EXPERIMENTAL

2-Hydroxydiethyl sulfoxide. 2-Hydroxydiethyl sulfide (74.3 g., 0.70 mole) was placed in an 800 ml. beaker containing 225 ml. water and 10 ml. concentrated hydrochloric acid. Bromine was added to the well stirred mixture from a buret having a long capillary tip that extended below the surface of the solution. The rate of addition was regulated so that the bromine reacted as fast as it was added. Water was added at intervals to reduce the hydrobromic acid concentration, until the final volume of the mixture was about 500 ml. Near the equivalence point (indicated by slight persistence of color) the rate of addition of bromine was reduced and the final additions were made dropwise until one drop colored the mixture yellow.

The mixture was diluted to 2000 ml. and passed in two 1000 ml. portions through a column containing about 400 g. moist IR-4B resin. The column was washed with water until a total of 3000 ml. neutral solution had been collected.

The sulfoxide solution was concentrated in a flash vacuum evaporator and the remaining water removed at 60° C. under 10 mm. pressure. The product was finally distilled in a molecular still at 54° C. A yield of 70% was obtained with much of the loss mechanical. Analysis by a modified method of Barnard[7-9] for sulfoxide indicated 100.4 ± 0.7% sulfoxide.

Calcd. for $C_4H_{10}OS$: S, 26.26. Found: S, 26.47.

The product had a density of 1.1685 25°/4°, and a refractive index, n_D^{25} 1.5019. The vapor pressure at 54° C. was estimated from molecular distillation data at about 3 microns.

Department of Agricultural Chemistry
State College of Washington
Pullman, Wash.

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(7) D. Barnard and K. R. Hargrave, *Anal. Chim. Acta*, 5, 476 (1951).

(8) D. Barnard and K. R. Hargrave, *Anal. Chim. Acta*, 5, 536 (1951).

(9) R. R. Legault and K. Groves, unpublished manuscript.

Nitric Acid Oxidation of 5,14-Octadecanedione

Charles M. Selwitz and A. C. Whitaker

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To study the effect of the nitric acid oxidation of a long paraffin chain containing two distantly placed carbonyl groups, 5,14-octadecanedione was oxidized with 50% nitric acid at 55°. The diketone was prepared in 50% yield by a modification of Cason's[1] method for preparing keto esters, whereby sebacyl chloride was added to di-*n*-butyl cadmium. Random attack on either side of the carbonyl groups of the diketone should have given 25% sebacic, 50% azelaic, and 25% suberic acid, and the theoretical amounts of the eight and ten carbon dibasic acids were found (Table I). However, far less than the theoretical yield of azelaic acid resulted, and smaller quantities of the four to seven carbon acids were also found.

TABLE I

Molar Yield of Dibasic Acids

Acid	Yield: %
Sebacic	25.8
Azelaic	14.6
Suberic	24.2
Pimelic	8.7
Adipic	7.0
Glutaric	8.2
Succinic	5.3
	93.8

Apparently azelaic acid was degraded to the smaller acids. This tendency of higher molecular weight dicarboxylic acids having an odd number of carbon atoms to break down more readily into shorter chain dicarboxylic acids than those having an even number of carbon atoms has been noted by others.[2]

EXPERIMENTAL

Preparation of Diketone. To 24.3 g. (1.0 mole) of magnesium covered with 150 ml. of dry ether was added 137 g. (1.0 mole) of *n*-butyl bromide in 350 ml. of ether over a period of 1.5 hr. The reaction mixture was refluxed for 15 min. and cooled, and to it was added 100 g. (0.54 moles) of anhydrous cadmium chloride. After the mixture was refluxed with stirring for 1 hr., the ether was stripped, 350 ml. of benzene was added, and, after the removal of 100 ml. of benzene by distillation, an additional 350 ml. of benzene was added. The mixture was stirred and refluxed for a few minutes to disperse solids, the heat was removed, the mixture was cooled with an ice bath, and 100 g. (0.40 moles) of sebacyl chloride, dissolved in 150 ml. of benzene, was added to the vigorously stirred solution over a 0.5 hr. period. The heat of reaction caused the mixture to reflux, although the flask was immersed in an ice bath. After the addition was complete, stirring and refluxing were continued for 2 hr., during which time it was necessary to apply heat.

