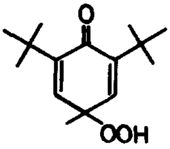
d) Oxidation of O-Containing Functional Groups

Oxidation of malic acid by bromate catalyzed by Ce(III) in the presence of Hg(II) and Tl(III) as bromide-scavengers leads to the formation of $OHCCH_2COOH$. The rate-determining step is the oxidation of the Ce(III)-malic acid complex by bromate [602].

Primary and secondary benzyl alcohols were selectively oxidized with high yields to the corresponding aldehydes or ketones using tBuOOH and catalytic amounts of $Ti(OPr^i)_4$ or $Zr(OPr)_4$ at 20 °C [603].

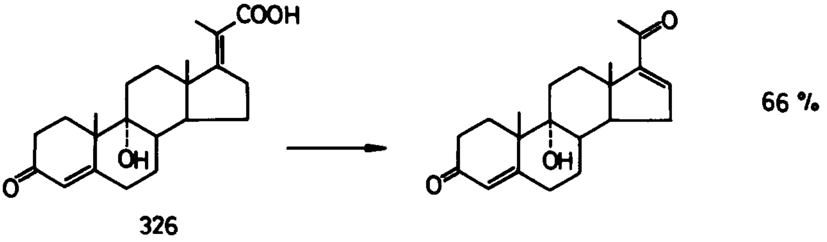
A novel vanadium pillared clay was prepared by refluxing chloromontmorillonite with NH_4VO_3 in dry acetone followed by washing with KOH to remove excess vanadate; the product was used as a shape-selective catalyst for the oxidation of benzylic alcohols with H_2O_2. Benzyl alcohols and *para*-substituted benzyl alcohols were readily oxidized to the corresponding benzoic acids, *ortho*-substituted benzyl alcohols and 1-penylethanol were recovered unchanged [604].

The oxidation of 2,6-di-*tert*-butyl-4-methyl-phenol with H_2O_2 in the presence of heteropolyacids was studied. In the presence of 12-molybdophosphoric acid as a catalyst at 30 °C, (**325**) was obtained as the major product [605].

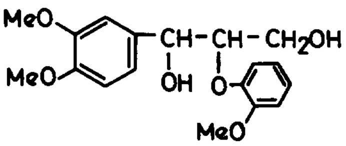


325

17(20)-Dehydro-23,24-dinorcholan-22-oic acids like (**326**) were converted with H_2O_2 in the presence of molybdate or tungstate ions into 16-unsaturated 20-oxo-pregnanes in a simple one step reaction at 30 °C in 1 h [606].

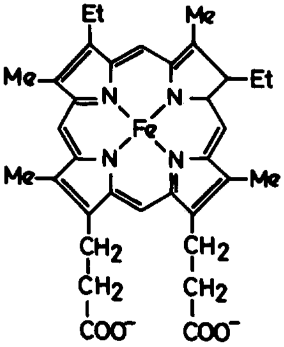


Biomimetic models of ligninase (a peroxidase which catalyzes the oxidation of lignin with H_2O_2) based on anionic iron- or manganese-porphyrin complexes and K_2SO_5 have been developed. Veratryl alcohol and (**327**) were used as lignin models [607].



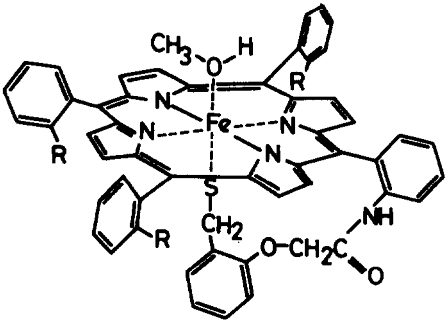
327

Oxidation of alkyl and aromatic aldehydes by an $(Fe_{20}TPP)Fe(III)$- *m*-chloroperbenzoic acid system at -78 °C led to carboxylic acids in good yields. Based on kinetic studies, a direct hydrogen abstraction mechanism was suggested [608]. The peroxidatic activity of the intermediate species, obtained from mesoferriheme (**328**) and NaOCl, toward the oxidation of phenol with NaOCl was studied by the stopped-flow technique [609].



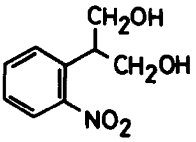
328

A novel iron porphyrin coordinated by thiolate anion (**329**; R = NHCOBu^t) has been synthesized and tested as catalyst for the oxidation of 2,4,6-tri-*tert*-butylphenol(TBPH) and 1,1-diphenyl-2-picrylhydrazine (DPPH) by alkyl hydroperoxides to the corresponding TBP$^\cdot$ and DPP$^\cdot$ radicals. The new catalyst was found to be about 100 times more effective than (TPP)FeCl [610].



329

The Ru(III) chloride catalyzed oxidation of C_3 and C_4 alkanols by $[Fe(CN)_6]^{3-}$ in mild alkaline medium is first order in alcohol, OH^-, and zero order in oxidant. A mechanism based on these results has been proposed [611]. The Ru(III)-catalyzed oxidation of cyclopentanol and cyclohexanol by an acidic solution of $KBrO_3$ in the presence of mercuric acetate was found to be second order in substrate, first order in Ru(III) and zero order in bromate [612]. The kinetics of the Ru(III)-catalyzed oxidation of lactic acid by *N*-bromosuccinimide have been investigated in perchloric acid medium in the presence of mercuric acetate as scavenger. Pyruvic acid has been identified as a reaction product [613]. The kinetics of the Ru(III) chloride catalyzed oxidation of glycolic acid and ethanol by alkaline $[Fe(CN)_6]^{3-}$ have been determined. A similar mechanism was proposed for both substrates [614]. The kinetics of oxidation of digol and ethyl digol by *N*-bromoacetamide catalyzed by $RuCl_3$ were determined in the presence of $Hg(OAc)_2$. Digolic aldehydes were identified as the end products [615]. The catalytic oxidation of alcohols in the presence of excess *N*-methylmorpholine-*N*-oxide by $RuCl_2(PPh_3)_2(acac)$ has been reported [616]. The kinetics of the Ru(III) chloride-catalyzed oxidation of glycolic acid and mandelic acid to glyoxylic acid and benzoyl formic acid, respectively, by *N*-bromosuccinimide (NBS) at 30–45 °C show first-order dependencies each on NBS, substrate, Ru(III), and Cl^-, and a negative effect of succinimide [617]. Primary alcohols were selectively oxidized to the corresponding aldehydes by the $RuCl_3$/*N*-methylmorpholine-*N*-oxide system in DMF at 35 °C. The unsaturated alcohols allyl alcohol and cinnamyl alcohol gave selectively acrolein and cinnamaldehyde, respectively. Based on kinetic results, Ru(V)=O species were suggested to be involved in the reaction mechanism [618]. Oxidation of (**330**) with $NaIO_4$ in the presence of a catalytic amount of RuO_2 or with CrO_3 in aqueous sulfuric acid (Jones reagent) gave 2-nitrobenzoic acid in 96% yield [619].



330

The oxidation of (**331**) and (**333**) using $NaIO_4$ in the presence of catalytic amounts of $RuCl_3.H_2O$ in $CCl_4/MeCN/H_2O$ afforded (**332**) and (**334**) in 69 and 72% yield, respectively [620].

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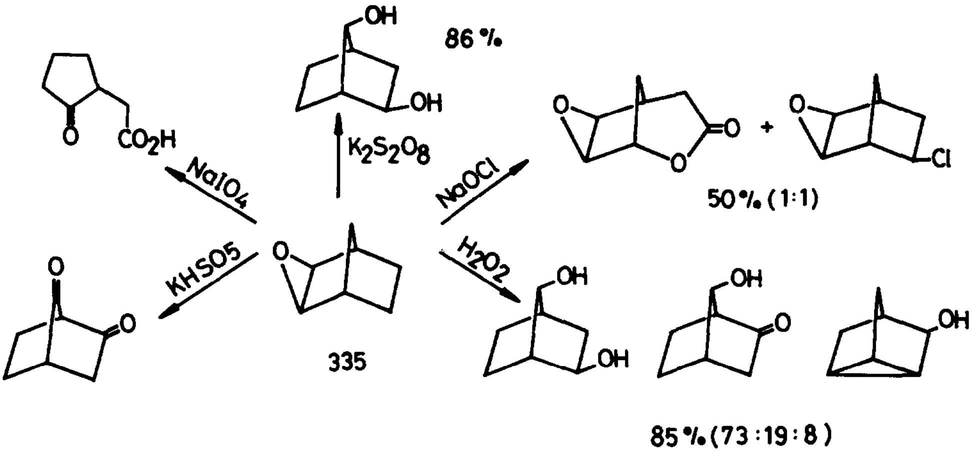
334

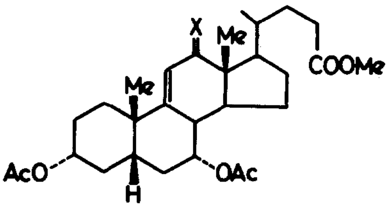
Selective and fast conversion of primary ethers to esters (or lactones) were achieved by using LiClO in the presence of catalytic amounts of $RuCl_2L_4$ (L = Me_2SO, $(L)_2$ = dppp) complexes at 22 °C (eq.**23**):

$$CH_3OCH_2CH_2CH_2CH_3 + 2[O] \longrightarrow CH_3OC(=O)CH_2CH_2CH_3 + H_2O \qquad \text{(eq.23)}$$

Isopropyl ether gave acetone, while secondary ethers bearing methylene groups in β-position were converted into β-keto ethers [621].The products of the RuO_4-catalyzed oxidation of 2,3-epoxy-norbornane (**335**) at 60 °C have been found to depend strongly upon the nature of the reoxidizing compound [622].



Oxidation of iPrOH to acetone by N-bromosuccinimide in basic solution was investigated in the presence Ru(III), Os(VIII), and Ru(III) + Os(VIII) ions. The order in metal ion was found to be nearly unity in all the three catalyzed reactions; the orders in oxidant and substrate varied with the catalyst. Suitable mechanisms have been proposed [623]. Oxidation of (**336**; X = H, OH) with OsO_4 and *N*-methylmorpholine-*N*-oxide gave (**336**; X = O) in 91% yield. Other cyclic allylic alcohols were also oxidized by this method [624].



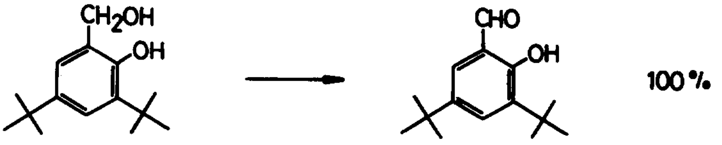
336

Cobalt and iron salts strongly reduced the yields of benzenediol in the oxidation of phenol with peracetic acid due to their catalytic effect on the consecutive oxidation of these diols. This unfavorable effect could be eliminated by adding diphosphate which acts as a complexing agent [625].

The Rh(III)-catalyzed oxidation of 1,2-glycols to the corresponding carbonyl compounds by acid bromate is first order with respect to both Rh and glycol and independent of bromate concentration. A mechanism was proposed [626].

The kinetics of the uncatalyzed and of the Ir(III)-catalyzed oxidation of oxalate ion by *N*-bromosuccinimide have been determined. A mechanism involving the hypobromite ion as the reactive species of the oxidant was proposed [627].

