cm^{-1}; exact mass ($M^+ - 18$) calcd 604.5797, found 604.5786. Anal. Calcd for $C_{40}H_{78}O_4$: C, 77.11; H, 12.62. Found: C, 76.84; H, 12.72.

Dihydro-3,3,4,4-tetraoctadecyl-2,5-furandione (30). To a solution of diisopropylamine (0.57 mL, 4.1 mmol) in 25 mL THF at -25 °C was added *n*-butyllithium (2.56 mL, 1.6 M, 4.1 mmol). The mixture was stirred below -20 °C for 5 min and then at room temperature 25 min and then cooled to 0 °C. 2-Octadecyleicosanoic acid (1.13 g, 2.0 mmol) in 12 mL of THF was added over 3 min, and the resulting pale yellow heterogeneous solution was stirred at 0 °C for 30 min and at room temperature for 30 min. After being stirred at 50 °C for 3 h, the clear yellow dianion solution was cooled to room temperature over 30 min and then to 0 °C. I_2 (0.254 g, 1.0 mmol) in 9 mL of THF was added over 1.5 min, resulting in a clear pale yellow solution. The mixture was allowed to stir for 18 h while being warmed to room temperature. The solvents were then evaporated, and the residue was acidified with 50 mL of 1:1 4 N HCl/brine. The aqueous solution was extracted 3× with 75 mL of 2:1 $Et_2O/CHCl_3$, and the combined organic layers were washed 1× with brine. After drying over $MgSO_4$ and filtering, the solvents were evaporated, leaving a waxy yellow solid. This was purified by flash chromatography (12 g of silica gel; 3:1 ligroin/$CHCl_3$ to remove starting materials, followed by EtOAc to remove diacid). Starting material (0.552 g) was recovered, as well as 0.330 g (29.3%) of diacid. A second chromatography (15 g of silica gel, 3:1 ligroin, then $CHCl_3$) performed on the semipure diacid afforded 0.112 g of anhydride. The waxy anhydride was unsuitable for recrystallization. However, material isolated by chromatography gave a satisfactory combustion analysis: mp 53-54 °C; ^1H NMR ($CDCl_3$) δ 1.653 (t, J = 6.6 Hz, 8 H), 1.257 (br s, 128 H), 0.880 (t, J = 6.6 Hz, 12 H); ^{13}C NMR ($CDCl_3$) δ 175.560 (s), 54.746 (s), 31.969 (t), 30.157 (t), 29.696 (t), 29.362 (t), 24.438 (t), 22.720 (t), 14.101 (q); IR (CCl_4) 2920 (s), 2860 (s), 1780 (s), 1460 (m), 940 (m) cm^{-1}. Anal. Calcd for $C_{76}H_{148}O_3$: C, 82.24; H, 13.44. Found: C, 82.52; H, 13.17.

Acknowledgment. We gratefully acknowledge the financial support of the National Institutes of Health. This investigation was supported by PHS grant 1 R01 CA40105-01 awarded by the National Cancer Institute, DHHS. Preliminary research on this project was funded by grants from the Lalor Foundation, The American Cancer Society, and the Research Corporation. The 300-MHz NMR spectrometer used in this study was purchased with the aid of an NSF instrumentation grant (CHE-8102974). The Kratos mass spectrometer used in this study was purchased with the aid of an NSF instrumentation grant (PCM-8219912).

Catalytic Reactions of Metalloporphyrins. 3.[1] Catalytic Modification of Hydroboration–Oxidation of Olefin with Rhodium(III) Porphyrin as Catalyst[2]

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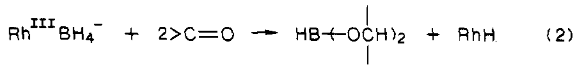
Received November 24, 1986

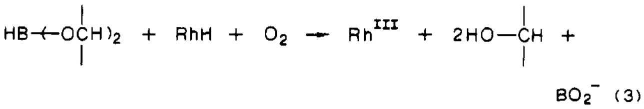
(Octaethylporphyrinato)- or (tetraphenylporphyrinato)rhodium(III) chloride catalyzes the anti-Markovnikov "hydration" of olefin with $NaBH_4$ and O_2 in THF. 1,5-Cyclooctadiene gives rise to cyclooctanol and 1,5-cyclooctanediol (in a ratio of approximately 1:2), and acetylenes are converted directly to alcohols under similar conditions. The initial step in the catalytic reaction of olefin is the hydride and borane transfers from BH_4^- respectively to Rh^{III} porphyrin and olefin to give hydridorhodium (RhH) porphyrin and alkylborane. The RhH species undergoes oxidation with O_2 back to Rh^{III} with concomitant oxidation of alkylborane with *retention of configuration*. This coupled oxidation of alkylborane is in competition with its nonstereospecific autoxidation without assistance of Rh–H. The present system provides a catalytic modification of hydroboration–oxidation of olefin in the presence of oxygen, as illustrated by the one-pot conversion of 1-methylcyclohexene to (*E*)-2-methylcyclohexanol with 100% regioselectivity and up to 97% stereoselectivity.

