Hydrogen Peroxide Oxidation. I. A New Selenium Dioxide-Catalyzed Synthesis of Carboxylic Acids from Aliphatic Ketones Accompanied by Rearrangement of Alkyl Groups

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In the selenium dioxide oxidation of aliphatic carbonyl compounds, α-dicarbonyl compounds are generally obtained, whereas in the presence of hydrogen peroxide the oxidative reaction proceeds quite differently. For instance, selenium dioxide was used as catalyst for hydroxylation of olefins[1,2], and recently the use of selenium dioxide catalyst for the hydrogen peroxide oxidation of acrolein to acrylic acid has been reported by Smith and Holm[3], and the ring contraction of cycloalkanones to cycloalkanecarboxylic acids has also been confirmed by Payne and Smith[4].

We had tried to hydroxylate olefins with hydrogen peroxide in the presence of selenium dioxide catalyst and by using a mixed solvent of *tert*-butyl alcohol and a ketone. It was interesting to note that the oxidation of the ketone, used as solvent, proceeded mainly to form carboxylic acid accompanied by a migration of an alkyl group of the ketone.

For the purpose of elucidating the new reaction mode, acetone, methyl ethyl ketone, methyl *n*-propyl ketone and diethyl ketone were chosen as the starting materials. In the presence of a catalytic

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[1] M. Mugdan and D. P. Young, *J. Chem. Soc.*, **1949**, 2988.

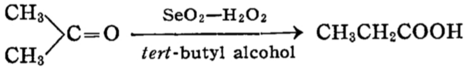
[2] P. Seguin, *Compt. rend.*, **216**, 667 (1943).

[3] C. W. Smith and R. T. Holm, *J. Org. Chem.*, **22**, 746 (1957).

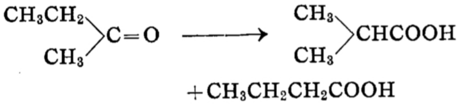
[4] G. B. Payne and C. W. Smith, ibid., **22**, 1680 (1957).

amount of selenium dioxide, the oxidation of ketones was carried out with a slight excess of hydrogen peroxide in *tert*-butyl alcohol in gentle reflux condition (78～82 °C) for 5～6 hr. At the end of the oxidation the deposition of metallic selenium was observed by which the reaction mixture was colored brownish red, while the hydrogen peroxide completely disappeared. The oxidation products were separated by fractional distillation and analyzed.

When acetone was treated according to the above method, propionic acid, which arose by the shift of either of the methyl carbons to another, was isolated in a yield of 40.7% based on the acetone used. The oxidation of methyl ethyl ketone under similar conditions gave isobutyric acid as the main product in a 27.3% yield and *n*-butyric acid in a 4.8% yield. Both products were formed by the respective migration of the methyl and ethyl groups to the α-carbon atom of the carbonyl group.



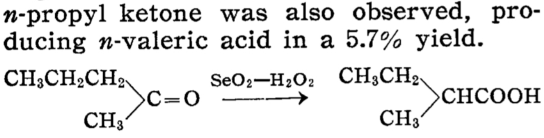
$$(CH_3)_2C{=}O \xrightarrow[\textit{tert}\text{-butyl alcohol}]{SeO_2-H_2O_2} CH_3CH_2COOH \quad (1)$$



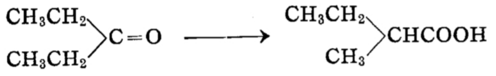
$$CH_3CH_2(CH_3)C{=}O \longrightarrow (CH_3)_2CHCOOH + CH_3CH_2CH_2COOH \quad (2)$$

All the acids obtained were identified by their physical properties, preparation of the derivatives (*p*-bromophenacyl esters), and their infrared spectra.

When methyl *n*-propyl ketone and diethyl ketone were oxidized under similar conditions to those described above, methyl ethyl acetic acid, which was formed by the respective migration of methyl and ethyl groups to the α-carbon atoms of the carbonyl groups, was isolated in a yield of 22.8% and 32.4%, respectively. The migration of *n*-propyl group of methyl *n*-propyl ketone was also observed, producing *n*-valeric acid in a 5.7% yield.

