Hydrogen Peroxide Oxidation. V. Selenium Dioxide Catalyzed Oxidative Rearrangement Reaction of Desoxybenzoin[1]

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The previous papers[2-4] in this series described the fact that the selenium dioxide catalyzed hydrogen peroxide oxidation of enolizable ketones produces carboxylic acids by the intramolecular migration of alkyl or aryl group to the α-carbon atom of the carbonyl group. The present study was undertaken to provide additional informations pertinent to active species of these reactions and the reaction processes.

For this purpose, desoxybenzoin was selected as a starting material. According to the procedure[4] previously employed for phenyl alkyl ketones, desoxybenzoin (I) was oxidized with hydrogen peroxide in the presence of a catalytic amount of selenium dioxide in tertiary butyl alcohol at 82°C. The formation of diphenyl acetic acid (II) was observed and benzoic acid was also isolated as a acidic product.

After unreacted desoxybenzoin was removed, small amounts of benzil (III) and benzoin (IV) were isolated from the neutral part of the reaction products, and an oily substance was also isolated as the residue. The strong infrared absorption bands at 1110 (sym. C-O-C), 1270 (asym. C-O-C) and 1710 cm^{-1} (C=O) of the residue indicated the presence of an ester group, and it was confirmed to be benzyl benzoate (V) by gaschromatographic analysis.

Diphenyl acetic acid (II) should be produced by the migration of phenyl group to the α-carbon atom of the benzyl group in conformity

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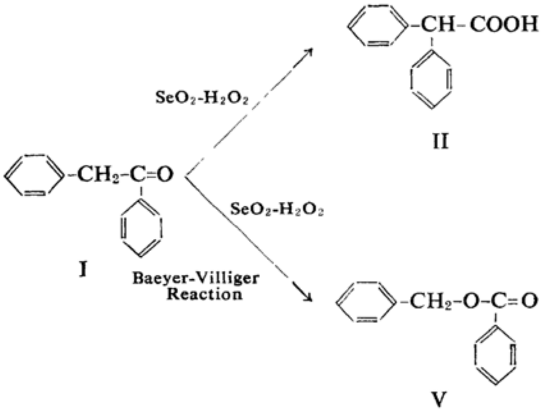
[1] Reported at the Autumn Meeting of Chemical Society of Japan, Tokyo, October, 1959.

[2] N. Sonoda and S. Tsutsumi, This Bulletin, 32, 505 (1959).

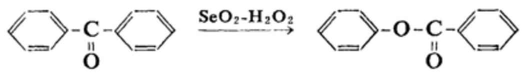
[3] N. Sonoda, T. Yamaguchi and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 63, 737 (1960).

[4] N. Sonoda and S. Tsutsumi, This Bulletin, 33, 1440 (1960).

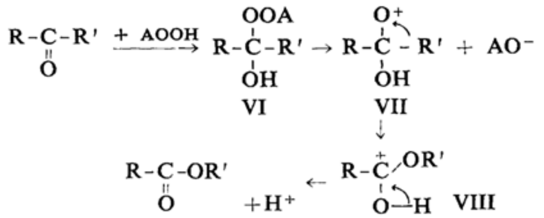
with the reaction aptitude observed in the previous paper[4], whereas the formation of benzyl benzoate (V) may be apparently due to Baeyer-Villiger oxidative rearrangement reaction[5,6].



It was confirmed experimentally that benzyl benzoate is not an intermediate in the reaction path of the production of diphenyl acetic acid. Therefore, both the rearrangement reactions described above may proceed competitively in the same reaction system. This is also supported by the fact that the Baeyer-Villiger reaction is generally applicable to the non enolizable ketones which can not produce the rearranged carboxylic acids. For example, benzophenone was oxidized by the selenium dioxide catalyzed hydrogen peroxide yielding phenyl benzoate or its hydrolyzed products.



