265. *Anhydrides of Polyhydric Alcohols. Part VIII. Some Alkenyl Ethers of* 1 : 4-3 : 6-*Dianhydromannitol and* 1 : 4-3 : 6-*Dianhydrosorbitol.*

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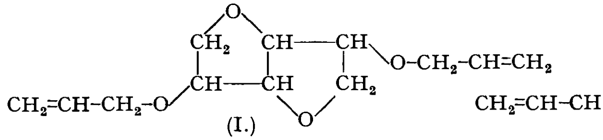
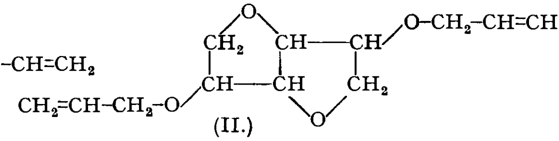
Diallyl and dimethallyl ethers of the 1 : 4-3 : 6-dianhydrides of mannitol and sorbitol have been prepared. They polymerise slowly in a stream of oxygen, the allyl at a greater rate than the methallyl ethers.

In continuation of our studies of 1 : 4-3 : 6-dianhydro-mannitol and -sorbitol described in Parts I and IV—VII of this series, we have sought to obtain unsaturated ethers of these compounds. In a previous communication (Haworth, Gregory, and Wiggins, *J.*, 1946, 488) we have described unsaturated acyl derivatives of these dianhydrides, namely the diacrylyl and dimethacrylyl esters, which were found to polymerise very rapidly to glass-like resins; saturated ether derivatives have also been reported (Haworth and Wiggins; Patent Application 1945).

The allyl ethers of certain carbohydrates have recently been obtained by Nichols and Yanovsky and their associates; these include allyl sucrose (Nichols and Yanovsky, *J. Amer. Chem. Soc.*, 1945, **67**, 47), tetra-allyl α-methylglucoside (*idem, ibid.*, 1944, **66**, 1625), and allyl starch (Nichols, Hamilton, Smith, and Yanovsky, *Ind. Eng. Chem.*, 1945, **37**, 206). By treating 1 : 4-3 : 6-dianhydro-mannitol and -sorbitol with allyl bromide and concentrated sodium hydroxide solution according to the procedure of Nichols and Yanovsky, we have obtained 2 : 5-*diallyl* 1 : 4-3 : 6-*dianhydromannitol* (I) and 2 : 5-*diallyl* 1 : 4-3 : 6-*dianhydrosorbitol* (II), complete allylation being accomplished in one treatment, giving 70% yields of the products. Both compounds were yellow liquids, quite stable to distillation. Although they polymerised slowly in a stream of oxygen, no appreciable effect was observed on heating them in the presence of benzoyl peroxide, a fact previously noted by Nichols and Yanovsky for tetra-allyl α-methylglucoside. The rates of polymerisation of the dianhydrohexitol derivatives at 97° have been followed viscometrically in an Ostwald viscometer modified as shown in Fig. 1, so that oxygen could be bubbled through the substance and the viscosity measured in the same apparatus.


(I.)


(II.)

Preliminary experiments showed that the rate of polymerisation depended upon the rate of flow of oxygen through the apparatus, hence the flow of gas was kept constant throughout the polymerisation. It was found that the rate of polymerisation as measured by the viscosity for both the mannitol and the sorbitol derivatives (see Fig. 2) followed closely the behaviour of tetra-allyl α-methylglucoside, described by Nichols and Yanovsky (*loc. cit.*). Fig. 2 shows that the polymerisation of the mannitol derivative was very slightly faster than that of its sorbitol analogue. Both liquids became darker at the beginning of the heating, but became progressively lighter in colour as the polymerisation continued. The viscosity increased slowly for about 180 minutes, followed by a rapid increase to the gelation point, at which the substances were almost colourless. Both end-products were soft and rubbery, completely infusible and insoluble.

On treatment of dianhydromannitol with methallyl chloride and concentrated sodium hydroxide solution at ordinary pressures, 2 : 5-*dimethallyl* 1 : 4-3 : 6-*dianhydromannitol* was obtained in poor yield, owing probably to loss of reagent and incompletion of reaction. Some improvement was effected by carrying out the reaction in an autoclave fitted with a stirring device, and by this method 2 : 5-*dimethallyl*-1 : 4-3 : 6-*dianhydrosorbitol* was obtained. Both of the methallyl derivatives were yellow liquids which polymerised slowly on being heated in a stream of oxygen. Neither, however, gelatinised, or reached a state of acetone insolubility, as distinct from the behaviour of the corresponding allyl derivatives. The rates of polymerisation (see Fig. 2) when investigated under the same conditions as described previously were also markedly slower than those of the allyl ethers; even after 24 hours at 97° in a stream of oxygen at 10 l./hour, no gel formation had occurred and the viscous liquid remained acetone soluble.

