portions of water, 10% sodium thiosulfate solution, saturated sodium bicarbonate solution, and saturated sodium chloride. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation to afford 1.11 g of a yellow oil. The oil was eluted through a silica column with dichloromethane, and the solvent was removed by rotary evaporation. Recrystallization from hot methanol afforded 480 mg (55%) of iodide **17**-*2-d* as colorless needles: mp 47–48 °C; 0% d_0, 100% d_1.

B. Irradiation. A 10-mL ethereal solution containing 130 mg (0.500 mmol) of iodide **17**-*2-d* and 50 mg (0.50 mmol) of triethylamine was irradiated at 254 nm as described above for 1.5 h. The principal product was isolated by preparative gas chromatography (column A) and its isotopic composition determined by mass spectroscopy: 100% d_1.

Irradiation of 1-(Iodomethyl)norbornane (22). A 10-mL solution of 236 mg (1.00 mmol) of iodide **22**[26] in methanol-*d* was irradiated at 254 nm as described above for 4.5 h. The products were isolated by preparative gas chromatography (column A) and characterized as described previously.[2] Their isotopic compositions were determined by mass spectroscopy (Scheme VII).

Quantum Yields. Solutions containing 1 mmol each of iodides **1** and **13** and 1-iodonorbornane (actinometer[2]) in 20 mL of methanol containing a hydrocarbon internal standard were placed in 11-mm i.d. (13-mm o.d.) × 140-mm quartz tubes and dearated for 15 min with nitrogen bubbling. The tubes were sealed, placed in a merry-go-round apparatus in a RPR-100 Rayonet photochemical reactor equipped with a circular array of 16 G8T5 lamps, and irradiated for 15 min. The progress of the photolyses was monitored by gas chromatographic analysis, and the quantum yields for the disappearance of iodide were calculated (Table VI).

Acknowledgment. Generous financial assistance by the National Science Foundation is gratefully acknowledged.

Registry No. **1**-*1,1*-d_2, 89232-08-6; **1**-*2,2*-d_2, 89232-09-7; **6**, 111-66-0; **6**-*1-d*, 72084-42-5; **6**-*2-d*, 72084-45-8; **6**-*1,1*-d_2, 54439-94-0; **6**-*1,2*-d_2, 89232-14-4; **10**, 106-32-1; **11**-*1,1*-d_2, 78510-02-8; **11**-*2,2*-d_2, 89232-16-6; **12**, 124-13-0; **12**-*2,2*-d_2, 89232-15-5; **13**, 626-62-0; **13**-*1-d*, 89232-10-0; **15**, 110-83-8; **15**-*1-d*, 42843-17-4; **16**, 931-56-6; **17**-*2-d*, 89232-13-3; **19**-*2-d*, 89232-17-7; **22**, 61192-16-3; **23**, 7697-14-5; **24**, 61192-23-2; **25**, 89232-12-2; **28**, 89232-11-1; CH_3OD, 1455-13-6; $(PhO)_3P$, 101-02-0; CH_3I, 74-88-4; cyclohexanol, 108-93-0; cyclohexanol-*1-d*, 21273-02-9; 2-adamantanone, 700-58-3; 2-adamantanol-*2-d*, 55834-71-4.

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Oxygenation of Olefins under Reductive Conditions. Cobalt-Catalyzed Selective Conversion of Aromatic Olefins to Benzylic Alcohols by Molecular Oxygen and Tetrahydroborate

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A high-yield catalytic conversion of aryl olefins **1** to benzylic alcohols **2** was developed by the use of molecular oxygen and BH_4^- in the presence of a catalytic amount of Co(TPP). Acid-labile alcohols were prepared in good yields. The reaction was regioselective to give benzylic alcohols exclusively and nonstereoselective. Comparison of the results of the catalytic oxygenation of styrene, the stoichiometric oxygenation of alkylcobalt complex **6**, and the decomposition of 1-phenylethyl hydroperoxide (**7**) in distribution of products and deuterium incorporation at room and low temperatures indicated the participation of **7** as the primary product, which is formed by the reaction of **6** with molecular oxygen. Co(TPP) catalyzed three elementary reactions in the overall catalytic process: formation of **7**, decomposition of **7** to **2** and aryl ketone **5**, and reduction of **5**.

