

THE TRITYLATION OF SUGAR MERCAPTALS

Sir:

In view of the publication of Micheel and Spruck [*Ber.*, **67**, 1665 (1934)] on the tritylation of galactose ethyl mercaptal, we wish to report the work completed in this Laboratory on the tritylation of a number of sugar mercaptals. The work herein reported was completed before the above article of Micheel and Spruck appeared and was also well under way before the publication of Micheel and Suckfüll [*Ann.*, **502**, 85 (1933)] on the action of mercuric chloride on 6-iodogalactose ethyl mercaptal tetraacetate. All compounds now reported were obtained in crystalline form and were recrystallized to constant melting point and rotation. All rotations are recorded in U. S. P. chloroform. *d*-Glucose ethyl mercaptal was successively treated in pyridine solution with triphenylchloromethane (trityl chloride) and benzoyl chloride to produce (I) 6-tritylglucose ethyl mercaptal tetrabenzoate (m. p. 161–162°; $[\alpha]_D +49^\circ$). This tritylation procedure was originally applied to carbohydrates by Helferich and co-workers [B. Helferich and J. Becker, *Ann.*, **440**, 1 (1924)]. Similar procedures produced the tetrabenzoate of 6-trityl-*d*-galactose ethyl mercaptal (m. p. 138–139°; $[\alpha]_D -22.5^\circ$). By substituting acetic anhydride for the benzoyl chloride there was obtained 6-tritylgalactose ethyl mercaptal tetraacetate (m. p. 123–124°; $[\alpha]_D -22.5^\circ$), trityl-*l*-arabinose ethyl mercaptal triacetate (m. p. 101–102°; $[\alpha]_D -24^\circ$), and trityl-*d*-xylose ethyl mercaptal triacetate (m. p. 149–150°; $[\alpha]_D -20.5^\circ$).

Attempts to hydrolyze the trityl group in 6-tritylglucose ethyl mercaptal tetrabenzoate with hydrogen bromide always produced (II) 6-bromogalactose ethyl mercaptal tetrabenzoate (m. p. 169–170°; $[\alpha]_D +39^\circ$). The position of the bromine atom was proved by the identity of this compound with the product obtained by benzylation of the 6-bromogalactose ethyl mercaptal of E. Fischer [E. Fischer, B. Helferich and P. Ostmann, *Ber.*, **58**, 873 (1920)]. Iodine replacement of the bromine atom was effected by sodium iodide in acetone [J. C. Irvine and J. W. Oldham, *J. Chem. Soc.*, **127**, 2729 (1925)] to produce (III) 6-iodogalactose ethyl mercaptal tetrabenzoate (m. p. 165–166°; $[\alpha]_D +39^\circ$) with constants practically identical with those of the 6-bromo compound. The iodine was removed with silver nitrate in dilute acetone and the mercaptal groups with

mercuric chloride and cadmium carbonate in moist acetone [M. L. Wolfrom, *THIS JOURNAL*, **51**, 2188 (1929)]. The product obtained was the glucopyranose tetrabenzoate of E. Fischer [E. Fischer and H. Noth, *Ber.*, **51**, 321 (1918)] and a benzoyl migration had accordingly occurred.

Cautious hydrolysis of 6-tritylgalactose ethyl mercaptal tetraacetate with hydrogen bromide produced 6-hydroxygalactose ethyl mercaptal tetraacetate (m. p. 96–97°; $[\alpha]_D -7^\circ$). More vigorous hydrolysis produced 6-bromogalactose ethyl mercaptal tetraacetate (m. p. 110–111°). Removal of the mercaptal groups from 6-hydroxygalactose ethyl mercaptal produced the galactose 2,3,4,5-tetraacetate hydrate of Micheel and Suckfüll. When recrystallized from water this substance melts sharply at 168°.

Removal of the mercaptal groups from 6-tritylgalactose ethyl mercaptal tetraacetate produced 6-tritylgalactose tetraacetate, isolated as a compound with one mole of ethanol (m. p. 153°; $[\alpha]_D -28^\circ$) and also as its semicarbazone ($[\alpha]_D +20^\circ$).

The above work on the glucose compounds was presented completely on March 30, 1934, at the 44th Meeting of the Ohio Academy of Science at Columbus, Ohio. Compounds I, II and III are recorded in the M.A. thesis of Mr. Clarence C. Christman, The Ohio State University, Dec. 15, 1933. Full details of all this work will be published at a later date.