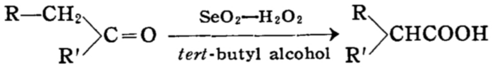


$$CH_3CH_2CH_2(CH_3)C{=}O \xrightarrow{SeO_2-H_2O_2} CH_3CH_2(CH_3)CHCOOH + CH_3CH_2CH_2CH_2COOH \quad (3)$$



$$(CH_3CH_2)_2C{=}O \longrightarrow CH_3CH_2(CH_3)CHCOOH \quad (4)$$

The above results suggest that similar treatments can be applied to other dialkyl ketones. Thus, the oxidative reactions may be generalized as follows;



$$R{-}CH_2(R')C{=}O \xrightarrow[\textit{tert}\text{-butyl alcohol}]{SeO_2-H_2O_2} R(R')CHCOOH \quad (5)$$

R=H or alkyl R′=alkyl

It is inferable that the main rearrangement in these oxidative reactions is due to the migration of the alkyl group having a smaller number of carbon atoms to the α-carbon atom of the larger alkyl group, and, in consequence, the generated acids have the same number of carbon atoms as the original ketones. On the other hand, the migration of the alkyl group with a larger number of carbon atoms to the smaller one occurs simultaneously in some degree, so that the corresponding isomers are obtainable when unsymmetrical dialkyl ketones are used.

Small amounts of cleavage products were obtained as by-products in all cases. These are listed in Table I.

TABLE I. CLEAVAGE PRODUCTS FROM OXIDATIVE REACTION OF KETONES

Reactants	Products confirmed	Yield
acetone	acetic acid(a)	trace
methyl ethyl ketone	acetic acid	trace
	propionic acid	trace
methyl *n*-propyl ketone	acetic acid(b)	trace
diethyl ketone	acetic acid(a)	trace
	propionic acid	4.1%

(a) The presence of acetic acid was confirmed by the boiling point, the refractive index and the value of neutral equivalent, and the other acids were identified in the form of *p*-bromophenacyl esters.

(b) Propionic acid and *n*-butyric acid are assumed to be present, but were not detected.

These products have apparently formed by the cleavage of the bond between the α-carbon atom and the carbonyl group, although, propionic acid can partly be furnished from oxidation of the solvent; because acetone and methyl alcohol are presumed to be generated from the decomposition of *tert*-butyl hydroperoxide and di-*tert*-butyl peroxide which are produced by the reaction of *tert*-butyl alcohol, used as solvent, with hydrogen peroxide. Actually, the formation of a small amount of aceton was observed (identified as its 2, 4-dinitrophenylhydrazone; the melting point and mixed melting point with authentic sample were 123°C[5]) when the

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[5] W. Dirscherl and H. Nahm, *Ber.*, **73**, 448 (1940).

selenium dioxide-hydrogen peroxide solution used above was heated without ketones.

The presence of acetic acid and propionic acid in the oxidation products of diethyl ketone indicates that both of the cleavaged groups from one ketone can be oxidized to acids in these reaction systems. In addition, the occurrence of formic acid due to the cleavage of methyl alkyl ketones or oxidation of methyl alcohol produced from solvent may be possible, but it was not detectable.

