Preparation of Carboxylic Acids from Hydroxy Compounds by Oxidation with Ozone

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ABSTRACT

Various mono- and dicarboxylic acids were obtained with appreciable yields from saturated hydroxy compounds by oxidation in aqueous acetic acid with a mixture of ozone and oxygen followed with oxygen. The starting materials and the mono- and dicarboxylic acids obtained were as follows: Primary alcohols $RCH_2OH \rightarrow RCOOH$; α,ω-glycols $HOCH_2(CH_2)_nCH_2OH \rightarrow HOOC(CH_2)_nCOOH$; secondary alcohols and 12-hydroxyoctadecanoic acid $R_1CH_2CH(OH)CH_2R_2 \rightarrow R_1COOH + R_2CH_2COOH + R_1CH_2COOH + R_2COOH$; alicyclic alcohols $CH_2(CH_2)_nCHOH \rightarrow HOOC(CH_2)_nCOOH$; 9,10-dihydroxyoctadecanoic acid $CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7COOH \rightarrow CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$. Small amounts of aldehydes, ketones, and carboxylic acids having fewer carbon atoms than those of the carboxylic acids formed as main products were also detected from some of the oxidation products.

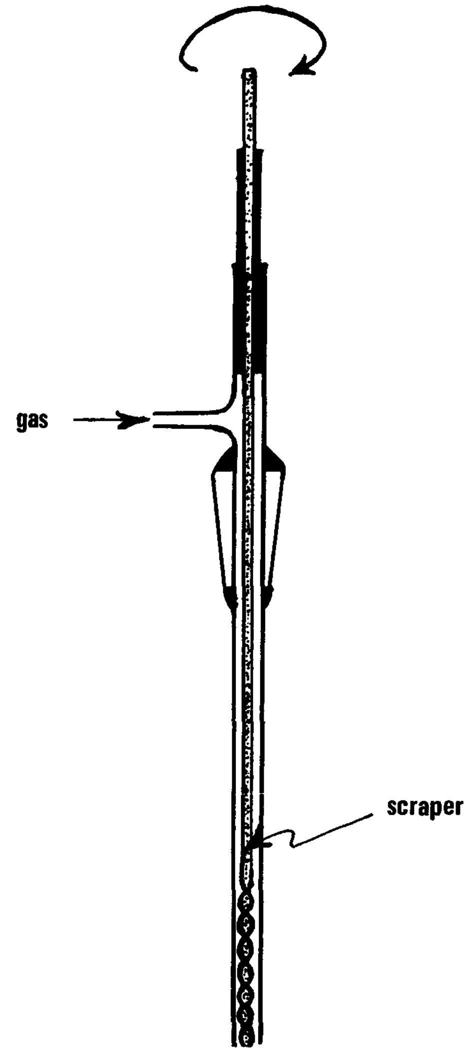


FIG. 1. The glass tube with a scraper.

INTRODUCTION

Many papers on the addition of ozone to unsaturated compounds have been published, but studies on the oxidation of saturated compounds with ozone have been rarely carried out. Alcohols are converted to aldehydes, ketones, or carboxylic acids by a variety of oxidizing agents, but reports are infrequent on the use of ozone as an oxidant for this purpose. By oxidation with ozone, carboxylic acids were formed from lower aliphatic (1-6) or alicyclic (7-12) alcohols, and ketones were also formed from secondary alcohols (10-13). But investigations of oxidation with ozone as a general preparative method for carboxylic acids have not been carried out.

The authors have tried to obtain mono- and dicarboxylic acids by the oxidation of saturated compounds with ozone. In the present investigation, hydroxy compounds such as aliphatic and alicyclic alcohols, α,ω-glycols, and mono- and dihydroxycarboxylic acids were used as the saturated compounds. The reaction consisted of two steps in which a hydroxy compound was oxidized with an ozone-oxygen mixture followed with oxygen. By the first-step oxidation, hydroxy compounds were converted to mono- and dicarboxylic acids. In the second-step oxidation, unstable compounds such as peroxides and carbonyl compounds which were existent in the solution after the first-step oxidation had been carried out were decomposed or oxidized.

By the oxidation procedure described above, mono- and dicarboxylic acids were obtained with appreciable yields from saturated hydroxy compounds.

EXPERIMENTAL PROCEDURES

Starting Materials

3-Methyl-1-butanol, 2-ethyl-1-hexanol, 1-decanol, 1-hexadecanol, 4-nonanol, 2-tetradecanol, and cyclohexanol were purified by distillation. 12-Hydroxyoctadecanoic acid was purified by recrystallization from aqueous acetone. 9,10-Dihydroxyoctadecanoic acid (mp 94-95 C) was prepared by the oxidation of oleic acid with hydrogen peroxide-formic acid, and the crude product obtained was purified by recrystallization from 95% ethanol (14). 1,4-Butanediol, 1-10-decanediol, and cyclododecanol were purchased from Tokyo Chem. Ind. Co., and used without purification.

Gas chromatograms of each starting material showed a single peak.

