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EFFICIENT OLEFIN OXYGENATION WITH TETRAHYDROBORATE AND DIOXYGEN CATALYZED BY A RHODIUM PORPHYRIN COMPLEX

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Abstract: Octaethylporphyrinatorhodium(III) shows an excellent catalytic activity in the oxygenation of simple olefins with tetrahydroborate and dioxygen in tetrahydrofuran to give alcohols via an anti-Markownikoff addition.

The combination of a reductant (BH_4^- or H_2/colloidal Pt), manganese porphyrin, and O_2 has been demonstrated to constitute a functional model of cytochrome P_{450},[1] a class of heme-containing monoxygenases, the essential catalysis of which lies in the reductive activation of dioxygen. We wish to report here the oxygenation of simple olefins using a closely related system composed of $NaBH_4$, rhodium porphyrin, and O_2. A regioselective anti-Markownikoff addition and an excellent catalysis of the rhodium porphyrin are demonstrated.

An apparently heterogeneous mixture of cyclohexene (12 mmol), $NaBH_4$ (1.3-16 mmol), and a catalytic amount of octaethylporphyrinatorhodium(III) chloride [(OEP)-Rh(III), 6.0-30 μmol] in dry THF was stirred at 20-25°C under aerobic condition for 48-130 h (depending on the amounts of reagents). Work-up gave cyclohexanol together with a trace amount of cyclohexenol (<2% of cyclohexanol).[2] $NaBH_4$, (OEP)Rh(III), and O_2 were essential for the effective formation of cyclohexanol as evidenced from control reactions in which one of these was omitted.[3] The time course of the alcohol formation consisted of a smooth progression curve followed by a plateau after complete consumption of $NaBH_4$. The yield of the alcohol depended on the amount of $NaBH_4$ and the rate of reaction depended on that of (OEP)-Rh(III). A typical run using $NaBH_4$ (7.9 mmol) and (OEP)Rh(III) (6.0 or 30 μmol) afforded ca. 1.2 mmol of cyclohexanol with initial rate of its formation of 0.036 or 0.22 mmol/h, respectively (Figure 1). The yield of the alcohol is 15% based on $NaBH_4$ and 20000% based on 6.0 μmol of (OEP)Rh(III), the turnover number of the catalyst being 200 and its turnover rate 6-7 cycles/h at earlier stage of reaction. There was no indication of significant decomposition or deactivation of metalloporphyrin during reaction. Addition of an appropriate amount (7.9 mmol) of $NaBH_4$ to the reaction mixture after complete consumption of that initially added (1.3 mmol) initiated the reaction again to give a nearly corresponding amount of cyclohexanol. These results demonstrate that (OEP)Rh(III) catalyzes efficiently oxygenation of cyclohexene with aid of BH_4^-.

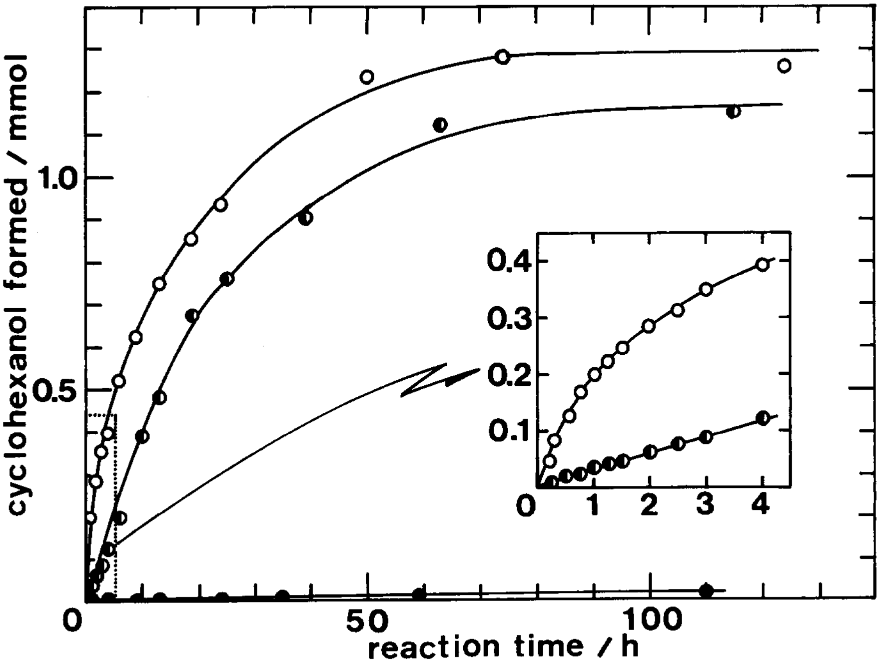

Figure 1. Time courses of cyclohexanol formation using cyclohexene (12 mmol), $NaBH_4$ (7.9 mmol), and (OEP)Rh(III) (30 (-○-○-), 6.0 (-◐-◐-), and 0 μmol (-●-●-)) in THF (10 mL).