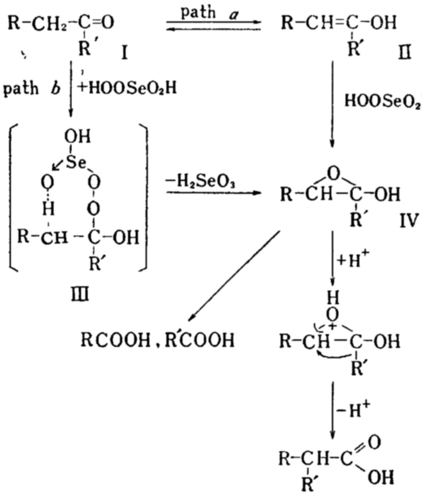
Synthesis of carboxylic acids from ketones by the use of aqueous ammonium polysulfide or a mixture of sulfur and water has been known as Willgerodt-reaction⁶⁾, in which aromatic-aliphatic ketones are mainly used as the starting materials, and no change of the carbon skeleton has been observed because of the consecutive reduction and oxidation of the carbon atoms in the aliphatic carbon chain. In the reaction described here the rearrangement of alkyl group occurs apparently and therefore the reaction mode is different from the Willgerodt-reaction. On the other hand, oxidation of ketones accompanying the rearrangement of alkyl group, by peracids or hydrogen peroxide in the presence of acidic catalyst, has been well known as Baeyer-Villiger reaction⁷⁾, but in this case the migrating alkyl group becomes the ester group of the resulting carboxylic acid so that the carbon numbers of the generated carboxylic acid are less than those of the starting ketone used. It is of interest to note that the rearrangement by the selenium dioxide-hydrogen peroxide system is applicable to such lower ketones as acetone and methyl ethyl ketone which produce monomeric or polymeric ketone-peroxides under the conditions of Baeyer-Villiger reaction. The ring contraction of cycloalkanones reported by Payne and Smith⁴⁾ may be interpreted as one of the rearrangement reactions described here.

Although little evidence was obtained about the mechanism of the rearrangement, the reaction would obviously proceed owing to the peculiar action of the catalyst. It seems to us that selenium dioxide may not affect the reaction directly but a further oxidized form of selenium dioxide by hydrogen peroxide may be the most probable catalytic form. Because α-dicarbonyl compound is not the intermediate⁴⁾; for example, diacetyl was cloven into two molecules of acetic acid under the same reaction conditions and C_4-acid was not obtained.

The oxidation of selenium dioxide with hydrogen peroxide has been reported by several workers⁸⁻¹⁰⁾. Hughes and Martin⁹⁾ proposed the formation of peroxyselenious acid in the course of the oxidation of selenium dioxide to selenic acid as shown below.

$$SeO_2 + H_2O_2 \rightleftharpoons HOOSeO_2H$$

We investigated¹¹⁾ previously the fact that the hydroxylation of a double bond was possible by applying the same oxidative method to olefins, and this fact would be elucidated by considering the formation of some kind of peracid in the reaction system. In the present case, the peroxyselenious acid may be formed in *tert*-butyl alcohol solution and may attack ketones in an ionic fashion; thus the following mechanism will be presumed.



Path a indicates that the epoxidation of *enol*-form II by the peroxyselenious acid may occur and addition of proton to the resulting epoxyalcohol IV may cause the migration of an alkyl group. Formation of epoxyalcohol IV will be also expected

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6) For a review of this reaction, see (a) M. Carmack, "Organic Reactions", Vol. III, John Wiley and Sons, Inc., New York, N. Y. (1946), p. 83-107; (b) R. Wegler, E. Kühle and W. Schäfer, *Angew. Chem.*, **70**, 351 (1958).

7) For a review of this reaction, see C. H. Hassall, "Organic Reactions", Vol. IX, John Wiley and Sons, Inc., New York, N. Y. (1957), p. 73-106.

8) L. I. Gilbertson and G. B. King, *J. Am. Chem. Soc.*, **58**, 180 (1936).

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

10) B. Maliñák, *Chem. Listy.*, **50**, 160 (1956); *Chem. Abstr.*, **50**, 3939*a* (1956).

11) The results were presented at the 11th Annual Meeting of the Chemical Society of Japan held in Tokyo, April 3, 1958.

from path b which may include the combination between the α-hydrogen and the oxygen of peroxyselenious acid at the same time of addition of peroxyselenious acid to the carbonyl group. The former path would be more favorable to the latter because of the difficulty of such ring formation III. After the epoxidation, the peroxyselenious acid may become selenious acid which is in equilibrium with selenium dioxide and water (equation 7)[9],

$$H_2SeO_3 \rightleftarrows SeO_2+H_2O \qquad (7)$$

and the reproduced selenium dioxide will be again oxidized to peroxyselenious acid with hydrogen peroxide (equation 6).

