[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE]

# Higher 2-Alkyl Ethers of 1,3-Dibromopropane

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Studies in the synthesis of 2-alkoxyl-1,3-dihalogenated propane have been made by Reboul-Lourenço[2] and Paal.[3] These investigators have synthesized the mixed 1,3-dihalogenated substituted compounds. Hess[4] and Hibbert,[5] however, have prepared the symmetrical dichloro methyl ether of propane.

It has been shown[6] that 1,3-dibromo-2-methoxypropane is formed by the action of mercuric acetate in methanol upon allyl bromide, with subsequent treatment of the resulting 1-bromo-2-methoxy-3-acetoxymercuripropane with bromine. In the present paper it is shown that this reaction can be applied to the preparation of higher homologous alkyl ethers. It is of interest that the alkoxyl group invariably attaches itself to the center carbon atom rather than at the end of the chain, as would be predictable from the electronic conception $C^+H_2{=}C^-H{-}C^+H_2Br^-$.

## Experimental

In the preparation of the higher homologous ethers 0.3 mole of pure, dry, redistilled allyl bromide, 83.7 g. of mercuric acetate, and 0.8 liter of the necessary absolute alcohol were used in each case. In order to give an idea of the procedure, the one used in the case of the methoxy compound[6] is presented in brief.

**Preparation of 1,3-Dibromo-2-methoxypropane.**—One mole of pure, dry, redistilled allyl bromide was dissolved in absolute methanol, and 5–10% less than one mole of mercuric acetate was added. The best ratio of the reagents appeared to be: 13 g. of allyl bromide, 30 g. of mercuric acetate, and 300 cc. of methyl alcohol. The mixture was allowed to stand at room temperature with occasional shaking. At the end of ten days the reaction was complete, as was evident by the test in which no yellow precipitate was obtained when a few drops of the reaction mixture were shaken with 5% sodium hydroxide solution. The reaction mixture was then filtered into a Claissen flask, and the contents distilled *in vacuo* from a water-bath. The distillation was continued until all of the methanol and most of the acetic acid were removed. At 13 mm. the temperature of the bath was allowed to rise to 65–70°. The residual liquid was a pale, yellowish-green oil. The yield at this point was quantitative. It was treated with distilled water (4 liters for 230 g. of allyl bromide), and one mole of potassium bromide was added. One-tenth mole of pure liquid bromine, in small portions at a time, was dropped slowly into the mixture. After this addition the supernatant water solution was siphoned off, and the oil was removed from any residual water by means of a separatory funnel. This oil (the mercuric salt complex) was found to be soluble in ether, and could not be distilled without decomposition. It was poured into a steam distilling apparatus to which were also added 100 cc. of water and 35 g. of potassium bromide (for 230 g. of allyl bromide), and the whole was steam distilled. The substance which passed over with the steam possessed a sharp, penetrating odor resembling closely that of horse-radish. It was extracted with diethyl ether, the ethereal extract dried over anhydrous sodium sulfate, and the product, after the removal of the diethyl ether, was finally distilled *in vacuo*. It was a colorless oil, b. p. 83.0° (13 mm.).

*Anal.* Calcd. for $C_4H_8OBr_2$: Br, 68.91. Found: Br, 69.13, 68.94.

In the preparation of the other members of the series the following were observed. First, the length of time necessary for the completion of the reaction increased with the size of the alkoxyl group, and, second, greater difficulty was encountered in purifying them. Three vacuum distillations gave practically pure substances. Samples for analysis (in the case of the first three ethers), however, were obtained after several redistillations using special precautions and special apparatus, *e. g.*, a receiver[7] provided adequate cooling and collection of the vapors, and a modified Claisen flask[8] made it possible to obtain fractions over a range of 0.5–1.0°. The constant boiling fractions were poured into amber-colored bottles from which the air was practically evacuated, and then subjected to micro-analysis.[9] The members of the homologous series

TABLE I

1,3-DIBROMO-2-ALKOXYLPROPANES

| Alkoxyl group | B. p., °C. | Mm. | Yield, % | Carbon, % Calcd. | Found | Hydrogen, % Calcd. | Found |
|---|---|---|---|---|---|---|---|
| Ethoxy[a] | 90.5 | 17.0 | 27.7 | 24.4 | 26.4 | 4.4 | 4.5 |
| Propoxy | 114.2 | 27.0 | 31.6 | 27.7 | 26.7 | 4.6 | 4.9 |
| Isopropoxy | 108.6 | 28.5 | 22.2 | 27.7 | 27.3 | 4.6 | 4.6 |
| Butoxy | 119.0 | 19.5 | 22.0 | | | | |
| Isobutoxy | 117.0 | 22.0 | 20.8 | | | | |
| Amyloxy[b] | 137.0 | 23.0 | 9.2 | | | | |
| Isoamyloxy | 137.5 | 27.0 | 21.5 | | | | |

[a] The ethoxy compound always underwent slight decomposition in spite of the effort made to obtain it in pure form. [b] The very low yield in the case of the amyloxy compound was due to accidental loss during its preparation.

