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Effect of Catalyst on the Oxygenation of Styrene with BH_4^- and Molecular Oxygen[1)]

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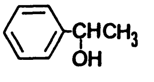
Synopsis. The effects of equatorial ligands and central metals on the catalytic conversion of styrene to 1-phenylethanol were examined. Accompanying hydrogenation and hydrodimerization of the substrate to ethylbenzene and 2,3-diphenylbutane, respectively, was facilitated in the presence of a catalyst ligated with an electron-releasing ligand such as 1,4,8,11-tetraazacyclotetradecane or sulfur-containing ligands.

Previously we reported the catalytic conversion of aryl-conjugated olefins to the derivatives of benzyl alcohol by molecular oxygen and tetrahydroborate ion at room temperature.[2,3)] The reaction proceeded with high reio- and chemoselectivities affording the corresponding alcohols in high yields. A related reaction by using nitrogen monoxide in place of molecular oxygen also presented a new process for preparation of oximes under mild reaction conditions.[4)] As for the catalyst of these reactions, successful results were reported with cobalt complexes of the monoanion of 2,3-butanedione dioxime (DMG)[2)] and tetraphenylporphyrin (TPP).[3)] The catalytic effects of some other transition metal complexes in the oxygenation of styrene was examined in the present study to reveal a distinctive effects of equatorial ligands and the central metals on the distribution of the products.

Results and Discussion

In the transition metal-catalyzed oxygenation of styrene with tetrahydroborate and molecular oxygen, the main product of 1-phenylethanol (**1**) was occasionally accompanied by three by-products. Two of them were ethylbenzene (**2**) and 2,3-diphenylbutane (**3**) which were produced by hydrogenation and hydrodimerization of styrene, respectively. The other was acetophenone, a compound formally produced by dehydrogenation of the alcohol **1**. The relative yields of these products were dependent on the various reaction conditions. Typically, the yields of products via hydrogenation, **2** and **3**, increased at the high concentration of tetrahydroborate ion. On the other hand, the yield of acetophenone increased when the low concentration of BH_4^- was used. At low reaction temperature the yield of acetophenone increased relative to the alcohol. The contribution of bimolecular process affording **3** was important at the high concentration of the catalyst.



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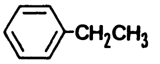

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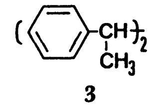

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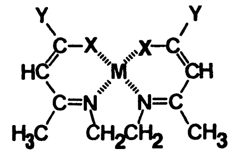
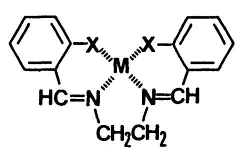
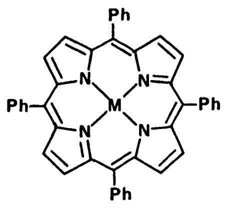
Except for these general phenomena, the product distribution was dependent on the metal complex used as the catalyst. The effect of equatorial ligand was compared with eight cobalt complexes having the equatorial coordinating atoms of nitrogen, oxygen, and sulfur such as **4**—**11**. The effect of central metal ion was also examined for complexes with a nitrogen



4 X=O, Y=Ph
5 X=S, Y=Ph
6 X=S, Y=CH_3



7 X=O
8 X=N



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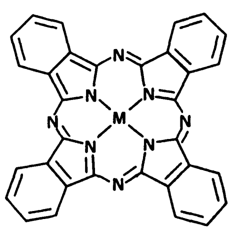

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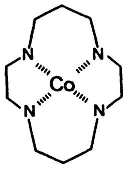

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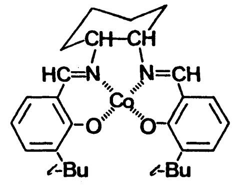

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Table 1. The Effect of Catalyst on the Oxygenation of Styrene[a)]

