TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

ANNUAL SURVEY COVERING THE YEAR 1988*

László Markó

Institute of Organic Chemistry, University of Veszprém,
H-8200 Veszprém, Hungary

CONTENTS

---

[*] No reprints available
Previous Annual Survey see J.Organomet.Chem. 357 (1988) 481.

I. THEORETICAL CALCULATIONS

The potential energy profile for the full catalytic cycle of olefin hydrogenation by $Rh(PPh_3)_3Cl$ has been studied with the *ab initio* MO method. Oxidative addition of H_2 and olefin coordination are exothermic and have no significant barrier. Olefin insertion combined with the first portion of isomerization of the resultant trans hydride alkyl complex to a cis complex constitutes the rate determining step [1,2].

Quantum chemical calculations were performed on the catalytically active species ($HCo(CO)_3$, $HCo(CO)_4$, and phosphine substituted derivatives) involved in cobalt carbonyl-catalyzed hydroformylation [3].

II. HYDROFORMYLATION AND RELATED REACTIONS OF CO

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

NaY zeolite-encapsulated $Rh_6(CO)_{16}$, reduced Rh_6 clusters, and bimetallic RhFe clusters were prepared and used as catalysts for the synthesis of hydrocarbons and lower alcohols from CO + H_2 [4].

The development and operation of a liquid-phase hydrogenation process for manufacturing of MeOH from synthesis gas using $Ni(CO)_4$ or $Fe(CO)_5$ were described [5]. Synthesis of EtOH from CO + H_2 with $Ru_3(CO)_{12}$ as catalyst dissolved in a high boiling solvent was studied in a continuous reactor at 220-240°C and 400-500 bar. The main byproducts were MeOH, PrOH, MeOAc, EtOAc, and CH_4. All these products left the reactor with the unreacted synthesis gas. If the small amount of Ru that evaporated with the products was replenished the system could be kept going for 40 hours [6]. Ethanol was produced with good selectivity from CO + H_2 at 220°C and 850 bar with homogeneous catalysts composed of Ru and Co together with alkali metal halide or Me_4NX promoters in methylpyrrolidinone-tetraglyme solvent [7].

Formaldehyde and glycolaldehyde have been identified as intermediates of ethylene glycol synthesis from CO and H_2 catalyzed by catalyst systems composed of Ru carbonyls and halide salts. At low temperature the rate of formaldehyde formation was found to be the rate-determining step. Selectivity of glycol aldehyde formation increased if a Rh complex was added to this catalyst system [8]. Addition of amines improved the activity and selectivity of Rh catalysts for the direct synthesis of ethylene glycol from CO and H_2 under high pressure (1800 bar). Bulky amines like triisobutylamine or tribenzylamine were especially effective. The optimum amine:Rh ratios for ethylene glycol formation strongly depended on the polarity of the solvent [9].

The reaction between CO_2, H_2 and Me_2NH to yield dimethyl formamide

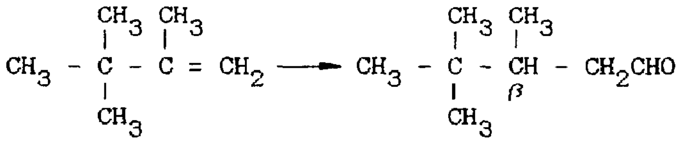
$$CO_2 + H_2 + Me_2NH \longrightarrow HCONMe_2 + H_2O$$

was realized with the diplatinum complex $Pt_2(\mu\text{-dppm})_3$ as catalyst under mild conditions (25-100°C, 1-100 bar). The reaction is reversible; at higher temperatures and lower pressures DMF was decomposed by water into CO_2, H_2 and Me_2NH. The selectivity of this new reaction was found to be 90-95%, some Me_3N was formed as byproduct [10].

2. Hydroformylation

a) Co Catalysts

If hexene-1 is added to a THF solution of $CoCl_2$ and $Co_2(CO)_8$ (1:1) and the reaction mixture treated with CO and H_2 (1:1, total pressure 600 mmHg) at room temperature, C_7 aldehydes are formed in a slow reaction (one day or more). Dihydrogen is activated under these unusually mild conditions by highly polarized Co^{2+} cations generated from $CoCl_2$ [11]. Stoichiometric hydroformylation of allylbenzene with $HCo(CO)_4$ is catalyzed by $Co_2(CO)_8$. The main aldehydic product is PhCHEtCHO which is formed via a mechanism characteristic for aliphatic olefins and not by one operative for styrenes [12]. Stoichiometric hydrogenation and hydroformylation of cyclopentene with $HCo(CO)_4$ has been studied under 100 bar D_2 pressure. About 30% of the alkane and aldehyde formed contained deuterium showing that some "semi-catalytic" reaction also took place under such conditions [13]. Deuterioformylation of 2,2,3-trimethyl-1-butene (**1**) leads to labeled 3,4,4-trimethylpentanal (**2**) as the sole aldehyde product; in the β-position to the aldehyde group mainly H is found in the case of cobalt while in the case of rhodium the product has only D on that position. This suggests different mechanisms for the two metals [14].



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{C}=CH_2 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{\beta}{CH}}-CH_2CHO}$$

1 **2**

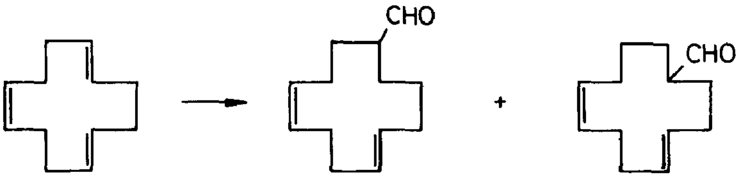
The complex $Sn[Co(CO)_4]_4$ catalyzes the hydroformylation of 1-hexene with rather low activity. In the presence of propylene glycol significant amounts of acetals are formed - more than in the presence of $Co_2(CO)_8$ suggesting, that the mixed metal complex promotes the consecutive aldolization of the aldehydes formed [15]. Hydroformylation of $tBuCH=CH_2$ to $tBuCH_2CH_2CHO$ (25% conversion after 24 hours) is catalyzed by $CoRh(CO)_7$ at 0°C and 10 bar (H_2:CO =4:1). Pure $HCo(CO)_4$, $Co_2(CO)_8$, or $Rh_4(CO)_{12}$ show very little, if any, catalytic activity under these conditions [16].

See also [41].

b) Rh Catalysts

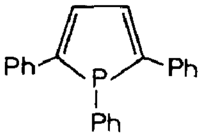
Regioselectivity of the Rh-catalyzed hydroformylation of 1-hexene was investigated [17]. Hydroformylation of dimethyl itaconate with Rh carbonyl catalyst gives preferentially dimethyl 2-(formylmethyl)butanedioate. In the presence of phosphines this regioselectivity is completely reversed [18]. The hydroformylation of cyclohexene at low pressure (34 bar CO + H_2) and 125°C with $Rh_4(CO)_{12}$ as catalyst was found to be first order each in catalyst, olefin, CO, and H_2 concentration. This suggests that under such conditions the reaction is catalyzed by a Rh_4 carbonyl cluster species [19]. Hexene-1 was hydroformylated at 60-100°C and 20-60 bar using $[Rh(CO)_2Cl]_2$ or $Rh_4(CO)_{12}$ as catalysts. The effect of solvents and PPh_3 on the activity and selectivity of the catalysts was studied. The activity of $Rh_4(CO)_{12}$ sharply increased above a molar ratio of P:Rh = 2:1 [20]. Deuteroformylation of styrene was carried out at 90° and 160 bar (CO/D_2 = 1/1) in the presence of $Rh_4(CO)_{12}$ as catalyst precursor. At partial conversion β-deuterostyrene, PhCH=CHD and β,β-dideuterostyrene, $PhCH=CD_2$ were recovered. This result suggests that under hydroformylation conditions the branched alkylrhodium intermediate in part dissociates into rhodium hydride and deuterated olefin [21].

The kinetics of hydroformylation of 1-hexene have been studied using $HRh(CO)(PPh_3)_3$ as catalyst in EtOH solution at 30-50°C and 1-60 bar total pressure. The reaction was found to be first order with respect to catalyst and H_2, the rate versus p_{CO} and olefin passed through maxima [22]. A cracking fraction containing 74-86% 1-hexene was hydroformylated at 100°C and 15 bar using $Rh(acac)(CO)(PPh_3)$ as catalyst. The use of a very high PPh_3:Rh ratio (400:1) promoted the formation of n-heptaldehyde and retarded catalyst deactivation [23]. Indene was hydroformylated using $Rh(CO)(PAr_3)_2Cl$ complexes as catalysts. The catalyst containing the tri-*o*-tolylphosphine ligand gave a high selectivity to 1-indancarboxaldehyde [24]. The complex (triphos)$RhH(C_2H_4)$ has been used as catalyst for the hydrogenation and hydroformylation of hexene-1. The n:i ratio of C_7 aldehydes formed was higher than that obtained with $HRh(CO)(PPh_3)_3$ under similar conditions [25]. Hydroformylation of cyclododecatriene (**3**) with $HRh(CO)(PPh_3)_3$ as catalyst afforded only aldehydes (**4**) and (**5**) corresponding to selective monohydroformylation of the trans double bond. No selectivity was found, however, if the same catalyst was employed for hydrogenation of (**3**) [26].



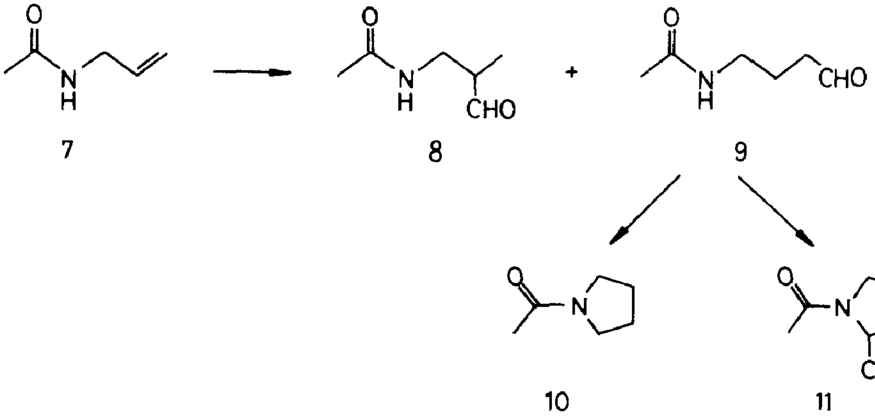
3 4 5

Hexene-1 was hydroformylated at 40°C and 1 bar with $HRh[P(OPh)_3]_4$ and $Rh[P(OPh)_3]_3[P(OPh)_2(OC_6H_4)]$ as catalysts. Catalytic activity of both catalysts was comparable to that found for the $Rh(acac)[P(OPh)_3]_2$ + n $P(OPh)_3$ systems [27]. The deactivation of Rh-PPh_3 complex catalysts in the presence of oxygen, sulfur, chlorine, and their compounds in hydroformylation of propene was studied. The poisoning effect caused by oxygen was temporary while the deactivation of the catalyst by sulfur, chlorine, and their compounds was permanent [28]. The effect of tris(3,4-dimethylphenyl)phosphite as ligand in hydroformylation of 1-heptene using $Rh(CO)_2(acac)$ as catalyst was studied. The ratio of straight to branched chain aldehydes formed was larger than in the case of PPh_3 [29]. The catalytic activity of the Rh(I) complexes $Rh(acac)[P(OPh)_3]_2$, $Rh(acac)(CO)_2$ and $Rh(acac)(CO)(PPh_3)$ for hydroformylation of 1-hexene at 40°C and 1 bar was examined in the presence of phenylphosphites containing Me, NO_2, or Cl substituents in the phenyl ring. No effect was observed in the case of $Rh(acac)[P(OPh)_3]_2$ [30]. The activity and regioselectivity of Rh-phosphine catalysts used for the hydroformylation of styrene did not change with the P:Rh ratio above 2:1 and 1:1 respectively, if the phosphine ligand (6) was used. This proves that under the conditions used (40°C, 20 bar) only a disubstituted Rh carbonyl hydride species was active as catalyst [31].

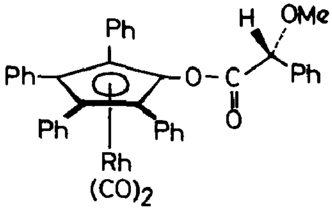


6

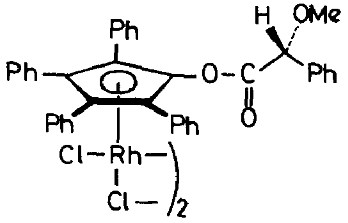
Hydroformylation of N-allylacetamides (e.g.7) in the presence of Rh carbonyls as catalysts yields as first products the expected aldehydes (8) and (9). The linear isomer (9), however, reacts further under the reaction conditions forming ring-closure products (10) and (11). Highest yields of the cyclic aldehyde (11) (the product of double carbonylation) were achieved with [Rh(dppb)(NBD)]ClO_4 as catalyst [32].



Chiral cyclopentadienyl complexes of Rh have been tested as catalysts for hydroformylation and hydrogenation. Complex (12) catalyzed the hydroformylation of vinyl acetate to give 2-acetoxypropanal with 3% enantiomeric excess and complex (13) catalyzed the hydrogenation of methyl α-acetamidocinnamate to give 6% enantiomeric excess [33].



12



13

Dinuclear Rh complexes of the type $Rh_2(\mu\text{-}SBu^t)_2(CO)_2L_2$, where L_2 is a diphosphine, were used as catalysts for the hydroformylation of 1-hexene. Those complexes in which the diphosphine ligands maintained a short Rh-Rh distance were the most active [34]. The dinuclear Rh(I) complexes with mixed bridging ligands $Rh_2(\mu\text{-}L)(\mu\text{-}SBu^t)(CO)_2[P(OMe)_3]_2$ (L = pyrazolate or benzotriazolate) were tested as hydroformylation catalysts at 80°C and 6 bar. These complexes were almost as active as the well-established thiolato bridged analog $Rh_2(\mu\text{-}SBu^t)_2(CO)_2[P(OMe)_3]_2$ [35].

Hydroformylation of 1-hexene in a two-phase system using water-soluble Rh-phosphine complexes formed *in situ* was studied in detail. The IR spectra showed that the same water-soluble active species were formed starting from $Ph_2P(m\text{-}C_6H_4SO_3Na)$ and $[Rh(COD)Cl]_2$, $Rh(acac)(CO)_2$, or $RhCl_3.3H_2O$ [36]. Hydroformylation of linear α-olefins in a water/organic two-phase system using Rh complexes of $Ph_2PC_6H_4COOH\text{-}p$ as catalysts at 80°C and 5.5 bar H_2+CO has been described. Very high normal:iso aldehyde ratios (up to 100:1) were achieved at pH 10 in the presence of a surfactant like $C_{12}H_{25}NMe_3Br$ [37].

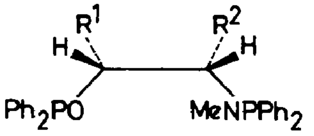
The heterobimetallic complex $Cp_2Zr(\mu\text{-}PPh_2)_2RhH(CO)PPh_3$ was applied as catalyst for the hydroformylation of 1-hexene at 25-50°C and 1 bar CO + H_2. Although the rate of reaction was lower than with $HRh(CO)(PPh_3)_3$, the selectivity for terminal aldehydes was significantly higher [38]. The catalytic activity of $[Rh(COD)(PPh_3)_2]^+$ for hydroformylation of olefins was decreased by the addition of the diphosphines $Cp_2M(CH_2PPh_2)_2$ (M = Ti,Zr). In accordance with this finding also the mixed-metal catalysts $[Cp_2M(CH_2PPh_2)_2Rh(COD)]^+$ showed only moderate catalytic activity [39]. Polybutadienes were hydrogenated, hydroformylated and

hydroxymethylated using $Rh(PPh_3)_3Cl$, $HRh(CO)(PPh_3)_3$, and $HRu(CO)(PPh_3)_3Cl$ as catalysts. No changes in chain length properties were observed on hydrogenation [40]. Allyl alcohol, allyl acetate, and allylamine were hydroformylated or homologated with CO + H_2 using $HRh(CO)(PPh_3)_3$, RuO_2, or $Co_2(CO)_8$ catalysts [41].
See also [14,16,84,122].

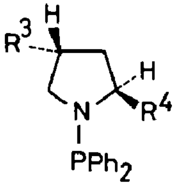
c) Other Metals as Catalysts

The catalytic activities of $[HRu(CO)_4]^-$, $[HRu_3(CO)_{11}]^-$, and $Ru_3(CO)_{12}$ for hydroformylation of olefins were compared. In the case of styrene and ethyl acrylate, $[HRu(CO)_4]^-$ was found to be the most active [42]. Alkali metal halides increase the catalytic activity of $Ru_3(CO)_{12}$ in the hydroformylation of ethene; the $Ru_3(CO)_{12}$ + CsI + CsOH + THF system showed the highest activity. IR spectroscopy indicated the presence of $[HRu_3(CO)_{11}]^-$ as the main Ru component in the reaction mixture [43]. Hydroformylation of 1-hexene was carried out using the water-soluble Ru(III) complex $K[Ru(EDTA-H).2H_2O$ as catalyst at 130°C and 50 bar CO + H_2 in $EtOH/H_2O$ = 4/1 solvent mixture. The reaction was slow but yielded exclusively linear heptadehyde [44]. Hydroformylation of allyl alcohol in aqueous solution using a Ru(III)-EDTA complex as catalyst at 90-130°C and 25-65 bar CO_2 + H_2 furnishes γ-hydroxybutyraldehyde as the primary product. Secondary reactions (cyclization and hydrogenation) result in the formation of γ-butyrolactone, dihydrofuran and 1,4-butanediol as side products [45]. The dinuclear Ru carboxylato complexes $Ru_2(\mu\text{-}OOCR)_2(CO)_4L_2$ (R = Me,Ph,CF_3,tBu; L = PPh_3,PBu_3,$P(OPh)_3$,$P(OMe)_3$) catalyze the hydroformylation of linear 1-alkenes at 10-30 bar and 80°C, provided that a small amount of a base is added to the reaction mixture. A mechanism involving dinuclear intermediates in the catalytic cycle was proposed [46]. Terminal olefins could be hydroformylated to aldehydes with predominantly linear structure with Ru catalysts (RuO_2 or $Ru_3(CO)_{12}$) modified by N- or P-ligands such as bpy or dppe and working in low-melting quaternary phosphonium salts (e.g. Bu_4PBr) as solvents. The influence of reaction conditions (temperature, pressure, catalyst concentration, and structure of ligands) has been investigated in detail [47].

The complex *trans*-[$PtCl_2(COCH_2CH_2Ph)(PPh_3)_2$].EtOH, in combination with $SnCl_2.2H_2O$, was found to be an active catalyst for the hydroformylation of styrene. The complex was synthesized from styrene, *cis*-[$PtCl_2(PPh)_3)_2$], CO, and H_2 under hydroformylation conditions (100°C,100 bar) [48]. Platinum(II)-aminophosphinephosphinite complexes combined with $SnCl_2$ were used as catalysts for the hydroformylation of styrene. The complexes were prepared from K[$Pt(C_2H_4)Cl_3$] and chiral ligands of type (**14**) and (**15**). Best optical yield (48%) was achieved with the ligand (**15**; R^3 = $OPPh_2$, R^4 = COOEt) [49].

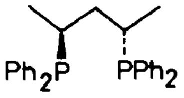


14



15

Asymmetric hydroformylation of prochiral olefins is catalyzed by PtCl($SnCl_3$)[(S,S)-BDPP] ((S,S)-BDPP = **16**). The linear (non chiral) regioisomer 3-phenylpropanal is the main product of styrene hydroformylation, but the enantioselectivity of 2-phenylpropanal is unusually strongly influenced by the reaction temperature: the S-enantiomer predominates at lower and the R-enantiomer at higher temperatures [50].



16 ; (S,S)-BDPP

The effect of styrene polymer ligand and transition metal complexes on the selectivity and activity of the catalysts in hydroformylation of 1-hexene was studied [51].

See also [15,19,38,39,40,41,122].
40,41,122].

d) Heterogeneous Systems (Supported Complexes)

The catalytic activity in hydroformylation of $HCo(CO)_4$, substituted by mono- and bidentate phosphines and silylphosphine ligands was studied. The results were used to obtain a heterogeneous catalyst which is active, selective and stable in the gas-phase hydroformylation of propene [52]. Adding silica gel during the formation of $HCo(CO)_2(PBu_3)_2$ from $HCo(CO)_4$ and PBu_3 (1:5) partially deactivated the homogeneous catalyst in the hydroformylation of propene. Immobilizing the ligand by using silica gel with $MeOSiMe(CH_2CH_2PBu_2)_2$ gave a selective catalyst which was stable for more than 300 hours at 180°C and 100 bar [53].

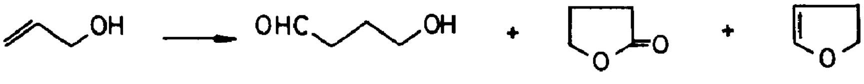
Cyclohexene was hydroformylated with a catalyst consisting of a polyalumazane-Co-Ru bimetallic complex supported on silica. The cyclohexanecarboxaldehyde formed as primary product was partly hydrogenated to the corresponding alcohol in a consecutive reaction. The amount of alcohol increased with increasing Ru:Co ratio of the catalyst [54]. Higher activities for the gas-phase hydroformylation of ethene and propene were achieved on carbon-supported Rh-Co bimetallic clusters than on Rh-only and Co-only catalysts. Cobalt is supposed to prevent sintering of the Rh aggregates [55]. Homo- and heteronuclear Pd- and Co-containing complexes anchored on phosphinated silica have been used for gas phase hydroformylation of propene. Due to synergistic effects products were produced in the presence of Pd-Co catalysts already at 40-70°C [56].

Propene was hydroformylated at 90-140°C and 20 bar using a supported liquid phase catalyst composed of styrene-divinylbenzene copolymer and $HRh(CO)(PPh_3)_3$ dissolved in PPh_3. Aldehyde selectivity was 100% at 120°C [57]. Five kinds of polymer-anchored aminophosphine-Rh complexes were prepared and used as catalysts for the hydroformylation of diisobutylene [58]. Several polymeric ligand-bound Rh complexes were prepared starting from $[Rh(CO)_2Cl]_2$ and functional cross-linked polystyrenes containing amine, aminophosphine, or phosphite groups. These polymeric complexes were used as catalysts for hydroformylation of diisobutylene at 110°C and 60-100 bar. Most of the catalysts showed good catalytic properties. The elution of Rh was studied in most detail [59]. The kinetics of hydroformylation of propene with a supported liquid phase catalyst containing Rh-dibenzophosphole complexes have been determined. The reaction was zero order in CO and H_2, and first order in propene [60]. Several new types of polymeric ligands based on polystyrene and their Rh complexes were synthesized and tested as catalysts for the hydroformylation of diisobutylene [61].

Mercaptopropyl-containing siloxane and mercaptomethylated polystyrene were used as supports for Rh catalysts for hydroformylation of cyclohexene. These catalysts showed higher activity and stability than the phosphine-containing polymer-supported Rh catalyst [62]. Hydroformylation of propene was carried out with a catalyst obtained by supporting solutions of $HRh(CO)(PPh_3)_3$ in phenyldibenzophosphole on silica. The reaction was first order in propene and zero order in both H_2 and CO [63]. Cyclohexene was hydroformylated using a SiO_2-supported polytitazane rhodium complex catalyst at 120°C and 60 bar. The catalyst was stable for turnover numbers higher than 20.000 [64]. Reduced Rh/SiO_2 catalysts were exposed to a flow of H_2 containing 10.9 ppm H_2S and then reduced again. Sulfur preadsorbed in this way strongly suppressed the hydrogenation of ethene but increased the rate of hydroformylation. Consequently, the selectivity of propionaldehyde formation was substantially improved [65]. Ethene was hydroformylated in the vapor phase at 180° and 20 bar using Rh/SiO_2 catalysts. The activity of the catalysts increased remarkably if the Rh particle size was below approximately 30 Å [66].

e) Modified Hydroformylations

In the presence of tertiary amines, iron carbonyls catalyze the hydroformylation of styrene with CO and H_2O, and the reduction of aldehydes and ketones by CO and H_2O, or with H_2. Hydrogenation and dimerization are important side reactions in the hydroformylation of styrene. Hydrogenation of Schiff bases with H_2 and iron carbonyls does not require addition of an extra base [67]. Allyl alcohol was hydroformylated with CO + H_2O using a Ru(III)-EDTA complex as catalyst. The product composition (**17**, 35%; **18**, 25%; **19**, 25%) was like that obtained with the same catalyst using a CO + H_2 gas mixture [68].

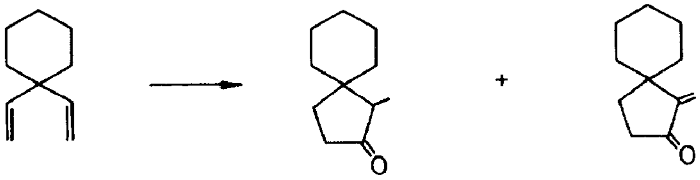


17 **18** **19**

Hydrocarbonylation of diphenylacetylenes (20) with CO + H_2O and $Co_2(CO)_8$ + PR_3 (R = Bu, Ph) catalysts at 220°C and 100 bar furnishes indanones (21) in good yields. With H_2 instead of H_2O only hydrogenation to the corresponding ethylbenzene derivative takes place [69].

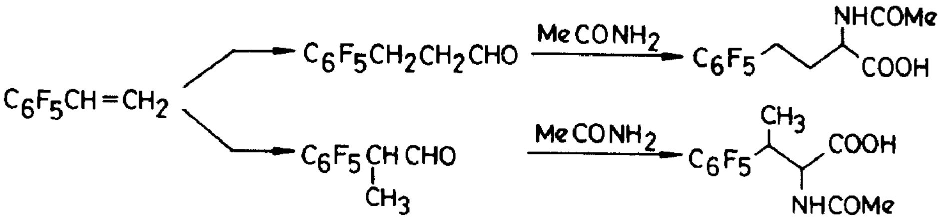
20 21

Synthesis of substituted cyclopentanones (23) via hydrocarbonylation-cyclization of 1,4-dienes (22) has been studied. Both Co and Rh carbonyl catalysts could be applied either with CO+H_2, or with CO+H_2O; best results were achieved with Rh and CO+H_2O at 100°C and 30 bar. At low catalyst concentrations *exo*-methylenecyclopentanones (24) were formed as byproducts [70].



22 23 24

Hydroformylation of the fluoroolefin $C_6F_5CH{=}CH_2$ and *in situ* amidocarbonylation of the aldehydes formed catalyzed by $Co_2(CO)_8$-$Rh_4(CO)_{12}$ systems proceeds with excellent regioselectivity forming predominantly the branched chain aminoacid isomer:

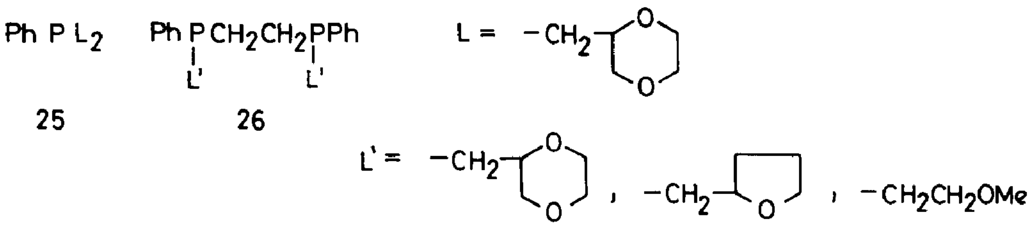


It has been proved that hydroformylation in this system is catalyzed by the mixed metal complex $CoRh(CO)_7$, the relative activity of which to $Co_2(CO)_8$ is about 22.000 per metal atom (i.e. $Co_2(CO)_8$ is practically inert under the reaction conditions) [71].

See also [32].

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

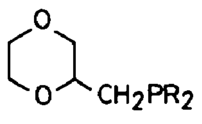
Iron pentacarbonyl combined with cyclic amines, e.g. N-methylpiperidine was found to be the most active and selective catalyst of methanol homologation [72]. The ether-phosphine ligands (25,26) gave high selectivities and conversions in the Co-catalyzed hydrocarbonylation of MeOH to MeCHO [73].



25

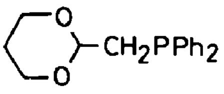
26

Hydrocarbonylation of methanol to acetaldehyde (and carbonylation to acetic acid) were investigated with CoI_2 as catalyst and the phosphines (27) and (28) containing ether groups as ligands. Best results (turnover numbers up to 1300/hour) were achieved with the ligand (27a) [74].



27

R
a) Ph
b) mesityl
c) Cy



28

Homologation of methanol to ethanol was achieved at unusually low pressure and temperature (70 bar, 140°) using a catalyst system composed of $Rh(CO)_2(acac)$, $RuCl_3.3H_2O$, a diphosphine and

MeI (1:2:2:40). The best diphosphine was dppp with which ethanol selectivity reached 80%. The remainder of the liquid product was acetic acid which could not be reduced to ethanol under these conditions [75]. Hydrocarbonylation of C_2-C_4 alcohols with Co + Ru catalyst and I_2 or KI as promoter has been studied at 170-200°C and about 500 bar syngas pressure. Highest yields of the next higher alcohols were obtained with catalyst compositions of 80-85 mol% Co and 15-20 mol% Ru. A mechanism was proposed according to which an intermediate olefin is hydroformylated by cobalt and the acylcobalt complex is attacked by a ruthenium hydride [76]. The reaction of ethyl orthoformate with CO + H_2 in the presence of Rh carbonyl catalysts has been studied at 80 bar and 150-170°C. The main reaction was hydrogenation leading to EtOH and $CH_2(OEt)_2$; with $Rh(OEt)_2$+ MeI catalyst systems some carbonylation to ethyl propionate, 1,1-diethoxypropane, and diethyl carbonate were observed (maximum total selectivity 12%) [77]. Reductive carbonylation of methyl formate at 180°C and 80 bar CO with $Rh+I^-$ catalyst leads to acetaldehyde in about 80% yield:

$$HCOOCH_3 + CO \longrightarrow CH_3CHO + CO_2$$

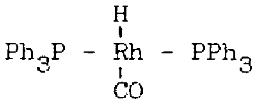
The main side product is MeOH [78]. The yield of ethylene glycol in the hydroformylation of formaldehyde with Co carbonyl catalyst could be increased by addition of $Ru_3(CO)_{12}$ and phenol to about 65% at 180°C and 200 bar [79].

See also [33].

4. Coordination Chemistry Related to Hydroformylation

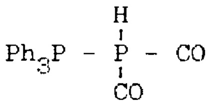
Kinetic investigation of the reductive elimination reactions of $RCOCo(CO)_4$ (R = Pr, iPr) with H_2 or $HCo(CO)_4$ showed that under conditions of catalytic hydroformylation of propene, butyraldehydes are formed mainly by the reaction with H_2 [80]. The reaction of $HRh(CO)(PPh_3)_3$ with CO has been studied by ^1H, ^{13}C, and ^{31}P NMR and the results of these investigation were used to interpret the regioselectivities (normal:branched aldehyde ratios) observed in the hydroformylation of olefins catalyzed by $Rh-PPh_3$ complexes. It was concluded that the catalytic results can be best explained by the two co-ordinatively unsaturated intermediates

(29) and (30) assuming that the monophosphine complex reacts with lower regioselectivity toward terminal olefins [81].



$$\mathrm{Ph_3P - \overset{H}{\underset{CO}{Rh}} - PPh_3}$$

29



$$\mathrm{Ph_3P - \overset{H}{\underset{CO}{P}} - CO}$$

30

5. Water Gas Shift Reaction

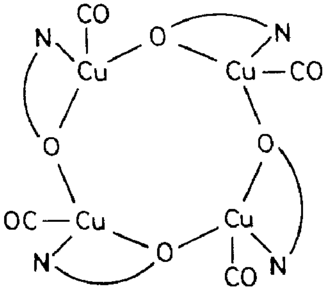
The water gas shift reaction is catalyzed by K[Ru(HEDTA)(CO)] even at 20°C and 1 bar CO pressure. The turnover number is under optimal conditions (50°C and 15 bar) 350 mol CO/H_2 per mol catalyst and hour, which is the highest value observed up till now for a homogeneous catalyst [82]. The kinetics of the water-gas shift reaction catalyzed by Os carbonyls supported on X-type zeolite were studied by using a flow reactor. The nature of the carbonylic surface species and their interconversions were studied by spectroscopic techniques [83]. Several Rh(I) complexes containing the ligand $P(C_6H_4SO_3Na\text{-}m)_3$ (L) catalyze the water-gas shift reaction and the hydroformylation of hexene-1 at 80°C and 8 bar in water as solvent. Highest rates were obtained with the complex $Rh_2(\mu\text{-}SBu^t)_2(CO)_2L_2$ [84]. The Ir(III) complexes $[Cp^*Ir(bpy)Cl]^+$, $[Cp^*Ir(bpy)H]^+$, and $[Cp^*Ir(phen)Cl]^+$ were shown to be active catalysts for the water gas shift reaction at room temperature under irradiation with visible light [85].

6. Reduction with CO or CO + H_2

$KHFe(CO)_4^-$ generated *in situ* from $Fe(CO)_5$ and K_2CO_3 in MeOH catalyzes the reduction of aryl iodides to the corresponding hydrocarbons under CO at 60°C. Reduction of 1 mol of ArI needs 1 mol of CO and 2 mol of K_2CO_3. Up to 18 catalytic cycles could be achieved [86]. Aldoximes could be selectively transformed by CO into nitriles using $Rh_6(CO)_{16}$ as catalyst according to the following reaction:

$$R\text{-}CH{=}N\text{-}OH + CO \longrightarrow R\text{-}CN + CO_2 + H_2$$

Reaction conditions were 40°C and 8 bar, basic additives as KOH or diamines were necessary. The corresponding alcohols were formed as byproducts [87]. Reduction of nitrobenzene with CO in the presence of protonated Pd carbonyl phosphine complexes formed *in situ* from $Pd(OAc)_2$, PPh_3, and $HClO_4$ was studied [88]. The trinuclear complex $PhCCo_3(CO)_9$ catalyzes the reduction of aromatic nitro compounds to the corresponding anilines under phase transfer conditions in the presence of NaOH and CO. Carbon dioxide is formed and a significant part of the complex is transformed into $Co(CO)_4^-$ under the reaction conditions [89]. The tetranuclear complex (**31**) ($O\frown N$ = 2-methylquinolin-8-ol) catalyzes the deoxygenation of some nitro- or nitroso-compounds by CO under pressure (6-100 bar) at relatively high temperatures (80-100°C). For example aliphatic nitroalkanes are transformed into the corresponding nitriles or oximes; nitrobenzene, however, does not react under such conditions [90].



31

Deoxygenation of aliphatic nitro compounds to nitriles and of hydroxylamines to amines by CO + H_2 at 40°C and 16 bar is catalyzed by polymeric Rh carbonyl clusters which are formed *in situ* from $Rh_6(CO)_{16}$ and aminated polystyrenes. The catalyst may be easily separated from the reaction mixture by filtration; its IR spectrum indicates the formation of Rh carbonyl cluster anions under the reaction conditions [91].
See also [67].

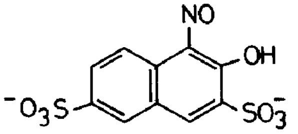
7. Miscellaneous Reductive Transformations of CO and CO_2

Ethyl iodide or benzyl bromide could be hydrocarbonylated to yield propionaldehyde and phenyl acetaldehyde, respectively, by controlled-potential electrolysis of their solution in THF in the presence of $Fe(CO)_5$, followed by treatment with CO and finally with AcOH. Probably $RFe(CO)_4^-$ complexes are intermediates of the reaction [92]. $Ru_3(CO)_{12}$ and (less efficiently) $Ru(CO)_3(PPh_3)_2$ catalyze the reductive carbonylation of nitrobenzene and of substituted aromatic mononitro compounds in toluene-MeOH to give the corresponding methylcarbamates at 160°C and 60 bar, with high selectivity, in the presence of Et_4NCl as cocatalyst:

$$ArNO_2 + 3\ CO + MeOH \longrightarrow ArNHCOOMe + 2\ CO_2$$

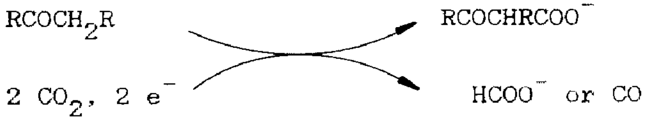
If water is added to the reaction mixture, aniline is the main product [93]. Dissolving potassium in THF containing $V(C_6H_6)_2$ gives a solution of $K[V(C_6H_6)_2]$ which reduces CO_2 or CO to oxalate and small amounts of formate and glycolate [94]. Carbon dioxide reduction to CO on electrodes coated with polymeric films obtained by oxidative electropolymerization of $Re(L)(CO)_3Cl$ complexes, where L is a 2,2'-bipyridine derivative substituted by pyrrole-containing groups, has been investigated. Small amounts of formate and oxalate were also formed [95]. Reductive carbonylation of Me_2NH to DMF with $CO_2 + H_2$ and the (simultaneous) reduction of DMF by H_2 to Me_3N have been investigated with Ru,Os,Rh,Ir, and Pt complexes as catalysts at 125-150°C and about 100 bar. Platinum complexes were found to be the most active in both cases [96].

Photochemical reduction of CO_2 to CO and $HCOO^-$ was achieved by using 1-benzyl-1,4-dihydronicotinamide (BNAH) as electron donor and $[Ru(bpy)_3]^{2+}$ as catalyst, in H_2O/DMF. The reductant was oxidatively dimerized to $(BNA)_2$ [97]. Electroreduction of CO_2 is catalyzed by Co(II)-, Fe(II)-, Ni(II)-, and Cu(II)-complexes of 1,10-*o*-phenanthroline. The ligand participates in the reaction [98]. Carbon dioxide has been reduced electrocatalytically to methanol at Pt electrodes modified with different metal porphyrins (Co,Fe,Ni,Cr) in the presence of $[Fe(CN)_5(H_2O)]^{3-}$ or the Co(II) complex of (**32**) as homogeneous catalyst. The highest current efficiency (15.1%) was achieved with (TPP)Co and the Co complex of (**32**) [99].

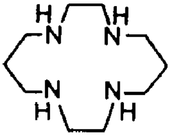


32

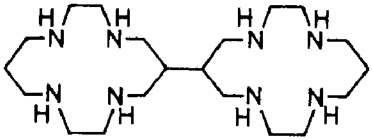
Electrochemical reduction of CO_2 to formate and CO, and simultaneous carboxylation of ketones at the α-carbon were carried out in the presence of $[Ru(bpy)_2(CO)_2]^{2+}$. Ketones play the role of the proton source in these reactions [100]:



The complex *cis*-$[Rh(bpy)_2(Tf)_2](Tf)$ is an electrocatalyst for the reduction of CO_2 to formate in MeCN solution. The protons required for the reduction are furnished by the $[NBu_4]^+$ ions of the supporting electrolyte [101]. Carbon dioxide coordinated to Ni(0) in $(Cy_3P)_2Ni(CO_2)$ is easily reduced to bound CO in $(Cy_3P)_2Ni(CO)_2$ by aliphatic or aromatic thiols. The reduction is selective (no formates or oxalates are formed), and the system provides a reasonable model for the Ni-containing enzyme carbon monoxide dehydrogenase [102]. The complexes $Ni(cyclam)^{2+}$ and $Ni_2(biscyclam)^{4+}$ have been tested as electrocatalysts for the reduction of CO_2. Both catalysts gave only C_1 products; in water only CO was formed, whereas in low water content DMF high faradaic yields of formate were observed [103].



33 ; cyclam



34 ; biscyclam

The complexes $[PdPPh(CH_2CH_2PPh_2)_2(PR_3)](BF_4)_2$ (R = Et,OMe) were found to be catalysts for the electroreduction of CO_2 [104].

See also [180].

III. HYDROGENATION AND REDUCTION

1. Hydrogenation of Olefins

a) Ru and Os Catalysts

The complexes $H_2Ru(CO)_2L_2$ (L = PMe_2Ph or $AsMe_2Ph$) hydrogenate ethene in a stoichiometric reaction; the starting complexes may be regenerated by treatment with H_2 [105]. Catalysts prepared from Rh^{2+} or Ru^{3+} and trioctylamine with amine:metal molar ratios of 2-6 were used for the hydrogenation of olefins in toluene at 20-60°C [106]. The Ru(II) complexes of the types $(R_3P)_2Ru(CO)_2Cl_2$ and $(R_3P)_3Ru(CO)Cl_2$ (R_3P = alkyl or aryl phosphines) were tested as catalyst for the hydrogenation of 1-hexene at 100°C and 7 bar in EtOH/benzene. Reaction rates decreased with decreasing size and increasing basicity of the phopsphines [107]. The trinuclear cluster $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}O)(CO)_5(dppm)_2$ was found to be a catalyst for the hydrogenation of 1-hexene at 55°C and 7.4 bar. The reaction is first order in complex concentration indicating that the cluster remains intact during the catalytic cycle [108].

The silica-supported cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Si\leqslant)$ catalyzes the hydrogenation of ethene at 90°C and 1 bar; reaction kinetics, volumetric and IR studies indicate a mechanism involving the intact triosmium framework in all the elementary steps forming the catalytic cycle. However, complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)$ is quickly transformed in solution under catalytic conditions with loss of PhOH and formation of $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$ [109].

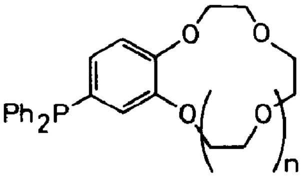
See also [162,195].

b) Co, Rh, and Ir Catalysts

Cobalt-ethylenediamine and Co-glycine complexes were supported on divinylbenzene-styrene macroporous beads and their catalytic activity tested for the hydrogenation of 1-octene [110]. Several dinuclear Rh complexes containing hydride bridges like $[(triphos)Rh(\mu-H)_3Co(triphos)]^{2+}$ were found to be catalysts for the hydrogenation of dimethyl maleate and dimethyl acetylenedicarboxylate. In the catalytic cycles some of these compounds were resistant to fragmentation and therefore responsible for the catalysis [111].

Homogeneous hydrogenation of cyclohexene catalyzed by $Rh(PPh_3)_3Cl$, $Rh(dppe)Cl_2$ and $Rh(NP_2)Cl$ ($NP_2 = HN(CH_2CH_2PPh_2)_2$) was investigated at 10-40°C and 0.6 bar. Thermodynamic parameters for the formation of the corresponding dihydrido and olefin complexes of Rh(I) were calculated. The insertion of the olefin into the Rh-H bond seems to be controlled mainly by the entropy factor in the reaction rather than the enthalpy [112]. The kinetics of homogeneous hydrogenation of α-methylstyrene with $Rh(PPh_3)_3Cl$ as catalyst has been studied in a well-stirred bubble reactor. It was shown that an overall rate constant, combining rate contants of reversible adition of H_2 to the catalyst and the subsequent irreversible reaction, can describe the overall rate [113]. Homogeneous hydrogenation of olefinic steroids has been investigated using Rh-phosphine catalysts prepared *in situ*. Reducing 3-oxo-4-ene steroids gave mainly the *trans*-anellated α-derivatives; the most favorable isomer ratio (5α:5β = 9:1) was observed in the hydrogenation of 4-androstene-3,17-dione using a $[Rh(NBD)Cl]_2 + PPh_2Me$ (P:Rh = 3:1) catalyst [114]. Simultaneous hydrogenation and esterification of α,β-unsaturated carboxylic acids is catalyzed by $[RhCl(1,5\text{-hexadiene})]_2$ or $RhCl_3$ in MeOH. When an aryl group is present in the reactant, the reduction of the arene ring also takes place under the reaction conditions. No reaction occurs in the absence of H_2 suggesting that a Rh hydride is the key catalytic species for both reduction and esterification [115].

Cyclopentene was hydrogenated in a two-phase system with $RhCl_3$ and the water-soluble ligand triphenyl phosphine *meta*-trisulfonate under room conditions. It was shown that the phosphine is oxidized to the corresponding phosphine oxide and that catalytic activity is associated with colloidal Rh stabilized by this protective dispersent [116]. The crown ether-modified phosphines (35; n = 1-4) were used as ligands combined with $[Rh(COD)Cl]_2$ for the hydrogenation of K and Cs cinnamates in a two-phase (benzene/water) system. Hydrogenation took place in the organic phase due to the extraction of the alkali metal cation by the crown ether moiety [117].



35

Polyethylene hollow fibers were brominated, phosphinated, and treated with $Rh(PPh_3)_3Cl$ to give a catalyst useful for hydrogenation of olefins in a fixed-bed flow reactor. The catalyst could be easily separated and reused without loss of activity [118]. A catalyst for hydrogenation of olefins was developed consisting of $Rh(PPh_3)_3Cl$ bound to the surface of polyethylene single crystals. These single crystals had a high surface:volume ratio and the catalysts was more active than a similar bead system [119]. The following catalysts fixed to functionalized silica gel were prepared and tested for hydrogenation of olefins: neutral Rh complexes immobilized by bidentate phosphines, cationic Rh complexes attached via monodentate phosphines, and Ti(IV) complexes attached to an immobilized Cp ligand [120].

Rhodium(I) and iridium(I) complexes of the type $[M(diene)(L)_2](ClO_4)$ containing phosphine sulfide (L) ligands were used as catalysts for the hydrogenation of olefins [121]. Organometallic Keggin ion complexes like $[Rh(CO)(PPh_3)]_4SiW_{12}O_{40}$ and $[H_2Ir(PPh_3)_2]_3PW_{12}O_{40}$ were tested as catalysts for the hydrogenation, dehydrogenation, and hydroformylation of olefins and in C-H activation processes [122]. The η^2-H_2 complex $[Ir(H)_2(H_2)(PMe_2Ph)_3]^+$ catalyzes the hydrogenation of ethene under mild conditions. The catalytic cycle starts with the substitution of the η^2-H_2 ligand by ethene [123].
See also [25,26,33,194,244].

c) Ni, Pd, and Pt catalysts

Optimal conditions for the preparation of catalysts for the hydrogenation of cyclohexene based on Ni(II) salts (acetylacetonate, stearate, etc.) and Al or Li alkyls were described. Solvent effects were studied [124].

