

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

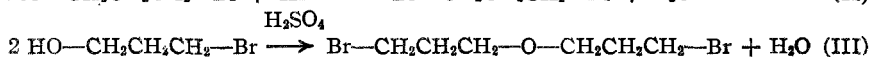
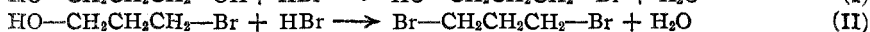
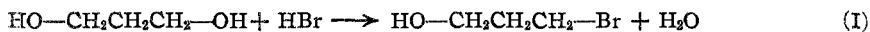
 γ, γ' -DIHALOGENO-DIPROPYL ETHERS.

BY OLIVER KAMM AND WALTER H. NEWCOMB.

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The present work was undertaken in order to prepare the symmetrical γ -dichloro and dibromo substitution products of dipropyl ether, compounds which may prove of value in the synthesis of certain heterocyclic derivatives containing rings of more than 6 atoms. By analogy to the preparation of β, β' -dichloro-diethyl ether described in the preceding paper, the derivatives of dipropyl ether were prepared by subjecting trimethylene-chloro- and bromohydrins to dehydration.

Trimethylene bromide is readily prepared from the corresponding glycol, even with aqueous hydrobromic acid. The presence of sulfuric acid increases the yield.¹ Accordingly an attempt was made to prepare the bromohydrin by an analogous reaction. Since trimethylene glycol is practically non-volatile with water vapor while the bromohydrin is appreciably volatile, the latter compound may be continuously removed from the reaction mixture, a procedure which should tend to favor Reaction I at the expense of Reaction II.



Unfortunately, the reaction velocity of the step illustrated by Equation II is far greater than that of Step I, and consequently in spite of the use of a considerable excess of trimethylene glycol, the dibromide represents the largest percentage of the yield. Simultaneously with the formation of the first two products a third reaction takes place as represented by Equation III. The desired dibromo ether may therefore be isolated during the preparation of the bromohydrin.

Preliminary experiments have been conducted in the endeavor to convert γ, γ' -dibromo-dipropyl ether into hexamethylene oxide by the removal of the bromine atoms by means of metals. These reactions, however, have yielded products contaminated with di-allyl ether and dipropyl ether, together with products which are probably mixed ethers, and we are unable at present to offer a feasible method for the preparation of this unknown cyclic ether.

Experimental Part.

Trimethylene chlorohydrin was prepared with aqueous hydrochloric acid in a manner analogous to that described (p. 2229) for the preparation of the bromohydrin. In view of the fact that an improved method has

¹ THIS JOURNAL, 42, 301 (1920).

recently been contributed from the Eastman Laboratory² we omit a discussion of our own results.

γ, γ' -Dichloro-dipropyl ether was obtained in 10–15% yield by refluxing trimethylene chlorohydrin with 20% of its weight of sulfuric acid. The ether is a colorless oil boiling at 215° at 745 mm., d_{20}^{20} 1.140.

Preparation of Trimethylene Bromohydrin and of γ, γ' -Dibromo-dipropyl Ether.

To 3 moles of trimethylene glycol in a 1-liter distilling flask add 1 mole of sulfuric acid and 1½ moles of hydrobromic acid in the form of the aqueous 48% solution. This mixture is distilled until the distillate is equal in volume to the hydrobromic acid solution added. 1 mole of the glycol and 1 mole of hydrobromic acid are added and the distillation repeated until the volume of the distillate is again equal to the volume of the hydrobromic acid solution added. The molar additions of hydrobromic acid and of the glycol and the distillations may be repeated as many times as may be desired. The halogen derivatives of the glycol distil over with water and the distillate separates into two layers. At the end of the distillation, which is finally carried to the stage at which considerable charring takes place, the distillate is neutralized with sodium carbonate and the two layers separated. The oily layer containing the organic derivatives is dried over anhydrous sodium sulfate. The aqueous layer is extracted with ether in order to remove any of the bromohydrin which is dissolved therein, and the ether extract is also dried with anhydrous sodium sulfate. The ether is distilled leaving the nearly pure bromohydrin which is subjected to fractional distillation. The main product is distilled until a temperature of 170° is reached, in order to remove most of the trimethylene bromide, and the remaining residue is distilled under diminished pressure. By means of a careful refractionation with the use of a column, a separation of the trimethylene bromide from the trimethylene bromohydrin may be attained.

