Tetrahedron Letters, Vol.22, No.23, pp 2191 - 2194, 1981
Printed in Great Britain

0040-4039/81/232191-04$02.00/0

COBALT-CATALYZED REGIOSPECIFIC CONVERSION OF ARYL-SUBSTITUTED OLEFINS INTO ALCOHOLS USING MOLECULAR OXYGEN AND TETRAHYDROBORATE.
THE REACTION OF OXYGEN WITH ACTIVATED SUBSTRATES

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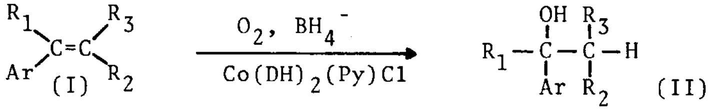
Abstract: Aryl-substituted olefins were converted to benzyl alcohols regioselectively by the use of oxygen and tetrahydroborate in the presence of a catalytic amount of bis(dimethylglyoximato)chloro(pyridine)cobalt(III).

Reactions of molecular oxygen with hydrocarbons under mild conditions are one of the most challenging topics nowadays in the fields of reaction mechanisms and also synthetic chemistry.[1] Besides a large number of studies for elucidation of the function of biological heme-containing oxygenation systems, many model systems have been constructed to introduce its activity and specificity into organic syntheses,[2] however, bearing a limited success so far for aliphatic substrates.[3]

Here, we would like to communicate a catalytic reaction of molecular oxygen with alkenes to give alcohols under a reductive atmosphere which represents an example of a preference of the activation of substrate over the activation of oxygen. When styrene was stirred in the presence of a catalytic amount of bis-(dimethylglyoximato)chloro(pyridine)cobalt(III) and an excess amount of sodium tetrahydroborate under oxygen, 1-phenylethanol was obtained selectively with no detectable amount of 2-phenylethanol accompanied.[4] Control experiments without oxygen or tetrahydroborate gave no alcohol in either case. The main product in the former was ethylbenzene.



The results with some aryl substituted olefins are summarized in Table 1. Addition of hydroxy group took place at the phenyl-substituted olefinic carbon exclusively and so this reaction has a practical meaning for carrying out a Markownikoff-type hydroxylation under basic conditions.[5]

Two alternative routes are suggested for this reaction, namely: (1) The reaction of an activated oxygen with a substrate. (2) The reaction of an activated substrate with oxygen. Cobaloxime(III) is reduced by tetrahydroborate to Co(I) state[6] and Co(I) is known to react with oxygen quickly to give superoxide anion radical and Co(II).[7] Superoxide might react with olefin to give al-

Table 1. Hydroxylation of Alkenes with O_2 and $NaBH_4$ Catalyzed by $Co(DH)_2ClPy$[a]

Olefin (I)	Time (h)	Solvent	Yield of (II)[b] (%)[c]	Yield of (II)[b] (%)[d]
Ar = phenyl, $R_1 = R_2 = R_3 = H$	14	Me_2SO	17[e]	2340
Ar = phenyl, R_1 =Me, $R_2 = R_3 = H$	60	Me_2SO	28[e]	1730
Ar = phenyl, $R_1 = R_2 = H$, R_3 = Me	20	$(CH_3OCH_2)_2$	5	160
Ar = R_1 = phenyl, $R_2 = R_3 = H$	20	$(CH_3OCH_2)_2$	14	430
Ar + R_2 = 1,9-naphtyl, $R_1 = R_3 = H$	20	$(CH_3OCH_2)_2$	11	60
Ar = phenyl, $R_1 = R_2 = H$, $R_3 = CH_2OH$	20	$(CH_3OCH_2)_2$	22	630
Ar = R_3 = phenyl, $R_1 = R_2 = H$	20	$(CH_3OCH_2)_2$	0	0

[a] See reference 4 for reaction procedure. Reaction conditions were not optimized. [b] Isolated yield through silica-gel column. [c] Caluculated on the basis of I used. [d] Catalyst base. [e] Yield was determined by GC.

cohol. The reaction of cobalt(II)-oxygen complex[8] with olefin is also a possibility. On the other hand cobaloxime(I) reacts with olefins generating an alkyl cobaloxime(III),[9] which reacts with oxygen photochemically or thermally to give alkylperoxo complex.[10] Alkylperoxo complex gives alcohol in the presence of tetrahydroborate.