Homogeneous hydrogenation of cyclohexene with [Pd(L)Cl]Cl (L = $PhCH_2N(CH_2CH_2PPh_2)_2$ has been studied at 25-40°C and 0.1-1 bar H_2. Several hydride complexes were characterized by NMR spectroscopy. Two mechanisms were proposed [125]. The catalytic activity of the complexes [Pd(L)Cl]Cl (L = $NH(CH_2CH_2PPh_2)_2$ or $N(CH_2CH_2PPh_2)_3$) for the homogeneous hydrogenation of cyclohexene has been tested. The rate of hydrogenation was found to be first order in catalyst, fractional order in substrate and independent of H_2 pressure. Several hydride species were identified as intermediates by NMR spectroscopy [126].

Rate constants were determined for the hydrogenation of alkenes on Pd-polyheteroarylene catalysts. The activity of the catalysts was governed largely by the degree of charge transfer from Pd to the electronic system of the polymer [127]. A polymer-bound Pd(II) complex has been prepared by the reaction of $PdCl_2$ with a chelate resin of 8-aminoquinoline and used as catalyst for the hydrogenation of olefins. No obvious loss of Pd from the catalyst was observed [128]. Poly(vinylpyridine) complexes of Pd catalyze the hydrogenation of allyl alcohol. Activity of the catalysts depends on the position of the vinyl group on the pyridine ring: complexes prepared from polymers of 4-vinylpyridine were found to be the most active [129]. Palladium complexes fixed on an ethene-propene-ethylidenenorbornene copolymer grafted with vinylpyridine were used as catalysts for the hydrogenation of alkenes. The nature of the solvent strongly influenced the reaction; highest rates were obtained in MeOH + benzene [130]. Palladium chloride fixed on polyethyleneimine catalyzes the hydrogenation of allylphenols to propylphenols at 25-50°C and 6-20 bar. Under similar conditions a $RhCl_3$-polyethyleneimine catalyst leads to products formed by ring hydrogenation [131].

Platinum and palladium complexes of the crosslinked polymers prepared from poly(vinyl alcohol), SiO_2, p-$Me_2NC_6H_4CHO$ and glutaraldehyde were used as catalyst for the hydrogenation of several simple and functionalized olefins. The polymer Pt complex was more effective than H_2PtCl_6 [132]. Platinum(IV) complexes of poly(vinylpyridines) reduced with $NaBH_4$ or H_2 catalyze the hydrogenation of aqueous allyl alcohol. Selectivity of these catalysts is higher than that of Pt black [133].

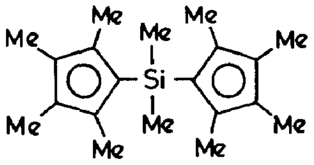
See also [189].

d) Other Metals as Catalysts

Hydrogenation of mono- and disubstituted alkenes is catalyzed by $Cp_2TiCl(AlH_3)$, a complex prepared from Cp_2TiCl_2 and $LiAlH_4$ [134]. When supported on dehydroxylated or partly dehydroxylated alumina, the complexes Cp_2ZrMe_2, $Cp^*_2ZrMe_2$, and Cp^*ZrMe_3 are highly active catalysts for propene hydrogenation, even at -63°C [135].

Aluminosilicate-supported $Cr(\pi\text{-}C_3H_5)_3$ catalyzes the hydrogenation of α-olefins [136]. The cluster complex $Re_3(CO)_6(\mu_3\text{-}H)_2(\mu\text{-}PPh_2)_3$ catalyzes the hydrogenation of cyclohexene at 20°C and 10 bar [137].

The dimeric hydride $(LThH_2)_2$ (L = 36) catalyzes the hydrogenation of 1-hexene about 1000 times faster than the structurally similar $[Cp^*_2ThH_2]_2$. Preliminary kinetic measurements indicate that the rate-limiting step is the hydrogenolysis of the intermediate Th-alkyl complex [138].

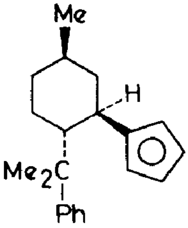


36

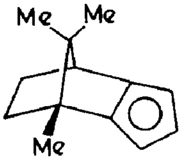
See also [120].

2. Asymmetric Hydrogenation of Olefins

The titanocene complexes L_2TiCl_2 containing the chiral cyclopentadienyl ligands L = (37) and (38) were used as catalyst precursors for the hydrogenation of 2-phenyl-1-butene. The complexes were transformed into the catalitically active species by addition of BuLi. Optical yields up to 34% were achieved [139].

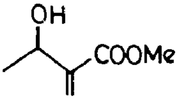


37

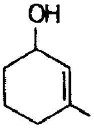


38

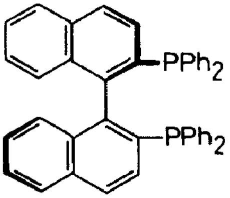
Chiral allylic secondary alcohols like (**39**) and (**40**) have been resolved efficiently by homogeneous hydrogenation catalyzed by (R)- or (S)-BINAP-Ru diacetate complexes. Up to 76:1 differentiation was obtained between the enantiomeric unsaturated alcohols resulting in 99% optically pure unreacted alcohols [140].



39

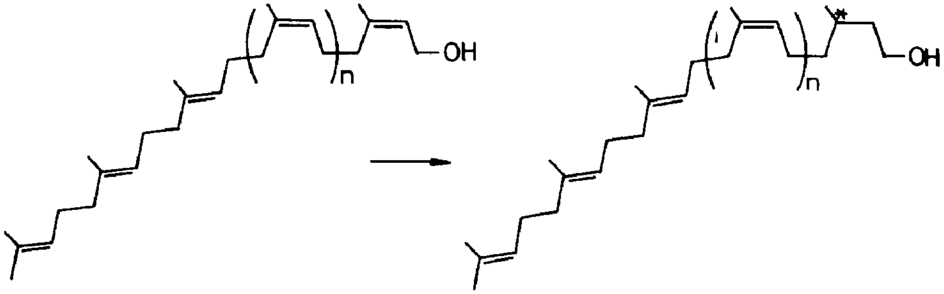


40



41 ; (R)-BINAP

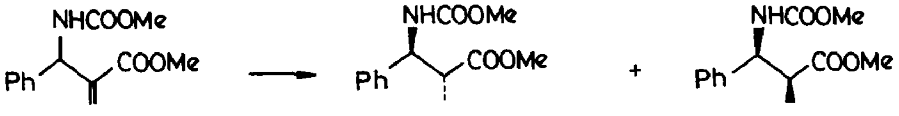
Naturally occurring plant polyprenols (**42**; n = 13,14,15) were asymmetrically hydrogenated to the corresponding dihydroisoprenols (dolichols) (**43**) using (BINAP)Ru(OOCCF$_3$)$_2$ as catalyst. Only 2% hydrogenation was observed at any other olefinic double bond and the optical yield was at least 95% [141].



42

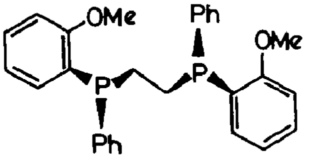
43

Homogeneous hydrogenation of (**44**) with $(PPh_3)_2Ru(OOCCF_3)_2$ or $[Rh(COD)(dppe)]^+$ as catalyst gave the diastereomer (**45a**) with 95-99% selectivity. The results indicate that the group NHCOOMe (which binds to the catalyst) directs the addition of hydrogen to the olefinic diastereoface proximate to this group [142].



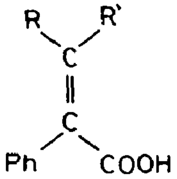
44 45a 45b

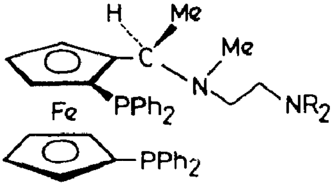
Rhodium complexes containing chiral P ligands and used for the asymmetric hydrogenation of PhCH=C(NHAc)COOR (R = H, alkyl, benzyl) were classified according a conformational angle. The absolute configurations of the products depended on the sign of this angle [143]. Simple stereochemical rules were established for the relationship between product configuration and catalyst or reactant configuration for asymmetric hydrogenation of dehydroacylamino acids in the presence of Rh-phosphine complexes [144]. The interconversion of diastereomeric N-acyl dehydroamino acid or ester ligands in Rh diphosphine complexes which occurs under the conditions of asymmetric hydrogenation has been studied using the DANTE magnetisation transfer technique. Two pathways were identified, one involving dissociation of the enamide ligand followed by recombination from the solute pool, and an intramolecular reaction characterized by the dissociation of the olefinic part of the ligand with the amide group remaining co-ordinated throughout this process. Interestingly, the N-pivaloyl derivative showed the slowest rate of exchange and at the same time the lowest optical yield in asymmetric hydrogenation using dipamp (**46**) as chiral ligand [145].



46 ; dipamp

Analogues of DIOP bearing *para*-Me_2N groups were used as chiral ligands in asymmetric hydrogenation of ketopantolacetone, itaconic acid, or dimethyl itaconate with Rh(I) complex catalysts. Reaction rates and enantioselectivities were higher than those obtained with the conventional Rh-DIOP systems [146]. Ruthenium(II)-BINAP complexes were found to be effective catalysts for asymmetric hydrogenation of itaconic acid and its derivatives; 86-90% optical yields were achieved [147]. Trisubstituted acrylic acids (**47**; R,R' = Me,CD_3,Et,Ph; R $\neq$ R') were asymmetrically hydrogenated with Rh(I) catalysts formed *in situ* from $[Rh(NBD)Cl]_2$, $AgBF_4$, and the chiral ferrocenylphosphines (**48**; R_2 = $(CH_2)_5$, Et_2, Bu_2). Optical yields as high as 80% were achieved at room temperature and 100 bar H_2 [148].


47


48

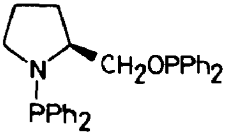
Rhodium(I) complexes of the type [(COD)Rh(L)Cl] and $[(COD)RhL]^+$ containing the chiral phopsphines L = PR_3, $PhPR_2$, Ph_2PR, and Me_2PR where R is the (S)-(+)-2-methylbutyl substituent, were applied as catalysts in asymmetric hydrogenation of Z-α-N-acetamidocinnamic acid. Highest optical yield was 15% [149]. N-substituted α-(aminoalkyl) acrylates (**49**; R = Me,Et; Y = COMe, $COOBu^t$) were hydrogenated with cationic Rh(I) complexes containing achiral (dppb) or chiral (dipamp) diphosphine ligands. In both cases the *anti* isomers were obtained with high stereoselectivity; in the case of the dipamp-containing catalyst good kinetic resolution was observed and the (R) product was obtained at about 50% conversion [150].


49

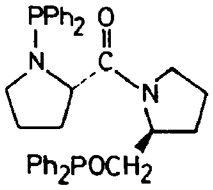
O,N-Bis(diphenylphosphino) derivatives of chiral *trans-* and *cis*-2-aminocyclohexanols were prepared and used as ligands in enantioselective hydrogenation of dehydro-α-acylamino acids with cationic Rh(I) complexes as catalysts. In some cases high (>97%) optical yields were achieved [151]. The two enantiomers of the O,N-bis(diphenylphosphino)aminoalkanol (50) have been prepared and used as ligands in asymmetric hydrogenation of olefins with Rh(I) complexes. Optical yields between 85 and 89% were achieved with acetamidocinnamic and acetamidoacrylic acids as substrates [152].

50

The chiral aminophosphine-phosphinites (51) and (52) were applied in the asymmetric hydrogenation of acetamidocinnamic acid with Rh complexes as catalysts. In the case of ligand (52) optical yields were dramatically affected by the solvent used. The enantiodifferentiating ability of the catalysts was better if the ligands were added in the form of their Cu complexes and the Rh complexes were generated in situ [153].

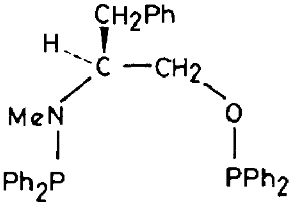


51



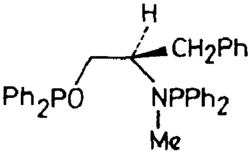
52

The chiral complex $[(NBD)RhL]^+(ClO_4)^-$ (L = 53) was prepared and used as catalyst for asymmetric hydrogenation of α-acetamido cinnamic acid derivatives. Based on X-ray structure determination a correlation was found between the configuration of the phosphino Ph groups and that of the products [154].



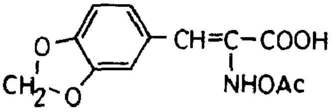
53

α-Acetamidocinnamic acid was hydrogenated to the (S)-enantiomer with 60% enantioselectivity using $[Rh(L)(COD)](ClO_4)$ (L = **54**) as catalyst [155].

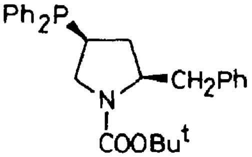


54

Asymmetric hydrogenation of (**55**) was carried out in the presence of $[Rh(COD)(BPPM)](ClO_4)$ adsorbed on methylated silica gel. The adsorption of the complex could be improved by introducing a stearoyl group instead of the butoxycarbonyl group of BPPM . When the recovered catalyst was reused three times the optical yield decreased gradualy from 85 to 69% [156].



55



56 ; BPPM

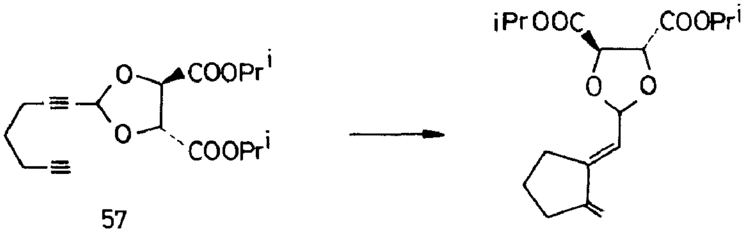
Palladium catalysts obtained *in situ* from $PdCl_2$ and either (S)-α-phenylethylamine, (S)-N-isopropyl-α-phenylethylamine, or (S)-phenylalaninol as chiral ligands were applied in the hydrogenation of α-nitrocaprolactam to (S)-α-aminocaprolactam. Optical yields varied between 1-13% [157].

See also [435].

3. Hydrogenation of Dienes and Alkynes

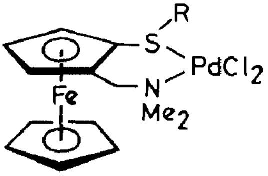
Hydrogenation of butadiene was carried out over molybdenum carbonyl/zeolite catalysts at 50-150° and 0.2 bar. Based on the results of IR spectroscopic investigations it was concluded that the catalytically active species was adsorbed $Mo(CO)_3$ [158]. Hydrogenation of phenylacetylene to styrene with $FeSt_3$-$AlEt_3$ and $NiSt_2$-$AlEt_3$ catalysts was studied using D-labeling experiments [159]. When olefins or acetylenes were hydrogenated with para-enriched H_2 in the presence of $H_4Ru(PPh_3)_3$, strong induced polarization leading to enhanced ^1H NMR absorptions and emissions could be observed. This observation proves the pairwise transfer of para-enriched H_2 to the substrate [160]. Phosphine substituted derivatives of $CpNiM_3(\mu\text{-}H)_3(CO)_9$ and $M_3(CO)_{12}$ clusters (M = Ru, Os) were tested as catalysts for hydrogenation of 1,4-pentadiene at 120°C. Most complexes showed a slight catalytic activity [161]. The η^2-H_2 complex $Os(H_2)(H)(CO)(PPr^i_3)_2Cl$ catalyzes the hydrogenation of alkenes and alkynes [162].

Hydrogenation of styrene-butadiene rubber using $Rh(PPh_3)_3Cl$ as catalyst was reported [163]. The rubbery center block of a triblock styrene-butadiene rubber could be converted into a semicrystalline, low density polyethylene-like polymer by treating it with H_2 in the presence of $[Ir(COD)(py)(PCy_3)]PF_6$ as catalyst [164]. The Pd(II) complex of interlamellar montmorillonite-2-diphenylphosphinoethylsilane catalyzes the hydrogenation of alkynes to alkenes with >95% *cis*-selectivity. The catalyst is superior in this respect to the conventional Lindlar catalyst [165]. The insoluble Pd(salen) complex was found to be an active and selective heterogeneous hydrogenation catalyst for the reduction of alkynes in the presence of alkenes and of alkenes in the presence of other functional groups. The activity of the complex is not due to the formation of metallic Pd [166]. The $PdCl_2$ complex of a polymeric support bearing isonitrile groups was tested as hydrogenation catalyst at 21°C and 3 bar. Phenylacetylene was hydrogenated to stilbene and ethylbenzene, benzaldehyde to benzylalcohol [167]. The clusters $[Pd_4(SnCl_2)_2(SnCl_3)_m]^{n-}$ (m = 8, n = 5; m = 4, n = 3) catalyze the hydrogenation of dienes [168]. Reductive cyclization of 1,6-diynes (e.g.57) to dialkylidenecycloalkanes with Et_3SiH as reductant is catalyzed by $(dba)_3Pd_2.CHCl_3$ in the presence of tri-*o*-tolylphosphine and AcOH in benzene solution. The catalytically active species is presumably a hydridopalladium carboxylate [169].



57

Palladium(II) ferrocenyl sulfide complexes of the type (58; R = C_1-C_5 alkyl, phenyl, *p*-tolyl) catalyze the hydrogenation of conjugated dienes to monoenes with good selectivity. Addition of $AgNO_3$ in the absence of water increases the selectivity [170].



58

Homogeneous and supported Pd and Pt complex catalysts with N-containing ligands were prepared and used for the hydrogenation of olefins, dienes and alkynes. Molar activities of the supported complexes were in the range 20.000-100.000 mol substrate/metal hour [171].

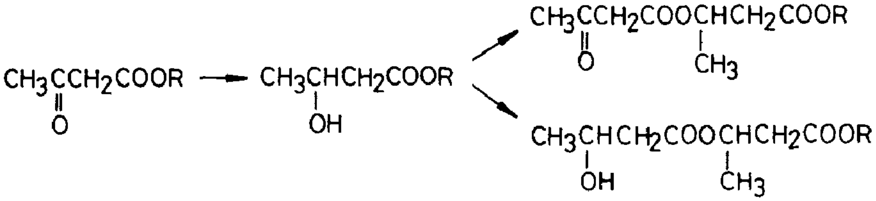
See also [189].

4. Hydrogenation of Arenes and Heterocyclic Compounds

Benzene is hydrogenated in MeOH solution on Pd/carbon at 30°C and 1 bar to cyclohexane if $Ru(NH_3)_5(OTf)_3$ is present; in the absence of the Ru complex the catalyst is ineffective. The effect of the Ru complex is probably due to the intermediate formation of η^2-benzene complexes in which ligation disrupts the aromacity of the arene [172]. The use of $Rh(PPh_3)_3Cl$ and $Ru(PPh_3)_3Cl_2$ as catalysts for the reduction of the heteroatom-containing ring in polynuclear heteroaromatic compounds has been investigated. The reduction of quinoline was found to start with the reversible hydrogenation of the C=N bond followed by an irreversible reduction of the C3-C4 bond. Several quinoline-Rh complexes have been identified in the reaction mixtures [173]. Naphthalene, quinoline, isoquinoline, and substituted quinolines were hydrogenated to the corresponding tetrahydro derivatives at 90°C and 50 bar using the Ziegler-type catalyst $CoSt_2$ + $AlEt_3$ in hexane. Compounds containing sulfur, nitro, and chlorine functional groups deactivated the catalyst [174]. Regioselective hydrogenation of quinoline, isoquinoline, and 2-methylquinoline to the corresponding 1,2,3,4-tetrahydro derivatives is catalyzed by $[Cp^*Rh(p\text{-xylene})]^{2+}$or $[Cp^*Rh(MeCN)_3]^{2+}$in MeOH solution at 80°C and 35 bar. Further reduction does not take place under such conditions [175]. Pyrene could be hydrogenated in 60% yield to symmetrical hexahydropyrene with a Ziegler-Sloan-Lapporte catalyst based on $Ni(acac)_2$ and Et_3Al [176].
See also [115,131,223].

5. Hydrogenation of Carbonyl Compounds

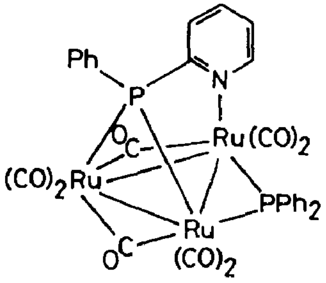
The kinetics of the catalytic hydrogenation of cyclohexanone with $RuH_4(PPh_3)_3$ or $[RuH_3(PPh_3)_3]^-$ were measured. Based on these results it was concluded that anionic character of the Ru complex is not a significant contributor to its catalytic activity [177]. Dimethyl oxalate could be hydrogenated at 180°C and 200 bar H_2 in the presence of $Ru(CO)_2(PBu_3)_2(OAc)_2$ first to methyl glycolate (in a rapid reaction) and subsequently to ethylene glycol (in a significantly slower reaction). Pretreatment of the catalyst with ethylene glycol increased its activity [178]. The cluster anion $[H_2Ru_4(CO)_{12}]^-$ was found to catalyze the hydrogenation of the keto group in acetacetic amides and esters at $10^{\circ}C$ and 40 bar in THF solution. Acetacetic esters were converted in a consecutive coupling step into new diester derivatives (59, 60) [179].



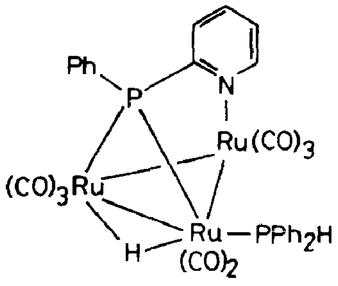
59

60

The complexes $Ru(CO)_3(PPh_3)_2$ and $Ru(CO)_4(PPh_3)$ were found to catalyze the hydrogenation of benzaldehyde to benzyl alcohol photochemically. Since both complexes also catalyze the photochemical carbonylation of benzene to benzaldehyde, carbonylation in the presence of H_2 leads directly to benzyl alcohol. Although this reaction is thermodinamically more favorable than carbonylation alone, no significant increase in yield could be observed [180]. The trinuclear Ru cluster (61) was found to be a good catalyst precursor for the hydrogenation of cyclohexanone at $120^{\circ}C$ and 40 bar. It was transformed under the reaction conditions partly into (62). This result suggests, that a bridging phosphido group may serve in catalytic cycles as hydrogen "reservoir" through intermediates containing secondary phosphines as ligands [181].



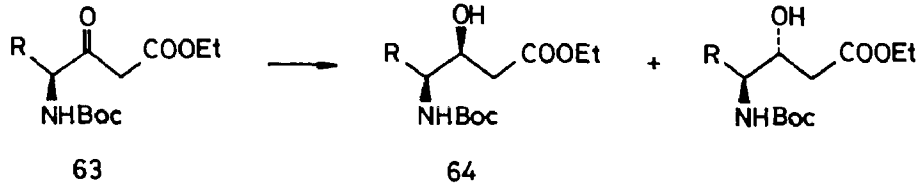
61



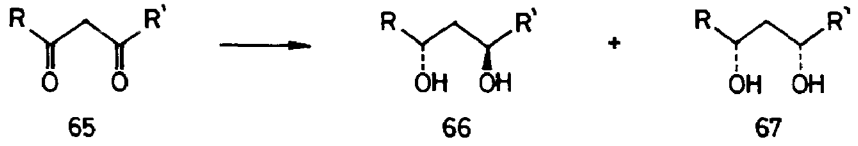
62

Chiral ketones of type (63) (R = $PhCH_2$, iBu, cyclohexyl-methyl) were asymmetrically hydrogenated with

$RuBr_2$[(S)-BINAP] to give the desired threo products (**64**) in over 99% yield and better than 97% enantiomeric excess. The latter value shows that the γ-stereocenter does not racemize under the reaction conditions (20°C, 100 bar, EtOH solution) [182].



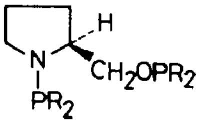
The chiral Ru complex Ru_2Cl_4[(R)-BINAP$]_2(NEt_3)$ has been used as an efficient catalyst for the asymmetric hydrogenation of 1,3-diketones (**65**) to the corresponding diols (**66** and **67**). In all the cases examined (R,R' = Me, Et, iPr, iBu, or Ph) a high excess (89-99%) of the (R,R)-anti isomer (**66**) was formed [183].



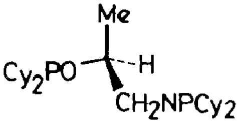
Asymmetric hydrogenation of many functionalized ketones was performed with high enantioselectivity (optical yields above 90%) using Ru(II)-BINAP complexes as catalysts. Reaction conditions were 30°C, 40-100 bar and 8-185 hours reaction time. The key factor in stereodifferentiation is the simultaneous coordination of the carbonyl oxygen and the heteroatom to the Ru atom, making a five- or six-membered chelate ring; N- or O-containing functional groups or even halogen atoms may serve as directing groups [184]. Enantioselective hydrogenation of the chloro ketone (**68**) with $Ru(OAc)_2$(BINAP) as catalyst precursor at 100°C and 100 bar afforded the chloro alcohol (**69**) in 97% optical yield within 5 minutes. If the reaction was conducted at room temperature (necessary reaction time was 25-40 h) optical yield was below 70% [185].

68 69

The chiral aminophosphinephosphinite ligands (70) and (71) were found to give with $[Rh(COD)Cl]_2$ *in situ* active and selective catalysts for hydrogenation of activated ketones like (72) or (73). Enantioselectivities were in the range of 70–80% [186].

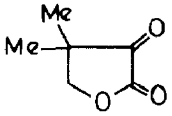


70 ; R = Cy, cyclopentyl



71

$PhCH_2COCONHCH_2Ph$ 72



73

See also [67,146,167,195,210].

6. Hydrogenation of Nitro Compounds

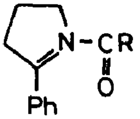
Hammett plots were obtained for the hydrogenation of $RC_6H_4NO_2$ and the reductive amination of iPrCHO with a Pd/poly(4-vinylpyridine)-polyethylene graft copolymer as catalyst [187]. Aromatic nitro compounds were hydrogenated under normal pressure using $M(acac)_2$ (M = Pd,Pt) complexes as catalysts. The Pd complex was more active than its Pt analog. Partly reduced nitroaromatics could be hydrogenated only in the presence of $PhNO_2$ [188]. Complexes of Pd and Pt with organic dyes were immobilized on organic and inorganic supports and used as catalysts for the hydrogenation of nitro groups, conjugated double bonds and acetylenic bonds [189]. Pd(II) and Pt(II) anchored to 2- and

4-vinylpyridine polymers of different molecular weights were used for the hydrogenation of nitro aromatics to anilines at 50°C. Palladium complexes were far more effective than their platinum analogs; the activity of the catalysts decreased with increasing molecular weight of the polymers [190].
See also [194].

7. Miscellaneous Hydrogenations

Hydrogenolysis of alkanes and cycloalkanes was observed at 180°C and 50 bar H_2 in the presence of a $Re_2(CO)_{10}$ + iBu_2AlH catalyst system. All possible lower molecular weight alkanes were formed as products and turnover numbers per Re atom were around 100 in a few hours [191].

Aromatic imines $ArC(Me)=NCH_2Ph$ (Ar = Ph, 2-MeO-C_6H_4, 4-MeO-C_6H_4) were hydrogenated to the corresponding secondary amines at 70 bar in 1:1 MeOH:C_6H_6 using a chiral *in situ* catalyst system formed from $[Rh(NBD)Cl]_2$ and (R)-$Ph_2PCH(C_6H_{11})CH_2PPh_2$. A maximum of 91% enantiomeric excess was achieved at low temperatures in the presence of iodide as cocatalyst. The system was ineffective for the asymmetric hydrogenation of aliphatic imines [192]. Asymmetric hydrogenation of the substituted phenylpyrrolines (**74**; R = H,CF_3) with catalysts formed *in situ* from $Rh(COD)Cl_2$ and chiral phosphines gave the corresponding pyrrolidines in max. 36% optical yield [193].



74

A catalyst for the hydrogenation of olefins, MeCN, and $PhNO_2$ was prepared by treating SiO_2 with hydrolyzed poly {[γ-(*m*-diphenylphosphinophenyl)propyl]siloxane} and then reacting with rhodium trichloride. The catalyst could be recovered and reused with little loss of activity [194]. Olefins, aldehydes, ketones, α,β-unsaturated carbonyl compounds and nitriles were hydrogenated at 100°C and 14-70 bar using $RuCl_2[PhP(CH_2CH_2PPh_2)_2]$ as catalyst. Hydrogenation of nitriles furnished a mixture of

primary, secondary, and tertiary amines [195].
See also [67,96].

8. Dehydrogenation

Polyquinoline was synthesized from 1,2,3,4-tetrahydroquinoline by dehydrogenative polymerization using as catalyst precursor Re *o*-aminobenzenethiolate which transformed *in situ* into an active dehydrogenation catalyst [196].

Dehydrogenation of 1,4-cyclohexadiene to benzene is catalyzed at 25°C by the radical anions derived from $(C_6H_6)_2Cr$ or $(C_6H_6)_2Mo$ and Na sand in 1,2-dimethoxyethane. Under the same conditions, (benzene)(1,3-cyclohexadiene)Fe(0) promotes both dehydrogenation and disproportionation to benzene and cyclohexene [197]. The polyoxotungstates $(Bu_4N)_4W_{10}O_{32}$, $H_3PW_{12}O_{40}$, and $(Bu_4N)_3PW_{12}O_{40}$ were tested as catalysts for the photochemical dehydrogenation of alkanes and cycloalkanes. Strong acids increased the selectivity and rate of the reaction, in some cases quantum yields around 100% have been achieved [198].

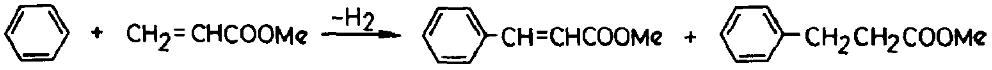
Dehydrogenation of methanol to formaldehyde is catalyzed at reflux temperature by $Ru(OAc)Cl(PEtPh_2)_3$. The catalyst is gradually transformed into $RuClH(CO)(PEtPh_2)_3$ and thus looses its activity [199]. The complex $RuH_2(N_2)(PPh_3)_3$ catalyzes the dehydrogenation of alcohols and diols at 150°C in the presence of NaOH. The catalytic cycle probably involves $RuH_4(PPh_3)_3$ which contains coordinated dihydrogen [200]. Dehydrogenation of secondary and allylic primary alcohols to carbonyl compounds with allyl methyl carbonate was carried out in the presence of Ru or Pd complexes. The reaction proceeded under neutral conditions and hence various acid- or base-sensitive functional groups were not affected [201].

n-Heptane and n-octane were dehydrogenated to the corresponding 1- and 2-alkenes at 70-90°C under photocatalytic conditions using $Rh(CO)(PR_3)_2Cl$ (R = Ph, Et, Me) complexes. Activity of the catalysts increased in the stated order of phosphine ligands; the largest turnover frequency was 795 h^{-1} [202,203]. Dehydrogenation of alkanes or cycloalkanes is catalyzed by $Rh(CO)(PMe_3)_2Cl$ under mercury-lamp irradiation at room temperature. Cyclohexene and benzene are formed from cyclohexane (turnover numbers 132 and 3, respectively), 2-hexenes are the main products of the dehydrogenation of n-hexane. No H acceptor is necessary [204]. Catalyzed by $Rh(CO)(PMe_3)_2Cl$ under irradiation, 1-decene undergoes dehydrogenation, hydrogenationand dimerization reactions leading to a mixture of isomeric C_{20} dienes and saturated hydrocarbons. Small amounts of intramolecular dehydrogenation products (decadienes, cyclodecane,and cyclodecene) were also formed [205]. Methyl propionate could be photocatalytically dehydrogenated to methyl 4-propionyloxybutyrate (73) (head-to-tail dimer) in the presence of $Rh(CO)(PMe_3)_2Cl$ at room temperature. Methyl acrylate was presumed to be an intermediate of the reaction [206].

$$2\ CH_3CH_2COOCH_2 \xrightarrow{-H_2} CH_2CH_2COOCH_2CH_2CH_2COOCH_3$$

75

Dehydrogenative cross coupling of benzene with methyl acrylate to yield methyl cinnamate (75; mainly *trans*-isomer) was accomplished with $Rh(CO)(PMe_3)_2Cl$ as catalyst under irradiation. 3-Phenylpropionate was formed as minor byproduct. The reaction of toluene afforded *meta*-substituted isomers as main products [207].



76

The catalyst system generated from $RhCl.3H_2O$ and Aliquat 336 or some other phase-transfer catalyst catalyzes the dehydrogenation and disproportionation of 1,3-cyclohexadiene into benzene and cyclohexene at 70°C. Polar organic solvents promote dehydrogenation (more benzene than cyclohexene is formed), in toluene only disproportionation takes place. Water is essential for the activity of the catalyst [208]. Irradiating a benzene solution of Et_3SiH containing $Rh(CO)(PMe_3)_2Cl$ as catalyst, triethylphenylsilane and biphenyl are formed and H_2 is evolved:

$$PhH + Et_3SiH \longrightarrow PhSiEt_3 + Ph\text{-}Ph + H_2$$

A rhodium hydride species is assumed as the key intermediate of the catalytic cycle [209]. The complex $Ir(CO)(PPh_3)_2(ClO_4)$ stoichiometrically dehydrogenates $PhCH{=}CHCH_2OH$ to $PhCH{=}CHCHO$ and catalyzes the hydrogenation of $PhCH_2CH_2CHO$ to $PhCH_2CH_2CH_2OH$ at room temperature and atmospheric pressure [210].
See also [122].

9. Hydrogen Transfer Reactions

a) Hydrogenation of C=C Bonds

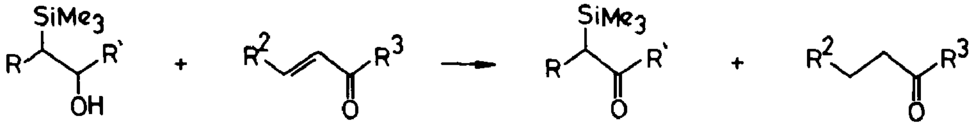
Transfer hydrogenation of anthracene with tetralin as H source was investigated with Co(II), Fe(III), and Cr(III) TPP complexes as catalysts at 70°C. (TPP)Co(II) exhibited the highest activity [211].
See also [212].

b) Hydrogen Transfer Reactions Involving $>C{=}O$ and $>CHOH$ Groups

Group 4 metallocene complexes such as Cp_2ZrH_2, and Cp_2HfH_2 catalyze the chemoselective reduction of polycarbonyl compounds to hydroxycarbonyl compounds by iPrOH. Reduction of keto aldehydes proceeds selectively at the aldehyde group to provide the corresponding hydroxy ketones. Under similar conditions, however, cyclohexanediones are aromatized to benzenediols. The two complexes also catalyze the selective reduction of various α,β-unsaturated carbonyl compounds to the corresponding allylic alcohols in good to excellent yields [212]. The titanium system obtained from Cp_2TiCl_2 and Et_3Al, followed by thermal treatment in tetralin at 200-220°C, catalyzes hydrogen transfer reactions of CH_2O (added as trioxane) at 210°C resulting in the formation of methanol, methyl formate, methylal and CO [213].

Selective transfer hydrogenation of α,β-unsaturated aldehydes to α,β-unsaturated alcohols by iPrOH is catalyzed by $H_4Ru_4(CO)_8(PBu_3)_4$. Kinetic data support a mechanism according to which the catalyst remains a Ru_4 cluster and is not fragmented into smaller species [214]. Transfer hydrogenation of cyclohexanone or acetophenone with iPrOH and $HMCl(CO)(PPr^i_3)_2$ (M = Ru,Os) as catalyst proceeds with reasonable rate only in the presence of $NaBH_4$ or KOH as cocatalysts. Probably the polyhydrides $H_4M(CO)(PPr^i_3)_2$ are formed under such conditions and these act as catalysts [215]. Transfer hydrogenation of hexane-2-one by iPrOH is catalyzed at 110-190°C by an osmium cluster catalyst prepared by refluxing an n-octane solution of $Os_3(CO)_{12}$ with silica under Ar [216].

The binuclear complexes $H(CO)(PPh_3)_2Ru(L\text{-}L)M(COD)$ (HL-LH = = 2,2'-biimidazole, M = Rh,Ir) were found to be more active as catalysts for the transfer hydrogenation of cyclohexanone or cyclohexene by iPrOH than the mononuclear parent (Ru, Rh, or Ir) compounds. The binuclear complexes could be recovered unchanged after the reactions [217]. In the presence of some ligands $Rh_2(OAc)_4$ showed good catalytic activity for H transfer from iPrOH to cyclohexanone or other unsaturated compounds. The most active system was obtained from $Rh_2(OAc)_4$ and bpy in a molar ratio 1:6 [218]. Synthesis of α-trimethylsilyl ketones (77; R,R' = H or different alkyl groups) was achieved from β-trimethylsilyl alcohols by using α,β-unsaturated carbonyl compounds (e.g. 2-cyclohexanone) as hydrogen acceptors and $HRh(PPh_3)_4$ as transfer hydrogenation catalyst at 100°C [219].



77

c) Reduction of Nitro Compounds

Transfer hydrogenation of aromatic nitro compounds by hydrazine to the corresponding anilines is catalyzed by $(Bu_4N)[Ni(tdt)_2]$ (tdt = toluene-3,4-dithiolate) and analogous Ni complexes in refluxing THF. Hydroxylamine derivatives are formed as intermediates [220]. Reduction of aromatic nitro compounds by benzoin and Et_3N is catalyzed by $[Fe_4S_4(SPh)_4]^{2-}$ in MeCN solution. Nitrobenzene is reduced to aniline, *m*-dinitrobenzene to *m*-phenylene diamine or *m*-amino nitrobenzene, depending on the excess of reducing agent [221].

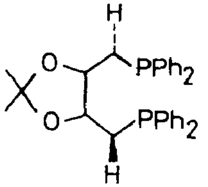
d) Formates as Hydrogen Donors

Ketones and aldehydes were reduced with good yields to alcohols with Cp_2TiCl_2 as catalyst and HCOOH + Et_3N as H source [222].

Cationic Rh(III) complexes like $[Cp^*(bpy)RhCl]^+$ catalyze the reduction of $NAD(P)^-$ by formate:

$$NAD(P)^+ + HCOO^- \longrightarrow NAD(P)H + CO_2$$

Reduction of $NAD(P)^+$ by H_2 is also catalyzed by these complexes but this reaction is slow compared to the reduction by formate [223]. Enantioselective transfer hydrogenation of α,β-unsaturated carboxylic acids by triethylammonium formate is catalyzed by Rh complexes formed *in situ* from $[Rh(COD)Cl_2$ and chiral diphosphines. Highest reaction rates and optical yields were achieved with DIOP (78) or BPPM which form seven membered chelate rings. The best solvent was DMSO [224].



78 ; (-)-DIOP

Selective hydrogenolysis of alkenylcyclopropanes (79) having two electron-withdrawing groups (E = COMe, COOMe) was carried out using a Pd-phosphine catalyst (formed *in situ* from $Pd_2(dba)_3 \cdot CHCl_3$ and PBu_3) and ammonium formate in dioxane at reflux temperature. Cyclopropane ring opening proceeds with inversion [225].

79

Hydrogenolysis of propargyl carbonates (80) with ammonium formate in the presence of a Pd complex and a tertiary phosphine

(PBu_3, PPh_3, or dppe) gave 1,2-dienes (**81**) along with smaller amounts of simple alkynes (**82**) [226].

$$\underset{\mathbf{80}}{HC\equiv CCRR'OCOOMe} \longrightarrow \underset{\mathbf{81}}{CH_2{=}C{=}CRR'} + HC\equiv CCH_2R' + \underset{\mathbf{82}}{CH_3C\equiv CR'}$$

R = H, Me; R' = n-C_8H_{17}, $(CH_2)_2CH{=}CMe_2$, Ph

Isomerization/hydrogenation of 4-hydroxy-2-alkynoates and 4-hydroxy-2-alkyn-1-ones (**83**; R = aryl, heteroaryl, vinyl; R' = OEt, aryl) to give 1,4-dicarbonyl derivatives (**84**) has been achieved by treatment with tributylammonium formate in the presence of $Pd(OAc)_2(PPh_3)_2$ as catalyst. The presence of both carbonyl and aryl/heteroaryl/vinyl groups in the starting material is necessary, otherwise base-catalyzed isomerization of the propargylic system is prevented and only hydrogenation of the C,C triple bond can be observed [227].

83 84

In the presence of formic acid, Et_3N, and a Pd(II) catalyst the alkyl 4-hydroxy-2-alkynoates (**85**; R = H,Me; R' = Me,Et,Ph; RR' = cycloalkyl; R'' = Me,Et) undergo a one-pot hydrogenation-cyclization reaction to form the butenolides (**86**). Increasing the excess of formic acid results in the formation of saturated γ-lactones [228].

85 86

10. Reduction without Molecular Hydrogen

a) Stoichiometric Reduction with Low-Valent Transition Metal Complexes

Pyridine N-oxides, Ph_3AsO and $(C_8H_{17})_3NO$ were deoxidized by SmI_2 and nitrobenzenes were reduced to anilines with SmI_2 in MeOH [229]. Nitroarenes were reduced by Sm (and less effectively, Yb) metal to azoxy compounds. Best yields were achieved in the presence of small amounts of MeOH and HMPA [230]. Benzil could be asymmetrically reduced to benzoin by SmI_2 in THF solution in the presence of a chiral auxiliary like quinine or diethyl L-(+)-tartrate. Addition of HMPA increased the enantioselectivity of the system; best optical yields (up to 56%) were achieved with quinidine [231]. Samarium diiodide promotes intramolecular reductive coupling of functionalized keto aldehydes (87), generating stereoselectively *cis*-2,3-dihydroxycyclopentane derivatives (88) [232].

87 88

R = alkyl,Ph
R' = H,Me,Et
Y = OEt,NMe_2

In the reduction of α-keto esters by Ti(III) the dimeric or monomeric reduction products (pinacols or secondary alcohols, respectively) could be made to predominate by the choice of the solvent. Dimerization increased with increasing dielectric constant and/or increasing hydrogen ion concentration [233]. Heterocyclic aromatic disulfides with a N α to the S atom could be reduced to the corresponding thiols by $TiCl_3$ in the presence of citrate. Simple alkyl or aryl disulfides did not react [234].

Reduction of nitroarenes to the corresponding amines, of alkyl or aryl halides to hydrocarbons and of acylic α,β-unsaturated ketones to saturated ketones was achieved with $CpV(CO)_3$ under phase transfer conditions using 5N NaOH and $(Bu_4N)HSO_4$. The reactions proceed probably via electron transfer pathways [235]. The kinetics and mechanism of the reduction of cystine to cysteine by vanadium(II) in slightly alkaline medium has been studied. The data were consistent with a mechanism involving two parallel paths leading to vanadium(II) and vanadium(IV), with precursors differing by one cystine ligand [236].

Epoxides could be selectively deoxygenated to the corresponding alkenes by treating with $MoO(S_2CNEt_2)_2$ in toluene at 80-130°C. Over 98% retention of stereochemistry was observed [237]. Thiols (RSH) were reduced with good yields to the corresponding hydrocarbons (RH) by treatment with stoichiometric amounts of $W(CO)_6$ in chlorobenzene solution at reflux temperature. Small amounts of the dimers R-R were formed as byproducts [238].

The anionic hydride $[HFe(CO)_4]^-$ reduces aldehydes and ketones to alcohols in THF solution in the presence of CF_3COOH at reflux temperature. The reduction of nitrobenzene to aniline, of benzoyl chloride to benzaldehyde and benzyl alcohol and of benzyl chloride to toluene proceeds already at room temperature [239]. The rubredoxin model complex $[Fe(SC_6H_4Me\text{-}p)_4]^-$ stoichiometrically reduces tBuOOH to tBuOH [240]. N-Aryl-O-pivaloylhydroxylamines (89; X = *m*-Br, *p*-Cl, 3,4-Cl_2, *p*-NO_2) are rapidly reduced by an excess of Fe^{2+} to the corresponding anilines. The reaction requires complexation of the ester with Fe^{2+} and proceeds with hydrolysis of the N-O bond since nearly quantitative yields of pivalic acid can be isolated too [241].

89

Second-order rate constants were determined for the reduction of indigo carmine by several amino alcohol coplexes of Co in aqueous solution [242]. The kinetics of stoichiometric hydrogenation of α,β-unsaturated esters or ketones by $HCo(CO)_4$ were determined. Both reactions are catalyzed by $Co_2(CO)_8$ [243]. The η^2-H_2 complex $[(H_2)Rh(PP_3)]^+$ [PP_3 = $P(CH_2CH_2PPh_2)_3$] stoichiometrically hydrogenates the C=C double bond of dimethyl maleate at room temperature in THF solution. The analogous Co and Ir complexes (the latter is a dihydride) are inactive [244].

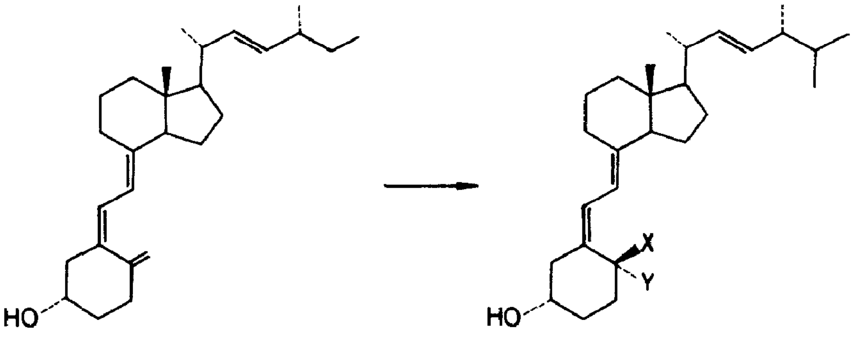
Selective reduction of the C=C bond in α,β-unsaturated ketones or esters has been achieved with the Cu(I) hydride cluster

$[(PPh_3)CuH]_6$ in benzene at room temperature. The reduction was stereoselective and the major products arose from hydride addition to the least hindered face of the substrate [245].

b) Inorganic Reductants in the Presence of Transition Metal Complexes

Chemoselectivity could be achieved in the reduction of D-fructose and D-glucose when $CeCl_3$ was used with $NaBH_4$ [246]. A highly selective reduction of α,β-carbonyl compounds to the corresponding allylic alcohols has been achieved by $NaBH_4/LnCpCl_2(THF)_3$ (Ln = Sm or Er) in MeOH [247]. Reduction of 1-hexene with Cp_3Ln/NaH (Ln = La,Pr,Nd,Sm,Tb,Y,Er,Yb,Lu) in THF at 45°C gave hexane after hydrolysis. The Cp_3Sm/NaH system was the most active. This latter reagent also catalyzed the hydrogenation of 1-hexene at 45°C and 4 bar [248].