A catalytic synthesis of nitriles from aldehydes and alcohols in the presence of aqueous ammonia by oxidation with $NiSO_4$-$K_2S_2O_8$ at room temperature has been described. In particular, benzaldehyde and benzyl alcohol gave 100% conversion in 3 h, yielding 76% and 82% benzonitrile, respectively [628]. Transition metal ions like Ag(I), Mn(II), Cu(II), Co(II), and Ni(II) catalyze the oxidation of diacetone alcohol by Ce(IV). A mechanism involving the formation of a complex between the substrate and the catalyst in a fast step followed by oxidation of this complex by Ce(IV) in a slow step was proposed [629]. Oxidation of ascorbic acid by peroxodiphosphate is catalyzed by trace metal-ion impurities of Cu(II) and Fe(III) present in the reagents. The catalytic activity of Cu(II) is especially high and is so specific that the amount of Cu(II) present in a system as impurity can be calculated from the initial reaction rates [630]. Copper(I) and copper(II) mediated two-electron oxidations of benzylic alcohols like (**337**) and diaryl acetic acids like (**338**) to the corresponding carbonyl compounds by trimethylamine-*N*-oxide occur at 60 °C in acetonitrile [631].



337

$Ph_2CH\text{-}COOH \longrightarrow Ph_2C{=}O$ 70%

338

The oxidative cyclization of ω-hydroxy alkenes (e.g.**339**) to ω-lactones in 52-84% yield was achieved with a slightly wet mixture of $KMnO_4$ and $CuSO_4.5H_2O$ in CH_2Cl_2. Dry $KMnO_4$ and $CuSO_4.5H_2O$, or $KMnO_4$ alone do not effect this transformation. At least one carbon atom is lost in the process [632].

339

81%

The kinetics of oxidation of benzoin and substituted benzoins [633], of benzylphenylglycolic and substituted benzylphenylglycolic acid [634], and of chalcones and substituted chalcones [635] by $S_2O_8^{2-}$ in the presence of Ag^+ have been investigated. Free radical mechanisms were proposed in all the three cases. Oxydation of MeOEt, HF, and anisole by $S_2O_8^{2-}$ is also catalyzed by Ag^+. The reaction is first order in oxidant and catalyst and is zero order in substrate. Acetaldehyde, 2,3-dihydrofuran and benzaldehyde were identified as products [636].

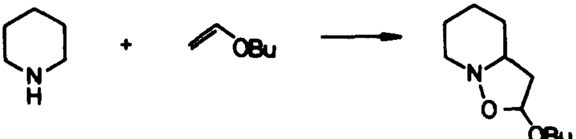
See also [420, 527, 542, 655, 657, 711, 755].

e) Oxidation of N-Containing Organic Compounds

Oxidation of secondary amines with H_2O_2 in the presence of $Na_2WO_4.H_2O$ catalyst at room temperature in methanol or water gives nitrones (**340**) in good to excellent yields. In the presence of alkenes at 90 °C isoxazolidines (**341**) were obtained in one step [637].

340

89 %



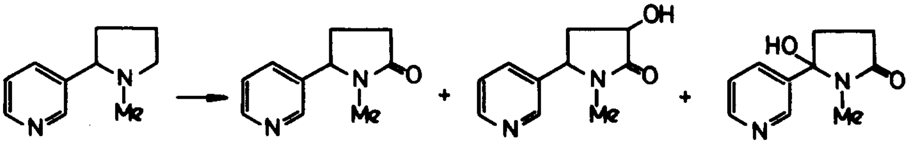
341

54 %

1-Hydroxy-3,4-dihydroquinolin-2(1H)-ones (**342**; R = H, 4-Me, 6-Me, 6-MeO, 6-MeCONH, 6-Cl, 6-Br, 6-MeCO, 6-CN, 8-Me) have been prepared in good to excellent yields by the sodium tungstate catalyzed oxidation of 1,2,3,4-tetrahydroquinolines with 30% aqueous H_2O_2 in methanol at room temperature [638].

342

Oxidation of L-glutamic acid by $Ce(SO_4)_2$ in the presence of $MnSO_4$ is first order in both oxidant and substrate. A mechanism was proposed [639]. Oxidation of DL-alanine by $Ce(SO_4)_2$ in the presence of Mn^{2+} ions was found to be first order in oxidant and fractional order in substrate. A mechanism has been suggested [640]. In a HCO_3^-/CO_2 buffer Mn(II) and Fe(II) catalyze the oxidation of amino acids by H_2O_2. Oxidation products are carbonyl compounds; in a parallel reaction about 50% of the H_2O_2 consumed is decomposed to O_2 and H_2O [641]. Nicotine was oxidized with PhIO in the presence of $(Cl_4TPP)M(III)$ (M = Fe, Mn) as catalyst in dry CH_2Cl_2 solution at RT. The iron catalyst gave (**343**) and (**344**) with low yields; the yields were higher with the Mn porphyrin complex and additionally also (**345**) was formed [642].

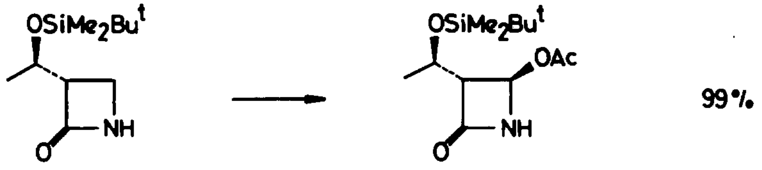


343 344 345

The biomimetic hydroxylation of 5-nitroacenaphthene with PhIO in CH_2Cl_2 in the presence of Cr(III), Mn(III), or Fe(III) tetraphenylporphyrins was studied in order to distinguish between mechanistic alternatives [643]. The oxidation of *N,N*-dimethylbenzamides to the corresponding *N*-formyl-*N*-methylbenzamides using (TPP)Fe(III) as catalyst and tBuOOH as oxidant was studied. The rate of oxidation was found to be independent from the substituents in the aryl ring and a kinetic deuterium isotope effect of 5.6 was observed. These results are consistent with a mechanism involving direct H atom abstraction from the substrate [644].

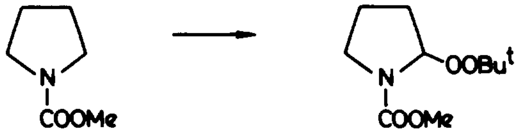
Oxidation of α-substituted nitriles PhCHRCN (R = Me, Ph, CH_2COOEt, $CH_2CH_2CH=CH_2$, $OSiMe_3$) with tBuOOH in the presence of $RuCl_2(PPh_3)_3$ yields the peroxides tBuOOCPhRCN. Under the same conditions, nitriles $ArCH_2CN$ (Ar = 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$) give ArCOCN [645]. Ruthenium-catalyzed oxidation of amides (e.g.**346**) and lactams (e.g.**347**) with tBuOOH or AcOOH at room temperature and $RuCl_2(PPh_3)_3$ as catalyst precursor gave good to excellent isolated yields of the corresponding oxygenated products [646].

346



347

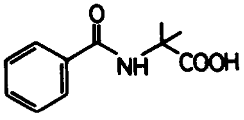
tert-Butyldioxyamides were obtained from amides by the ruthenium-catalyzed oxidation with tBuOOH. E.g. the treatment of (**348**) with tBuOOH in the presence of 3 mol% of $RuCl_2(PPh_3)_3$ in benzene gave (**349**) in 60% isolated yield [647].



348 349

Aliphatic primary amines gave the corresponding nitriles in 84-97% isolated yields on treatment with $NiSO_4$ as catalyst and $K_2S_2O_8$ as an oxidant at room temperature [648].

N-benzoylhistidine was oxidized with H_2O_2 in the presence of Cu^{2+} under physiological conditions (pH 7.2, RT). Seven different oxidation products were detected, among them four asparagine derivatives which were formed by rupture of the imidazole ring [649]. A new reagent, $CuCl_2$ + DMSO was developed for oxidation, oxidative cyclization, and chlorination. Thus, isoxazoline was oxidized to isoxazole and dibenzoylmethane underwent oxidative cyclization to flavone [650]. *N*-benzoyl-2-methylalanine (**350**) was quantitatively orthohydroxylated through its copper(II) salt by oxidation with trimethylamine-*N*-oxide at 75 °C in acetonitrile. Transitory formation of a copper(III) species was proposed [651].



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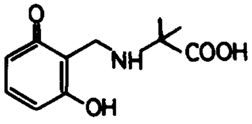
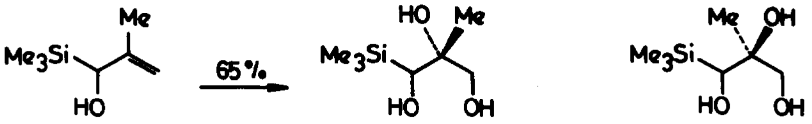


Oxidation of (dimethylamino)ethanol by KSO_5 in the presence of Ag^+ is first order in alcohol, half order in Ag^+ and zero order in persulfate. A mechanism was proposed [652].

See also [655].

f) Oxidation of Si-, P-, S-, or Br-Containing Organic Compounds

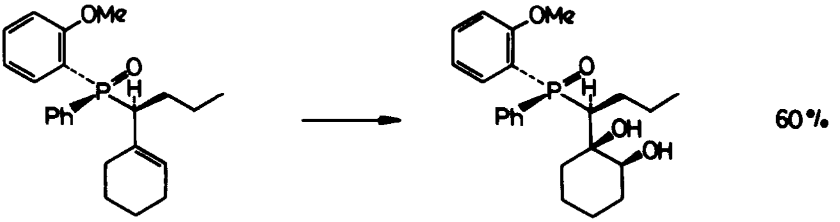
Predominantly 1,2-*anti*-1,2,3-triol units (e.g. **351**:**352** = 97:3) are formed from oxygen-substituted allylic and crotyl silanes with trimethylamine-*N*-oxide at room temperature in the presence of catalytic amounts of OsO_4 [653].



351

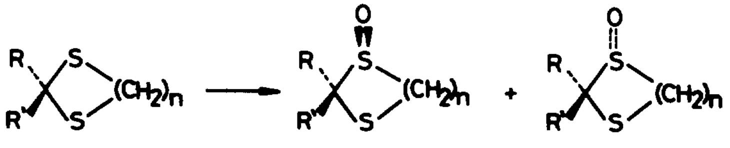
352

The oxidation of PPh_3 to $OPPh_3$ by Me_2SO is catalyzed by $\{HB(Me_2pz)_3\}MoO_2X$ complexes at 40 °C ($X = Cl^-$, SPh^-, OPh^-; Me_2pz = 3,5-dimethyl-1-pyrazolyl) [654]. The kinetics of the oxidation of PPh_3 with NaOCl catalyzed by aquo-ethylenediaminetetraacetato ruthenate(III) in a water/dioxane medium were studied [655]. Ruthenium complex/*N*-methylmorpholine-*N*-oxide systems oxidize alcohols, olefins, sulfides, and PPh_3. The reactions proceed via the formation of a higher valent metal oxo species. Alcohols are oxidized by hydride ion abstraction, in the other cases there is a net oxygen atom transfer onto the substrate [656]. Hydroxylation with OsO_4 and *N*-methylmorpholine-*N*-oxide was applied to obtain diols from cyclic allylic phosphine oxides like (**353**) [657]. A new oxidizing reagent prepared from Cu(II) ion and H_2O_2 gave acetaldehyde from ethanol in 100 yield at 45 °C. The reagent readily oxidized PPh_3 to $O{=}PPh_3$, diphenyl acetic acid to benzophenone, benzylamine to benzaldehyde and toluene to benzyl alcohol [658].



