Hydroxylation of Olefins with Hydrogen Peroxide in the Presence of Selenium Dioxide Catalyst

By Noboru SONODA and Shigeru TSUTSUMI

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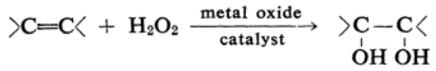
Oxidation by hydrogen peroxide in the presence of a metal oxide catalyst is known as one of the simplest procedures for effecting the hydroxylation of olefins.[1]



$$\rangle C{=}C\langle \; + \; H_2O_2 \xrightarrow[\text{catalyst}]{\text{metal oxide}} \rangle\underset{OH}{C}-\underset{OH}{C}\langle$$

Although many catalysts for this reaction are known, osmium tetroxide and tungstic acid (or tungsten trioxide) are especially useful for the practical syntheses of *cis*- and *trans*-α-diols from the corresponding olefins. Selenium dioxide, which can be used in organic or aqueous solution, has found favor with some investigators,[2-5] but is not so well established a catalyst as osmium tetroxide or tungstic acid. Mugdan and Young[2] have suggested that it may be possible to hydroxylate allyl alcohol with hydrogen peroxide in the presence of selenium dioxide. It has been confirmed that cyclohexene and cyclopentene are hydroxylated to give the corresponding *trans*-α-diols[3,4] under similar conditions; recently we also have reported the hydroxylation of some gaseous olefins.[5]

The purpose of the present investigation is to study the use of selenium dioxide as a catalyst in the hydroxylation of olefins with hydrogen peroxide, and also to extend the application of this catalyst.

In order to examine the ionic character of the hydroxylation, oxidation of norbornene was undertaken, because addition of a cation to the double bond of norbornene should cause a Wagner-Meerwein rearrangement via the norbornyl cation.[6,7]

When norbornene (II) was oxidized with 30% hydrogen peroxide in tertiary butyl alcohol in the presence of a catalytic amount of selenium dioxide, the only product was *exo-syn*-norbornane-2, 7-diol (V) which was identified by comparison with an authentic sample. The diol was best isolated as the diacetate (62% yield based on the norbornene used) which was obtained by treatment of the crude product with acetic anhydride. The formation of *exo-syn*-norbornane-2, 7-diol (V) may be due to the hydration of a norbornyl cation (III or IV) produced by the cationic addition of a hydroxyl group to the double bond of norbornene.[6] Although it is still not clear whether rearrangement of the norbornyl cation proceeds via a nonclassical structure (III) or an equilibrium of classical structures (IV),[8] it is evident that the high propensity and stereospecificity of the rearrangement, in this oxidation, indicate the cationic nature of the reaction,[6] since no rearrangement product is known to arise from a radical addition to norbornene[9,10] or in reactions of the norbornyl free radical.[10,11]

On the other hand, the formation of the norbornyl cation (III or IV) suggests that some active oxidizing species having a peroxy acid function may be formed from the selenium dioxide and hydrogen peroxide in the reaction system, and the mechanism of the hydroxylation may be analogous to that proposed for oxidations with organic peracids[12,13] or pertungstic acid.[14] We have assumed[15,16] that peroxyselenious acid (I) is probably the active oxidizing species in the oxidation of ketones under the above reaction conditions. Thus, a likely mechanism for the hydroxylation of norbornene (II) is that shown below.

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1) For a review, see F. D. Gunstone, "Advance in Organic Chemistry," Vol. I, Interscience Pub., New York (1960), p. 103.

2) M. Mugdan and D. P. Young, *J. Chem. Soc.*, **1949**, 2988.

3) P. Seguin, *Compt. rend.*, **216**, 667 (1943).

4) A. Stoll, A. Lindenmann and E. Jucker, *Helv. Chim. Acta*, **36**, 268 (1953).

5) N. Sonoda and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 110 (1960).

6) P. de Mayo, "Molecular Rearrangements," Part I, Interscience Pub., New York (1963), p. 111.

7) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

8) For one of the recent discussions of these topics, see P. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1856 (1964); and earlier papers therein cited.

9) H. Kwart and J. L. Nyce, ibid., **86**, 2601 (1964).