Transition-metal-catalyzed reactions of molecular oxygen with organic compounds are important processes for the mimesis of various metal-containing oxidases and oxygenases.[1] Since an electron donor such as NADH or ascorbic acid is usually required for the reaction catalyzed by monooxygenases,[2] a catalyst composed of a reductant and a transition-metal complex attracted attention as the model system of NADH-dependent oxygenases. Tabushi[3] and Gaudemer[4] reported the reactions of hydrocarbons with molecular oxygen to give an alcohol, a ketone, or an epoxide by the catalysis of (tetraphenylporphyrinato)manganese(III) under the influence of a reducing agent such as tetrahydroborate or molecular hydrogen over colloidal platinum. However, the mechanisms of these model reactions are not elucidated at present and it is a question whether a true activation of molecular oxygen is involved during the reaction. We communicated previously the reaction of aryl olefins with molecular oxygen and BH_4^- (eq 1) to give low yields of benzyl alcohols in the presence of a catalytic amount of bis(dimethylglyoximato)chloro(pyridine)cobalt.[5] In this paper the

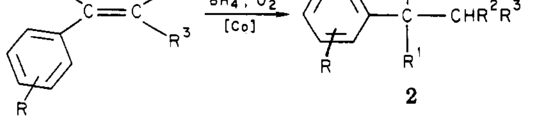

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Table I. Oxygenation of 1 with Co(TPP) and Et$_4$NBH$_4$[a]

	substrate (1, R^3 = H)			reaction time, day	yield of 2, %
	X	R^1	R^2		
a	H	H	H	2	87
b	*p*-chloro	H	H	2	92
c	*o*-methyl	H	H	3	98
d	*p*-methyl	H	H	3	94
e	*p*-methoxy	H	H	5	78
f	*p*-bromo	H	H	2.5	84
g	*m*-nitro	H	H	3	79
h	H	CH$_3$	H	2	94
i	H	H	CH$_3$	10	48[b]
j	H	H	CH$_2$OH	8	91
k		acenaphthylene		8	76
l		indene		0.8	14[b]
m	H	phenyl	H	0.8	30[b]
n	H	H	CH=CH$_2$	6	93[c]
o	H	H	CH$_2$CH=CH$_2$	5	45[d]
p	H	H	(CH$_2$)$_2$CH=CH$_2$	5	68[b]

[a] Yield was calculated on the basis of 1 used. [b] Reaction was not completed. [c] *trans*-1-Phenyl-1-buten-3-ol. [d] 1-Phenyl-4-penten-1-ol (34%) and 1-phenyl-1-penten-3-ol (11%).

mechanism of the apparent hydration reaction is discussed for more productive systems mainly consisting of (tetraphenylporphyrinato)cobalt and tetraalkylammonium tetrahydroborate.

The catalytic reaction showed the following characteristics: (1) The reaction was chemoselective, yielding substituted benzyl alcohols in good yields. (2) Addition of a hydrogen atom and a hydroxyl group was regioselective and nonstereoselective. (3) Free radical inhibitors such as hydroquinone had no influence. (4) 1-Phenyl-1,4-pentadiene or 1-phenyl-1,5-hexadiene did not give any cyclized products. On the basis of the experimental results a mechanism of the reaction is proposed which proceeds via the activation of organic substrates to give a benzylic cobalt intermediate followed by the reaction of the complex with molecular oxygen.[6]

Experimental Section

Materials. All reagents used were analytical grade unless otherwise mentioned. Substituted styrenes,[7] 1-phenyl-1,3-butadiene,[8] 1-phenyl-1,4-pentadiene,[9] 1-phenyl-1,5-hexadiene,[10] cyclam,[11] and cobalt complexes[12] were prepared by the methods in the literature. The method of Espenson was followed in the dark for the preparation of the (1-phenylethyl)peroxycobalt complex.[13]