Oxidation Procedure

A starting material (4-5 g) was dissolved in 25 to 30 ml of 80 to 90% aqueous acetic acid in a 50 ml three-necked flask equipped with a gas inlet, a stirrer, and a condenser. A trap immersed in an ice-cold bath was connected to an outlet of the condenser. The gas inlet was used with a glass ball filter (Kinoshita Co., No. 1) or a glass tube with a scraper shown in Figure 1. The glass tube was employed in case a stream of the reaction gas was interfered with by the products or starting materials which were deposited as crystals on the glass ball filter during the reaction (e.g., glycols, alicyclic alcohols, and dihydroxy acid).

In the first-step oxidation, the reaction temperature for

TABLE I

Oxidation Results of Various Hydroxy Compounds

Starting material	Conversion, %	Compound	Yield, %	By-products[a]
3-Methyl-1-butanol	87.4	Isovaleric acid	82.4	Isovaleraldehyde, isobutyraldehyde, acetone
2-Ethyl-1-hexanol	98.5	2-Ethylhexanoic acid	84.1	Butyric and propionic acids, 3-heptanone
1-Decanol	79.0	Decanoic acid	88.6	Nonanoic acid, decanal
1-Hexadecanol	74.5	Palmitic acid	76.8	Pentadecanoic, myristic, tridecanoic, and lauric acids, hexadecanal
1,4-Butanediol	100.0	Succinic acid	57.5	– – – –
1,10-Decanediol	95.4	Sebacic acid	68.9	10-Hydroxydecanoic and sebacaldehydic acids
4-Nonanol	83.7	Propionic acid	15.8	– – – –
		Butyric acid	33.6	
		Valeric acid	14.3	
		Hexanoic acid	18.5	
2-Tetradecanol	53.8	Tridecanoic acid	27.3	Undecanoic (7.4), decanoic, nonanoic, octanoic, and heptanoic acids, 2-decanoene (5.4)
		Lauric acid	28.3	
12-Hydroxyocata decanoic acid	73.0	Dodecanedioic acid	31.8	12-Oxsodecanoic acid
		Undecanedioic acid	19.4	
		Heptanoic acid	42.6	
		Hexanoic acid	23.5	
Cyclohexanol	93.0	Adipic acid	60.2	Glutaric (10.6) and succinic (4.3) acids, cyclohexanone (14.0)
Cyclododecanol	92.9	Dodecanedioic acid	38.8	Undecanedioic (8.6), sebacic (2.9), azelaic, suberic, pimelic, and adipic acids, cyclododecanone (15.9)
9,10-Dihydroxy octadecanoic acid	92.0	Nonanoic acid	78.0	– – – –
		Nonanedioic acid	89.8	

[a] Figures in parenthesis: yield %; others were trace amounts.

the compounds having a primary hydroxyl group was kept to 20-40 C according to the solubilities of starting materials in the solvent, and that for the compounds having a secondary hydroxyl group was kept to 85-90 C, except 2-tetradecanol and 9,10-dihydroxyoctadecanoic acid which were carried out at 25 C and 47 C, respectively.

The flask was put in a water bath warmed or cooled to the reaction temperature of the first step of the oxidation. Then the aqueous acetic acid solution of the starting material was stirred and ice-cold water was passed through the condenser.

The ozone-oxygen mixture (flow rate: 270 ml/min, O_3: 0.35 mmol/min) was blown into the solution until the amount of ozone reached the molar ratio of 2-3 mol of ozone to 1 mol of a hydroxyl group or vicinal hydroxyl groups.

The second-step oxidation was performed by the blowing of oxygen (flow rate: 200 ml/min) at 85 to 90 C for 15 to 30 min.

Treatment of the Oxidation Products

After the oxidation, the reaction solution of 3-methyl-1-butanol or 4-nonanol was poured into a 100 ml measuring flask, and the volume was adjusted to 100 ml with acetone. The other reaction solutions were distilled at 24-40 C/65-80 mmHg, and the oxidation products were obtained as the residues. No further treatment was applied to the oxidation products from 12-hydroxyoctadecanoic acid and cyclohexanol. The oxidation product of 1,4-butanediol was dissolved in chloroform, and dibasic acid was obtained as an insoluble substance. The oxidation product of 9,10-dihydroxyoctadecanoic acid was extracted with a mixture of hot water (50-60 C) and hexane, and dibasic and monobasic acids were obtained from the water layer and hexane layer, respectively. The unreacted dihydroxy acid was also obtained as an insoluble substance in the solvents. The oxidation products of 2-ethyl-1-hexanol, 1-decanol, 1-hexadecanol, 1,10-decanediol, 2-tetradecanol, and cyclododecanol were saponified with an ethanol solution of potassium hydroxide (1N). After some of the water was added, unsaponified materials were extracted with ether. The water layer was acidified with hydrochloric acid (1:1), and acidic substances were extracted with ether.