Our recent study indicates that the combination of $NaBH_4$, O_2, and rhodium(III) porphyrin as catalyst constitutes a highly efficient, catalytic modification of synthetic reactions of borane in the presence of oxygen.[3] The reduction of ketone with this catalytic system involves (1) the rate-determining complexation of BH_4^- with Rh^{III} porphyrin (eq 1, where and hereafter OEP ligand is omitted), (2) rapid borane transfer from the adduct to ketone to give dialkoxyborane and hydridorhodium species (eq 2), and (3) oxidation of hydridorhodium species with O_2 back to Rh^{III} with concomitant "hydrolysis" of dialkoxyborane to alcohol (eq 3).

$$Rh^{III} + BH_4^- \rightarrow Rh^{III}BH_4^- \qquad (1)$$



$$Rh^{III}BH_4^- + 2{>}C{=}O \rightarrow HB(OCH)_2 + RhH \qquad (2)$$



$$HB(OCH)_2 + RhH + O_2 \rightarrow Rh^{III} + 2HO{-}CH + BO_2^- \qquad (3)$$

The essential reaction of the ternary system of $NaBH_4$, O_2, and rhodium porphyrin can be regarded as borane generation with concomitant reduction of O_2 upon metal-controlled, two-electron aerial oxidation of BH_4^- (eq 4).

$$BH_4^- + O_2 \xrightarrow{\text{Rh porphyrin}} \text{"}BH_3\text{"} + \text{"}HO_2^-\text{"} \qquad (4)$$

In the present work we have taken up olefins and acety-

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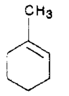
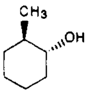
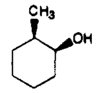
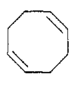
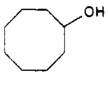
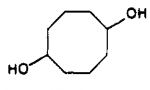
[1] Part 2 of this series: Aoyama, Y.; Tanaka, Y.; Yoshida, T.; Toi, H.; Ogoshi, H. *J. Organomet. Chem.*, in press.

[2] Preliminary accounts of this work: Aoyama, Y.; Watanabe, T.; Onda, H.; Ogoshi, H. *Tetrahedron Lett.* **1983**, *24*, 1183.

[3] Aoyama, Y.; Fujisawa, T.; Watanabe, T.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1986**, *108*, 943.

0022-3263/87/1952-2555$01.50/0

Table I. Product Distribution in the Oxygenation of Olefin, Diene, and Acetylene with $NaBH_4$, O_2, and (OEP)$Rh^{III}Cl$ in THF[a]

substrate	$[Rh^{III}]$ (mM)	product: major	product: minor	% yield[b]	ratio
	1.2			12 000	93:7
	12				97:3
$CH_3(CH_2)_2CH{=}CH_2$	0.6	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_2CH(OH)CH_3$	21 000	91:9
$PhCH{=}CH_2$	0.6	$Ph(CH_2)_2OH$	$PhCH(OH)CH_3$	5 800	61:39
	0.3			37 500	36:64
	0.3[c]			27 800[c]	32:68[c]
$CH_3(CH_2)_2C{\equiv}CCH_2CH_3$	0.3	$CH_3(CH_2)_3CH(OH)CH_2CH_3$	$CH_3(CH_2)_2CH(OH)(CH_2)_2CH_3$	16 300	53:47
$CH_3(CH_2)_4C{\equiv}CH$	0.3	$CH_3(CH_2)_6OH$	$CH_3(CH_2)_4CH(OH)CH_3$	4 800	82:18

[a] Reaction conditions: $NaBH_4$ (0.3 g, 7.9 mmol), substrate (1 g for olefin or 0.3 g for diene and acetylene) in THF (10 or 20 mL) exposed to dry air at 20–25 °C for 50 h. [b] Based on (OEP)$Rh^{III}Cl$. [c] With (TPP)$Rh^{III}Cl$.

lenes as substrates. One of the most important reactions involving borane is the conversion of olefin to anti-Markovnikov alcohol via hydroboration followed by alkaline hydrogen peroxide oxidation of the resulting alkylborane.[4] We report here the application and limitation therein of the present system to the catalytic modification of hydroboration–oxidation of olefin.

