

3-Alkoxypropionic acids were readily prepared by the cyanoethylation of an alcohol<sup>4</sup> and hydrolysis of the 3-alkoxypropionitrile thus formed with mineral acid.<sup>5</sup> Esterification was accomplished by the usual azeotropic technique. Physical properties for the several 3-alkoxypropionic acids are given in Table I and the data concerning the glycol esters are shown in Table II.

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(4) H. A. Bruson, *Org. Syntheses*, **V**, 122 (1948).

(5) R. V. Christian and R. M. Hixon, *J. Am. Chem. Soc.*, **70**, 1334 (1948).

### Cyclic Peroxide By-product from the Alkaline Epoxidation of Mesityl Oxide

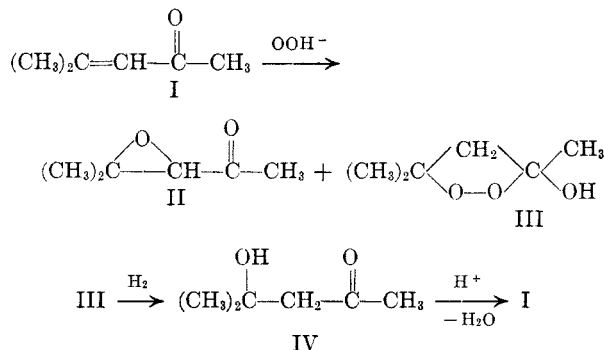
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The alkaline epoxidation of mesityl oxide, 4-methyl-3-penten-2-one (I), to give 3,4-epoxy-4-methyl-2-pentanone (II), has been carried out several times in the past.<sup>1</sup> Nazarov and Akhrem,<sup>1d</sup> however, were the only ones to separate and purify a slightly higher boiling by-product. They established its formula as C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>(OH) by carbon and hydrogen and hydroxyl analysis.

Using a modification of the procedure employed by Wilder and Dolnick<sup>1b</sup> we have carried out the epoxidation of mesityl oxide and obtained the high boiling impurity in 3% yield along with an 85% yield of II. Its structure has been established as 3-hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane (III) by ultimate analysis, peroxide titration, qualitative reaction with ferrous ion and by quantitative hydrogenation to 4-methyl-4-hydroxy-2-pentanone (IV). The latter, when allowed to react with 2,4-dinitrophenylhydrazine under acidic conditions, afforded the 2,4-dinitrophenylhydrazone of mesityl oxide (I). An authentic sample of IV exhibited this same behavior.

(1) (a) Weitz and Scheffer, *Ber.*, **54**, 2327 (1921); (b) Wilder and Dolnick, U. S. Patent **2,431,718** (Dec. 2, 1947); (c) Bunton and Minkoff, *J. Chem. Soc.* 665 (1949); (d) Nazarov and Akhrem, *J. Gen. Chem. (U.S.S.R.)*, **20**, 2183 (1950); *Chem. Abstr.*, **45**, 7062 (1950); (e) House and Wasnon, *J. Am. Chem. Soc.*, **78**, 4394 (1956).



The infrared spectrum of III, with the exception of the presence of a strong band for hydroxyl, was markedly similar to that recently given for 3,3,5,5-tetramethyl-1,2-dioxacyclopentane.<sup>2</sup>