A typical procedure of the reaction in a preparative scale follows: A mixture of olefin (1 mmol), (*meso*–tetraphenylporphyrinato)cobalt(II), (Co(TPP)), (9 × 10^{-3} mmol), and Et$_4$NBH$_4$ (0.5 mmol) was stirred under air in 5 mL of a 50% mixture of 1,2-dimethoxyethane (DME) and 2-propanol at room temperature. Stirring was continued with an occasional addition of BH$_4^-$ until all the substrate was consumed. When the reaction was completed, 15 mL of water was added to the reaction mixture and the precipitated catalyst was removed by filtration. The filtrate was extracted by ether, and the organic layer was dried over Na$_2$SO$_4$. The product alcohol was obtained in an almost pure form after evaporation of the solvent. Spectroscopic data of products are as follows. ***trans*-1-Phenyl-3-hydroxy-1-butene**: NMR 1.38 (d, 3 H, J = 6 Hz), 1.71 (br s, 1 H), 4.48 (pen, 1 H, J = 6 Hz), 6.24 and 6.54 (ABX, 2 H, J_{AB} = 16, J_{AX} = 6 Hz), 7.2–7.4 ppm (m, 5 H); MS (EI), m/e (relative intensity) 43 (100), 105 (89), 148 (51), 91 (48), 115 (41), 55 (40), 77 (40), 129 (36), 51 (34), and 133 (28). **1-Phenyl-5-hexen-1-ol**: NMR 1.23–1.89 (m, 4 H), 2.06 (q, J = 6.84 Hz, 2 H), 4.65 (t, J = 2.35 Hz, 1 H), 4.89 (m, 1 H), 5.02 (d, 1 H), 5.58–5.99 (m, 1 H), 7.31 ppm (s, 5 H); MS, m/e (relative intensity) 107 (100), 79 (74), 77 (37), 120 (23), 133 (23), 105 (14), 41 (14), 51 (12), 108 (9), 78 (9), M$^+$/e, 176 (2.3). **1-Phenyl-4-penten-1-ol**: NMR 1.82 (q, 2 H), 2.12 (q, 2 H), 4.65 (t, 1 H), 4.90–5.10 (m, 2 H), 5.60–6.30 (m, 1 H), 7.29 ppm (s, 5 H); MS (EI), m/e (relative intensity) 107 (100), 79 (85), 77 (52), 120 (32), 105 (22), 51 (19), 78 (12), 104 (12), 108 (9), 55 (8), 144 (5). ***trans*-1-Phenyl-1-penten-3-ol**: NMR 0.94 (t, 3 H), 1.59 (q, 2 H), 4.15 (q, 1 H), 6.00–6.60 (m, 2 H), 7.25 ppm (s, 5 H); MS (EI), m/e (relative intensity) 133 (100), 55 (80), 105 (58), 115 (52), 129 (51), 77 (45), 91 (43), 57 (34), 128 (33), 51 (27), M$^+$/e, 162 (26).

Experiments of deuterium incoporation were carried out in DME by the use of NaBD$_4$ as the reductant. The procedure for isolation of the product was the same as described above. Deuterium contents of products or recovered olefins were determined on a Hewlett-Packard 5992B GCMS spectrometer for the ether extract of the reaction product.[14]

Results

Scope, Limitation, and Regioselectivity. The results of oxygenation of aromatic olefins by the catalysis with Co(TPP) are listed in Table I. Alcohols were isolated in good to excellent yields with 100% selectivities of benzylic alcohols **2**. The other regioisomer of 2-arylethanol was not found in the reaction products. Nitro, methoxy, bromo, and chloro substituents on the aromatic ring were unaffected under the reaction conditions, but cyanide and ester groups were converted to carboxylic acid and some unidentified products. Reaction of 1-phenylpropene was slow compared with those of terminal olefins, and *cis*- and *trans*-stilbenes were unreactive. Electron-releasing substituents on the aromatic ring retarded the reaction as is exemplified by the result that the reaction of *p*-methoxystyrene took 5 days for completion in contrast to 2 days for reaction of *p*-chlorostyrene under the given reaction conditions.

1-Phenyl-1,5-hexadiene gave 1-phenyl-5-hexen-1-ol in a yield of 68% in 5 days. A 13% yield of unreacted substrate was recovered after that period, but no cyclization product such as (2-phenylcyclopentyl)methanol was detectable. Similarly 1-phenyl-1,4-pentadiene gave 1-phenyl-4-penten-1-ol in a yield of 34% accompanied by

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(14) Because relative abundance of peaks was dependent on the absolute abundance of samples analyzed on MS, similar amounts of samples were used for analyses.

Table II. Effect of Catalysts in the Oxygenation of Styrenes

catalyst	substrate	condn[b]	time, h	conv, %	yield,[a] % 2	3	4
$CoCl\cdot 6H_2O$	1h	A	16	28	3	23	
Co(salen)	1h	A	16	54	54	1	
$Co(DH)_2(H_2O)_2$[c]	1h	A	16	31	42	8	
$Co(DH)_2(H_2O)_2$[d]	1h	A	16	24	0	30	
$Co(DH)_2(py)Cl$	1h	B	20	46	86		
$Co(DH)_2(py)Cl$	1a	B	20	72	80	9	7
$Co(cyclam)Cl_2$[e]	1a	B	15	79	3	29	33
$Co(cyclam)(py)Cl_2$	1a	B	168	61	14	32	40
Co(TPP)	1a	B	25	100	83	1	9
$Pd(OAc)_2$	1a	B	18	94	1	96	trace
$Rh(DH)_2(py)Cl$	1a	B	20	100	1	62	0
Fe(phthalocyanin)	1a	B	25	100	97	0	0

[a] Calculated on the basis of consumed **1**. [b] A: catalyst, 0.37 mmol; **1**, 3.8 mmol; $NaBH_4$, 1.3 mmol. B: catalyst, 0.09 mmol; **1**, 0.87 mmol; $NaBH_4$, 1.3 mmol. [c] DH = monoanion of dimethylglyoxime. [d] Under nitrogen. [e] cyclam = 1,4,8,11-tetraazacyclotetradecane.