Results

Oxygenation of Cyclohexene. In the presence of a catalytic amount of (octaethylporphyrinato)rhodium(III) chloride, (OEP)$Rh^{III}Cl$, in THF, cyclohexene underwent facile oxygenation with $NaBH_4$ and O_2 to give cyclohexanol together with a trace amount of cyclohex-2-enol (ca. 1% of cyclohexanol). $NaBH_4$, O_2, and rhodium porphyrin were essential for the formation of cyclohexanol. The amount of the alcohol formed depended on that of $NaBH_4$ used. A typical run using olefin (1.0 g, 12 mmol), $NaBH_4$ (300 mg, 7.9 mmol), and rhodium complex (4.0 mg, 6.0 μmol) in dry THF (10 mL) exposed to dry air at 20–25 °C for 50 h afforded ca. 1.2 mmol of cyclohexanol after complete consumption of $NaBH_4$.[2] The yield of alcohol is 15% based on $NaBH_4$ (on mol basis) and 20 000% based on (OEP)$Rh^{III}Cl$, the turnover rate of the catalyst being 6–7 cycles/h at early stages of reaction. There was no indication of significant decomposition or deactivation of rhodium porphyrin catalyst during the reaction. Addition of $NaBH_4$ (7.9 mmol) to the reaction mixture after consumption of that initially added (1.3 mmol) started the reaction again with a reasonable rate (Figure 1). Cyclohexene oxide was not detected among products. Independent experiments also ruled out its intermediacy as a precursor of cyclohexanol. (Tetraphenylporphyrinato)rhodium(III) chloride, (TPP)$Rh^{III}Cl$, in THF exhibited a similar catalysis as (OEP)$Rh^{III}Cl$. When $NaBH(OCH_3)_3$ was used instead of $NaBH_4$, the rhodium porphyrin was readily reduced but showed no catalytic activity at all for the formation of cyclohexanol from cyclohexene.

Oxygenation of Unsymmetrical Olefins, Diene, and Acetylenes. The oxygenation of 1-methylcyclohexene took place in a similar manner as that of cyclohexene and afforded 2-methylcyclohexanol exclusively; the *E*/*Z* ratio was 93:7 for a run using 1.2 mM of (OEP)$Rh^{III}Cl$ but was enhanced up to 97:3 when the catalyst concentration was increased to 12 mM. A selective anti-Markovnikov addition was also observed for the "hydration" of 1-pentene by the present catalytic system, 1-pentanol and 2-pentanol being formed in a ratio of 91:9 (yield 21 000% based on the catalyst). The regioselectivity was much poorer, however, when the substrate was styrene. Allylic oxidation was negligible in all the cases examined. The product distributions are summarized in Table I. The oxygenation of 1,5-cyclooctadiene gave rise to a mixture of cyclooctanol and 1,5-cyclooctanediol in a ratio of approximately 1:2 as the major oxygenation products accounting for 90% of the substrate consumed. The present catalytic system was used also for the direct conversion of acetylenes, both internal and terminal, to alcohols. Under conditions of acetylene (300 mg, 3.1 mmol), $NaBH_4$ (300 mg, 7.9 mmol), and (OEP)$Rh^{III}Cl$ (4.0 mg, 6 μmol) in dry THF (20 mL) exposed to dry air, 3-heptyne was converted to a mixture

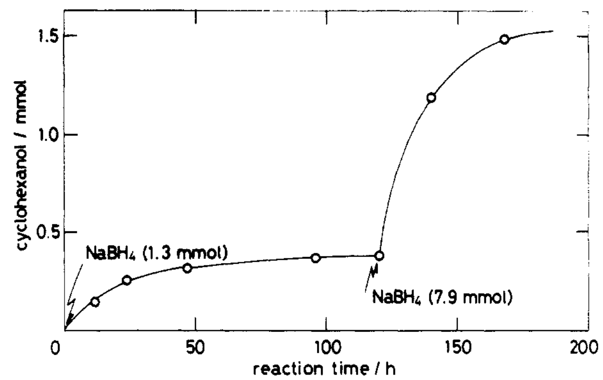


Figure 1. Time course of the oxygenation of cyclohexene (12 mmol) in THF (10 mL) exposed to air at 20–25 °C in the presence of (OEP)$Rh^{III}Cl$ (6 μmol), 1.3 mmol of $NaBH_4$ being used at time 0 and 7.9 mmol of that added 120 h later.

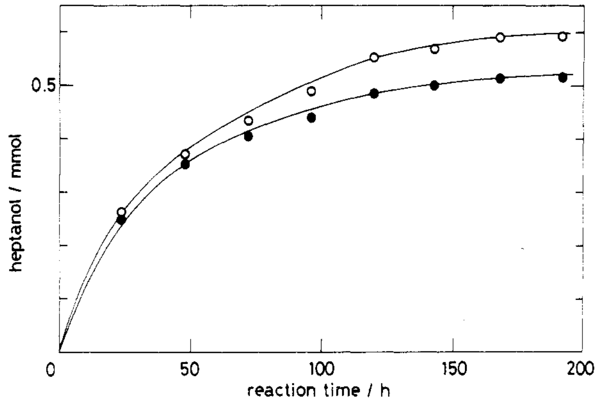


Figure 2. Time course of the formation of 3-heptanol (○) and 4-heptanol (●) from the oxygenation of 3-heptyne (3.1 mmol) in THF (20 mL) exposed to air at 20–25 °C in the presence of $NaBH_4$ (7.9 mmol) and (OEP)$Rh^{III}Cl$ (6 μmol).