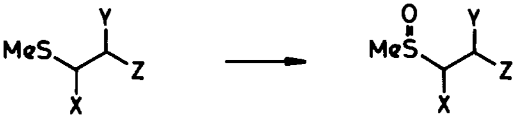
353

The chemical and enzymatic S-oxygenation of 2-(*p*-methoxyphenyl)-1,3-dithiolane and 2-(*p*-cyanophenyl)-1,3-oxathiolane has been investigated. By using the chiral sulfoxidizing system consisting of $Ti(OPr^i)_4$, (+)-diethyl tartarate, tBuOOH, and water, S-oxides were obtained in 76% and 54% ee, respectively [659]. Asymmetric oxidation of dithio acetals and dithio ketals (**354**; R,R' = H, Me, tBu, Ph, EtOOC, PhOOC; n = 2-4) to the corresponding monosulfoxides (**355**) by tBuOOH with the catalyst system $Ti(OPr^i)_4$ + (+)- or (-)-diethyl tartrate has been carried out. Simple 1,3-dithiolanes (**354**; n = 2) provided the best results (70-80% ee). As catalyst, $VO(acac)_2$, and as a stoichiometric oxidant, $MoO_2(acac)_2$ were also tested [660].



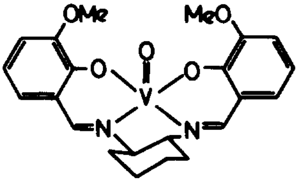
354 355

S-methyl β-hydroxysulfides, or their acetylated or silylated derivatives (**356** = H, Ph; Y = H, Ph, Me; Z = OH, $OSiPh_3$, $OSiBuPh_2$, $OSiMe_2Bu^t$, OAc) were asymmetrically oxidized to the corresponding sulfoxides (**357**) of fairly high enantiomeric purity (up to 80%) with tBuOOH, $Ti(OPr^i)_4$, and (+)-diethyl tartrate [661].



356 357

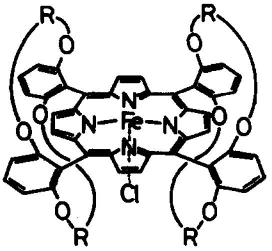
The catalytic asymmetric oxidation of sulfides into sulfoxides with organic hydroperoxides in the presence of optically active Schiff base - oxovanadium complexes was investigated. The best result was obtained in the oxidation of methyl phenyl sulfide with cumene hydroperoxide at 0 °C. Up to 96% isolated yield and 42% ee was found using (**358**) in CH_2Cl_2 [662].



358

Asymmetric hydroxylation of benzylic methylene in methylene chloride solution with 20-72% yield and 41-72% ee, asymmetric epoxydation of olefins in toluene with 9-73% yield and 20-72% ee, and asymmetric sulfoxidation of aryl alkyl thioethers with 67-88% yield and 14-48% ee was achieved at 0 °C by iodosylbenzene in the presence of chiral, vaulted binaphthyl porphyrinato chloroiron(III) or chloromanganese(III) catalyst (cf. AS 1989, ref.480) [663]. Catalytic oxygen atom transfer from PhIO to cyclohexene, methyl phenyl sulfide and methyl phenyl sulfoxide in CH_2Cl_2/DMF solution by a binuclear non-heme iron complex $[Fe^{2+}(H_2HBAB)(N\text{-MeIm})]_2$ (H_4HBAB = 1,2- bis(2-hydroxybenzamido)-benzene, *N*-MeIm = *N*-methyl imidazole) was reported [664]. Sulfides of type (**359**; X = H, NO_2, Me, F_5) were oxidized to sulfoxides by PhIO in CH_2Cl_2 at -15 °C using the chiral iron porphyrins (**360**) and (**361**) as catalysts. Fair to good ee-s (24–73%) and excellent turnover numbers (up to 168) were obtained in the presence of 1-methylimidazole as axial ligand [665].

359



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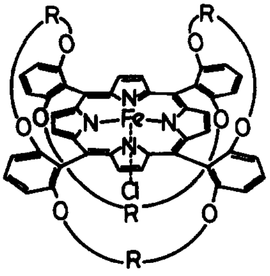
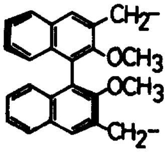


361

R =

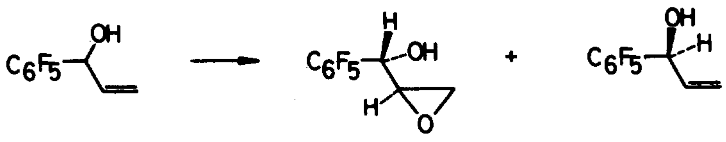


(S)

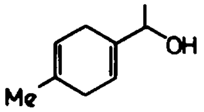
Tetrabromoaurate(III) is an efficient catalyst for the oxidation of sulfides to sulfoxides by HNO_3 in a biphasic system ($MeNO_2/H_2O$). The method can be applied to all kinds of dialkyl and alkyl aryl sulfides and also to diaryl sulfides activated by electron-releasing substituents. No sulfone formation is detected and other oxidizable groups like allyl, tertiary amino, and hydroxy are not affected [666].
See also [792, 794].

g) Kinetic Resolution by Asymmetric Oxidation

Reaction of the racemic allylic alcohol (**362**) with (+) diisopropyl tartrates, tBuOOH and $Ti(OiPr)_4$ in CH_2Cl_2 at −20 °C produced the optically active epoxy alcohol (**363**) and the kinetically resolved allylic alcohol (**364**) in 45% yield, 97% ee and 46% yield, 97% ee, respectively [620].



Epoxidation of racemic (365) using the Sharpless procedure gave the epoxides (366) and (367) [667].



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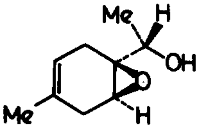

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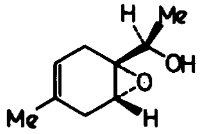
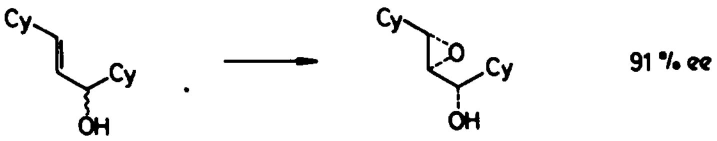


367

The racemic secondary allylic alcohol (368) was epoxidized using the Sharpless method (Ti(OPr^i)$_4$ + L-(+)-diisopropyl tartrate + tBuOOH in CH_2Cl_2). As a consequence of kinetic resolution only the (S)-enantiomer of (368) reacted and gave the epoxide (369) [668].

Substituted racemic *trans*-secondary allylic alcohols (for example 370) were converted to the corresponding *erythro* glycidols with excellent ee, applying the Sharpless kinetic resolution procedure (tBuOOH, (+)-diisopropyl tartrate, Ti(OPr^i)$_4$ [669].



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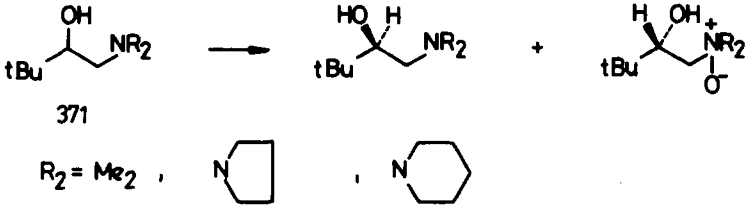
The coupling of telluride chemistry with the Sharpless kinetic resolution (Ti(O-i-Pr)$_4$, tBuOOH, (+) or (−) diisopropyl tartrate) of secondary allyl alcohols was found to be a powerful method for the conversion of a racemic allyl alcohol to either enantiomer in high (70-90%) yield and high enantiomeric purity. The procedure is based on the reduction of the epoxidized alcohol by Te^{2-} to the alcohol having the configuration of the unreacted alcohol enantiomer [670]. *β*-Hydroxy amines with high optical purity could be prepared by kinetic resolution of racemic *β*-hydroxy amines (**371**) via enantioselective *N*-oxide formation. Oxidation was performed by tBuOOH using Ti(OPr^i)$_4$ and L-(+)-diisopropyltartrate as catalysts [671].

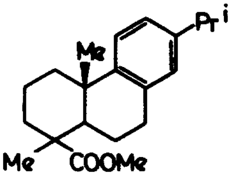


6. Stoichiometric Oxidation of Organic Compounds with High Valent Transition Metal Complexes

a) *Oxidation of Hydrocarbons or Hydrocarbon Groups*

Oxidation of the Na adducts of anthracene and pyrene with $(NH_4)_2Ce(NO_3)_6$ is accompanied by chemiluminescence [672].

Oxidation of succinic acid by acid dichromate was found to be first order in both substrate and oxidant [673]. The oxidation of glutaric acid by chromic acid in $HClO_4$ showed first and second order kinetics with respect to the substrate and oxidant, respectively. Activation parameters were determined [674]. The relative rates of oxidation of the methyl group in substituted toluenes by CrO_3 or $K_2Cr_2O_7$ in AcOH under thermal and photochemical conditions have been determined. The results support a single hydrogen-transfer mechanism for both reactions [675]. Oxidation of dehydroabietic acid Me ester (**372**) with various Cr(VI) reagents led to the formation of the compounds (**373-375**) [676].



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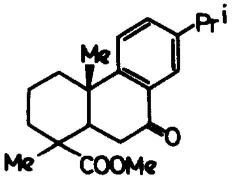

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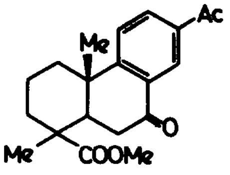

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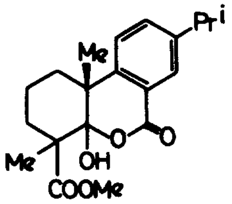
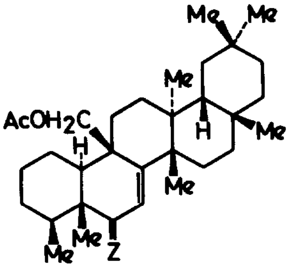


375

Oxidation of (376; Z = H,H) with Na$_2$Cr$_2$O$_7$ in AcOH gives (376; Z = O); oxidation of (377; R = CH$_2$OH) with CrO$_3$ in aqueous sulfuric acid gives (377; R = CHO) [677].



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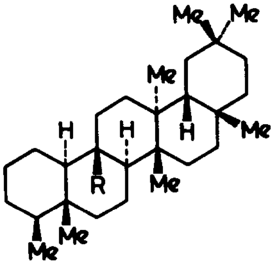
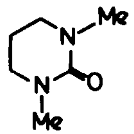


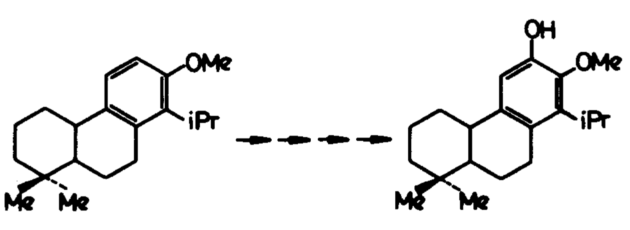
377

The oxodiperoxomolybdenum complex [MoO$_5$.py.L] (L = 378) was found to be as effective as [MoO$_5$.py.HMPA] in the α-hydroxylation of enolate anions. The new complex is a safer alternative to the HMPA complex since (378) has no carcinogenic properties [678].