### EXPERIMENTAL

3-Hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane (III) and 3,4-epoxy-4-methyl-2-pentanone (II). To a 3-l. round-bottom flask equipped with stirrer, thermometer, and dropping funnel were charged 450 ml. of water and 392 g. (4.0 moles) of freshly distilled mesityl oxide. With stirring was added a solution of 8 g. of sodium hydroxide in 100 ml. of water followed by 5 g. of magnesium sulfate dissolved in 50 ml. of water. With vigorous stirring and ice bath-cooling to maintain a temperature of 25–30°, there was then added 555 g. (5.0 moles) of 30% hydrogen peroxide over a period of 40 min. After stirring an additional 2 hr., 200 g. of sodium sulfate was added followed, 0.5 hr. later, by 400 ml. of benzene. After another 0.5 hr. of stirring, excess salt was removed by filtration and washed with 50 ml. of benzene. Distillation of the benzene layer of the filtrate through a 10-tray Oldershaw column afforded 387 g. (85%) of 3,4-epoxy-4-methyl-2-pentanone, b.p. 61–62° (20 mm.);  $n_D^{20}$  1.4235 (reported<sup>1b</sup> values: b.p. 155.5–157.5°;  $n_D^{20}$  1.4238).

The 28 g. residue from the above distillation was distilled through an 18-in. glass spiral packed column to give 16 g. (3%) of 3-hydroxy-3,5,5-trimethyl-1,2-dioxacyclopentane, b.p. 69–70° (10 mm.);  $n_D^{20}$  1.4320 (reported<sup>1d</sup> values: b.p. 79–81°/15 mm.;  $n_D^{20}$  1.4328).

The infrared spectrum exhibits strong bands at 2.91 $\mu$  (hydroxyl) and at 6.88, 7.32, 7.68, 10.31, 11.25, 11.52 (probably O—O stretching) and 12.6 $\mu$ . 3,3,5,5-Trimethyl-1,2-dioxacyclopentane is reported<sup>2</sup> to exhibit strong bands at 6.86, 7.32, 7.67, 11.47, and 12.55 $\mu$  along with weaker bands at 10.28 and 11.22 $\mu$ .

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>O<sub>3</sub>: C, 54.5; H, 9.2; active O, 12.1. Found: C, 54.5; H, 9.2; active O, 11.8.<sup>3</sup>

*Reaction of III with hydrogen.* Conversion to 4-methyl-4-hydroxy-2-pentanone (IV). Ten g. of cyclic peroxide III (0.076 mole) and 100 ml. of methanol were charged to a 450 ml. capacity glass hydrogenation bottle along with 1 g. of 5% palladium on barium sulfate catalyst. The mixture was shaken at room temperature with hydrogen at a starting pressure of 50 lb. Within 1 hr., 0.074 mole of hydrogen had been absorbed and the rate of uptake was then very slow. Distillation of the filtered solution afforded 7.2 g. of 4-methyl-4-hydroxy-2-pentanone, b.p. 56–61° (10 mm.);  $n_D^{27}$  1.4204. The refractive index of Eastman Kodak Co. White Label diacetone alcohol, taken at the same time, was  $n_D^{27}$  1.4200.

(2) Criegee and Paulig, *Ber.*, **88**, 712 (1955).

(3) Sample heated with 56% aqueous hydrogen iodide in glacial acetic acid at 60° for 45 minutes, liberated iodine titrated with standard thiosulfate; milder methods of analysis gave lower values.

The 2,4-dinitrophenylhydrazone<sup>4</sup> of the distillate melted initially at 175–180°, but after two recrystallizations from ethyl acetate it melted at 196–197°. The 2,4-DNP prepared from authentic diacetone alcohol exhibited the same melting point behavior. The mixed melting point between the two recrystallized samples was not depressed. A mixed melting point with the 2,4-DNP prepared from I (m.p. 196–197°) was also not depressed.

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(4) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York 1948, p. 143.

### Bromination of Naphthalene with Dioxane Dibromide

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Yanovskaya<sup>1,2</sup> has reported the quantitative preparation of 1,4-dibromonaphthalene by the reaction of naphthalene with dioxane dibromide in a one to two mole ratio, at 40°. We have attempted this preparation and find that it is neither quantitative nor specific for the 1,4-dibromonaphthalene, 1,5-dibromonaphthalene and 2-bromonaphthalene also being formed.