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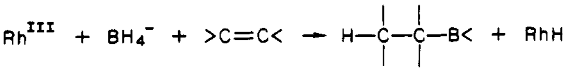
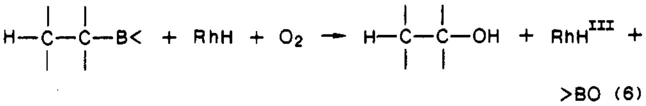
[4] (a) Cragg, G. M. L. *Organoboranes in Organic Synthesis*; Marcel Dekker: New York, 1973. (b) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975.

of 3-heptanol and 4-heptanol in approximately equal amounts in a total yield of 16300% based on rhodium catalyst. The time course of their formation is shown in Figure 2. A similar reaction of 1-heptyne gave the terminal anti-Markovnikov alcohol predominantly (Table I).

Formation and Oxidation of Alkylborane. Stoichiometric reactions of (OEP)Rh^{III}Cl, NaBH$_4$, and 1-pentene in THF in the absence of O$_2$ gave hydridorhodium species ((OEP)RhH) and tripentylborane as a result of concomitant hydride and borane transfers from BH$_4^-$ to (OEP)Rh^{III} and 1-pentene, respectively (eq 5). The alkylborane was identified by comparison with the authentic specimen prepared by the standard procedure for olefin hydroboration.[4] When exposed to air, the mixture of alkylborane and RhH thus obtained (eq 5) underwent facile oxidation to give a Rh^{III} complex and a mixture of 1-pentanol and 2-pentanol (94:6 in a total yield of 45% based on mol of Rh complex used) (eq 6). The oxidation of RhH

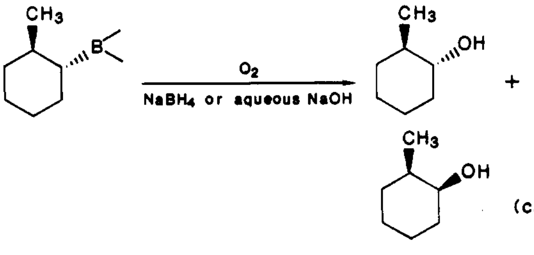


$$\mathrm{Rh^{III}} + \mathrm{BH_4^-} + \mathrm{{>}C{=}C{<}} \rightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}B{<}} + \mathrm{RhH} \qquad (5)$$

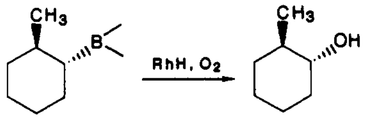


$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}B{<}} + \mathrm{RhH} + \mathrm{O_2} \rightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH} + \mathrm{RhH^{III}} + \mathrm{{>}BO} \qquad (6)$$

and that of alkylborane were found to be not independent but rather "coupled". This conclusion came from the examination of the stereochemistry of alcohol products. Air oxidation of (*E*)-bis(2-methylcyclohexyl)borane in THF in the presence of either NaBH$_4$ or aqueous NaOH gave rise to a mixture of (*E*)- and (*Z*)-2-methylcyclohexanol in a ratio of approximately 8:2 (eq 7). In the presence of an equivalent amount of (OEP)RhH, however, a stereospecific oxidation of the dialkylborane took place and gave *E* alcohol exclusively (eq 8).



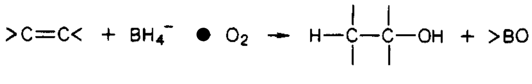
(ca. 8:2) (7)



(8)

Discussion

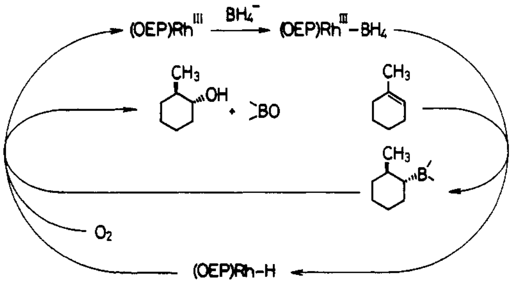
Two stoichiometric reactions (eq 5 and 6) have been demonstrated which, when combined, give the reaction scheme observed for the present oxygenative transformation of olefin (eq 9). The Rh^{III}-assisted hydroboration of



$$\mathrm{{>}C{=}C{<}} + \mathrm{BH_4^-} \bullet \mathrm{O_2} \rightarrow \mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH} + \mathrm{{>}BO} \qquad (9)$$