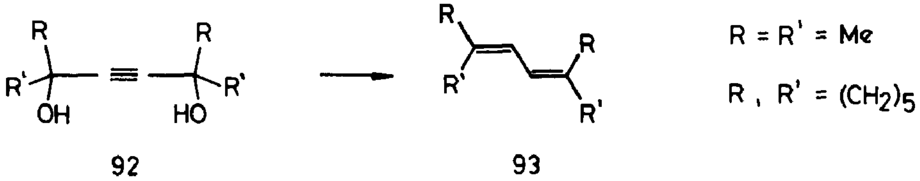
Vitamin D_2 (**90**) and its derivatives were regioselectively reduced to the corresponding 10,19-dihydrovitamins D_2 (e.g. **91a** and **91b**) by treatment with Cp_2TiCl_2 + $LiAlH_4$ followed by hydrolysis [249].



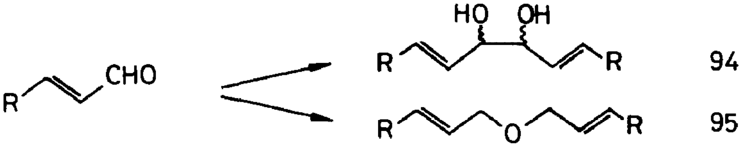
90

91a, X = Me, Y = H
91b, X = H , Y = Me

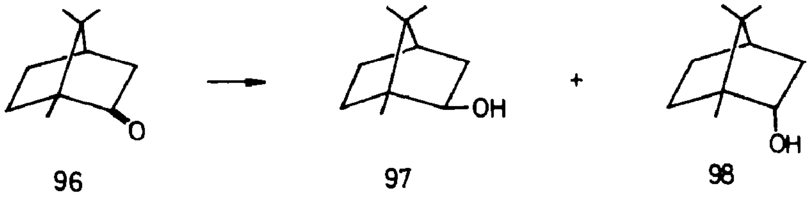
Low-valent titanium, prepared from $TiCl_3$ and $LiAlH_4$, was used to reduce 2-yne-1,4-diols (**92**) to 1,3-dienes (**93**). The reaction was not stereospecific and monoolefins were formed as byproducts [250].

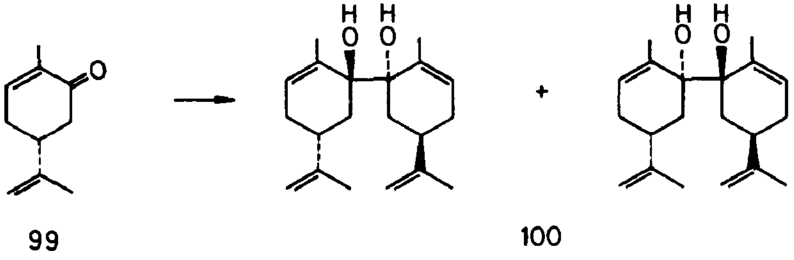


Aliphatic, aromatic, and α,β-unsaturated ketones are readily reduced to the corresponding secondary alcohols by iPrMgBr in the presence of a catalytic amount of bis(neomenthylcyclopentadienyl) titanium dichloride. The effective reducing agent is probably $(nmenCp)_2TiH$ [251]. Epoxides can be deoxygenated to alkenes by "reactive titanocene" prepared *in situ* from Cp_2TiCl_2 and Mg in THF solution. The same reducing agent transforms unsaturated aldehydes at -78°C into dimeric diols (**94**) or at room temperature into divinyl ethers (**95**) [252].

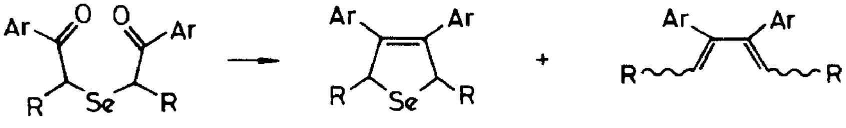


Camphor (**96**) is reduced by $TiCl_4$ + Mg in the presence of tBuOH to isoborneol (**97**, 58%) and borneol (**98**, 32%). The same reagent reduces (R)-(+)-carvone (**99**) to the corresponding pinacols (**100**) [253].



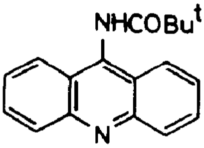


Reduction of diketo selenides (**101**; R = H,Me) with a low-valent Ti reagent prepared from $TiCl_4$ and Zn powder in THF, afforded 2,5-dihydroselenophenes (**102**) and 1,3-dienes (**103**) in comparable yields [254].



101 **102** **103**

Reduction of acetylene by Zn amalgam is catalyzed by $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_4(C_2H_4)$ [255]. Reduction of sulfoxides and pyridine N-oxides with low-valent tungsten reagents derived from WCl_6/BuLi or WCl_6/Zn gave the corresponding sulfides and pyridines in almost quantitative yields. At low temperatures $WCl_4(THF)_n$ was isolated from the WCl_6/BuLi reaction mixture [256]. The cubane clusters $[MoFe_3S_4(SC_6H_4\text{-}p\text{-n-octyl})_3(O_2C_6Cl_4)L]^{2-}$ (L = DMF, Me_2CO) and $[Fe_4S_4(SC_6H_4\text{-}p\text{-n-octyl})_4]^{-}$ function as catalysts for the reduction of $n\text{-}C_5H_{11}N_3$ by $Na_2S_2O_4$ in aqueous Triton X-100 micellar solutions, giving $n\text{-}C_5H_{11}NH_2$ and N_2. The reduction is enhanced by the methyl viologen dication and in its presence also N_2H_4 and NH_3 are formed by the FeMo cluster catalyst [257]. The kinetics of the reduction of (**104**) with dithionite catalyzed by the Fe-S clusters $[Fe_4S_4(SR)_4]^{n-}$ (R = $CH_2CH(COONa)NHCOMe$, $CH_2CH(COONa)NHCO(CH_2)_{16}Me$; n = 1,2) in cetyltrimethylammonium bromide micelles have been studied. Both electron transfer reactions (from dithionite to the catalyst and from the catalyst to the substrate) showed almost the same efficiencies as those of native ferredoxins [258].

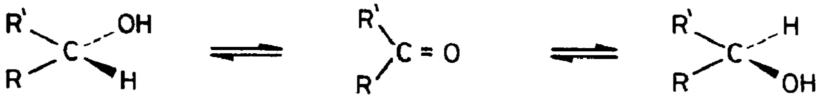


104

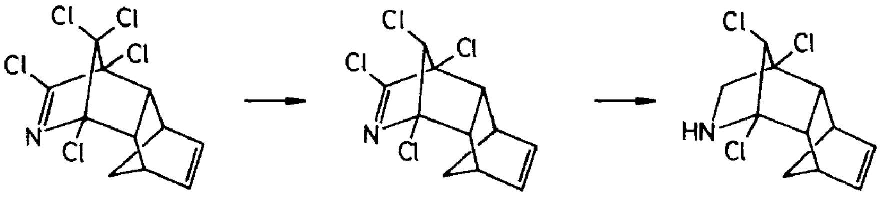
The stereochemistry of reduction of several cyclic ketones by a variety of complex reducing agents composed of NaH + MX_2 + Me_3SiCl (MX_2 = $CoCl_2$, $MnCl_2$, or $Ni(OAc)_2$) has beeen investigated.

Stereochemistry was principally determined by the metal salt; Ni and Co had a strong tendency to produce the more stable alcohol [259]. The 2-oxo group on triterpenoid pentacyclic skeletons was selectively reduced to give 2β-OH axial derivatives using chloroiridic acid and $P(OMe)_3$. Oxo groups in other positions did not react [260].

A homogeneous organonickel reagent prepared from nickelocene and $LiAlH_4$ was shown to be effective for the reduction of carbon-sulfur bonds in thiols, thioethers, sulfoxides, and sulfones to the corresponding carbon-hydrogen bonds. Other functional groups such as isolated double bonds, esters, carbonyls, and halides remained intact under such conditions [261]. Olefinic doble bonds were hydrogenated by adding the substrate and water or Me_3SiCl simultaneously to a complex reducing agent (CRA) composed of anhydrous nickel acetate, NaH, and tert.-pentyl alcohol in THF. Olefins were hydrogenated to saturated hydrocarbons, diolefins to monoolefins and unsaturated ketones or esters to the corresponding saturated derivatives [262]. Epimerization of diastereomeric secondary alcohols has been achieved by the complex reducing agent composed of NaH + 2,5-dimetyl-2,5-hexanediol + $Ni(OAc)_2$ + $MgBr_2$ via successive dehydrogenation-hydrogenation as shown below (R or R' = chiral alkyl or cycloalkyl group):

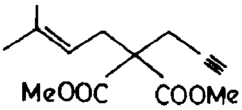


These reactions are controlled by thermodynamic factors [263]. The complex reducing agent (CRA) composed of $Ni(OAc)_2$, NaH, and tert.-pentyl alcohol was used for the reductive desulfurization of thioketals, thiophenes, sulfoxides, and sulfones to the corresponding hydrocarbons. The new reagent proved to be as effective as Raney Ni [264]. Reduction of azaaldrin (**105**) by the NaH-t-pentylONa - $Ni(OAc)_2$ complex reducing agent (NiCRA) yields the tetrachloro (**106**) and trichloro derivatives (**107**) [265].

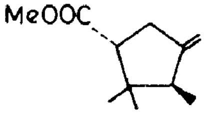


105 106 107

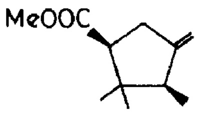
Reduction of propargyl alcohol derivatives RC≡CCHRR' (R = H,alkyl; R' = Br, SO_3Me, $OP(O)(OEt)_2$) with $LiALH_4$, $NaBH_4$, or $LiBHEt_3$ catalyzed by $Pd(PPh_3)_4$ gave mainly allenes RHC=C=CHR and $RC{\equiv}CCH_2R$. Highest yields of allenes were obtained with $LiBHEt_3$ [266]. Reductive cyclization of the enyne (**108**) catalyzed by $(dba)_3Pd_2.CHCl_3$ + $(o\text{-}MeC_6H_4)_3P$ and using Me_3SiH as hydride source gave the two diastereomeric cyclopentane derivatives (**109a**) and (**109b**) in a 5:1 ratio [267].



108



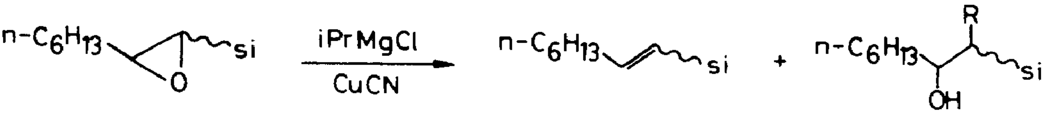
109 a



109 b

Reduction of MeOH to CH_4 by HI is catalyzed by Pt ions [268].

Reaction of iPrMgCl with α,β-epoxy silanes (**110**) in the presence of CuCN was found to result in deoxygenation and ring-opening to give vinylsilanes (**111**) and β-hydroxysilanes (**112**), respectively. The ratio of the two products depended on the structure of the silyl group (si): $SiMe_3$ led exclusively to the ring-opening product while $SiMe_2(OPr^i)$ gave almost exclusively the deoxygenation product [269].



110 111 112

Active uranium, prepared in hydrocarbon solvents from UCl_4 and $[TMEDA)Li]_2$(naphthalene) (TMEDA = N,N,N',N'-tetramethylethylenediamine), reduces benzil or benzoin to bibenzyl. The reaction proceeds over diphenylacetylene and stilbene as intermediates [270].
See also [306].

c) Organic Reductants in the Presence of Transition Metal Complexes

Several $Cr(CO)_3$-complexed aromatic ketones could be enantioselectively reduced by baker's yeast; in some cases (e.g. acetophenone) the reduction was faster and the enantioselectivity higher than with the uncomplexed ketone [271]. Aromatic nitro compounds were reduced to amines by 2-mercaptoethanol in the presence of $[Fe_3O(OAc)_6py_3]$ as catalyst in py as solvent at room temperature:

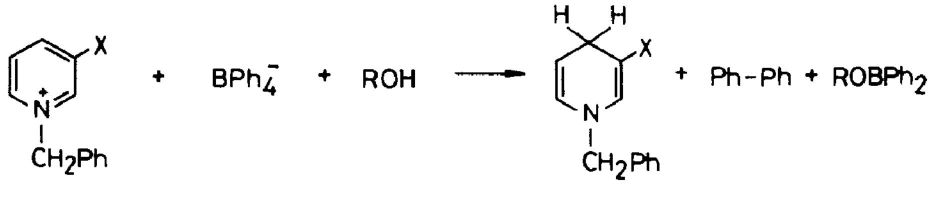
$$ArNO_2 + 6\ HOCH_2CH_2SH \longrightarrow ArNH_2 + 3\ (HOCH_2CH_2S-)_2 + 2\ H_2O$$

Several related mixed trinuclear acetate complexes of the type $[Fe_2^{III}M^{II}O(OAc)_6py_3]$ (M = Mn, Fe, Co, and Ni) were found to be also active and the catalysts could be used for the reduction of benzil to benzoin and of azobenzene to hydrazobenzene too [272].

d) Electroreduction and Photoreduction

The $Cp_2NbCl_2^-$ anion has been shown to be an efficient catalyst for the electrochemical reduction of benzyl chloride to bibenzyl [273]. Conditions for the electroreduction of *m*-nitroaniline to *m*-phenylenediamine were optimized using the Ti^{3+}/Ti^{4+} redox system [274]. Aromatic amines were obtained as the sulfates in 67-99% yield by electrochemical reduction of the corresponding nitro compounds in H_2SO_4 containing 2-3% $Ti(SO_4)_2$ [275]. Voltammetric studies on the electroreduction of *p*-nitrophenetole with and without Ti(IV) sulfate on a Cu cathode were reported. The catalytic influence of the Ti^{4+}/Ti^{3+} couple could be clearly established [276]. Electroreduction of nitrobenzene was studied on a glassy C electrode in the presence of Cr^{2+}/Cr^{3+}, V^{2+}/V^{4+}, Ti^{3+}/Ti^{4+}, Fe^{2+}/Fe^{3+}, and Fe^{o}/Fe^{2+} redox systems. The most effective were V^{2+}/V^{4+} systems which quickly reduced phenylhydroxylamine, the intermediate product of the reaction [277]. Aromatic hydrocarbons can be activated for electrochemical reduction (hydrodimerization or hydrogenation) by transforming them into $Cr(CO)_3$ complexes. Stilbene was hydrodimerized in this way via its mono $Cr(CO)_3$ complex into 1,2,3,4-tetraphenylbutane [278]. The reduction of allyl halides to 1,5-hexadiene at glassy carbon electrodes is catalyzed by bipyridyl complexes of Co(II) in aqueous micellar solutions containing Na dodecyl sulfate or cetyltrimethylammonium bromide. An organocobalt(I) intermediate was observed [279].

Visible-light-photoinduced hydrogenation of acetylene and ethene was accomplished employing an aqueous system containing $[Ru(bpy)_3]^{2+}$ as photosensitizer, ascorbate as sacrificial electron donor, and $[RhCl(dpm)_3]^{3-}$ (dpm = diphenylphosphinobenzenesulfonate) as catalyst. In the presence of CO hydroformylation of ethene took place [280]. Photoreduction of the NAD(P)$^-$ model compounds (**113**; X = $CONH_2$, Ac) with BPh_4^- in an alcohol containing solvent mixture (benzene/MeCN/iPrOH) using (OEP)RhAc as catalyst gave the corresponding 1,4-dihydropyridine derivatives (**114**). Hydride transfer was supposed to take place via an intermediate Rh-hydride complex [281].



113 114

See also [95,97-99,101,103,104].

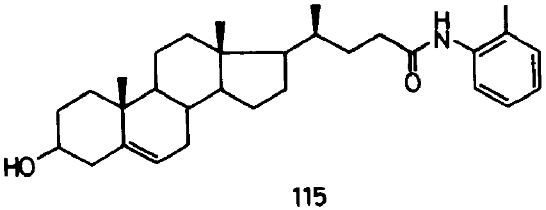
IV. OXIDATION

1. Catalytic Oxidation of Hydrocarbons and Hydrocarbon Groups with O_2

a) Oxidation of Alkanes

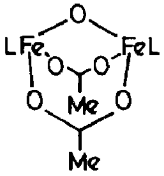
The activity of catalysts in the oxidation of cyclohexane by O_2 decreases in the following order: $CrSt_3 \sim VOSt_2 > MoO(acac)_2 > CoSt_2 > MnSt_2 > NiSt_2 > CuSt_2 > CeSt_4 > TiSt_4$ [282]. The rate constants of oxidation of cholesterol by O_2 in the presence of tetra-*meso*-substituted metalloporphyrins (containing Cr, Mn, Fe, Co, or Ni) have been determined. The reaction proceeded rapidly in those cases where the intermediate metalloporphyrin-O_2 complex contained singlet oxygen [283].

Oxidation of polyethylene dissolved in hexadecane by O_2 with a $MnSt_2$ + NaSt catalyst was faster than the oxidation of hexadecane alone [284]. Autocatalysis is completely eliminated in the first step of the liquid-phase oxidation of n-dodecane by O_2 if Mn naphthenate is added to the reaction mixture [285]. The optimum temperature for the oxidation of paraffin mixtures to fatty acids by O_2 and $KMnO_4$ as catalyst was found to be 130^oC [286]. In the oxidation of alkanes with O_2 in the presence of $CpMn(CO)_3$ as catalyst carboxylic acid formation was inhibited by other O-containing products in the order aldehydes > ketones > alcohols. The rate of formation of organic carbonyl compounds increased in the presence of aldehydes and acids, and decreased in the presence of ketones [287]. Hydroxylation of simple alkanes and the selective C-25 hydroxylation of cholesterol by O_2 in the presence of ascorbic acid have been achieved using as catalyst a Mn(III) porphyrin having the groups (**115**) at the four *meso* positions of the porphyrin ring and intercalated into a synthetic bilayer liquid membrane composed of dimeristoylphospholine. The system strikingly mimicks the C-26 hydroxylation of cholesterol by liver mitochondrial cytochrome P-450 [288].

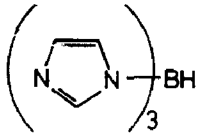


115

Adamantane and cyclohexane could be oxidized to the corresponding alcohols and ketones by O_2 in CH_2Cl_2 in the presence of AcOH, Zn powder and the iron complex (**116**) at room temperature and 1 bar [289].



116 ; L =



The kinetics of the Ru(III)-EDTA catalyzed oxidation of cyclohexane to cyclohexanol and of cyclohexanol to cyclohexanone by O_2 in acidic medium have been determined and the activation parameters were calculated [290]. The rates of these oxidations increased in the presence of cetyltrimethylammonium bromide, mainly because of a decrease in activation energy [291].

Liquid-phase oxidation of cyclohexane to dibasic acids has been studied in glacial acetic acid solution with the Co-form of a weak acid resin as catalyst at 85-105^{o}C and 5-20 bar O_2. Addition of cyclohexanone decreased the induction period of the reaction. The yield of adipic acid was higher than that in cyclohexanone oxidation alone [292]. The influence of water on the oxidation of cyclohexane by O_2 catalyzed by $Co(OAc)_2.4H_2O$ was determined [293].

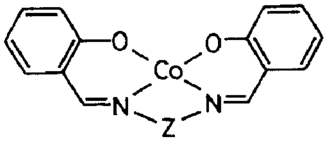
Cyclohexane is oxidized to cyclohexanone by air at room temperature and atmospheric pressure in pyridine solvent using $Cu(ClO_4)_2.6H_2O$ or $Fe(ClO_4)_2.6H_2O$ as catalyst. Small amounts of cyclohexanol are also formed but the alcohol is not an intermediate of ketone formation [294].

See also [326,417].

b) Oxidation of Olefins

Olefins were oxidized to alcohols by O_2 in MeOH solution in the presence of metal porphyrin complexes and $NaBH_4$. Metal *meso*-tetrakis(sulfophenyl)porphines showed higher activity than metal TPP complexes [295]. Oxygenation of ethyl oleate in the presence of M(TPP) + $NaBH_4$ + Avicel (a microcrystalline form of cellulose) or M(TPP) + thiolato ligand (cysteine or N-acetyl cysteine) has been studied (M = Mn, Fe, Cr). The products were either ketones (at the 9- or 10-position), mono-ols (at the 9- or 10-position) or diols (at the 8- and 11-positions) [296]. Thiolate-metalloporphyrin complexes were reported to catalyze the oxygenation of cyclohexene with O_2, yielding mainly cyclohexanone and cyclohexanol acting thus as model systems of cytochrome P-450. The system composed of (TPP)Mn, cysteine, Mn^{3+}, and $NaBH_4$ was found to be the most effective but also (TPP)Cr or (TPP)Fe could be used instead of (TPP)Mn [297]. Oxidation of olefins with O_2 and a reducing agent was studied with different metal *meso*-tetrakis(*p*-sulfonatophenyl)porphins (TPPS) in MeOH as solvent. The best system was that comprising Mn(TPPS) and $NaBH_4$. It was concluded that the active species of the catalytic process was not a metal-oxo complex. The olefin was mainly transformed into the corresponding alcohol [298].

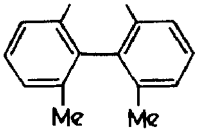
Oxidation of propene to propylene oxide and allyl alcohol on an immobilized complex of iron protoporphyrin has been studied [299]. The effect of Fe(III) palmitate on the rate of oxidative deterioration of palm oil was evaluated. Iron(III) palmitate mainly increased the rate of formation of secondary products [300]. The oxidation of 1-hexene to 2-hexanone by O_2 is catalyzed by $[RuCl_2(H_2O)_4]^+$ at 35°C in a water/dioxane solution; the product ketone is formed in 54% yield. This system represents the first monometallic catalyst system for Wacker oxidation of olefins to ketones [301]. Liquid-phase oxidation of cyclohexene with O_2 in the presence of cobalt-containing polymer catalysts has been studied. A Co diacrylate-polyethylene graft polymer was found to be the most active. No correlation was found between the type of coordination and catalytic activity [302]. The liquid-phase oxidation of 3-carene with O_2 in the presence of $Co(acac)_2$ as catalyst to give 3-caren-5-one was studied. The main byproduct was the corresponding peroxide [303]. Liquid-phase oxidation of 1-decene with O_2 and $Co(acac)_2$ as catalyst gave 1-decen-3-one with 80% selectivity [304]. Cobalt(II)-Schiff base complexes Co(L) (**117**) were used as catalysts for the oxidation of alkenes to ketones with O_2 at 60°C in primary or secondary alcohols as solvents. No reaction took place in aprotic solvents; using benzyl alcohol as solvent it was shown that the reaction proceeds as a co-oxidation and benzaldehyde is formed [305].



117

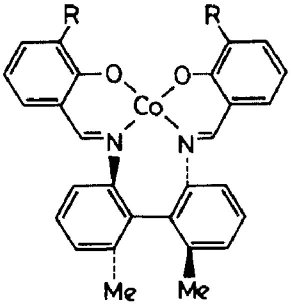
Z = $(CH_2)_n$; n = 2-4

$(CH_2)_3NR(CH_2)_3$; R = H,Me

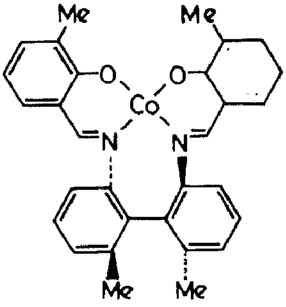


2 nPr

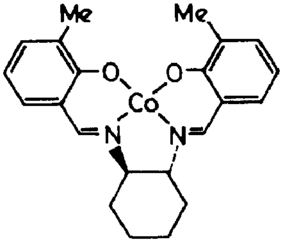
Oxygenation of styrene with O_2 and BH_4^- using dmgH, TPP, salen or phthalocyanine complexes of Co, Fe, and Mn as catalysts was investigated. Main product of the reaction was 1-phenylethanol but some hydrogenation to ethylbenzene and 2,3-diphenylbutane also took place [306]. The chiral Co Schiff base complexes (**118–121**) have been used as catalysts for the oxidation of styrene to 1-phenyl ethanol. Modest enantioselectivities were observed; the best value was 38% which was achieved with the complex (**121**; R = H) [307,308].



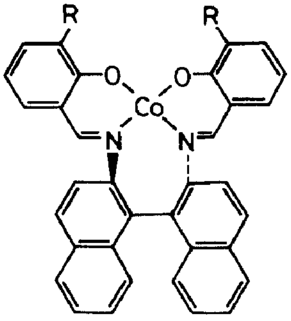
118 ; R = H, Me, MeO



119

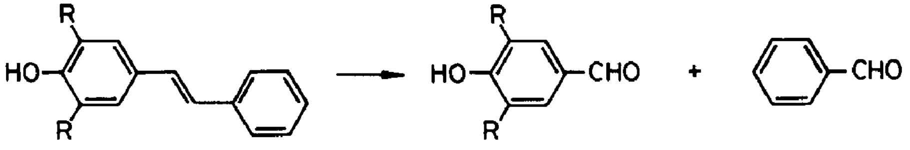


120



121
R = H,Me

The Co(II) Schiff base chelate (152) catalyzes the oxygenation of 4-stilbenols (122; R = H,Me,tBu) to give two molecules of aldehydes. Both O atoms are incorporated into the products, providing a good model for dioxygenase reactions [309].



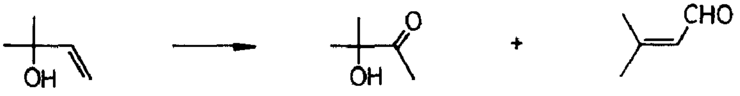
122

Liquid-phase oxidation of styrene by O_2 in toluene solution and with $Rh(PPh_3)_3Cl$ as catalyst gave selectively benzaldehyde and formaldehyde as primary products. Optimum reaction temperature was 75°C; higher temperatures and styrene conversions led to the formation of benzoic acid [310]. The same reaction was performed at 100°C also with $Rh(PPh_3)_3Cl$ anchored to polymeric Amberlite beads. In this case styrene conversion depended on catalyst loading and distribution [311].

Mono- and binuclear polyketone complexes of Ni(II) and Cu(II) were tested as catalysts for the oxidation of propene with O_2 [312].

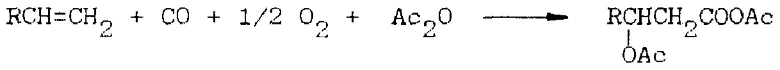
Nitro and nitrate complexes of Pd(II) with the general formula $Pd(NO_n)_{2-m}Cl_m(MeCN)_2$ ($n = 2,3$; $m = 0,1,2$) were tested as catalysts for the oxidation of ethene and propene [313]. Cyclopentene is oxidized to cyclopentanone by O_2 in tetralin containing dichloropalladium complexes. The reaction proceeds by oxidation of tetralin to α-tetralyl hydroperoxide which then initiates radical chain processes [314]. Oxidation of 1-decene by O_2 in the presence of Pd(II) complexes as catalysts gave 1-decene-3-one in 60% yield [315]. Acetoxylation of propene to allyl acetate with O_2 and AcOH was performed using as catalysts the Pd clusters $Pd_{561}X_{60}(OAc)_{180}$ and $Pd_{561}X_{60}(PF_6)_{60}$ (X = phen) [316].

Alkenes were oxidized to ketones with O_2 in EtOH containing $PdCl_2$, $BiCl_3$, and LiCl. One oxygen atom was incorporated into the ketone, the second co-oxidized a solvent molecule [317]. A chloride-free catalytic system composed of $Pd(OAc)_2$, hydroquinone and iron phthalocyanine has been developed for the oxidation of olefins to methyl ketones with O_2. The iron complex catalyzes the oxidation of hydroquinone to quinone which acts as the oxidant of the Pd-catalyzed oxidation of the olefin. The reactions were performed in aqueous DMF [318]. The oxidation of ethene to acetaldehyde with O_2 on a supported liquid-phase Wacker catalyst adsorbed on alumina was investigated. The active phase of the catalyst was a chlorinated aqueous solution of $CuCl_2$, $PdCl_2$, and $Cu(NO_3)_2$; reaction temperature was 40-80°C [319]. The allyl alcohol derivative (**123**) was oxidized to the corresponding ketone (**124**) with good yields using the following systems: O_2 + $PdCl_2$ + CuCl, quinone + $PdCl_2$, and O_2 + $PdCl(NO_2)(MeCN)_2$. Best selectivity (99%) was obtained with the last combination, the other systems furnished minor amounts of (**125**) too [320].

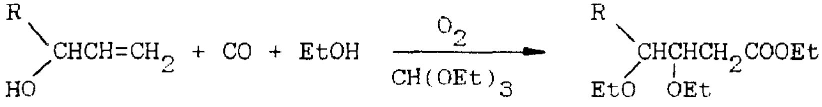


123 124 125

Acetyl derivatives of β-hydroxyalkanoic acids (**126**) were prepared by oxidative carbonylation of terminal olefins with CO + O_2 in Ac_2O solution catalyzed by $PdCl_2$ + $CuCl_2$ at 80°C and atmospheric pressure. Allylic alcohols were transformed in EtOH solution under similar conditions into β,γ-diethoxybutanoates (**127**) [321].



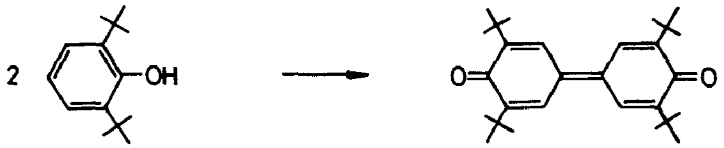
$$RCH{=}CH_2 + CO + 1/2\ O_2 + Ac_2O \longrightarrow \underset{\displaystyle OAc}{RCH}CH_2COOAc \qquad 126$$



$$\underset{HO}{\overset{R}{>}}CHCH{=}CH_2 + CO + EtOH \xrightarrow[CH(OEt)_3]{O_2} \underset{EtO}{\overset{R}{>}}CH\underset{\displaystyle OEt}{CH}CH_2COOEt \qquad 127$$

The $Cu(OAc)_2$ - LiBr system catalyzes the oxidation of 1,4-diphenyl-1,3-butadiene to 2,5-diphenylfuran (**128**) and that of 2,6-di-t-butylphenol to the diquinone (**129**) by O_2 in an AcOH - Ac_2O 1:1 mixture. The two products were isolated in 30 and 60% yield, respectively [322].

128



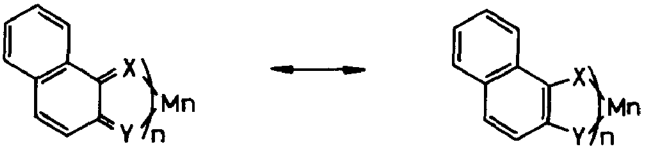
129

See also [480].

c) Epoxidation of Olefins

Polymer-supported $(NH_4)_6Mo_7O_{24}$, $MoO_2(acac)_2$, and MoO_2Cl_2 catalyze the epoxidation of cyclohexene [323].

Cyclohexene was epoxidized with O_2 using a catalyst which consisted of Pt on silica and a homogeneously dissolved (TPP)Mn(III) complex. The reaction was carried out in the presence of H_2 as cooxidized species [324]. Alkenes were epoxidized by O_2 at 60°C using the complexes (**130**) as catalysts. The induction period of the reaction could be reduced by the addition of pyridine [325].

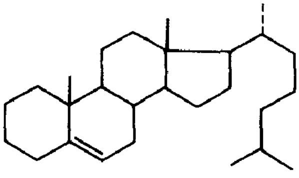


130

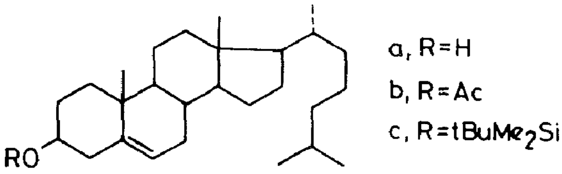
n = 2,3

X,Y = O or NO

The Ru(III) Schiff base complexes Ru(saloph)(Im)Cl and Ru(salen)(Im)Cl (Im = imidazole) catalyze the oxidation of cyclohexene predominantly to cyclohexene oxide and cyclohexanone, respectively [326]. Cyclohexene was epoxidized with O_2 using Rh(saloph)(L)Cl complexes (L = Cl^-, imidazole, 2-methylimidazole, or py) as catalysts in water/dioxane as solvent at 35°C. The catalytic activity of the complexes increased in the stated order of ligands L [327]. Cholest-5-ene (**131**) and cholesterol derivatives in which the OH group is protected (**132b**,**132c**) were epoxidized highly stereospecifically to the β-derivatives by air with $(TMP)Ru(O)_2$ as catalyst. Cholesterol (**132a**) itself was unreactive [328].



131



132

Liquid-phase oxidation of 4-vinylcyclohexene by O_2 catalyzed by $CoBr_2$ and a complex Mo catalyst gave 4-vinyl epoxycyclohexane along with unsaturated alcohols and ketones [329].
See also [459].

d) Oxidation of Aromatics

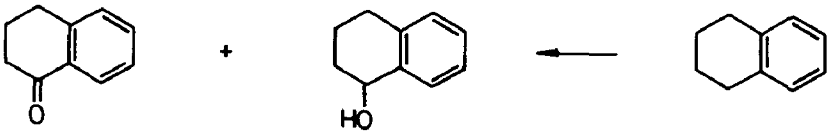
Rate constants for the oxidation of anthracene to anthraquinone by O_2 in the presence of Mn porphyrins and $NaBH_4$ were determined [330].

The system Ru(III)-EDTA-ascorbic acid-O_2 selectively oxidizes toluene to *o*-creols. Based on kinetic, spectrophotometric and potentiometric measurements a mechanism was proposed which involves the formation of an intermediate Ru(IV) dioxygen complex [331].

Methyl acetate is one of the main byproducts in the air oxidation of *p*-xylene to terephthalic acid in acetic acid solution and with a Co-Mn-Br catalyst system. It has been shown, that by recycling the ester to the oxidation process it is oxidized under the technological conditions (220^oC and 24 bar) into acetic acid, CO, and CO_2 [332]. In the oxidation of *m*-xylene with O_2 and a Co-Mn catalyst system, Co^{2+} plays the main role in chain initiation while Mn^{2+} reacts with peroxy, acylperoxy, and acyloxy radicals [333]. Liquid-phase oxidation of *p*-methoxytoluene to *p*-anisaldehyde with O_2 in the presence of Co based catalysts has been studied. With $Co(OAc)_2.4H_2O$ alone only traces of the desired product could be obtained; upon addition of $Mn(OAc)_2.4H_2O$ or $Ce(OAc)_3.H_2O$ a considerable improvement was observed. The most effective catalyst system (76% yield of *p*-anisaldehyde) was composed of Co, Ce, and Cr acetates [334]. In a similar system, the yield of 3,4,5-trimethoxybenzaldehyde from

3,4,5-trimethoxytoluene was highest (92%) if a $Co(OAc)_2.4H_2O$ + $Mn(OAc)_2.4H_2O$ (3 + 1) catalyst mixture was used [335]. Complexes of Co, Ni, and Cu with aromatic Schiff bases containing sulfur, nitrogen, and phosphoryl donor groups were tested as catalysts in the liquid-phase oxidation of cumene. Both catalysis and inhibition were observed [336].

Fluorene was oxidized to phthalic acid with O_2 in the liquid phase in the presence of Co complexes, e.g. $[Co(nicotinate)_2](NCS)_2$ or activated carbon containing Co^{2+} and Br^- [337]. Effects of temperature, catalyst, initiator concentration, and addition of MeCOPh initially to the reaction mixture were determined for the liquid-phase oxidation of ethylbenzene to acetophenone in the presence of Co salt catalysts. The Co naphthenate + dibenzoylperoxide system was the most convenient to handle [338]. Both $Co(St)_2$ andf $Cr(St)_3$ catalyze the oxidation of xylenes by O_2; combinations of the two catalysts show the highest activity [339]. Cobalt complexes with N,N'-methylene-diacrylamide-crosslinked acrylic acid-di-ethyl vinyl phosphonate copolymer showed a high catalytic activity in liquid-phase oxidation of xylenes to toluic acids [340]. Complexes of Co with a copolymer of vinylphosphonic acid diethyl ester and acrylic acid were prepared in the presence of ethylbenzene and after the removal of the substrate were used as catalysts for the liquid-phase oxidation of ethylbenzene with O_2. The prearrangement of the complexes in this way resulted in a considerable increase in activity and selectivity [341]. Cobalt(II)-pyridine complexes bound to latex copolymers of styrene, divinylbenzene, and either acrylic or methacrylic acid catalyze the autoxidation of tetralin:



These heterogenized catalysts are more active than Co(II)-py complexes in aqueous solution or Co-acetate in acetic acid [342].

The $Ni(acac)_2$-HMPA catalyst used in the oxidation of ethylbenzene by O_2 is oxidized during the process at the methine C-H bond. This results in an increase of selectivity of hydroperoxide formation [343]. If N-methyl-2-pyrrolidinone (L) is used as electron donor ligand instead of HMPA in this system, the active catalyst formed during oxidation has the composition $Ni_2(acac)(OAc)_3.L.2H_2O$ [344].

Oxidation of benzene with O_2 in the presence of CuCl as catalyst in a water-benzene two-phase system has been studied. Phenol and hydroquinone were the main products; their ratio strongly depended on the pH of the solution. The results were compared to those obtained with $CuCl/H_2O_2$ and $FeSO_4/H_2O_2$ systems [345]. Benzene dispersed in aqueous sulfuric acid was hydroxylated with O_2 in the presence of CuCl to give phenol and hydroquinone in yields of 24 and 8%, respectively. The active species generated by the Cu-O_2 system was reported to be the hydroxyl radical [346]. Oxidation of cumene by O_2 is catalyzed by $CuCl_2$ fixed on aminopropyl Aerosil. The catalyst increases the rate of hydroperoxide decomposition and thereby initiates a radical-chain process [347]. The Cu(I) phenolato complex (**133**) reacts with excess phenol under O_2 to give the Cu(II) catecholato complex (**134**). The catecholato group originates from a phenol hydroxylation reaction assisted by the Cu center [348].

$$\underset{\mathbf{133}}{(phen)(Ph_3P)Cu(OPh)} \longrightarrow \underset{\mathbf{134}}{(phen)Cu(OPh)(OC_6H_4OH\text{-}o)}$$

See also [74,710].

2. Catalytic Oxidation of O-Containing Organic Compounds

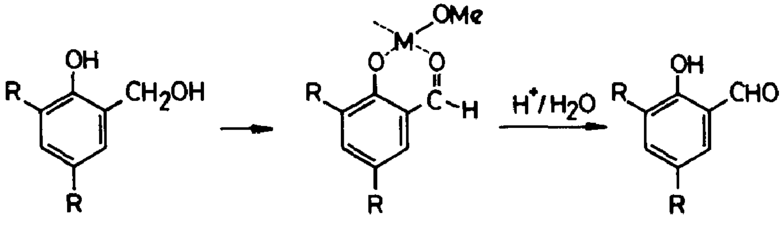
a) Oxidation of Alcohols

The Pt/C - $CeCl_3$- $Bi_2(SO_4)_3$ system in aqueous MeOH has been found to catalyze the selective oxidation of *m*-hydroxybenzyl alcohol by O_2 to *m*-hydroxybenzaldehyde (83% yield). The role of $CeCl_3$ is not clear [349]. Benzoins, $p\text{-}RC_6H_4CH(OH)COC_6H_4R\text{-}p$ (R = H,MeO,Cl), were oxidized to the corresdponding benzils with air or amine N-oxides in the presence of Mo(VI) complexes of cysteine esters or cysteine-containing peptides [350]. Catalytic oxidation of alcohols with O_2 in the presence of silica-supported transition metal chlorides has been studied. The highest selectivity in oxidation of EtOH to AcH was obtained with supported $MnCl_2$ [351].

Aryl-substituted 1,2-diols were selectively cleaved to aldehydes or ketones as oxidation products at room temperature by O_2 in the presence of catalytic amounts of (TPP)FeCl and stoichiometric amounts of 1-benzyl-3-carbamoyl-1,4-dihydropyridine (BNAH). Reduction of the Fe(III) complex by BNAH to Fe(II) starts the catalytic cycle: (TPP)Fe(II) reacts with O_2 to form (TPP)Fe=O which oxidizes the diol and Fe(III) formed is again reduced by BNAH to Fe(II) [352]. Oxidation of alcohols to the corresponding carbonyl compounds by air is catalyzed by $[Bu_4N][Os(N)(CH_2SiMe_3)_2(CrO_4)]$ in MeCN solution at 70°C. The catalyst is highly selective: only aldehydes are formed from primary alcohols, and PPh_3 or olefins are not oxidized under such reaction conditions [353].

In the oxidation of cyclohexanol to cyclohexanone by O_2 at 120-165°C and 10 bar, high conversion and selectivity were obtained with $PdCl_2$ and $Fe_2(SO_4)_3$ as catalysts [354]. A silica-supported polysilazane-Pt complex has been prepared and used as catalyst for the oxidation of alcohols to the corresponding carbonyl compounds with O_2 at room temperature. The catalyst could be reused several times [355].

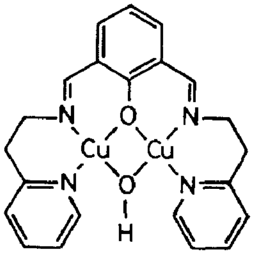
Saligenols (**135**, R = H,tBu) were oxidized by O_2 in the presence of an excess of metallic Cu or Fe and a catalytic amount of Cu_2Cl_2 or $FeCl_2$ in MeOH solution to the Cu or Fe complexes of salicylaldehydes (**136**). The complexes may be easily converted into the free salicylaldehydes (**137**) [356].



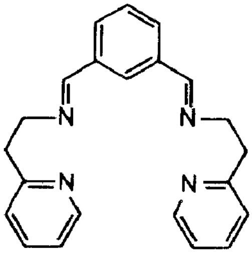
135 **136** **137**

Oxidation of primary alcohols to carboxylic acids by O_2 is catalyzed by Cu-phen complexes in the presence of bases. Cu(I) complexes catalyzed the formation of aldehydes; in the presence of Cu(II) complexes carboxylic acids were formed. In aqueous media, PrOH was preferentially oxidized to formic acid whereas in nonaqueous media PrOH and $PhCH_2OH$ were oxidized to propionic and benzoic acids, respectively [357,358]. The Cu^{2+} complex of a

14-membered macrocyclic dioxotetramine ligand catalyzes the oxidation of benzyl alcohol by O_2 to benzaldehyde in MeCN solution containing $PhCH_2ONa$. Oxygen is transformed into H_2O_2 [359]. The binuclear Cu(II) complex (**138**), prepared from Cu(I) and the ligand (**139**) followed by oxidation with O_2, catalyzes the oxidation of α-hydroxy ketones to diketones and of hydroquinones to quinones. Thus benzoin was quantitatively oxidized in a few minutes with O_2 to benzil in MeOH solution [360].



138

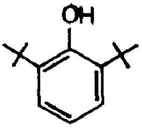


139

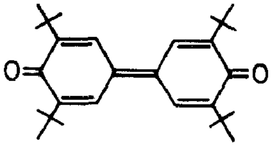
See also [290,291,305].

b) Oxidation of Phenols

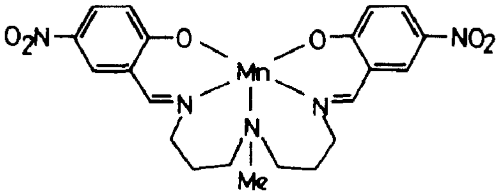
Catalytic oxidation of (**140**) to (**141**) by O_2 in the presence of the Mn(II) complex (**142**) is influenced by an external magnetic field (highest rate was measured at about 1.4 kG). If the substrate contained D at the *para* position, a magnetic kinetic isotope effect was observed. Catalyst regeneration by forming the phenol radical is the most likely origin of the magnetic field effect [361].



140

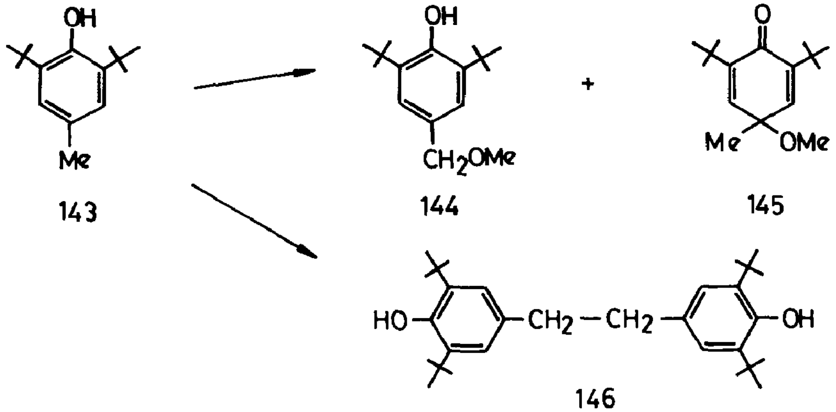


141



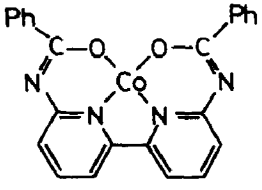
142

The catalytic oxidation of (**143**) to (**144**) and (**145**) in MeOH solution using a catalyst prepared by impregnation of an acid-modified τ-Al_2O_3 with an aqueous solution of $K_4[Fe(CN)_6]$ was reported. If the reaction was carried out in a chloroform suspension, the dimeric derivative (**146**) was the product. The actual catalytic species is probably $[Fe(CN)_6]^{3-}$ [362].



143 **144** **145** **146**

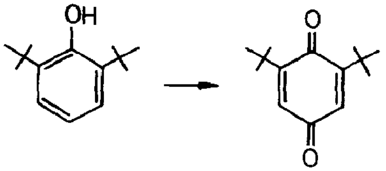
Cobalt(II) complexes of TPP-OR-*p* (R = Me or polymer-bonded benzyl) were prepared and used as catalysts for the oxidation of hydroquinone to quinone. The monomeric catalyst was more active but difficult to reuse whereas the polymeric catalyst showed unchanged activity even after 3 uses [363]. Several hydrophobic derivatives of vitamin B_{12} have been tested as catalysts for the air oxidation of ubihydroquinone. Complexes with CN group(s) on Co showed no activity [364]. The Co(II) complex (**147**) catalyzes the oxidation of (**148**) to (**149**) at room temperature and atmospheric pressure in toluene solution containing >1% pyridine. The new catalyst was found to be more active than Co(salen) and its derivatives [365].