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[1] Assigned to part of this investigation as partial fulfilment of the undergraduate chemistry specialization at Brooklyn College.

(2) Reboul-Lourenço, *Ann.*, **119**, 239 (1861).

(3) Paal, *Ber.*, **21**, 2971 (1888).

(4) Hess, *ibid.*, **48**, 2003 (1915).

(5) Hibbert, THIS JOURNAL, **51**, 1944 (1929).

(6) Sattler, Doctor's Dissertation, University of Chicago, 1925.

(7) M. Altamura, *Chem. Analyst*, **22**, 18 (1933).

(8) M. Altamura, to be published.

(9) Sincere thanks and appreciation are extended to Miss R. T. Roth for the analytical work performed at the Washington Square College of New York University.

prepared, together with their corresponding boiling points and yields and analyses for the first three, are listed in Table I.

**General Properties of these Ethers.**—They are colorless oils, extremely diffusible, heavier than water, insoluble in water, but soluble in fat solvents. They possess a pungent odor and undergo gradual decomposition on standing as shown by discoloration. Physiological tests[10] gave evidence that these substances are hypnotics and toxic.

### Summary

1. Several new 2-alkyl ethers of 1,3-dibromopropane are reported and their properties studied.

2. The method of preparation appears to be a general one for the series.

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[10] Sincere thanks and appreciation are extended to Dr. J. G. Harwell for the physiological tests.

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# The Optical Rotatory Dispersion of Terpenes

BY R. PADMANABHAN AND S. K. KULKARNI JATKAR

The terpenes form an interesting series of optically active isomers, the rotatory dispersion of which has not been examined in detail. As they are colorless, measurements can be extended into the ultraviolet and information obtained regarding the natural frequencies of the electrons which determine the optical activity. The rotatory dispersions of pinene and limonene have been studied by Nutting[1] in the visible, and by Ingersoll[2] in the infra-red region of the spectrum. Darmois[3] investigated the dispersion of pinene up to 3130 Å. Recently, M. Servant[4] using alcoholic solutions of pinene found that the dispersion was anomalous in the region of 2800 Å.

A serious drawback to the use of the terpenes in an investigation of this nature is the great difficulty of obtaining them in a state of purity. The values for the rotation given in the literature vary, as will be shown later, in a marked manner and it is the exception rather than the rule to find *d*- and *l*-varieties of the same terpene with a rotation which is numerically the same. These discrepancies may be due either to (1) admixture with small quantities of the same terpene in an inactive form or of opposite sign, (2) admixture of other terpenes, or (3) as suggested by Simonsen, the existence of terpenes as an equilibrium mixture, the proportion of the constituents varying for reasons at present not understood. In case (1) dispersion results will be approximately correct, the error occurring only in the absolute magnitude of the rotation. Case (2) will be similar provided the quantity of impurity is small, while in case (3) the results will be very difficult to interpret.

In view of the above we have taken great pains to obtain our materials in as pure a condition as possible, but in spite of this it is evident that in some of the cases the final product cannot be regarded as quite satisfactory. The terpenes we have examined are *d*-pinene, *d*-limonene, *d*-camphene, *d*-$\Delta^3$-carene, *d*-$\Delta^4$-carene, *d*-$\alpha$-thujene and *d*-sabinene. The report on the Raman spectrum of these terpenes will be published in the near future.

## Experimental

### Preparation of Materials

**Pinene.**—A sample of this terpene with $[\alpha]_D$ 51.14° was obtained in 2% yield by Thurber and Thielke[5] by regeneration from the active nitrosochloride. We did not succeed, however, in obtaining any product by this method, probably on account of the extremely low yields reported by these authors and consequently recourse was had to fractional distillation. A fairly pure sample of *d*-pinene of unknown origin was taken as the starting material; 500 g. was dried for a day over anhydrous magnesium sulfate and then subjected to fractional distillation over sodium at a pressure of 30 mm. using a Widmer–Schenck column nearly half a meter in length. Three such distillations, neglecting the head and tail fractions, gave the following fairly agreeing values for the rotation.

| Fraction | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Rotation | 40.48 | 40.57 | 40.57 | 40.58 | 40.57 | 40.50 |

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[1] Nutting, *Phys. Rev.*, **17**, 1 (1903).

[2] Ingersoll, *ibid.*, **9**, 257 (1917).

[3] Darmois, *Ann. chim. phys.*, **22**, 281 (1911).

[4] Servant, *Compt. rend.*, **194**, 368 (1932).

[5] Thurber and Thielke, THIS JOURNAL, **53**, 1030 (1931).