olefin with BH$_4^-$ leaving RhH (eq 5)[5] seems to constitute an essential process also in the catalytic reactions.[6] An analogous borane transfer to ketone has been discussed thoroughly.[3] Involvement of borane transfer is consistent with the regioselectivity of alcohol products arising from anti-Markovnikov addition (Table I), so characteristic of olefin hydroboration,[10] and is also consistent with the lack of any reactivity of NaBH(OCH$_3$)$_3$ in place of NaBH$_4$ in the present olefin oxygenation reaction.[14] A cytochrome P$_{450}$ model composed of NaBH$_4$, O$_2$, and manganese porphyrin has been shown to be effective in epoxidation of olefins,[16] while a similar system with cobalt complexes has been demonstrated to give organocobalt derivatives, which undergo oxidative C–Co bond cleavage by O$_2$ in a subsequent step.[17] An essential feature of these reactions lies in the reductive activation of oxidants (O$_2$ or central metal). The present reaction, on the contrary, involves oxidative activation of a reductant (BH$_4^-$ → H$^-$ + BH$_3$) (eq 5).

Scheme I



Alkylboranes readily undergo autoxidation with O$_2$ to give alcohols after workup.[18] This is a free radical chain

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(5) Brown and Narasimhan have recently shown that the BH$_4^-$ reduction of esters is catalyzed by olefins and suggested that the hydride transfer could be facilitated by a concurrent reaction of the leaving group, borane, with the catalyst as borane acceptors: Brown, H. C.; Narasimhan, S. *J. Org. Chem.* **1984**, *49*, 3891. This mechanism is essentially the same as that for the present reaction involving concurrent borane and hydride transfers (eq 5).

(6) The combination of NaBH$_4$ and metal salts or complexes has been used for the reduction of a variety of functional groups[7] and oxygenative transformations of olefins possibly via organoborane intermediates.[8,9] However, the mechanism of these reactions is not clear. A recent study on the mechanism of NaBH$_4$–CoCl$_2$ reduction indicates that cobalt boride (Co$_2$B), by coordinating to functional groups, catalyzes their heterogeneous reduction by NaBH$_4$.[6] An interesting possibility of surface-generated borane has been suggested.

(7) Heizman, S. W.; Ganem, B. *J. Am. Chem. Soc.* **1982**, *104*, 6801 and references cited therein.

(8) (a) Kano, S.; Tanaka, Y.; Hibino, S. *J. Chem. Soc., Chem. Commun.* **1980**, 414. (b) Lee, H. S.; Isagawa, K.; Otsuji, Y. *Chem. Lett.* **1984**, 363.

(9) Satyanarayana, N.; Periasamy, M. *Tetrahedron Lett.* **1984**, *25*, 2501.

(10) The isomer ratios of anti-Markovnikov to Markovnikov addition of borane to 1-methylcyclohexene[11] and simple 1-olefins such as 1-hexene[12] and styrene[13] have been reported to be ~100:0, 94:6, and 81:19, respectively.

(11) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 2544. (b) Brown, H. C.; Suzuki, A. *Ibid.* **1967**, *89*, 1933.

(12) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708.

(13) Brown, H. C.; Sharp, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5851.

(14) (OEP)Rh^{III}Cl is readily reduced with BH(OCH$_3$)$_3^-$ to (OEP)RhH (⇌[(OEP)Rh^{I}]$^-$ + H$^+$) but fails to catalyze the oxygenation of olefin. This is taken as evidence ruling out the possibility of direct addition of (OEP)RhH to an olefin followed by oxidation of the resulting alkylrhodium species with O$_2$ as the mechanism of the present oxygenation of olefin. In fact, an attempted reaction of (OEP)RhH[15] with a large excess of cyclohexane in THF gave only trace, if any, of alkylrhodium complex. Furthermore, the hexylrhodium complex in THF was found to be stable at least for a day under air atmosphere or in the presence of equimolar amount of BH$_3$ under N$_2$. These results indicate that even if alkylrhodium complex is formed in the present reaction, the oxidation thereof with O$_2$ or transfer of alkyl ligand therefrom to borane would be too slow to account for the observed turnover rate of 6–7 cycles/h at early stages of reaction. Involvement of alkylrhodium complex as a reactive intermediate can be ruled out on these grounds.

(15) (a) Ogoshi, H.; Setsune, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869. (b) Setsune, J.; Yoshida, Z.; Ogoshi, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 983.

(16) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456.

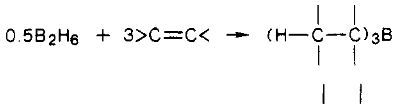
(17) (a) Okamoto, T.; Oka, S. *Tetrahedron Lett.* **1981**, *22*, 2191. (b) Okamoto, T.; Oka, S. *J. Chem. Soc., Chem. Commun.* **1984**, 289.