To the product was added 600 ml. of ice water and then a large excess of 20% sulfuric acid. After the further addition of benzene and the separation into two phases, the undissolved solids were removed from each layer by filtration. The benzene solution was extracted successively with 200 ml. of water, 200 ml. of 5% sodium carbonate, 200 ml. of water, and 100 ml. of saturated sodium chloride solution and then passed through a column of anhydrous sodium sulfate. The aqueous phase was extracted with three 150 ml. portions of benzene, which were added to 200 ml. of a hot benzene solution of the gum in the original flask. This was washed and dried as above and added to the initial solution. After stripping the benzene the diketone was obtained by distillation as 56 g. (0.20 moles; 50%) of a colorless, hard, waxy solid boiling at 191° at 6.7 mm., and melting, after two recrystallizations from hexane, at 75.6–76.0°.

Anal. calcd. for $C_{18}H_{34}O_2$: C, 76.50; H, 12.08; mol. wt., 282. Found: C, 75.87; H, 11.87; mol. wt., 270.

Oxidation of Diketone. To 100 ml. of 50% nitric acid and 0.1 g. vanadium pentoxide in a 500 ml. 3-neck flask equipped with stirrer and vented reflux condenser was added 5.64 g. (0.05 moles) of 5,14-octadecanedione in small increments over a 4 hr. period while the temperature was maintained at 54.8–55.3°. The oxidation was marked by the evolution of brown nitrogen oxide fumes. Heating was maintained for another 2.5 hr.

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(1) J. Cason and F. S. Prout, *Org. Syntheses*, **Coll. Vol. III**, 601 (1955).

(2) R. L. Logan, U. S. Patent **2,662,908** (December 15, 1953).

The oxidation product was neutralized with 20% NaOH at 0°, and water was carefully evaporated from aliquot portions. The dry salts were acidified with minimum quantities of concentrated hydrochloric acid, and then extracted with four 10-ml. portions of ether. The residues after the evaporation of ether and monobasic acids were analyzed for dibasic acids by liquid partition chromatography.[3]

Gulf Research and Development Company
Post Office Box 2038
Pittsburgh 30, Pa.

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(3) T. Higuchi, N. C. Hill, and G. B. Corcoran, *Anal. Chem.*, **24**, 491 (1952).

Reaction of *Exo*-norbornylene Oxide with Hydrogen Bromide[1,2]

H. M. Walborsky and D. F. Loncrini

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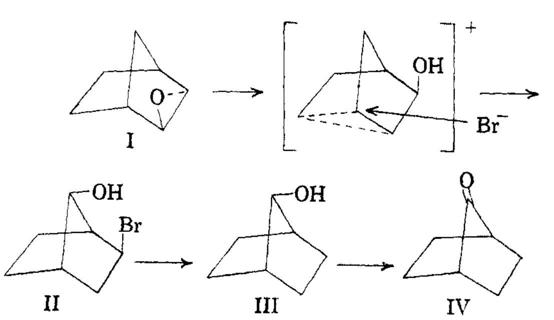
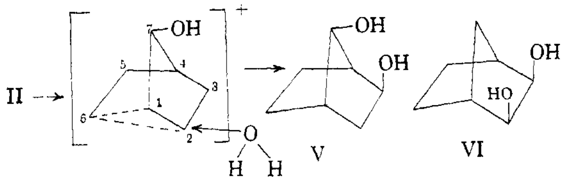
It has previously been demonstrated[3] that the reaction of norbornylene with peracetic acid yields the *exo*-norbornylene oxide (I). Treatment of I with hydrogen bromide produced a bromohydrin (II) as the main product.[2] The structure of II has been tentatively assigned as 2-*exo*-bromo-7-*syn*-hydroxy-norbornane based on analogy to the product formed by the hydrolysis[3] of I.