Experimental[12]

Starting Materials.—The ketones and the solvent used in this study were commercial products. Acetone and methyl ethyl ketone were carefully purified by treatment with potassium permanganate solution according to the usual method[13]. The other ketones and *tert*-butyl alcohol, used as the solvent, were purified by fractional distillation prior to their uses. Hydrogen peroxide (30%) and selenium dioxide were from Wako Pure Chemical Industries, Ltd.

Reagent for Oxidation.—A solution containing 150 ml. of 30% hydrogen peroxide and 600 ml. of *tert*-butyl alcohol was dried over 200 g. of anhydrous sodium sulfate overnight. After separating the sodium sulfate, the concentration of hydrogen peroxide in the solution was determined by iodometry. A solution containing 68~69 mg. of hydrogen peroxide per 1 ml. was obtained, and 2 g. of selenium dioxide was dissolved in 500 ml. of the solution (corresponding to about 1 mol. of hydrogen peroxide) with stirring. Selenium dioxide-hydrogen peroxide reagent thus obtained was used in all experiments.

Oxidation of Acetone.—A 1 l. round bottomed flask was charged with 500 ml. of the selenium dioxide-hydrogen peroxide reagent (2 g. of selenium dioxide and 1 mol. of hydrogen peroxide), and 50 g. (0.86 mol.) of acetone was added slowly with stirring. The flask was then fitted with an efficient reflux condenser and was heated on a steam bath. After refluxing (79~81°C) the mixture gently for about 5 hr., the solution became brownish red owing to the deposition of metallic selenium, and the hydrogen peroxide had been completely consumed at this stage. The reaction mixture was allowed to cool to room temperature, the reflux condenser was exchanged for a Widmer-spiral and the distillation was then carried out to remove the remaining acetone-*tert*-butyl alcohol azeotropic mixture. When about 400 ml. of the azeotropic mixture was distilled off, the residue was cooled and the precipitated metallic selenium was filtered off. Ten g. of anhydrous sodium sulfate and 50 ml. of ether were added to the filtrate. After the solution was allowed to stand overnight, it was transferred to a separatory funnel and the water layer was removed and dried over anhydrous sodium sulfate. The ether and the products boiling up to 83°C were distilled off and materials of higher boiling point were fractionated through a 1×40 cm. packed column. The fraction boiling at 139.5~141°C was collected, and 26.0 g. of propionic acid was obtained (40.7% of the theoretical amount based on the quantity of acetone used); n_D^{25} 1.3852, neut. equiv. 74.8; lit.[14] b. p. 140.3°C, n_D^{25} 1.3848. Calcd. for $C_3H_6O_2$: neut. equiv. 74.1.

The infrared spectrum of the acid coincided with that of an authentic sample. *p*-Bromophenacyl ester of the acid was prepared by an usual method[15], m. p. 63.5~64°C, reported[16] 63°C. The mixed melting point with an authentic sample (63.5~64°C) was not depressed.

Anal. Found: C, 48.64; H, 4.23%. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.74; H, 4.09%.

The results of fractional distillation and the characterization of each fraction were listed in Table II.

TABLE II. DISTILLATION OF OXIDATION PRODUCTS FROM ACETONE

Fraction	B. p. °C	Vol. ml.	Characterization n_D^{25}	neut. equiv.
a-1	82~108	6.0	1.3738	90.2
a-2	108~115	2.0	1.3721	69.2
a-3	115~125	0.5	1.3781	78.5
a-4	125~135	0.6	1.3810	83.7
a-5	135~138	0.5	1.3822	80.0
a-6	138~139.5	0.9	1.3844	78.9
a-7	139.5~141	26.0	1.3852	74.8
	residue	1.7(g.)		