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CRYSTALLINE β -GLUCOHEPTOSE AND ITS MUTAROTATION

Sir:

A sirup containing β -glucoheptose was synthesized by E. Fischer [*Ann.*, **270**, 87 (1892)] but he and subsequent workers were unable to obtain the crystalline sugar. The writer has now prepared β -glucoheptose in crystalline form. The mutarotation is very unusual and resembles that of ribose, reported in a previous publication [*THIS JOURNAL*, **56**, 747 (1934)].

The first crystals separated spontaneously from a product obtained by Fischer's method from β -glucoheptonic γ -lactone by reduction with sodium amalgam. The new sugar crystallizes in slender prisms, melting at 121°, very soluble in water but

not deliquescent. After recrystallization from aqueous alcohol and drying over calcium chloride it was analyzed. *Anal.* Calcd. for $C_7H_{14}O_7$: C, 39.98; H, 6.72. Found: C, 40.06; H, 6.62.

MUTAROTATION OF β -GLUCOHEPTOSE AT 20° IN 5% AQUEOUS SOLUTION

$$[\alpha]_D^{20} = +11.31 \times 10^{-0.050t} - 11.28 \times 10^{-0.0108t} - 0.13$$

Time, minutes	$[\alpha]_D^{20}$ Obs.	k Initial period	$k_1 + k_2$ Final period	$[\alpha]_D^{20}$ Calcd. from eq.
0	(-0.1)	-0.1
1.3	-1.4	-1.31
3.2	-2.7	0.0496	...	-2.73
5.1	-3.7	.0489	...	-3.78
7.5	-4.7	.0497	...	-4.72
10	-5.2	.0483	...	-5.35
15	-5.8	.0487	...	-5.89
18	-5.93	.0503	...	-5.92
20	-5.9	.0507	...	-5.86
30	-5.2	-5.12
40	-4.3	-4.19
50	-3.4	...	0.0106	-3.38
60	-2.70105	-2.67
70	-2.10108	-2.11
80	-1.60113	-1.67
90	-1.30110	-1.33
100	-1.10106	-1.06
120	-0.70108	-0.70
24 hrs.	-0.13	- .13

The mutarotation cannot be expressed by the usual first order equation but, as may be seen from the calculated values given in the table, it is adequately expressed by an equation containing two exponential terms corresponding to two well-defined reactions. The velocity constants for the initial reaction were calculated by the method of Lowry and Smith [*J. Phys. Chem.*, **33**, 9 (1929)]. The uniform values show that the initial change follows approximately the course of a first order reaction. The constants calculated from forty minutes on are uniform also, which shows that the final change follows the course of a first order reaction. The initial change is approximately five times as fast as the final and is sufficiently large to permit its study in more detail than is possible with ribose and other known sugars which exhibit this type of mutarotation.

The complex character of the mutarotation reaction is evidence that the original substance on dissolving in water changes into another form or forms which slowly pass, at least in part, into one or more additional substances. The various sub-

stances may contain different ring structures or possibly the changes in rotation may be due in part to the presence of endocyclic bridge isomers [Fuson, *Chem. Reviews*, **7**, 347 (1930)] of one ring type. In any case the new crystalline form of β -glucoheptose may contain an open chain, furanose or pyranose structure. Hence the writer refrains from classifying it until its reactions and properties have been studied further.

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THE REACTION OF ETHYLENE OXIDE WITH ACETYLENIC GRIGNARD REAGENTS

Sir:

In a recent article Faucounau [*Compt. rend.*, **199**, 605 (1934)] describes the preparation of some acetylenic alcohols by the action of ethylene oxide on acetylenic Grignard reagents and the subsequent hydrolysis of the products obtained. During the past year we have been working on the same reaction [Danehy, Master's dissertation University of Notre Dame, 1934] and have prepared 3-nonyl-1-ol and 1-phenyl-1-butyn-4-ol as reported by Faucounau, obtaining yields corresponding with his; we have also prepared 3-octyn-1-ol, b. p. 97° (15 mm.); n_D^{25} 1.4542; d_4^{25} 0.8765. We also have obtained other products from these reactions in yields at least as large as the yields of the alcohols by extracting the aqueous layer with ether after hydrolysis of the Grignard complex. Faucounau has failed to report these non-alcoholic products. Because of the water solubility, molecular weight and other physical properties of these compounds, it is very likely that the phenyl-substituted product (b. p. (15 mm.) 55°) isolated by us along with the 1-phenyl-1-butyn-4-ol is identical with the 2-phenyl-4,5-dihydrofuran obtained by Faucounau in a series of reactions subsequently carried out with the 1-phenyl-1-butyn-4-ol, and that the amyl and butyl compounds isolated by us are similar in nature. We are investigating the structures of these compounds.

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