

Communications TO THE EDITOR

Novel Rearrangement of 1,3-Glycols

Sir:

Recently, Gillis¹ has reported the isolation of small quantities of propionaldehyde from the attempted Bissinger rearrangement² 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 sulfites³ on rearrangement with sodium or potassium hydroxide alone gave comparable yields of the same monoalcohols as shown in Fig. 1.

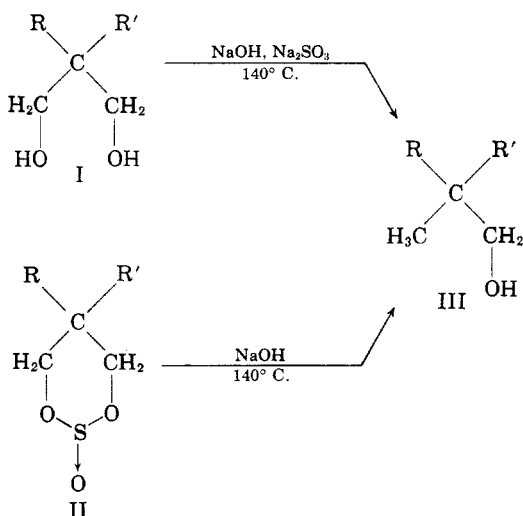


Fig. 1. Base catalyzed rearrangements of 1,3-glycols and cyclic sulfites

- 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

(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).

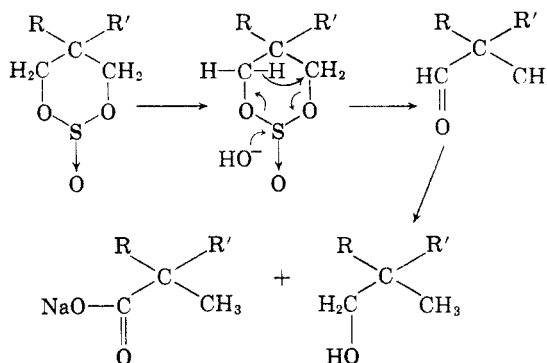


Fig. 2. Mechanism of 1,3-glycol rearrangement

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%.

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 α -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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Synthesis of Ethyl 2- and 4-Pyridylpyruvates

Sir:

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

simple esters and much work has gone into the investigation of possible synthetic methods.¹ To date the compounds have not been available. We wish to report the synthesis of esters of both the acids by a simple modification of the Claisen ester condensation of ethyl oxalate with α - and γ -picoline.

For reasons which will be given later, it appeared to us that previous attempts failed because of either too great or too little activity of the basic co-reactant used, and a metal derivative of the picolines of somewhat intermediate reactivity seemed to be indicated. If 2-picolyllithium is treated with anhydrous cadmium chloride and the resulting picolylium is treated at -70° in ether with ethyl oxalate a 10% yield of easily purified ethyl 2-pyridylpyruvate is obtained as light-yellow crystals melting at 82.5 – 83.5° (*Anal.* Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.35; H, 5.85; N, 7.18).

Use of cadmium chloride was not effective in the case of 4-picoline but when mercuric chloride was substituted for it, under almost identical conditions, a 10% yield of ethyl 4-picolylypyruvate was obtained. This ester was also easily isolated and purified and appeared as an orange-yellow powder which melted at 138 – 139° . (*Anal.* Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.3; H, 5.95; N, 7.08).

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(1) C. R. Hauser and W. J. Humphlett, *J. Am. Chem. Soc.*, **72**, 3805 (1950); R. Adams and S. Miyano, *J. Am. Chem. Soc.*, **76**, 3168 (1954).

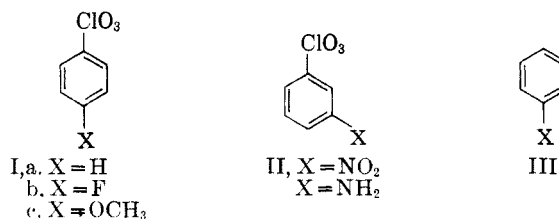
Hydrogenolysis of Perchloryl Aromatic Compounds

Sir:

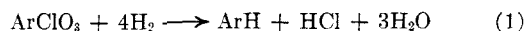
When some representative perchloryl aromatic compounds, I and II, dissolved in glacial acetic acid, were stirred in contact with a palladium-on-charcoal catalyst and with hydrogen,¹ they absorbed the latter rapidly.² The products were identified by ultraviolet spectral data as being the

(1) These hydrogenolyses were all run at room temperature and on a micro scale. The apparatus, technique, and catalyst used were as described by C. L. Ogg and F. J. Cooper, *Anal. Chem.*, **21**, 1400 (1949).

(2) An earlier probing experiment failed to reveal appreciable reaction between hydrogen with palladium catalyst and perchlorylbenzene [C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 5286 (1958)]. The present data now amend this erroneous impression. Other than the possibility that the earlier run may have contained some impurities which poisoned the catalyst, and the fact that it was not run on a quantitative scale, we cannot explain the negative result.

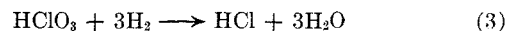
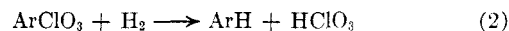


deperchlorylated compounds (III). The stoichiometry of the reaction corresponds generally to



There are two qualifications we must offer to the above statements. First, *m*-nitroperchlorylbenzene absorbed not 4, but 7 moles of hydrogen corresponding to reduction of the nitro-group as well as hydrogenolysis of the perchloryl moiety. Second, our qualitative series of runs revealed no apparent structural influence on rate of hydrogenolysis, the uptake of hydrogen being quite rapid and essentially complete in 30 minutes at room temperature. The only exception was *m*-aminoperchlorylbenzene which as the free base readily underwent reaction (1) but which when placed in solution as its hydrochloride, was resistant to hydrogenolysis. The cause of this anomaly is being examined further.

When 95% ethanol was used as solvent the absorption of hydrogen observed was step-wise, one mole being taken up very rapidly and the other three much more slowly. These data suggest the following sequence for the overall hydrogenolysis (1).



Calibrating experiments with chloric acid solutions in both glacial acetic acid (where reduction is rapid) and 95% ethanol (where reduction is slow) confirm this sequence of cleavage. In a critical experiment, a solution of Ia in 95% ethanol was allowed to take up one molar proportion of hydrogen, it was then filtered, extracted with ether, and the aqueous mother liquor was shown to contain 88% of the calculated chlorate content in accord with equation (2). An alternative mode of scission to the observed initial C—Cl rupture would involve initial Cl—O cleavages (to yield Ar—Cl) followed by its hydrogenolysis. This Ar—Cl intermediate in the case of Ia, *viz.* chlorobenzene was not hydrogenolyzed under our conditions.

These results also have some implication with regard to the structure of compounds of type (I). If the perchloryl compounds had the structure Ar—O—ClO₂ instead of the well established one, ArClO₃,³ then one might anticipate their hydrogenolysis being akin to those of the analogous nitrate esters⁴ and they should then proceed as follows:

(3) See Inman, *et al.*, *J. Am. Chem. Soc.*, **80**, 5286 (1958).

(4) L. P. Kuhn, *J. Am. Chem. Soc.*, **68**, 1761 (1946).