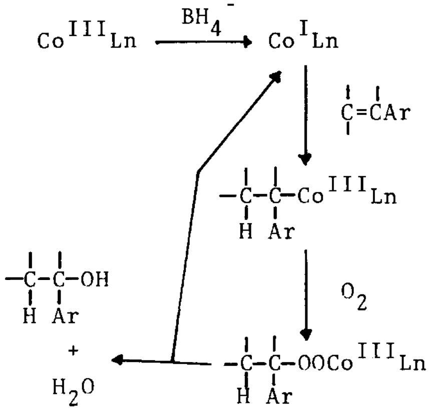
The time-dependent yield and deuterium incorporation of alcohol presented evidence to determine the two alternatives. The yields shown in Fig. 1 suggest that the reaction of Co(I) with olefin gives a reactive intermediate in a higher concentration which gives alcohol by the treatment of oxygen, whereas initial addition of oxygen to Co(I) produces alcohol slowly, indicating that the reactive intermediate is not made from Co(I) and O_2. Phenylethanol formed in the presence of $NaBD_4$ instead of $NaBH_4$ showed a substantial incorporation of deuterium while the deuterium content of recovered styrene was remarkably less (Table 2). Similar incorporation was seen for 1-phenylethanol formed by the reaction of bis(dimethylglyoximato)(1-phenylethyl)pyridinecobalt(III) with oxygen in the presence of BD_4^- and also for recovered cobalt complex.[11]

Table 2. Deuterium Content of 1-Phenylethanol[a]

Conditions[b]	Deuterium Content (%) d_0	d_1	d_2	d_3
Styrene + BD_4^- + Catalyst + O_2, 2h[c]	9	52	38	2
1-Phenylethanol + BD_4^- + Catalyst + O_2, 42.5h	98	2	0	0
$C_6H_5(CH_3)CHCo(DH)_2Py$ + BD_4^- + O_2, 17h	33	38	23	6

[a] Determined by GCMS. [b] Catalyst: $Co(DH)_2(Py)Cl$. [c] Deuterium content of recovered styrene was: d_0, 100%; d_1, 0 in 2h and d_0, 98%; d_1, 2% after 4 day.

These results support the mechanism of (2), which would take place as described in the following equation.[12] The observed regioselectivity is in accordance with the selectivity of the reaction of Co(I) with olefins.[14]



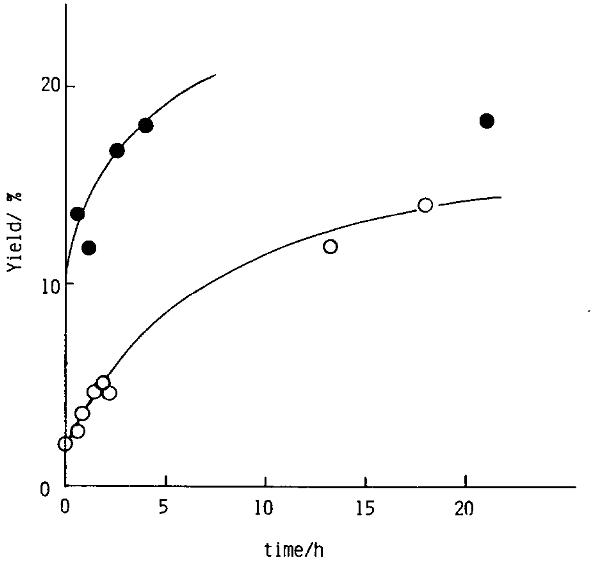


Figure 1. Yields of 1-phenylethanol at the early stage of the reaction of styrene. The order of addition: ●, catalyst + BH_4^-, olefin, and O_2; ○, catalyst + BH_4^-, O_2, and olefin.

Although the mechanism of deuterium incorporation is still unclear,[15] the presented results illustrate the importance of the activation of substrate in the reaction of molecular oxygen with organic substrates and, together with the rather low reactivity of metal-coordinated oxygen,[16] suggests this methodology promising for a purpose of organic syntheses.

References and notes

1) See for example review articles; (a) V. Ullrich, *Angew. Chem., Int. Ed. Engl.* **11**, 701 (1972). (b) O.Hayaishi, Ed., "Molecular Mechanisms of Oxygen Activation", Academic Press, New York, 1974. (c) C. K. Chang, D. Dolphin, "Bioorganic Chemistry", E. E. van Tamelen, Ed., Academic Press, New York, 1978; Vol. 4, Chapter 2. (d) Papers in *J. Mol. Catalysis*, **7**, 1-334 (1980).

2) T. Matsuura, *Tetrahedron*, **33**, 2869 (1977).