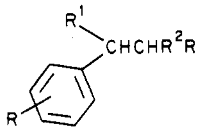
Table III. Deuterium Distribution in the Products of Oxygenation of Styrene

			deuterium distribution, %									
			2a, *d* =				**5a**, *d* =			**1a**, *d* =		
reactn[a]	conv, %	temp, °C	0	1	2	3	0	1	2	0	1	2
A	83	rt[b]	12	43	42	4				65	32	3
A	24	rt	9	52	38	2				100	0	
A	20	−50	18	70	12	0	33	64	3	94	6	
B	74	rt	33	38	23	6						
B	60	−40	85	15	1		99	1				

[a] A: reaction of styrene catalyzed by Co(TPP). B: reaction of $PhCH(CH_3)Co(DH)_2(py)$ with oxygen in the presence of $NaBD_4$. [b] rt = room temperature.

a 11% yield of 1-phenyl-1-penten-3-ol. 1-Phenyl-1,3-butadiene afforded *trans*-1-phenyl-3-hydroxy-1-butene as the sole product in a yield of 93%.

In addition to **2**, arylethanes **3** and 2,3-diarylbutanes **4** were identified as byproducts at room temperature when a high concentration of catalyst was used. The selectivity of the reaction was dependent on the catalyst used as shown in Table II. Cobalt complexes of Schiff bases and dimethylglyoximato ligands were also effective for the oxygenation. In the presence of cobalt(II) chloride as catalyst, however, hydrogenation of olefin was dominant and oxygenation did not take place significantly. FeCl(TPP) or Mn(OAc)(TPP) catalyzed the reaction, but the selectivity of alcohol was low. (Phthalocyaninato)iron(II) was also a good catalyst for the oxygenation. In the catalytic reactions reported here, Co(TPP) was recovered quantitatively after the reaction without any change in NMR and IR spectra, but Co(salen) decomposed to give a substantial amount of salicylaldehyde.



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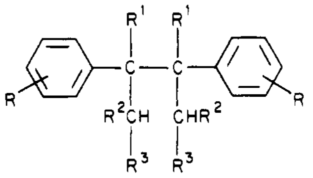

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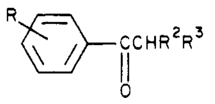

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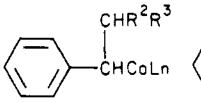

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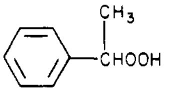

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Although **2** was the sole product of the reaction catalyzed by a low concentration of cobalt complex at room temperature, ketone **5** was found to be the main product when the reaction was carried out at low temperature. A 16% yield of acetophenone was formed in the reaction of styrene together with a 5% yield of 1-phenylethanol in 46 h at −50 °C.

Aliphatic olefins also gave the corresponding alcohols, but a high concentration of olefin was required for a good turnover of the catalyst. Furthermore, the regioselectivity of addition was low. Thus, 1-hexene without solvent yielded 1-hexanol (45%) and 2-hexanol (55%) with a total catalyst turnover of 32 in 12 h.

Deuterium Incorporation and Stereochemistry. When $NaBD_4$ was used in the catalytic reaction, mainly monodeuterated products together with considerable amounts of nondeuterated products were found at −40 °C. Further complex deuteration of the primary products took place at room temperature as shown in Table III. Deuterium was found also in recovered styrene when the conversion was high.

In the presence of BD_4^- and O_2, bis(dimethylglyoximato)(1-phenylethyl)(pyridine)cobalt (**6a**) gave **2a** at room temperature and **2a** and **5a** with the ratio of 17:83 at −40 °C. Deuterium was incorporated in the products slightly at low temperature, but complex deuterium incoporation similar to that for the product of catalytic reaction was observed in the reaction at room temperature.