10) S. J. Cristol, G. D. Brindell and J. A. Reeder, ibid., **80**, 635 (1958).

11) S. J. Cristol and R. P. Arganbright, ibid., **79**, 6309 (1957).

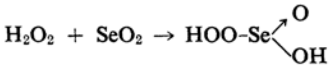
12) H. Kwart and W. G. Vosburgh, ibid., **76**, 5400 (1954).

13) H. M. Walborsky and D. F. Loncrini, ibid., **76**, 5396 (1954).

14) K. A. Saegebarth, *J. Org. Chem.*, **24**, 1212 (1959).

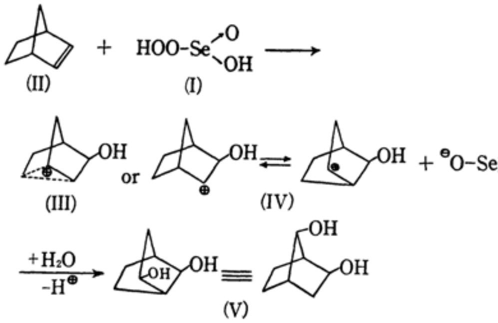
15) N. Sonoda and S. Tsutsumi, This Bulletin, **34**, 1006 (1961).

16) N. Sonoda and S. Tsutsumi, *Technol. Repts. Osaka Univ.*, **13**, 223 (1963).



$$H_2O_2 + SeO_2 \rightarrow HOO\text{-}Se(=O)OH \quad (1)$$

(I)



(2)

These results suggest that hydroxylation of ordinary olefins, which do not suffer a Wagner-Meerwein rearrangement through attack of a cationic species, may proceed via the corresponding epoxide, a stable intermediate produced by the epoxidation with the active oxidizing species in a similar fashion to the first step of the oxidation of norbornene (II). Oxidation of styrene, with hydrogen peroxide and selenium dioxide in methanol, gave mainly 2-phenyl-2-methoxyethyl alcohol (VIII);[17] this may have been formed by methanolysis of the hydronium ion (VI) which is in equilibrium with styrene oxide (VII) as shown below.

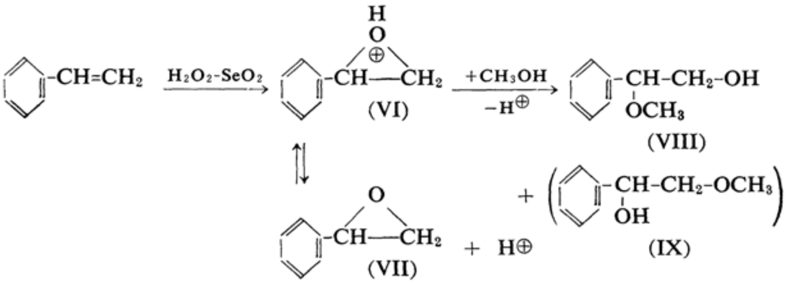
Further evidence for the presence of an epoxide intermediate was obtained by the hydroxylation of cyclohexene in various alcohols. The oxidation of cyclohexene with hydrogen peroxide and selenium dioxide in

TABLE I. HYDROXYLATION OF CYCLOHEXENE WITH HYDROGEN PEROXIDE IN THE PRESENCE OF SELENIUM DIOXIDE IN VARIOUS ALCOHOLS

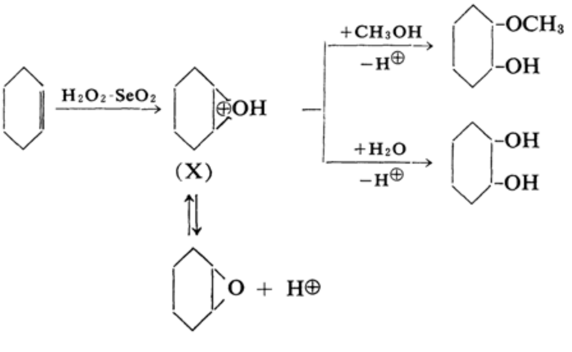
	Product	
Alcohol	Yield,* % α-Alkoxycyclohexanol	Yield,* % *trans*-Cyclohexane-1, 2-diol
Methanol	78	10
Ethanol	56	20
n-Propanol	51	23
n-Butanol	35	27
Isopropanol	24	47
t-Butyl alcohol	<1**	65

* Yields are based on the hydrogen peroxide used.