(18) (a) Davies, A. G.; Roberts, B. P. *J. Chem. Soc. B* **1969**, 311. (b) Brown, H. C.; Midland, M. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 1024.

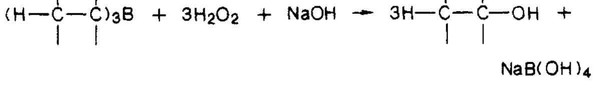
process.[19] Involvement of alkyl radicals as intermediates is responsible for the loss of stereospecificity (eq 7).[18] For synthetic purposes, alkylboranes are often oxidized with alkaline hydrogen peroxide with *retention of configuration.*[4] Interestingly enough, this is what was observed when (*E*)-bis(2-methylcyclohexyl)borane was allowed to be oxidized in the presence of (OEP)RhH (eq 8). The mechanism of coupled oxidation of Rh–H and B–C bonds is not clear at present, but it is likely that the initial oxidation product of (OEP)RhH, (OEP)RhOOH[20] attacks alkylboranes in a similar manner as does hydrogen peroxide anion. The actual E/Z ratio for the catalytic oxygenation of 1-methylcyclohexene is dependent on the catalyst concentration; E/Z = 93:7 and 97:3 for [Rh] = 1.2 and 12 mM, respectively (Table I). These results suggest that in the catalytic reaction the coupled oxidation of (*E*)-(2-methylcyclohexyl)borane intermediate[21] (leading to $E/Z = \sim 100{:}0$) is in competition with its simple autoxidation (leading to $E/Z = \sim 80{:}20$), and that the former process becomes the major reaction at higher catalyst concentrations. The suggested catalytic mechanism under these circumstances is shown in Scheme I. The intermediate, (OEP)$Rh^{III}BH_4$,[3] might be in equilibrium with (OEP)RhH + BH_3. Rather poor yields of alcohols based on $NaBH_4$ consumed (15% in the case of cyclohexane oxygenation) suggest that the borane-transfer step from either (OEP)-$Rh^{III}BH_4$ or -BH_3 itself to olefin is in competition with its oxidative degradation. This is in a marked contrast to the rapid and highly efficient borane transfer from (OEP)-$Rh^{III}BH_4$ to ketone.[3] The notable difference in the reactivities of ketone and olefin as borane acceptors indicates that (OEP)$Rh^{III}BH_4$ is better formulated as BH_4^- complex of (OEP)Rh^{III} rather than BH_3 complex of (OEP)RhH.[3] The electronic structure of the $Rh^{III}BH_4$ moiety, and its borane-transferring activity may be controlled by the inplane electronic effects of porphyrin ligands. Further work is now under way along this line.

The formation of anti-Markovnikov alcohols via hydroboration of olefins followed by oxidation is an important synthetic method.[4] The standard procedure involves three independent, stoichiometric reactions: borane generation from BH_4^- using a Lewis acid (eq 10), borane transfer to olefin (eq 11) and alkaline hydrogen peroxide oxidation of the resulting alkylborane (eq 12); each reaction should be carried out under inert atmosphere. The present system provides a catalytic modification of hydroboration–oxidation of olefin in the presence of O_2. The essential reaction is the rhodium–porphyrin-catalyzed two-electron oxidation of BH_4^- with O_2 (eq 4), where autorecycling (OEP)Rh^{III} and (OEP)RhH act as generators of "BH_3" and "HO_2^-", respectively (Scheme I). The characteristic catalysis observed for the present rhodium porphyrin seems to arise from its strong tendency to undergo two-electron or equivalent hydride-transfer redox reactions with the formal oxidation-state change of $Rh^{III} \rightleftharpoons Rh^{I}$. Metal-catalyzed autoxidation of olefin, on the other hand, is a common process leading mainly to allylic oxidation products.[22] This reaction involves metal-induced one-electron reduction of O_2 as an essential step. It is significant to note that allylic oxidation takes place only to a negligibly small extent in the present rhodium-catalyzed reactions.

$$3NaBH_4 + 4BF_3{\cdot}OEt_2 \rightarrow 2B_2H_6 + 3NaBF_4 + 4Et_2O \qquad (10)$$



$$0.5B_2H_6 + 3{>}C{=}C{<} \rightarrow (H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_3B \qquad (11)$$



$$(H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_3B + 3H_2O_2 + NaOH \rightarrow 3H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH + NaB(OH)_4 \qquad (12)$$

The formation of characteristic diol from 1,5-cyclooctadiene indicates that it undergoes hydroboration to give 9-borabicyclo[3.3.1]nonane (9-BBN),[23] which is subsequently oxidized either to 1,5-diol or to cyclooctanol via cyclooctanone;[24] the present system is known to be very efficient for the reduction of ketone.[3] The mechanism for acetylene to alcohol conversion can also readily be suggested: hydroboration to give vinylborane, oxidation to vinyl alcohol[26] and hence carbonyl compound after keto–enol tautomerism, and reduction (eq 13).