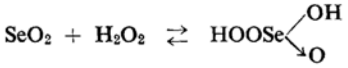
Baeyer-Villiger reaction is interpreted as one of the reactions of ketones with peroxyacids. The favored reaction mechanism was first proposed by Criegee[7], who assumed that the addition of peroxyacid to the carbonyl group produced a hydroxyperoxide VI (referred to as "Criegee Intermediate"), which dissociated to give an electron-deficient ion VII, and then was rearranged to form carbonium ion VIII with cleavage of a carbon-carbon bond, and VIII decomposed to the ester.



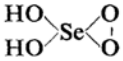
AOOH : peroxyacid

Accordingly, the formation of benzyl benzoate from desoxybenzoin may be due to some kind of peroxyacid as the active oxidizing species in the selenium dioxide-hydrogen peroxide system, and this fact is also consistent with our previous assumption[2] that peroxyselenious acid is the most probable catalyst.

The formation of peroxyselenious acid was first assumed by Hughes and Martin[8] from the kinetic study of the oxidation of selenium dioxide with hydrogen peroxide to selenic acid.



$$\mathrm{SeO_2 + H_2O_2 \rightleftarrows HOOSe}\begin{matrix}\mathrm{OH}\\ \mathrm{O}\end{matrix}$$

Recently, Ogata and Tabushi[9] have reported in the kinetic study of the oxidation of dimethylaniline that a kind of peroxide such as peroxyselenious acid or  is assumed to be produced as the active oxidizing species.

Although the formation of selenic acid would be possible in this reaction system, the selenic acid might not be the active species, because desoxybenzoin was oxidized with selenic acid to yield benzil as well as in the case of the selenious acid oxidation, and no rearrangement reaction was observed. In addition, Ogata and Tabushi[9] have shown in the kinetic study that peroxyselenic acid[10] may not be an active oxidizing species.

Hawthorne and his co-workers[11] reported that the Baeyer-Villiger rearrangement of desoxybenzoin with trifluoroperoxyacetic acid gave benzyl benzoate and phenyl phenylacetate in the ratio of 51 : 39. In contrast to this result, only benzyl benzoate was isolated as ester in the selenium dioxide catalyzed hydrogen peroxide oxidation, and phenyl phenylacetate was not detected by the gas chromatography which was capable of analyzing both the esters. It is interesting to note that the rearrangement aptituds of the two possible

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5) For a review of the Baeyer-Villiger reaction, see C. H. Hassall, "Organic Reactions", Vol. IX, John Wiley & Sons, Inc., New York, N. Y. (1957), pp. 73—106.

6) Recently, Hellman and Rosegay have also reported the occurrence of the Baeyer-Villiger reation from the isolation of 6-hydroxycaproic acid in the oxidation products of cyclohexanone with selenic acid-hydrogen peroxide reagent; H. M. Hellman and A. Rosegay, *Tetrahedron Letters*, **1959**, No. 13, 1∼3; *Chem. Abstr.*, **54**, 4345 (1960).