Oxygenation of acenaphthylene (0.4 mmol) with $NaBD_4$ (0.8 mmol) and Co(TPP) (0.02 mmol) at −40 °C gave acenaphthylenol (**2k**) in a yield of 35% in 45 h. The NMR spectrum of isolated **2k** showed that deuterium was introduced on the vicinal carbon of the hydroxyl group with a similar abundance of cis and trans hydrogen as shown in Figure 1, indicating a nonstereoselective 1,2-addition.

Discussion

Although acid-catalyzed hydration of olefins is a conventional method for the preparation of alcohol via the Markovnikov-type addition reaction, a strong acid is necessary for the reaction and the yield of alcohol is as

Table IV. Product Distribution

substrate	condn[a]	cat.[b]	temp, °C	time, h	conv, %	selectivity, %	
						2a	5a
1a	A	Co	rt[d]	6	95	94	3
1a	A	Co[c]	rt	21	80	91	5
1a	A	Co	−50	46	20	23	77
1a	A	Mn	rt	6	18	54	42
6	B		rt	5	74	89	11
6	B		−40	17	60	17	83
7	C	Co	rt	1.4	100	94	4
7	C	Co	−50	26		32	69
7	C	Mn	rt	2	99	28	67

[a] A: catalyst, 0.02 mmol; Et_4NBH_4, 0.50 mmol; 1a, 0.50 mmol. B: 6a (Ln = $(DH)_2(py)$), 0.50 mmol; $NaBD_4$, 1.20 mmol. C: 7, 0.50 mmol; catalyst, 0.01 mmol; Et_4NBH_4, 0.50 mmol. [b] Co: Co(TPP); Mn: Mn(OAc)(TPP). [c] $Co(DH)_2(py)Cl$, 0.124 mmol. [d] rt = room temperature.

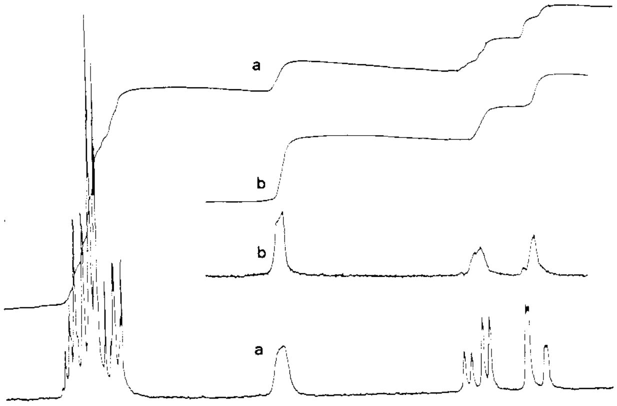

Figure 1. ^1H NMR spectra of acenaphthylenol in $CDCl_3$: (a) nondeuterated; (b) product from the catalytic reaction of acenaphthylene with O_2 and $NaBD_4$ in the presence of Co(TPP) in methanol-d_4.

much as 50%.[15] In contrast, the oxygenation presented here proceeded under basic or slightly basic reaction conditions with the production of high yields of alcohols even for acid-unstable products such as acenaphthylenol or 1-phenyl-1,3-propanediol. Thus it offers a new method of selective synthesis for substituted benzyl alcohols. In spite of the utility, the present redox system which is comprised of cobalt complex, tetrahydroborate, olefin, and molecular oxygen is a complicated system having many possibilities of elementary reactions.[16] Hence, it is not easy to predict a priori which of the two reactants, oxygen or olefin, is activated for the reaction by the catalyst.

However, formation of alcohol and ketone as the catalytic products at low temperature presented a clue to the reaction mechanism. Since these products are often formed in the decomposition of hydroperoxide,[17] its participation can be suggested as the intermediate of the catalytic reaction.[18] In fact, hydroperoxide 7 decomposed quickly in the coexistence of BH_4^- and cobalt catalyst, although 7 itself was fairly stable in the absence of either BH_4^- or Co(TPP).[19] In the presence of BH_4^- and Co(TPP), 7 decomposed quickly to give **2a** at room temperature and 32% of **2a** and 69% of **5a** at −50 °C. The distribution of products in the decompositon of 7 resembled closely that in the catalytic reaction both at low and room temperatures (Table IV). In addition to the similarity of the product distributions, the distribution of the products at low temperature curiously coincides with the reported values of deuterium incorporation in 1-arylethanol produced by the reaction of substituted (1-arylethyl)peroxycobaloxime with $NaBD_4$ in methanol.[20] Although the result suggests a facile reduction of the ketone with BH_4^- or BD_4^-, **5a** was unchanged in the presence of BH_4^- in DME and 2-propanol at room temperature, suggesting that cobalt complexes may catalyze not only the decomposition of hydroperoxide but also the reduction of **5a** with tetrahydroborate, which was confirmed separately.[21] A control reaction at −50 °C revealed that only 6% of **5a** was reduced to **2a** in 17 h under the catalytic reaction conditions. No exchange of hydrogen was found in the recovered ketone. However, with increasing temperature, methyl protons of acetophenone quickly exchanged with the solvent proton. At room temperature in 2-propanol-d_8, the NMR signal of acetyl protons (ca. 4 M) of **5a** completely disappeared in 5 min in the presence of a catalytic amount of Et_4NBH_4. Thus under the catalytic reaction conditions of deuteration at room temperature, initially formed **5a** exchanges the acetyl protons with deuterium in the solvent and BD_4^- and then it is reduced by $NaBD_4$–cobalt complex to give complicatedly deuterated 1-phenylethanol. 1-Phenylethanol itself was confirmed to be unchanged under the reaction conditions.