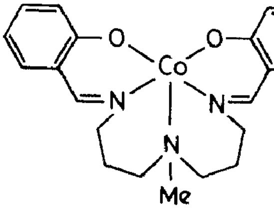
147

148 **149**

The catalytic efficiency of cobalt complexes with tetra- and quinquedentate Schiff base ligands in the oxidation of 2,6-di-tert-butylphenol by O_2 was studied. The complexes CoL and CoL(OAc) contained Schiff bases (H_2L) prepared from 5-formyluracil or 5-formyl-1,3-dimethylbarbituric acid and different aliphatic diamines or $H_2N(CH_2)_3NMe(CH_2)_3NH_2$ [366]. The effect of magnetic field between 0 and 70 kG on the oxidation of (**150**) by O_2 to form (**151**), and catalyzed by (**152**) has been reported. The rate was highest around 1 kG: the relative rate as compared to that measured at zero magnetic field was about 1.7. Magnetic isotope effects were observed for (**150**)-4-d_1-OD and ^{17}O-enriched O_2 [367].

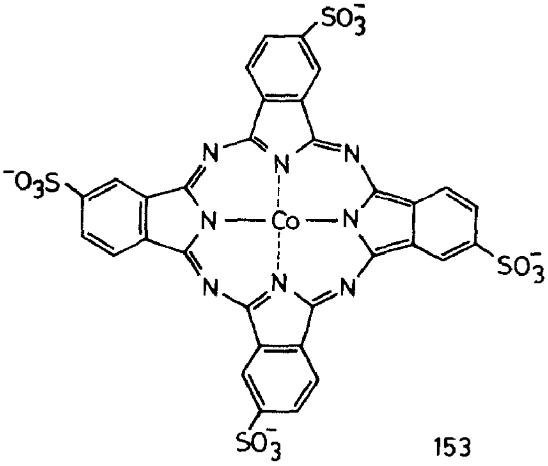


150 **151**



152

Autoxidation of 2,6-di-*tert*-butylphenol to diphenoquinone (**129**) is catalyzed by Co phthalocyaninetetrasulfonate (**153**). It was shown that the rate of O_2 consumption is about 10 times higher if (**153**) is bounded to styrene-divinylbenzene latexes substituted with quaternary ammonium ions than if it is acting in aqueous solution [368].



153

The mechanism of the oxidation of naphthols by O_2 mediated by CuCl depends on the solvent: in MeCN a radical-ion pair mechanism was observed whereas in MeOH hydrogen abstraction by free radicals was involved [369]. The kinetics of oxidation of 2,6-dimethylphenol (DMP) by O_2 to the corresponding

polyphenyleneoxide (as main product) and diphenoquinone (as minor product) catalyzed by Cu(II) complexes of 4-(N,N-dimethylamino) pyridine or its polystyrene-bound analog were studied. Based on the results it was suggested that DMP is oxidized by mononuclear Cu(II) complexes but reoxidation of Cu(I) needs dimerization [370]. The $Cu(acac)_2$-pyridine system and Cu(II)-poly (vinylpyridine) complexes were used as catalysts for the oxidation of 3,5-di-tert-butylpyrocatechol with O_2 to the corresponding o-benzoquinone. A dimeric Cu(II) complex was assumed to be the active species in the homogeneous system [371]. Copper(II) chelate-amine complexes catalyze the oxidative coupling of 2,6-dialkylphenols by O_2. The rate-determining step is the reaction between O_2 and the Cu-phenol adduct [372].
See also [318,322,360.389].

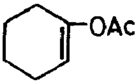
c) *Oxidation of Aldehydes and Ketones*

The chlorine-bridged binuclear complex $Mn_2Cl_2(PPr_3)_2$ catalyzes the oxidation of acrolein under mild conditions. The reaction proceeds via a $Mn-O_2$ complex [373]. Monocyclic ketones are oxidized in glycoldimethylether solution by O_2 in the presence of KOH, K_2CO_3, and catalytic amounts of $Re_2(CO)_{10}$ and polyethyleneglycol at room temperature and 1 bar to give dicarboxylic acids in good yield. The mechanism of this phase-transfer catalytic reaction is unclear [374]. Oxidation of benzaldehyde with O_2 in the presence of (TPP)Co, (TPP)FeCl, and (TPP)MnCl has been investigated. The reaction is catalyzed by species which are formed from the metalloporphyrin and perbenzoic acid with the destruction of the porphyrin ring [375]. Oxidation of cyclohexanone by O_2 catalyzed by $Co(OAc)_2.4H_2O$ and NaBr leads to at least five different products with more than 5% yield. The system shows oscillatory behavior with respect to redox potential, concentrations of dissolved O_2, Co^{3+}, and Br^-, conductivity, and in chemiluminescence [376]. A kinetic study of the oxidation of iPrCHO with O_2 in the presence of $Co(OAc)_2$ indicated that the catalyst participated only in the abstraction of the aldehydic H from the substrate [377]. Liquid-phase oxidation of cyclohexanone to dicarboxylic acids has been studied in AcOH solution using the Co-form of a weak acid cation exchanger as the catalyst at 83-118°C and 5-10 bar O_2. Water was detrimental to the catalyst due to the elution of Co; addition of Ac_2O reduced the amount of Co ion eluted and also increased the reaction rate [378]. A heterogenized homogeneous catalyst for the oxidation of acetaldehyde to peracetic acid was prepared by Co ion exchange on a polymer support. The selectivity and yield obtained with this catalyst were higher than when using a homogeneous catalyst [379].

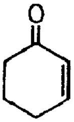
See also [332].

d) Miscellaneous Oxidations

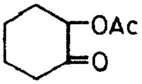
Oxidation of (**154**) by O_2 is catalyzed by $VO(acac)_2$, $MoO_2(acac)_2$, and $Cr(acac)_3$; (**155**) and (**156**) are formed as main products. The yield of (**155**) decreases in the stated order of complexes, epoxidation and the yield of (**156**) increases in the order Cr < V < Mo [380].



154

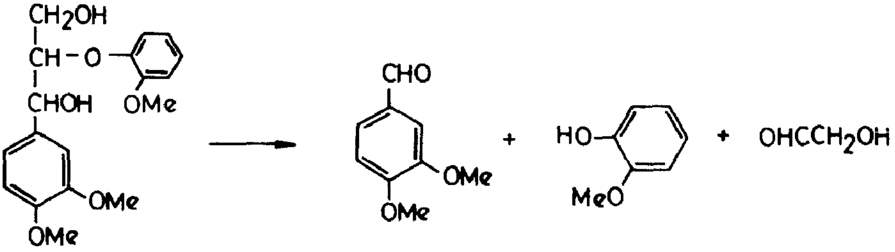


155



156

Oxidation with C-C bond cleavage of the lignin model compound (**157**) by O_2 was achieved with a Mn(II) acetate + Co(II) acetate (1:9) + acetaldehyde catalyst system in acetic acid at 170°C and 35 bar 96% N_2 + 4% O_2. The same reaction took place with stoichiometric amounts of Co(III) acetate in refluxing acetic acid [381].

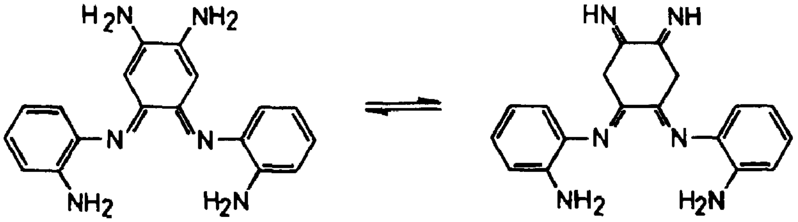


157

Sucrose increases the rate of the Cu-catalyzed oxidation of ascorbic acid by air [382].

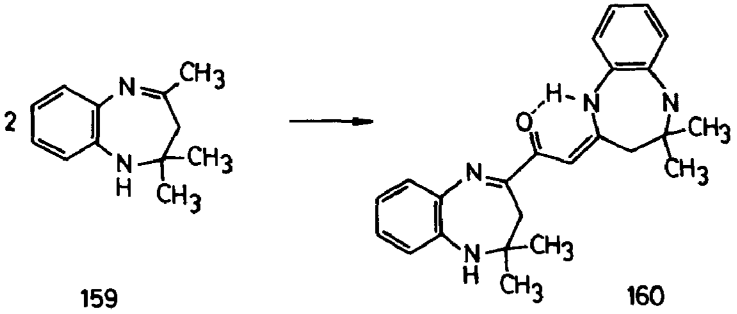
3. Catalytic Oxidation of N-Containing Compounds with O_2

A radical mechanism was confirmed for the oxidation of indigocarmine by O_2 in the presence of a Mn(II)-histidine complex catalyst [383]. Oxidation of *o*-phenylene diamine with O_2 in MeOH solution in the presence of Mn(II) perchlorate gave the complex MnL_2 containing the ligand (L = **158**) formed by trimerization of oxidized *o*-phenylene diamine [384].



158

Manganese(II) chloride promotes the oxidation of the benzodiazepine derivative (**159**) by O_2 in MeOH solution to the dimeric product (**160**) [385].

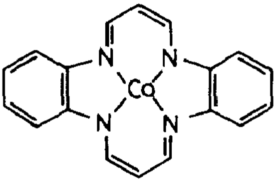


159 **160**

Hydroxylation of L-phenylalanine by O_2, Fe^2, and EDTA was performed in an electrochemical cell in which the cathode acted as the reductant which is necessary for the regeneration of Fe^{2+}. In addition to several unidentified products, *o*-, *m*-, *p*-tyrosine, and DOPA were also formed but the overall yield of these valuable compounds did not exceed 12% [386].

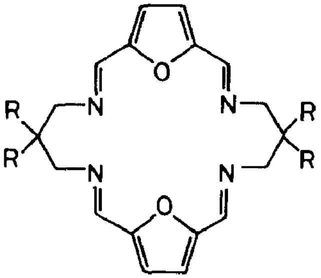
1,2-Diphenylhydrazine is catalytically oxidized by O_2 to zobenzene in the presence of $(Ph_3P)Co(dmg)_2$ at 30°C. The reaction does not involve H_2O_2 as an intermediate. Superoxo and oxo cobaloxime species were supposed to act as two-electron oxidants

[387]. Catalytic oxidation of secondary aromatic amines with O_2 + Co(salen) in ethanol at 60°C affords the corresponding imines in high yields. The electron accepting reactive reagents probably the hydroxocobalt(III) species [388]. The N_4-macrocyclic Co(II) complex (**161**) was used as catalyst for the oxidation of hydroquinones to quinones and hydrazobenzene to azobenzene by air in chloroform solution. Activity of the catalyst decreased upon the addition of a N-base like pyridine [389].



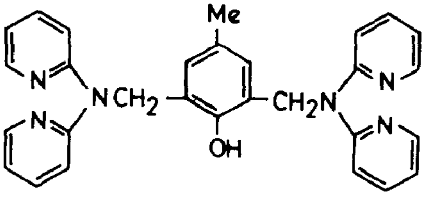
161

Co(salen) catalyzes the oxygenation of indoles in micellar solutions [390]. Dicopper(II) complexes of the macrocyclic ligands (**162**; R = H,Me) stoichiometrically oxidize hydrazobenzene to azobenzene; under O_2, the dicopper(I) complexes of the same ligand act as catalysts for this oxidation [391].



162

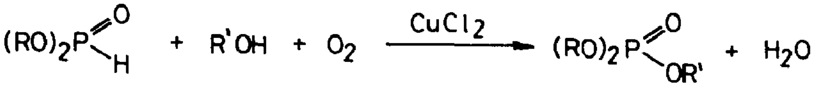
The catalytic activities of the binuclear complexes of Cu(II), Co(II) and Mn(II) with the ligand (**163**) were compared for the oxidation of N,N,N',N'-tetramethyl-*p*-phenylenediamine by O_2. The highest activity was observed for the Cu(II) complex [392].



163

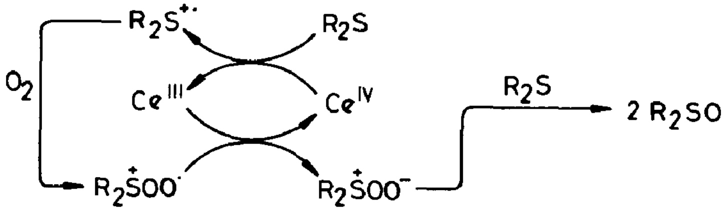
4. Catalytic Oxidation of P-, S-, Se-, or Cl-Containing Organic Compounds with O_2

Mixed trialkyl phosphates (**164**; R,R' = alkyl,Ph) were synthesized by oxidative phosphorylation of alcohols with dialkyl phosphonates and O_2 in the presence of $CuCl_2$ at 50°C [393].

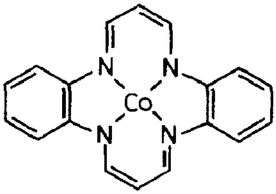


164

Selective oxidation of thioethers to sulfoxides by O_2 at 70°C and 8 bar is catalyzed by $(NH_4)_2Ce(NO_3)_6$. Both atoms of O_2 are incorporated into the product sulfoxide. The following mechanism has been proposed for the reaction [394]:



Hemin catalyzes the oxidation of dithiothreitol by O_2 to its intramolecular disulfide [395]. The kinetics of oxidation of cysteine with O_2 and Fe acetate complexes as catalysts was studied. The data suggest that polynuclear Fe(II,III) complexes are the catalytically active species [396]. Polymeric catalysts consisting of Co(II)phthalocyanine-tetrasodium sulfonate bound to basic polymers [water soluble polyamines or poly(quaternary ammonium hydroxides)] exhibit a high activity in the oxidation of water soluble thiols to disulfides with O_2 in aqueous media [397]. The kinetics of oxidation of 2-mercaptoethanol were investigated in the presence of such catalysts. Reaction rates followed the two-substrate Michaelis-Menten law [398]. The kinetics of cysteine autoxidation catalyzed by Co(II) tetrasulphophthalocyanine has been studied by the polarographic method. An intermediate complex composed of the catalyst, cysteine, O_2, and probably a second cysteine as an RS˙ radical was proposed [399]. The reaction was inhibited by the products [400]. Cobalt phthalocyanine-tetrasulfonate was bound to cationic latexes prepared from styrene, divinylbenzene, ethyldivinylbenzene, and surface active monomer and used as catalyst for the oxidation of 1-decanethiol by O_2 [401]. The Co-tetraaza[14]annulene complex (**165**) catalyzes the oxidation of aromatic thiols by air to disulfides with good yields. No byproducts are formed [402].



165

Reaction of $CuCl_2.2H_2O$ with alkyl thioethers in air yields the tetranuclear clusters $Cu_4Cl_6O(OSR_2)_4$ containing the corresponding sulfoxides as ligands. Copper (I)-thioether complexes were proposed as intermediates which in turn are oxidized by air to the final products [403].

Saturated hydrocarbons could be transformed into phenylseleno derivatives by oxidation with air in the presence of Ph_2Se_2 and iron powder (or $Fe_3O(OAc)_6py_{3.5}$ + Zn) in acetic acid/pyridine. Species containing iron-carbon σ-bonds were postulated as intermediates which react with Ph_2Se_2 to produce RSePh [404].

Kinetic data of the oxidation of *o*-chlorotoluene, 2,3,6-trichlorotoluene and *p*-toluic acid with O_2 in the presence of $Co(OAc)_2$ and NaBr were determined [405]. The kinetics of oxidation of *p*-chlorophenol in supercritical water (400°C and 240 bar) have been investigated. Addition of Cu(II) and Mn(II) salts as catalysts resulted in modest increases of the oxidation rate [406].

See also [660].

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

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

Cerium(IV) ammonium nitrate has been investigated as catalyst for the hydroxylation of aromatic substrates (toluene, phenol, 2-methylphenol, and 2,6-dimethylphenol) by H_2O_2 in water/AcOH solution at 30°C. Addition of surface active agents had a marked influence on selectivity: anionic sodium dodecyl sulfate increased the yield of hydroxylated products, while the yields of oxidatively coupled and nitro-substituted phenolic side products increased in the presence of cationic cetyltrimethylammonium bromide [407,408].

Cyclohexane was oxidized to cyclohexanol and cyclohexanone by H_2O_2 in AcOH + H_2O_2 containing NH_4VO_3 or $VO(acac)_2$. Interestingly cyclohexanol was not converted to cyclohexanone under these conditions [409]. Regioselective α-oxidation of alkynes to conjugated ynones (**166**; R,R' = alkyl, phenyl) was achieved with tBuOOH and catalytic amounts of CrO_3. Yields were superior to those with stoichiometric chromium procedures. Probably propargylic alcohols are the intermediates of this oxidation [410].

166

Terminal alkynes were oxidized to α-keto aldehydes with H_2O_2 in a two-phase (H_2O/dichloroethane) system containing a phase-transfer catalyst (e.g. Aliquat), Na_2MoO_4 as oxidation catalyst, and $Hg(OAc)_2$ as alkyne activating agent. In the presence of Na_2WO_4 as catalyst, carboxylic acids were formed as main products [411]. 12-Heteropolyacids were used as catalysts for the oxidation of cyclopentene to glutaraldehyde with H_2O_2 in PBu_3 solution. Best results were obtained with Mo-W mixed heteropolyacids with the composition $H_3PMo_{12-x}W_xO_{40}$ (x = 1-9) [412]. The heteropolytungstates $PW_{11}O_{39}^{7-}$, $SiW_{11}O_{39}^{8-}$, and $PMW_{11}O_{39}^{n-}$ (M = Ni, Co, Cu, n = 5; M = Fe, n = 4) were used in the form of their tetracyclohexylammonium salts as catalysts for the oxidation of olefins with H_2O_2 in a water/dichloroethane two-phase system. In the case of cyclohexene as model substance *trans*-1,2-cyclohexanediol, adipaldehyde, and adipic acid were formed [413].

Reaction of iodosylarenes with alkenes in a water/organic two-phase system in the presence of sodium halides or azide and catalyzed by Mn tetrarylporphyrin complexes yields both alcohols and alkyl halides (or azides). Selectivity for oxygen incorporation increases with increasing electron withdrawing character of the porphyrin ring [414]. Addition of the tin Lewis acids $Ph_3SnOOCC_7F_{15}$ and $Ph_3SnO_3SC_6F_{13}$ increased the reactivity and reduced the radical character of hydrocarbon oxidation reactions in CH_2Cl_2 solution using PhIO and Mn porphyrins, (TPP)MnOAc and (TpyP)MnOAc, due to substitution of AcO^- by the perfluoro anions. Accordingly, less chlorinated byproduct and less allylic oxidation was observed when oxidizing cyclohexane and cyclohexene, respectively [415]. Ethane, propane, and cyclohexane were oxidized in MeCN solution at room temperature to EtOH, iPrOH, and cyclohexanol or cyclohexanone, respectively, with tBuOOH in the presence of manganese clusters, $Mn_{3-4}O_{1-2}(OOCR)_{6-7}L_{2-3}$ (R = Me,Ph; L = py, bpy), as catalysts. Radical traps did not inhibit the reaction suggesting that free alkoxyl or peroxyl radicals are not involved in the process [416].

The complex $Fe_2O(OAc)_2Cl_2(bpy)_2$ was used as catalyst for the hydroxylation of ethane, propane, and cyclohexane with tBuOOH in MeCN solution at room temperature. Highest yield of alcohol was achieved with cyclohexane (32%). Using this catalyst with O_2 as the monooxygen donor in the presence of zinc powder and glacial acetic acid only small amounts of cyclohexanone were formed [417]. Hydroxylation of benzene with H_2O_2 in the presence of Fe(II)- or Fe(III)-crown ether complexes was studied in aqueous solution at 50^oC. The Fe(III)-dibenzo-18-crown-6 system gave the best results; the yield of PhOH reached 60% under optimal reaction conditions [418]. Hydroxylation of substituted benzenes with H_2O_2 in the presence of Fe^{3+} or Cu^{2+} has been studied in relation to the rearrangement of hydrogen atoms (NIH shift). High shift values (40%-50%) were observed indicating one-electron oxidation of the dienyl radical as one of the principal processes occurring under such conditions [419]. Complexes of Fe(II), Fe(III), Cu(II), Rh(II), and Pd(II) were used as catalysts for the hydroxylation of benzene with H_2O_2 in the presence of polymers, e.g. poly(ethylene glycol) or poly(acrylic acid). Yields of phenol were about 50% [420].

The *cis*-$[Ru(L)_2(OH_2)_2]^{2+}$ complexes (L = substituted bpy or phen) catalyze the oxidation of saturated hydrocarbons to alcohols and ketones by tBuOOH in acetone as solvent. The oxidations are inhibited by MeCN and proceed by a radical mechanism [421]. The Ru(III)-EDTA-ascorbic acid-H_2O_2 system oxidized cyclohexane to cyclohexanol. On the basis of kinetic results it was proposed that ascorbic acid reduces the metal chelate Ru(III)-EDTA to Ru(II)-EDTA and this latter complex catalyzes the oxidation of cyclohexane [422]. Oxidation of alkenes by O_2 is catalyzed by $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$ (pfb = perfluorobutyrate) in MeCN as solvent at 65°C and 3 bar. Mechanistic studies indicate that these oxidations involve a free radical chain pathway [423]. The side chain of alkyl aromatic compounds could be oxidized to aldehydes, ketones, or alcohols by aqueous H_2O_2 in the presence of a Ru(III) salt and a quaternary ammonium phase-transfer catalyst. Thus, tetraline was transformed with 65% yield into 1-tetralone [424]. The kinetics of oxidation of alkylbenzenes by Cr(VI) catalyzed by Ru(IV) were studied. The results indicated a mechanism involving equilibrium formation of a Cr(VI)-Ru(IV) complex followed by the rate-determining electron transfer from alkylbenzene to this complex [425].

A new catalytic, asymmetric dihydroxylation of alkenes has been developed. The method is based on the asymmetric stoichiometric hydroxylation of alkenes with OsO_4 in the presence of chiral tertiary amines (e.g. cinchona alkaloids like quinine or quinidine). The procedure was transformed into a catalytic process by using N-methylmorpholine N-oxide as oxidant and only catalytic amounts of OsO_4. Unlike asymmetric epoxidation or asymmetric hydrogenations this method requires no directing functional group on the olefin; optical yields are usually above 50% [426]. Dihydroxylation of olefins with a catalytic amount of OsO_4 and N-methylmorpholine N-oxide was achieved with high yields in CH_2Cl_2 solution in the presence $PhB(OH)_2$, giving the corresponding phenylboronic esters (e.g.167). The dihydroxyphenylborane acts as a diol captor thus preventing further oxidation [427].

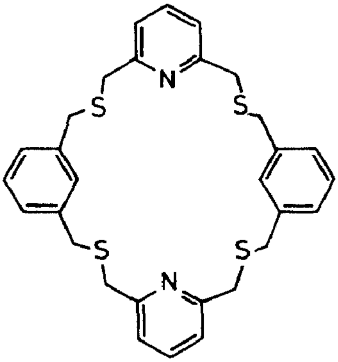
167

Anthracene is converted into anthraquinone, 1-octene into 2-octanone, and 1-phenylethanol into acetophenone with 95-100%

isolated yields by oxidation with tBuOOH in the presence of $Rh(PPh_3)_3Cl$ or $[(dppe)Rh(MeOH)_2]^+$ as catalysts. The phosphine ligands of the catalysts are rapidly attacked during these oxidations but this does not decrease the activity of the catalytic system. A metal-centered mechanism is believed to be more probable than a free radical pathway [428].

The kinetics of oxidation of allyl alcohol by Pd(II) and quinone as reoxidant of Pd(0) have been determined using a potentiometric procedure. The results allow the conclusion that the mechanism of allyl alcohol oxidation involves an irreversible *cis* hydroxypalladation step [429].

The dinuclear copper complex $L.2Cu^{2+}$ (L = **168**) was used as catalyst for the oxidation of styrene and *trans*-stilbene by PhIO. Both styrene oxide and benzaldehyde were formed from styrene; however, benzaldehyde was the only product of *trans*-stilbene oxidation [430].



168

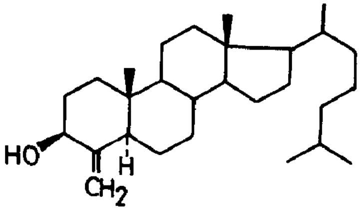
See also [451,457,469,473,479].

b) Epoxidation of Olefins

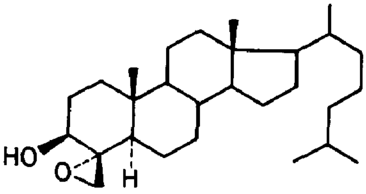
Epoxidation of primary and secondary alcohols with the $Ti(OPr^i)_4$ - tartrate - tBuOOH system has been studied using model substrates having bulky substituents at the olefinic terminus. Moderate increase of bulk increased the rate of epoxidation and the kinetic resolution operating in these systems [431]. Asymmetric epoxidation of (**169**) by tBuOOH in CH_2Cl_2 in the presence of $Ti(OPr^i)_4$ and diisopropyl L-(+)-tartrate gave 65% (**170**) [432].

169 170

Epoxidation of the allylic alcohol (**171**) with $tBuOOH/Ti(OPr^{i})_4$ and (+)- or (-)-diethyltartrate gave in both cases stereospecifically (**172**), although the reaction with (-)-diethyl tartrate was noticeably slower. Accordingly the hydroxyl group showed no directional effect which is an unusual result [433].

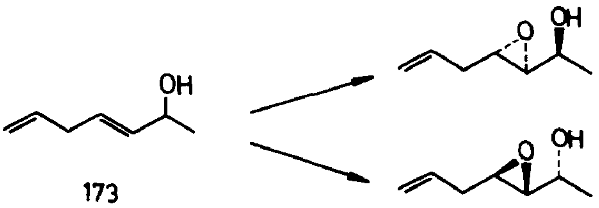


171



172

Kinetic resolution of the racemic allylic alcohol (**173**) by the Sharpless method ($tBuOOH + Ti(OPr^{i})_4$ + diisopropyl tartrate) afforded the epoxy alcohols (**174a**) or (**174b**) depending on whether L-(+)- or D-(-)-diisopropyl tartrate, respectively, were used as chiral auxiliary reagents [434].

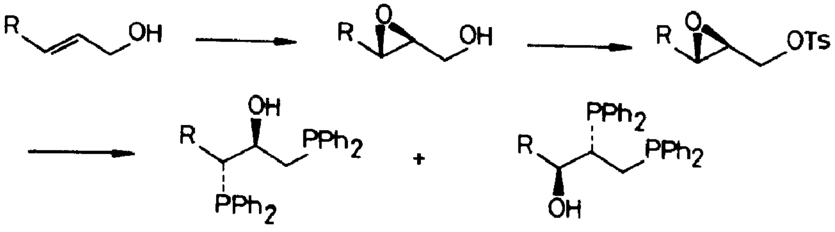


173

174 a

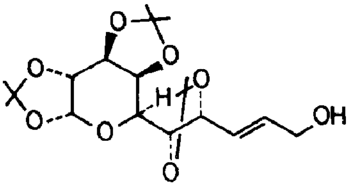
174 b

The Sharpless-epoxidation of allylic alcohols (Ti catalyst, AS 1986 ref.430) has been applied for the preparation of chiral bisphosphines as shown below:

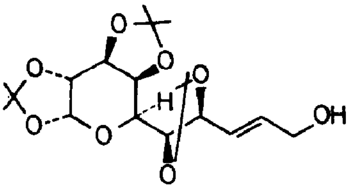


175 176

The phosphines (175) and (176) were used as ligands in the asymmetric hydrogenation of (Z)-α-acetamidocinnamic acid [435]. Sharpless epoxidation of the unsaturated C_{10} sugar derivatives (177) and (178) gave in each case two corresponding diastereomeric epoxides. The ratio of the two diastereomers could be changed by using L-(+)- or D-(-)-diisopropyl tartrate as chiral auxiliary [436].

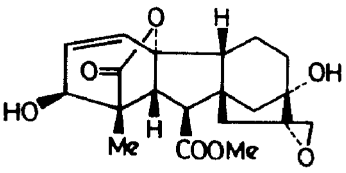


177



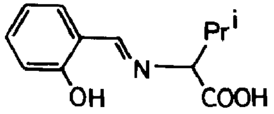
178

Methyl gibberellate gave the epoxide (179) when treated with a modified Sharpless reagent [437].

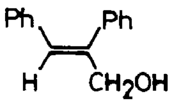


179

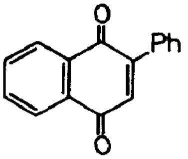
The complexes LTiO and $LMoO_2$ (L = 180) were used as catalysts for the epoxidation of olefins (181) and (182) with tBuOOH. Good chemical yields but only low optical yields (<15%) were achieved [438].



180

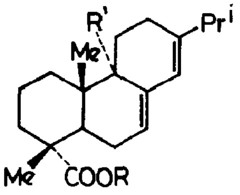


181

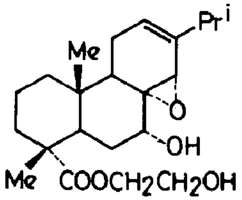


182

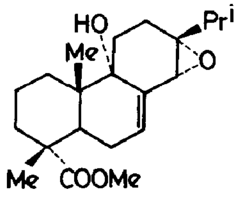
Epoxidation of the abietic acid esters (**183**; R = CH_2CH_2OH, R' = H; or R = Me, R'= OH) with tBuOOH and $VO(acac)_2$ gave the epoxides (**184**) or (**185**) and (**186**), respectively [439].



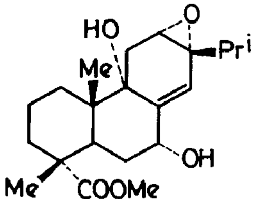
183



184

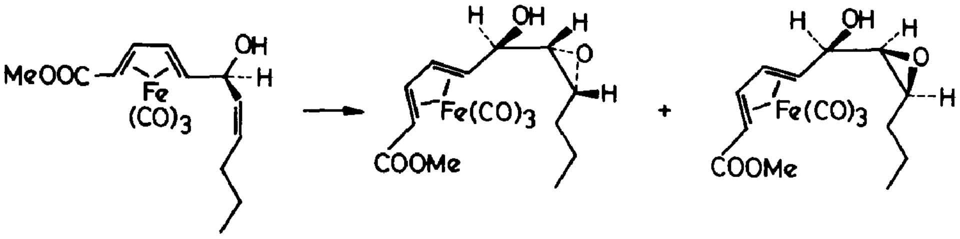


185



186

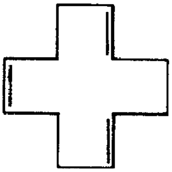
The Sharpless epoxidation procedure using tBuOOH and $VO(acac)_2$ has been applied to for allylic alcohols bearing a (diene)$Fe(CO)_3$ moiety. For example, the two diastereomeric epoxides (**188**) were prepared starting from the organoiron complex (**187**) [440].



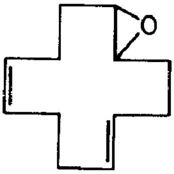
187

188

Several olefins were epoxidized with tBuOOH using MoO_2(salen) as catalyst. The relative rates followed the order cyclooctene > norbornene > cyclopentene > cycloheptene > cyclohexene [441]. Addition of amines significantly improved the activity and selectivity of $MoO_2(acac)_2$ catalyst used in the epoxidation of alkenes with tBuOOH. Among the amines tested pyridine was found to be the most effective [442]. The kinetics of epoxidation of isopropyl oleate with cumyl hydroperoxide and Mo acetylacetonate as catalyst were studied [443]. Epoxidation of butyl oleate with cumyl hydroperoxide using Mo acetylacetonate as catalyst proceeds through formation of a hydroperoxide-metal complex and the irreversible reaction of this complex with the olefin to form the epoxide [444]. The epoxidation of rapeseed oil was carried out using cumyl hydroperoxide, Mo acetylacetonate as catalyst and Na stearate as stabilizer. The process parameters were optimized [445]. The liquid-phase epoxidation of corn oil with cumylhydroperoxide and Mo acetylacetonate as catalyst at 110-125°C was studied. Increasing the unsaturation of the oil (i.e. its linoleic acid content) increased the rate of epoxide formation [446]. Complex formation between $Mo(CO)_6$ and hydroperoxides has been studied using NMR paramagnetic shifts. Based on these data the mechanism of alkene epoxidation in systems containing $Mo(CO)_6$ and hydroperoxides was discussed [447]. Heterogenized catalysts prepared from dihydroxyboryl-substituted polymeric resins and Na_2MoO_4 were used for the epoxidation of cyclohexene with tBuOOH or $PhCH(OOH)CH_3$. The catalyst could be recovered by filtration and showed no apparent loss of activity [448]. Several Mo-containing catalysts were tested for the epoxidation of the cyclododecatriene isomer (**189**). Highest yields of the desired epoxide (**190**) were obtained with a complex formed from MoO_3 and H_2O_2 in the presence of HMPA [449].

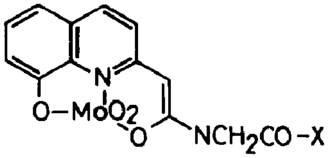


189

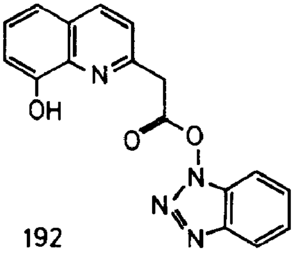


190

The supported molybdenum catalyst (**191a**) was prepared starting from polystyrene-supported glycine and the 8-hydroxyquinoline derivative (**192**) and used for the epoxidation of olefins with tBuOOH in CH_2Cl_2. Conversions and selectivities were the same as those obtained with the homogeneous analog (**191b**) [450].



191 a; X = polymer
191 b; X = OMe



192

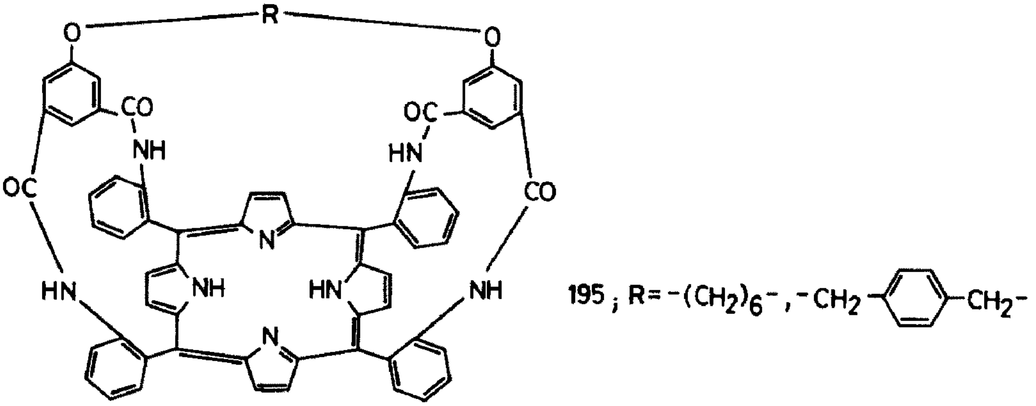
Epoxidation of olefins and allylic alcohols, oxidation of secondary alcohols to ketones, and oxidative cleavage of olefins and diolefins to carboxylic acids were accomplished with H_2O_2 under two-phase conditions ($CHCl_3$/water) using $H_3PMo_{12}O_{40}$ or $H_3PW_{12}O_{40}$ as catalyst and cetylpyridinium chloride as phase-transfer agent. The tris(cetylpyridinium) salt of 12-tungstophosphate, prepared independently could be used as catalyst under homogeneous conditions in tBuOH as solvent for the same reactions [451,452]. The peroxotungstates $Q_3(PO_4[W(O)(O_2)]_4)$ containing strongly lipophilic ammonium cations Q = R_2NMe^+ (R = n-octyl, n-palmityl, or n-stearyl) catalyze the epoxidation of olefins by H_2O_2 in an aqueous/organic biphase system. A variety of water-insoluble alkenes were epoxidized in high yields by this method if an excess of olefin was used [453].

The catalytic epoxidation activity of $[(salen)Mn(H_2O)](PF_6)$ could be improved by adsorbing the complex on kaolinite clay. It was demonstrated that the radical pathway for tBuOOH decomposition leading to side-product formation with cyclohexene was supressed and the oxometal route became the predominant pathway for epoxidation [454]. Manganese(III) tetraarylporphyrins were tested as catalysts for epoxidation of olefins with NaOCl in aqueous CH_2Cl_2 in the presence of N-hexylimidazole as axial ligand, and of a phase-transfer catalyst. Most of the complexes were rapidly deactivated with the exception of $(Cl_8TPP)MnOAc$ which epoxidized olefins at 0°C in very short reaction times [455]. Results of kinetic experiments on olefin epoxidation in a CH_2Cl_2/H_2O system containing a phase-transfer agent with NaOCl as oxidant and (TPP)Mn(III) complexes as catalysts do not support the formation of an intermediate composed of an alkene and a hypervalent metaloxo porphyrin [456]. In the presence of 10-20 equivalents of imidazole, $(Cl_8TPP)MnCl$ is a highly efficient catalyst for the epoxidation of alkenes with H_2O_2 (90-100% in less than 1 hour at room temperature). Epoxidation is stereospecific and corresponds to a *syn* addition of O to the double bond. The same system can also be used for the oxidation of alkenes leading to the corresponding alcohols and ketones with 40-80% yields [457]. The dienes (E)- and (Z)-(**193**) (R = Me, CH_2Ph) were regioselectively epoxidized to the monoepoxides (**194**) by NaOCl + (TPP)MnOAc. Epoxidation of the second double bond was less efficient [458].

$$Me_2C{=}CHCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2OR \longrightarrow Me_2\overset{O}{C{-}}CHCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CHCH_2OR$$

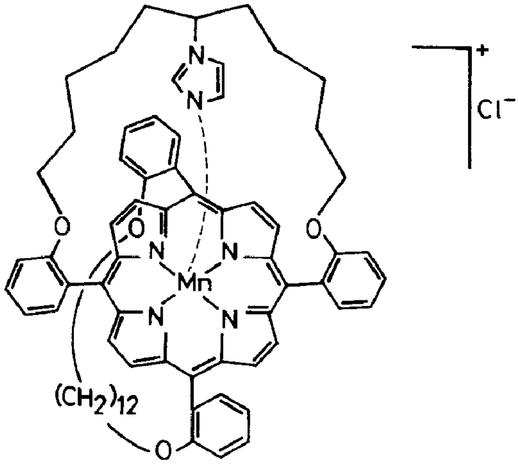
193 194

Epoxidation of *cis-β*-methylstyrene with (TMP)Mn(O) as catalyst was investigated using different oxidants (NaOCl, H_2O_2, cumyl hydroperoxide, IO_4^-, PhIO, and O_2). It was shown that both $Mn^{IV}(O)$ and $Mn^{V}(O)$ are competent oxidants and display different reactivities: Mn(IV) complexes produce predominantly *trans*-epoxides from *cis*-olefins while Mn(V) complexes epoxidize olefins in a predominantly stereoretentive fashion [459]. Manganese tetrakis(halogenoaryl)porphyrins were tested as catalysts for the epoxidation of cyclooctene with NaOCl. Those complexes which had the halogen in *ortho* positions of the phenyl rings, like Mn tetrakis(2,6-dichlorophenyl)porphyrin were found to be stable under the conditions of epoxidation, while for example Mn tetrakis(3,5-dichlorophenyl)porphyrin was totally unstable. This proves that both steric and electronwithdrawing effects of the substituents are important [460]. Atropisomeric porphyrins having 3,5-di-tBu-2-nitrophenyl groups at the *meso* positions were prepared and their MnBr and FeBr complexes used as catalysts for epoxidation of olefins with PhIO or NaOCl. These catalysts were somewhat more active than the corresponding TPP complexes but no significant differences were found between the individual atropisomers [461]. Complexes of 5,10,15,20-tetrakis (4-aminophenyl)porphyrin with Mn, Fe, and Cr were incorporated into water-soluble polymers and used as catalysts for the epoxidation of 2,5-dihydrofuran with NaOCl [462]. Manganese(III) complexes of the "picnic basket" porphyrins (PBP, **195**) were tested as catalysts for the epoxidation of olefins using different oxidants (PhIO, NaOBr, H_2O_2). Competitive epoxidations of *cis/trans* olefin mixtures proved that these catalysts show practically no selectivity for *cis*-olefins like it has been observed with sterically strongly hindered catalysts as (TMP)MnBr. This suggests that epoxidation takes place at the unhindered face of the complex despite the presence of a large excess of nitrogeneous base (1,5-diphenylimidazole) [463].



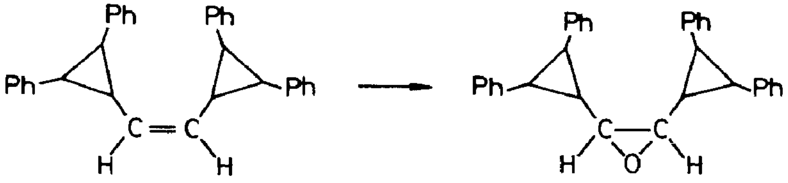
195; R = $-(CH_2)_6-$, $-CH_2-$

Manganese porphyrin complexes containing a pyridine or imidazole ring fixed in the axial coordination position by two chains attached to the macrocycle (for example see **196**) have been used as catalysts for the epoxidation of olefins with NaOCl. With such catalysts and stilbene as olefin, the *cis*-stilbene oxide percentage was always in the range 85-93%, whereas without N-donors (for example with (TPP)MnOAc) the configuration of the starting olefin was nearly lost during catalytic epoxidation [464].

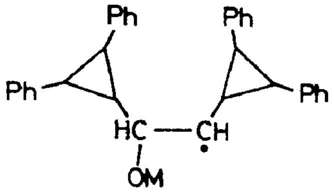


196

Several olefins have been epoxidized with NaOCl in the presence of Fe(III) and Mn(III) complexes of Me$_8$TPP. The *ortho* substituents showed little influence on the kinetic parameters in the case of iron complexes in contrast to the case of manganese complexes [465]. The alkene (197) has been epoxidized in high yield (>80%) with C_6F_5IO as oxidant applying the following complexes as catalysts: (F$_{20}$TPP)FeCl, (Cl$_8$TPP)FeCl, and (Cl$_8$TPP)MnOH. Epoxidation with (F$_{20}$TPP)FeCl provided (198) in 95% yield and no other O-containing products were formed. The absence of any rearrangement of the cyclopropyl substituents excludes the intermediacy of a radical intermediate with the structure (199) [466,467].

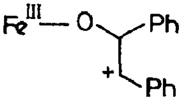


197 198

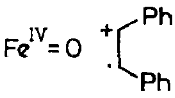


199

A kinetic method for measuring the relative rates of epoxidation of various alkenes has been developed. With this technique a linear relationship between the logarithm of the rates of epoxide formation and the ionization potential of the alkene has been observed in the case of epoxidation with C_6F_5IO catalyzed by $(Cl_8TPP)FeCl$ [468]. The stereoselectivity of epoxidation of *cis*-stilbene by the Fe(TPP)Cl-tBuOOH system depended on the concentration of the catalyst. In the reaction of cholesteryl acetate with the same system both allylic oxidation and epoxidation took place; epoxidation was β-selective independently of catalyst concentration [469]. Alkenes were epoxidized with high yield using C_6F_5IO and (*meso*-tetrakis(2,6-dibromophenyl) porphinato)iron(III) chloride, $(Br_8TPP)FeCl$, as catalyst. Due to severe steric hindrance caused by the *o*-bromine substituents alkene orbitals can only interact with the orbitals on iron bound oxygen in this system; the high efficiency of this catalyst proves that this is the only interaction which is needed for epoxidation [470]. Olefins are epoxidized and α-diols are cleaved into carbonyl compounds by F_5C_6IO or *m*-chloroperbenzoic acid in the presence of $(Cl_8TPP)Fe(III)^+(ClO_4)^-$ as catalyst. In a stoichiometric reaction this catalytically active complex can be transformed by these oxidants into $[(Cl_8TPP^{\cdot -})Fe(II)(O)^+]$ which, in turn, oxidizes olefins in a stoichiometric reaction to epoxides and cleaves α-diols into carbonyl compounds. The chemistry of this intermediate species parallels that of cytochrome P-450 [471]. The rate of reaction between *p*-cyano-N,N-dimethylaniline N-oxide and $[(TPP)Fe]_2O$ was found to be independent of the concentration of 2,3-dimethylbutene-2 added to the reaction mixture although the olefin was transformed into its epoxide. This shows that olefin epoxidation is not the rate-limiting step in this system [472]. Product yields were determined for the reactions of *cis*-stilbene with C_6F_5IO in the presence of $(Cl_8TPP)FeCl$ and $(F_{20}TPP)FeCl$ as epoxidation catalysts. It was concluded that *cis*-stilbene oxide, diphenylacetaldehyde and deoxybenzoin were formed through the carbocation (**200**) whereas benzaldehyde and polymeric products were produced from the carbocation radical (**201**) through interaction with atmospheric oxygen [473].



200



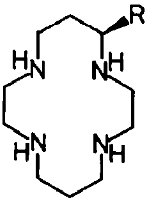
201

Cyclohexene and styrene were epoxidized with $KHSO_5$ in a CH_2Cl_2/H_2O two-phase system using Fe(II)-phthalocyanine as catalyst and dimethylbenzyltetradecylammonium chloride as phase-transfer agent. Addition of N-bases as axial ligands had no significant effect on catalyst activity and selectivity [474]. Anhydrous $FeCl_3$, dissolved in MeCN, catalyzes the epoxidation of olefins and the oxidative cleavage of 1,2-diols by H_2O_2. A highly electrophilic Fe(III)-oxene species is supposed to be an intermediate [475].

The complexes $[(dppp)MCl](ClO_4)$ (M = Ru, Os) promote the oxidation of alkenes by H_2O_2, NaOCl or PhIO; usually epoxides are the main reaction products but in some cases other oxidation pathways are dominant. Osmium is more active than ruthenium but less selective for epoxide formation [476].