378

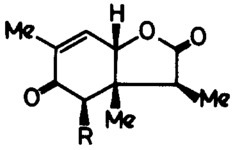
The regioselective hydroxylation of ring-C aromatic diterpenoids like (379) via their (η-arene)tricarbonylchromium(0) complexes was performed after lithiation with BuLi, cupration with CuBr.SMe, and oxidation with MoO$_5$.py.HMPA [679].



379

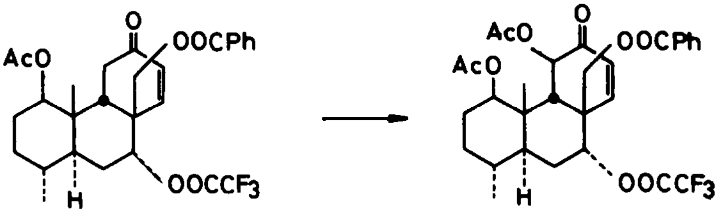
66 %

Methane is oxidized to CO_2 by $KMnO_4$ in aqueous sulfuric acid at 40–100 °C and 20–200 bar. If the reaction is performed in CF_3COOH, CF_3COOMe is formed selectively [680]. Aromatization of 1,4-dihydroarenes by MnO_2 or the $KMnO_4$-dicyclohexano-[18]crown-6 complex has been studied. Abstraction of the two H atoms occurs successively, the rate-determining step is the abstraction of the first H atom. A moderate *cis*-selectivity was found for the abstraction of the second H atom by MnO_2 [681]. Based on the spectroscopic behavior and the kinetics of the permanganate oxidation of *endo*-dicyclopentadiene in CH_2Cl_2 at 25 °C, the formation of a manganese(V) ester intermediate was observed. It was pointed out that these types of intermediates tend to be confused with soluble (colloidal) MnO_2 [682]. Oxidation of the benzofuranedione (**380**; R= H) with $Mn(OAc)_3$ gave (**380**; R = OAc) [683].



380

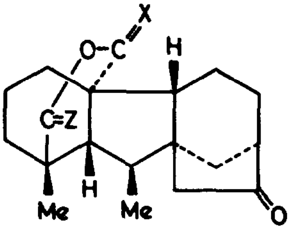
The tricyclic enone (**381**) was acetoxylated with $Mn(OAc)_3$ to give the enolone acetate (**382**) [684].



381 382

The rate of oxidation of substituted 1,4-cyclohexadienes by $Fe(phen)_3^{3+}$ to the corresponding arenes was studied. The results suggest a "homoconjugative" π-interaction between the double bonds of the 1,4-diene in the rate-determining step [685].

Oxidation of gibberellin ether (**383**; Z = X = H_2) with RuO_2 gave predominantly lactone (**383**; Z = H_2, X = O) with small amounts of isomeric lactone (**383**; Z = O, X = H_2) [686].



383

Methane was oxidized stoichiometrically by $Co(OOCCF_3)_3$ in CF_3COOH solution at 150-180 °C and 10-40 bar to give CF_3COOCH_3 in 90% yield based on cobalt. In the presence of 1-5 bar of O_2, the reaction was catalytic with respect to the cobalt salt. Smaller yields were obtained using $Mn(OOCCF_3)_3$ as stoichiometric reagent [687,688]. Oxidation of β-methylstyrenes by Co(III) and Mn(III) acetates in AcOH has been studied. Main products were *threo*-1-arylpropane-1,2-diol monoacetates in all cases [689]. The kinetics of the oxidation of ethyl acetoacetate and diethyl malonate by dodecatungstocobaltate(III) have been studied in aqueous acidic medium at 60 °C. A first order dependence of rate on both the concentrations of oxidant and reductant was obtained and the reaction was found to be catalyzed by alkali metal ions. An outersphere association between the complex and the reductant has been suggested as a plausible mechanism [690]. The kinetics of oxidation of ketones by dodecatungstocobaltate(III) have been determined in aqueous acidic media. A general rate expression was derived and a mechanism was proposed which assumes the corresponding enol as the reactive species [691].

The product distribution and kinetics of the oxidation of 3-buten-2-ol and 2-buten-1-ol by $PdCl_4^{2-}$ in aqueous solution at 25 °C have been investigated. The same rate equation was found as in the case of other acyclic olefins: $d[olefin]/dt = k[PdCl_4^{2-}][olefin][H^+]^{-1}[Cl]^{-2}$, suggesting similar mechanisms in all cases [692].

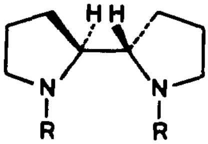
Rate constants and activation parameteres have been determined for the Os(VIII)-catalyzed and the uncatalyzed oxidation of C_5-C_7 cyclic ketones by $[Ag(IO_4)_2]^-$ [693].
See also [404, 791].

b) Epoxidation and Dihydroxylation of Olefins

3-Cyclohexene-1-carboxylic acid and 2-cyclopentene-1-acetic acid gave the corresponding epoxides in 53% and 21% yield in a stoichiometric reaction with oxo(5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)chromium(V) in aqueous solution [694].

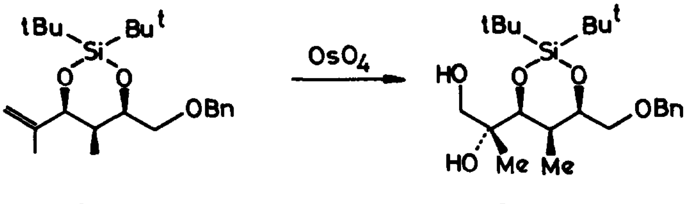
The nitrato complex $Fe(NO_3)_2Cl(OPPh_3)_2$ selectively epoxidizes cyclohexene; this is the first example of oxygen transfer from a nitrato ligand to an olefin [695]. The Ru(IV) oxo complex $[Ru(terpy)(tmen)O](ClO_4)_2$ oxidizes olefins to epoxides and secondary alcohols to ketones. The second order rate constants for the reactions have been determined [696].

Oxidation of some olefinic compounds (allyl alcohol, acrolein, acrylic acid, maleic acid, and cinnamic acid) by Os(VIII) has been studied in a H_2SO_4-AcOH medium. The order in Os(VIII) and substrate was unity in all cases; acid decreased the rate [697]. A simple mechanistic explanation for enantioselectivity in the catalytic dihydroxylation of certain olefins by OsO_4 under the influence of quinine and quinidine derivatives has been proposed [698]. The effect of the structure of chiral diamines in the enantioface differentiating dihydroxylation of styrene and styrene derivatives by diamine-OsO_4 complexes has been studied. It was concluded that the observed dramatic changes in enantioselectivity are essentially governed by steric factors in a tight conformation of the proposed intermediate [699]. The chiral 2,2'-bipyrrolidine (**384**; R = neohexyl) combined with OsO_4 was found to be an excellent stoichiometric enantioselective dihydroxylation reagent for *trans*-disubstituted and monosubstituted olefins. E.g. (E)-stilbene, dimethyl fumarate, (E)-2-heptene or 1-heptene gave excellent yields and 91-100% ee of the corresponding dihydroxylated product at -79 °C in toluene or methylene chloride solution [700].



384

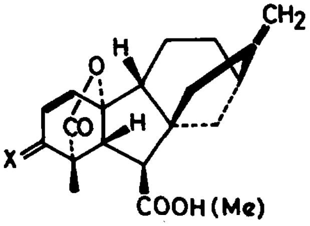
High diastereoselectivity (up to 61:1) has been found in osmylation of 1,1-disubstituted olefins like (385) possessing an allylic, oxygen-bearing stereocenter [701].



385

94%

The OsO_4-oxidation of C=C double bonds to *syn* diols was applied in the preparation of several hydroxylated gibberellins (77-92% yields) from gibberellin ring A olefins (386; X = H,H; H,OH; H,OAc; O). These experiments are claimed to be the first systematic study of the influence of two allylic substituents on the stereoselectivity of osmylation reactions [702].

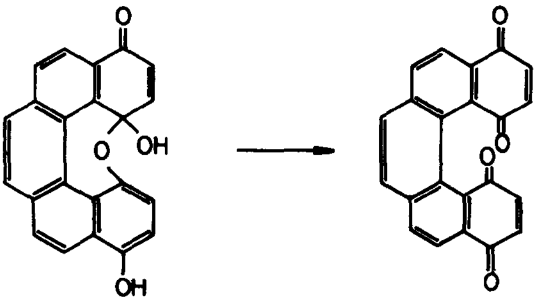


386

The osmylation of C_{60} (Buckminsterfullerene) with OsO_4 in toluene at 0-25 °C in the presence of pyridine gave an 81% yield of osmate ester corresponding to the addition of two Os(VI) units per carbon cluster without disrupting the carbon framework [703]. See also [801].

c) Oxidation of O-Containing Functional Groups

Cyclohexanol, 2-methylcyclohexanol, and 2,6-dimethylcyclohexanol were oxidized by Ce(IV) and some intermediate products were identified. The oxidizing agent was recovered anodically [704]. The oxidation of D-glucose, D-ribose, D-erythrose, and DL-glyceraldehyde by Ce(IV) was studied spectrophotometrically in aqueous H_2SO_4. The reactions were first order in both Ce(IV) and aldose [705]. The effect of acrylamide on the kinetics of oxidation of tartaric acid by Ce(IV) in sulfuric-perchloric acid media has been determined. A polymerization mechanism was proposed [706]. Cerium(IV) trifluoromethanesulfonate was found to be a powerful and selective oxidant of benzyl alcohols and alkylbenzenes to form the corresponding aldehydes or ketones at room temperature in MeCN/H_2O = 1/1 solution [707]. The hemiketal (**387**) was oxidized by $(NH_4)_2Ce(NO_3)_6$ in acetonitrile-water to give 100% yield of the helical quinone (**388**) [708].

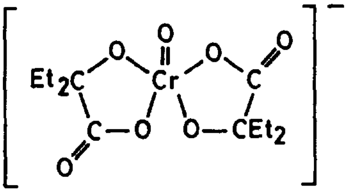


387 **388**

Benzyl alcohols and benzaldehydes were oxidized to benzoic acids by $NaVO_3$, NH_4VO_3, or $K_2Cr_2O_7$ in dilute perchloric acid [709]. The effect of pressure on the rates of oxidation of polyhydric alcohols by vanadium(V) has been studied. Radical formation by H-atom transfer was proposed as the mechanism of the rate-determining decomposition of a substrate-vanadium(V) complex [710]. Oxidation of D-galactose by vanadium(V) in aqueous acid solutions is first order in vanadium, second order in $HClO_4$ (or HCl) and shows weak catalysis by $RuCl_3$ [711].