The comparable results given in Tables III and IV of the patterns of deuterium incorporation and the distributions of products between the catalytic reaction of styrene, the reaction of (1-phenylethyl)cobaloxime with oxygen, and cobalt-catalyzed decomposition of 1-phenylethyl hydroperoxide at both low and room temperatures indicate that these reactions proceed by similar mechanisms, that is, by the intermediacy of a hydroperoxide, which decomposes to a mixture of ketone (ca. 80%) and alcohol (ca. 20%) (eq 2–5). Although the formation of an alkylcobalt complex in the catalytic oxygenation is not unequivocal, the result of deuterium incorporation in recovered styrene supports the presence of an equilibrium of eq 2 in the light of the report by Halpern and others.[22] Presence of Co(I) under the reaction conditions was confirmed by the addition of methyl iodide to the system. Methyl iodide

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[18] Stirring a solution of bis(dimethylglyoximato)(1-phenylethyl)peroxy(pyridine)cobalt(III) in 50% DME/2-propanol overnight gave 0.2% of **2a**, 0.5% of **5a**, and 99.2% of recovered substrate. This result eliminates the possibility of unimolecular decomposition of the alkylperoxy complex to give the products.

[19] More than 90% of 7 remained intact after 17 h in the presence of a catalytic amount of Co(TPP), and 70% of 7 remained under the reaction conditions of column 7 in Table IV if metal complex was absent.

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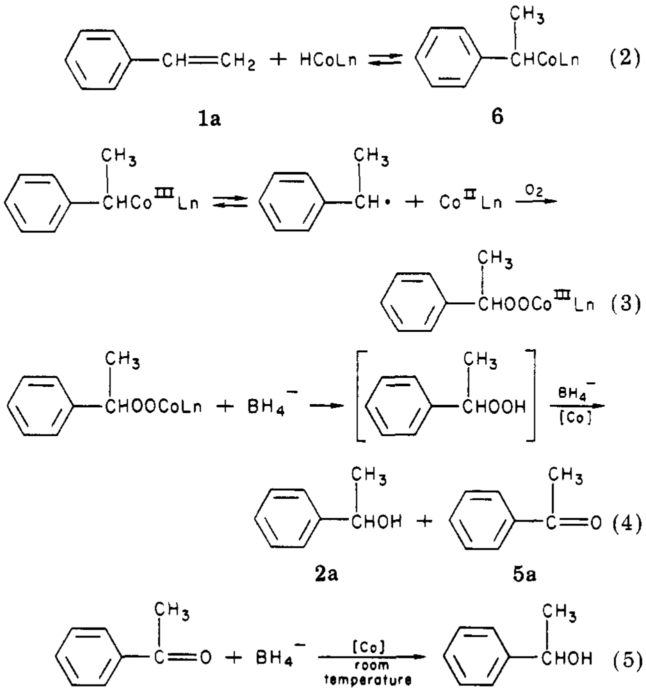
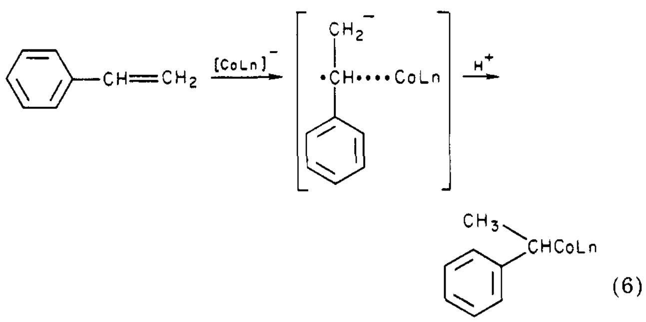


competes with olefin for Co(I) at the early stage of the reaction, thus decreasing the rate of oxygenation and subsequently inhibiting the reaction because Co(I) is trapped as the methylcobalt(III) complex (Figure 2).[23]