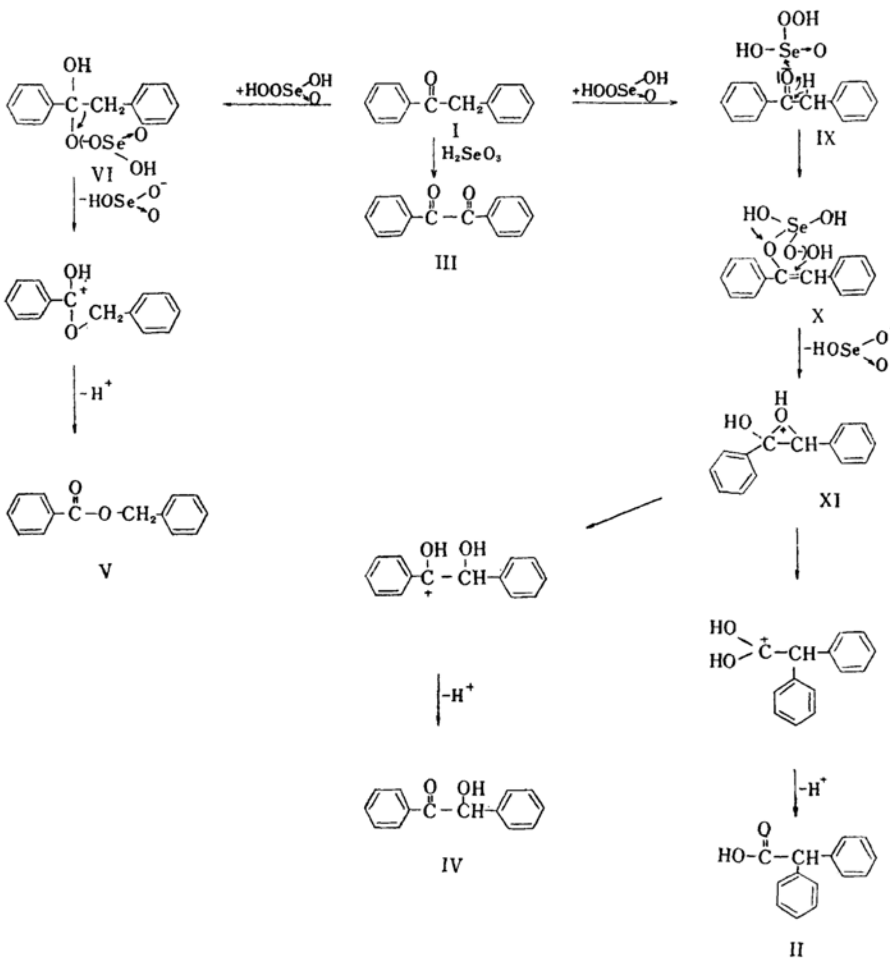
7) R. Criegee, *Ann*, **560**, 127 (1948).

8) F. J. Hughes and D. S. Martin Jr., *J. Phys. Chem.*, **59**, 410 (1955).

9) Y. Ogata and I. Tabushi, This Bulletin, **32**, 215 (1959).

10) The formation of peroxyselenic acid (H_2SeO_5) was assumed by several workers; (a) R. R. Worsley and H. B. Baker, *J. Chem. Soc.*, **123**, 2870 (1923). (b) C. W. Smith and R. T. Holm, *J. Org. Chem.*, **22**, 746 (1957). But the evidence and the other information of the peroxyselenic acid were not obtainable. See (c) W C. Schumb et al., "Hydrogen Peroxide", Reinhold Pub., New York, N. Y (1955), p. 477.

11) M. F. Hawthorne, W. D. Emmons and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958).



migrating groups, phenyl and benzyl groups, are largely dependent on the kind of the oxidative reagent in the Baeyer-Villiger reaction. Such a difference in the migrating aptitude was also reported by Howthorne and the co-workers[11], who showed that the greater selectivity between migrating groups was observed in the cleavage of phenyl cyclohexyl ketone with peroxyacetic acid as compared with the similar reaction with trifluoroperoxyacetic acid.

The simplest interpretation of the reaction mechanism of the diphenyl acetic acid formation may involve the electrophilic attack of the peroxyacid to a double bond formed between the carbonyl carbon and the methylene carbon atoms. The formation of this double bond was assumed from the observation[2,3,12] that the orientation of the migration of alkyl groups in the selenium dioxide catalyzed rearrangement reaction of aliphatic unsymmetrical ketones with hydrogen peroxide was comparable to the orientation of the enol form or of diketone formation with selenious acid. Accordingly, it is reasonable to say that the initial state of the attack of peroxyselenious acid to the ketone will be analogous to that of selenious acid. Although we have proposed the inferential mechanism[2] which comprises the enol formation followed by the attack of the peroxyselenious acid, the other possible reaction path will be suggested from the recent study on the mechanism of selenium dioxide oxidation of ketones, in which Corey and Schaefer[13] have pointed out that the electrophilic character to the carbonyl group may be served by 4d-orbitals of selenium in the first step of the reaction. In the present case the formation of the double bond may be induced by the electrophilic addition of the peroxyselenious acid to the carbonyl oxygen (IX), and then electrophilic attack by hydroperoxy group occurs intramolecularly (X) as shown below.