Catalyst	Conversion/%	Product yield/%[b)]			
		1	**2**	**3**	$PhCOCH_3$
$Co(DMG)_2$[c)]	92	80	7	9	—
4	100	80	7	10	—
5	98	41	16	18	—
6	93	53	18	19	—
7	50	30	9	4	—
8	69	56	6	25	—
9 (M=Co)	100	83	9	1	—
10 (M=Co)	96	86	0	0	—
11	79	3	33	29	—
9 (M=FeCl)	100	91	3	1	1
10 (M=Fe)	100	97	0	0	0
$Fe(DMG)_2$	27	75	0	Trace	—
9 (M=MnOAc)	100	42	0	0	51
12[d)]	100	57	16	—	7

a) Reaction conditions: styrene/catalyst=10, in 50% 1,2-dimethoxyethane/isopropyl alcohol at room temperature, 25 h. b) Yields were calculated on the basis of the amounts of consumed substrate. c) DMG: monoanion of 2,3-butanedione dioxime. d) At −60 °C; optical yield, 2%.

ligand such as DMG (Co and Fe complexes) or TPP (Co, Fe, and Mn complexes). The results are summarized in Table 1.

The effect of metal ion is characterized by the tendency that the activity for hydrogenation increases in the order of the periodic table, Mn(III)<Fe(III)<Co(II). In the case of TPP complex, nearly one tenth of the total products was converted to hydrogenation and hydrodimerization products, **2** and **3** by using Co(tpp), while the corresponding value by the use of Fe(tpp)Cl was less than 5%. For the catalysis by Mn(tpp)(OAc), no hydrogenation to **2** and **3** proceeded and the main product was acetophenone instead of **1**. Thus hydrogenation is not a favorable process by the use of Mn(tpp)(OAc) as the catalyst. The related tendency was observed in the catalysis by DMG complexes; the relative amount of hydrogenation product increased in the order, Fe<Co.

The effect of equatorial ligand also showed a distinct tendency. A cobalt complex of a chelating ligand bearing four coordination sites with two nitrogen and two oxygen atoms **4** gave quite similar results with the DMG complex. The change of carbon framework of the ligand has minor importance. The results show that the oxygen and nitrogen atoms have similar effect on the catalytic reaction. However, when two coordinating oxygen atoms of the ligand were substituted by sulfur atoms such as **5** and **6**, the yields of **2** and **3** increased significantly at the expense of oxygenation product **1**. Again, the change of organic substituents, Y, from phenyl to methyl group had little effect compared with the ligating atoms. Related result was obtained with the complex of saturated cyclic ligand **11**. In the reaction by the catalysis of this electron-rich complex, the formation of the oxygenation product **1** was almost inhibited. The results of Schiff base complexes **7** and **8** were not straightfoward. The low conversion and low yields of products as well as its distribution should be accounted for by the instability of the Schiff bases under the reaction conditions. In fact, almost quantitative amount of salicylaldehyde was found after the reaction by the catalysis of **7**. The effect of equatorial ligand are thus interpreted that the cobalt complex ligiated with an electron-releasing ligand promotes hydrogenation and hydrodimerization relative to oxygenation. Electron-releasing ligand increases the electron density of the central cobalt ion and stabilizes the alkyl-cobalt bond against homolytic dissociation to cobalt(II) and alkyl radical.[5] In this context the observed tendency supports the mechanism of a free radical combination process for the oxygenation step. As the catalyst of oxygenation, rigid cyclic tetraaza ligands such as porphyrin and phthalocyanine gave the best results with respect to both stability of the catalyst and the selectivity of the product alcohol. An attempt for the asymmmetric catalysis by using complex (1*R*,2*R*)-**12** at −60 °C resulted in only the isolation of **1** with optical yield of 2% (S) in 50% 1,2-dimethoxyethane-isopropyl alcohol. Intermediate formation of π-type free radical might be a possible explanation of the low optical yield.

Experimental

Complexes **4**—**11** were prepared according to the methods in literature.[6–10] Styrene was distilled before use. Other chemicals were commercial products and used as received. Experimental procedure of catalytic oxygenation was similar as the previous study. Reaction conditions were; Catalyst, 0.05 mmol; styrene, 0.5 mmol; tetraethylammonium tetrahydroborate, 1 mmol; in 5 ml of 50% 1,2-dimethoxyethane-isopropyl alcohol under atmospheric pressure of oxygen at room temperature. The yields of the reaction products were determined by Yanaco G2800 gas chromatography fitted with OV 101 packed column and calculated on the basis of the consumed amounts of the substrate.

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