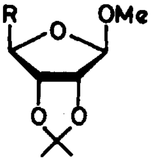
Acid improved procedure for the preparation of pyridinium chlorochromate (Corey's reagent) has been described. The synthetic utility of this reagent increased if it was applied in anhydrous acetic acid for the oxidation of alcohols [712]. Based on experimental data (among them kinetic isotope studies) a mechanism for the oxidation of primary and secondary alcohols by pyridinium chlorochromate and two other, newly synthesized Cr(VI) reagents has been proposed [713]. Trimethylammonium chlorochromate, alone or in the presence of molecular sieves, oxidizes alcohols in aprotic solvents to carbonyl compounds with quantitative yields [714]. Oxidation of cyclohexanol by CrO_3 in aqueous medium is accelerated by micelles of sodium lauryl sulfate. Catalysis has been attributed to enhanced concentration of the substrate in the micellar phase [715]. The activity and selectivity of CrO_3 + Me_3SiCl for oxidation of alcohols could be significantly improved by the addition of alumina. For example, 1-hexanol was oxidized to hexanal with 83% yield [716]. Oxidation of cholesterol with pyridinium dichromate in DMF at room temperature gave cholest-Δ^4-3,6-dione in 63% yield [717]. Immobilized pyridinium dichromates were prepared using crosslinked co-poly(styrene-4-vinylpyridine) converted with HBr or alkyl bromides as supports. These reagents were used for the oxidation of secondary alcohols to ketones [718]. Oxidation of ethylene glycol with pyridinium chlorochromate is first order in both oxidant and substrate and the reaction is catalyzed by acids. The thermodynamic parameters have been determined [719].

Primary aliphatic and aromatic alcohols were oxidized to aldehydes in up to 94% yield in Et_2O by treatment with aqueous chromic acid at 25-30 °C [720]. Oxidation of aromatic alcohols with CrO_3 in the presence of "wet-aluminium-oxide" in hexane at room temperature gave the corresponding carbonyl compounds in excellent yields [721]. The kinetics of oxidation of substituted benzyl alcohols by quinolinium dichromate in the presence of an acid were studied. The observed experimental data were rationalized in terms of a hydride ion transfer in the rate-determining step [722]. The kinetics of oxidation of benzyl alcohols by bis[2-ethyl-2-hydroxybutanoato]oxochromate(V) has been investigated in aqueous acetic acid in the presence of $HClO_4$. A mechanis involving hydride transfer from alcohol to Cr(V) was suggested [723]. Oxidation of benzyl alcohol by $K_2Cr_2O_7$ in aqueous $HClO_4$ in the presence of sodium dodecyl sulfate (SDS) micelles follows a pseudo-first order kinetics and the rate increases with increasing surfactant concentration. The rate of oxidation of 1-hexanol, however, reaches a maximum and then decreases with SDS concentration [724]. Kinetic deuterium isotope effect studies have been made on the oxidation of several benzhydrols by $K_2Cr_2O_7$ both in the presence and absence of oxalic acid. The k_H/k_D values indicate a direct transition from Cr(VI) to Cr(III) in the cooxidation reaction [725]. The kinetics of oxidation of unsaturated primary alcohols to the corresponding aldehydes with the Cr(V) complex (**389**) have been investigated in aqueous AcOH/$HClO_4$. The order of reactivity was cinnamyl>crotyl>allyl alcohol; the reactivity of these alcohols was about two orders of magnitute higher than that of saturated primary alcohols [726].



389

Oxidation of glycolic acid by chromic acid was studied in strong acid solutions. The reaction rate depended not only on the acidity of the medium but also on the mineral acid used [727]. Oxidation of lactic acid by CrO_3 was studied at high concentrations of $HClO_4$, HNO_3, and H_2SO_4. The reaction rate depended not only on the acidity of the medium but also on the nature of the mineral acid [728]. Oxidation of mandelic acid by chromic acid has been studied in highly acidic media [729]. Oxidation of tartaric acid by $Na[(Et_2COHCH_2COO)_2CrO].H_2O$ to glyoxal is first order in both oxidant and substrate. Experiments support the formation of a radical intermediate and the intermediacy of a Cr(IV) complex [730]. Oxidation of the ribofuranoside derivative (**390**; R = CH_2OH) with pyridinium dichromate yields, in addition to the expected aldehyde (**390**; R = CHO) also lactone (**391**). A mechanism was proposed [731].



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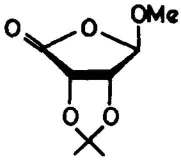
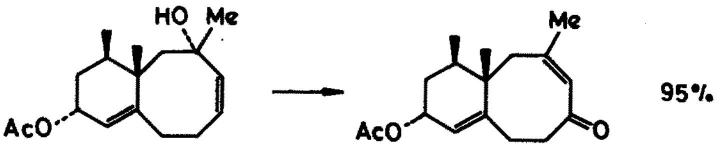


391

The oxidative rearrangement of the allylic alcohol (392) to the α,β-unsaturated ketone (393) by pyridinium dichromate has been used as a step in the direct synthesis of heolemnanyl acetate [732].

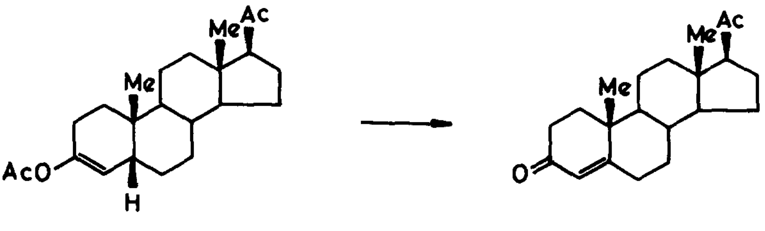


392 393

Treatment of tetrahydrofuran methanol derivatives (for example (394)) with pyridinium chlorochromate in boiling CH_2Cl_2 gives the corresponding γ-butyrolactones with the loss of one or more carbon atoms in 52-95% isolated yields [733].

394

Oxidation of benzyl ethers by pyridinium fluorochromate in aqueous acetic acid was found to be first order each in substrate, oxidant, and pH [734]. In the chromic acid oxidation of partially acylated sugar derivatives to form the respective uronic acids, acyl migration to the primary alcoholic group is a frequent cause of interference. It has now been found, that the O-levulinoyl group is far less prone to migration [735]. The kinetics of oxidation of aliphatic aldehydes by pyridinium fluorochromate in DMSO have been determined. A linear isokinetic correlation suggests that all aldehydes are oxidized by the same mechanism. A hidride-ion transfer from the aldehyde to pyridinium fluorochromate was proposed as the rate-determing step [736]. The oxidation kinetics of aromatic aldehydes by Cr(VI) have been determined in perchloric acid. Kinetic and spectrophotometric results indicate the formation of a 1:1 intermediate ester between the reactive Cr(VI) species and protonated benzaldehyde [737]. The enol acetate (**395**) was oxidized with $CrO_3.2py$ to the enone (**396**). This method was found to be useful also for the synthesis of other Δ^4-3-keto steroids [738].

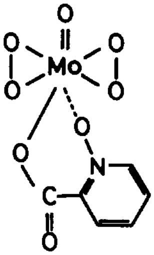


395 396

Oxidation of ascorbic acid by $Mo(CN)_8^{3-}$ in a buffered acidic aqueous methanolic medium was studied and compared with oxidations by $Fe(CN)_6^{3-}$ and $W(CN)_8^{3-}$. The reaction was first order in both oxidant and substrate. The rates decreased in the order Mo>Fe>W [739]. Oxidation of benzoin with $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ was found to be first order in benzoin, oxidant and OH^-. A mechanism was proposed [740]. Treatment of 4-hydroxy[2.2]paracyclophane (**397**) with $[Mo(O_2)_2O].py.HMPA$ in dry CH_2Cl_2 at 0 °C gave (**398**) in 75% yield [741].

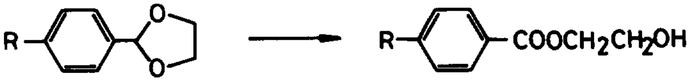
397 398

Primary and secondary alcohols were selectively oxidized to the corresponding aldehyde or ketone even in the presence of other functional groups (like epoxy, C≡C, C=C, and NH) at 50% by the anionic molybdenum picolinate *N*-oxidoperoxo complex (**399**) in CH_2Cl_2 with 60 to 97% isolated yields [742].



399

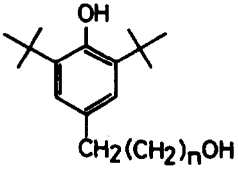
Barium permanganate can be used for the oxidation of alcohols and acyloins to the corresponding carbonyl compounds and of thiols to disulfides in acetonitrile at reflux temperature [743]. Oxidation of 2-methoxy- and 2-ethoxyethanols by permanganate is first order in substrate and higher than first order in H^+ concentration [744]. A new ultrasound reaction apparatus was applied for the oxidation of alcohols with $KMnO_4$. With the new apparatus $PhCH_2OH$ was converted to PhCO with 90% yield [745]. Potassium permanganate adsorbed on alumina was used to oxidize alcohols to carbonyl compounds [746]. A kinetic study of the oxidation of formic acid by permanganate indicated that the reaction is autocatalyzed by colloidal MnO_2 and by Mn^{2+} formed as intermediates and reaction products, respectively. Including the non-catalytic reactions six different reaction pathways were supposed [747]. Oxidation of the cyclic acetals (**400**; R = H, MeO, Me) by $KMnO_4$ under phase-transfer conditions (dichloromethane/water, $PhCH_2NEt_3{}^+Cl^-$) gave the hydroxyalkyl carboxylates (**401**) with good yields [748].



400 401

Oxidation of L-ascorbic acid by Fe(III) in the presence of 2,2'-bipyridyl is first order each in substrate and oxidant. The kinetic results provide evidence for the reaction between $Fe(bpy)_2{}^{3+}$ and the non-ionized form of ascorbic acid as the rate-limiting step [749]. The kinetic study of the oxidation of

L-ascorbic acid by $Fe(CN)_6^{3-}$ in strongly acidic media suggests a mechanism depending on the pH of the reaction mixture [750]. The oxidation of ascorbic acid by $Fe(CN)_6^{3-}$ and $W(CN)_8^{3-}$ has been studied. The reaction has been found first order in both oxidant and substrate. Entropies and enthalpies of activation were calculated [751]. Oxidation of 2,6-di-*tert*-butylphenols (**402**; n = 1,2) by $K_3[Fe(CN)_6]$-KOH in benzene gave the methylenequinones (**403**) in 43 and 60% yield [752].



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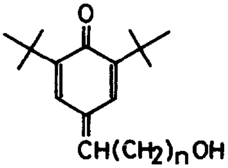


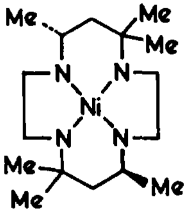
403

The kinetics of oxidation of alcohols by ruthenate and perruthenate ions have been determined. Both ions give concave Hammett plots which probably can be explained by the involvement of free radical-like transition states formed by the decomposition of organometallic intermediates [753]. The kinetics of oxidation of ascorbic acid and substituted 1,2- and 1,4-dihydroxybenzene compounds (H_2Q) by $Ru(CN)_6^{3-}$ have been investigated in acidic perchlorate media. One-electron oxidations of H_2Q or HQ^- to the corresponding semiquinone or ascorbate radical intermediate were proposed as rate-determing steps [754]. Several Ru(VI) oxo complexes of the types $Ru_2O_6L_4$, $RuO_2L_4^{2+}$, $RuO_2Cl_2L_2$, and $RuO_2Cl_3L^-$ (L = pyridine or pyridine derivatives) have been prepared. These complexes function as overall 4-electron oxidants (per Ru atom) and convert alcohols into carbonyl compounds. With *N*-methylmorpholine-*N*-oxide as cooxidant they act as catalysts [755].

The kinetics of the oxidation of L-ascorbic acid (AH_2) by chloropentamminecobalt(III) ions was studied by means of spectroscopic methods and using a stopped-flow technique. A mechanism involving the radical $AH^\bullet$ for the acidic and the radical $A^{\bullet -}$ for the basic region was suggested [756,757].