Fraction a-1 contained small amount of azeotropic mixture of acids and water. From the value of neutral equivalent, fraction a-2 seemed to contain the carboxylic acid lower than propionic acid. The *p*-bromophenacyl ester of fraction a-2 had melting point of 79~105°C, which indicated presumably the presence of formic acid and acetic acid: reported melting point of *p*-bromophenacyl ester of acetic acid, 85°C[16]; *p*-bromophenacyl ester of formic acid, 135°C[15]. It was presumed from the value of neutral equivalent that fraction a-3 was acetic acid which was contaminated by impurities other than carboxylic acid. Fraction a-4 was also an acid component but was contaminated by impurities. *p*-Bromophenacyl ester of fractions a-5 and a-6 were confirmed to be that of propionic acid

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[12] The boiling and melting points are uncorrected.

[13] A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, Inc., New York, N.Y. (1955).

[14] H. U. v. Vogel, "Chemiker Kalender", Springer-Verlag OHG., Berlin (1956).

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

[16] W. L. Judefind and E. E. Reid, *J. Am. Chem. Soc.*, **42**, 1043 (1920).

respectively from their melting points and mixed melting points with an authentic sample. Fraction a-7 was propionic acid, and the residue in the distilling flask consisted mainly of metallic selenium.

Oxidation of Methyl Ethyl Ketone. — To a 500 ml. of the selenium dioxide-hydrogen peroxide reagent (2 g. of selenium dioxide and 1 mol. of hydrogen peroxide) was added 62g. (0.86 mol.) of a methyl ethyl ketone, and the reaction was carried out under gentle reflux condition for 5.5 hr. The reaction mixture was concentrated through a Widmer-spiral to about 150 ml., and conducted in the same manner as described for the oxidation of acetone. The results of the fractional distillation were listed in Table III.

TABLE III. DISTILLATION OF OXIDATION PRODUCTS FROM METHYL ETHYL KETONE

Fraction	B. p. °C	Vol. ml.	Characterization n_D^{25}	neut. equiv.
b-1	102~115	1.0	1.3715	80.7
b-2	115~121	1.0	1.3756	67.7
b-3	121~137	0.4	1.3799	73.0
b-4	137~142	0.5	1.3838	77.4
b-5	142~152	1.2	1.3904	85.5
b-6	152~153.5	1.8	1.3923	88.1
b-7	153.5~156.5	21.2	1.3928	88.9
b-8	156.5~162	2.3	1.3950	89.2
b-9	162~164	4.1	1.3965	88.3
	residue	1.8(g.)		

Fraction b-1 consisted principally of the azeotropic mixture between lower carboxylic acids and water from the standpoint of the values of neutral equivalent and the refractive idex. Fraction b-2 was acetic acid which was identified, from its *p*-bromophenacyl ester m. p. 84~84.5°C; reported[16] m. p. 85°C; the depression of melting point was not shown when the ester was mixed with an authentic sample (m. p. 84.5°C).

Fraction b-3 would be possibly a mixture of acids. Fraction b-4 was identified to be propionic acid from the melting point of its *p*-bromophenacyl ester, m. p. 62.5~63°C, reported[16] m. p. 63°C; the mixed melting point with an authentic sample was not depressed. Fraction b-5 would be a mixture of acids. Fractions b-6 and b-7 were isobutyric acid, 23 g. (27.3% yield of the theoretical amont based on the quantity of methyl ethyl ketone used); the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p. 154.6°C, n_D^{20} 1.3930; Calcd. for $C_4H_8O_2$, neut. equiv. 88.1.

p-Bromophenacyl ester of the acid was prepared, m. p. 75~75.5C°, reported[16] m. p. 76.2°C. The mixed melting point with an authentic sample (m. p. 75.5°C) was not depressed.

Anal. Found: C, 50.68; H, 4.59. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.55; H, 4.60%.

Fraction b-8 would be obviously a mixture of isobutyric acid and *n*-butyric acid.