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[12] The detailed results were presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[13] E. J. Corey and J. P. Schaefer, *J. Am. Chem. Soc.*, **82**, 918 (1960).

Elimination of selenious acid from X may yield hydronium ion (XI) which will be rearranged to produce the carboxylic acid (II).

Our results are not sufficient to allow a choice between the two proposed reaction paths; however, the latter may be more favorable because of the distinctive character of the peroxyselenious acid as compared with the other peroxyacids.

Since no products other than benzil have been found[13] in the oxidation of desoxybenzoin with selenious acid, the formation of benzoin might be illustrated in the path via hydronium ion intermediate (XI).

Experimental[14]

Materials.—Desoxybenzoin was prepared from phenyl acetic acid, phosphorus trichloride and benzene according to the procedure of Allen and Barker[15]; b. p. 158°C (4 mmHg). A sample, m. p. 57°C, was obtained by the recrystallization from methanol.

Reagent for Oxidation. — A solution containing 20 ml. of 30% hydrogen peroxide and 80 ml. of tertiary butyl alcohol was dried over 60 g. of anhydrous sodium sulfate for two days. After filtration of sodium sulfate, 0.2 g. of selenium dioxide was dissolved in 25 ml. of this solution. The solution prepared was used as a reagent for oxidation.

Oxidation of Desoxybenzoin.—In a 15 ml. of tertiary butyl alcohol, was dissolved 4.9 g, (0.025 mol.) of desoxybenzoin by slight heating, and 25 ml. of hydrogen peroxide-selenium dioxide reagent (0.05 mol. of hydrogen peroxide and 0.2 g. of selenium dioxide) was added. The reaction mixture was refluxed for 17 hr., and was distilled under reduced pressure to remove the solvent and water. The residue was diluted with 100 ml. of ether and was filtered to remove a small amount of metallic selenium deposited. The ethereal solution was extracted with 10% potassium carbonate solution.

Acidic Products.—The potassium carbonate solution was acidified with 4 N hydrochloric acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and removal of the ether left 1.3 g. of mixture of acids. Benzoic acid (0.6 g.) was separated as the soluble part of the mixture in warm water, m. p. 121°C (lit.[16] 121°C), mixed melting point with an authentic sample was not depressed.

The insoluble part (0.5 g.) was recrystallized from a small amount of benzene to remove the brown impurities and was further recrystallized from hot water. This yielded white crystals, 0.2 g. of diphenyl acetic acid (6% yield based on the unrecovered desoxybenzoin); m. p. 145°C (lit.[16] 145°C), mixed melting point with an authentic sample showed no depression.

Found: C, 79.00; H, 5.52. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Neutral Products. — The ethereal solution, from which the acidic products were removed was dried over anhydrous sodium sulfate, and the ether was evaporated. On distillation of the residual brown oily liquid under reduced pressure, 3.0 g. of yellow oily products were obtained, b. p. 140~166°C (4 mmHg). After cooling overnight, crystals deposited were filtered and recrystallized from methanol giving 1.6 g. of recovered desoxybenzoin, m. p. 55°C. The filtrate was further cooled at 0°C for two days, and crystals deposited were filtered and recrystallized from ethanol giving a small amount of recovered desoxybenzoin and 35 mg. of benzil; faint yellow crystalline solid, m. p. 94~95°C (lit.[16] 95°C), undepressed when mixed with an authentic sample.

Found: C, 80.15; H, 5.11. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79%.

The filtrate was cooled further at 0°C for 3 weeks and isolated crystalline solid was recrystallized from ethanol; 25 mg. of white crystals were obtained, m. p. 130~132°C; the infrared spectrum[17] exhibited strong absorption bands at 3320 (OH) and 1680 cm^{-1} (conjugated C=O), and was identical with an authentic benzoin; vicinal hydroxy ketone test[18] by periodic acid reagent gave positive result. In the above respects this sample was confirmed to be mainly benzoin (lit.[16] m. p. 133°C).