Oxygenation of 1-methylcyclohexene under the present condition gave highly regioselective product of 2-methylcyclohexanol.[4] Similarly, 1-octene was converted to a mixture of 1-octanol and 2-octanol in a ratio of 84:16.[5] The alcohols thus formed exclusively or predominantly were derived in the manner of an anti-Markownikoff addition. The present system shows a marked contrast to the oxygenation of 1-hexene by the system, $NaBH_4$-(TPP)Mn-O_2, which leads to a predominant formation of 2-hexanol, the Markownikoff addition product.[1a] Furthermore, the oxygenation of cyclohexene catalyzed by the manganese porphyrin system has been claimed to afford cyclohexene oxide as the direct oxygenation product, which is reduced to cyclohexanol with excess BH_4^-.[1a] In the present reaction, however, cyclohexene oxide was not detected among products. Independent experiments also ruled out its intermediacy as a precursor of cyclohexanol.

The reactivity of olefins provided another interesting point. Competition experiments using cyclohexene as a standard indicated the relative reactivities of olefins as listed in Table I. For comparison, the relative reactivities of olefins toward the (H_2/colloidal Pt)-(TPP)Mn-O_2 system[1b] and those in hydroboration[6] are also included. 1-Alkenes show a significant diversity in reactivity

Table I. Relative Reactivities of Olefins in Various Systems.

	relative reactivity		
system	1-methylcyclohexene	cyclohexene	1-octene or 1-hexene
$NaBH_4$-(OEP)Rh-O_2[a]	1.0	1.0	0.70[d]
H_2(Pt)-(TPP)Mn-O_2[b]	1.4	1	<0.05[e]
hydroboration[c]	1.2	1	7.5[d]

(a) In THF. (b) In benzene-ethanol (2:1 v/v). (c) By using $NaBH_4$-BF_3 in diglyme at 0°C. (d) For 1-octene. (e) For 1-hexene.

As stated above, no appreciable oxygenation takes place when one of the components ($NaBH_4$, (OEP)Rh(III), and O_2) is omitted. It is possible that two of the components react catalytically with substrate to accumulate an intermediate which then reacts with the third component to give the final product. This is, however, not the case. Addition of the third component to the reaction mixture after removal of cyclohexene afforded no appreciable amount of cyclohexanol. This is true for each of the three components. A possible mechanism of the present reaction involves hydroboration as the key step. The reduction of (OEP) Rh(III) with BH_4^- may concomitantly generate diborane, which hydroborates olefins effectively even under aerobic conditions. The oxidative C-B bond cleavage of the resulting organoboranes may be effected by O_2 with or without activation by rhodium. The reduced porphyrin is also oxidized back to (OEP)Rh(III). A shortcoming of this mechanism is that there is a noticeable difference in the reactivity of 1-alkene in the present and hydroboration systems (Table I). An alternative mechanism would involve the dioxygen adduct of (OEP)Rh(II) as a key intermediate. Rh(III) porphyrin is readily reduced with BH_4^-.[7] It is also reported that relatively stable O_2 adduct of Rh(II) porphyrin is obtainable from reaction of a Rh(II) porphyrin with O_2 or directly from BH_4^- reduction of a Rh(III) porphyrin with subsequent addition of O_2.[8] As has been shown for the manganese porphyrin system,[1] (OEP)Rh(II)-O_2 may undergo further reaction(s)[9] to give an electrophilic and bulky Rh-O derivative as the active species which oxygenates olefins. The anti-Markownikoff addition is also explainable in terms of this mechanism.

The present reaction is almost completely free from metal-ion catalyzed olefin autoxidation where allylic oxidation is the principal pathway leading usually to a mixture of products.[10] From a synthetic point of view, this reaction provides a new route to anti-Markownikoff alcohols. In this respect, the present system constitutes a catalytic modification of the hydroboration of olefins followed by oxidation of the resulting organoboranes with alkaline hydrogen peroxide. Further work is now under way to get deeper insight into the mechanism of the present reaction.

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2. When the reaction was carried out in dichloromethane or benzene, (OEP)Rh underwent gradual decomposition on one hand and significant autoxidation took place to give considerable amounts of allylic oxidation products on the other hand. A small amount of cyclohexene oxide was also detected. Product ratios after 72 h from initiation of reaction were cyclohexene oxide:cyclohexanol: cyclohexenone:cyclohexenol = 0.07:1:2.6:2.9 for reaction in benzene and 0.13: 1:0.08:4.7 for reaction in dichloromethane. The ratio of cyclohexenol to cyclohexenone increased with increasing reaction times.
3. The cyclohexanol formation was also catalyzed by the pyridine adduct of cobalt(III) porphyrin [(OEP)Co(III)(Py)(Br)] in place of (OEP)Rh(III). However, the cobalt porphyrin underwent gradual bleaching and its catalytic activity at earlier stage of reaction was small (0.25 times as effective as (OEP)Rh(III). The pyridine-free Co(III) derivative [(OEP)Co(III)(Br)] was far less effective.
4. 1- and 3-Methylcyclohexanol were not detectable by gas chromatography. The lack of the 3-alcohol eliminates the possibility of allylic oxidation followed by reduction as the mechanism of the present oxygenation.
5. For comparison, simple 1-alkenes such as 1-hexene undergo hydroboration to place 94% of the boron on the 1-position and 6% at the 2-position: H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 82, 4708 (1960).
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