That the hydroxyl group is located at the 7-position was established by treating II with hydrogen and palladium to yield the known 7-hydroxynorbornane (III).[4] Oxidation of III yielded ketone IV which was isolated as the 2,4-dinitrophenylhydrazone.



Hydrolysis of II did not produce the rearranged product (VI) but yielded V.[2] Apparently the hydroxyl group at C-7 shields C-1 from attack by solvent so that reaction occurs at C-2. A similar observation has been made by Roberts[5] who obtained 2-*exo*-hydroxy-*syn*-7-chloronorbornane from the basic hydrolysis of *exo*-*syn*-2,7-dichloronorbornane.

EXPERIMENTAL[6]

2-exo-Bromo-7-syn-hydroxy-norbornylene (II). To 36 ml. of 48 per cent hydrobromic acid, cooled to 10°, was slowly added 20 g. (0.18 mole) of *exo*-norornylene oxide. The temperature was not allowed to rise above 15° during the addition. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium carbonate, dried over anhydrous sodium sulfate, and stripped. The residual oil was distilled to yield 13.5 g. (39%) of product, b.p. 98–100° (5 mm.), m.p. 75.5–76° from ether-pentane. An oil was also isolated but not identified.

Anal. calcd. for $C_7H_{11}BrO$: C, 43.94; H, 5.80; Br, 41.82. Found: C, 43.97; H, 6.00; Br, 41.78.

7-Hydroxynorbornane (III). Five grams (0.026 mole) of II dissolved in ethanol was hydrogenated using one gram of 10% palladium on charcoal catalyst. The reaction mixture was filtered, solvent stripped *in vacuo*, and the residue taken up in pentane. The pentane solution was dried over Drierite and stripped to yield 2.7 g. (92%) of III, m.p. 149–150° (Lit.[4] m.p. 149–150°).

The phenylurethan derivative melted at 138–139° from acetonitrile.

Anal. calcd. for $C_{14}H_7O_2N$: C, 72.72; H, 7.31; N, 6.66. Found: C, 72.78; H, 7.38; N, 6.69.

Norbornone-7. To a solution of 1 g. (0.008 mole) of III in 4 ml. of glacial acetic acid was slowly added a solution of 0.54 g. (0.0054 mole) of chromium trioxide in 10 ml. of acetic acid. The mixture was stirred for several hours at room temperature and extracted with pentane. Removal of the solvent yielded 0.2 g. (20%) of an oil with a strong camphoraceous odor. The oil was converted to the 2,4-dinitrophenylhydrazone which melted at 133–134° (Lit.[4] 133–134°).

exo-syn-2,7-Dihydroxynorbornane (V). To an aqueous solution of lithium carbonate was added 2 g. (0.001 mole) of II. The mixture was refluxed for several hours and then continuously extracted with ether. The ether extract was dried over anhydrous sodium sulfate and stripped to yield 1.1 g. (91%) of V, m.p. and mixed m.p. 180–181°. The diphenylurethan derivative m.p. and mixed m.p. 221–222°.

Department of Chemistry
Florida State University
Tallahassee, Fla.

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(1) This paper is based on a portion of the thesis submitted by D. F. L. in 1956 to the Florida State University in partial fulfillment of the requirements for the Ph.D. degree in chemistry.

(2) During the preparation of this manuscript a communication appeared describing this reaction (Winstein and Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957)).

(3) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

(4) Dissertations by P. Wilder, Jr. (1950) and R. E. Vanelli (1950) at Harvard University. S. Winstein, M. Shatovsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatovsky, **78**, 592 (1956).

(5) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

(6) All melting points and boiling points are uncorrected.