Kinetic parameters were reported for the second-order oxidations of benzenediols (4-*tert*-butylcatechol, hydroquinone, and 2-*tert*-butylhydroquinone) to the corresponding quinones with $IrCl_6^{2-}$ in several solvents and solvent mixtures [758]. The peroxo complex $(MeC(CH_2PPh_2)_3)IrCl(\eta^2-O_2)$ transforms primary alcohols (methanol, ethanol, propanol, butanol, and benzyl alcohol) into carboxylates at room temperature in a stoichiometric reaction [759].

The Ni(III) complex $(NiL)HSO_4$ (NiL = **404**) oxidizes *para*- and *meta*-cresol first to the corresponding hydroxybenzyl alcohols and further to the corresponding hydroxybenzaldehydes. No hydroxybenzoic acids are formed [760].



404

The oxidation of ascorbic acid by Cu(II) in aqueous perchloric acid has been studied under anaerobic conditions. Both acetate and chloride ions accelerate the reaction [761]. The rate constant for one-electron oxidation of D-lyxose with Cu^{2+}, Fe^{3+}, and Ce^{4+} increases semilogarithmically with the redox potential of the oxidant [762]. Oxidation of oxalate and malonate by diperiodatocuprate(III) is first order in both substrate and oxidant and is inhibited by excess KIO_4. A free radical mechanism was proposed [763]. Ethers (**405**) were oxidized and cleaved to the corresponding aldehydes and ketones by $Cu(NO_3)_2$ on silica gel under mild conditions (reflux in CCl_4 or isooctane as solvent). Overoxidation of aldehydes was not observed [764].

405

Kinetic data were obtained for the oxidation of EtOH, iPrOH, and $PhCH_2OH$ by [ethylenebis(biguanidine)]silver(III) in aqueous $HClO_4$ acid solutions. The reactions were found to be ESR-silent [765].

See also [525, 696, 768, 791, 798-800].

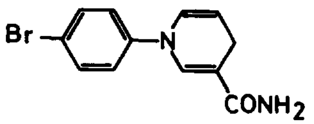
d) Oxidation of N-Containing Organic Compounds

The mechanism of oxidation of alkyl and aryl derivatives of aniline and *p*-phenylenediamine by Ce(IV) in aqueous perchloric acid solution has been studied by UV-spectroscopic methods [766]. Second-order rate constants for the oxidation of picolines and lutidines by cerium perchlorate have been determined. The rate of oxidation increased with increasing electron density on the nitrogen atom [767].

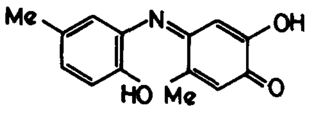
Imidazolium and 2-methylimidazolium chlorochromates [HL] [$ClCrO_3$] (L = imidazole, 2-methylimidazole) have been prepared. The compounds oxidize alcohols, ketoximes, and aldoximes to the corresponding carbonyl compounds [768]. 3'-Keto-5'-O-tritylthymidine was prepared in high yield by molecular sieve-catalyzed pyridinium dichromate oxidation of 5'-O-tritylthymidine [769].

Oxidation of DL-alanine by $KMnO_4$ in aqueous H_2SO_4 was found to be first order with respect to both substrate and oxidant [770]. The kinetics of oxidation of DL-isoleucine by acid permanganate have been investigated by spectrophotometric methods. The overall rate expression was determined [771]. The stoichiometry and kinetics of oxidation of leucine by acid permanganate have been determined. A Mn(IV) intermediate was identified spectroscopically [772]. The oxidation of serine by acid permanganate is faster in the presence of sodium dodecyl sulfate (SDS). The reaction is retarded by H^+ in the absence of SDS but catalyzed in the presence of SDS [773]. Autocatalytic behavior ascribed to Mn^{2+} was observed in the oxidation of L-serine by MnO_4^-. Two oxidation pathways were proposed which correspond to the presence or absence of Mn^{2+} [774]. The kinetics of Mn(III) oxidation of L-histidine in aqueous H_2SO_4 was studied spectrophotometrically. Second order kinetics in [Mn(III)], first order in [histidine], and a negative effect of increasing [H^+] and [Mn(II)] was found [775].

Oxidation of lysine, arginine, and histidine by alkaline $Fe(CN)_6^{3-}$ is first order in substrate and oxidant, but is independent of alkali concentration. The reaction proceeds via formation of α-imino acid which undergoes then hydrolysis to give the corresponding α-keto acid [776]. The kinetics of oxidation of dithiocarbamate anions to thiuram disulfides by $Fe(CN)_6^{3-}$ and I1 other substitution-inert metal complexes have been investigated. Outer-sphere electron transfer, resulting in the formation of dithicarbamate thio radicals, was proposed as the rate-determining step [777]. The kinetics of oxidation of various 1-(4-substituted phenyl)-1,4-dihydro- nicotinamides, e.g. (**406**) with $Fe(CN)_6^{3-}$ were determined. The results suggest that the rate-determining step is the loss of an electron from the substrates [778].


406

Oxidation of 2-amino-4-methylphenol by $Fe(CN)_6^{3-}$ in AcOH yields several quinonimine and oxazine derivatives like (**407**) and (**408**) [779].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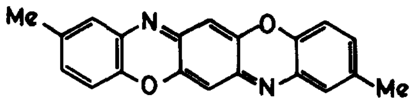
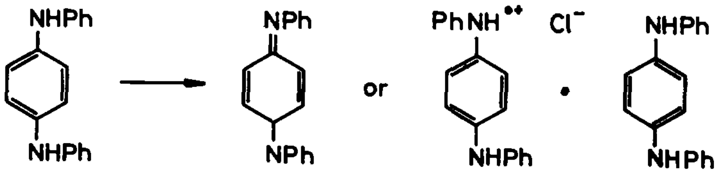
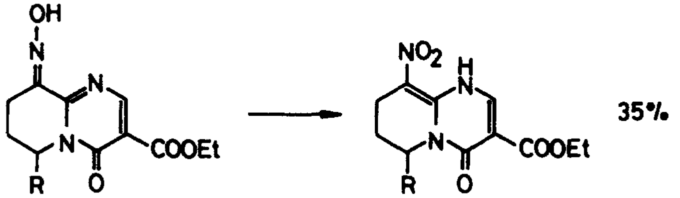

408

Oxidation of *N,N'*-diphenyl-*p*-phenylenediamine (**409**) with $FeCl_3.6H_2O$ in aqueous acetone gives - depending on the amount of oxidant used - the diimine (**410**) or the radical cation salt (**411**) [780].


409 410 411

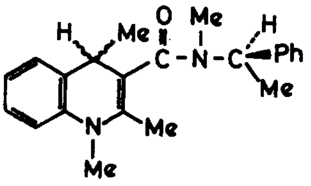
Clay-supported iron(III) nitrate was found to oxidize (**412**; R = H, Me) to (**413**) in CH_2Cl_2 at 25 °C [781].



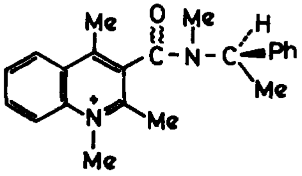
412 413

Oxidation of 3,4-dihydroisoquinoline-1(2H)-ones with RuO_4 gives the corresponding isoquinoline-1,3,4(2H)-triones in good yields [782].

The two diastereomers of the NADH model compound (**414**) are oxidized by $Fe(phen)_3^{3+}$ or $Co(bpy)_3^{3+}$ to (**415**). In this latter compound the free rotation of the carbonyl group is hindered and therefore two stereoisomers may be formed. The stereospecificity of this oxidation is influenced by the addition of amines; this indicates that the stereodetermining step in the reaction with the metal ion involves a process which is the subject of base-catalysis [783].



414



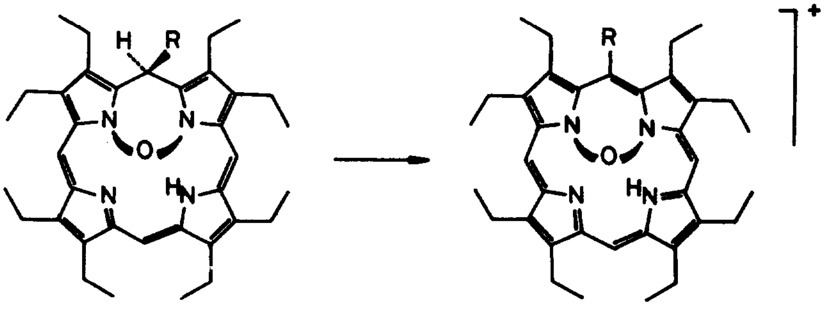
415

Oxidation of aliphatic amines by $IrCl_6^{2-}$ is first order each in Ir(IV), amine, and H^+ concentration in the pH range between 3.25-4.5. A suitable mechanism was suggested [784].

Oxidation of 1,5-substituted 1,2,3-triazolines (**416**; R,R' = Ph, substituted phenyl, pyridyl) with NiO_2 in refluxing benzene provides an efficient general route for the synthesis of a wide variety of both 1,5-diaryl- and 1-aryl-5-heteroaryl-1H-1,2,3-triazoles (**417**) [785].

416 **417**

The kinetics of oxidation of benzaldoxime by Cu(IO$_4$)$_3^+$ was studied photometrically in tBuOH/H$_2$O; the rate was first order in both oxidant and substrate [786]. The phlorins (**418**; Q = *cis*-PhCH=CHPh; R = CN, C=CPh, CH$_2$COMe, CH$_2$COPh, CH$_2$CN) were oxidized with Cu(BF$_4$)$_2$ to give the corresponding 5-alkylporphyrins as monoprotonated forms (**419**) [787].

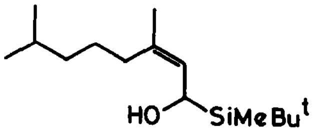


418 **419**

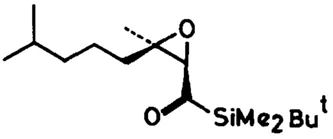
See also [640].

e) *Oxidation of Si-, P-, S-, or Halogen-Containing Organic Compounds*

Based on the kinetics of the pyridinum chlorochromate oxidation of phosphinic, phenylphosphinic, and phosphonic acids a rate-determining hydride ion transfer from the P-H bond to the pyridinum chlorochromate was proposed [788]. Silyl allyl alcohols like (**420**) were transformed into the corresponding epoxy silyl ketones (e.g.**421**) by epoxidation with tBuOOH followed by oxidation with Collins reagent (CrO$_3$/pyridine) [789].

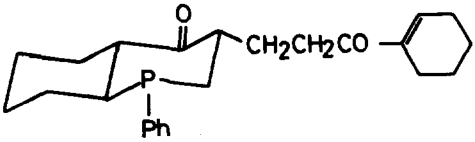


420



421

The phosphine (**422**) was oxidized with $KMnO_4$ to the corresponding phosphine oxide [790].

