Communications TO THE EDITOR

Novel Rearrangement of 1,3-Glycols

Sir:

Recently, Gillis[1] has reported the isolation of small quantities of propionaldehyde from the attempted Bissinger rearrangement[2] of trimethylene sulfite in the presence of triethylamine. For some time we have been investigating the base catalyzed rearrangement of 1,3-glycols (Ia–c) and the corresponding cyclic sulfites (IIa–c). In each case studied, it has been observed that treatment of the glycol with strong base, sodium or potassium hydroxide, in the presence of sodium sulfite, arsenite, or phosphite has resulted in rearrangement to form the monoalcohols (IIIa–c) in good yields (approximately 50%). The corresponding cyclic sulfites[3] on rearrangement with sodium or potassium hydroxide alone gave comparable yields of the same monoalcohols as shown in Fig. 1.

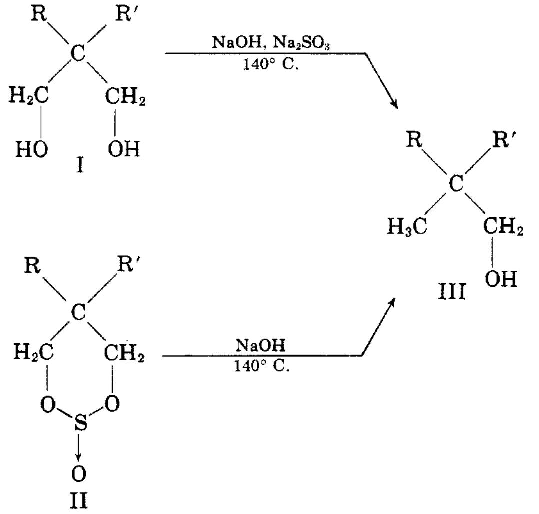

Fig. 1. Base catalyzed rearrangements of 1,3-glycols and cyclic sulfites

A. R = Methyl, R′ = Ethyl
B. R = Ethyl, R′ = Ethyl
C. R = Ethyl, R′ = Butyl

The reaction is experimentally quite simple to carry out and offers promise for the synthesis of a variety of neopentyl-type alcohols, difficult to obtain by other techniques. To a slurry of water (1.0 mole), sodium hydroxide (3.0 moles) and sodium sulfite (1.0 mole), the glycol (1.0 mole) was slowly added at a reaction temperature of 130–140°. After the addition was complete, the mixture was slowly cooled, water added, and the monoalcohol isolated by extraction in the normal fashion. Alternately, the cyclic sulfite was treated in a similar fashion with the exception that the sulfite was omitted. The yields obtained by either procedure were between 46 and 49%.

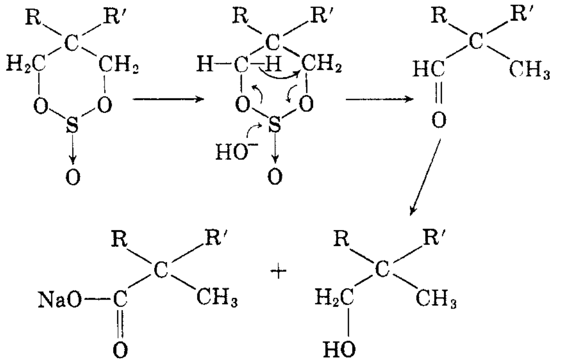

Fig. 2. Mechanism of 1,3-glycol rearrangement

Apparently, this is an extremely interesting example of a direct 1,3-hydride shift concurrent with the elimination of one of the hydroxyl groups. The resulting aldehyde, although not isolated among the reaction products, would be expected to undergo the Cannizzaro reaction in the strongly basic medium to yield the observed product, the monoalcohol. Basically, this mechanism is consistent for the rearrangement of either the cyclic sulfite or the glycol and can be visualized as indicated in Fig. 2. Using scale molecular models, the hydride migration postulated is easily visualized. In the case of the glycol, however, it must be assumed that only the monosulfite is formed and that the steric compression of the substituents on the *alpha*-carbon facilitates the rearrangement.

Further examples of this novel and interesting rearrangement are presently under investigation and a full account of this study with supporting data concerning the postulated mechanism will be published soon.

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[1] R. G. Gillis, *J. Org. Chem.*, **25**, 651 (1960).

[2] W. E. Bissinger, F. E. Kung, and C. W. Hamilton, *J. Am. Chem. Soc.*, **70**, 3940 (1948).

[3] For preparation see: A. C. Farthing, *J. Chem. Soc.*, 3648 (1955).

Synthesis of Ethyl 2- and 4-Pyridyplyruvates

Sir:

Considerable interest attaches to 2-pyridylpyruvic acid, 4-pyridylpyruvic acid, and their