3) G. A. Hamilton, R. J. Workman, and L. J. Woo, *J. Am. Chem. Soc.*, **86**, 3390 (1964). V. Z. Ullrich, *Z. Naturforsch. B*, **24**, 699 (1969). V. Ullrich and H. Staudinger, *ibid*., **24**, 583 (1969). V. S. Belova, L. A. Nikonova, L. M. Raikman, and M. R. Vorukaeva, *Dokl. Akad. Nauk SSSR*, **204**, 897 (1972). D. R. Poulson, R. Ullman, R. B. Sloane, and G. L. Closs, *J. Chem. Soc., Chem. Commun.*, **1974**, 186. J. T. Groves and M. Van der Puy, *J. Am. Chem. Soc.*, **96**, 5274 (1974). J. T. Groves and G. A. McClusky, *ibid*., **98**, 859 (1975). M. Baccouche, J. Ernst, J.-H. Furhop, R. Schlözer, and H. Arzoumanian, *J. Chem. Soc., Chem. Commun*. **1977**, 821.

4) Reaction procedure: Catalyst, $NaBH_4$, and olefin were stirred in the solvent

under the atmosphere of oxygen for a specified period, and the mixture was extracted with ether-H_2O. Ether extract was subjected to column chromatography to isolate the product, or GC analysis. Relative amount of catalyst was not the same for runs in Table 1.

5) The regioselectivity is worthy of note in the light of a recent publication on the hydroxylation of olefin with $TiCl_4$-$NaBH_4$, where completely reversal selectivity is reported; S. Kano, Y. Tanaka, and S. Hibino, J. Chem. Soc., Chem. Commun., 1980, 414.

6) G. N. Schrauzer, R. J. Windgassen, and J. Kohnle, Chem. Ber., 98, 3324 (1965).

7) R. M. Sellers and M. G. Simic, J. Am. Chem. Soc., 98, 6145 (1976).

8) M. M. T. Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Academic Press, New York, 1974; Vol. I., p 79. F. Basolo, Chem. Rev., 1979, 139.

9) G. N. Schrauzer and R. J. Windgassen, J. Am. Chem. Soc., 88, 3738 (1966).

10) K. N. V. Duong, C. Fontaine, G. Giannotti, and A. Gaudemer, Tetrahedron Lett., 1971, 1187. C. Fontaine, K. N. V. Duong, C. Marianne, A. Gaudemer, and C. Giannotti, J. Organomet. Chem., 38, 167 (1972). F. R. Jensen and R. C. Kiskis, J. Am. Chem. Soc., 97, 5825 (1975).

11) $NaBD_4$ (1.2 mmol) and 1-phenylethylcobaloxime (0.5 mmol) were stirred in dimethoxyethane (5 ml) under air for 17h. After quenching the reaction with water (10 ml), deuterium content of 1-phenylethanol (0.05 mmol, 10% yield) was determined by GCMS. ^{1}H-NMR analysis of recovered cobaloxime (0.2 mmol, 40%) revealed a $29 \pm 5\%$ incorporation of deuterium in the ethyl part of the complex.

12) In contrast to $NaBH_4$-Mn porphirine system, styrene oxide was unreactive under the present reaction conditions (99% recovery after 15.5h), indicating the mechanism of the two reactions being different: I. Tabushi and N. Koga, J. Am. Chem. Soc., 101, 6456 (1979). There is a possibility of other mechanisms such as the reaction of Co(II) with olefins similar to the Co(II)-RX system[13] and the reaction of Co-substrate complex with Co-O_2 complex. Ln in the equation represents only the presence of ligands and does not mean the coordination number being unchanged.

13) P. W. Schneider, P. F. Phelan, and J. Halpern, J. Am. Chem. Soc., 91, 77 (1969). L. G. Marzilli, P. A. Marzilli, and J. Halpern, ibid., 92, 5752 (1970), ibid., 93, 1374 (1971).

14) G. N. Schrauzer and R. J. Windgassen, J. Am. Chem. Soc., 89, 1999 (1967).

15) A simple mechanism of fast reversible formation of alkyl complex from Co(I) and free olefin does not explain the low deuterium content of recovered styrene.

16) Successful catalytic reactions of transition-metal dioxygen complexes in literature are with only reactive substrates toward oxygen such as triphenylphosphine and isocyanides: S. Takahashi, K. Sonogashira, and N. Hagihara, Nippon Kagaku Zassi, 87, 610 (1966) and S. Otsuka, A. Nakamura, and Y. Tatsuno, J. Chem. Soc., Chem. Commun., 1967, 836.

(Received in Japan 21 February 1981)