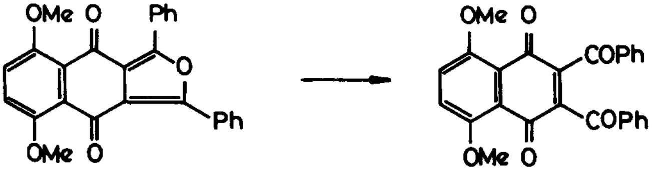


422

The *dioxoruthenium(VI) complexes* $O_2Ru(py)_2(O_2CR)$ *were found* to be active but non-selective oxo transfer agents in stoichiometric oxidations of olefins, phenols, alkanes, and ethers in CH_2Cl_2 at room temperature. A quantitative yield of triphenylphosphine oxide was obtained in the reaction with PPh_3 in acetonitrile [791]. The complex $[Ph_4P][RuO_2(OAc)Cl_2]$ was found to be an efficient two-electron oxidant at room temperature, both stoichiometrically and, in the presence of *N*-methylmorpholine-*N*-oxide as a co-oxidant, catalytically for halides, alcohols, sulfides, and phosphines. For example in MeCN, in the presence of powdered molecular sieves, benzyl bromide was converted to benzaldehyde (49% yield) in 3 h with a catalytic turnover of 115 [792]. The four-electron dioxo oxidant, *trans*-$[Ru(tpy)(O)_2(H_2O)]^{2+}$ oxidizes arylphosphines at 20 °C in MeCN solution to the corresponding phosphine oxides. It was shown, that both P atoms of chelating diphosphines like dppe are oxidized by the same complex: the key to this mechanism is the intramolecular rearrangement of the oxo group from a *trans* to a *cis* position [793]. Triphenylphosphine *m*-trisulfonate, $P(C_6H_4SO_3Na\text{-}m)_3$, is stoichiometrically oxidized by $RhCl_3.3H_2O$ in aqueous solution under anaerobic conditions. Under aerobic conditions the oxidation becomes catalytic in Rh [794].

A mononuclear (acylperoxo)copper(II) complex, Cu(*m*-chloroperbenzoate) (hydrotris(3,5-diisopropyl-1-pyrazolyl borate)) readily oxidized PPh_3 to $OPPh_3$ at -20 °C [795].

Sulfides are oxidized to sulfoxides by $(NH_4)_2Ce(NO_3)_6$ in AcOH. Kinetic data suggest that a sulfur radical cation is formed in an electron-transfer process; this cation is transformed into the sulfoxide mainly by NO_3^- [796]. Oxidation of *N*-arylsulfonamides with $(NH_4)_2Ce(NO_3)_6$ gives moderate yields of *p*-benzoquinones [797]. Ceric ammonium nitrate oxidizes isobenzofuranquinones (e.g.**423**) to diacylquinones (**424**) but the analogous thiophene derivative (**425**) to (**426**) [798].



423 424

425 426

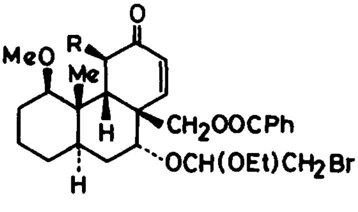
Oxidation of lactic and thiolactic acids by Cr(V) has been studied. Oxidation of lactic acid exhibits saturation kinetics while that of thiolactic acid is first order in both reactants. Probably the Cr(V)-S bond is weaker than the Cr(V)-O bond and electron transfer mediated through the sulfur system is facile [799]. Oxidation of cysteine, ascorbic acid, and several monosaccharides with Cr(VI) was studied using EPR and absorption spectroscopic methods. Chromium(V) was shown to be a definite intermediate [800]. Aryl methyl sulfides have been oxidized to sulfoxides and olefins to epoxides with the neutral peroxo complex $MoO(O_2)_2(HMPA)$ and the anionic peroxo complex obtained by treating the cetylpyridinium salt $[C_5H_5N(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})$ with H_2O_2. Kinetic data revealed that the anionic complex was more active in sulfide oxidation while the opposite was true in alkene epoxidation [801].

Oxidation of thioacids by acidic permanganate involves the formation of an intermediate thioester and yields a sulfenium cation [802]. The kinetics of oxidation of thiourea by MnO_4^- in aqueous solution at pH 6–8 were studied by the stopped-flow method. Two different mechanisms were proposed for the reaction at pH<7 and pH>7 [803].

Oxidation of cysteine by alkaline $Fe(CN)_6^{3-}$ gives cystine. A radical intermediate was identified by means of ESR spectroscopy [804]. The kinetics of oxidation of (phenylthio)acetates by $K_3[Fe(CN)_6]$ in aqueous NaOH have been determined. The reaction was first order in oxidant, substrate, and OH^-. Rate studies with substituted (phenylthio)-acetates gave an excellent Hammett correlation [805]. Various thiols [806] and thiol acetates [807] were oxidized mostly quantitatively into the corresponding disulfides by $FeCl_3$ in acetonitrile at room temperature in the presence of alkoxystannanes.

Selective hydroxylation of the methyl groups in *p*-toluenesulfonic acid, *p*-ethylbenzenesulfonic acid and ethanol was observed at 80–120 °C with stoichiometric amounts of Na_2PtCl_6 in aqueous solution [808].

Oxidation with $Na_2Cr_2O_7$–H_2SO_4 was applied for the preparation of trichloromethyl ketones ($RCOCCl_3$) from the corresponding secondary alcohols. Yields ranged between 74–92% [809]. Oxidation of 2-chloropropionamide by $KMnO_4$ in alkaline medium is first order in amide and zero order in oxidant. A mechanism was proposed [810]. Oxidation of (**427**) with $Mn_3O(OAc)_7$ gave (**428**) with 67% yield. This method of acetoxylation tolerates ether, ester, and acetal functionalities, but not hydroxyl or ketone groups [811].



427 ; R = H

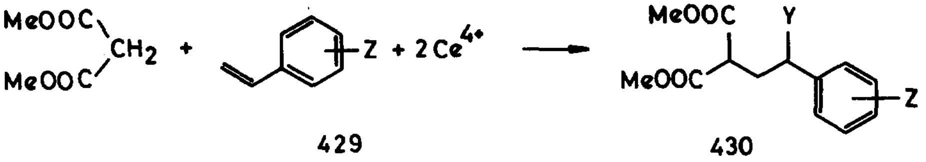
428 ; R = OAc

See also [480, 660].

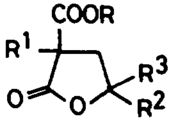
f) Oxidative Coupling Reactions

Oxidation of dimethyl malonate and styrene derivatives (**429**; Z = H, *p*MeO, *p*Me, *p*Cl, *m*Cl, *m*NO_2, *p*NO_2) with $(NH_4)_2Ce(NO_3)_6$ at 20

°C in methanol solution gave the adducts (**430**; Y = ONO_2 and OMe) in about 90% yields [812].



The γ-lactones (**431**) (R = Me, Et, $PhCH_2$; R^1 = H, Me, Bu, aralkyl; R^2 = H, Me; R^3 = hexyl, tBu, alkenyl, aryl) were prepared by oxidation of malonic esters $R^1CH(COOR)_2$ with $Fe(ClO_4)_3 \cdot 9H_2O$ in the presence of olefins $CH_2 = CR^2R^3$ [813].



431

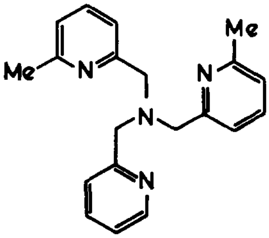
Ruthenium (III) complexes of 2-(phenylazo)pyridine have been prepared. The complexes bring about the oxidative coupling of *N,N*-dimethylaniline and oxidize 1,2-naphthoquinone 1-oxime to the corresponding iminoxy radical [814].

7. Electrooxidation and Photooxidation

The electrochemical oxidation of hydroquinone and catechol have been studied by cyclic voltammetry at glassy carbon electrodes coated with electropolymerized films of metal phthalocyanines. The presence of the polymer coating led to an enhancement of the heterogeneous electron transfer rate [815].

Liquid-phase electrochemical oxidation of sulfate lignin was applied to increase its carboxyl group content. Electron transfer was facilitated in the presence of Cr(III) sulfate [816]. Polyaniline was modified by incorporating $[SiW_{12}O_{40}]^{4-}$ into the polymer. Electrodes coated with this modified polymer showed increased catalytic activity for the oxidation of formic acid [817].

Electrochemical reduction of $[Mn(III)(salen)]^+$ complexes in MeCN solution in the presence of benzoic anhydride, 1-methylimidazole, O_2 and an olefin yields the epoxide of the olefin in as much as 48% yield based on electrochemical charge passed. A manganese-peroxo and a manganese(V)-oxo complex are intermediates of the reaction. Allylic alcohols and ketones are formed as byproducts [818]. The selective oxidation of cinnamyl alcohol to cynnamaldehyde, by the Mn^{2+}/MnO_2 couple incorporated into a Pt-Nafion composite electrode, was examined. The oxidation proceeded smoothly in THF solution and the current efficiency was as high as 85% [819]. The complex $(LMnO)_2(NO_3)_2.6H_2O$ (L = **432**) catalyzes the electrochemical oxidation of benzyl alcohol to benzaldehyde with high selectivity (about 100%) [820].



432

Electrocatalytic hydroxylation of cyclohexane to cyclohexanol, and n-octane to a 1:1:1 mixture of 2-octanol, 3-octanol and 4-octanol occurs in the presence of $[(F_8TPP)FeF_2]^-$ as catalyst [821]. The electrochemical reduction of Fe^{3+} to Fe^{2+} was applied for the regeneration of Fenton's reagent used to hydroxylate aromatic substrates. Based on this method a continuous process was developed for the hydroxylation of benzene and 70% current yield of phenol was achieved. Experiments to apply the same method for the hydroxylation of fluorobenzene were not successful [822]. The electrolytic hydroxylation of benzoic acid and Na benzoate on iron was studied in sulfuric acid or NaCl solutions in the presence of O_2. It was shown that the oxidation of Fe(II) (formed by corrosion) to Fe(III) by O_2 is responsible for hydroxylation [823]. Electrooxidation of ascorbic acid was studied on glassy carbon electrodes modified by the 3,3',3",3"'-tetranitrophthalocyanine complexes of Fe(II), Co(II), Ni(II), and Cu(II). Because the oxidation peak voltage of ascorbic acid was near the oxidation voltage of M(II) to M(III) it was proposed, that the M(II)/M(III) redox sites transport the electrons from ascorbic acid to the electrodes [824].

Methylbenzenes can be electrocatalytically oxidized in MeCN by electrogenerated $Ru(bpy)_3^{3+}$. The kinetics of the process were determined [825]. Electrocatalytic oxidations of alcohols were carried out using $Ru(trpy)(bpy)O^{2+}$ as catalyst. Primary aliphatic alcohols were oxidized to aldehydes, secondary aliphatic and aromatic alcohols to ketones, and allyl and benzyl alcohols to carboxylic acids [826]. Electrooxidation of benzyl alcohol in aqueous sulfuric acid at a ruthenium oxide-coated Ti anode has been studied. A mechanism was proposed for the reaction [827]. Optimum conditions for the electrooxidation of 1,3-dichloro-2-propanol to 1,3-dichloroacetone by using a double redox system consisting of Ru(VIII)/Ru(IV) and $[Cl^+]/Cl^-$ have been determined. In an AcOEt-aqueous NaCl (2:3 v/v) system buffered at pH 2-4 in a divided cell at 0-5 °C the oxidized product was obtained in 98% selectivity with 92% current efficiency. Similar results were reported in the case of other halohydrins [828].

Electrocatalytic oxidation of cysteine at glassy carbon electrodes coated with a Nafion-$[Os(bpy)_3]^{2+}$ film was studied [829].

Meso-tetrakis(1-methylpyridinium-4-yl)porhinatocobalt(I), $[(TM_{py}P)Co]^{3+}$, was found to be active in the electrocatalytic epoxidation of cyclohexene by O_2 in the presence of benzoic anhydride (which is reduced to benzoate) [830].

