CLII.—*The Partial Esterification of Polyhydric Alcohols. Part VIII. The Proposed Standards of Reference in Work on the Configuration of Glycerol Derivatives.*

By ARTHUR FAIRBOURNE.

SINCE the publication of Part V (J., 1926, 3148; *Ann. Reports*, 1927, 90), showing the illusory nature of synthetic processes for the preparation of "β"-mono-derivatives of glycerol, Helferich and Sieber (*Z. physiol. Chem.*, 1927, **170**, 31; 1928, **175**, 311) have made the true β-monobenzoate by a method which seems capable of general application for β-esters, and Hill, Whelen, and Hibbert (*J. Amer. Chem. Soc.*, 1928, **50**, 2235) have synthesised the true β-methyl ether, believed to be the first true β-ether of glycerol ever isolated.

Hibbert, Whelen, and Carter (*J. Amer. Chem. Soc.*, 1929, **51**, 302), referring to Part V of this investigation, and emphasising the difficulties of identification which have resulted, propose that the ethers of glycerol should now be adopted as the standards of reference in work on configuration, and mention that the isolation of the new compound renders available all five of the possible glycerol methyl ethers :

I. α-Monomethyl ether (Irvine, Macdonald, and Soutar, J., 1915, **107**, 337).
II. β-Monomethyl ether (now isolated).
III. αβ-Dimethyl ether (Gilchrist and Purves, J., 1925, **127**, 2735).
IV. αγ-Dimethyl ether (Zunino, *Atti R. Accad. Lincei*, 1897, **6**, 348).
V. αβγ-Trimethyl ether (Gilchrist and Purves, *loc. cit.*).

Before these ethers are used as standards of reference, however, it is desirable that their structures should be thoroughly established : I, II, and V are clearly trustworthy, but it is doubtful (see Part VII, this vol., p. 129) whether the "αβ"-dimethyl ether (III) really has the structure which Gilchrist and Purves assign to it. For the same reasons, the structure of the "αγ"-dimethyl ether (IV) also ought to be regarded as unproven.

These two supposed isomerides have been examined and found to be identical. One dimethyl ether (III or IV), therefore, is still unknown.

A communication will be made later on the similar preparation recorded by Gilchrist and Purves (*loc. cit.*) for the "α"-methyl ether (I).

EXPERIMENTAL.

Glycerol Dimethyl Ether (III or IV).—Glycerol "αβ"-dimethyl ether, prepared from αγ-dichlorohydrin by Gilchrist and Purves' method (*loc. cit.*), and glycerol "αγ"-dimethyl ether, prepared from epichlorohydrin by Zunino's method (*loc. cit.*), could not be distinguished from each other, both possessing specifically identifying properties recorded by Gilchrist and Purves. As glycerol isomerides of low molecular weight, differing by the interchange of groups in the α- and β-positions, exhibit appreciably different characteristics, there is no doubt that the above products are identical. Their being so is in accordance with Zunino's own expectations. He pointed out that the two methods normally lead to an identical product, and instanced glycerol diethyl and di*iso*amyl ethers (Reboul, *Annalen, Suppl.*, 1862, **1**, 238), which were prepared in both these ways.

That Gilchrist and Purves' alternative preparation from αβ-dibromohydrin also yields the same product has already been proved by them (*loc. cit.*). The preparation has, however, been repeated, and the product found indistinguishable from either of the two specimens mentioned above.

This work has been closely paralleled by Boyd and Marle (J., 1901, **79**, 1221; 1908, **93**, 838; 1909, **95**, 1807), who, using phenol instead of methyl alcohol, investigated all three of these reactions and obtained an apparently identical glycerol diphenyl ether in each case.

p-*Nitrobenzoyloxydimethoxypropane*, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_3H_5(OMe)_2$.—The glycerol dimethyl ethers obtained by the methods mentioned above (*viz.*, from αγ-dichlorohydrin, from epichlorohydrin, and from αβ-dibromohydrin) were separately warmed (5 g.) with 4 g. of pyridine and 28 c.c. of a solution of *p*-nitrobenzoyl chloride in chloroform (containing 27·5 g. in 100 c.c.). After 48 hours, ether and water were added and the ethereal extract was washed with water, dilute sulphuric acid, dilute sodium bicarbonate solution and again with water, dried with calcium chloride, concentrated, and heated in the steam-oven for 1 hour. The product was induced to crystallise by scratching; after recrystallisation from light petroleum, it melted in each case at 43°, alone or when mixed with either of the other two (Found: $NO_2{\cdot}C_6H_4{\cdot}CO$, 56·0. $C_{12}H_{15}O_6N$ requires $NO_2{\cdot}C_6H_4{\cdot}CO$, 55·8%).

In view of the evidence of Hibbert, Whelen, and Carter (*loc. cit.*) that methoxy-groups do not migrate during esterifications of this type, these mixed melting points serve to confirm the identity of (III) and (IV).

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