Alkenes were epoxidized in a two-phase system using iodosylbenzene as oxidant, $Co(salen)(H_2O)_2Cl$ as catalyst and β-cyclodextrin as phase-transfer agent. Addition of 4-methylpyridine increased the rate of epoxidation [477].

The use of Ni(salen) as catalyst for the epoxidation of olefins with NaOCl has been reported. Electron-rich aromatic olefins like β-methyl styrene were converted to epoxides in excellent yields, aliphatic olefins were reactive but gave large amounts of byproducts [478]. Cyclohexene and various aryl-substituted alkenes were oxidized with the cyclam complex of $Ni(NO_3)_2$ as catalyst and PhIO as terminal oxidant. Epoxides were the major products; however small amounts of ring-opened products were formed and over-oxidation to ketones or aldehydes, furthermore allylic oxidation of cyclohexene were also observed. Using Ni(II) complexes of chiral cyclam derivatives (202), no enantioselectivity was obtained. If epoxidation of styrene was perfomed in the presence of O_2, significant amounts of benzaldehyde were also formed [479,480].



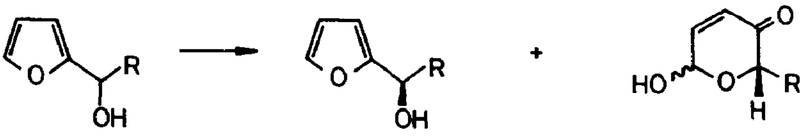
202; R = CH_2OH, $CH_2OSiMe_2Bu^t$

A detailed kinetic study of the epoxidation of 1-octene with H_2O_2 catalyzed by $(L)Pt(CF_3)OH$ or $[(L)Pt(CF_3)(CH_2Cl_2)](BF_4)$ (L = *cis*-1,2-bis(diphenylphosphino)ethylene) has been reported. In both cases the kinetic analysis suggested a mechanism in which the actual oxidant is a PtOOH species that reacts with a Pt-olefin complex to give the epoxide and a PtOH species [481].

See also [430].

c) Oxidation of O-Containing Functional Groups

The kinetics of the Ce(III))-catalyzed oxidation of oxalic acid by bromate were determined [482]. Enantioselective oxidation of racemic 2-furylcarbonyls (**203**; R = alkyls,Ph) using tBuOOH, L-(+)-diisopropyl tartrate and $Ti(OPr^i)_4$ provides by asymmetric kinetic resolution optically active 2-furylcarbinols (**204**) in 32-42% yield and better than 95% optical purity [483].

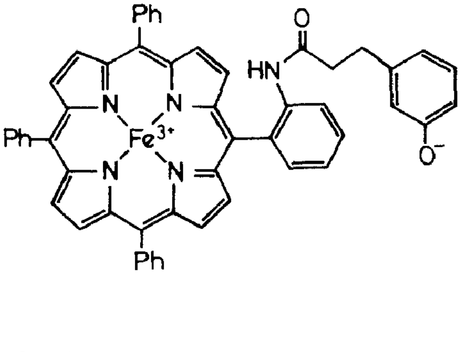


203 **204**

Oxidation of iPrOH by H_2O_2 to acetone catalyzed by $MoO_2(acac)_2$ or $VO(OPr^i)_3$ was studied using kinetic and ^{18}O-labeling experiments. Evidence was presented for a radical pathway. If the experiments were conducted under air, atmospheric O_2 also participated in the reaction [484]. Tetrabromooxomolybdate(V) immobilized on alkylammonium cation-type polymers is an active catalyst for the oxidation of alcohols and epoxidation of olefins with tBuOOH [485]. Tertiary and secondary glycols are oxidatively cleaved by tBuOOH and $MoO_2(acac)_2$ with high yields to ketones and carboxylic acids, respectively. If used in stoichiometric quantities, $MoO_2(acac)_2$ alone also cleaves glycols to the corresponding carbonyl compounds [486]. Oxidation of α,ω-diols to lactones was performed with good to excellent yields with H_2O_2 and tris(cetylpyridinium) 12-tungstophosphate as catalyst in tBuOH solvent at reflux temperature. The analogous Mo complex was much less active [487].

The kinetics of chromic acid oxidation of dimethyl malonate in aqueous $AcOH-H_2SO_4-H_3PO_4$ in the presence and absence of Mn^{2+} were determined [488]. The chromic oxidation of oxalic acid at high acid concentrations was found to be catalyzed by Mn^{2+}, Fe^{2+}, and Ce^{3+} [489].

Agglomerated $[Fe_4S_4]^{2+}$ clusters multiply bridged by 2,4,6-trimethylbenzene-1,3-dithiolate, benzene-1,3-dithiolate, or benzene-1,4-dithiolate and soluble in DMF catalyze the oxidation of benzoin to benzil by *p*-benzoquinone [490]. The rate of O atom transfer from *m*-chloroperoxybenzoic acid to the iron(III) tetraphenylporphyrin (**205**) with a covalently-attached phenolate tail was monitored by trapping the high-valent oxo-iron intermediate with 2,4,6-tri-*tert*-butylphenol and observing the rate of formation of the 2,4,6-tri-*tert*-phenoxide radical. This process was approximately four times faster than with (TPP)FeCl [491].



205

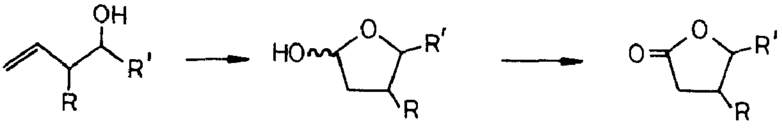
Bis(trimethylsilyl) peroxide effectively oxidizes alcohols to the corresponding carbonyl compounds in the presence of Cr(VI) or Ru(II) complexes as catalysts in dichloromethane. Using

$Ru(PPh)_3Cl_2$ as catalyst, primary alcohols can be selectively oxidized in the presence of secondary alcohols [492]. The kinetics of oxidation of diethylene glycol and its monomethyl ether by N-bromoacetamide catalyzed by Ru(III) chloride have been determined. The products of the reactions were identified as the corresponding acids [493]. Based on kinetic measurements a mechanism was proposed for the oxidation of 1,2-diols with $[Fe(CN)_6]^{3-}$ catalyzed by RuO_4. Accordingly, the slow step is the decomposition of a diol-Ru(VIII) complex into aldehyde and a Ru hydride which is then reoxidized by $[Fe(CN)_6]^{3-}$ [494]. The ruthenate ion-catalyzed oxidation of Na malate and Na mandelate by alkaline $[Fe(CN)_6]^{3-}$ showed Michaelis-Menten behavior [495]. The kinetics of oxidation of 2,3-butanediol and 2-ethyl-1,3-hexanediol by $[Fe(CN)_6]^{3-}$ catalyzed by Ru(VI) were determined. The data suggest a complex formation between ruthenate and diol prior to oxidation [496]. The kinetics of oxidation of cyclic ketones to dicarboxylic acids by periodate in the presence of Ru(III) and Os(VIII) have been studied. Catalytic activity of the complexes increased in the stated order [497]. Oxidation of 2-octanol by $NaBrO_3$ in a biphasic system (water/CCl_4) mediated by RuO_4 generated *in situ* has been optimized. A phase-transfer catalyst like Aliquat 336 was not necessary for the reaction [498]. The selective oxidation of primary alcohols to carboxylic acids, secondary alcohols to ketones and primary benzylic alcohols to aldehydes was performed with good yields in a $RuCl_3.3H_2O$ - H_2O_2 phase-transfer catalyst system. Similar catalyst systems containing $PdCl_2$, $RhCl_3.3H_2O$, $MnCl_2.4H_2O$, or $CoCl_2.6H_2O$ showed poor activity and selectivity [499].

Oxidation of aliphatic aldehydes by $[Fe(CN)_6]^{3-}$ catalyzed by Os(VIII) was found to be zero order in oxidant and first order in both aldehyde and catalyst. The data suggest that the anion of the aldehyde hydrate is involved in the oxidation [500]. The kinetics of uncatalyzed and Os(VIII)-catalyzed oxidations of acetophenone and some substituted acetophenones by diperiodatoargentate(III) have been investigated. The order in Ag(III) was one in the absence and zero in the presence of Os(VIII) [501].

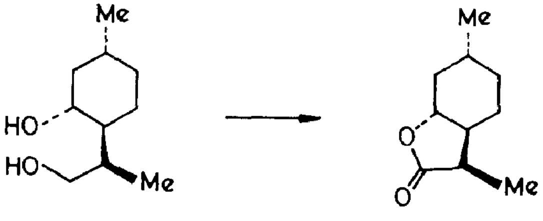
The kinetics of oxidation of diacetone alcohol by Ce(IV) both in the absence and presence of Ir(III) as catalyst has been determined. It was proposed that Ce^{4+} oxidizes an Ir(III)-substrate complex to give an Ir(IV)-substrate complex which decomposes into Ir(III) and first stage intermediate products [502].

3-Substituted 1-alken-4-ols (206; R = Me,$(CH_2)_7COOMe$,COOMe, Ts,OCH_2Ph; R'=n-hexyl,H,$CH=CHCH_3$,CH_2OCOPh,CH_2OCOPh,CH_2OCH_2Ph) were oxidized with $PdCl_2$-benzoquinone regioselectively at the terminal carbon to afford cyclic hemiacetals (207), which were converted to γ-butyrolactones (208) by CrO_3-H_2SO_4 in acetone (Jones oxidation). When the 4-hydroxy group was blocked by acetylation, the oxidation became slower and gave only methyl ketones in low yield [503].



206 207 208

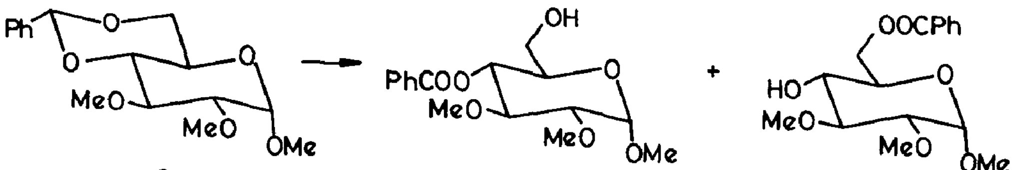
The rate of oxidation of mannitol and sorbitol by vanadium(V) in sulfuric acid was significantly increased by Cu(II) ions. This was attributed to the formation of a Cu-substrate complex in the initial step [504]. Primary alcohols could be conveniently oxidized to carboxylic acids using solid $KMnO_4/CuSO_4.5H_2O/KOH$ in an organic solvent. No added base was necessary for the oxidation of 1,4- and 1,5-diols which were transformed by solid $KMnO_4/CuSO_4.5H_2O$ into the corresponding lactones. For example, the insect repellent (210) was prepared from (209) in 83% yield [505].



209 210

Oxidation of glycolic acid with H_2O_2 in the presence of Cu^{2+} is first order in substrate and half order in catalyst and oxidant [506]. The kinetics of oxidation of malic acid by alkaline $[Fe(CN)_6]^{3-}$ catalyzed by Cu(II) have been determined. Cu(II)- and Cu(III)-malate complexes were suggested as intermediates [507].

Copper complexes of Schiff bases bound to styrene-divinylbenzene copolymers were used as catalysts for the oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethylbenzoquinone by H_2O_2 [508]. Copper(II) chloride has been found to be a highly effective catalyst for the oxidative cleavage of O-benzylidene rings by tBuOOH. The reaction was successfully used for the conversion of 4,6-O-benzylidenehexapyranoside derivatives (e.g. 211) into the corresponding 4- and 6-benzoates. Pd, Fe, and Ni salts also showed catalytic activity [509].

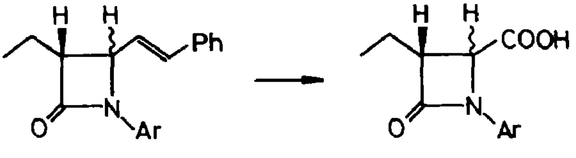


211

See also [451,471,475].

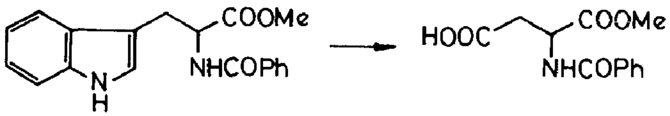
d) Oxidation of N-Containing Functional Groups

The kinetics of the oxidation of aspartic acid by Ce(IV) in the presence of Mn^{2+} have been determined [510]. Oxidative cleavage of the double bond in (212) to prepare the carboxylic acid derivative (213) could be accomplished with 70-80% yield either directly with $KMnO_4$ + $NaIO_4$, or with OsO_4 + $NaIO_4$ followed by oxidation of the resulting aldehyde with $KMnO_4$ [511].



212 213

The kinetics of the Ru(III)-catalyzed oxidation of some aminoalcohols by chloramine-T in $HClO_4$ medium have been studied. The reactions are first order with respect to oxidant and catalyst and independent of substrate concentration [512]. Quinoline was oxidized to pyridine-2,3-dicarboxylic acid by NaOCl in the presence of high valenced Ru complexes [513]. The kinetics of the Ru(VI)-catalyzed oxidation of benzyl amine and *n*-butyl amine by alkaline $[Fe(CN)_6]^{3-}$ were studied [514]. Pseudo-second order rate constants were determined for the Ru(III)-catalyzed oxidation of diethanolamine by alkaline $[Fe(CN)_6]^{3-}$ [515]. Oxidative degradation of biologically important α-amino acids to dicarboxylic acids could be performed with $NaIO_4$ in a biphasic CCl_4 + $MeCN/H_2O$ system in the presence of $RuCl_3.3H_2O$ as catalyst. Thus, tryptophan (**215**) was transformed into aspartic acid and phenylalanine (**216**) into phenylacetic acid [516].

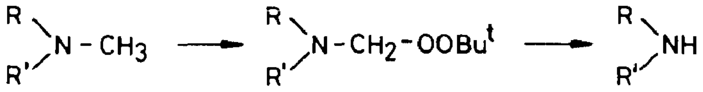


215

$$PhCH_2\underset{NH_2}{CH}COOH \longrightarrow PhCH_2COOH$$

216

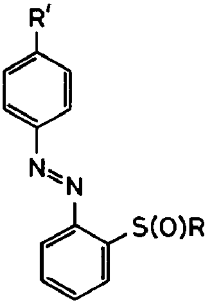
Oxidation of tertiary amines with tBuOOH in the presence of $Ru(PPh_3)_3Cl_2$ gives the corresponding α-(*tert*-butyldioxy)alkylamines (**218**). In the case of tertiary methylamines (**217**) subsequent hydrolysis with aqueous HCl leads via selective N-demethylation to secondary amines (**219**). This reaction sequence mimics biological oxidative demethylation of amines catalyzed by P-450 [517].



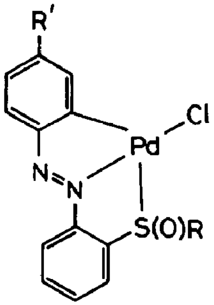
217 218 219

The kinetics of the Os(VIII)-catalyzed oxidation of aminoalcohols by chloramine-T in alkaline medium have been investigated. The rates were first order in Os(VIII) for primary amino alcohols whereas in the case of diethanolamine and triethanolamine parallel catalyzed and uncatalyzed reaction pathways were found [518].

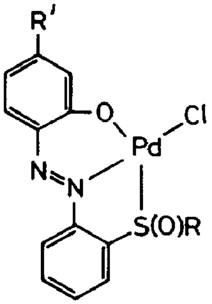
The kinetics of oxidation of mono-, di-, and triethanolamines by chloramine-T were studied in the presence and absence of Ir(III) as catalyst in aqueous acetic acid solution. A mechanism was proposed [519]. Regiospecific aromatic hydroxylation of azobenzenes was accomplished by complexing the azo sulfoxides (220; R' = Me, CH_2Ph) to Pd, oxidizing the complexes (221) with *m*-chloroperbenzoic acid to (222) and eliminating the ligands (223) by reductive treatment with hydrazine [520].



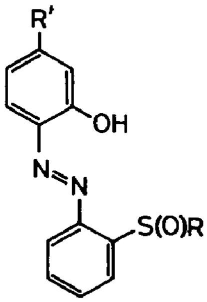
220



221

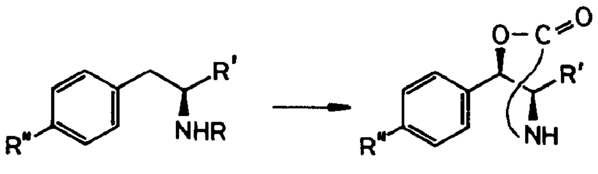


222



223

Derivatives of L-tyrosine (224; R = Z, Boc, COOEt; R' = COOMe,CH_2OAc,H; R'' = OMe,OAc,H) were oxidized with high *threo* selectivity at the benzylic position to yield the corresponding cyclic carbamates (225) with $K_2S_2O_8$ and catalytic amounts of $CuSO_4$ [521].



224 225

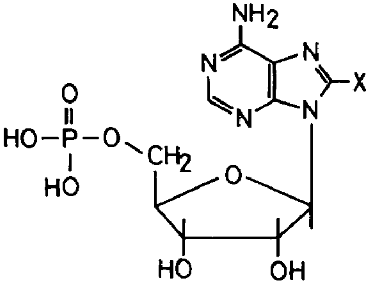
The Ag(I) catalyzed oxidation of alanine, valine, leucine, aspartic acid, and glutamic acid by Ce(IV) in HNO_3 was found to be first order each in Ag(I), Ce(IV), and the amino acids [522,523]. Rates of oxidation of aliphatic amines with Ce^{4+} in HNO_3, both in the presence and absence of Ag^+ were determined. Linear Taft's plots were obtained [524]. Oxidation of $PhCONHNH_2$ with peroxydisulfate catalyzed by Ag^+ yields PhCOOH and N_2 [525].

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

Sharpless epoxidation (tBuOOH + $Ti(OPr^i)_4$ + (+)-diethyl tartrate) of the alkenylsilanol (226) gave the epoxide (227) in 50% yield. After cleavage with fluoride (Et_4NF), (S)-styrene oxide was obtained with 85-95% enantiomeric excess [526].

226 227

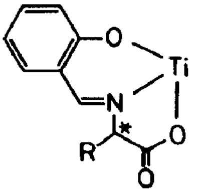
Oxidative desulfurisation (AS. 1987, ref.481) of pentacovalent phosphorus compounds was achieved with cumyl hydroperoxide and Mn(III) or Fe(III) TPP complexes as catalysts. Because of side reactions a tenfold excess of hydroperoxide had to be used [527]. Adenosine-5'-monophosphate (228; X = H) was hydroxylated with $KHSO_5$ as oxidant and the pentaacetate of *meso*-tetrakis-(N-methyl-4-pyridyl)porphyrinato-Mn(III) as catalyst in a buffered aqueous solution to 8-hydroxyadenosine-5'-monophosphate (228; X = OH) with 25% yield. The reaction went to completion within a few seconds [528].



228

The cyctochrome P 450 monooxygenase model system consisting of iodosylbenzene and derivatives as oxidants and metalloporphyrins as catalysts was studied to determine the influence of catalyst structure on S-oxidation and of oxidant structure on S-dealkylation [529].

The following asymmetric oxidations of organic sulfur compounds were performed with tBuOOH in the presence of $Ti(OPr^i)_4$ and (+)-diethyl tartrate: RSSR to RS(O)SR, $4\text{-}MeC_6H_4SNR_2$ to $4\text{-}MeC_6H_4S(O)NR_2$, and RSOR to RS(O)OR (R = alkyl or aryl). Enantiomeric excesses up to 50% were obtained [530]. Asymmetric oxidation of sulfides by hydroperoxides mediated by chiral Ti complexes has been further developed. It was shown, that cumyl hydroperoxide gives higher enantioselectivities than tBuOOH and that molecular sieves have a beneficial effect [531]. Oxidation of alkyl, aryl, and heterocyclic sulfides with tBuOOH and the chiral Ti complexes (229) as catalyst (R = iPr, tBu) gave the corresponding sulfoxides with up to 21% optical yields [532].

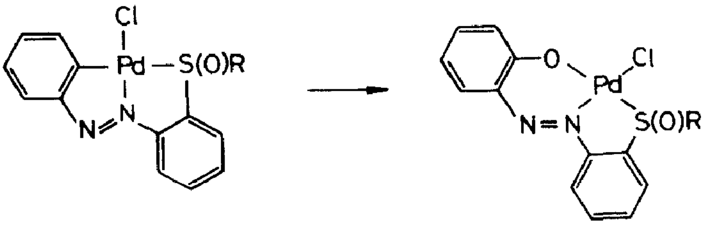


229

The effect of $(NH_4)_2MoO_4$, $H_3[P(W_3O_{10})_4]$, $H_3[P(Mo_3O_{10})_4]$, and Na_2WO_4 as catalysts on the oxidation of penicillins G and V to their S-oxides by H_2O_2 has been investigated. The best yield of penicillin G S-oxide was obtained with Na_2WO_4 [533].

Oxidation of L-cysteine by H_2O_2 in the presence of $[Fe(tetpy)(OH)_2]^+$ ions anchored to poly(D-glutamate) or poly(L-glutamate) matrixes has been studied. The reaction did not exhibit any stereoselectivity [534]. Oxidation of cimetidine with the Fenton reagent (Fe^{2+}/H_2O_2) was studied in the presence of various chelating ligands. Ligands with high affinity to Fe^{2+} inhibited the reaction; ligands with high affinity to Fe^{3+} selectively promoted either hydroxylation, N-demethylation or sulfoxidation [535].

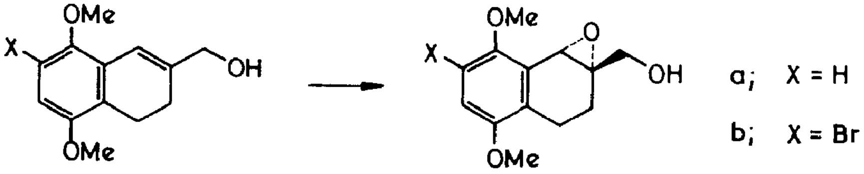
The Pd complexes (**230**; R = Me,$PhCH_2$) could be oxidized with percarboxylic acids into the complexes (**231**). Since complexes (**230**) are easily synthesized from the corresponding 2-(alkylsulfinyl) azobenzenes and the phenolic ligands in (**231**) can be set free by demetallation with hydrazine hydrate in MeCN, this reaction sequence is actually a regiospecific *ortho* hydroxylation of the aromatic ring [536].



230 231

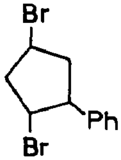
The complete oxidative destruction of polychlorinated biphenyls with RuO_4 and aqueous NaOCl at 64°C was reported [537]. The kinetics of oxidation of mono-, di-, and trichloroacetic acids by chloramine-T in acid medium were determined in the absence and in the presence of Ir(III) as catalyst. A first-order dependence in Ir(III) was found [538].

Asymmetric epoxidation of the bromo allylic alcohol (**232b**) with tBuOOH in the presence of $Ti(OPr^i)_4$ and L-(+)-dimethyl tartrate gave epoxide (**233b**) in 85% yield (99% o.y.). The bromine-free epoxy alcohol was, however, unstable under the conditions of Sharpless epoxidation of (**232a**) [539].

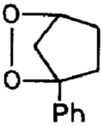


232 233

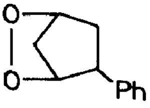
Oxidation of β-bromopropionic acid by alkaline $[Fe(CN)_6]^{3-}$ catalyzed by OsO_4 produced $HOCH_2CH(OH)COOH$ [540]. 1,3-dibromo-4-phenylcyclopentane (234) is transformed by anhydrous H_2O_2 in ether in the presence of silver acetate into the endoperoxides (235) and (236), and the hydroperoxides (237) and (238) [541].



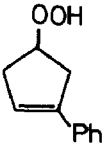
234



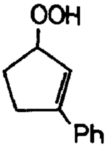
235



236



237

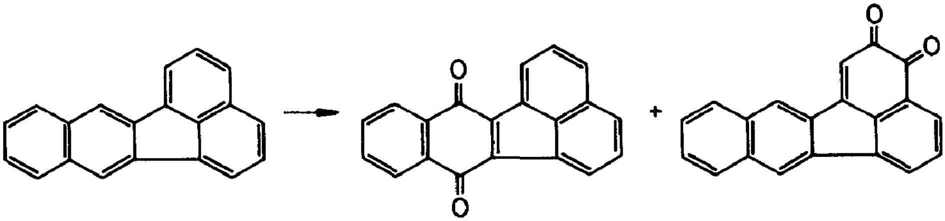


238

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

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

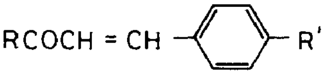
Oxidation of anthracene, naphthalene, *p*-xylene, *p*-methoxytoluene and toluene by Ce(IV) in a two-phase system containing a phase transfer catalyst was reported [542]. Ceric ammonium sulfate in sulfuric acid was found to be a useful reagent for the oxidation of polynuclear aromatic hydrocarbons to lactones or quinones. Thus, for example, benzofluoranthene (239) gave a mixture of the quinones (240) and (241), while chrysene (242) could be transformed into the lactone (243) [543].



239 240 241

242 243

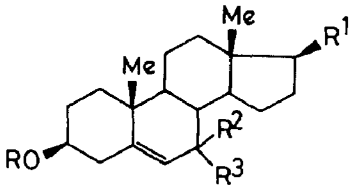
The α,β-unsaturated ketones (**244**; R = Ph, PhCH=CH; R' = H,Me,OMe) were oxidized by ceric ammonium nitrate into a mixture of RCOOH and $R'C_6H_4COOH$ [544].


244

Oxidation of tetrarylpropenes, e.g. $Ph_2C=C(Me)CHPh_2$ with CrO_3–Ac_2O gave epoxides and cleavage products, in this case Ph_2CO and $Ph_2CHCOMe$ [545]. Oxidation of methylbenzenes with trimethylsilyl chlorochromate in CCl_4 gave the corresponding benzaldehydes in good yields. The oxidant was prepared by treating Me_3SiCl with CrO_3 [546]. 2-Cyanopyridinium chlorochromate has been found to be the reagent of choice for the oxychlorination of alkenes into α-chloroketones. For example, norbornene was cleanly oxidized to *exo*-(**245**); in the case of cyclohexene some allylic oxidation was also observed [547].

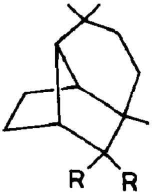

245

Pyridinium chlorochromate in refluxing benzene was an effective and convenient reagent for the oxidation of cholesteryl benzoate to 7-oxocholesteryl benzoate in 87% yield [548]. Pyridinium chlorochromate in refluxing benzene or DMSO and pyridinium dichromate in pyridine were effective reagents for allylic oxidation of steroids (**246**) to give steroids (**247**) [549].



246; R = PhCO, $R^1 = C_8H_{17}$,
$R^2 = R^3 = H$
$R = R^1 = Ac$, $R^2 = R^3 = H$
247; $R^2R^3 = O$

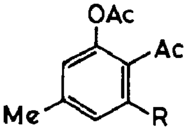
The influence of *meta*- and *para*-substituents on the kinetics of oxidation of phenoxyacetic acids by $KMnO_4$ in aqueous AcOH was studied [550]. Benzylic CH_2 or CHOH groups were transformed into keto groups, benzylic tertiary CH groups into tertiary carbinol groups by oxidation with $KMnO_4$ in the presence of Bu_4NHSO_4. Thus, for example, fluorene gave fluorenone and Ph_3COH gave [551]. Kinetic data for the oxidation of $MeCR_2COONa$ (R = H,D) by MnO_4^- in water show that the rate-determining step is the transfer of H from the methylene group to the oxidant [552]. Anethole was oxidized to anisaldehyde with $KMnO_4$ in water-dichloromethane solution using $(cetyl)Me_3N^+Br^-$ as phase-transfer catalyst. The yield was 68% [553]. Longicamphenilone (**248**) was prepared by phase-transfer-catalyzed $KMnO_4$ oxidation of longifolene (**249**) [554].



248; RR = O

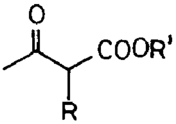
249; RR = CH_2

The kinetics of oxidation of cinnamic acid by $(NMeBu_3)(MnO_4)$ have been determined. The reaction was found to be first order in both reactants. A Hammett plot was determined for *m*- and *p*-substituted cinnamic acids [555]. Oxidation of compounds (**250**) with $[Et_3(PhCH_2)N]^+(MnO_4)^-$ proceeded regioselectively at the methyl groups located on the aromatic ring and gave the corresponding mono- or dicarboxylic acids [556].

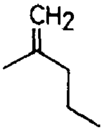


250; R = H, Me

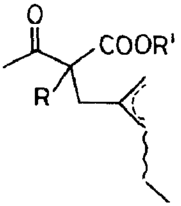
Oxidation of *β*-keto esters (**251**) by $Mn(OAc)_3.2H_2O$ in the absence or presence of olefins (e.g.**252**) was studied. Unsaturated esters like (**253**) were formed in the presence of the olefin; in the absence of olefins the main products were either volatile compounds (in the case of unsubstituted esters; **251**; R = H, R' = Me) or dimers (in the case of 2-substituted esters; **251**; R = Me, R' = Et) [557].



251

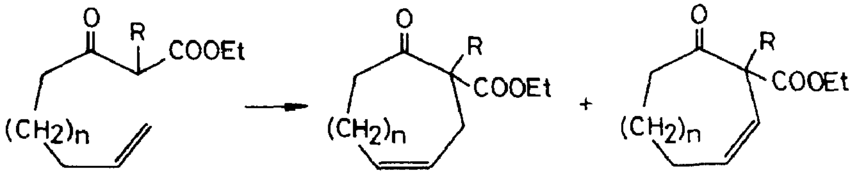


252



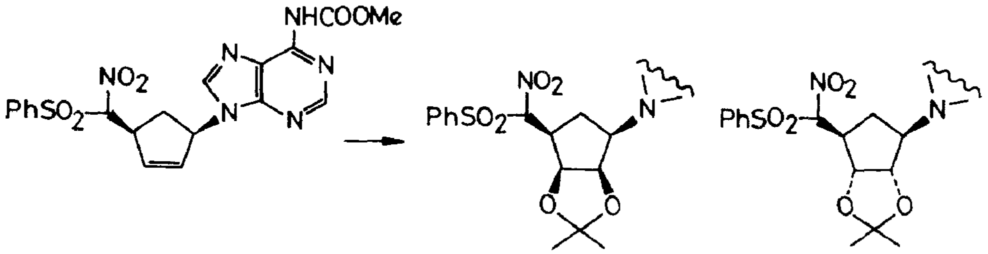
253

Oxidative cyclization of the unsaturated β-ketoesters 254; R = H,Me,Cl,allyl; n = 1,2) with $Mn(OAc)_3.2H_2O$ and $Cu(OAc)_2.H_2O$ gave the seven- and eight-membered ring compounds (255,256) in moderate yields. Oligomers were formed as byproducts [558].

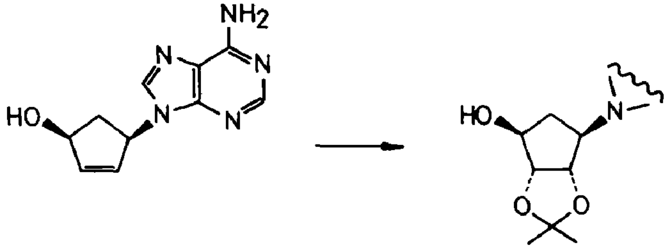


254 255 256

The stereochemistry of *cis* hydroxylation of substituted cyclopentenes with OsO_4 and basic $KMnO_4$ have been investigated. Hydroxylation of (257) by OsO_4 followed by conversion to the corresponding acetonide furnished (258) (i.e. hydroxylation occurred at the sterically hindered face) while the same procedure furnished isomer (259) if $KMnO_4$ was employed. Hydroxylating (260) with OsO_4 gave, however, compound (261) showing that osmylation is directed by the nitrosulfonylmethane substituent [559].

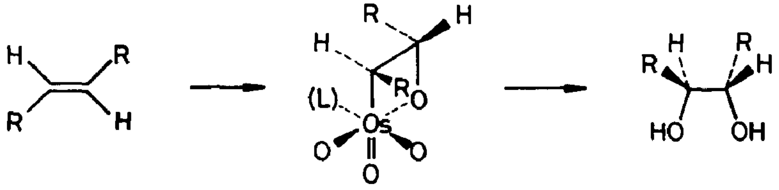


257 258 259

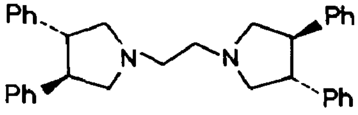


260 261

Oxidation of *trans*-olefins (262) with OsO_4 employing the chiral diamine (265) at $-110^{\circ}C$ in THF afforded, after reduction of the osmate esters with $LiAlH_4$, the corresponding *cis*-diols (264) having the absolute configuration shown, with high enantioselectivity. The organometallocycle (263; L = 265) was proposed as a plausible intermediate [560].



262 263 264

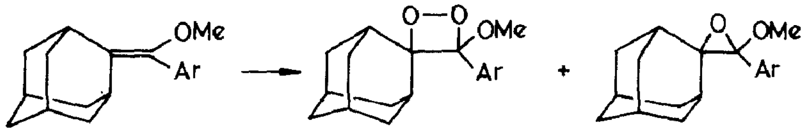


265

See also [410,426,495,545,599,626,639,640,645].

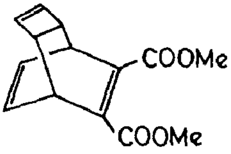
b) Epoxidation of Olefins

The enol ethers (266; Ar = Ph, naphthyl) react with the metal(VI) oxodiperoxo complexes $(py)MO(O_2)_2$ (M = Cr,Mo) to give, among other oxidized products, dioxetanes (267) and epoxides (268). It was shown that epoxides are the intermediates of dioxetane formation [561].

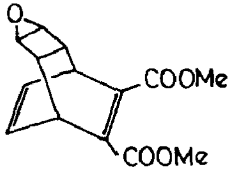


266 267 268

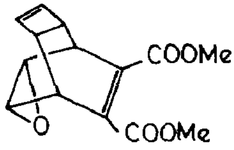
Epoxidation of the tricyclodecatriene derivate (269) with $MoO_5 \cdot 2HMPA$ gave the epoxides (270) and (271) in a 5:1 ratio [562].



269



270



271

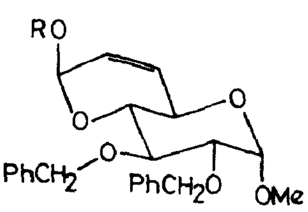
The Ru(III) nitro complex *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)]^{2+}$ (272) oxidizes alcohols to aldehydes and epoxidizes olefins according the following reactions [563]:

$$2\ (272) + PhCH_2OH \longrightarrow [Ru(NO_2)(PMe_3)_2(trpy)]^{+} + PhCHO + 2H^{+}$$

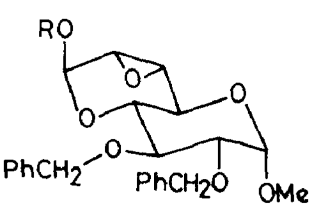
$$(272) + \text{norbornene} \longrightarrow [Ru(NO)(PMe_3)_2(trpy)]^{2+}$$

$$+\ exo\text{-}2,3\text{-epoxynorbornane}$$

A general procedure for epoxidation of olefinic bipyranosides (273; R = Me, benzyl, and substituted benzyls) was developed which gives the diastereomerically pure epoxides (274). The procedure involves hydroxylation with OsO_4 followed by reaction with phosgene iminium chloride and treatment of the resulting chlorocarbamates with NaOMe [564].



273

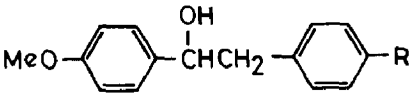


274

See also [483,526,539].

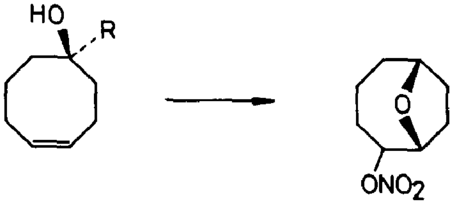
c) Oxidation of O-Containing Functional Groups

Kinetic measurements were carried out for the oxidation of allyl alcohol and its derivatives with Ce(IV) in aqueous solutions of perchloric acid [565]. Oxidation of crotyl alcohol, crotonaldehyde, and crotonic acid by Ce(IV) affords AcOH, HCOOH, and CO_2. Mechanisms were proposed [566]. The kinetics of the oxidation of several C_5 and C_6 monosacharides by Ce(IV) in $HClO_4$ were studied. Two complexes were formed in each case [567]. The methoxy compounds (275; R = NO_2,Cl,H,Me,OMe) were rapidly oxidized by $(NH_4)_2Ce(NO_3)_6$ at room temperature to give *p*-anisaldehyde in near quantitative yield. Analogous compounds with OH instead of the OMe group gave, however, a red Ce complex which did not oxidize under these reaction conditions [568].



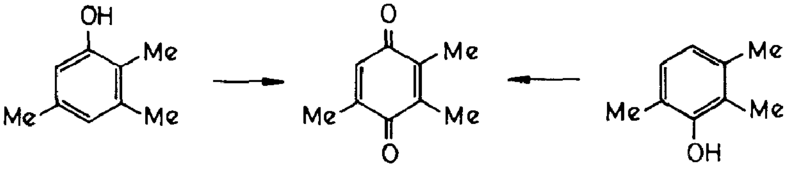
275

Oxidation of cyclooctenols (276; R = H,Me) with ceric ammonium nitrate afforded regio- and stereoselectively the bicyclic ethers (277) [569].



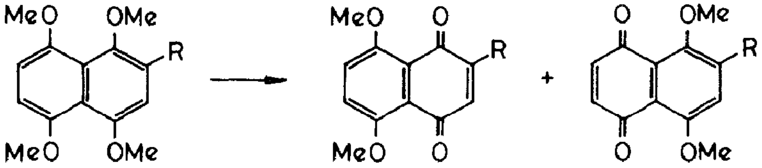
276 277

The kinetics of oxidation of *o*-cresol by Ce(IV) were determined [570]. A method for the synthesis of methylquinones from methylphenols by oxidation with anodically regenerated Ce^{4+} hasbeen developed. For example, (279) could be prepared either from (278) or from (280) in 70-80% yield [571].



278 279 280

Oxidation of the tetramethoxynaphthalene derivatives (281) with $(NH_4)_2Ce(NO_3)_6$ gave two isomeric dimethoxynaphthaquinones (282) and (283) (R = H, CHO, α-hydroxyalkyl, α-oxoalkyl) [572].



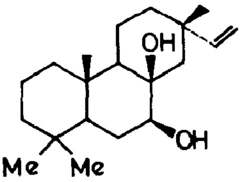
281 282 283

Rate constants for the oxidation of methyl ketones by Ce(IV) were determined [573]. Ceric ammonium nitrate was found to be an effective reagent for the oxidative decarboxylation of α-alkoxymaloic acids like (284) into the corresponding lactones (285) [574].

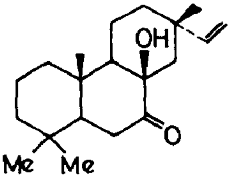
284 285

A linear dependence on acidity was found for the oxidation of lactic acid and tartaric acid by vanadium(V) in a nitric acid medium [575].

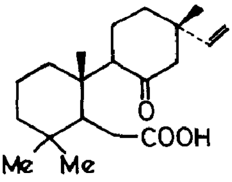
Magnetic measurements on the inorganic residue from chromate oxidation of alcohols indicated formation of Cr(III) in the reaction [576]. Primary alcohols were oxidized with H_2CrO_4 adsorbed on aluminium silicate to give the corresponding aldehydes in 74-90% yields [577]. Allyl alcohols were oxidized to acrolein derivatives in 69-80% yield by H_2CrO_4 adsorbed on silica gel using CCl_4 as solvent [578]. The oxidation of aliphatic acetals by CrO_3 in aqueous AcOH is first order each in oxidant and acetal, and yields the corresponding ester as the main product. Kinetic data suggest that the elimination of a proton from the complex involving the acetal and Cr is the rate-determining step [579]. Oxidative cleavage of secondary-tertiary 1,2-glycols or α-hydroxy ketones (e.g. 286 or 287) with the Jones reagent (CrO_3 in aqueous sulfuric acid) gave the corresponding ketoacids (e.g. 288) in excellent yields [580].



286

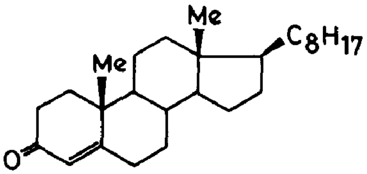


287



288

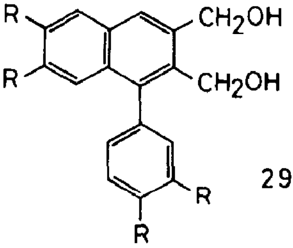
The oxidation kinetics of citric acid with $K_2Cr_2O_7$ in acid medium were studied spectrophotometrically [581]. Cholesterol was oxidized to the α,β-unsaturated ketone (289) with $K_2Cr_2O_7$ deposited on $AlPO_4$, BPO_4, or $AlPO_4$-BPO_4 as inert supports. Solid supports with small surface areas and large pore diameters gave more active reagents [582].



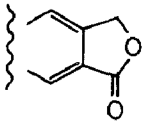
289

In 90% aqueous acetone the rate of allyl alcohol oxidation by Cr(VI) is markedly decreased by chloride ion; this effect is due to the formation of $ClCrO_3^-$ which is a less powerful oxidant

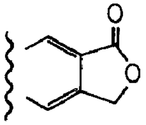
[583]. Potassium chlorochromate was found to be a versatile oxidant for the conversion of secondary saturated, as well as allylic and benzylic alcohols, to the corresponding carbonyl compounds. The reagent was less useful for the conversion of saturated primary alcohols [584]. The kinetics of the oxidation of 30 monosubstituted benzyl alcohols to the corresponding benzaldehydes by pyridinium fluorochromate (PFC) have been studied. The reactions were first order in oxidant and showed a Michaelis-Menten type kinetics with respect to the substrates, indicating the formation of a PFC-alcohol complex in the preequilibrium [585]. Primary and secondary alcohols were oxidized by 1-methylimidazolium chlorochromate to the corresponding aldehydes and ketones. The same reagent oxidatively cleaved oximes to the corresponding carbonyl compounds [586]. Oxidation of the lignan model compounds (**290**; R,R = $(OMe)_2$ or OCH_2O) by pyridinium chlorochromate gave the lactones (**291**) and (**292**) in a 2:1 ratio [587].



290



291

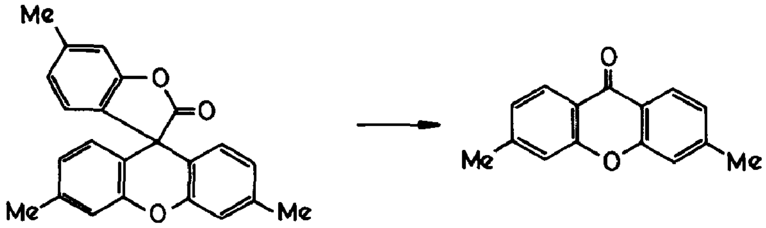


292

Trimethylsilylchromate, prepared *in situ* from CrO_3 and $Me_3SiOSiMe_3$, oxidizes primary and secondary alcohols to the corresponding carbonyl compounds in 75-93% yields [588].

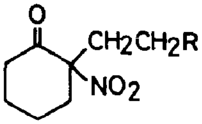
The kinetics of oxidation of D-fructose, D-glucose, and D-mannose by $[CoW_{12}O_{40}]^{5-}$ in aqueous media have been investigated. The reactions were catalyzed by alkali metal ions [589].

Cinnamyl, cyclopentyl, and cyclohexyl alcohols were easily oxidized to aldehydes in good yield by barium manganate in CH_2Cl_2 [590]. Oxidation of primary alcohols with $KMnO_4$ in a two-phase system using tris[2-(methoxyethoxy)ethyl]amine as phase-transfer catalyst gave the corresponding aldehydes in 54-91% yield [591]. Based on kinetic measurements it was concluded that the oxidation of formic acid by permanganate in aqueous $HClO_4$ proceeds via several parallel reactions [592]. Symmetrical xanthones (e.g.**294**) were prepared by alkaline $KMnO_4$ oxidation of the corresponding spirolactones (**293**) [593].

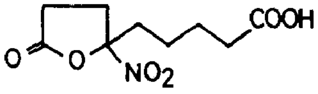


293 294

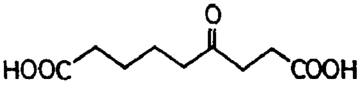
Oxidation of (**295**; R = CHO) with $KMnO_4$ gave the corresponding acid (**295**; R = COOH) and the two rearranged products (**296**) and (**297**) [594].



295



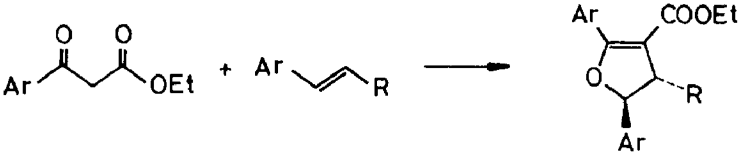
296



297

Oxidation of formic acid by $(Bu_3MeN)^+(MnO_4)^-$ in CH_2Cl_2 solution proceeds by a non-catalytic and an autocatalytic pathway; in the latter, one of the reaction products, colloidal MnO_2 acts as the catalyst. Both mechanisms are strongly inhibited by water [595]. Treating crystalline MnO_2 with ultrasound increased its activity as oxidant for the transformation of alcohols to carbonyl compounds [596]. The kinetics of oxidation of benzaldehyde by manganese(III) pyrophosphate were determined [597]. The selectivity of radical generation in the oxidation of carbonyl compounds by Mn(III)acetate was studied. The effects of chain propagation and initiation by Mn(III) could be separated; the C(1) position was found to be the most reactive in the initiation step [598]. Manganese(III) acetate oxidation of aroylacetates (**298**; Ar = Ph or substituted Ph) in the presence of a styrene derivative

(299; R = Me, CH_2OAc, COOEt) gave the dihydrofuran derivatives (300) in 40-70% yield [599].