The separation of the bromohydrin from the dibromo-dipropyl ether which is also formed in the reaction can be easily accomplished because of the wide difference between the boiling points of the two products. The yield of the derivatives depends somewhat on the number of additions of glycol and hydrobromic acid. The increase in the number of additions decreases the yield of the dibromide and increases the yield of the bromohydrin and of the dibromoether. A limit to the number of additions, however, is reached because of the charring of the reaction mixture.

The following table gives the average yields of several runs by the above process. The percentage yields are calculated on the possible theoretical yield for each substance based upon the amount of hydrobromic acid used. 85 to 95% of this amount is accounted for in the combined yields.

| No. of extra additions of HBr and glycol. | Glycol used G. | HBr used G. | Yield of dibromide. | Yield of bromohydrin. | Grams of dibromo ether. |
|---|----------------|-------------|---------------------|-----------------------|-------------------------|
| 2 | 380 | 283.5 | 214 g. 60% | 86 g. 17% | 48 g. 10.7% |
| 5 | 608 | 526.5 | 372.5 g. 57% | 210.5 g. 23% | 126.7 g. 15% |

The dibromo-dipropyl ether is a colorless liquid which undergoes slight decomposition when distilled under ordinary pressure. It boils at 128° at 19 mm.; d_{20}^{20} 1.574. As might be expected from its structure, this ether is insoluble in water, but is soluble in the common organic solvents; it is also appreciably volatile with water vapor. In solubility and volatility, dichloro-ethers derived from ethylene- and trimethylene chlorohydrins, show a close resemblance to dibromo-dipropyl ether.

² THIS JOURNAL, 43, 369 (1921).

Analysis. Subs., 0.2030, 0.1716; AgBr, 0.2902, 0.2456. Calc. for $C_6H_{12}OBr_2$: Br, 61.5. Found: 60.8. 60.9.

Summary.

γ, γ' -Dichloro- and dibromo-dipropyl ethers have been prepared and their physical properties recorded.

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[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY.]

THE ACTION OF AMMONIA WATER ON DICYANDIAMIDE.¹

BY TENNEY L. DAVIS.

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Dicyandiamide hydrolyzed with sulfuric acid produces one molecule of guanidine sulfate and one of ammonium sulfate, and guanidine sulfate may be obtained in satisfactory yields by this process.² But dicyandiamide is most readily prepared from Lime-nitrogen, from which ammonia may be produced more readily by simpler methods—and the production of ammonia from dicyandiamide in a process where guanidine is the object might well be regarded as the virtual loss of one quarter of the nitrogen which has earlier been "fixed" in the form of Lime-nitrogen and of dicyandiamide. We¹ have studied the reaction of ammonia on dicyandiamide with the expectation that it would lead to the formation of guanidine or of guanidine carbonate without the agency of mineral acid, and in the hope that it might perhaps lead to the formation of two molecules of guanidine from one of dicyandiamide.

We find that the action of ammonia water on dicyandiamide when the materials are heated together in a sealed tube is simple hydrolysis, water only being effectively involved and the dicyandiamide being converted first into guanylurea and later into guanidine carbonate. We have followed the progress of the reaction by precipitating the solution with ammonium picrate and have been able to judge from the melting point whether the precipitate consisted of picrate of guanidine or of picrate of guanylurea. After relatively short durations of heating at 150°, guanylurea was found in the product and the reaction mixture contained no appreciable amount of insoluble material. When the reaction was of longer duration or at a higher temperature, guanidine was formed and the reaction mixture contained considerable quantities of ammeline and ammelide. When the reaction was carried on for a still longer time, no guanidine was found and

¹ This investigation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance. In this work I have been assisted by William S. Johnson. T. L. D.

² THIS JOURNAL, 43, 669 (1921).