Conclusion

The ternary system composed of Rh^{III} porphyrin, $NaBH_4$, and O_2 with olefin as substrate provides a catalytic modification of the oxygenative transformation of olefin via hydroboration followed by oxidation, although the catalytic efficiency based on the reductant is not very high. The essential role of Rh porphyrin is that of a two-electron or equivalent hydride-transfer catalyst, preventing one-electron processes from taking place. The present reaction thus presents a new catalytic method for selective transformations of olefin, as demonstrated by the highly regioselective (~100%) and stereoselective (up to 97%), one-pot transformation of 1-methylcyclohexene to (*E*)-2-methylcyclohexanol. A problem is that oxidative degradation directly with O_2 of "borane" generated and alkylborane intermediate accompanies the catalytic pathway shown in Scheme I to lower the efficiency and selectivity of the catalytic processes. Suitable modification of the present rhodium porphyrin catalyst could minimize the contribution of these undesired side reactions.

Experimental Section

Gas chromatographic analyses were performed with a Shimadzu GC-4C or GC-8A gas chromatograph on a column of poly(ethylene glycol)-20M or silicone DCQF-1. Substrate hydrocarbons were purified either by distillation or chromatography on silica gel with pentane as eluant. Sodium tetrahydroborate ($NaBH_4$) was dried in vacuo for 3 h just prior to use. Tetrahydrofuran (THF) was dried with benzophenone ketyl and distilled under inert atmosphere. Rhodium porphyrin complexes, (OEP)Rh^{III}Cl and (TPP)Rh^{III}Cl, were obtained as described.[27]

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[19] (a) Allies, P. B.; Brindly, P. B. *J. Chem. Soc. B* **1969**, 1126. (b) Davies, A. G.; Ingold, K. U.; Roberts, B. P.; Tudor, R. *Ibid.* **1971**, 698.

[20] The product of the reaction of (OEP)RhH and O_2 has been assigned to (OEP)RhOOH: James, B. R., personal communication. For the hydroperoxorhodium(III) (RhOOH) complexes from the reaction of other hydridorhodium(III) species and O_2, see: (a) James, R. B. In *Biomimetic Chemistry*; Dolphin, D., McKenna, C., Murakami, Y., Tabushi, I., Eds.; Advances in Chemistry 191; American Chemical Society: Washington, DC, 1980; Chapter 14. (b) Thomas, K.; Osborn, J. A.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 1801. (c) Johnston, L. E.; Page, J. A. *Can. J. Chem.* **1969**, *47*, 4241. (d) Roberts, H. L.; Symes, W. R. *J. Chem. Soc. A* **1968**, 1450.

[21] The hydroboration of 1-methylcyclohexene is highly stereoselective, affording the *E* isomer almost exclusively.[11]

[22] (a) Ohkatsu, Y.; Tsuruta, T. *Bull. Chem. Soc. Jpn.* **1974**, *48*, 1747. (b) Baccouche, M.; Ernst, J.; Furrhop, J.-H.; Schlozer, R.; Arzoumanian, H. *J. Chem. Soc., Chem. Commun.* **1977**, 821.

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[24] Aerial oxidation of 9-butyl-BBN[25] in THF afforded cyclooctanone in a similar manner.

[25] Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1.

[26] This process may be in competition with doubled hydroboration to give diboro derivatives.

[27] Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* **1986**, *5*, 168.

General Oxygenation Procedure. An apparently heterogeneous mixture of an olefin (cyclohexene, 1-pentene, or styrene, 1 g), NaBH$_4$ (300 mg, 7.9 mmol), (OEP)Rh^{III}Cl (4.0 mg, 6 μmol; [Rh] = 0.6 mM), and an internal standard (*p*-xylene, mesitylene, or durene, appropriate amount) in dry THF (10 mL) exposed to dry air was stirred at 20–25 °C. The oxygenation of 1-methylcyclohexene was carried out by using the rhodium catalyst in an amount 2 or 20 times as much as that used above ([Rh] = 1.2 or 12 mM). The electronic spectra of the reaction mixture underwent no significant change even after 100 h. The formation of oxygenation products was monitored by gas chromatography. Similarly was carried out the oxygenation of 1,5-cyclooctadiene and acetylenes (1-heptyne and 3-heptyne) by using substrate (300 mg), NaBH$_4$ (300 mg), and (OEP)Rh^{III}Cl or (TPP)Rh^{III}Cl (4.0 mg) in THF (20 mL). Reaction products, after conversion if necessary to silylated derivatives, were identified by gas chromatography on the basis of coinjection with authentic samples, and their yields determined also by gas chromatography. 2-Methylcyclohexanol as a mixture of stereoisomers arising from the oxygenation of 1-methylcyclohexene was purified by preparative gas chromatography. The stereoisomer distribution was determined by ^{1}H NMR spectroscopy by taking advantage of the characteristic signals for hydroxymethine protons at δ 3.1 (for *E* isomer) and 3.75 (for *Z* isomer).