Found: C, 79.23; H, 5.78. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

The residual liquid was redistilled under reduced pressure, and 0.9 g. of oily product, benzyl benzoate, was obtained. The infrared spectrum[17] of analytical sample, b. p. 156~157°C (3 mmHg), showed strong bands at 1710 (C=O), 1270 (asym. C-O-C) and 1110 cm^{-1} (sym. C-O-C), and was identical with an authentic sample.

Found: C, 79.50; H, 5.54. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Presence of phenyl phenylacetate was not detected by the gaschromatography which was capable of separating phenyl phenylacetate and benzyl benzoate: column, Silicone-550; column temperature, 205°C; carrier gas, H_2.

Oxidation of Benzophenone.—To a 25 ml. of selenium dioxide-hydrogen peroxide reagent (0.05 mol. of hydrogen peroxide and 0.2 g. of selenium dioxide) was added 50 ml. of tertiary butyl alcohol and 9.1 g. (0.05 mol.) of benzophenone, and the mixture was refluxed for 24 hr. After removal of the solvent from the reaction mixture, the residual products was separated into acidic and neutral parts according to the usual procedure. From the acidic part was isolated 0.2 g. of benzoic acid. For the purpose of saponification of the ester contained, the neutral product was treated with 5 g. of sodium hydroxide in 90% aqueous methanol solution at 65°C for 2 hr. After removal of the methanol, 20 ml. of water was added and the neutral substance was extracted with ether. The ether extract gave 6.8 g. of unreacted benzophenone, b. p. 124~129°C

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[14] The boiling and the melting points are uncorrected.

[15] C. F. H. Allen and W. E. Barker, "Organic Syntheses", Coll. Vol. II (1948), p. 156.

[16] R. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th Ed., John Wiley & Sons, Inc., New York, N. Y. (1956).

[17] The infrared spectra were obtained on a Shimadzu Model IR-27A instrument.

[18] Ref. 16, p. 129.

(3 mmHg). Acidification of the water soluble part yielded 0.4 g. of benzoic acid, and small amount of phenol was also isolated; the tribromide was prepared which melted at 94°C (lit.[16] m. p. 95°C), mixed melting point with an authentic sample showed no depression. The formation of phenyl benzoate was confirmed from the above experiments.

Oxidation of Desoxybenzoin with Selenic Acid. —To a mixed solution of 50 ml. of tertiary butyl alcohol and 50 ml. of methanol was added 9.8 g. (0.05 mol.) of desoxybenzoin. The solution was heated to 70°C, and 18 g. of 40% aqueous selenic acid (0.05 mol.) was added dropwise to the solution. After the solution was maintained at 70°C for 24 hr., metallic selenium deposited was filtered off. The filtrate was distilled to remove the solvent, and the residue was separated into acidic and neutral parts according to the usual procedure. From the acidic part was isolated 0.15 g. of benzoic acid. The neutral part gave 7.6 g. of benzil, m. p. 94~95°C, and 1.8 g. of unidentified substance (probably, some organo selenium compound).

Summary

1) Selenium dioxide catalyzed oxidation of desoxybenzoin with hydrogen peroxide in tertiary butyl alcohol gave diphenyl acetic acid which was produced by the rearrangement of phenyl group to the methylene carbon atom.

2) Baeyer-Villiger reaction was also occurred competitively in this reaction system, and benzyl benzoate was isolated as ester from the neutral products. Such an observation shows that the active oxidizing species may be some kind of peroxyacid. This fact is consistent with our previous assumption that peroxyselenious acid is the most probable catalytic form.

3) It is assumed in the reaction path of the formation of the rearranged carboxylic acid that the initial state of the attack of the peroxyselenious acid to the ketone may be analogous to that of selenious acid. From this point of view, a possible reaction path was proposed.

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