The observed regioselectivity of reaction was in accordance with those of addition of Co(I) to substituted olefins,[24] which apparently is not determined by the thermodynamic stability of the resulting carbon–cobalt bond.[22] Electron transfer from Co(I) to olefin followed by the coupling of generated Co(II) and organic anion radical in the solvent cage (eq 6) can be a mechanism to satisfy the result of regioselectivity. The lack of stereoselectivity observed for acenaphthylene can also be explained by the mechanism if the rotation of carbon–carbon bond is allowed in the radical ion pair as was observed in organic anion radicals.[25] Electron transfer from Co(I) finds precedent in the reaction with organic halides.[26]



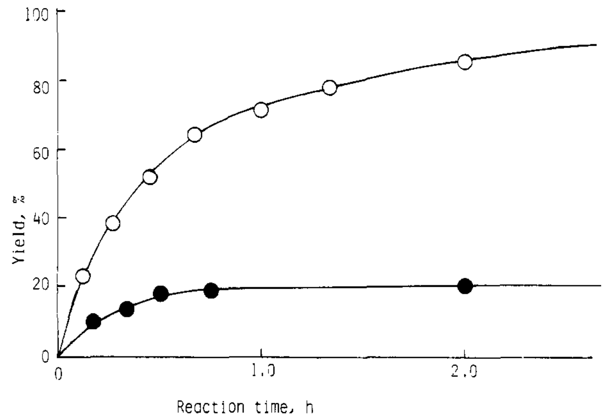


Figure 2. Time-dependent yield of the oxygenation of styrene: (○) without MeI; (●) in the presence of MeI. Reaction conditions; Co(TPP), 0.03 mmol; Et_4NBH_4, 1.03 mmol; styrene, 0.87 mmol; in 5 mL of 50% DME/2-propanol. [MeI]/[St] = 4.6.

Cyclization of the 5-hexenyl radical was used as mechanistic evidence for a free radical intermediate in the photoinduced oxygenation of alkylcobaloximes.[27] 1-Phenyl-5-hexenyl- or 1-phenyl-4-pentenylcobaloxime, which will be formed by the reaction of HCoLn or its conjugate base with 1-phenyl-1,5-hexadiene or 1-phenyl-1,4-pentadiene,[24] would generate the corresponding benzylic radicals by homolytic dissociation.[28] The reactions of stable benzyl radicals with molecular oxygen are shown to be slightly slow compared with that of nonconjugated alkyl radicals.[29] Since 1-phenyl-5-hexenyl radicals cyclize to (2-phenylcyclopentyl)methyl and 3-phenylcyclohexyl radicals,[30] cyclization product may be expected if the oxygenation proceeds via an alkyl free-radical intermediate. However, there was no indication of cyclization product in the oxygenation of these dienes. This result recalls the absence of a cyclized product in the alkyl transfer reaction of hexenylcobalt(III) with cobalt(II) reported by Dodd and others.[31] The experimental results can be interpreted as follows: (1) Oxygenation proceeds via the S_H2 substitution[32] of **6** by molecular oxygen without formation of a benzylic radical or (2) the free-radical intermediate is involved, but the rate of intramolecular cyclization is slow compared with the rate of the reaction with oxygen. The latter situation holds even in the photochemical oxygenation of 5-hexenylcobaloxime if the supply of oxygen is sufficient.[27] Judging from the slow rate of catalytic oxygenation, it seems likely that the rate of the reaction of generated free radical with oxygen is faster than the rate of cyclization.

Thus, the present reaction proceeds primarily by the activation of hydrocarbons. The low bond energy of cobalt–carbon bond of the benzyl–cobalt complex[22] seems to be the key point of the successful thermal catalytic reaction. In fact, (2-phenylethyl)cobaloxime was unreactive under the present reaction conditions. Abstraction of a hydrogen atom from the substrate with oxygen radicals generated by the reaction of dioxygen with reduced metal species[33] did not contribute to the oxygenation except for 1-phenyl-1,4-pentadiene, which has a highly activated allylic hydrogen. Thus, the contribution of activation of dioxygen by transition-metal complexes is, even if it might