Fraction b-9 was *n*-butyric acid, 4.1 g. (4.8% yield based on the quantity of methyl ethyl ketone used); the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p, 164°C, n_D^{20} 1.3979; Calcd. for $C_4H_8O_2$, neut. equiv. 88.1.

p-Bromophenacyl ester of the acid was prepared, m. p. 62.5°C reported[16] m. p. 63°C. The mixed melting point with an authentic sample (62.5°C) was not depressed.

Anal. Found: C, 50.39; H, 4.70. Calcd. for $C_{12}H_{13}O_3Br$: C, 50.55; H, 4.60%.

Oxidation of Methyl *n*-Propyl Ketone. — To a 250 ml. (1 g. of selenium dioxide and 0.5 mol. of hydrogen peroxide of the selenium dioxide-hydrogen peroxide reagent was added 37 g. (0.43 mol.) of a methyl *n*-propyl ketone, and the mixture was treated under the gentle reflux condition for 6 hr. The reaction mixture was concentrated through a Widmer-spiral to about 70 ml. (when aqueous layer had separated) followed by addition of 5 g. of anhydrous sodium sulfate to saturate the aqueous layer. After separation, the aqueous layer was extracted with 20 ml. of ether. A mixture of the ether extract and the separated organic layer was dried over anhydrous sodium sulfate, and fractional distillation was carried out through the same column described as in the case of acetone. The results of the fractional distillation were listed in Table IV.

TABLE IV. DISTILLATION OF OXIDATION PRODUCTS FROM METHYL *n*-PROPYL KETONE

Fraction	B. p. °C	Vol. ml.	Characterization n_D^{25}	neut. equiv.
c-1	110~117	0.9	1.3733	67.5
c-2	117~122	0.3	1.3752	—
c-3	122~160	1.3	1.3875	81.3
c-4	160~166	0.4	1.3977	97.2
c-5	166~172	1.0	1.4008	101.3
c-6	172~175	3.1	1.4030	103.0
c-7	175~177	7.5	1.4044	103.7
c-8	177~182	1.1	1.4059	102.8
c-9	182~186	2.7	1.4074	104.0
	residue	2.2(g.)		

Fraction c-1 would be a mixture of lower carboxylic acids which consisted mostly of acetic acid. Fraction c-2 was identified as acetic acid from its *p*-bromophenacyl ester, m. p. 84.5°C, reported[16] 85°C; the mixed melting point with an authentic sample was not depressed. Fractions c-3 and c-4 would be a mixture of acids, and a detectable amount of *n*-butyric acid was not obtained. The greater part of fraction c-5 would consist of methyl ethyl acetic acid similar to the next fraction.

Fractions c-6 and c-7 were identified to be methyl ethyl acetic acid, 10.0 g. (22.8% yield of the theoretical amount based on the methyl *n*-propyl ketone used), the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p. 174°C (reported[15] 176°C), n_D^{20} 1.4051; Calcd. for $C_5H_{10}O_2$, neut. equiv. 102.1.

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[17] O. T. Schmidt, *Ann.*, 483, 115 (1930).

p-Bromophenacyl ester of the acid was prepared from the fraction c-7, m. p. 54.5~55°C, reported[15] 55°C; mixed melting point with an authentic sample was not depressed.

Anal. Found: C, 52.34; H, 5.36. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.06%.

Fraction c-9 was confirmed to be *n*-valeric acid, 2.5 g. (5.7% yield based on the ketone used); the infrared spectrum of the acid coincided with that of an authentic sample; lit.[14] b. p. 186.4°C, n_D^{20} 1.4086; Calcd. for $C_5H_{10}O_2$, neut. equiv. 102.1.

p-Bromophenacyl ester of the acid was prepared; m. p. 73.5~74°C, reported[17] m. p. 74°C; the mixed melting point with an authentic sample was not depressed.

Anal. Found: C, 52.01; H, 5.33. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.06%.

