The Structure of Stoehr's Glycerinäther

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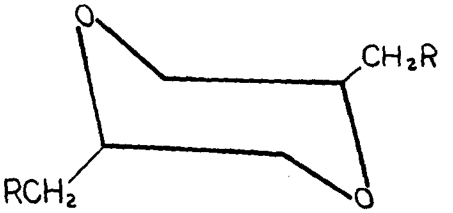
Abstract

Stoehr's Glycerinäther has been shown to be the ether of *cis* 2,6-bis(hydroxymethyl)dioxane.

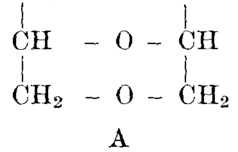
THE DETERMINATION of the structure and configuration of diepiiodohydrin as *trans* 2,5-bis(iodomethyl)dioxane (I) by work in our laboratory several years ago (1) permitted the assignment of structures and configuration to a number of known diglycerol derivatives. We were able to relate diglycerol (2), diglycerol diacetate (2), diepichlorohydrin (2,3), a diaminocompound (4) and the dibenzamide (4) of that diaminocompound directly to our key compound, I. Thus all of these were shown to be *trans* 2,5-disubstituted dioxanes.



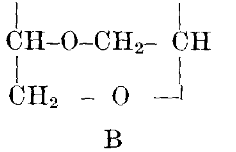
$\mathrm{R = I, OH, O\overset{O}{\overset{\|}{C}}CH_3, Cl, NH_2, NH\overset{O}{\overset{\|}{C}}C_6H_5}$

The original isolations of some of these compounds from glycerine condensation reactions were in small yields. The fact that the isolated compounds were all *trans* 2,5-disubstituted dioxanes does not necessarily indicate that other isomers such as *cis* 2,5-, *cis* 2,6- and *trans* 2,6-disubstituted dioxanes were not formed. These other isomers would be expected to have lower melting points and higher solubilities, and thus be more difficult to obtain in a pure solid form.

In addition to the amine and its derivative, Stoehr (4) also isolated a compound which he believed to be the complete ether or anhydride of two molecules of glycerine. It was obtained by distilling glycerine with ammonium phosphate or phosphoric acid and was best isolated by the somewhat novel procedure of precipitating an insoluble mercuric chloride addition compound from the aqueous distillate. The analysis and the molecular weights determined both by vapor density and cryoscopically in benzene indicated the formula $C_6H_{10}O_3$. Inertness towards several reagents indicated the absence of functional groups other than ether. Stoehr proposed structures A and B, but his experimental evidence did not permit him to choose between them.



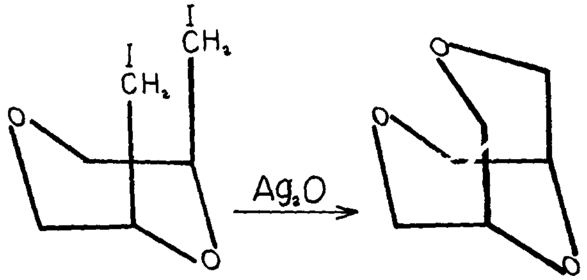
A



B

In terms of our own past work, A would be the ether of 2,6-bis(hydroxymethyl)dioxane (5) and B the ether of 2,5-bis(hydroxymethyl)dioxane (1). Models indicate that both A and B would have to be derived from the *cis* disubstituted dioxanes, as the ethers of the *trans* forms would be impossibly strained.

We have synthesized Stoehr's Glycerinäther in a rational manner that proves the structure and sterochemistry. Treatment of *cis* 2,6-bis(iodomethyl)dioxane (6) with silver oxide according to the Erlenmeyer procedure (7) produced a compound which possessed the reported properties of Stoehr's Glycerinäther.



Thus, Stoehr's Glycerinäther is not the complete ether of the partial ether diglycerol (2). The former is a derivative of a *cis* 2,6-disubstituted dioxane and the latter is a *trans* 2,5-disubstituted dioxane.

Experimental

Preparation of Stoehr's Glycerinäther of 3,7,9-trioxabicyclo(3,3,1)-nonane (A). A mixture of 0.0928 mole *cis*-2,6-bis(iodomethyl)dioxane (6), 0.0934 mole silver oxide (commercial), and 100 ml water was stirred while being heated for 1½ days. After the mixture was cooled, the filtered solids consisted of 37.2 g silver iodide and some unreacted starting material. Saturated mercuric chloride solution was added to the filtrate and an immediate precipitate formed. After crystallization from ethanol, it melted at 220–22° [lit. (4) mp 223C]. The complex was dissolved in chloroform and hydrogen sulfide was bubbled into the solution. After the yellow mercuric sulfide was filtered off, the solvent was evaporated in a jet of air. The residue was recrystallized from ether and sublimed at 100C, mp 122–122.5C corr., sealed capillary [lit. (4) mp 124C].

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.35; H, 7.34.

Acknowledgment

This research was supported by National Science Foundation Grant 7355.

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[Received September 14, 1961]