FIG. 1.

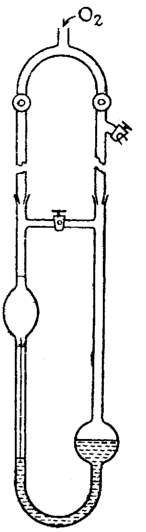
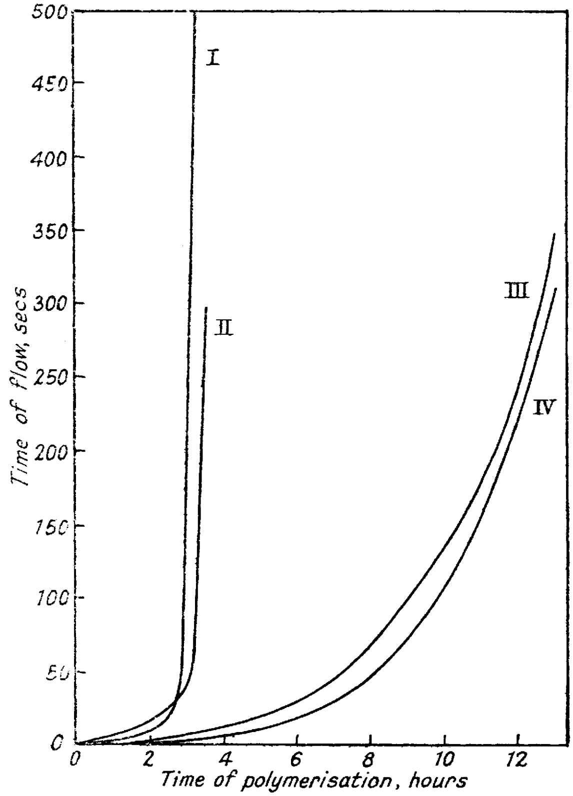


FIG. 2.



I. 2 : 5-*Diallyl* 1 : 4-3 : 6-*dianhydromannitol.*
II. 2 : 5-*Diallyl* 1 : 4-3 : 6-*dianhydrosorbitol.*
III. 2 : 5-*Dimethallyl* 1 : 4-3 : 6-*dianhydrosorbitol.*
IV. 2 : 5-*Dimethallyl* 1 : 4-3 : 6-*dianhydromannitol.*

The difference in the rates of polymerisation of the allyl and methallyl ethers and the difference in properties of the final product must be due to the presence of the methyl group. Therefore, since the methallyl ethers polymerise more slowly and to a lesser degree than the allyl ethers, the methyl group must exhibit an inhibitory effect upon polymerisation. This tendency has been observed previously in many cases. For instance, whereas styrene will undergo addition polymerisation very rapidly, to form long-chain macromolecules, α-methylstyrene will only form an octamer (Staudinger and Breusch, *Ber.*, 1929, **62**, 442), and β-methylstyrene, dimeric molecules (Errera, *Gazzetta*, 1884, **14**, 504).

EXPERIMENTAL.

2 : 5-*Diallyl* 1 : 4-3 : 6-*Dianhydrosorbitol.*—Dianhydrosorbitol (50 g.) was suspended in allyl bromide (85 c.c.) in a three-necked bolthead flask, fitted with a dropping funnel, condenser, and mechanical

stirring device. The well-stirred reaction mixture was maintained at 70°. Sodium hydroxide solution (53 c.c. of a 52% solution, w/v) was added slowly during 1·25 hours, and stirring continued for a further 1·75 hours. Water (100 c.c.) was then added, and any unsaturated volatile compounds present were removed by steam distillation. The mixture was then extracted with ether, the ethereal extract washed with water and dried ($MgSO_4$), and the ether removed, leaving a light brown, mobile liquid. This was fractionally distilled under reduced pressure in an atmosphere of carbon dioxide. The bulk distilled at 157—161°/20 mm. One further distillation gave pure *diallyl dianhydrosorbitol* as a colourless liquid in 70·3% yield, b. p. 185°/40 mm., $n_D^{21°}$ 1·4812, $[\alpha]_D^{22°}$ + 93·4° (*c*, 1·756 in chloroform) (Found : C, 63·4; H, 7·7. $C_{12}H_{18}O_4$ requires C, 63·6; H, 8·0%).

The rate of polymerisation of 2 : 5-diallyl dianhydrosorbitol was followed viscometrically. The results below give the time of flow in seconds for the corresponding time of polymerisation in minutes (in parentheses) : 1·9 (0); 2·4 (20); 2·8 (45); 18 (130); 37·0 (166); 118·0 (196); 160 (205); 245·0 (210); ∞ (216). During the last reading the material gelled in the tube. These results are shown graphically in Fig. 2.