Oxidation of Diethyl Ketone.—To a 150 ml. (0.6 g. of selenium dioxide and 0.3 mol. of hydrogen peroxide) of selenium dioxide-hydrogen peroxide reagent was added 22.4 g. (0.26 mol.) of diethyl ketone, and the mixture was gently refluxed for 5.5 hr. The resulting reaction mixture was concentrated through a Widmer-spiral to about 50 ml. and was treated according to the same method as described in the case of methyl *n*-propyl ketone. The results of the fractional distillation were listed in Table V.

TABLE V. DISTILLATION OF OXIDATION PRODUCTS FROM DIETHYL KETONE

Fraction	B. p.	Vol.	Characterization	
	°C	ml.	n_D^{25}	neut. equiv.
d-1	103~112	1.2	—	—
d-2	112~124	0.5	1.3770	68.4
d-3	124~135	0.3	—	—
d-4	135~142	0.8	1.3860	75.4
d-5	142~160	0.6	1.3891	82.8
d-6	160~170	0.5	1.3960	91.0
d-7	170~174	0.8	1.4033	101.5
d-8	174~177	8.0	1.4040	103.1
d-9	177~179	0.3	1.4051	104.8
	residue	1.1(g.)		

Fraction d-1 was an azeotropic mixture of acids and water. Fraction d-2 was a mixture of acids which would consist mainly of acetic acid from the standpoint of the boiling range, the refractive index and the value of neutral equivalent, but the *p*-bromophenacyl ester did not give the constant melting point owing to the presence of the ester of the other acids. Fraction d-3 would be a mixture of acetic acid and propionic acid.

Fraction d-4 was identified to be propionic acid (4.1% yield based on the ketone used); *p*-bromophenacyl ester, m. p. 62.5~63.5°C, reported[16] m. p. 63°C, the mixed melting point with an authentic sample was not depressed. Fractions d-5 and d-6 would be a mixture of acids which were not identified.

Fractions d-7 and d-8 were identified to be methyl ethyl acetic acid, 8.6 g. (32.4% yield based on the quantity of diethyl ketone used); the infrared spectra of these fractions coincided with that of an authentic sample; lit.[14] b. p. 174°C (reported[15] 176°C); n_D^{20} 1.4051; Calcd. for $C_5H_{10}O_2$, neut. equiv. 102.1.

p-Bromophenacyl ester was prepared from the fraction d-8, m. p. 55°C, reported[15] m. p. 55°C; the mixture melting point with an authentic sample was not depressed.

Anal. Found: C, 51.94; H, 5.06. Calcd. for $C_{13}H_{15}O_3Br$: C, 52.19; H, 5.06%.

Oxidation of Diacetyl.—To a 130 ml. (0.52 g. selenium dioxide and 0.26 mol. hydrogen peroxide) of the selenium dioxide-hydrogen peroxide reagent was added 21.5 g. (0.25 mol.) of diacetyl. The mixture was refluxed for 6.5 hr. and then was treated in the same manner as described for the oxidation of acetone. Acetic acid (b. p. 117~119°C) was isolated by distillation and the yield was 10.8 g. (36.0% based on diacetyl used).

Summary

1) Selenium dioxide catalyzed oxidation of aliphatic ketones with hydrogen peroxide gave carboxylic acids which were produced by the rearrangement of the alkyl group as shown by equation 5.

2) Acetone, methyl ethyl ketone, methyl *n*-propyl ketone and diethyl ketone were selected as starting materials. The main rearrangement observed is due to the migration of the alkyl group having a smaller number of carbon atoms to the α-carbon atom of the larger alkyl group, and the migration of the alkyl group with a larger number of carbon atoms to the smaller one also occurs in some degree.

3) The yield of the generated acids were about 30~40% of the theoretical amounts based on the ketones used. Small amounts of cleavage products were obtained as the by-products in all cases. Both of the cleavaged groups from a ketone were oxidized to acids in these reaction systems.

4) The most probable catalytic form seems to be peroxyselenious acid which may be produced by the oxidation of selenium dioxide with hydrogen peroxide (equation 6). Inferential reaction mechanism was discussed.

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