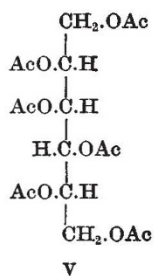
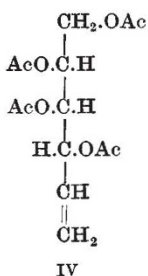
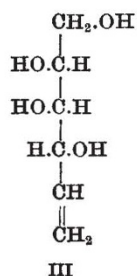
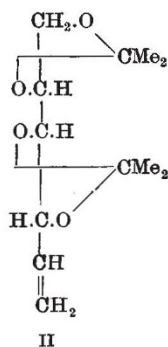
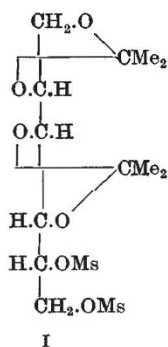


Reaction of Vicinal Dimesyl Compounds with Sodium Iodide, and its Application to the Interconversion of Hexitols

THE recent paper of Karrer and Davis¹ prompts us to report some work of a similar nature, on which we have been recently engaged.

Previous investigators²⁻⁴ have shown that treatment of a compound containing two or more vicinal tosyloxy groups, with sodium iodide, leads to the elimination of all these groups, whether primary or secondary, with formation of an unsaturated compound, and the liberation of iodine. We have been using this type of reaction mainly for the preparation of intermediates for the synthesis of polyhydroxy dithiols (cf. Evans and Owen⁵), and have found that it is equally applicable to mesyl (methanesulphonyl) compounds.



(Ms = CH₃.SO₂—)

Treatment of 5:6-dimesyl 1:2-3:4-diacetone D-mannitol (I) (m.p. 117.5–120°, $[\alpha]_D^{20} + 25.1^\circ$; all rotations in this communication were determined in chloroform solution unless otherwise stated) with sodium iodide in acetone solution at 100° gave a 65.5 per cent yield of 1:2-3:4-diacetone 5:6-mannitoleen (II), a colourless liquid, b.p. 41°/0.1 mm., $n_D^{20} 1.4401$, $[\alpha]_D^{21} - 5.49^\circ$ (found: C, 63.4; H, 8.6. C₁₂H₂₀O₄ requires C, 63.1; H, 8.8 per cent), together with a small amount of 5:6-mannitoleen (III), (Karrer's D-arabo-3:4:5:6-tetrahydroxyhex-1-ene), m.p. 147–149°, $[\alpha]_D^{20} + 30.9^\circ$ (water). Hydrolysis of the diacetone compound in the usual way gave a 69 per cent yield of 5:6-mannitoleen, [tetraacetate (IV) m.p. 80–81°, $[\alpha]_D^{21.5} + 49.4^\circ$]. Karrer and Davis¹, who employed 5:6-ditosyl 1:2-3:4-diacetone mannitol as starting material in a similar reaction, failed to isolate diacetone mannitoleen, and obtained only mannitoleen in 26 per cent yield.

Similar treatment of 5:6-dimesyl 1:3-2:4-diethylidene sorbitol with sodium iodide gave a theoretical yield of 1:3-2:4-diethylidene 5:6-

sorbitoleen, m.p. 122–123°, $[\alpha]_D^{21} - 21.6^\circ$ (found: C, 60.4; H, 7.9. C₁₀H₁₆O₄ requires C, 60.1; H, 8.1 per cent), acid hydrolysis of which afforded 5:6-sorbitoleen (97 per cent yield), a colourless syrup, b.p. 100–130° (bath)/10⁻⁴ mm., $n_D^{15} 1.5068$, $[\alpha]_D^{19} + 19.8^\circ$ (water) (found: C, 48.5; H, 8.3. C₆H₁₂O₄ requires C, 48.6; H, 8.2 per cent) (tetra-acetate, m.p. 57–58.5°, $[\alpha]_D^{22} - 13.6^\circ$). 5:6-Ditosyl 1:3-2:4-diethylidene sorbitol gave the same products, though in poorer yield.

Incidental to the main work, the following new method for the interconversion of hexitols has been evolved. Treatment of 5:6-mannitoleen tetra-acetate with hypobromous acid, according to the method of Raphael⁶, and reaction of the crude bromohydrin with a mixture of acetic acid, acetic anhydride, and fused sodium acetate, yielded D-sorbitol hexa-acetate (V), m.p. and mixed m.p. 97–98°, $[\alpha]_D^{20} + 9.04^\circ$. No mannitol hexa-acetate, the other possible product, could be detected. Similarly, from sorbitoleen tetra-acetate, L-iditol hexa-acetate, m.p. 119–120°, $[\alpha]_D^{22} - 26.8^\circ$, was obtained, no sorbitol hexa-acetate being encountered.

Full details will be published elsewhere. One of us (P.B.) desires to thank the Department of Scientific and Industrial Research for a maintenance grant.

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¹ Karrer, P., and Davis, P. C., *Helv. Chim. Acta*, **31**, 1611 (1948).

² Tipson, R. S., and Cretcher, L. H., *J. Org. Chem.*, **8**, 95 (1943).

³ Hann, R. M., Ness, A. T., and Hudson, C. S., *J. Amer. Chem. Soc.*, **66**, 73 (1944).

⁴ Karrer, P., Schick, E., and Schwyzer, R., *Helv. Chim. Acta*, **31**, 784 (1948).

⁵ Evans, R. M., and Owen, L. N., *J. Chem. Soc.* (in the press).

⁶ Raphael, R. A., *J. Chem. Soc.* (in the press).

Position of the Hydroxyl Group in Lanosterol

DEHYDRATION of alcohols of the lanosterol series to the corresponding hydrocarbons has recently been reported by us¹, when the action of both phosphorus pentachloride and phosphorus oxychloride was described. Dihydroagnosterol and dihydrolanosterol, when treated with phosphorus pentachloride, gave *iso*-agnostadiene (*iso*-γ-lanostatriene²), C₃₀H₄₈, and *iso*-lanostadiene, C₃₀H₅₀, respectively, and hydrocarbons isomeric with the above dehydration products were obtained with phosphorus oxychloride. We expressed the opinion, based on a consideration of analogous cases in triterpene chemistry, that the phosphorus pentachloride dehydration involved a retro-pinacol rearrangement accompanied by a contraction of the terminal ring A of lanosterol, and stated that experiments to confirm this view were in progress. In the meantime, Ruzicka *et al.*³, following our method of preparation, have reported the results of oxidation experiments on the dehydration product from dihydrolanosterol, and afforded evidence in support of the reaction mechanism suggested above, establishing at the same time the position of the secondary hydroxyl group in lanosterol. The continuation of our work has involved the study of the same series of reactions applied both to *iso*-agnostadiene and *iso*-lanostadiene, and in view of Ruzicka's publication, we now present a brief summary of our results.