Identification and Determination of the Oxidation Products

Gas liquid chromatography (GLC) and gas chromatography-mass spectrometry (GC-MS) were used for the identification and determination of the oxidation products. GLC was carried out with a Shimadzu Gas Chromatograph 4BPTF equipped with dual columns (3 mm x 2 m) packed with Tenax GC or 15% SE-30/Chromosorb WAW. GC-MS was carried out with a Shimadzu LKB-9000 Gas Chromatograph-Mass Spectrometer equipped with a column (3 mm x 2 m) packed with Tenax GC or 10% SE-30/Chromosorb WAW, and the ionization intensity was 70 eV.

The Tenax GC columns were used for the solution prepared from the reaction solution of 3-methyl-1-butanol or 4-nonanol, and for the oxidation product of 2-ethyl-1-hexanol. The SE-30 columns were used for samples obtained by the reaction of other oxidation products with diazomethane.

The identification of the oxidation products was established by the comparison of the data from GLC and GC-MS of the products with those of authentic samples.

RESULTS AND DISCUSSION

Table I presents the results of the oxidation of various hydroxy compounds.

Primary alcohols and α,ω-glycols were oxidized to the corresponding mono- and dicarboxylic acids, respectively. The conversion of each starting material was fairly high, therefore, it was shown that a primary hydroxyl group is oxidized with ozone easily under mild conditions. The formation of aldehydes corresponding to the starting materials suggests that the aldehydes are intermediates on the reaction.

Four kinds of carboxylic acids were formed by the oxidation of secondary alcohol and the monohydroxycarboxylic acid, respectively.

Alicyclic alcohols were also oxidized to dicarboxylic acids.

In the oxidation of 4-nonanol and 12-hydroxyoctadecanoic acid, it was shown that the yields of butyric and heptanoic acids were higher than the yields of other acids (Table I), but the cause of these selective high yields is not clear.

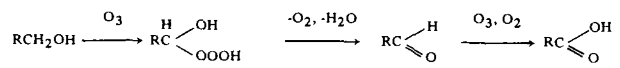
Acetic and formic acids which may be formed in oxidation of 2-tetradecanol were not analyzed because the lower acids were indistinguishable from aqueous acetic acid used as the solvent.

Ketones were contained in the oxidation products of 2-tetradecanol, 12-hydroxyoctadecanoic acid, cyclohexanol, and cyclododecanol, and their amounts were fairly large in alicyclic alcohols. From these results, it is assumed that the oxidation of compounds having secondary hydroxyl group proceeds via ketone formation.

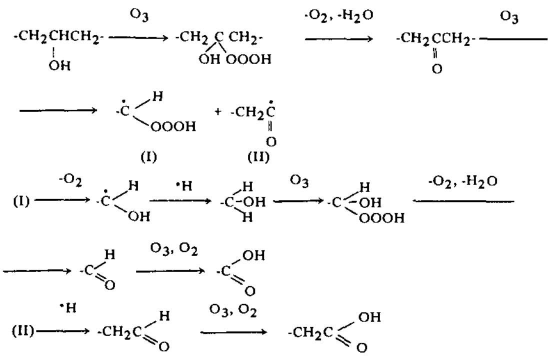
The carbon-carbon bond of vicinal hydroxy groups of 9,10-dihydroxyoctadecanoic acid was cleaved selectively with ozone, and the conversions to nonanoic and nonanedioic acids were both satisfactory.

For the reaction steps from hydroxyl groups to carboxylic groups, a mechanism involving the formation of hydrotrioxide (4,15) has been considered.

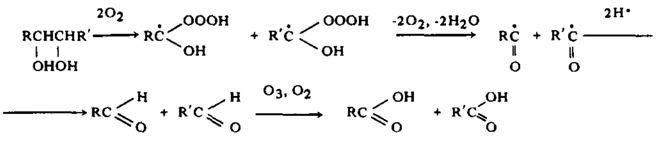
Primary hydroxyl group:



Secondary hydroxyl group:



Vicinal hydroxyl groups:



Carboxylic acids having fewer carbon atoms than those of the starting materials or main products were also formed in the oxidation of 2-ethyl-1-hexanol, 1-hexadecanol, 2-tetradecanol, cyclohexanol, and cyclododecanol. It is assumed that the shorter chain carboxylic acids were formed by the oxidative cleavage of a carbon-carbon bond of methylene linkage and/or the decarboxylation of carboxylic acid formed.

Substances collected in the trap were 0.2-0.5 g in each experiment. The main substance collected was acetic acid used as the solvent, though trace amounts of oxidation products of lower acids or carboxyl componds were contained in the substances collected in the oxidation of 3-methyl-1-butanol, 2-ethyl-1-hexanol, 4-nonanol, and cyclohexanol.

The compounds having a primary hydroxyl group or vicinal hydroxyl groups were oxidized with ozone easily to carboxylic acids at lower temperature. On the other hand, the ozone oxidation of the compounds having a secondary hydroxyl group to carboxylic acids required generally higher temperatures than the former.

The present investigation shows that ozone is an effective oxidant for the preparation of carboxylic acids from aliphatic and alicyclic compounds having a hydroxyl group.

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