#### EXPERIMENTAL

The bromination was studied varying the temperature and the time of the reaction. In two runs, solutions of the products were analyzed by means of infrared spectrophotometry. The absorption frequencies (in wave numbers) used for analysis are: naphthalene, 782, 955, 1010; 1-bromonaphthalene, 768, 794; 2-bromonaphthalene, 742, 812, 887; 1,4-dibromonaphthalene, 760, 823; 1,5-dibromonaphthalene, 704, 782.

Bromine, 17.0 g. was added to 9.5 g. of dioxane (0.106 moles of dioxane dibromide) in a 100 ml. round-bottom flask. To this solid complex, 6.4 g. (0.05 moles) of naphthalene was added. The reaction began immediately, the mixture turned a deep red, the temperature rose to 39° and HBr fumes were evolved. The mixture was stirred periodically for 3 hr. and some solid formed; it was left standing overnight. After being made basic to litmus with 10% NaOH, white crystals formed and were filtered, washed with water, and recrystallized from 95% ethanol. The yield was 9.9 g. of crude material, (70%) and had a melting point of 77–80°. It contained about 78% of the 1,4-isomer, the balance being the 1,5-isomer with a trace of 1-bromonaphthalene.

The above crude product was recrystallized twice from absolute methanol. The melting point was 83–83.5°. The infrared spectrum showed trace amounts of impurities.

Dioxane dibromide, 24.8 g. (0.1 moles) was added to 6.4 g. of naphthalene (0.05 moles) in a 300 ml., three neck round-bottom flask. Two of the necks were left open so that there was ample room for the HBr to escape. After standing

(1) L. A. Yanovskaya, *Doklady Akad. Nauk SSSR*, **17**, 693 (1950).

(2) A. P. Terent'ev, L. I. Belen'kii, and L. A. Yanovskaya, *Zhur. Obshchei Khim.*, **24**, 1265 (1954).

an hour, the liquid mixture was stirred and maintained at 40° for 6 hr. by means of a water bath. It was then allowed to stand overnight. The reaction mixture was neutralized with 10% NaOH and filtered. A white crystalline residue (7.240 g.) was air dried. It contained about 95% 1,4-dibromonaphthalene, the remainder being the 1,5-isomer and 1-bromonaphthalene. The oil, (3.6068 g.) from the above filtration, was washed with water, and taken up in ether. A qualitative analysis showed it to be mainly 1-bromonaphthalene and 1,4-dibromonaphthalene. There was estimated to be about 10% 1,5-dibromonaphthalene and about 5% 2-bromonaphthalene in the oil.

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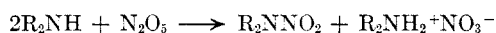
### Nitration of Amines with Dinitrogen Pentoxide<sup>1</sup>

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In spite of the fact that dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, has been known for many years, its use as an alkaline nitration reagent for amines has not been investigated generally. A number of aromatic amines have been converted to the corresponding nitramines with dinitrogen pentoxide<sup>4,5</sup> but other than a report that triethylamine and dinitrogen pentoxide form an unstable explosive complex,<sup>6</sup> aliphatic amines do not appear to have been investigated.

It has been found that secondary aliphatic amines react smoothly with dinitrogen pentoxide to give secondary nitramines in excellent yields.



The reactions were carried out by addition of dinitrogen pentoxide in carbon tetrachloride solution to excess amine also in carbon tetrachloride at –25°. Yields obtained with a number of amines are summarized in Table I. The yields of nitramines obtained in this way are excellent testimony to the effectiveness of dinitrogen pentoxide for the preparation of secondary nitramines. This is particularly true for the branched secondary amines which gave essentially quantitative conversions to the nitramines; it will be recalled that acetone cyanohydrin nitrate was virtually ineffective with those

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(4) E. Bamberger, *Ber.*, **27**, 584 (1894); **28**, 397 (1895).

(5) E. Hoff, *Ann.*, **311**, 91 (1900).

(6) L. B. Haines and H. Adkins, *J. Am. Chem. Soc.*, **47**, 1419 (1925).