** The pure product was not isolated.



(3)



(4)

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[17] Identification of 2-phenyl-2-methoxyethyl alcohol (VIII) was established by elementary analysis, and by the mixed melting point of the α-naphthylurethan derivative with an authentic sample, m. p. 119°C (lit.[18] m. p. 119.5°C). Acid or base catalyzed methanolysis of styrene oxide[7] gave generally a mixture of 2-phenyl-2-methoxyethyl alcohol (VIII) and 1-phenyl-2-methoxyethyl alcohol (IX) (α-naphthylurethan, m. p. 105°C[18]), and it has been reported[18] that the α-naphthylurethan of a sample of 2-phenyl-2-methoxyethyl alcohol (VIII) containing a small amount of the 1-phenyl isomer (IX) also showed a m. p. of 119.5°C, identical with that of the α-naphthylurethan of a pure sample of the 2-phenyl isomer (VIII). Accordingly, it is possible that a small amount of the 1-phenyl isomer may have been formed in this experiment, but no attempt was made to determine the content of the 1-phenyl isomer.

[18] W. Reeve and I. Christoffel, *J. Am. Chem. Soc.*, **72**, 1480 (1950).

methanol gave α-methoxycyclohexanol as a main product and *trans*-cyclohexane-1, 2-diol in a small amount. α-Methoxycyclohexanol may be fomed by the methanolysis of the hydronium ion intermediate (X), and the production of *trans*-cyclohexane-1, 2-diol may be attributable to competitive hydrolysis of the same intermediate (X).

The results obtained for the oxidation of cyclohexene with 30% hydrogen peroxide in various alcohols are summarized in Table I.

The yields of α-alkoxycyclohexanol and *trans*-cyclohexane-1, 2-diol shown in Table I are comparable to those obtained by Payne and Smith,[19] and the decrease in the yields of α-alkoxycyclohexanol with the kind of alcohol used can be attributed to the decrease in the polarity of the alcohol.

Experimental

Hydroxylation of Norbornene.—To a solution of hydrogen peroxide in tertiary butyl alcohol, prepared by dilution of 5 ml. (0.05 mol.) of 30% hydrogen peroxide with the alcohol, was added 0.1 g. of selenium dioxide. After the selenium dioxide was dissolved completely, 5 g. (0.04 mol.) of norbornene was added and the solution was heated at 70°C for 13 hr. Most of the solvent and unreacted norbornene was removed by distillation, 50 ml. of ethyl acetate was added to the residue and the ethyl acetate solution was extracted with 10 ml. of 10% sodium hydroxide solution to remove the catalyst. After the ethyl acetate solution had been dried over anhydrous magnesium sulfate, the solvent was removed by distillation under reduced pressure. Sublimation of a small part of the residual crystalline solid gave *exo-syn*-norbornane-2, 7-diol, m. p. 176—177°C (sealed tube) (lit.[20] m. p. 174—176°C), the mixed melting point with an authentic sample (m. p. 176—177°C), synthesized by the procedure described by Kwart,[20] showed no depression, and the infrared spectrum of the product was identical with that of the authentic sample.

Found: C, 65.38; H, 9.32. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44%.

Since the crude *exo-syn*-norbornane-2, 7-diol was slightly hygroscopic, the diol was acetylated. The residual crystalline solid obtained by the removal of solvent was added to 50 ml. of acetic anhydride containing one drop of sulfuric acid; a slightly exothermic reaction was observed. After the reaction mixture had been allowed to stand overnight at room temperature, a small amount of calcium carbonate was added to neutralize the sulfuric acid, and then filtered off. Removal of the unreacted acetic anhydride by distillation under reduced pressure, gave 5.2 g. of *exo-syn*-2, 7-diacetoxynorbornane in a yield of 62% based on the norbornene used; b. p. 128—132°C (10 mmHg), n^{20}_{D} 1.4626 (lit.[14] b.p. 130—134°C (11 mmHg), n^{25}_{D} 1.4620), the infrared spectrum was identical with that of an authentic sample.