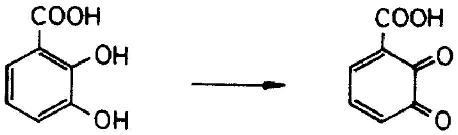
298 299 300

The kinetics of oxidation of ascorbic acid by Fe(III) have been investigated in aqueous solution using the stopped-flow technique [600]. Barium ferrate monohydrate $BaFeO_4.H_2O$ was found to be a useful oxidant for the oxidation of a large number of organic compounds under aprotic conditions. Alcohols and hydroquinones were converted into the corresponding carbonyl compounds, aromatic amines into their azo compounds, benzylamine to benzaldehyde, and thiols to disulfides in high yields [601]. Acyloins, RCOCH(OH)R (R = H,alkyl,Cy) were oxidized with $[Fe(CN)_6]^{3-}$ in alkaline medium. The reactivity of the substrates decreased with increasing bulkyness of the groups R [602]. The aromatic pinacol type compounds (301) could be oxidatively cleaved into the corresponding ketones by $Fe(phen)_3$. Pinacol itself proved to be inert against this type of oxidative cleavage [603].

R = Me, Ph

301

2,3-Dihydroxybenzoic acid (302) is oxidized by aqueous Fe^{3+} to the corresponding quinone (303). Based on kinetic measurements a mechanism was proposed for the reaction [604].



302 303

Phenol is oxidized to quinones (88% *para* and 12% *ortho* isomer) and cyclohexene to cyclohexen-3-one by $[(bpy)_2(py)Ru(O)]^{2+}$ in acetonitrile solution. The mechanism of these reactions has been studied by kinetic and spectroscopic methods [605]. The kinetics of oxidation of phenol and alkylated phenol derivatives by $[(bpy)_2(py)Ru^{IV}(O)]^{2+}$ and $[(bpy)_2(py)Ru^{III}(OH)]^{2+}$ to give the corresponding quinones have been studied in aqueous solution and in MeCN. Isotopic labeling experiments with ^{18}Ohave shown that the transfer of the oxo group from $[Ru^{VI}=O]^{2+}$ to phenol is quantitative. A Ru(II) complex has been detected as intermediate [606]. The kinetics of oxidation of ascorbic acid by $[RuCl_2(H_2O)_4]^+$, $[Ru(iminodiacetate)]^+$, and $[Ru(EDTA)]^+$ have been determined. Kinetic, spectroscopic, and thermodinamic parameters were reported for the formation of intermediate Ru(III)-ascorbate (1:1) and Ru(III)-chelate-ascorbate complexes [607].

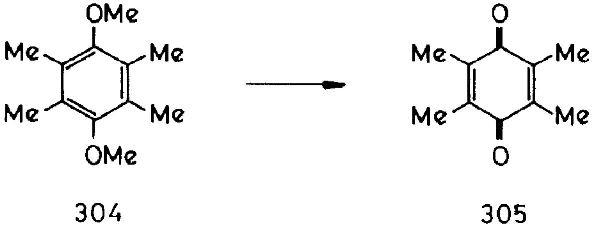
Based on spectrophotometric studies, a mechanism has been suggested for the oxidation of 2,2'-dihydroxy diethyl ether by OsO_4 [608].

Benzyl alcohol and substituted benzyl alcohols were oxidized to the corresponding benzaldehydes with Co(III) acetate in the presence of NaBr. If allylic alcohols were oxidized with Co(III) acetate, no NaBr was necessary but a larger excess of oxidant had to used [609]. Activity of Co(III) in the oxidation of hydroxyethyl cellulose is decreased by the addition of organic acids. This effect is due to the formation of inactive $CoOH^{2+}$ - acid complexes [610]. The kinetics and mechanism of the oxidation of ascorbic acid by trisoxalatocobaltate(III) were studied. As shown by the pH dependence of the process, oxidation of the doubly deprotonated substrate was the fastest in the system [611]. Oxidation of catechol and 3,5-di-*tert*-butylcatechol by $[IrCl_6]^{2-}$ in an SDS/1-butanol/toluene/water microemulsion has been investigated [612].

Oxidation of iPrOH by H_2PtCl_6 is significantly accelerated by metallic Pt [613].

The influence of acetonitrile on the kinetics of oxidation of ascorbic acid by Cu(II) and the ferrocenium ion in MeCN - H_2O solvent mixtures was determined [614]. Oxidation of D-lyxose by Cu^{2+} in H_2SO_4 at 130°C gave a mixture of C_2-C_4 hydroxycarboxylic acids. Kinetic parameters of the oxidation were determined [615]. Oxidation of dihydroxystilbene with Cu^{2+} at 155°C gave

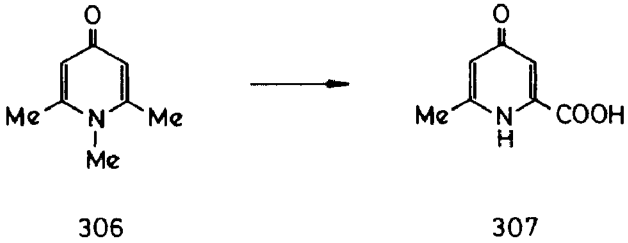
p-hydroxybenzoic acid [616]. Copper(II) nitrate (and to a lesser extent also Cr, Fe, Ce, Mn, and Ag nitrates) supported on silica gel were used to oxidize secondary alcohols to ketones and benzylic alcohols to aldehydes in refluxing CCl_4 or hexane. Yields were much lower in the absence of silicagel [617]. Oxidation of 1,2-ethanediol, 1,2-propanediol, and 1,2-butanediol with $[Cu(IO_4)_3]^-$ in an aqueous alkaline medium furnishes formaldehyde and the corresponding aldehydes. The rate of oxidation decreases with increasing IO_4^- concentration [618]. The hydroquinone derivative (304) was oxidized to (305) in a two-phase system by AgO in the presence of 2,6-pyridinedicarboxylic acid or with Ce(IV) in the presence of Na dodecyl sulfate. The latter system oxidized substituted toluenes to the corresponding benzaldehydes [619].



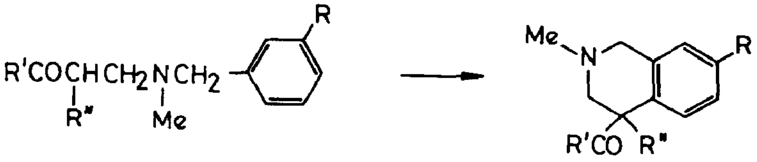
See also [381,488,501-504,511,544,545,551,563,648,657,664].

d) Oxidation of N-Containing Organic Compounds

The kinetics of oxidation of 1,8-diamino-4,5-dihydroxyanthraquinone-2,7-disulfonate with Ce(IV) were determined [620]. Oxidation of (306) with cerium perchlorate in perchloric acid gave (307) [621].

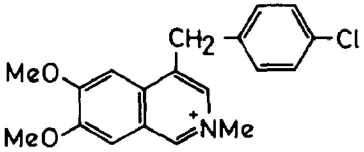


Tetrahydroisoquinolines (**309**) were obtained by the oxidative cyclization of β-amino ketones (**308**; R = HNO_2; R',R'' = $(CH_2)_n$, n = 3-5) by $Ce(SO_4)_2$-H_2SO_4 [622].

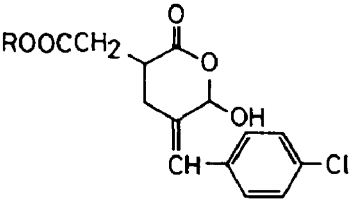


308 **309**

Oxidation of (**310**) with V_2O_5 in sulfuric acid gave p-$ClC_6H_4COCH_2OH$, p-$ClC_6H_4CH_2CH_2COOH$, p-$ClC_6H_4CH_2COCOOH$ and the δ-valerolactones (**311**; R = H,Me) [623].

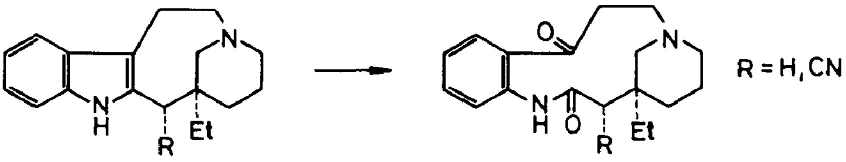


310



311

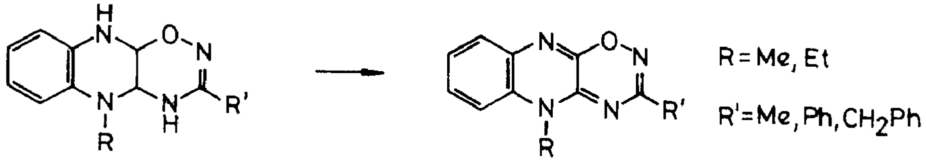
Oxidation of β-hydroxynitrosamines or β-nitrosoureas with CrO_3-celite or CrO_3-Florisil in EtOAc gave the corresponding β-oxo derivatives in 38-70% yield [624]. Oxidation of indigo carmine by chromic acid in acidic media was found to be first order in substrate, oxidant and perchloric acid [625]. Oxidation of the vinca alkaloid derivatives (**312**) with chromyl acetate (CrO_3/Ac_2O) in dichloromethane/acetic acid resulted, by ring cleavage in the macrocyclic compounds (**313**) [626].



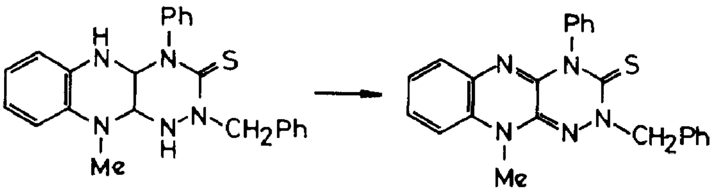
312 **313**

Oxidation of N,N-diethyl-p-phenylenediamine by 12-tungstocobaltate was studied in a stopped-flow apparatus [627].

The kinetics of permanganate oxidation of β-phenylalanine in aqueous $HClO_4$ have been studied spectrophotometrically. Evidence for the formation of an intermediate complex between the amino acid and the oxidant was presented [628]. The kinetics of oxidation of α-leucine, isoleucine and benzoylglycine in alkaline medium by $KMnO_4$ were studied [629]. Oxidation of L-isoleucine with MnO_4^- in buffered neutral aqueous solution showed autocatalysis by colloidal MnO_2 [630]. Oxidation of L-alanine [631], L-threonine [632], and L-glutamic acid [633] by permanganate in aqueous phosphate buffers is autocatalyzed by the inorganic reaction product, colloidal MnO_2 stabilized in solution by adsorption of phosphate ions on its surface. A catalytic and a non-catalytic reaction pathway are simultaneously operating in this system. Oxidation of ethylenediaminetetraacetate by MnO_4^- was found to be second order in oxidant, first order in substrate and inverse first order in H^+. Mn(II) retarded the reaction [634]. Oxidation of n-caproamide and i-caproamide with $KMnO_4$ in alkaline medium was found to be first-order with respect to amide and zero-order with respect to permanganate [635]. The kinetics of oxidation of phthalimide by $KMnO_4$ in aqueous NaOH have been studied. A radical mechanism was proposed [636]. The kinetics of oxidation of 2,6-diphenylpiperidin-4-one and its 3-methyl derivative by acidic $KMnO_4$ has been studied in $AcOH-H_2O$. A suitable mechanism was suggested [637]. Oxidation of the quinoxaline derivatives (**314**) and (**316**) with $KMnO_4-Me_2CO$ gave the corresponding dehydro compounds (**315**) and (**317**) [638].



314 **315**



316 **317**

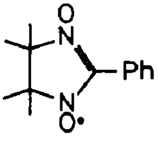
Aryl-substituted pyrazoles were obtained by the oxidation of the corresponding pyrazolines with MnO_2 [639]. Manganese(III) acetate was found to be a mild and selective reagent for the oxidation of a variety of N-protected indolines (318; R = H, CH_2Ph, Et, COPh, COMe, $CONEt_2$, Br; X = $CONEt_2$, SO_2Ph, COMe) to the corresponding indoles (319) [640].

318 319

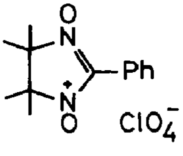
The kinetics of oxidation of phenylalanine and leucine by alkaline $[Fe(CN)_6]^{3-}$ have been determined. The products obtained were the corresponding keto acids [641]. Oxidation of arginine by alkaline $[Fe(CN)_6]^{3-}$ was found to be first order in substrate, oxidant, and OH^-. Oxidation of tryptophan to the corresponding keto acid by the same reagent, however, was independent of alkali concentration [642,643]. Oxidation of glycine with alkaline $[Fe(CN)_6]^{3-}$ gave glyoxylic acid. The slow step of the reaction involved the formation of a radical intermediate [644].

Oxidation of 2-picoline and 3-picoline by Co(III) acetate afforded the corresponding carboxylic acids in up to 52% yield [645].

Copper perchlorate in MeCN oxidizes the nitronyl nitroxide radical (320) to the nitrosonium perchlorate (321) in good yield [646].

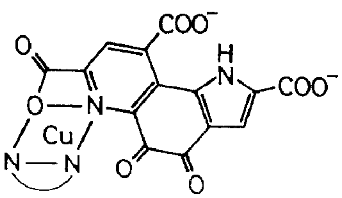


320

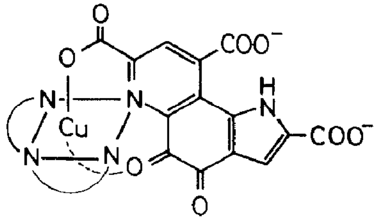


321

The ternary Cu(II) complexes (322) and (323), containing coenzyme PQQ and bpy or trpy oxidize benzylamine to benzaldehyde. In the case of (323) this oxidation is faster by a factor of about 15 than the control reaction with free PQQ [647].



322

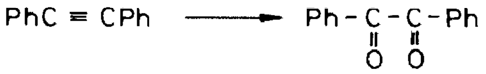


323

See also [391,524,559,594,601].

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

Oxidation of alcohols by pyridinium fluorochromate, $C_5H_5NHCrO_3F$, in CH_2Cl_2 requires 1 mol of oxidant for 1 mol of substrate. Oxidation of PPh_3 is a clear-cut example of oxygen transfer, the oxidant is transformed into $C_5H_5NHCrO_2F$ [648]. The Cr(V) complex $[(salen)Cr{=}O]^+(CF_3SO_3)^-$ oxidizes alkynes to 1,2-diones and phosphorous ylides to phosphine oxides and organic carbonyl compounds:



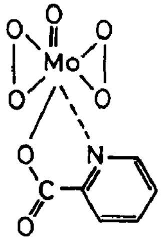
$$PhC\equiv CPh \longrightarrow Ph-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-Ph$$

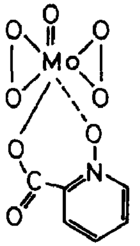
$$Ph_3PCRR' \longrightarrow Ph_3PO + O{=}CRR'$$

The oxidation requires two molecules of the complex for one molecule of substrate; an alkylidene complex of the type $(salen)Cr{=}CR_2$ is assumed as an intermediate [649]. The bis-μ-oxo complex $[Cp^*IrO]_2$ rapidly oxidizes CO to CO_2 and PPh_3 to $OPPh_3$ [650].

The kinetics of oxidation of cysteine with chromate in acid solutions were determined by spectrophotometric methods [651]. The oxidation kinetics of methionine by Cr(VI) in aqueous perchloric acid have been studied and the activation parameters determined [652]. Oxidation of EtSH by chromic acid proceeds via the reversible formation an intermediate chromic acid thioester. If EtSH is present in large excess, Cr(III) and EtSSEt are formed as products [653]. Oxidation of dipentyl and diphenyl sulfoxides with Cr(VI) in sulfuric acid was found to be first order each in oxidant and substrates [654]. Rate constants for the pyridinium chlorochromate oxidation of several *ortho*-substituted phenyl methyl sulfides have been determined. The reaction is sterically hindered by the *ortho* substituents in the benzene ring [655].

The anionic and coordinatively saturated oxodiperoxomolybdenum complexes (**234**) and (**235**) have been used for the stoichiometric oxidation of sulfides to sulfoxides and of sulfoxides to sulfones. Oxidation appears to proceed through an electrophilic oxygen transfer from the peroxo complexes to the substrates [656].


324

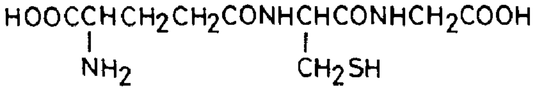

325

The kinetics of oxidation of thioglycolic acid and structurally related hydroxy acids with manganic pyrophosphate in sulfuric acid medium was studied. A cyclic 1:1 complex was proposed as an intermediate [657].

The kinetics and mechanism of the oxidation of 1-butanethiol and 2-butanethiol by $[Fe(CN)_6]^-$ have been studied and activation parameters evaluated in $MeOH\text{-}H_2O$ solution [658]. The kinetics of oxidation of cysteine to cystine by Fe(III) in acidic solution were determined [659]. Sodium nitroprusside, $Na_2[Fe(CN)_5NO].2H_2O$ oxidizes glutathione (GSH, **326**) to diglutathione according to the following stoichiometry:

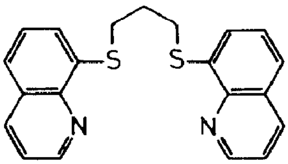
$$GSH + [Fe(CN)_5(NO))]^{2-} \longrightarrow 1/2\ GSSG + NO\ + H^+$$
$$+\ 5/6\ [Fe(CN)_6]^{4-} + 1/6\ Fe^{2+}$$

In the presence of air, oxidation becomes in part catalytic [660]. The kinetics of oxidation of thiophene by Pd(II) aqua complexes in acidic solution have been studied. 2-Hydroxythiophene was produced [661]. Glutathione (326) is oxidized to the corresponding disulfide (diglutathione) by Cu(II) complexes of thioaza ligands like (327). These complexes may be regarded as models of "blue" copper proteins [662].



$$\mathrm{HOOC\underset{NH_2}{C}HCH_2CH_2CONH\underset{CH_2SH}{C}HCONHCH_2COOH}$$

326



327

Tellurophosphoranes $R_3P{=}Te$ (R = iPr, tBu) are oxidized by ferricenium salts to give the dications $R_3P{-}Te{-}Te{-}Te{-}PR_3^{2+}$ [663]. Oxidation of 1-chloro-3-alkoxy-2-propanols with $K_2Cr_2O_7{-}H_2SO_4$ gave the corresponding propanones in 43-50% yield [664]. Oxidation of branched-chain internal fluoroolefins with 0.3-0.7 equiv. $KMnO_4$ in aqueous acetone below $0^{o}C$ gave diketones and tertiary diols [665].

See also [559,601,640].

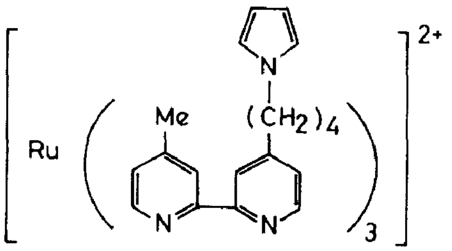
7. Electrooxidation and Photooxidation

Electrochemical oxidation of MeOH on Pt electrodes is catalyzed by adsorbed Mo species. The rate of oxidation increases several thousand fold; a detailed analysis of the results suggests that the adsorbed Mo(IV)/Mo(III) couple is catalytically active [666].

Epoxidation of *cis*-cyclooctene by O_2 is catalyzed by a Mn porphyrin polymer film deposited on an electrode. The catalyst was prepared from a pyrrole-substituted Mn porphyrin monomer by electrochemical polymerization [667]. An electrochemical system consisting of (TPP)MnCl and imidazole as catalyst, $MeCN{-}H_2O$ as solvent and acetic acid as proton donor activates O_2 and epoxidizes various alkenes with yields around 50% based on consumed electrons and oxidizes alkanes into alcohols and ketones (with significantly lower yields, however). Acetic acid is consumed during the electrolysis as expected for a monooxygenase reaction [668]:

$$RH + O_2 + 2e^- + 2H^+ \longrightarrow ROH + H_2O$$

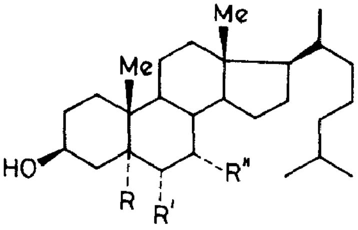
Catalytic oxidation of alkanes to alcohols and ketones was shown to take place in an electrochemical cell with an Fe porphyrin complex deposited on a graphite electrode [669]. Using iron bpy or phen complexes as redox catalysts NAD(P)H could be electrochemically oxidized to $NAD(P)^+$ in a tris-H_2SO_4-buffer solution. This enabled the electrochemically driven enzymatic oxidation of 2-hexen-1-ol or 2-butanol to the corresponding carbonyl compounds [670]. Electrocatalytic oxidation of cyclohexene in dichloromethane containing Pr_4NClO_4 and $Bu_4NF.3H_2O$ is catalyzed by $(TPP)FeF_2^-$. The products are cyclohexenone, 2-cyclohexen-1-ol, and cyclohexene oxide in approximately equal amounts. Water introduced in the form of the hydrated fluoride salt apparently provides the source of oxygen [671]. Electrooxidation of alkyl phenyl sulfides to chiral sulfoxides was performed using an electrode coated by Na montmorillonite, ion-exchanged with optically active $[Ru(phen)_3]^{2+}$ [672]. The electrochemical oxidation of alcohols to aldehydes or ketones and tetrahydrofuran to γ-butyrolactone is catalyzed by *cis*-$[Ru(Cl_2bpy)_2(OH)_2]^{2+}$ (Cl_2bpy = 6,6'-dichloro-2,2'-bipyridine). Current efficiencies were between 80 and 97% [673]. An electrocatalytic procedure has been described for the oxidation of alkenes to carbonyl compounds and of ketones to carboxylic acids using the Ru(IV) oxidant $[Ru(trpy)(bpy)O]^{2+}$, generated in situ from$[Ru(trpy)(bpy)(H_2O)]^{2+}$. Thus, for example, 2-cyclohexene-1-one was obtained from cyclohexene in 48% yield [674]. Electrolysis of an aqueous solution of benzyl alcohol containing Na_2CO_3 on a carbon-felt electrode coated by poly $[Ru(L)_3]^{2+}$ and RuO_2 produced benzaldehyde with 76% current efficiency. The Ru-containing polypyrrole film was prepared by controlled-potential oxidation of $[Ru(L)_3]^{2+}$ (**328**) in MeCN on a Pt disk [675].



328

Silver ion catalyzes the indirect electrochemical oxidation of toluene to benzaldehyde with Ce^{3+}/Ce^{4+} as mediator [676].

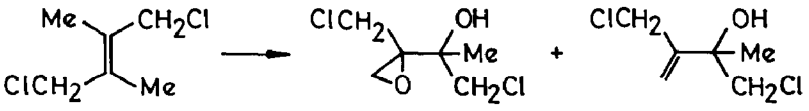
The Ti(IV) complexes formed from $TiCl_4$ and H_2O_2 in alcoholic solutions decompose on UV irradiation with formation of Ti(III) compounds and oxidation of the alcohol to aldehyde [677]. A convenient one-pot procedure for the synthesis of epoxy alcohols (**329**) and (**330**) by photooxygenation of cholesterol in the presence of $Ti(OPr^i)_4$ was developed. The ratio of the two products depended on the solvent used [678].



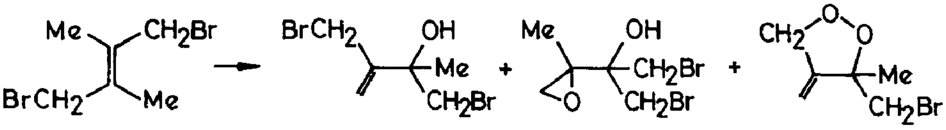
329; R = OH, R'R'' = O

330; R,R' = O, R'' = OH

Photooxygenation of the dichloro olefin (**331**) in the presence of $Ti(OPr)_4$ resulted in the formation of the epoxy alcohol (**332**) and the allylic alcohol (**332**). In contrast, the dibromo olefin (**334**) was transformed under the same conditions into a complex mixture containing, among other compounds, (**335**), (**336**), and (**337**) [679].

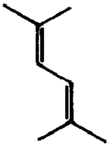


331 **332** **333**

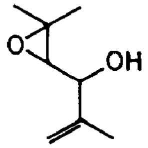


334 **335** **336** **337**

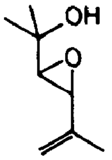
Photooxygenation of 2,5-dimethyl-2,4-hexadiene (**338**) gave epoxy alcohol (**339**) if $Ti(OPr^i)_4$ was used as catalyst while epoxy alcohol (**340**) was the sole product if the reaction was performed in the presence of $VO(acac)_2$. The reason for this unexpected regioselectivity difference is that the vanadium catalyst effects isomerization of the intermediate allylic alcohol (**341**) into (**342**) [680].



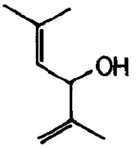
338



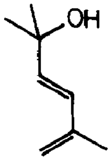
339



340



341



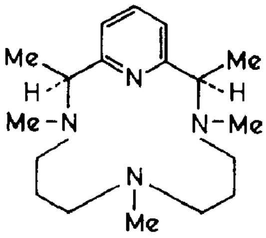
342

Photocatalytic liquid-phase oxidation of MeOH, EtOH, and PrOH with O_2 and $VOCl_3$ or $NH_4V(SO_4)_2$ as catalysts was studied. Photocatalytic activity decreased with increase of temperature [681].

Photochemical epoxidation of olefins by O_2 was achieved with the Mo(V) complex catalyst Mo(O)(OEt)(TPP-Me-*p*); terminal olefins, however, did not react under these conditions. The actual catalyst was the Mo(IV) complex Mo(O)(TPP-Me-*p*) formed *in situ* [682]. Photochemical oxidation of alkanes (mainly to alkenes) is catalyzed by α-$H_3PW_{12}O_{40}.nH_2O$ in acetonitrile solution.

Reoxidation of the photoreduced polytungstate is facilitated by Pt and its presence results therefore in increased turnover rates but at the same time decreases alkene selectivities [683]. The chemical and photochemical characteristics of the polytungstates involved in this process were investigated in detail [684].

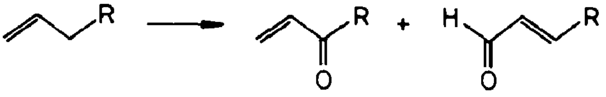
The kinetics of oxidation of formic acid by O_2 under photocatalytic conditions in the presence of iron ions was investigated. The catalytic cycle is composed of two main steps: formic acid is oxidized by Fe^{3+} to CO_2 and H_2O and Fe^{2+} is reoxidized by O_2 [685]. Visible irradiation of a methanolic solution of furfural containing dilute aqueous H_2O_2 and $[FeCp(C_6H_5R)]PF_6$ (R = H,Cl,Me) as catalyst yields methyl 2-furoate quantitatively. The catalyst can be isolated from the reaction mixture and recycled [686]. Photo-oxidation of organic substrates is catalyzed by *trans*-$[Ru^{VI}(L)(O)_2](ClO_4)_2$ (L = **343**) and $(Ph_4As)_2[Os^{VI}(CN)_4(O)_2]$ in MeCN at 25°C. Olefins are transformed into epoxides and carbonyl compounds, alcohols into aldehydes or ketones, toluene into benzaldehyde and dibenzyl sulfide into the corresponding sulfoxide [687].



343

Irradiation at λ > 480 nm of the purple solution of OsO_4 and anthracene in hexane yielded anthraquinone as the major product. Interestingly, the same product was formed also from 9-substituted (Br,NO_2) anthracenes [688].

The light-promoted oxidation of terminal alkenes by O_2 in the presence of Pd(II) complexes leads to α,β-unsaturated carbonyl compounds (**344,345**). The formation of isomeric olefins is retarded if the reaction is performed in acetone [689].



344 345

Photochemical oxidation of adamantylideneadamantane in the presence of $UO_2(NO_3)_2.6H_2O$ as sensitizer gave adamantylideneadamantane-1,2-dioxetane and adamantanone (3:1) in 70% yield [690]. Photo-oxidation of L-aspartic acid by uranyl ions in acidic medium gave malonic acid [691].

See also [386,571].

V. REVIEWS

Homogeneous catalysis by transition-metal complexes. 335 refs. [692].

Homogeneous catalysis by transition-metal complexes. 378 refs. [693].

Metal carbonyl catalysts for synthesis of organic compounds from CO and H_2. 165 refs. [694].

Syngas chemistry to chemical feedstocks: new frontiers. 102 refs. [695].

Carbon monoxide hydrogenation catalysis and supported metal clusters [696].

Transformations of carbon monoxide and related ligands on metal ensembles. 63 refs. [697].

Electrocatalytic CO_2 reduction. 11 refs. [698].

Carbon monoxide and carbon dioxide fixation: relevant C_1 and C_2 ligand reactions emphasizing $(\eta^5-C_5H_5)Fe$ complexes. 290 refs. [699].

The technology of oxo alcohols. [700].

Production of higher alcohols from α-olefins by the oxo process. 16 refs. [701].

Steric effects on the synthesis, structure, reactivity and selectivity of *tert*-phosphine rhodium complex hydroformylation catalysts. 10 refs. [702].

Some rules of catalytic activity in hydroformylation with transition metal complexes (metal clusters). 19 refs. [703].

New catalytic reactions with transition metal clusters. 25 refs. [704].

Aspects of intermediacy of carbalkoxymetal complexes in CO reactions (CO hydrogenation). 42 refs. [705].

Metal catalyzed carbonylation and oxidation-reduction reactions. 26 refs. [706].

New aspects of carbonylations catalyzed by transition metal complexes. 52 refs. [707].

Industrially relevant homogeneous catalysis using platinum-group metal complexes (hydroformylation, hydrogenation). 12 refs. [708].

Making pharmaceuticals via homogeneous catalysis (hydrogenation, hydroformylation). 43 refs. [709].

Homogeneous catalysis of the water-gas shift reaction. 97 refs. [710].

Metal-catalyzed deoxygenation reactions by carbon monoxide of nitroso and nitro compounds. 328 refs. [711].

Hydrogenation. 665 refs. [712].

Mechanism of homogeneous hydrogenation. 990 refs. [713].

Enantioselective synthesis with optically active transition-metal catalysts (hydrogenation, oxidation). 157 refs. [714].

Preparation of chiral ligands from amino acids, application to catalytic asymmetric synthesis. 43 refs. [715].

Novel reactions catalyzed by $H_5Ir(PPr^i_3)_2$ (H transfer). 26 refs. [716].

Stereochemistry of H_2 oxidative addition and dihydride-transfer reactions involving Ir(I) complexes. 42 refs. [717].

Organoiridium complexes as models for homogeneously catalyzed reactions. 86 refs. [718].

Homogeneous catalysis with platinum-group complexes. 12 refs. [719].

Palladium clusters - catalysts for reactions of unsaturated compounds. 43 refs. [720].

An introduction to the field of catalysis by molecular clusters and by supported molecular clusters and complexes. 37 refs. [721].

Mechanistic relationships between homogeneous and heterogeneous catalysis: some concepts arising from surface organometallic chemistry. [722].

Hydrogenation of aromatic nitro compounds in the presence of transition metal complexes. 96 refs. [723].

Cobalamin derivatives and analogs as catalysts and their use in organic synthesis. 65 refs. [724].

Methods of chloroaniline production from chloronitrobenzenes.II. Metal complex-catalyzed reductions. 32 refs. [725].

Synthesis, structure and reactivity or organometallic complexes of samarium(II) (reductions). 15 refs. [726].

Oxidation and reduction. 510 refs. [727].

Utilization of O_2 for the specific oxidation of organic substrates with Co(II) catalysts. 29 refs. [728].

Homogeneous liquid-phase oxidation of alkylaromatic compounds catalyzed by Co salts - activation with bromides. 41 refs. [729].

Soluble and supported metal catalysts for hydrocarbon oxidation in liquid and vapor phase. 76 refs. [730].

Phase-transfer systems in oxygen-transfer processes (epoxidations with Mo and W). 12 refs. [731].

Catalytic asymmetric epoxidation. 15 refs. [732].

New developments in the chemistry of peroxo-metal and chromium(VI) oxidant systems. 62 refs. [733].

Polymer-supported metal complex oxidation catalysts. 69 refs. [734].

Industrially relevant homogeneous catalysis utilizing platinum group metal complexes. 12 refs. [735].

Catalytic co-oxygenation of alkenes and other ligands by molecular oxygen at rhodium centers. 42 refs. [736].

Organometallic chemistry of electrophilic transition and lanthanide metal ions. The dominant pathways for reactions involving C=C, C-C, and C-H bonds (oxidations). 49 refs. [737].

Catalysis of electrode processes by metal complexes (electroreduction and electrooxidation). 177 refs. [738].

List of Abbreviations

acac	acetylacetonate
AS	Annual Survey on Hydroformylation, Reduction and Oxidation
BINAP	see Fig.41
BPPM	see Fig.56
Boc	*tert*-butoxycarbonyl, $-COOBu^t$
bpy	2,2'-bipyridine
Cl_8TPP	*meso*-tetrakis(2,6-dichlorophenyl)porphinato
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp^*	pentamethylcyclopentadienyl
cyclam	see Fig.33
dba	dibenzylideneacetone
DIOP	see Fig.78
dipamp	see Fig.46
dmgH	dimethylglyoxime
dppb	1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
dppm	bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$
dppp	1,3-bis(diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$
$F_{20}TPP$	*meso*-tetrakis(pentafluorophenyl)porphinato
HMPA	hexamethylphosphoric triamide
Me_8TPP	*meso*-tetrakis(2,6-dimethylphenyl)porphinato
OEP	2,3,7,8,12,13,17,18-octaethylporphinato
o.y.	optical yield
phen	1,10-phenathroline
py	pyridine
salen	N,N'-bis(salicylidene)-ethylenediaminato
saloph	N,N'-bis(salicylaldehyde)-*o*-phenylenediaminato
St	stearate, $nC_{17}H_{35}COO$
tetpy	2,2':6',2'':6",2'''-tetrapyridyl
Tf	trifluoromethanesulfonate (triflate), $CF_3SO_3^-$
TMP	*meso*-tetramesitylporphinato
TPP	5,10,15,20-tetraphenylporphinato
TpyP	*meso*-tetrakis(4-pyridylphenyl)porphinato
triphos	$MeC(CH_2PPh_2)_3$
trpy	2,2':6'2"-terpyridine

Ts	*p*-toluenesulfonyl (tosyl), *p*-$CH_3C_6H_4SO_2$-
Z	benzyloxycarbonyl, -$COOCH_2Ph$

Metal index

REFERENCES

1 C.Daniel, N.Koga, J.Han, X.Y.Fu and K.Morokuma, J.Am.Chem.Soc. 110 (1988) 3773.
2 N.Koga and K.Morokuma, Yuki Gosei Kagaku Kyokaishi 45 (1987) 1055; CA 109 (1988) 110467.
3 Z.Wang, W.Cao and J.Zhang, J.Mol.Sci.(Int.Ed.) 4 (1986) 365; CA 108 (1988) 130815.

4 N.Kosugi, H.Kuroda, L.Rao, A.Fukuoka and M.Ichikawa, Shokubai 29 (1987) 438; CA 108 (1988) 188848.

5 T.R.Tsao and P.Rao, Electr.Power Res.Inst.,[Rep.] EPRI AP (Palo Alto, Calif.) (1987) EPRI AP-5043-SR; CA 108 (1988) 223406.

6 H.Ono, K.Fujiwara, E.Sugiyama and K.Yoshida, Kagaku Kogaku Ronbunshu 14 (1988) 449; CA 109 (1988) 151864.

7 R.A.Head and R.Whyman, New.J.Chem. 12 (1988) 675; CA 109 (1988) 233133.

8 M.Ishino, M.Tamura, T.Deguchi and S.Nakamura, J.Catal. 105 (1987) 478; CA 108 (1988) 55277.

9 T.Masuda, K.Murata and A.Matsuda, Bull.Chem.Soc.Jpn. 61 (1988) 2865.

10 S.Shreiner, J.Y.Yu and L.Vaska, J.C.S.Chem.Commun. (1988) 602.

11 G.Fachinetti, T.Funaioli and M.Marcucci, J.Organomet.Chem. 353 (1988) 393.

12 F.Ungváry, L.Markó, T.M.Bockman, J.F.Garst and R.B.King, Isr.J.Chem. 27 (1986) 262; CA 109 (1988) 128307.

13 A.Major, I.T.Horváth and P.Pino, J.Mol.Catal. 45 (1988) 275.

14 G.Consiglio, Organometallics 7 (1988) 778.

15 A.Cabrera, A.Mortreux and F.Petit, J.Mol.Catal. 47 (1988) 11.

16 I.T.Horváth, M.Garland, G.Bor and P.Pino, J.Organomet.Chem. 358 (1988) C17.

17 B.E.Hanson and M.E.Davis, J.Chem.Educ. 64 (1987) 928; CA 108 (1988) 55087.

18 L.Kollár, G.Consiglio and P.Pino, Chimia 40 (1986) 428; CA 109 (1988) 54227.

19 N.Rosas, C.Márquez, H.Hernández and R.Gómez, J.Mol.Catal. 48 (1988) 59.

20 X.Li, Y.Chen, H.Xie and Y.Chen, Fenzi Cuihua 1 (1987) 1; CA 109 (1988) 189795.

21 R.Lazzaroni, R.Settambolo, A.Raffaelli, S.Pucci and G.Vitulli, J.Organomet.Chem. 339 (1988) 357.

22 R.M.Deshpande and R.V.Chaudhari, Ind.Eng.Chem.Res. 27 (1988) 1996.

23 W.Xie, Y.Chen, X.Huang, F.Jiao, Y.Yin and S.Yang, Fenzi Cuihua 1 (1987) 87; CA 109 (1988) 233100.

24 A.Cabrera, J.L.Arias and J.Gomez Lara, Acta Cient.Venez. 37 (1986) 512; CA 108 (1988) 21448.

25 C.Bianchini, A.Meli, M.Peruzzini, F.Vizza, Y.Fujiwara, T.Jintoktu and H.Taniguchi, J.C.S.Chem.Commun (1988) 299.

26 A.J.Chalk, J.Mol.Catal. 43 (1988) 353.

27 A.M.Trzeciak and J.J.Ziółkowski, J.Mol.Catal. 43 (1988) 335.

28 J.Lui, Y.Xia, W.Yuan and D.Liu, Fenzi Cuihua 1 (1987) 101; CA 109 (1988) 75652.

29 K.Sha, R.Yang and X.Guo, Fenzi Cuihua 1 (1987) 166; CA 109 (1988) 192532.

30 A.M.Trzeciak and J.J.Ziółkowski, J.Mol.Catal. 48 (1988) 319.

31 C.Bergounhou, D.Neibecker and R.Réau, J.C.S.Chem.Commun. (1988) 1370.

32 I.Ojima and Z.Zhang, J.Org.Chem. 53 (1988) 4425.

33 N.A.Bailey, V.S.Jassal, R.Vefghi and C.White, J.C.S. Dalton Trans. (1987) 2815.

34 P.Kalck, M.Ridmy and A.Thorez, C.R.Acad.Sci., Ser.2, 305 (1987) 953; CA 109 (1988) 6716.

35 C.Claver, P.Kalck, M.Ridmy, A.Thorez, L.A.Oro, M.T.Pinillos, M.Carmen Apreda, F.H.Cano and C.Foces-Foces, J.C.S.Dalton Trans. (1988) 1523.

36 Z.Wang, G.Yuan and Q.Zhou, Shiyou Huagong 16 (1987) 691; CA 109 (1988) 109832.

37 M.J.H.Russel, Platinum Metals Rev. 32 (1988) 179.

38 L.Gelmini and D.W.Stephan, Organometallics 7 (1988) 849.

39 R.Choukroun, A.Iraqui, C.Rifai and D.Gervais, J.Organomet. Chem. 353 (1988) 45.

40 N.A.Mohammadi and G.L.Rempel, ACS Symp.Ser. 364 (1988) 393; CA 108 (1988) 113113.

41 J.J.Lin, J.M.Larkin and J.F.Knifton, New.J.Chem. 12 (1988) 669; CA 109 (1988) 233132.

42 T.Hayashi, Z.H.Gu, T.Sakakura and M.Tanaka, J.Organomet. Chem. 352 (1988) 373.

43 J.Gao and J.Evans, Cuihua Xuebao 8 (1987) 384; CA 108 (1988) 169602.

44 M.M.Taqui Khan, S.B.Halligudi and S.H.R.Abdi, J.Mol.Catal. 48 (1988) 313.

45 M.M.Taqui Khan, S.B.Halligudi and S.H.R.Abdi, J.Mol.Catal. 45 (1988) 215.

46 J.Jenck, P.Kalck, E.Pinelli, M.Siani and A.Thorez, J.C.S. Chem.Commun. (1988) 1428.

47 J.F.Knifton, J.Mol.Catal. 47 (1988) 99.

48 R.Graziani, G.Cavinato, U.Casellato and L.Toniolo, J.Organomet.Chem. 353 (1988) 125.

49 S.Mutez, A.Mortreux and F.Petit, Tetrahedron Lett. 29 (1988) 1911.

50 L.Kollár, J.Bakos, I.Tóth and B.Heil, J.Organomet.Chem . 350 (1988) 277.

51 C.Pan, Y.Zhao and Y.Chen, Zhongguo Kexue Jishu Daxue Xuebao 17 (1987) 160; CA 108 (1988) 7853.

52 G.A.Korneeva, O.L.Butkova, L.I.Zvedkina, N.A.Pritula, S.M.Loktev and Yu.B.Kagan, Homogeneous Heterog.Catal.,Proc. Int.Symp.Relat.Homogeneous Heterog.Catal., 5th (1986) 587; CA 108 (1988) 149744.

53 O.L.Butkova, G.A.Korneeva, N.A.Pritula and S.M.Lokterv, Izv. Akad.Nauk SSSR, Ser.Khim. (1987) 1643; CA 108 (1988) 204196.

54 S.K.Cao, M.Y.Huang and Y.Y.Jiang, Polym.Bull.(Berlin) 19 (1988) 353; CA 109 (1988) 128415.

55 M.Ichikawa, Homogeneous Heterog.Catal.,Proc.Int.Symp.Relat. Homogeneous Heterog.Catal.,5th (1986) 819; CA 108 (1988) 111577.

56 B.L.Moroz, O.N.Shumilo, E.Paukstis, V.A.Likholobov, N.N.Bulgakov, E.N.Yurchenko and Yu.I.Ermakov, Homogeneous Heterog.Catal.,Proc.Int.Symp.Relat Homogeneous Heterog. Catal.5th (1986) 1127; CA 108 (1988) 93874.

57 C.Zheng, Y.Yin, G.Su and R.Rao, Fenzi Cuihua 1 (1987) 243; CA 109 (1988) 75655.

58 B.He, J.Sun, H.Li, F.Zheng, H.Cai, Q.Zhou, X.Yang, G.Liu, D.Liu and X.Wang, Sci.Sin.,Ser.B (Eng.Ed.) 30 (1987) 16; CA 108 (1988) 76291.

59 B.He, J.Weng, J.Sun, H.Li, Q.Zhou, G.Liu, X.Yang and C.Fu, Sci.Sin., Ser.B (Engl.Ed.) 31 (1988) 269; CA 109 (1988) 47335.

60 J.Hjortkjaer and P.Torotanova-Petrova, Mezhdunar.Simp.Svyazi Gomogennym Geterog.Katal.,5th 2 (1986) 233; CA 108 (1988) 21293.

61 J.Sun, J.Weng, H.Li and B.He, Gaodeng Xuexiao Huaxue Xuebao 8 (1987) 653; CA 108 (1988) 193373.

62 X.Liu and Y.Jiang, Cuihua Xuebao 9 (1988) 107; CA 109 (1988) 39724.

63 J.Hjortkjaer, Homogeneous Heterog.Catal.,Proc.Symp.Relat. Homogeneous Heterog.Catal.,5th (1986) 563; CA 108 (1988) 130830.

64 Y.Yuan, M.Huang and Y.Jiang, Gaofenzi Xuebao (1987) 356; CA 108 (1988) 152488.

65 Y.Konishi, M.Ichikawa and W.M.H.Sachtler, Shokubai 29 (1987) 462; CA 108 (1988) 188853.

66 H.Arakawa, N.Takahashi, T.Hanaoka, K.Takeuchi, T.Matsuzaki, and Y.Sugi, Chem.Lett. (1988) 1917.

67 L.Markó, M.A.Radhi, J.Palágyi and G.Pályi, Kém.Közl. 65 (1986) 144; CA 108 (1988) 204079.

68 M.M.Taqui Khan, S.B.Halligudi and S.H.R.Abdi, J.Mol.Catal. 48 (1988) 7.

69 K.Doyama, K.Fujiwara, T.Joh, K.Maeshima and S.Takahashi, Chem.Lett. (1988) 901.

70 P.Eilbracht, M.Acker and I.Hadrich, Chem.Ber. 121 (1988) 519.

71 I.Ojima, M.Okabe, K.Kato, H.B.Kwon and I.T.Horváth, J.Am. Chem.Soc. 110 (1988) 150.

72 M.Tanaka and I.Ogata, Chem.Express 2 (1987) 479; CA 108 (1988) 74784.

73 E.Lindner, U.Schober, E.Glaser, H.Norz and P.Wegner, Z.Naturforsch.,B: Chem.Sci. 42 (1987) 1527; CA 109 (1988) 149740.

74 E.Lindner, A.Sichinger and P.Wegner, J.Organomet.Chem. 349 (1988) 75.

75 K.G.Moloy and R.W.Wegman, J.C.S.Chem.Commun. (1988) 820.

76 G.Jenner, J.Organomet.Chem. 346 (1988) 237.

77 A.M.Raspolli Galletti, G.Braca and C.Sbrana, J.Organomet. Chem. 356 (1988) 221.

78 D.Vanhoye, S.Melloul, Y.Castanet, A Mortreux and F.Petit, Angew.Chem. 100 (1988) 711.

79 K.Murata, A.Matsuda and T.Masuda, Bull.Chem.Soc.Jpn. 61 (1988) 325.

80 F.Ungváry, A.Sisak, I.Kovács and L.Markó, Kém.Közl. 65 (1986) 127; CA 108 (1988) 204078.

81 J.M.Brown and A.G.Kent, J.C.S.Perkin Trans.II (1987) 1597.

82 M.M.Taqui Khan, S.B.Halligudi and S.Shukla, Angew.Chem. 100 (1988) 1803.

83 M.Lenarda, J.Kaspar, R.Ganzerla, A.Trovarelli and M.Graziani, J.Catal. 112 (1988) 1; CA 109 (1988) 135803.

84 P.Escaffre, A.Thorez and P.Kalck, New.J.Chem. 11 (1987) 601; CA 108 (1988) 186148.

85 R.Ziessel, J.C.S.Chem.Commun. (1988) 16.

86 J.-J.Brunet and M.Taillefer, J.Organomet.Chem. 348 (1988) C5.

87 K.Kandea, K.Doken and T.Imanaka, Chem.Lett. (1988) 285.

88 A.I.Min'kov, O.A.Efimov, N.K.Eremenko and E.B.Klimenko, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 2076; CA 109 (1988) 190537.