Irradiating a solution of $K_2Cr_2O_7$, Bu_4NBr, and water by light in the presence of toluene leads to the oxidation of toluene by air to benzaldehyde in yields approaching 100% [831]. The photocatalytic oxygenation of cyclohexene or α-pinene with air using (TPP)Mo=O(OMe) or $[(TPP)Nb]_2O_2$ at RT results in the formation of epoxides and of oxygenated products formed by an allylic hydrogen abstraction mechanism. Radical intermediates were detected by ESR and spin-trapping experiments [832]. Photochemical oxidation of toluene and ethylbenzene with O_2 catalyzed by $PMo_{12}O_{40}^{3-}$ gave equimolar amounts of benzaldehyde and acetophenone [833]. In the anaerobic photooxidation of thioethers by polyoxotungstates $W_{10}O_{32}^{4-}$ simultaneous oxidative C-H bond cleavage and reductive C-S bond cleavage were observed at ambient temperature in MeCN solution. Under aerobic conditions, $W_{10}O_{32}^{4-}$

catalyzes the complete oxidative conversion of thioethers to sulfoxides and sulfones [834].

A photochemically driven biomimetic oxidation of alkanes and alkenes which operates two catalytic cycles has been developed. The first is a reductive photoredox cycle which uses Sn or Sb porphyrins to generate the necessary co-reductant and the second is the oxidative cycle in which Fe or Mn porphyrins catalyze the oxidation of hydrocarbons with O_2 [835]. Photooxidation of toluene in AcOH by O_2 to acetaldehyde is catalyzed by *o*-phenanthroline or α,α'-bipyridyl. The reaction is accelerated by the addition of $FeCl_3$ [836]. Photooxidation of phenol by O_2 is catalyzed by a suspension of oxygenated TiO_2 (anatase). The rate of this photoprocess is considerably increased in the presence of Fe^{3+} [837].

Complexes of the type $M(L\text{-}L)N_3$ (M = Pd(II) or Pt(II); L-L = bpy, phen, 2,2'-biquinoline, or 4,7-diphenyl-1,10-phenanthroline) act as sensitizers in the photooxidation of 2,2,6,6-tetramethyl-4-piperidinol in DMF to give the nitroxide radical [838].

The competitive photooxygenation of ethylbenzene and cyclohexane in the presence of $CuCl_2$ or $FeCl_3.6H_2O$ has been studied. The reactivity of the CH_2 group in PhEt relative to cyclohexane was 2.6 and 1.7, respectively [839]. The photocatalytic activity of TiO_2 in the oxidation of formic acid by O_2 is considerably enhanced in the presence of copper ions. The proposed mechanism of the reaction is based upon a redox cycle between Cu^{2+} and Cu^{+} species adsorbed on the surface of TiO_2 [840].

The kinetics of photooxidation of leuco thionine with uranyl nitrate was determined [841].
See also [675].

V. REVIEWS

Transition metal-hydrogen and metal-carbon bond strengths: the keys to catalysis. 505 refs. [842].

Homogeneous catalysis by transition-metal complexes. 309 refs. [843].

Homogeneous catalysis of organic reactions by transition metal complexes. 321 refs. [844].

The use of transition metal clusters in organic synthesis. 425 refs. [845].

Assembly of molecules in zeolites (catalytic activity of bimetallic carbonyl clusters). 5 refs. [846].

Current status of the problem of preparing catalysts through the fixing of metal complexes on the surfaces of inorganic supports. 91 refs. [847].

Metal carbonyl derivatives of lanthanides, actinides and early transition elements (applications in catalysis). 81 refs. [848].

Enantioselective catalysis with chiral cobalt and copper complexes. 67 refs. [849].

Palladium and platinum (catalysis by Pd and Pt complexes). 1160 refs. [850].

This(hydroxymethyl)phosphine platinum metal complexes: catalysts for water-based reactions. 4 refs. [851].

Opportunities in homogeneous catalysis (hydroformylation and reductive carbonylation) [852].

Syngas reactions involving C_8 substances (hydroformylation). 19 refs. [853].

Tetracarbonylhydridoferrates, $MHFe(CO)_4$: Versatile tools in organic synthesis and catalysis (reductions, water gas shift reaction, hydroformylation). 170 refs. [854].

Heterometallic clusters in catalysis (hydrogenation, hydroformylation). 320 refs. [855].

Lewis acid site-promoted carbon monoxide insertion in alkene hydroformylation on zeolite entrapped Rh-Fe bimetallic cluster-derived catalysts. 12 refs. [856].

Heterogenization of rhodium hydroformylation catalysts. 44 refs. [857].

Thermodynamic studies of the hydrogenation and reductive coupling of carbon monoxide by rhodium(II)porphyrins. 17 refs. [858].

Synthesis, reactivity, and redistribution reactions of homo- and hetero-binuclear Pd(II) and Pt(II) complexes (hydrogenation, hydroformylation). 16 refs. [859].

New palladium-complex catalysts for selective hydrogenation. 61 refs. [860].

Soluble metal-polymer catalysts in the hydrogenation of organic compounds. 51 refs. [861].

Enantioselective catalysis with metal complexes. 253 refs. [862].

Design of super catalysts for asymmetric hydrogenations and their utilization in practical asymmetric syntheses. 51 refs. [863].

Enantioselective syntheses with optically active transition metal catalysts. 285 refs. [864].

Right or left - this is the question (enantioselective catalysis with transition metal compounds). 24 refs. [865].

BINAP: an efficient chiral element for asymmetric catalysis (hydrogenation). 49 refs. [866].

Carbonyl complexes as homogeneous and supported catalysts (transfer hydrogenation). 28 refs. [867].

Photocatalytic carbon-hydrogen bond activation by $RhCl(CO)(PMe_3)_2$ (carbonylation, dehydrogenation). 14 refs. [868].

Photochemical dehydrogenation of alkanes catalyzed by *trans*-carbonylchlorobis(trimethylphosphine)rhodium: aspects of selectivity and mechanism. 6 refs. [869].

Control of metal-catalyzed reactions by organic ligands: from corrinoid and porphinoid metal compounds to tailor-made catalysts for asymmetric synthesis (conjugate reduction of unsaturated esters). 57 refs. [870].

Catalytic properties of metal hydrides. 91 refs. [871].

A new stage in the development of transition metal alumohydrides (hydrogenation). 87 refs. [872].

Structural and catalytic chemistry of transition-metal aluminium hydrides. 28 refs. [873].

Samarium diiodide as a useful reagent in organic synthesis (reductions). [874].

Metal complexes in conversions of saturated hydrocarbons of petroleum and gas (oxidation, carbonylation). 115 refs. [875].

Soluble polymer-bound catalysts (oxidation, hydrogenation). 28 refs. [876].

Some investigations in homogeneous catalysis (hydrogenation, oxidation). 17 refs. [877].

Synthesis and catalytic activity of carbonyl palladium clusters (hydrogenation, oxidation). 27 refs. [878].

Platinum group metals in phase-transfer catalysis (carbonylation, oxidation, reduction). 96 refs. [879].

Recent advances in catalytic asymmetric reactions promoted by transition metal complexes (hydrogenation, oxidation) 148 refs. [880].

Enantioselective synthesis of non-racemic chiral molecules on an industrial scale (asymmetric hydrogenation, epoxidation). 47 refs. [881].

Metallaoxetanes as intermediates in oxygen-transfer reactions - reality or fiction? 198 refs. [882].

Peroxo complexes of transition metals in the oxidation of organic substrates: some examples of selectivity (oxidation of thioethers and allyl alcohols). 57 refs. [883].

Transition metal dioxygen complexes as intermediates in homogeneous catalytic oxidations. 128 refs. [884].

Organometallic oxidation catalysts. 441 refs. [885].

Selective oxidations of organic substrates with hydroperoxides catalyzed by Group VIII transition metals. 320 refs. [886].

Recent progress in metalloporphyrin-catalyzed oxidation and oxygenation. 217 refs. [887].

Biomimetic catalysts for selective oxidation in organic chemistry. 35 refs. [888].

Asymmetric dihydroxylation via ligand-accelerated catalysis. 6 refs. [889].

Surfactant-assisted permanganate oxidation of aromatic compounds. 6 refs. [890].

Homogeneous catalysis of epoxidation of olefins by mono- and binuclear Schiff base complexes (Fe and Mn). 28 refs. [891].

Status and perspectives of Re chemistry in catalysis (epoxidation). 34 refs. [892].

A guided tour of electron transfer reactions (oxidations with $K_3[Fe(CN)_6]$. 38 refs. [893].

Organic oxidations by Os and Ru complexes. 71 refs. [894].

Autoxidation catalysts bound to polymer colloids (Co catalysts). 53 refs. [895].

Expanding industrial application of palladium catalysts (oxidative reactions). 89 refs. [896].

Photocatalysis induced by light-sensitive coordination compounds (photooxidation). 45 refs. [897].

List of Abbreviations

acac	acetylacetonate
As	Annual Survey on Hydroformylation, Reduction and Oxidation
BDPP	see Fig. 113
BINAP	see Fig. 64
Bn	benzyl, $PhCH_2-$
Boc	*tert*-butoxycarbonyl, $-COOBu^t$
BPPM	see Fig. 115
bpy	2,2'-bipyridine
Bz	benzoyl, PhC(O)-
chiraphos	see Fig. 112
Cl_4TPP	*meso*-tetrakis(*p*-chlorophenyl)porphinato
Cl_8TPP	*meso*-tetrakis(2,6-dichlorophenyl)porphinato
COD	1,5-cylooctadiene
Cp	cyclopentadienyl, $\eta^5-C_5H_5$
Cp^*	pentamethylcyclopentadienyl, $\eta^5-C_5Me_5$
Cy	cyclohexyl
DIOP	see Fig. 116
DIPAMP	see Fig. 67
dmgH	dimethylglyoxime
dpe	*cis*-1,2-bis(diphenylphosphino)ethylene, *cis*-$Ph_2PCH=CHPPh_2$
dppb	1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
dppp	1,3-bis(diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$
ee	enantiomeric excess

F$_{20}$TPP	*meso*-tetrakis(pentafluorophenyl)porphinato
HEPES	(N-(2-hydroxyethyl)piperazine-N'-ethanesulfinic acid
HMPA	hexamethylphosphoric triamide
ment	menthyl
NBD	norbornadiene
norphos	see Fig. 113
OEP	2,3,7,8,12,13,17,18-octaethylporphinato
Pc	phthalocyanato
PPN	bis(triphenylphosphine)iminium cation, (Ph$_3$P)$_2$N$^+$
py	pyridine
RT	room temperature
salen	N,N'-bis(salicylidene)-ethylenediaminato, see Fig. 273
saloph	N,N'-bis(salicylidene)-*o*-phenylenediaminato, see Fig. 22
St	stearate, n-C$_{17}$C$_{35}$COO-
terpy	2,2':6'2"-terpyridine
TfO	trifluoromethanesulfonate(triflate), CF$_3$SO$_3$-
tmen	N,N,N',N'-tetramethylethylenediamine
TMP	*meso*-tetramesitylporphinato
TPP	*meso*-tetraphenylporphinato
TPPTS	*meta*-trisulfonated triphenylphosphine Na salt, P(C$_6$H$_4$SO$_3$Na-*m*)$_3$
TTP	*meso*-tetratolylporphinato

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