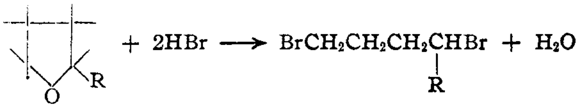
[CONTRIBUTION FROM THE JONES CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

Tetrahydrofuran Compounds. I. Cleavage by Hydrogen Halides

BY SHERMAN FRIED AND RICHARD D. KLEENE

The cleavage of tetrahydrofuran by hydrogen bromide has been investigated by various workers.[1] Likewise the cleavage of some substituted tetrahydrofurans has been studied by Paul.[2] The reaction may be represented as follows



$$+ 2\mathrm{HBr} \longrightarrow \mathrm{BrCH_2CH_2CH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{C}}}\mathrm{HBr} + \mathrm{H_2O}$$

where R = H, *n*-Pr, *n*-Bu or benzyl. In general it may be said that the method has proved to be an excellent one for the preparation of 1,4-dibromoalkanes.

The purpose of the present work has been to study the relative reactivities of the various hydrogen halides as cleaving agents. It has been observed that the general order of reactivity is hydrogen iodide > hydrogen bromide > hydrogen chloride. The yields of dihalides were also in the same order. In the case of hydrogen chloride, the addition of zinc chloride was necessary and products other than dichlorides were obtained.

Experimental

Preparation of Compounds.—Tetrahydrofuran was prepared by the hydrogenation of furan with a palladium oxide catalyst.[3] 2,5-Dimethyltetrahydrofuran was prepared from 2,5-dimethylfuran by the general hydrogenation method of Adkins,[4] using a nickel on kieselguhr catalyst. The yield of the desired product was only 40%, the rest of the starting product undergoing hydrogenolysis to yield hexanol-2.

Cleavage by Hydrogen Bromide and Hydrogen Iodide.—The cleavage experiments were performed in the manner previously described.[1b] Passage of dry hydrogen iodide through tetrahydrofuran resulted in a moderately vigorous reaction and the diiodide was isolated in 65% yield. Some tar also was formed.

Gaseous hydrogen bromide was bubbled through 17 g. of 2,5-dimethyltetrahydrofuran. A smooth reaction ensued and no tar was formed. The time required was six hours and the temperature was maintained at 90°. 2,5-Dibromohexane was isolated in 60% yield; b. p. 100° at 15 mm., m. p. 30°.

A similar reaction took place with hydrogen iodide. Sixty-one grams of 2,5-diiodohexane, b. p. 115–119° at 12 mm., was obtained from 24 g. of the ether; the yield was 75%.

Cleavage by Hydrogen Chloride.—The results of Starr and Hixon[3] on the cleavage of tetrahydrofuran with hydrogen chloride were confirmed, in that the chlorohydrin was the only product obtained. When the reaction was carried out with the addition of small amounts of fused zinc chloride from time to time, until 50% by weight of this salt was present, tetramethylene chloride was isolated in 59% yield.

When hydrogen chloride was passed into 2,5-dimethyltetrahydrofuran, no reaction occurred and the starting product was almost completely recovered. When the reaction was carried out in the presence of zinc chloride, the acid was slowly absorbed. After ten hours, the product was washed and distilled. A yield of 8% of 2,5-dichlorohexane boiling at 177° was obtained. The rest of the material was a clear liquid which boiled much higher and was not further investigated.

Summary

1. The action of the hydrogen halides (except hydrogen fluoride) upon tetrahydrofuran and 2,5-dimethyltetrahydrofuran has been studied and it has been shown that this constitutes a good method for the preparation of the corresponding dibromides and diiodides.

2. Hydrogen chloride reacts with these ethers in the presence of zinc chloride to give moderate yields of the desired dichlorides.

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[1] (a) Bourguinon, *Bull. soc. chim. Belg.*, **22**, 87 (1908); (b) Fried and Kleene, THIS JOURNAL, **62**, 3258 (1940); (c) Van Alphen, *Rec. trav. chim.*, **58**, 1105 (1939).

[2] Paul, *Bull. soc. chim.*, [5] **5**, 1053 (1938).

[3] Starr and Hixon, THIS JOURNAL, **56**, 1595 (1934).

[4] Burdick and Adkins, *ibid.*, **56**, 438 (1934).