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take place, not important in this catalytic reaction. At this stage, it would be worthwhile to refer to the similar cobalt-catalyzed reaction of nitric oxide and BH_4^- with styrene to give actophenone oxime.[34] Nitric oxide also has the characteristics of a free radical, and, in spite of the fact that it is a good ligand in transition-metal chemistry, no catalytic reaction of nitric oxide via migratory insertion process was ever known.[35] These results support the activation of hydrocarbons instead of a small molecule such as molecular oxygen or nitric oxide. Since the activation of oxygen is not important in the present catalytic oxygenation, the model reactions of cytochrome P-450 by the catalysis of Mn(TPP)X[3,4] needs further examination as to whether or not the activation of molecular oxygen is really involved during the course of reaction. Although Mn(OAc)(TPP) gave epoxide and alcohol from olefin and saturated hydrocarbons, respectively, the epoxidation of alkene and hydroxylation of alkane could be a reaction of alkenes or alkanes with generated hydroperoxide by the catalysis of Mn(OAc)(TPP).[36] Porphyrin complexes such as Mn(OAc)(TPP) or Fe(TPP)Cl likewise catalyzed the decomposition of 7 in the presence of BH_4^-, but contrary to Co(TPP), Mn(OAc)(TPP) did not show a catalytic effect for the reduction of acetophenone, which suggests a unique character of Mn(TPP)X.

It is noteworthy at this point that in the overall catalytic oxygenation, cobalt complex catalyzes at least three elementary reactions, that is, generation of an alkyl cobalt complex which subsequently reacts with dioxygen, decomposition of hydroperoxide or its derivative, and hydrogenation of ketone. It exemplifies the multifunctional behavior of transition-metal species in the redox reaction.

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Phase-Transfer-Catalyzed Gomberg-Bachmann Synthesis of Unsymmetrical Biarenes: A Survey of Catalysts and Substrates

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Two problems have hindered the Gomberg-Bachmann (GB) and Pschorr reactions of arenediazonium cations: the instability of the arenediazonium salts and side reactions. Arenediazonium tetrafluoroborate and hexafluorophosphate salts can be prepared in high yield and purity and can be stored safely. Unfortunately, these salts are insoluble in most nonpolar organic solvents. Crown ether complexation or other phase-transfer (pt) catalytic methodology can ameliorate this situation, and reactions conducted by the approaches outlined herein often afforded coupling or cyclization products in high yield and corresponding purity. The use of crown ethers, quaternary 'onium salts, lipophilic carboxylic acid salts, and even the polar cosolvent acetonitrile increase the utility of the ptGB reaction dramatically. Sixty examples of couplings are reported along with an assessment of selectivities. A number of examples are also presented of phase-transfer-type Pschorr cyclizations. In the latter case, the use of potassium superoxide, KO_2, is introduced to suppress indazole formation.

The so-called Gomberg-Bachmann reaction can be traced to the report of Mohlau and Berger in 1893[1] that anhydrous benzenediazonium chloride reacts with pyridine to afford 18% 2-phenylpyridine along with a smaller amount of the 4-isomer. The reaction is generally dated, however, from 1924 when Gomberg and Bachmann showed that anhydrous arenediazonium compounds were not required and that "diazonium salts in aqueous solution, under certain conditions, can couple with hydrocarbons and many diverse derivatives therefrom...".[2] The advantage of the Gomberg-Bachmann (GB) approach (eq 1) is

$$ArN_2^+ + HO^- \xrightarrow{Ar'H/H_2O} ArAr' \qquad (1)$$

that the "powerfully explosive"[2] dry diazonium salts did not have to be utilized, rather the salt could be formed in a normal diazotization reaction and then used directly in situ.

The advent of the phase-transfer method and the observation that macrocyclic (crown) polyethers can solubilize stable, solid arenediazonium tetrafluoroborates[3] have brought the method full circle by allowing one to avoid some of the complicating side reactions associated with the standard GB reaction. We have previously reported that considerably improved yields can be realized in this reaction by application of the phase-transfer technique.[4] We now report experimental details of these reactions and a survey that outlines the scope and utility of this modification.

Results and Discussion

Advantages of the Phase-Transfer Method. The phase-transfer Gomberg-Bachmann (ptGB) modification allows safe, stable arenediazonium tetrafluoroborates to be used in aromatic hydrocarbon solvents in the absence of water, thus avoiding some of the side reactions that have historically complicated this reaction. The ptGB reaction is conducted at room temperature by stirring the ArN_2^+-BF_4^- or -PF_6^- salt in an aromatic hydrocarbon solvent with solid KOAc and a phase-transfer catalyst for 1-2 h. Our early work involved only crown ethers as catalysts, but

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