2 : 5-*Diallyl* 1 : 4-3 : 6-*Dianhydromannitol*.—This was prepared on the same scale and in the same way as its sorbitol analogue. The *compound* was obtained as a colourless, mobile liquid, b. p. 173°/10 mm., $n_D^{21°}$ 1·4847, $[\alpha]_D^{23°}$ + 160·3° (*c*, 1·51 in chloroform) (Found : C, 63·2; H, 8·3. $C_{12}H_{18}O_4$ requires C, 63·6; H, 8·0%).

The rate of polymerisation of 2 : 5-diallyl dianhydromannitol was investigated viscometrically. The following results give the time of flow in seconds for the corresponding time of polymerisation in minutes (in parentheses) : 1·4 (0); 1·8 (20); 2·4 (80); 5·6 (105); 15·1 (135); 32·4 (155); 82·0 (170); 120·0 (180); 495·2 (185); ∞ (193). These results are shown graphically in Fig. 2.

2 : 5-*Dimethallyl* 1 : 4-3 : 6-*Dianhydromannitol*.—A mixture of 1 : 4-3 : 6-dianhydromannitol (20·0 g.), methallyl chloride (100 c.c.), and sodium hydroxide (22 c.c. of a 52% solution, w/v) was heated on a boiling water-bath for 10 hours. The mixture was kept well stirred throughout the reaction to prevent the conversion of methallyl chloride into *iso*butaldehyde as a result of the development of local acidity. The mixture was then cooled, water (200 c.c.) was added, and the two layers were separated. The upper layer was dried ($CaCl_2$) and distilled on a boiling water-bath under reduced pressure to remove the more volatile components. The residual oil was fractionally distilled under reduced pressure in an atmosphere of carbon dioxide. The bulk distilled at 132—135°/10 mm. as a pale yellow liquid which darkened on standing. One further distillation under the same conditions gave 2 : 5-*dimethallyl* 1 : 4-3 : 6-*dianhydromannitol* (4·62 g.), b. p. 135°/10 mm., $n_D^{10°}$ 1·4979, $[\alpha]_D^{20°}$ + 71·4° (*c*, 1·168 in chloroform) (Found : C, 66·0; H, 8·3. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·6%). The rate of polymerisation of 2 : 5-dimethylallyl 1 : 4-3 : 6-dianhydromannitol was investigated viscometrically. The following results give the time of flow in seconds for the corresponding time of polymerisation in minutes (in parentheses) : 2·5 (0); 3·0 (60); 4·0 (120); 2 (150); 5·8 (195); 8·0 (240); 11·2 (300); 18·0 (360); 27·8 (420); 35·0 (450); 52·2 (480); 1400 (990). Further readings could not be taken owing to the high viscosity of the liquid. These results are shown graphically in Fig. 2.

2 : 5-*Dimethallyl* 1 : 4-3 : 6-*Dianhydrosorbitol*.—Dianhydrosorbitol (20 g.), methallyl chloride (100 g.), sodium hydroxide solution (22 c.c. of a 50% solution, w/v) and acetone (100 c.c.) were heated in a stamless steel autoclave, fitted with a stirring device, for 10 hours at 120°. The contents of the autoclave were then diluted with water (200 c.c.) and the mixture was steam distilled to remove acetone, methallyl chloride, and any methallyl alcohol and dimethallyl ether produced during the reaction. The remaining liquid was then cooled and extracted with ether, the ethereal extract was washed with water and dried ($MgSO_4$), and the ether was removed. The residual brown mobile liquid was fractionally distilled under reduced pressure in an atmosphere of carbon dioxide, whereby a pale yellow liquid was obtained, b. p. 150—160°/15 mm. The distillate was then redistilled using the same precautions; *dimethallyl dianhydrosorbitol* (6·4 g.) was obtained, b. p. 157°/15 mm., $n_D^{15°}$ 1·4843, $[\alpha]_D^{15°}$ + 37·1 (*c*, 1·40 in chloroform) (Found : C, 66·0; H, 8·7. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·66%).

The rate of polymerisation of 2 : 5-dimethallyl dianhydrosorbitol was followed viscometrically. The results below give the time of flow in seconds for the corresponding time of polymerisation in minutes (in parentheses) : 1·9 (0); 2·6 (60); 14·4 (255); 20·5 (295); 26·6 (330); 30·0 (360); 36·4 (390); 44·0 (420); 52·0 (440); 64·5 (475); 85·0 (515); 88·6 (540); 123·0 (570); 133·0 (600); 195·0 (675); 315·0 (750); 581·0 (810); 1423 (970). Further readings could not be taken in this apparatus owing to the high viscosity of the liquid. The results are shown graphically in Fig. 2.

The authors wish to express their thanks to Sir Norman Haworth, F.R.S., and Dr. J. L. Simonsen, F.R.S., for their interest, and to the Colonial Products Research Council for financial assistance.

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[*Received, December* 24*th*, 1946.]