89 M.Miura, M.Shinohare and M.Nomura, J.Mol.Catal. 45 (1988) 151.

90 C.Floriani, P.Fiaschi, A.Chiesi-Villa, C.Guastini and P.F.Zanazzi, J.C.S.Dalton Trans. (1988) 1607.

91 K.Kaneda, T.Takemoto and T.Imanaka, Chem.Lett. (1988) 1759.

92 D.Vanhoye, F.Bedioui, A.Mortreux and F.Petit, Tetrahedron Lett. 29 (1988) 6441.

93 S.Cenini, C.Crotti, M.Pizzotti and F.Porta, J.Org.Chem. 53 (1988) 1243.

94 G.Fochi, J.Organomet.Chem. 350 (1988) C1.

95 S.Cosnier, A.Deronzier and J.-C.Moutet, J.Mol.Catal. 45 (1988) 381.

96 S.Schreiner, J.Y.Yu and L.Vaska, Inorg.Chim.Acta 147 (1988) 139.

97 H.Ishida, K.Tanaka and T.Tanaka, Chem.Lett. (1988) 339.

98 T.C.Simpson and R.R.Durand, Electrochim.Acta 33 (1988) 581; CA 109 (1988) 28962.

99 K.Ogura and I.Yoshida, J.Mol.Catal. 47 (1988) 51.

100 K.Tanaka, H.Miyamoto and T.Tanaka, Chem.Lett. (1988) 2033.

101 C.M.Bolinger, N.Story, B.P.Sullivan and T.J.Meyer, Inorg. Chem. 27 (1988) 4582.

102 M.Aresta, E.Quaranta and I.Tommasi, J.C.S.Chem.Commun. (1988) 450.

103 J.-P.Collin, A.Jouaiti and J.P.Sauvage, Inorg.Chem. 27 (1988) 1986.

104 D.L.DuBois and A.Medianer, ACS Symp.Ser. 363 (1988) 42; CA 108 (1988) 175728.

105 J.M.Bray and R. J.Mawby, J.C.S.Dalton Trans. (1987) 2989; CA 108 (1988) 67771.

106 K.K.Turisbekova, L.P.Shuikina, O.P.Parenago and V.M.Frolov, Kinet.Katal. 29 (1988) 1020; CA 109 (1988) 192548.

107 D.W.Krassowski and J.H.Nelson, J.Organomet.Chem. 356 (1988) 93.

108 C.Bergounhou, P.Fompeyrine, C.Commenges and J.J.Bonnet, J.Mol.Catal. 48 (1988) 285.

109 A.Choplin, B.Besson, L.D'Ornelas, R.Sanchez-Delgado and J.-M.Basset, J.Am.Chem.Soc. 110 (1988) 2783.

110 D.T.Gokak, B.V.Kamath and R.N.Ram, J.Appl.Polym.Sci. 35 (1988) 1523; CA 109 (1988) 23720.

111 C.Bianchini, A.Meli, F.Laschi, J.A.Ramirez, P.Zanello and A.Vacca, Inorg.Chem. 27 (1988) 4429.

112 M.M.Taqui Khan, E.Rama Rao, M.R.H.Siddiqui, B.Taqui Khan, S.Begum, S.Mustafa Ali and J.Reddy, J.Mol.Catal 45 (1988) 35.

113 C.-C.Fu and B.J.McCoy, Ind.Eng.Chem.Res. 27 (1988) 233.

114 L.Kollár, S.Tőrös, B.Heil and Z.Tuba, J.Mol.Catal. 47 (1988) 33.

115 I.J.B.Lin, H.A.Zahalka and H.Alper, Tetrahedron Lett. 29 (1988) 1759.

116 C.Larpent and H.Patin, J.Mol.Catal. 44 (1988) 191.

117 T.Okano, M.Iwahara, H.Konishi and J.Kiji, J.Organomet.Chem. 346 (1988) 267.

118 J.S.Butler, B.Gordon and I.R.Harrison, J.Appl.Polym.Sci. 35 (1988) 1183; CA 108 (1988) 206628.

119 B.Gordon, J.S.Butler and I.R.Harrison, J.Polym.Sci.,Part A: Polym.Chem. 25 (1987) 2139; CA 108 (1988) 7863.

120 M.Capka, Mezhdunar.Simp.Svyazi Gomogennym Geterog.Katal., 5th 2 (1986) 182; CA 108 (1988) 21083.

121 C.Claver, F.Gili, J.Vinas and A.Ruiz, Polyhedron 6 (1987) 1329; CA 108 (1988) 204800.

122 A.R.Siedle, R.A.Newmark, W.B.Gleason, R.P.Skarjune, K.O.Hodgson, A.L.Roe and V.W.Day, Solid State Ionics 26 (1988) 109; CA 109 (1988) 85111.

123 E.G.Lundquist, J.C.Huffman, K.Folting and K.G.Caulton, Angew.Chem. 100 (1988) 1236.

124 J.Reguli and A.Stasko, Chem.Pap. 41 (1987) 299; CA 109 (1988) 5937.

125 V.V.S.Reddy, J.Mol.Catal. 45 (1988) 73.

126 M.M.Taqui Khan, B.Taqui Khan and S.Begum, J.Mol.Catal. 45 (1988) 305.

127 A.A.Belyi, L.G.Chigladze, A.L.Rusanov, M.O.Shalikiani, R.S.Tabidze, S.G.Gagarin, E.S.Shpiro, G.V.Antoshin, Kh.M.Minachev and M.E.Vol'pin, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 2153; CA 109 (1988) 128179.

128 B.He and L.Wang, Gaofenzi Xuebao (1987) 404; CA 109 (1988) 73046.

129 D.V.Sokol'skii, A.K.Zharmagambetova, S.G.Mukhamedzhanova, E.A.Bekturov and S.E.Kudaibergenov, React.Kinet.Catal. Lett. 33 (1987) 387; CA 108 (1988) 166807.

130 L.I.Gvinter, V.M.Ignatov, L.N.Suvorova and V.Z.Sharf, Neftekhimiya 27 (1987) 348; CA 108 (1988) 74884.

131 V.N.Perchenko, I.S.Kalashnikova, G.L.Kamneva, I.V.Obydennova and N.S.Nametkin, Neftekhimiya 27 (1987) 219; CA 108 (1988) 55576.

132 C.Jiang, X.Zhang, J.Du, J.Hua, S.Fang and Y.Jiang, Shanghai Keji Daxue Xuebao (1987) 81; CA 108 (1988) 132932.

133 D.V.Sokolskii, S.G.Mukhamedzhanova and A.K.Zharmagambetova, Izv.Akad.Nauk Kaz.SSR, Ser.Khim., (1988) 86; CA 109 (1988) 128345.

134 H.S.Lee, Taehan Hwahakhoe Chi 32 (1988) 79; CA 109 (1988) 189899.

135 K.H.Dahmen, D.Hedden, R.L.Burwell and T.J.Marks, Langmuir 4 (1988) 1212; CA 109 (1988) 129202.

136 T.A.Markova, S.A.Smirnov, I.A.Oreshkin and B.A.Dolgoplosk, Kinet.Katal. 28 (1987) 1229; CA 108 (1988) 204770.

137 H.-J.Haupt, P.Balsaa and U.Flörke, Angew.Chem. 100 (1988) 280.

138 C.M.Fendrick, L.D.Schertz, V.W.Day and T.J.Marks, Organometallics 7 (1988) 1828.

139 R.L.Halterman and K.P.C.Vollhardt, Organometallics 7 (1988) 883.

140 M.Kitamura, I.Kasahara, K.Manabe, R.Noyori and H.Takaya, J.Org.Chem. 53 (1988) 710.

141 B.Imperiali and J.W.Zimmerman, Tetrahedron Lett. 29 (1988) 5343.

142 K.Yamamoto, M.Takagi and J.Tsuji, Bull.Chem.Soc.Jpn. 61 (1988) 319.

143 V.A.Pavlov, A.A.Bagatur'yants, V.B.Kazanskii and E.I.Klabunovskii, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 508; CA 109 (1988) 37314.

144 V.A.Pavlov, E.I.Klabunovskii, Yu.T.Struchkov, A.A.Voloboev and A.I.Yanovsky, J.Mol.Catal. 44 (1988) 217.

145 J.M.Brown, P.A.Chaloner and G.A.Morris, J.C.S.Perkin Trans. II (1987) 1583.

146 T.Morimoto, M.Chiba and K.Achiwa, Tetrahedron Lett. 29 (1988) 4755.

147 M.Saburi, H.Kawano, Y.Ishii and Y.Uchida, Kenkyu Hokoku - Asahi Garasu Kogyo Gijutsu Shoreikai 50 (1987) 225; CA 109 (1988) 109958.

148 T.Hayashi, N.Kawamura and Y.Ito, Tetrahedron Lett. 29 (1988) 5969.

149 H.Brunner and H.Leyerer, Bull.Soc.Chim.Belg. 96 (1987) 353; CA 108 (1988) 167657.

150 J.M.Brown, A.P.James and L.M.Prior, Tetrahedron Lett. 28 (1987) 2179.

151 H.Pracejus, G.Pracejus and B.Costisella, J.Prakt.Chem. 329 (1987) 235; CA 108 (1988) 74414.

152 C.Döbler, H.-J.Kreuzfeld and H.Pracejus, J.Organomet.Chem. 344 (1988) 89.

153 E.Cesarotti, A.Chiesa, L.Prati and L.Colombo, Gazz.Chim. Ital. 117 (1987) 129; CA 108 (1988) 150930.

154 Yu.T.Struchkov, A.I.Yanovskii, V.A.Pavlov, A.A.Voloboev and E.I.Klabunovskii, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 518; CA 108 (1988) 75602.

155 V.A.Pavlov, A.A.Voloboev, L.Z.Gorshkova, E.I.Karpeiskaya and E.I.Klabunovskii, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 513; CA 109 (1988) 55180.

156 N.Ishizuka, M.Togashi, M.Inoue and S.Enomoto, Chem.Phar. Bull. 35 (1987) 1686; CA 108 (1988) 204296.

157 E.I.Klabunovskii, D.D.Gogoladze, E.S.Lavitina, E.I.Karpeiskaya, L.F.Godunova, L.N.Kaigorodova and G.O.Chivadze, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 1597; CA 108 (1988) 167910.

158 Y.Okamoto, H.Kane and T.Imanaka, Chem.Lett. (1988) 2005.

159 A.V.Korolev, A.R.Brodskii, N.F.Noskova and D.V.Sokol'skii, Dokl.Akad.Nauk SSSR 296 (12987) 379; CA 108 (1988) 149758.

160 R.U.Kirss, T.C.Eisenschmid and R.Eisenberg, J.Am.Chem.Soc. 110 (1988) 8564.

161 M.Castiglioni, R.Giordano and E.Sappa, J.Organomet.Chem. 342 (1988) 111.

162 M.A.Esteruelas, E.Sola, L.A.Oro, U.Meyer and H.Werner, Angew.Chem. 100 (1988) 1621.

163 L.R.Gilliom, Polym.Mater.Sci.Eng. 58 (1988) 908; CA 109 (1988) 94501.

164 L.R.Gilliom, Mater Res.Soc.Symp.Proc. 111 (1988) 365; CA 109 (1988) 130600.

165 B.M.Choudary,K.Mukkanti and Y.V.Subba Rao, J.Mol.Catal. 48 (1988) 151.

166 J.M.Kerr and C.J.Suckling, Tetrahedron Lett. 29 (1988) 5545.

167 B.Corain, M.Basato, P.Main, M.Zecca, R.De Pieri and R.Arshady, J.Organomet.Chem. 326 (1987) C43.

168 N.V.Borunova, P.G.Antonova, N.V.Antseva, V.Z.Sharf and Yu.N.Kukushkin, Zh.Obshch.Khim. 57 (1987) 265; CA 108 (1988) 37159.

169 B.M.Trost and D.C.Lee, J.Am.Chem.Soc. 110 (1988) 7255.

170 M.O.Okoroafor, L.-H.Shen, R.V.Honeychuk and C.H.Brubaker, Organometallics 7 (1988) 1297.

171 V.M.Frolov, O.P.Parenago, L.P.Shuikina, A.V.Novikova, A.I.El'natanova, G.M.Cherkashin, E.G.Kliger and E.Ya.Mirskaya, Homogeneous Heterog.Catal.,Proc.Int.Symp.Relat.Homogeneous Heterog.Catal.,5th (1986) 587; CA 108 (1988) 149745.

172 W.D.Harman and H.Taube, J.Am.Chem.Soc. 110 (1988) 7906.

173 A.D.Thormodsen, T.Vermeulen and R.H.Fish, Report 1985, LBL-22209; CA 108 (1988) 5846.

174 A.Alvanipour and L.D.Kispert, J.Mol.Catal. 48 (1988) 277.

175 R.H.Fish, H.-S.Kim, J.E.Babin and R.D.Adams, Organometallics 7 (1988) 2250.

176 B.Fell and P.Elsler, Erdöl, Erdgas, Kohle 103 (1987) 231; CA 108 (1988) 204314.

177 J.Halpern, Pure Appl.Chem. 59 (1987) 173; CA 108 (1988) 6166.

178 U.Matteoli, G.Menchi, M.Bianchi and F.Piacenti, J.Mol.Catal. 44 (1988) 347.

179 G.F.Schmidt, J.Reiner and G.Süss-Fink, J.Orgnanomet.Chem. 355 (1988) 379.

180 E.M.Gordon and R.Eisenberg, J.Mol.Catal. 45 (1988) 57.

181 N.Lugan, G.Lavigne, J.-J.Réau, D.Neibecker and I.Tkatchenko, J.Am.Chem.Soc. 110 (1988) 5369.

182 T.Nishi, M.Kitamura, T.Ohkuma and R.Noyori, Tetrahedron Lett. 29 (1988) 6327.

183 H.Kawano, Y.Ishii, M.Saburi and Y.Uchida, J.C.S.Chem.Commun. (1988) 87.

184 M.Kitamura, T.Ohkuma, S.Inoue, N.Sayo, H.Kumobayashi, S.Akutagawa, T.Ohta, H.Takaya and R.Noyori, J.Am.Chem.Soc. 110 (1988) 629.

185 M.Kitamura, T.Ohkuma, H.Takaya and R.Noyori, Tetrahedron Lett. 29 (1988) 1555.

186 C.Hatat, A.Karim, N.Kokel, A.Mortreux and F.Petit, Tetrahedron Lett. 29 (1988) 3675.

187 M.V.Klyuev, Zh.Org.Khim. 23 (1987) 581; CA 108 (1988) 5414.

188 P.Khandual and C.R.Saha, J.Indian Chem.Soc. 63 (1986) 901; CA 108 (1988) 111554.

189 D.Shopov and S.Rakovski, Homogeneous Heterog.Catal.,Proc. Int.Symp.Relat.Homogeneous Heterog.Catal., 5th (1986) 601; CA 108 (1988) 93919.

190 C.R.Saha and S.Bhattacharya, J.Chem.Technol.Biotechnol. 37 (1987) 233; CA 108 (1988) 55561.

191 I.S.Akhrem, S.V.Reznichenko, V.V.Grushin and M.E.Vol'pin, Dokl.Akad.Nauk CCCR 294 (1987) 363.

192 G.-J.Kang, W.R.Cullen, M.D.Fryzuk, B.R.James and J.P.Kutney, J.C.S.Chem.Commun. (1988) 1466.

193 H.Brunner, A.Kürzinger, S.Mahboobi and W.Wiegrebe, Arch. Pharm.(Weinheim, Ger.) 321 (1988) 73; CA 109 (1988) 38011

194 X.Lu, P.Xu and Y.Chen, Cuihua Xuebao 9 (1988) 111; CA 109 (1988) 57000

195 T.Suarez and B.Fontal, J.Mol.Catal. 45 (1988) 335.

196 L.Y.Chiang, J.W.Swirczewski and R.R.Chianelli, Polym.Prepr. (Am.Chem.Soc.,Div.Polym.Chem.) 29 (1988) 210; CA 109 (1988) 38280.

197 G.Fochi, Oragnometallics 7 (1988) 2255.

198 R.F.Renneke and C.L.Hill, Angew.Chem. 100 (1988) 1583.

199 H.Itagaki, S.Shinoda and Y.Saito, Bull.Chem.Soc.Jpn. 61 (1988) 2291.

200 D.Morton and D.J.Cole-Hamilton, J.C.S.Chem.Commun. (1988) 1154.

201 I.Minami and J.Tsuji, Tetrahedron 43 (1987) 3903; CA 108 (1988) 185843.

202 K.Nomura and Y.Saito, J.C.S.Chem.Commun. (1988) 161.

203 K.Nomura, H.Kumagai and Y.Saito, Shokubai 30 (1988) 204; CA 109 (1988) 56987.

204 T.Sakakura, T.Sodeyama, Y.Tokunaga and M.Tanaka, Chem.Lett. (1988)) 263.

205 T.Sakakura, Y.Tokunaga, T.Sodeyama and M.Tanaka, Chem.Lett. (1988) 885.

206 T.Sakakura, T.Sodeyama and M.Tanaka, Chem.Lett. (1988) 683.

207 K.Sasaki, T.Sakakura, Y.Tokunaga, K.Wada and M.Tanaka, Chem.Lett. (1988) 685.

208 I.Amer, V.Orshav and J.Blum, J.Mol.Catal. 45 (1988) 207.

209 T.Sakakura, Y.Tokunaga, T.Sodeyama and M.Tanaka, Chem.Lett. (1988) 2375.

210 C.S.Chin, J.H.Shin, and J.B.Kim, J.Organomet.Chem. 356 (1988) 381.

211 H.Kameyama and T.Tsuji, Sekiyu Gakkaishi 30 (1987) 312; CA 109 (1988) 6197.

212 T.Nakano, S.Umano, Y.Kino, Y.Ishii and M.Ogawa, J.Org. Chem. 53 (1988) 3752.

213 S.K.Tyrlik, A.Korda and L.W.Zatorski, J.Mol.Catal. 45 (1988) 161.

214 S.Bhaduri and K.Sharma, J.C.S.Chem.Commun. (1988) 173.

215 M.A.Esteruelas, E.Sola, L.A.Oro, H.Werner and U.Meyer, J.Mol.Catal. 45 (1988) 1.

216 J.Kaspar, A.Trovarelli, M.Graziani, C.Dossi, R.Psaro, R.Ugo, G.Zanderighi, M.Lenarda and R.Ganzerla, J.Mol. Catal. 44 (1988) 183.

217 M.P.Garcia, A.M.López, M.A.Esteruelas, F.J.Lahoz and L.A.Oro, J.C.S.Chem.Commun. (1988) 793.

218 R.Marcec, React.Kinet.Catal.Lett. 31 (1986) 337; CA 108 (1988) 5410.

219 S.Sato, I.Matsuda and Y.Izumi, J.Organomet.Chem. 344 (1988) 71.

220 A.Vizi-Orosz and L.Markó, Transition Met.Chem. 13 (1988) 221.

221 H.Inoue, E.Haruki and M.Shirai, Chem.Express 3 (1988) 195; CA 109 (1988) 73072.

222 T.Nakano, J.Ando, Y.Ishii and M.Ogawa, Technol.Rep.Kansai Univ. 29 (1987) 69; CA 109 (1988) 5839.

223 R.Ruppert, S.Herrmann and E.Steckhan, J.C.S.Chem.Commun. (1988) 1150.

224 H.Brunner and W.Leitner, Angew.Chem. 100 (1988) 1231.

225 I.Shimizu and F.Aida, Chem.Lett. (1988) 601.

226 J.Tsuji, T.Sugiura and I.Minami, Synthesis (1987) 603; CA 108 (1988) 55437.

227 A.Arcadi, S.Cacchi, F.Marinelli and D.Misiti, Tetrahedron Lett. 29 (1988) 1457.

228 A.Arcadi, E.Bernocchi, A.Burini, S.Cacchi, F.Marinelli and B.Pietroni, Tetrahedron 44 (1988) 481; CA 109 (1988) 73273.

229 Y.Zhang and R.Lin, Synth.Commun. 17 (1987) 329; CA 108 (1988) 37596.

230 Z.Hou, Y.Fujiwara and H.Taniguchi, J.Org.Chem. 53 (1988) 3118.

231 S.Takeuchi and Y.Ohgo, Chem.Lett. (1988) 403.

232 G.A.Molander and C.Kenny, J.Org.Chem. 53 (1988) 2132.

233 A.Clerici and O.Porta, J.Org.Chem. 52 (1987) 5099.

234 H.A.Akers, M.C.Vang and T.Updike, Can.J.Chem. 65 (1987) 1364; CA 108 (1988) 36847.

235 S.Falicki and H.Alper, Organometallics 7 (1988) 2548.

236 G.Kalatzis, D.Katakis, E.Vrachnou and J.Konstantatos, Inorg.Chim.Acta 151 (1988) 191.

237 K.G.Moloy, Inorg.Chem. 27 (1988) 677.

238 C.T.Ng, X.Wang and T.-Y.Luh, J.Org.Chem. 53 (1988) 2536.

239 P.L.Gaus, S.W.Gerritz and P.M.Jeffries, Tetrahedron Lett. 29 (1988) 5083.

240 K.Yanada, T.Nagano, and M.Hirobe, Chem.Pharm.Bull. 36 (1988) 353; CA 109 (1988) 106678.

241 M.Novak and R.K.Lagerman, J.Org.Chem. 53 (1988) 4762.

242 I.N.Terskaya, G.A.Romanova, V.N.Polyakov and V.V.Budanov, Izv.Vyssh.Uchebn.Zaved., Khim.Khim.Tekhnol. 30 (1987) (11) 62; CA 109 (1988) 148725.

243 J.A.Roth, K.Grega and M.Orchin, J.Organomet.Chem. 342 (1988) 129.

244 C.Bianchini, C.Mealli, A.Meli, M.Peruzzini and F.Zanobini, J.Am.Chem.Soc. 110 (1988) 8725.

245 W.S.Mahoney, D.M.Brestensky and J.M.Stryker, J.Am.Chem.Soc. 110 (1988) 291.

246 R.Roy, S.Gervais, A.Gamian and J.Boratynski, Carbohydr.Res. 177 (1988) C5; CA 109 (1988) 231388.

247 S.Komiya and O.Tsutsumi, Bull.Chem.Soc.Jpn. 60 (1987) 3423.

248 C.Qian, Y.Ge, D.Deng, Y.Gu and C.Zhang, J.Organomet.Chem. 344 (1988) 175.

249 J.G.Cota, M.C.Meilán, A.Mourino and L.Castedo, J.Org.Chem. 53 (1988) 6094.

250 J.Huang, V.Goedken and H.M.Walborsky, J.Org.Chem. 53 (1988) 4129.

251 Y.Zhang and Z.Hu, Tetrahedron Lett. 29 (1988) 4113.

252 R.Schobert, Angew.Chem. 100 (1988) 869.

253 M.Pierrot, J.-M.Pons and M.Santelli, Tetrahedron Lett. 29 (1988) 5925.

254 J.Nakayama, Y.Ikuina, F.Murai and M.Hoshino, J.C.S.Commun. (1987) 1072.

255 S.V.Kukharenko, I.V.Barinov and V.V.Strelets, Izv.Akad.Nauk SSSR, Ser.Khim. (1988) 464; CA 109 (1988) 230207.

256 W.Tang, J.Li and T.H.Chen, Huaxue Xuebao 45 (1987) 472; CA 108 (1988) 131530.

257 K.Tanaka, M.Moriya, S.Uezumi and T.Tanaka, Inorg.Chem. 27 (1988) 137.

258 I.Tabushi, Y.Kuroda and Y.Sasaki, Tetrahedron 44 (1988) 2843; CA 109 (1988) 206829.

259 A.Feghouli, Y.Fort, R.Vanderesse and P.Caubere, Tetrahedron Lett. 29 (1988) 1379.

260 J.Protiva, E.Klinotova, J.Klinot, M.Kusiak and A.Vystrcil, Collect.Czech.Chem.Commun. 51 (1986) 2029; CA 108 (1988) 6225.

261 M.-C.Chan, K.-M.Cheng, K.M.Ho, C.T.Ng, T.M.Yam, B.S.L.Wang and T.-Y.Luh, J.Org.Chem. 53 (1988) 4466.

262 Y.Fort, R.Vanderesse and P.Caubere, Chem.Lett. (1988) 757.

263 G.Feghouli, R.Vanderesse, Y.Fort and P.Caubere, Tetrahedron Lett. 29 (1988) 1383.

264 S.Becker, Y.Fort, R.Vanderesse and P.Caubere, Tetrahedron Lett. 29 (1988) 2963.

265 B.Kh.Rammash, J.F.Richardson and J.L.Wong, J.Org.Chem. 53 (1988) 4241.

266 Y.Colas, B.Cazes and J.Gore, Bull.Soc.Chim.Fr. (1987) 165; CA 108 (1988) 21306.

267 B.M.Trost, R.Braslau, Tetrahedron Lett. 29 (1988) 1231.

268 K.Onuki, S.Shimizu, H.Nakajima, Y.Ikezoe and S.Sato, Int. J.Hydrogen Energy 12 (1987) 555; CA 108 (1988) 111749.

269 K.Tamao, E.Nakajo and Y.Ito, J.Org.Chem. 53 (1988) 414.

270 B.E.Khan and R.D.Rieke, J.Organomet.Chem. 346 (1988) C45.

271 J.Gillois, D.Buisson, R.Azerad and G.Jaouen, J.C.S.Chem. Commun. (1988) 1224.

272 S.Murata, M.Miura and M.Nomura, Chem.Lett. (1988) 361.

273 A.Fakhr, Y.Mugnier, E.Laviron and J.Mofidi, J.Organomet. Chem. 346 (1988) C49.

274 M.D.Ravi, V.N.Sivasankaran Pillai and P.N.Anantharaman, Bull.Electrochem. 4 (1988) 241; CA 109 (1988) 28929.

275 H.V.K.Udupa, Indian Chem.Eng. 30 (1988) 53; CA 108 (1988) 223397.

276 P.Subbiah, M.Noel, S.Chidambaram and K.S.Udupa, J.Electrochem.Soc.India 37 (1988) 7; CA 109 (1988) 178887.

277 Yu.B.Khokhryakov, A.V.Shavykin and I.A.Avrutskaya, Elektrokhimiya 24 (1988) 1275; CA 109 (1988) 199806.

278 Y.Lin Chiu, A.E.G.Sant'ana and J.H.P.Utley, Tetrahedron Lett. 28 (1987) 1349.

279 G.N.Kamau and J.F.Rusling, J.Electroanal.Chem.Interfacial Electrochem. 240 (1988) 217; CA 108 (1988) 139644.

280 I.Willner and R.Maidan, J.C.S.Chem.Commun. (1988) 876.

281 Y.Aoyama, K.Midorikawa, H.Toi and H.Ogoshi, Chem.Lett. (1987) 1651.

282 O.A.Borislavskii, L.Ya.Lyuta, V.Ya.Suprun and E.N.Mokryi, Vestn.L'vov.Politekh.Inst. 211 (1987) 120; CA 108 (1988) 186188.

283 A.L.Chugreev, A.B.Solov'eva, A.I.Samokhvalova and I.A.Misurkin, Teor.Eksp.Khim. 23 (1987) 428; CA 108 (1988) 18385.

284 R.V.Kucher, L.I.Opeida, T.V.Novikova and A.A.Turovskii, Dokl.Akad.Nauk Ukr.SSR, Ser.B: Geol.,Khim.Biol.Nauki (1987) (5) 37; CA 108 (1988) 130838.

285 F.Diaz-Rodriguez and J.Fernandez Gonzales, Quim.Ind.(Madrid) 32 (1986) 837; CA 108 (1988) 7854.

286 I.H.Al-Wahaib, B.S.Al-Metweli and B.S.Razoki, Neftepererab. Neftekhim.(Moscow) (1988) (4) 24; CA 109 (1988) 8345.

287 R.A.Galimov, and I.M.Kuznetsova, Neftekhimiya 27 (1987) 223; CA 108 (1988) 5421.

288 J.T.Groves and R.Neumann, J.Org.Chem. 53 (1988) 3891.

289 N.Kitajima, H.Fukui and Y.Moro-oka, J.C.S.Chem.Commun. (1988) 485.

290 M.M.Taqui Khan and R.S.Shukla, J.Mol.Catal. 44 (1988) 85.

291 M.M.Taqui Khan, H.C.Bajaj, R.S.Shukla and S.A.Mirza, J.Mol. Catal. 45 (1988) 51.

292 H.-C.Shen and H.-S.Weng, Ind.Eng.Chem.Res. 27 (1988) 2254.

293 A.P.Pokutsa and S.S.Ratovskii, Vestn.L'vov.Politekh.Inst. 211 (1987) 23; CA 108 (1988) 130841.

294 Y.V.Geletii, V.V.Lavrushko and G.V.Lubimova, J.C.S.Chem. Commun. (1988) 936.

295 M.Shimizu, H.Orita, T.Hayakawa and K.Takehira, Stud.Org. Chem.(Amsterdam) 33 (1988) 311; CA 109 (1988) 189917.

296 H.Sakurai, M.Mizu, M.Nishiki, N.Mitsuo and Satoh, J.Mol. Catal. 48 (1988) 175.

297 H.Sakurai, J.Mol.Catal. 47 (1988) 1.

298 M.Shimizu, H.Orita, T.Hayakawa and K.Takehira, J.Mol.Catal. 45 (1988) 85.

299 T.M.Nagiev, Z.M.Nagieva and Sh.A.Tagieva, Heterog.Catal. 6th (1988) Pt.2, 13; CA 109 (1988) 148722.

300 M.Augustin and C.L.Chong, Food.Chem. 27 (1988) 123; CA 108 (1988) 149089.

301 M.M.Taqui Khan and A.Prakash Rao, J.Mol.Catal. 44 (1988) 95.

302 A.V.Nikitin, A.D.Pomogailo, S.A.Maslov and V.L.Rubailo, Neftekhimiya 27 (1987) 234; CA 108 (1988) 5423.

303 D.Mukesh, S.Bhaduri and V.Khanwalkar, Chem.Eng.J.(Lausanne) 38 (1988) 153; CA 109 (1988) 131168.

304 Kh.E.Kharlampidi, E.A.Efanova and N.N.Batyrshin, Neftekhimiya 27 (1987) 533; CA 109 (1988) 37487.

305 A.Nishinaga, T.Yamada, H.Fujisawa, K.Ishizaki, H.Ihara and T.Matsuura, J.Mol.Catal. 48 (1988) 249.

306 T.Okamoto, Y.Sasaki, K.Sasaki and S.Oka, Bull.Chem.Soc.Jpn. 60 (1988) 4449.

307 A.Nishinaga, H.Yamato, T.Abe, K.Maruyama and T.Matsuura, Tetrahedron Lett. 29 (1988) 6309.

308 A.Nishinaga, H.Yamato and T.Matsuura, Stud.Org.Chem. (Amsterdam) 33 (1988) 289; CA 109 (1988) 189916.

309 P.A.Ganeshpure and S.Satish, Tetrahedron Lett. 29 (1988) 6629.

310 K.Yogish and N.V.S.Sastri, Ind.Eng.Chem.Res. 27 (1988) 909.

311 K.Yogish and N.V.S.Sastri, Ind.Eng.Chem.Res. 27 (1988) 2214.

312 S.Shi, X.You, P.Li and D.Li, Wuji Huaxue 3 (1987) 104; CA 108 (1988) 166808.

313 I.E.Bekk, E.V.Gusevkaya, V.A.Likholobov and Yu.I.Yermakov, React.Kinet.Katal.Lett. 33 (1987) 209; CA 108 (1988) 93898.

314 K.Takehira, T.Hayakawa, H.Orita, M.Shimizu and I.H.Oh, Bull. Korean Chem.Soc. 8 (1987) 254; CA 108 (1988) 21367.

315 E.A.Efanova and D.N.Gazizova, Khim.Tekhnol.Pererab.Nefti Gaza (1985) 7; CA 108 (1988) 36976.

316 I.P.Stolyarov, M.N.Vargaftik and I.I.Moiseev, Kinet.Katal. 28 (1987) 1359; CA 108 (1988) 149761.

317 J.M.Bregault, M.Faraj, J.Martin and C.Martin, New.J.Chem. 11 (1987) 337; CA 108 (1988) 74801.

318 J.-E.Backwall and R.B.Hopkins, Tetrahedron Lett. 29 (1988) 2885.

319 I.S.Shaw, J.S.Dranoff and J.B.Butt, Ind.Eng.Chem.Res. 27 (1988) 935.

320 F.Derdar, J.Martin, C.Martin, J.-M.Brégeault and J.Mercier, J.Organomet.Chem. 338 (1988) C21.

321 H.Urata, A.Fujita, and T.Fuchikami, Tetrahedron Lett. 29 (1988) 4435.

322 I.Mamalis, A.F.Noels, G.Tihange, R.Warin, P.Teyssié and A.J.Hubert, J.Mol.Catal. 45 (1988) 327.

323 K.Vasilev, R.Stamenova, R.Boeva and C.Tsvetanov, Dokl.Bolg. Akad.Nauk 40 (1987) 95; CA 109 (1988) 110173.

324 J.Van Beinum, A.J.Van Dillen, J.W.Geus and W.Drenth, Homogeneous Herterog.Catal., Proc.Int.Symp.Relat.Homogeneous Heterog.Catal. 5th (1986) 293; CA 108 (1988) 130829.

325 D.Baluch, J.Charalambous and L.I.B.Haines, J.C.S.Chem. Commun. (1988) 1178.

326 M.M.Taqui Khan, S.A.Mirza, C.Sreelatha, S.H.R.Abdi and Z.A.Shaikh, Stud.Org.Chem.(Amsterdam) 33 (1988) 211; CA 109 (1988) 47311.

327 M.M.Taqui Khan, S.A.Mirza, A.Prakash Rao and C.Sreelatha, J.Mol.Catal. 44 (1988) 107.

328 J.-C.Marchon and R.Ramasseul, J.C.S.Chem.Commun. (1988) 298.

329 S.I.Sadykh-Zade, F.I.Garibov, R.A.Kuliev and N.I.Garibov, Izv.Vyssh.Uchebn.Zaved.,Khim.Khim.Tekhnol. 30 (1987) 32; CA 108 (1988) 75123.

330 E.A.Lukashova, A.B.Solov'eva, A.L.Chugreev and N.S.Enikolopyan, Dokl.Akad.Nauk SSSR 294 (1987) 1167; CA 108 (1988) 55291.

331 M.M.Taqui Khan and R.S.Shukla, J.Mol.Catal. 45 (1988) 25.

332 P.Roffia, P.Calini and S.Tonti, Ind.Eng.Chem.Res. 27 (1988) 765.

333 B.G.Bal'kov, L.V.Dalidovich, N.G.Ariko and N.I.Mitskevich, Vestsi Akad.Navuk BSSR, Ser.Khim.Navuk (1988) (2) 17; CA 109 (1988) 229979.

334 N.Kitamija, S.Sunaga, Y.Moro-oka, T.Yoshikuni, M.Akada, Y.Tomotaki and M.Taniguchi, Bull.Chem.Soc.Jpn. 61 (1988) 967.

335 N.Kitajima, K.Takemura, Y.Moro-oka, T.Yoshikuni, M.Akada, Y.Tomotaki and M.Taniguchi, Bull.Chem.Soc.Jpn. 61 (1988) 1035.

336 I.Petrova, S.Ivanov, M.Kirilov, H.Tom Dieck, E.T.K.Haupt, Z.Zdravkova and D.Stoianova, Izv.Khim. 20 (1987) 548; CA 109 (1988) 162245.

337 A.I.Kamneva, N.V.Koroleva and A.Baghdadi, Tr.Inst.-Mosk. Khim.-Tekhnol.Inst.im.D.I.Mendeleeva 139 (1985) 103; CA 108 (1988) 94184.

338 S.N.Vyas, S.R.Pathwardan and T.N.Pal, Indian Chem.Eng. 28 (1986) 44; CA 108 (1988) 188832.

339 B.N.Sukharev and N.I.Sukhareva, Zh.Prikl.Khim.(Leningrad) 61 (1988) 819; CA 109 (1988) 189647.

340 L.F.Vekilova, T.S.Alieva, D.D.Orudzhev, G.L.Shik, A.A.Efendiev and T.N.Shakhtakhtinskii, Dokl.Akad.Nauk Az. SSR 44 (2) (1988) 15; CA 109 (1988) 233106.

341 A.A.Efendiev, D.D.Orudzhev, T.N.Shakhtakhtinskii and V.A.Kabanov, Homogeneous Heterog.Catal., Proc.Int.Symp. Relat.Homogeneous Heterog.Catal.,5th (1986) 717; CA 108 (1988) 149746.

342 R.S.Chandran and W.T.Ford, J.C.S.Chem.Commun. (1988) 104.

343 L.A.Mosolova, L.I.Matienko and I.P.Skibida, Kinet.Katal. 28 (1987) 479; CA 108 (1988) 21204.

344 L.A.Mosolova, L.I.Matienko and I.P.Skibida, Kinet.Katal. 28 (1987) 484; CA 108 (1988) 21205.

345 S.Ito, A.Kunai, H.Okada and K.Sasaki, J.Org.Chem. 53 (1988) 296.

346 S.Ito, T.Yamasaki, H.Okada, S.Okino and K.Sasaki, J.C.S. Perkin Trans.II (1988) 285; CA 109 (1988) 189620.

347 N.P.Evmenenko, A.P.Filippov, B.I.Kolotusha and V.M.Zyatkovskii, Kinet.Katal. 28 (1987) 861; CA 108 (1988) 130834.

348 G.La Monica, M.A.Angaroni, F.Cariati, S.Cenini and G.A.Ardizzoia, Inorg.Chim.Acta 148 (1988) 113.

349 R.Oi and S.Takenaka, Chem.Lett. (1988) 1115.

350 N.Ueyama, N.Yoshinaga and A.Nakamura, Stud.Org.Chem. (Amsterdam) 33 (1988) 257; CA 109 (1988) 210629.

351 S.Ya.Aleksandrova, V.N.Belousova and A.Ya.Yuffa, Neftekhimiya 27 (1987) 813; CA 108 (1988) 111601.

352 T.Okamoto, K.Sasaki and S.Oka, J.Am.Chem.Soc. 110 (1988) 1187.

353 N.Zhang, C.M.Mann and P.A.Shapley, J.Am.Chem.Soc. 110 (1988) 6591.

354 J.Vojtko, M.Cihova and J.Ilavsky, Ropa Uhlie 30 (1988) 193; CA 109 (1988) 39711.

355 M.Y.Huang, C.Y.Ren and Y.Y.Jiang, J.Macromol.Sci.,Chem. A24 (1987) 269; CA 108 (1988) 74794.

356 P.Capdevielle, J.Baranne-Lafont, D.Sparfel, N.K.Cuong and M.Maumy, J.Mol.Catal. 47 (1988) 59.

357 A.M.Sakharov and I.P.Skibida, Kinet.Katal. 29 (1988) 118; CA 108 (1988) 163991.

358 A.M.Sakharov and I.P.Skibida, J.Mol.Catal. 48 (1988) 157.

359 J.T.Groves and K.-T.Park, Stud.Org.Chem. (Amsterdam) 33 (1988) 541; CA 109 (1988) 230442.

360 O.J.Gelling, F.van Bolhuis, A.Meetsma and B.L.Feringa, J.C.S.Chem.Commun. (1988) 552.

361 R.P.Perito and B.B.Corden, Inorg.Chem. 27 (1988) 1276.

362 N.Homs, P.Ramirez de la Piscina and F.Borrull, J.C.S.Chem. Commun. (1988) 1075.

363 Y.Lin, A.Han and Q.Dai, Youji Huaxue 8 (1988) 45; CA 108 (1988) 197218.

364 M.Yu.Tuvin, G.N.Novodarova and M.E.Vol'pin, Izv.Akad.Nauk SSSR, Ser.Khim. (1988) 759; CA 109 (1988) 230619.

365 M.Yamada, K.Araki and S.Shiraishi, J.C.S.Chem.Commun. (1988) J.C.S.Chem.Commun. (1988) 530.

366 I.Sasaki, D.Pujol, A.Gaudemer, A.Chiaroni and C.Riche, Polyhedron 6 (1987) 2103; CA 108 (1988) 142080.

367 R.P.Perito and B.B.Corden, J.Am.Chem.Soc. 110 (1988) 3472.

368 H.Turk and W.T.Ford, J.Org.Chem. 53 (1988) 460.

369 H.J.Duchstein, K.Müller and G.Wurm, Arch.Pharm.(Weinheim, Ger.) 321 (1988) 153; CA 109 (1988) 128209.

370 C.E.Koning, F.J.Viersen, G.Challa and J.Reedijk, J.Mol. Catal. 44 (1988) 245.

371 S.Tsuruya, H.Kuwahara and M.Masai, J.Catal. 108 (1987) 369; CA 109 (1988) 92101.

372 K.Nakagawa, S.Nishiyama, S.Tsuruya and M.Masai, Stud.Org. Chem.(Asmterdam) 33 (1988) 315; CA 109 (1988) 229941.

373 Yu.I.Bratushko, N.I.Ermokhina and K.B.Yatsimirskii, Zh. Neorg.Khim. 33 (1988) 636; CA 108 (1988) 193426.

374 K.Osowska-Pacewicka and H.Alper, J.Org.Chem. 53 (1988) 808.

375 X.Wang, R.Wang, G.Li and G.Li, Huaxue Xuebao 45 (1987) 780; CA 108 (1988) 111590.

376 J.D.Druliner and E.Wasserman, J.Am.Chem.Soc. 110 (1988) 5270.

377 E.A.Sandler, Kh.E.Khcheyan, A.V.Ryabukhin and B.N.Bobylev, Neftekhimiya 27 (1987) 242; CA 108 (1988) 5424.

378 H.C.Shen and H.S.Weng, Ind.Eng.Chem.Res. 27 (1988) 2246; CA 109 (1988) 212710.

379 T.C.Chou, B.J.Hwang and C.C.Lee, J.Chin.Inst.Eng. 10 (1987) 441; CA 108 (1988) 23656.

380 Yu.I.Gudimenko, V.E.Agabekov, L.V.Shibaeva and N.I.Mitskevich, Zh.Prikl.Khim.(Leningrad) 60 (1987) 1078; CA 108 (1988) 37258.

381 R.DiCosimo and H.-C.Szabo, J.Org.Chem. 53 (1988) 1673.

382 Y.P.Hsieh, and N.D.Harris, J.Food.Sci. 52 (1987) 1384; CA 108 (1988) 110909.

383 T.V.Niem, N.V.Xuyen and H.S.Thoang, Tap Chi Hoa Hoc 25 (1987) 7; CA 109 (1988) 128182.

384 M.L.Hsieh, M.C.Cheng and S.M.Peng, Inorg.Chim.Acta 145 (1988) 1.

385 Z.Szeverényi, V.Fülöp, A.Kálmán and L.I.Simándi, Inorg. Chim.Acta 147 (1988) 135.

386 M.Blanchard, C.Bouchoule, G.Djaneye-Boundjou and P.Canesson, Tetrahedron Lett. 29 (1988) 2177.

387 L.I.Simándi, A.Fülep-Poszmik and S.Németh, J.Mol.Catal. 48 (1988) 265.

388 A.Nishinaga, S.Yamazaki and T.Matsuura, Tetrahedron Lett. 29 (1988) 4115.

389 K.Sakata, T.Kikutake, Y.Shigaki, M.Hashimoto, H.I.Ogawa and Y.Kato, Inorg.Chim.Acta 144 (1988) 1.

390 A.Inada, Y.Nakamura and Y.Morita, Chem.Pharm.Bull. 36 (1988) 462; CA 108 (1988) 182729.

391 M.G.B.Drew, P.C.Yates, J.Trocha-Grimshaw, A.Lavery, K.P.McKillop, S.M.Nelson and J.Nelson, J.C.S.Dalton Trans. (1988) 347.

392 Y.Nishida, Inorg.Chim.Acta 152 (1988) 41.

393 Y.Okamoto, T.Kusano and S.Takamuku, Bull.Chem.Soc.Jpn. 61 (1988) 3359.

394 D.P.Riley, M.R.Smith and P.E.Correa, J.Am.Chem.Soc. 110 (1988) 177.

395 S.U.Devi and T.Ramasarma, Moll.Cell.Biochem. 77 (1987) 111; CA 108 (1988) 200544.

396 Kh.M.Yakubov, V.E.Bessarabenko, A.N.Astanina, E.Ya.Offengenden and A.P.Rudenko, Koord.Khim. 14 (1988) 792; CA 109 (1988) 80592.

397 W.M.Brouwer, A.J.M.S.Robeerst, P.Piet and A.L.German, Homogeneous Heterog.Catal., Proc.Int.Symp.Relat.Homogeneous Heterog.Catal. 5th (1986) 631; CA 108 (1988) 93920.