The following control runs were carried out by using cyclohexene as substrate: (1) without rhodium porphyrin catalyst, (2) without O$_2$, (3) without NaBH$_4$, and (4) with NaBH(OCH$_3$)$_3$ in place of NaBH$_4$. In neither case was detected oxygenation of substrate to any significant extent. Another control run using cyclohexene oxide in place of cyclohexene under otherwise identical oxygenation conditions did not give cyclohexanol.

Borane Transfer. A mixture of (OEP)Rh^{III}Cl (40 mg, 0.06 mmol), NaBH$_4$ (100 mg, 2.64 mmol), and 1-pentene (70 mg, 1.0 mmol) in THF (2 mL) in a vessel sealed with a rubber septum was degassed by freeze–pump–thaw cycles and was stirred at room temperature for 19 h. The electronic spectrum of the mixture showed λ_{max} at 395, 514, and 545 nm, indicating the formation of (OEP)RhH.[3] Following the standard procedure for the analysis of organoboranes,[28] the mixture was then subjected to gas chromatography at 170 °C on a column of silicone SE-30 (2 m), which had been treated with Silyl-8 (Pierce Chemical Co.) to mask protic sites with trimethylsilyl groups. The product was readily identified as tripentylborane on the basis of coinjection with the authentic sample prepared by hydroboration of olefin with diborane under standard conditions. The mixture was exposed to air, stirred for 20 min, and then analyzed by gas chromatography to show the formation of 1-pentanol and 2-pentanol (94:6, in a total yield of 45% based on mol of Rh complex used).

Oxidation of Alkylborane. A THF solution of (*E*)-bis(2-methylcyclohexyl)borane[11] was prepared by the hydroboration of 1-methylcyclohexene (96 mg, 1.0 mmol) with borane–THF (1 M) (0.5 mL, 0.5 mmol) in THF (1 mL) under nitrogen. To this was added 1 N aqueous NaOH (0.5 mL), and the mixture was stirred under air atmosphere for 20 h. Gas chromatographic analysis using silicone DCQF-1 showed the formation of 2-methylcyclohexanol with the stereoisomer ratio of $E/Z = 76{:}24$. Another control run for the oxidation of alkylborane with O$_2$ was carried out in the presence of NaBH$_4$ (38 mg, 1.0 mmol) instead of aqueous NaOH under otherwise identical conditions and gave the isomer ratio of $E/Z = 81{:}19$.

A solution of (*E*)-bis(2-methylcyclohexyl)borane in THF (0.21 mL) was prepared as above starting from the olefin (15.4 mg, 0.16 mmol). This solution was added to (OEP)RhH[15] (100 mg, 0.16 mmol) under nitrogen. The mixture was then allowed to contact with a gentle stream of THF-saturated air for 20 h. Gas chromatography coupled with ^{1}H NMR analysis indicated almost exclusive formation of (*E*)-2-methylcyclohexanol.

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(28) Reference 4b, pp 246–248.

Fast and Selective Oxidation of Primary Alcohols to Aldehydes or to Carboxylic Acids and of Secondary Alcohols to Ketones Mediated by Oxoammonium Salts under Two-Phase Conditions

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Received August 6, 1986

Primary alcohols are quantitatively oxidized to aldehydes in a few minutes at 0 °C in CH$_2$Cl$_2$–0.35 M aqueous NaOCl in the presence of catalytic amounts of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (**3b**). Cocatalysis by Br$^-$ and buffering of pH at 8.6 with NaHCO$_3$ are also required. Secondary alcohols are converted to ketones. Further oxidation of aldehydes to carboxylic acids is slow, but the reaction is completed in a few minutes under the same conditions by addition of catalytic amounts of phase-transfer catalyst. All reactions are highly selective. Only a slight excess of NaOCl is required. The method can be applied to saturated alkyl and aryl alkyl substrates.

Selective oxidation of primary alcohols to aldehydes is one of the long standing problems of organic chemistry. Although a huge number of methods of oxidation is known,[1] it is difficult to find a procedure which is selective, cheap, efficient, and easy to work up.

Oxoammonium salts **1** oxidize primary and secondary alcohols to the corresponding carbonyl derivatives.[2] Both stoichiometric[3] and catalytic procedures have been described. Catalytic cycles include electrooxidation,[4] and oxidations by CuCl$_2$–O$_2$[5] or by peroxy acids.[6] It has been

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