Oxidation of Styrene in Methanol Solution.—To a solution of 400 ml. of methanol containing 30 ml. (ca. 0.3 mol.) of 30% hydrogen peroxide was dissolved 0.5 g. of selenium dioxide. Then 31.2 g. (0.3 mol.) of styrene was added to the solution and the reaction mixture was gently refluxed for 20 hr. After decantation to remove the polystyrene deposited in the flask, the solvent and unreacted styrene were removed by distillation under reduced pressure, and the residual liquid was distilled; 8.5 g. of a fraction boiling at 108—113°C (6 mmHg) was collected. Purification by redistillation of this fraction gave 7.8 g. of 2-phenyl-2-methoxyethyl alcohol[17] (60% yield based on the unrecovered styrene); the infrared spectrum was practically identical with that of an authentic sample.

Found: C, 70.88; H, 7.72. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95%.

The α-naphthylurethan melted at 119°C (lit.[18] m. p. 119.5°C), the mixed melting point with an authentic sample (m. p. 119°C) showed no depression and the infrared spectrum was identical with that of an authentic sample.

Found: C, 74.92; H, 5.90. Calcd. for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.96%.

Hydroxylation of Cyclohexene in Methanol Solution.—To a solution of 18.4 ml. (0.18 mol.) of 30% hydrogen peroxide in 365 ml. (9.0 mol.) of methanol was added 0.8 g. of selenium dioxide and 29.5 g. (0.36 mol.) of cyclohexene. After the solution had been refluxed for 10.5 hr. (at this stage, hydrogen peroxide was completely consumed), the solvent and unreacted cyclohexene were removed by distillation under reduced pressure. The residual product was separated by distillation into the following three fractions: fraction A, b. p. 106—116°C (65 mmHg); fraction B, b. p. 105—128°C (20 mmHg); fraction C, b. p. 128—133°C (20 mmHg), which crystallized at once. Fraction B, on being allowed to stand overnight at 0°C, deposited a white crystalline solid which was filtered off; the filtrate was combined with fraction A. Redistillation of this mixture gave 18.2 g. of α-methoxycyclohexanol (78% yield based on the hydrogen peroxide used), b. p. 107—111°C (65 mmHg), n^{20}_{D} 1.4604 (lit.[19] b. p. 122—124°C (100 mmHg), n^{20}_{D} 1.4595). The infrared spectrum was identical with that of an authentic sample.

Found: C, 64.46; H, 10.78. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84%.

The crystalline solid collected from fractions A and B was recrystallized from ether to give 2.0 g. (10% yield) of *trans*-cyclohexane-1, 2-diol, m. p. 103—103.5°C (lit.[21] m. p. 103.5—104°C). The mixed melting point with an authentic sample (m. p. 103—103.5°C) was not depressed.

Found: C, 61.85; H, 10.83. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41%.

Hydroxylation of Cyclohexene in Ethanol Solution.—To a solution of 18.4 ml. (0.18 mol.) of 30% hydrogen peroxide in 420 ml. (7.2 mol.) of ethanol

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[19] G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1682 (1957).

[20] H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

[21] J. English and J. D. Gregory, *J. Am. Chem. Soc.*, **69**, 2120 (1949).

containing 0.8 g. of selenium dioxide was added 29.5 g. (0.36 mol.) of cyclohexene. The reaction mixture was heated at 55—60°C for 13.5 hr. The reaction products were separated in the same manner as described for the hydroxylation in methanol solution, and 14.5 g. (56% yield based on the hydrogen peroxide used) of α-ethoxycyclohexanol was obtained, b. p. 80—85°C (15 mmHg), n_D^{20} 1.4566 (lit.[19]) b. p. 65—67°C(4 mmHg), n_D^{20} 1.4562).

Found: C, 66.78; H, 11.21. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18%.

trans-Cyclohexane-1, 2-diol (4.2 g.) was also isolated in a yield of 20%, m. p. 103—103.5°C. The mixed melting point with an authentic sample showed no depression.