398 A.M.van Herk, A.H.J.Tullemans, J.van Welzen and A.L.German, J.Mol.Catal. 44 (1988) 269.

399 E.I.Kozlyak, A.S.Erokhin and A.K.Yatsimirskii, React,Kinet. Catal.Lett. 33 (1987) 113; CA 108 (1988) 37014.

400 A.K.Yatsimirskii, E.I.Kozlyak and A.S.Erokhin, Kinet.Catal. 29 (1988) 352; CA 109 (1988) 211423.

401 M.Hassanein and W.T.Ford, Polym.Prepr.(Am.Chem.Soc.,Div. Polym.Chem.) 29 (1988) 198; CA 109 (1988) 56982.

402 K.Sakata, S.Wada and M.Hashimoto, Inorg.Chim.Acta 148 (1988) 7.

403 J.T.Guy, J.C.Cooper, R.D.Gilardi, J.L.Flippen-Anderson and C.F.George, Inorg.Chem. 27 (1987) 635.

404 D.H.R.Barton, J.Boivin and P.L.Coupanec, J.C.S.Chem.Commun. (1987) 1379.

405 F.F.Shcherbina, Ukr.Khim.Zh.(Russ.Ed.) 53 (1987) 89; CA 108 (1988) 21186.

406 H.H.Yang and C.A.Eckert, Ind.Eng.Chem.Res. 27 (1988) 2009.

407 H.M.Chawla, S.K.Sharma, K.Chakrabarty and S.Bhanumati, J.C.S.Chem.Commun. (1988) 128.

408 H.M.Chawla, S.K.Sharma, K.Chakrabarty and S.Bhanumati, J.Mol.Catal. 48 (1988) 349.

409 A.E.Gekhman, D.I.Shishkin and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 1436; CA 108 (1988) 94091.

410 J.Muzart and O.Piva, Tetrahedron Lett. 29 (1988) 2321.

411 F.P.Ballistreri, S.Failla and G.A.Tomaselli, J.Org.Chem. 53 (1988) 830.

412 H.Furukawa, T.Nakamura, H.Inagaki, E.Nishikawa, C.Imai and M.Misono, Chem.Lett. (1988) 877.

413 H.Schwegler, M.Floor and H.van Bekkum, Tetrahedron Lett. 29 (1988) 823.

414 R.B.Brown and C.L.Hill, J.Org.Chem. 53 (1988) 5762.

415 M.J.Nappa and R.J.McKinney, Inorg.Chem. 27 (1988) 3740.

416 R.H.Fish, R.H.Fong, J.B.Vincent and G.Christou, J.C.S.Chem. Commun. (1988) 1504.

417 J.B.Vincent, J.C.Huffman, G.Christou, Q.Li, M.A.Nanny, D.N.Hendrickson, R.H.Fong and R.H.Fish, J.Am.Chem.Soc. 110 (1988) 6898.

418 E.A.Karakhanov, S.Yu.Narin, V.A.Artemov, T.Yu.Filippova and A.G.Dedov, Neftekhimiya 28 (1988) 352; CA 109 (1988) 75686.

419 T.Kurata, Y.Watanabe, M.Katoh and Y.Sawaki, J.Am.Chem.Soc. 110 (1988) 7472.

420 E.A.Karakhanov, S.Yu.Narin, T.Yu.Filippova, E.A.Ivanova, S.M.Volkov and A.G.Dedov, Neftekhimiya 27 (1987) 791; CA 109 (1988) 92383.

421 T.-C.Lau, C.-M.Che, W.-O.Lee and C.-K.Poon, J.C.S.Chem. Commun. (1988) 1406.

422 M.M.Taqui Khan and R.S.Shukla, J.Mol.Catal. 44 (1988) 73.

423 S.Davis and R.S.Drago, Inorg.Chem. 27 (1988) 4759.

424 G.Barak and Y.Sasson, J.C.S.Chem.Commun. (1988) 637.

425 V.P.Tret'yakov, G.P.Zimtseva, L.A.Min'ko, V.V.Chudaev, E.S.Rudakov and N.F.Tyupalo, Ukr.Khim.Zh.(Russ.Ed.) 53 (1987) 1176; CA 109 (1988) 189624.

426 E.N.Jacobsen, I.Markó, W.S.Mungall, G.Schröder and K.B.Sharpless, J.Am.Chem.Soc. 110 (1988) 1968.

427 N.Iwasawa, T.Kato and K.Narasaka, Chem.Lett. (1988) 1721.

428 P.Müller and H.Idmoumaz, J.Organomet.Chem. 345 (1988) 187.

429 W.K.Wan, K.Zaw and P.M.Henry, Organometallics 7 (1988) 1677.

430 C.A.Salata, D.van Engen and C.J.Burrows, J.C.S.Chem.Commun. (1988) 579.

431 P.R.Carlier, W.S.Mungall, G.Schröder and K.B.Sharpless, J.Am.Chem.Soc. 110 (1988) 2978.

432 A.M.Kornilov, A.E.Sorochinskii, I.A.Butovich and V.P.Kukhar, Zh.Org.Khim. 23 (1987) 2470; CA 108 (1988) 221507.

433 I.Victor Ekhato, J.V.Silverton and C.H.Robinson, J.Org.Chem. 53 (1988) 2180.

434 L.-X.Dai, B.-L.Lou and Y.Z.Zhang, J.Am.Chem.Soc. 110 (1988) 5195.

435 H.Brunner and A.Sicheneder, Angew.Chem. 100 (1988) 730.

436 J.S.Brimacombe, R.Hanna and A.K.S.Kabir, J.C.S.Perkin Trans. I (1987) 2421.

437 Z.Wang and W.Zhou, Tetrahedron 43 (1987) 2935; CA 108 (1988) 131442.

438 L.Casella, M.Gullotti, A.Pintar, S.Colonna and A.Manfredi, Inorg.Chim.Acta 144 (1988) 89.

439 J.Cristobal Lopez, R.M.Rabanal and S.Valverde, An.Quim., Ser.C 82 (1986) 245; CA 108 (1988) 94808.

440 J.P.Lellouche, P.Breton, J.P.Beaucourt, L.Toupet and R.Gree, Tetrahedron Lett. 29 (1988) 2449.

441 D.D.Agarwal, J.Mol.Catal. 44 (1988) 65.

442 J.-I.Kato, H.Ota, K.Matsukawa and T.Endo, Tetrahedron Lett. 29 (1988) 2843.

443 P.J.Martinez de la Cuesta, E.Rus Martinez and A.J.Medina, Grasas Aceites (Seville) 39 (1988) 13; CA 109 (1988) 130073.

444 P.J.Martinez de la Cuesta, E.Rus Martinez and A.Justicia Medina, An.Quim.,Ser.A 84 (1988) 378; CA 109 (1988) 233098.

445 P.J.Martinez de la Cuesta, E.Rus.Martinez, J.M.Rodriguez Maroto and F.Martin Jimenez, An.Quim.,Ser.A 84 (1988) 235; CA 109 (1988) 151862.

446 J.Aguiar Garcia and V.R.Cortes, Grasas Aceites (Seville) 39 (1988) 1; CA 109 (1988) 131158.

447 R.M.Azhikova, A.M.Syroezhko and V.A.Proskuryakov, Kinet. Katal. 29 (1988) 780; CA 109 (1988) 177665.

448 E.Tempesti, L.Giuffré, F.Di Renzo, C.Mazzocchia and G.Modica, J.Mol.Catal. 45 (1988) 255.

449 V.A.Likhomanenko, E.Kh.Ziganshina, V.F.Tsvetkov, S.P.Korshunov, V.V.Guseva and L.I.Zakharkin, Neftekhimiya 27 (1987) 544; CA 109 (1988) 22769.

450 Y.Okamoto and W.C.Still, Tetrahedron Lett. 29 (1988) 971.

451 Y.Ishii, K.Yamawaki, T.Ura, H.Yamada, T.Yoshida and M.Ogawa, J.Org.Chem. 53 (1988) 3587.

452 Y.Ishii, K.Yamawaki, T.Ura, H.Yamada, H.Nishihara, T.Yoshida and M.Ogawa, Stud.Org.Chem.(Amsterdam) 33 (1988) 325; CA 109 (1988) 170144.

453 C.Venturello and R.D'Aloisio, J.Org.Chem. 53 (1988) 1553.

454 P.S.Dixit and K.Srinivasan, Inorg.Chem. 27 (1988) 4507.

455 S.Banfi, F.Montanari, M.Penso, V.Sosnovskikh and P.Vigano, Gazz.Chim.Ital. 117 (1987) 689; CA 109 (1988) 110125.

456 R.W.Lee, P.C.Nakagaki, B.N.Balasubramanian and T.C.Bruice, Proc.Natl.Acad.Sci.U.S.A. 85 (1988) 641; CA 109 (1988) 229914.

457 P.Battioni, J.P.Renaud, J.F.Bartoli, M.Reina-Artiles, M.Fort and D.Mansuy, J.Am.Chem.Soc. 110 (1988) 8462.

458 M.Nali, B.Rindone, S.Tollari and L.Valletta, Gazz.Chim.Ital. 117 (1987) 207; CA 108 (1988) 94787.

459 J.T.Groves and M.K.Stern, J.Am.Chem.Soc. 110 (1988) 8628.

460 S.Banfi, F.Montnari and S.Quici, J.Org.Chem. 53 (1988) 2863.

461 T.K.Miyamoto, S.Tagaki, T.Hasegawa, S.Tsuzuki, E.Takahashi, K.Okude, I.Banno and Y.Sasaki, Bull.Chem.Soc.Jpn. 60 (1987) 1649.

462 D.Wöhrle and J.Gitzel, Makromol.Chem., Rapid Commun. 9 (1988) 229; CA 109 (1988) 74051.

463 J.P.Collman, J.I.Brauman, J.P.Fitzgerald, P.D.Hampton, Y.Naruta and T.Michida, Bull.Chem.Soc.Jpn. 61 (1988) 47.

464 B.Meunier, M.-E. de Carvalho, O.Bortolini and M.Momenteau, Inorg.Chem. 27 (1988) 161.

465 H.Amatsu, T.K.Miyamoto and Y.Sasaki, Bull.Chem.Soc.Jpn. 61 (1988) 3193.

466 A.J.Castellino and T.C.Bruice, J.Am.Chem.Soc. 110 (1988) 7512.

467 A.J.Castellino and T.C.Bruice, J.Am.Chenm.Soc. 110 (1988) 1313.

468 T.G.Traylor and F.Xu, J.Am.Chem.Soc. 110 (1988) 1953.

469 T.Muto, H.Masumori, T.Miura and M.Kimura, Chem.Pharm.Bull. 35 (1987) 2177; CA 108 (1988) 221955.

470 D.Ostovic and T.C.Bruice, J.Am.Chem.Soc. 110 (1988) 6906.

471 H.Sugimoto, H.-C.Tung and D.T.Sawyer, J.Am.Chem.Soc. 110 (1988) 2465.

472 C.M.Dicken, P.N.Balasubramanian and T.C.Bruice, Inorg.Chem. 27 (1988) 197.

473 A.J.Castellino and T.C.Bruice, J.Am.Chem.Soc. 110 (1988) 158.

474 R.Belal and B.Meunier, J.Mol.Catal. 44 (1988) 187.

475 D.T.Sawyer, L.Spencer and H.Sugimoto, Isr.J.Chem. 28 (1987) 3; CA 108 (1988) 146163.

476 M.Bressan and A.Morvillo, J.C.S.Chem.Commun. (1988) 650.

477 P.A.Ganesphure and S.Satish, J.C.S.Chem.Commun. (1988) 981.

478 H.Yoon and G.J.Burrows, J.Am.Chem.Soc. 110 (1988) 4087.

479 J.F.Kinneary, J.S.Albert and C.J.Burrows, J.Am.Chem.Soc. 110 (1988) 6124.

480 J.F.Kinneary, T.R.Wagler and C.J.Burrows, Tetrahedron Lett. 29 (1988) 877.

481 A.Zanardo, F.Pinna, R.A.Michelin and G.Strukul, Inorg.Chem. 27 (1988) 1966.

482 C.S.Reddy and E.V.Sundaram, React.Kinet.Catal.Lett. 36 (1988) 131; CA 109 (1988) 28201.

483 Y.Kobayashi, M.Kusakabe, Y.Kitano and F.Sato, J.Org.Chem. 53 (1988) 1586.

484 V.Conte, F.Di Furia and G.Modena, J.Org.Chem. 53 (1988) 1665.

485 Y.Kurusu and Y.Masuyama, J.Macromol.Sci., Chem. A24 (1987) 389; CA 108 (1988) 130806.

486 K.Kaneda, K.Morimoto and T.Imanaka, Chem.Lett. (1988) 1295.

487 Y.Ishii, T.Yoshida, K.Yamawaki and M.Owaga, J.Org.Chem. 53 (1988) 5549.

488 S.L.Oswal, J.Indian.Chem.Soc. 63 (1986) 738; CA 108 (1988) 21202.

489 M.C.Crespo-Pinilla, F.Mata-Perez, M.P.Alvarez-Macho and M.S.Crespo-Pinilla, An.Quim.,Ser.A 83 (1987) 130; CA 108 (1988) 130832.

490 N.Ueyama, T.Sugawara, A.Nakamura, K.Yamaguchi and T.Fueno, Chem.Lett. (1988) 223.

491 M.W.Nee, C.A.Kim, S.Garg, M.C.Griffith, L.S.Mizoue, P.E.Rauch and W.J.Dixon, Tetrahedron Lett. 29 (1988) 5345.

492 S.Kanemoto, S.Matsubara, K.Takai, K.Oshima, K.Utimoto and H.Nozaki, Bull.Chem.Soc.Jpn. 61 (1988) 3607.

493 B.Singh, A.K.Singh and D.Singh, J.Mol.Catal. 48 (1988) 207.

494 M.K.Verma, P.K.Tandon and M.P.Singh, Z.Phys.Chem.(Leipzig) 268 (1987) 565; CA 108 (1988) 74605.

495 K.C.Gupta, P.Kumar and K.Behari, Bull.Soc.Chim.Fr. (1987) 232.

496 K.Behari, M.Verma and M.Gautam, Z.Phys.Chem.(Leipzig) 268 (1987) 1208; CA 109 (1988) 72805.

497 N.Swarnalakshmi, V.Uma, B.Sethuram and T.N.Rao, Indian J. Chem. 26A (1987) 592; CA 108 (1988) 186005.

498 S.Giddings and A.Mills, J.Org.Chem. 53 (1988) 1103.

499 G.Barak, J.Dakka and Y.Sasson, J.Org.Chem. 53 (1988) 3553.

500 K.G.Khetawat and G.D.Menghani, J.Indian Chem.Soc. 64 (1987) 766; CA 109 (1988) 189628.

501 G.Sarala, P.J.P.Rao, B.Sethuram and T.N.Rao, Indian J.Chem. 26A (1987) 475; CA 108 (1988) 204097.

502 P.N.Char, S.Sondu, B.Sethuram and T.N.Rao, J.Indian Chem. Soc. 64 (1987) 209; CA 108 (1988) 221113.

503 J.Nokami, H.Ogawa, S.Miyamoto, T.Mandai, S.Wakabayashi and J.Tsuji, Tetrahedron Lett. 29 (1988) 5181.

504 V.L.Devi, G.S.S.Murty and S.Kandlikar, Acta Cienc.Indica, Chem. 12 (1986) 72; CA 108 (1988) 112863.

505 C.W.Jefford and Y.Wang, J.C.S.Chem.Commun. (1988) 634.

506 A.Ya.Sychev, G.G.Duka, L.S.Chub and S.I.Kampos, Izv.Akad. Nauk Mold.SSR, Ser.Biol.Chim.Nauk (1987) 62; CA 108 (1988) 93897.

507 S.S.Shrivastava and P.C.Mathur, Pol.J.Chem. 60 (1986) 531; CA 108 (1988) 55288.

508 V.D.Skobeleva, S.Yu.Men'shikov, L.S.Molochnikov, I.P.Kolenko, A.A.Novoselova, L.A.Petrov and O.N.Sabkin, Izv. Akad.Nauk SSSR, Ser.Khim. (1987) 1728; CA 108 (1988) 221116.

509 K.Sato, T.Igarashi, Y.Yanagisawa, N.Kawauchi, H.Nashimoto and J.Yoshimura, Chem.Lett. (1988) 1699.

510 S.L.Khandia, V.K.Vaidya and S.G.Ameta, Afinidad 45 (1988) 175; CA 109 (1988) 190785.

511 G.I.Georg and J.Kant, J.Org.Chem. 53 (1988) 692.

512 V.Ali, S.Gupta and S.K.Upadhyay, Transition Met.Chem. 13 (1988) 179.

513 T.Hara, and T.Matsuura, Stud.Org.Chem.(Amsterdam) 33 (1988) 347; CA 109 (1988) 229942.

514 K.Behari, R.K.Agarwal and M.Gautam, Natl.Acad.Sci.Lett. (Indian) 9 (1986) 233; CA 108 (1988) 55249.

515 A.K.Awasthi and S.K.Upadhyay, J.Indian.Chem.Soc. 64 (1987) 125; CA 108 (1988) 111574.

516 S.Ranganathan, D.Ranganathan and D.Bhattacharyya, J.C.S. Chem.Commun. (1987) 1085.

517 S.-I.Murahashi, T.Naota and K.Yonemura, J.Am.Chem.Soc. 110 (1988) 8256.

518 S.Gupta, V.Ali and S.K.Upadhyay, Transition Met.Chem. 13 (1988) 135.

519 S.Ramakrishna, I.B.Bhushan and S.Kandlikar, Oxid.Commun. 10 (1987) 293; CA 109 (1988) 128212.

520 G.Sinha, D.Bandyopadhyay and A.Chakravorty, Inorg.Chem. 27 (1988) 1173.

521 K.Shimamoto and Y.Ohfune, Tetrahedron Lett. 29 (1988) 1988.

522 A.Prakash, P.Dwivedi, M.N.Shrivastava and B.B.L.Saxena, Indian J.Chem. 26A (1987) 960; CA 109 (1988) 55193.

523 A.Prakash, P.Dwivedi, M.N.Shrivastava and B.B.L.Saxena, Natl.Akad.Sci.Lett.(India) 11 (1988) 107; CA 109 (1988) 211429.

524 M.A.Rao, J.Indian.Chem.Soc. 64 (1987) 213; CA 108 (1988) 149748.

525 M.B.Hogale, M.H.Jagdale and B.P.Nikam, J.Indian Chem.Soc. 63 (1986) 932; CA 108 (1988) 130814.

526 T.H.Chan, L.M.Chen and D.Wang, J.C.S.Chem.Commun. (1988) 1280.

527 R.S.Davidson and M.D.Walker, Tetrahedron Lett. 29 (1988) 1827.

528 J.Bernadou, P.Gelas and B.Meunier, Tetrahedron Lett. 29 (1988) 6615.

529 F.Pautet, R.Barret, L.Favre and M.Daudon, Pharmazie 43 (1988) 437; CA 109 (1988) 207400.

530 C.Nemecek, E.Dunach and H.B.Kagan, Nouv.J.Chim. 10 (1986) 761; CA 108 (1988) 5635.

531 S.H.Zhao, O.Samuel and H.B.Kagan, Tetrahedron 43 (1987) 5135; CA 109 (1988) 109573.

532 S.Colonna, A.Manfredi, M.Spadoni, L.Casella and M.Gullotti, J.C.S.Perkin.Trans.I (1987) 71; CA 108 (1988) 74908.

533 J.Cabre Castellvi and A.Palomo Coll, Afinidad 43 (1986) 505; CA 108 (1988) 21565.

534 B.Pispisa, G.Paradossi, A.Palleschi and A.Desideri, J.Phys. Chem. 92 (1988) 3422; CA 109 (1988) 6928.

535 S.Zbaida, R.Kariv and P.Fischer, Arch.Biochem.Biophys. 261 (1988) 12; CA 108 (1988) 160840.

536 C.R.Sinha, D.Bandyopadhyay and A.Chakravorty, J.C.S.Chem. Commun. (1988) 468.

537 C.S.Creaser, A.R.Fernandes and D.C.Ayres, Chem.Ind.(London) (1988) 499; CA 109 (1988) 98209.

538 S.Ramakrishna and S.Kandlikar, Indian J.Chem.,27A (1988) 27; CA 109 (1988) 169714.

539 T.Izawa, Z.-G.Wang, Y.Nishimura, S.Kondo and H.Umezawa, Chem.Lett. (1987) 1655.

540 R.K.Shukla and N.Anandam, Acta Cienc.Indica, Chem. 11 (1985) 242; CA 108 (1988) 21215.

541 K.Takahashi, M.Shiro and M.Kishi, J.Org.Chem 53 (1988) 3098.

542 D.Pletcher and E.M.Valdes, J.Chem.Res.,Synop. (1987) 386; CA 109 (1988) 6169.

543 G.Balanikas, N.Hussain, S.Amin and S.S.Hecht, J.Org.Chem. 53 (1988) 1007.

544 D.N.Dhar, S.Joshi and P.Dwivedi, Indian J.Chem. 26B (1987) 539; CA 108 (1988) 204299.

545 G.E.M.Moussa, M.R.Salem, M.E.Shaban and E.I.Nagdy, J.Chem. Soc.Pak. 9 (1987) 391; CA 109 (1988) 6339.

546 J.G.Lee, H.J.Lim and D.S.Ha, Bull.Korean Chem.Soc. 8 (1987) 435; CA 108 (1988) 111911.

547 A.F.Guerrero, H.Kim and M.F.Schlecht, Tetrahedron Lett. 29 (1988) 6707.

548 E.J.Parish, T.-Y.Wei and P.Livant, Lipids 22 (1987) 760; CA 109 (1988) 23199.

549 E.J.Parish and T.Y.Wei, Synth.Commun. 17 (1987) 1227; CA 109 (1988) 55048.

550 R.Gurumurthy and M.Gopalakrishnan, Acta Cienc.Indica, Chem. 12 (1986) 104; CA 108 (1988) 37002.

551 S.M.Gannon and J.G.Krause, Synthesis (1987)) 915; CA 109 (1988) 230486.

552 M.Zielinski, J.Radioanal.Nucl.Chem. 121 (1988) 499; CA 109 (1988) 229971.

553 W.Huang and Q.Jiang, Huaxue Shijie 29 (1988) 253; CA 109 (1988) 189937.

554 P.Weyerstahl and K.Krohn, Liebigs Ann.Chem. (1987) 1125; CA 108 (1988) 22074.

555 J.F.Perez-Benito, Chem.Scr. 27 (1987) 433; CA 109 (1988) 54136.

556 D.Murali and G.S.K.Rao, Indian.J.Chem. 26B (1987) 156; CA 108 (1988) 94794.

557 B.B.Snider, J.J.Patricia and S.A.Kates, J.Org.Chem. 53 (1988) 2137.

558 J.E.Merritt, M.Sasson, S.A.Kates and B.B.Snider, Tetrahedron Lett. 29 (1988) 5209.

559 B.M.Trost, G.-H.Kuo and T,Benneche, J.Am.Chem.Soc. 110 (1988) 621.

560 K.Tomioka, M. Nakajima, Y.Iitaka and K.Koga, Tetrahedron Lett. 29 (1988) 573.

561 R.Curci, L.Lopez, L.Troisi, S.M.K.Rashid and A.P.Schaap, Tetrahedron Lett. 29 (1988) 3145.

562 N.S.Zefirov, V.N.Kirin, N.M.Yur'eva and A.S.Koz'min, Zh.Org.Khim. 23 (1987) 1902; CA 108 (1988) 221506.

563 R.A.Leising and K.J.Takeuchi, J.Am.Chem.Soc. 110 (1988) 4079.

564 B.F.Molino and B,.Fraser-Reid, Can.J.Chem. 65 (1987) 2834; CA 108 (1988) 56472.

565 M.Ignaczak, M.Deka and S.Komisarski, Pol.J.Chem. 61 (1987) 331; CA 109 (1988) 210367.

566 M.Ignaczak, M.Deka and S.Komisarski, Kinet.Katal. 28 (1987) 1479; CA 109 (1988) 72808.

567 P.O.I.Virtanen, R.Lindroos, E.Oikarinen and J.Vaskuri, Carbohydr.Res. 167 (1987) 29; CA 108 (1988) 204898.

568 T.H.Fisher, S.M.Dershem and T.P.Schultz, J.Org.Chem. 53 (1988) 1504.

569 H.-J.Kim and M.F.Schlecht, Tetrahedron Lett. 29 (1988) 1771.

570 J.P.Singh, S.J.S.Sirohi and Miss Aishwati, J.Indian Chem. Soc. 64 (1987) 440; CA 109 (1988) 22435.

571 M.Ignaczak, J.Dzigiec and K.Prawiczki, Chem.Stosow. 31 (1987) 119; CA 108 (1988) 40066.

572 Y.Tanoue and A.Terada, Bull.Chem.Soc.Jpn. 61 (1988) 2039.

573 M.Ignaczak, J.Dzigiec and L.Leszczynski, Pol.J.Chem. 60 (1986) 11; CA 108 (1988) 5427.

574 R.G.Salomon, S.Roy, M.F.Salomon, Tetrahedron Lett. 29 (1988) 769.

575 G.S.S.Murty, V.L.Devi and S.Kandlikar, Acta Cienc.Indica, Chem. 12 (1986) 63; CA 108 (1988) 130813.

576 T.Brunelet and G.Gelbard, C.R.Acad.Sci.,Ser.2, 303 (1986) 1433; CA 108 (1988) 74557.

577 J.Lou and Y.Wu, Synth.Commun. 17 (1987) 1717; CA 109 (1988) 54288.

578 J.D.Lou and Y.Y.Wu, Chem.Ind.(London) (1987) 531; CA 109 (1988) 189792.

579 K.A.B.Ahamed, K.Nambi and S.J.Arulraj, Indian J.Chem. 26A (1987) 672; CA 109 (1988) 72792.

580 R.de A.Epifano, W.Camargo and A.C.Pinto, Tetrahedron Lett. 29 (1988) 6403.

581 M.P.Alvarez Macho and M.I.Montequi Martin, An.Quim.,Ser.A 83 (1987) 248; CA 108 (1988) 132217.

582 M.S.Climent, J.M.Marinas and J.V.Sinisterra, Tetrahedron 43 (1987) 3303; CA 109 (1988) 55049.

583 S.A.Chimatadar, S.T.Nandibewoor and J.R.Raju, J.Indian. Chem.Soc. 64 (1987) 187; CA 108 (1988) 185985.

584 H.J.Carlsen and J.E.Braenden, Acta Chem.Scand. B41 (1987) 313; CA 108 (1988) 185838.

585 K.K.Banerji, J.Org.Chem. 53 (1988) 2154.

586 S.Kim and H.Chang, Bull.Korean Chem.Soc. 8 (1987) 183; CA 108 (1988) 5627.

587 A.S.R.Anjaneyulu, C.V.M.Sastry, P.Umasundari and P.Satyanarayana, Indian J.Chem. 26B (1987) 305; CA 108 (1988) 131395.

588 A.I.Moiseenkov, B.Ceskis, A.B.Veselovskii, V.V.Veselovskii, A.Yu.Romanovich and O.S.Chizhov, Zh.Org.Khim. 23 (1987) 1852; CA 108 (1988) 185842.

589 M.Gupta, S.K.Saha and P.Banerjee, J.C.S.Perkin Trans. II (1988) 1781.

590 G.L.Agrawal, J.Inst.Chem.(India) 59 (1987) 181; CA 109 (1988) 54289.

591 A.McKillop and L.S.Mills, Synth.Commun. 17 (1987) 647; CA 108 (1988) 131181.

392 I.S.Monzo, J.Palou, J.Penalver and R.Valero, Int.J.Chem. Kinet. 19 (1987) 741; CA 108 (1988) 111561.

593 M.Kimura and I.Okabayashi, Chem.Pharm.Bull. 35 (1987) 136; CA 108 (1988) 37627.

594 A.Zuercher and M.Hesse, Helv.Chim.Acta 70 (1987) 1937; CA 108 (1988) 186193.

595 D.G.Lee and J.F.Perez-Bonito, J.Org.Chem. 53 (1988) 5725.

596 T.Kimura, M.Fujita and T.Ando, Chem.Lett. (1988) 1387.

597 P.Oswal, S.L.Oswal and H.B.Naik, Proc.Indian Natl.Sci. Acad.,Part A 53 (1987) 200; CA 108 (1988) 130828.

598 G.Midgley and C.B.Thomas, J.C.S.Perkin Trans.I (1987) 1103; CA 108 (1988) 94043.

599 F.Z.Yang, M.K.Trost and W.E.Fristad, Tetrahedron Lett. 28 (1987) 1493.

600 M.J.Hynes and D.F.Kelly, J.C.S.Chem.Commun. (1988) 849.

601 H.Firouzabadi, D.Mohajer and M.Entezari-Moghadam, Bull. Chem.Soc.Jpn. 61 (1988) 2185.

602 A.A.Jarrar, R.A.El-Zaru and A.S.Shabin, Arabian J.Sci.Eng. 13 (1988) 65; CA 109 (1988) 169695.

603 J.H.Penn, D.-L.Deng and K.-J.Chai, Tetrahedron Lett. 29 (1988) 3635.

6o4 J.Xu and R.B.Jordan, Inorg.Chem. 27 (1988) 4563.

605 W.K.Seok, J.C.Dobson and T.J.Meyer, Inorg.Chem. 27 (1988) 3.

606 W.K.Seok and T.J.Meyer, J.Am.Chem.Soc. 110 (1988) 7358.

607 M.M.Taqui Khan and R.S.Shukla, Inorg.Chim.Acta 149 (1988) 89.

608 M.B.Singh, A.P.Singh, A.K.Singh and B.Singh, Natl.Acad.Sci. Lett.(India) 9 (1986) 175; CA 108 (1988) 55248.

609 M.Hirano, T.Morimoto and K.Itoh, Bull.Chem.Soc.Jpn. 61 (1988) 3749.

610 I.A.Nemchinov, V.A.Molotkov and V.I.Kurlyankina, Zh.Obshch. Khim. 57 (1987) 2019; CA 108 (1988) 206478.

611 P.Martinez, J.Zuluaga, J.Kraft and R.van Eldik, Inorg.Chim. Acta 146 (1988) 9.

612 C.Minero, E.Pramauro and E.Pelizzetti, Langmuir 4 (1988) 101; CA 108 (1988) 55303.

613 V.I.Perevalova, N.B.Shitova, L.Ya.Al't and V.K.Duplyakin, Zh.Obshch.Khim. 58 (1988) 1715; CA 109 (1988) 216823.

614 B.G.Cox, W.Jedral and J.Palou, J.C.S.Dalton Trans. (1988) 733; CA 109 (1988) 129549.

615 V.I.Krupenskii, Zh.Prikl.Khim.(Leningrad) 60 (1987) 675; CA 108 (1988) 38199.

616 S.M.Dershem, T.H.Fisher, S.Johnson and T.P.Schultz, Holzforschung 42 (1988) 163; CA 109 (1989) 131039.

617 T.Nishiguchi and F.Asano, Tetrahedron Lett. 29 (1988) 6265.

618 K.B.Reddy, B.Sethuram and T.N.Rao, Z.Phys.Chem.(Leipzig) 268 (1987) 706; CA 109 (1988) 72787.

619 J.Sharzewski, Pr.Nauk.Inst.Chem.Org.Fiz.Polytech.Wroclaw (1986) (No.30) 3; CA 109 (1988) 92399.

620 E.Alvarez-Manzaneda and T.Gamiz Garofano, Afinidad 44 (1987) 264; CA 108 (1988) 93903.

621 M.Ignaczak, M.Deka and S.Komisarski, Pol.J.Chem. 60 (1986) 357; CA 108 (1988) 112161.

622 U.Holzgrabe, Arch.Pharm.(Weinheim, Ger.) 321 (1988) 181; CA 109 (1988) 149318.

623 E.Postaire, C.Viel, M.Hamon and A.Gond, Talanta 34 (1987) 799; CA 108 (1988) 150232.

624 J.E.Saavedra, D.W.Farnsworth and G.K.Pei, Synth.Commun. 18 (1988) 313; CA 109 (1988) 109843.

625 P.Kamannarayana and K.Raghavachari, Acta Cienc.Indica, Chem. 12 (1986) 79; CA 108 (1988) 5430.

626 G.Kalaus, N.Malkieh, M.Kajtár-Peredy, J.Brlik, L.Szabó and C.Szántay, J.Org.Chem. 53 (1988) 42.

627 U.Nickel, B.Klein and H.Jen, Ber.Bunsen-Ges.Phys.Chem. 91 (1987) 997; CA 109 (1988) 5951.

628 R.M.Hassan, M.A.Mousa and M.H.Wahdan, J.C.S.Dalton Trans. (1988) 605; CA 109 (1988) 93559.

629 M.B.Hogale, P.K.Pawar and B.P.Nikam, Acta Cienc.Indica, Chem. 12 (1986) 228; CA 108 (1988) 22231.

630 J.A.Garrido, J.F.Perez-Benito, R.M.Rodriguez, J.De Andres and E.Brillas, J.Chem.Res.,Synop. (1987) 380; CA 108 (1988) 222074.

631 J.De Andres, E.Brillas and J.A.Garrido, J.C.S.Perkin Trans. II (1988) 107; CA 109 (1988) 6927.

632 R.M.Rodriguez, J.De Andres, E.Brillas, J.A.Carrido and J.Perez-Benito, New.J.Chem. 12 (1988) 143; CA 109 (1988) 211425.

633 J.De Andres, E.Brillas, J.A.Garrido, J.F.Perez-Benito and R.M.Rodriguez, Gazz.Chim.Ital. 118 (1988) 203; CA 109 (1988) 150011.

634 S.S.Anis, M.A.Mansour and S.L.Stefan, Microchem.J. 32 (1988) 170; CA 109 (1988) 238100.

635 K.R.Yadav, S.G.Sankpal, K.S.Warke and M.H.Jagdale, Acta Cienc.Indica,Chem. 11 (1985) 229; CA 108 (1988) 37001.

636 N.B.Hogale, B.P.Nikam, N.P.Dhore and P.K.Pawar, Acta Cienc.Indica, Chem. 12 (1986) 203; CA 108 (1988) 21213.

637 R.Varadachari, G.Mangalam and S.P.Meenakshisundaram, Acta Cienc.Indica, Chem. 12 (1986) 160; CA 108 (1988) 111553.

638 V.N.Charushin, L.M.Naumova, M.G.Ponizovskii, V.G.Baklykov and O.N..Chupakhin, Khim.Geterotsikl.Soedin. (1987) 1260; CA 108 (1988) 150439.

639 K.Agrawal, J.Indian Chem.Soc. 64 (1987) 408; CA 109 (1988) 54701.

640 D.M.Ketcha, Tetrahedron Lett. 29 (1988) 2151.

641 D.Laloo and M.K.Mahanti, Oxid.Commun. 10 (1987) 205; CA 109 (1988) 129627.

642 D.Laloo and M.K.Mahanti, Pol.J.Chem. 60 (1986) 589; CA 108 (1988) 6375.

643 D.Laloo and M.K.Mahanti, Afinidad 44 (1987) 324; CA 108 (1988) 6376.

644 D.Laloo and M.K.Mahanti, Afinidad 44 (1987) 123; CA 108 (1988) 22232.

645 M.Ahmed, T.A.Chaudhary and M.Azam, Pak.J.Sci.Ind.Res. 30 (1987) 182; CA 108 (1988) 221128.

646 A.Caneschi, J.Laugier and P.Rey, J.C.S.Perkin Trans. I (1987) 1077; CA 108 (1988) 21787.

647 S.Suzuki, T.Sakurai, S.Itoh and Y.Oshiro, Inorg.Chem. 27 (1988) 593.

648 M.N.Bhattacharjee, M.K.Chaudhuri and S.Purkayastha, Tetrahedron 43 (1987) 5389; CA 108 (1988) 130677.

649 B.Rihter and J.Masnovi, J.C.S.Chem.Commun. (1988) 35.

650 W.D .McGhee, T.Foo, F.J.Hollander and R.G.Bergman, J.Am. Chem.Soc. 110 (1988) 8543.

651 I.Baldea and G.Niac, Stud.Univ.Babes-Bólyai, Chem. 31 (1986) 41; CA 109 (1988) 149998.

652 M.A.Oletunji and G.A.Ayoko, Polyhedron 7 (1988) 11; CA 109 (1988) 190770.

653 G.Niac, S.Schon and I.Baldea, Stud.Univ.Babes-Bólyai, Chem. 31 (1986) 31; CA 109 (1988) 22431.

654 D.Bhatta, S.M.Behera and S.R.Mohanty, Indian J.Chem. 26A (1987) 778; CA 109 (1988) 37373.

655 K.Rajasekaran, T.Baskaran and C.Gnanasekaran, Indian J. Chem. 26A (1987) 956; CA 109 (1988) 229916.

656 S.Campestrini, V.Conte, F.Di Furia and G.Modena, J.Org. Chem. 53 (1988) 5721.

657 P.K.Ghandi and B.M.Rao, Z.Phys.Chem.(Leipzig) 268 (1987) 513; CA 108 (1988) 74604.

658 K.G.Kalla and K.K.Mishra, Phosphorus Sulfur 35 (1988) 183; CA 109 (1988) 169704.

659 R.F.Jameson, W.Linert, A.Tschinkowitz and V.Gutmann, J.C.S. Dalton Trans. (1988) 943; CA 108 (1988) 193483.

660 A.R.Butler, A.M.Calsy-Harrison, C.Glidewell, I.L.Johnson, J.Reglinski and W.E.Smith, Inorg.Chim.Acta 151 (1988) 281.

661 E.S.Rudakov and V.M.Ignatenko, Kinet.Catal. 28 (1987) 589; CA 108 (1988) 93901.

662 V.V.Pavlishchuk, J.Labuda and E.Sturdik, Iniorg.Chim.Acta 151 (1988) 261.

663 N.Kuhn, H.Schumann and R.Boese, J.C.S.Chem.Commun. (1987) 1257.

664 B.Kh.Kimsanov, L.A.Biryukova, S.A.Rasulov and L.A.Ismagilova, Zh.Vses.Khim.O-va im.D.I.Mendeleeva 32 (1987) 467; CA 109 (1988) 92249.

665 I.L.Knunyants, S.A.Postovoi, N.I.Delyagina and Yu.V. Zeifman, Izv.Akad.Nauk.SSSR, Ser.Khim. (1987) 2256; CA 109 (1988) 92244.

666 H.Kita, H.Nakajima and K.Shimazu, J.Electroanal.Chem. Interfacial Electrochem. 248 (1988) 181; CA 109 (1988) 137346.

667 P.Moisy, F.Bedioui, Y.Robin and J.Devynck, J.Electroanal. Chem.Interfacial Electrochem. 250 (1988) 191; CA 109 (1988) 158599.

668 P.Leduc, P.Battioni, J.F.Bartoli and D.Mansuy, Tetrahedron Lett. 29 (1988) 205.

669 A.M.Khenkin and A.E.Shilov, React.Kinet.Catal.Lett. 33 (1987) 125; CA 108 (1988) 37015.

670 J.Komoschinski and E.Steckhan, Tetrahedron Lett. 29 (1988) 3299.

671 D.L.Hickman, A.Nanthakumar and H.M.Goff, J.Am.Chem.Soc. 110 (1988) 6384.

672 A.Yamagishi, Chem.Aust. 54 (1987) 278; CA 108 (1988) 204030.

673 C.M.Che and W.O.Lee, J.C.S.Chem.Commun. (1988) 991.

674 J.M.Madurro, G.Chiericato, W.F.De Giovani and J.R.Romero, Tetrahedron Lett. 29 (1988) 765.

675 S.Cosnier, A.Deronzier and J.-C.Moutet, Inorg.Chem. 27 (1988) 2389.

676 J.J.Jow and T.C.Chou, J.Appl.Electrochem. 18 (1988) 298; CA 109 (1988) 558.

677 S.Ya.Kuchmii, A.V.Korzhak and A.I.Kryukov, Teor.Eksp.Khim. 24 (1988) 67; CA 108 (1988) 158882.

678 W.Adam and E.Staab, Liebigs.Ann.Chem. (1988) 757; CA 109 (1988) 110736.

679 A.Waldemar, S.Kömmerling, E.-M.Peters, K.Peters, H.G.von Schnering, M.Schwarm, E.Staab and A.Zahn, Chem.Ber. 121 (1988) 2151.

680 W.Adam and E.Staab, Tetrahedron Lett. 29 (1988) 531.

681 L.V.Lyashenko, E.V.Kashuba and V.M.Belousov, Kinet.Katal. 29 (1988) 218; CA 108 (1988) 158891.

682 Y.Matsuda, H.Koshima, K.Nakamura and Y.Murakami, Chem.Lett. (1988) 625.

683 R.E.Renneke and G.L.Hill, J.Am.Chem.Soc. 110 (1988) 5461.

684 C.L.Hill, D.A.Bouchard, M.Kadkhodayan, M.M.Williamson, J.A.Schmidt and E.F.Hilinski, J.Am.Chem.Soc. 110 (1988) 5471.

685 M.Bideau, L.Faure, Y.Assemian and B.Claudel, J.Mol.Catal. 43 (1988) 267.

686 F.Moulines, J.Ruiz and D.Astruc, J.Organomet.Chem. 340 (1988) C13.

687 V.W.-W.Yam, C.M.Che and W.-T.Tang, J.C.S.Chem.Commun. (1988) 100.

688 J.M.Wallis and J.K.Kochi, J.Am.Chem.Soc. 110 (1988) 8207.

689 J.Muzart, P.Pale and J.-P.Pete, J.Organomet.Chem. 353 (1988) 267.

690 A.I.Voloshin, G.L.Sharipov, V.P.Kazakov and G.A.Tolstikov, Izv.Akad.Nauk SSSR, Ser.Khim. (1987) 2837; CA 109 (1988) 149393.

691 R.Bhatt, P.B.Gandhi, S.C.Ameta and H.C.Chowdhry, Pak.J. Sci.Ind.Res. 30 (1987) 437; CA 108 (1988) 6379.

692 M.Bochmann, Organomet.Chem. 15 (1987) 382; CA 108 (1988) 6059.

693 M.Bochmann, Organomet.Chem. 16 (1987) 385; CA 108 (1988) 221737.

694 A.L.Lapidus and M.M.Savel'ev, Usp.Khim. 57 (1988) 29; CA 108 (1988) 115285.

695 B.Cornils, Crit.Rep.Appl.Chem. 14 (1987) 93; CA 108 (1988) 206603.

696 H.Knözinger and B.C.Gates, Stud.Surf.Sci.Catal. 29 (1986) 531; CA 108 (1988) 5316.

697 D.F.Shriver and M.J.Sailor, Acc.Chem.Res. 21 (1988) 374; CA 109 (1988) 157140.

698 B.P.Sullivan, M.R.M.Bruce, T.R.O'Toole, C.M.Bolinger, E.Megehee, H.Thorp and T.J.Meyer, ACS Symp.Ser. 363 (1988) 52; CA 108 (1988) 139596.

699 A.R.Cutler, P.K.Hanna and J.C.Vites, Chem.Rev. 88 (1988) 1363.

700 P.I.Bhuva, Chem.Age India 38 (1987) 101; CA 108 (1988) 152473.

701 R.Kubicka and V.Macek, Chem.Prum. 37 (1987) 590; CA 108 7831.

702 A.A.Oswald, D.E.Hendrikson, R.V.Kastrup, K.Irikura, E.J.Mozeleski and D.A.Young, Phosphorus Sulfur 30 (1987) 237; CA 108 (1988) 56141.

703 Y.Yin, Fenzi Cuhua 1 (1987) 246; CA 109 (1988) 75617.

704 G.Süss-Fink, Nachr.Chem.Tech.Lab. 36 (1988) 1110; CA 109 (1988) 237975.

705 D.Milstein, Acc.Chem.Res. 21 (1988) 428.

706 H.Alper, Pure Appl.Chem. 60 (1988) 35; CA 109 (1988) 230650.

707 I.Ojima, Chem.Rev. 88 (1988) 1011.

708 M.J.H.Russel, Chem.-Tech.(Heidelberg) (1988) (Int.Issue) 1721; CA 109 (1988) 112366.

709 G.W.Parshall and W.A.Nugent, CHEMTECH 18 (1988) 184; CA 109 (1988) 22318.

710 R.M.Laine and E.J.Crawford, J.Mol.Catal. 44 (1988) 357.

711 S.Cenini, M.Pizzotti and C.Crotti, Aspect Homogeneous Catal. 6 (1988) 97; CA 109 (1988) 109498.

712 D.Parker. Chem.Met.-Carbon Bond 4 (1987) 979; CA 108 (1988) 55116.

713 F.H.Jardine, Chem.Met.-Carbon Bond 4 (1987) 1049; CA 109 (1988) 37292.

714 H.Brunner, Synthesis (1988) 645; CA 109 (1988) 169579.

715 A.Mortreux, F.Petit, G.Buono and G.Peiffer, Bull.Soc.Chim. Fr. (1987) 631; CA 108 (1988) 185828.

716 X.Lu, Y.Lin and D.Ma, Pure Appl.Chem. 60 (1988) 1299; CA 109 (1988) 229694.

717 P.P.Deutsch and R.Eisenberg, Chem.Rev. 88 (1988) 1147.

718 J.D.Atwood, Coord.Chem.Rev. 83 (1988) 93; CA 109 (1988) 73497.

719 M.J.H.Russel, Chem.-Tech.(Heidelberg) 17 (1988) 148,151; CA 109 (1988) 116733.

720 A.S.Berenblyum, Zh.Vses.Khim.O-va im D.I.Mendeleeva 32 (1987) 82;; CA 108 (1988) 93797.

721 J.M.Basset, Ind.Appl.Homogeneous Catal. (1988) 293; CA 109 (1988) 237965.

722 J.M.Basset, J.P.Candy, A.Choplin, P.Dufour, P.Louessard and C.Santini, Stud.Surf.Sci.Catal. 41 (1988) 1; CA 109 (1988) 237964.

723 A.V.Bulatov, M.V.Klyuev and M.L.Khidekel, Kinet.Katal. 28 (1988) 263; CA 108 (1988) 74443.

724 O.E.Vendrova and A.M.Yurkevich, Khim.-Farm.Zh. 21 (1987) 339; CA 108 (1988) 221422.

725 Z.Sári, Magyar Kém.Lapja 43 (1988) 127; CA 109 (1988) 172471.

726 W.J.Evans, Inorg.Chim.Acta 139 (1987) 169.

727 G.W.J.Fleet, Org.React.Mech. (1984) 179; CA 109 (1988) 53988.

728 C.L.Bailey and R.S.Drago, Coord.Chem.Rev. 79 (1987) 321; CA 108 (1988) 74455.

729 F.F.Shcherbina, Neftekhimiya 27 (1987) 536; CA 108 (1988) 111409.

730 J.E.Lyons, NATO ASI Ser.,Ser.C 231 (1988) 97; CA 109 (1988) 172473.

731 O.Bortolini, V.Conte, F.Di Furia and G.Modena, Stud.Org. Chem.(Amsterdam) 33 (1988) 301; CA 109 (1988) 210234.

732 K.B.Sharpless, Janssen Chim.Acta 6 (1988) 3; CA 109 (1988) 128034.

733 M.K.Chaudhuri, J.Mol.Catal. 44 (1988) 129.

734 D.C.Sherrington, Pure Appl.Chem. 60 (1988) 401; CA 109 (1988) 38985.

735 M.J.H.Russel, Chem.-Tech.(Heidelberg) (1988) 17,21; CA 109 (1988) 172472.

736 G.Read, J.Mol.Catal. 44 (1988) 15.

737 A.Sen, Acc.Chem.Res. 21 (1988) 421.

738 O.N.Efimov and V.V.Strelets, Usp.Khim. 57 (1988) 228; CA 108 (1988) 175704.