Hydroxylation of Cyclohexene in *n*-Propanol Solution.—To a solution of 18.4 ml. (0.18 mol.) of 30% hydrogen peroxide in 540 ml. (7.2 mol.) of *n*-propanol containing 0.8 g. of selenium dioxide was added 29.5 g. (0.36 mol.) of cyclohexene. The reaction mixture was heated at 55—60°C for 16 hr. The reaction products were separated in the same manner as described for the hydroxylation in methanol solution, and 14.4 g. (51% yield based on the hydrogen peroxide used) of α-*n*-propoxycyclohexanol was isolated, b. p. 92—96°C (14 mmHg), n_D^{20} 1.4571 (lit.[22]) b. p. 205°C, n_D^{20} 1.4580).

Found: C, 67.89; H, 11.40. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47%.

trans-Cyclohexane-1, 2-diol (4.9 g.) was also isolated in a yield of 23%, m. p. 103—103.5°C. The mixed melting point with an authentic sample was not depressed.

Hydroxylation of Cyclohexene in *n*-Butanol.—To a solution of 18.4 ml. (0.18 mol.) of 30% hydrogen peroxide in 660 ml. (7.2 mol.) of *n*-butanol containing 0.8 g. of selenium dioxide was added 29.5 g. (0.36 mol.) of cyclohexene. The reaction mixture was heated at 55—60°C for 17 hr. The reaction products were separated in the same manner as described for the hydroxylation in methanol solution, and 10.8 g. (35% yield based on the hydrogen peroxide used) of α-*n*-butoxycyclohexanol was obtained, b. p. 106—110°C (13 mmHg), n_D^{20} 1.4562 (lit.[23]) b. p. 113—115°C (15 mmHg)).

Found: C, 69.49; H, 11.60. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%.

trans-Cyclohexane-1, 2-diol (5.7 g.) was also isolated in a yield of 27%, m. p. 103—103.5°C. The mixed melting point with an authentic sample showed no depression.

Hydroxylation of Cyclohexene in Isopropanol Solution.—To a solution of 18.4 ml. (0.18 mol.) of 30% hydrogen peroxide in 550 ml. (7.2 mol.) of isopropanol containing 0.8 g. of selenium dioxide was added 29.5 g. (0.36 mol.) of cyclohexene. The reaction mixture was heated at 55—60°C for 14 hr. The reaction products were separated in the same manner as described for the hydroxylation in methanol solution, and 6.7 g. (24% yield based on the hydrogen peroxide used) of α-isopropoxycyclohexanol was isolated, b. p. 89—93°C (18 mmHg), n_D^{20} 1.4520 (lit.[19]) b. p. 94—96°C (20 mmHg), n_D^{20} 1.4506).

Found: C, 68.22; H, 11.36. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47%.

trans-Cyclohexane-1, 2-diol (9.9 g.) was also isolated in a yield of 47%, m. p. 103—103.5°C. The mixed melting point with an authentic sample showed no depression.

Hydroxylation of Cyclohexene in *t*-Butyl Alcohol Solution.—To a solution of 18.4 ml. (0.18 mol.) of 30% hydrogen peroxide in 680 ml. (7.2 mol.) of *t*-butyl alcohol containing 0.8 g. of selenium dioxide was added 29.5 g. (0.36 mol.) of cyclohexene. The reaction mixture was heated at 55—60°C for 16 hr. The reaction products were separated in the same manner as described for the hydroxylation in methanol solution, and 0.4 g. of liquid, b. p. 86—91°C (14 mmHg), n_D^{20} 1.4598, was obtained as a first fraction. Although the infrared absorption of this fraction showed strong bands at 3350 cm^{-1} (O-H) and 1250 cm^{-1} (C-O-C), elementary analysis as α-tertiary-butoxy-cyclohexanol gave slightly unsatisfactory result which might be due to the presence of some impurities.

trans-Cyclohexane-1, 2-diol (13.5 g.) was also isolated in a yield of 65%, m. p. 103—103.5°C. The mixed melting point with an authentic sample showed no depression.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka

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[22] M. Mousseron and R. Granger, *Compt. rend.*, **205**, 327 (1937).

[23] E. Imoto and K. Azuma, *J. Soc. Org. Synthet. Chem. Japan*, **12**, 405 (1954).