[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Allyl Ethers of Carbohydrates. V. Preparation and Polymerization of β-Methallyl Ethers

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After a study of the properties of various allyl ethers of polyhydric compounds, it was deemed advisable to investigate the corresponding methallyl ethers. Preparative work followed the same pattern as that previously described for allyl ethers.[2,3]

In this paper the preparation of the β-methallyl ethers of sucrose, D-mannitol, D-sorbitol, pentaerythritol, dipentaerythritol, glycerol and ethylene glycol is described, their oxidation and polymerization are discussed, and comparisons are made with the corresponding allyl ethers. For the sake of comparison allyl dipentaerythritol, not described in previous articles, has been prepared.

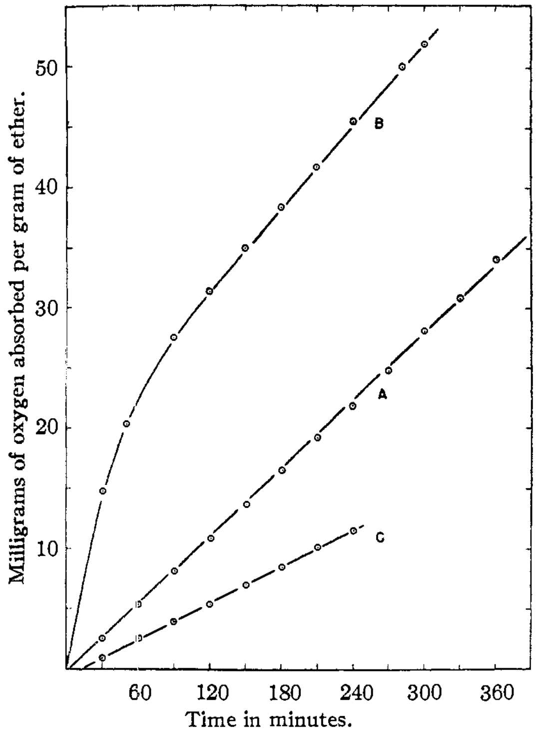

Fig. 1.—Influence of cobalt naphthenate and sodium hydroxide on oxygen absorption of methallyl pentaerythritol at 80°. A, methallyl pentaerythritol; B, methallyl pentaerythritol plus 0.2% cobalt; C. methallyl pentaerythritol plus 4.5% sodium hydroxide.

Oxidation and Polymerization.—As in the case of allyl ethers, methallyl ethers absorb appreciable amounts of oxygen during polymerization in an atmosphere of oxygen to an insoluble, infusible resin. Also, the oxidative attack occurs to some extent at the α-methylenic carbon atom of the methallyl group, as evidenced by the formation of methacrolein, which was identified as its 2,4-dinitrophenylhydrazone.

Two methods were used in determining the amount of oxygen absorbed. For relatively small amounts the usual Barcroft–Warburg apparatus and a technique essentially the same as that described in the literature[4,5,6] were employed. For gelled products, the percentage carbon was determined, and from this value the amount of added oxygen was calculated.

When the weight of oxygen absorbed per gram of material is plotted against time during the initial three to seven hours of the oxidation, a straight line is obtained. The slope of the resulting straight line, expressed in micrograms of the oxygen absorbed per gram of material per minute, is taken as the rate constant.

From results obtained with different preparations of the same substance, it appears that the oxidation reaction is very sensitive and the rate of oxidation might be affected by traces of extraneous materials acting as inhibitors or accelerators. As a result our data on the comparison of the rates of oxidation of methallyl ethers with those of the corresponding allyl ethers must be essentially qualitative. Table I shows the rates of oxidation of various methallyl and allyl ethers.

TABLE I

RATE CONSTANTS FOR OXYGEN ABSORPTION FOR ALLYL AND METHALLYL ETHERS OF POLYHYDRIC ALCOHOLS AT 80°

Polyhydric alcohol	Rate in micrograms per gram per minute Allyl[a]	Methallyl[a]
Mannitol	78	109
Sorbitol	73	104
Glycerol	. .	155
Pentaerythritol	74	93
Dipentaerythritol	50	63

[a] Values for completely substituted products.

The accelerating effect of cobalt naphthenate on the rate of oxidation is demonstrated in Fig. 1. Inhibition of oxidation by the addition of 0.143 g. of 30% aqueous sodium hydroxide to 0.929 g. of the ether is shown graphically in the same figure. Triethylene tetramine (2%) completely inhibited the oxidation. Other effective inhibitors of the oxidation and polymerization are hydroquinone and tertiary butyl catechol. In concen-

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(1) One of the Laboratories of the Bureau of Agricultral and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

(2) Nichols and Yanovsky, THIS JOURNAL, **66**, 1625 (1944).

(3) Nichols and Yanovsky, *ibid.*, **67**, 46 (1945).

(4) Johnston and Frey, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 479 (1941).

(5) Perkins, *ibid.*, **15**, 61 (1943).

(6) Stirton, Turer and Riemenschneider, *Oil & Soap*, **22**, 81 (1945).

tration of 0.1% the former reduced the rate of oxidation of allyl and methallyl pentaerythritol from 74 and 93 micrograms to 2.0 and 2.3, respectively; *t*-butyl catechol reduced it from 74 to 8.7 and from 93 to 2.7.

In Table II the amount of oxygen absorbed by several gelled methallyl and allyl ethers is shown. The values were calculated from the carbon analyses as described in a previous article.[2] The methallyl ethers apparently required considerably more oxygen to reach the gelation point.

TABLE II

OXYGEN ABSORBED DURING TIME REQUIRED FOR GELATION

Polyhydric alcohol	Atoms of oxygen absorbed per molecule Allyl	Methallyl
Mannitol	2.1	3.2
Sorbitol	1.8	2.9
Pentaerythritol	2.1	2.5
Ethylene glycol	1.6	2.2

Like the corresponding allyl ethers, the methallyl compounds polymerized in the presence of oxygen, yielding transparent, colorless, insoluble, infusible resins. The gelation times of methallyl and corresponding allyl ethers are shown in Table III. It is interesting that in the presence of cobalt naphthenate gelation times for the corresponding allyl and methallyl ethers are more nearly the same, whereas without the catalyst methallyl ethers gel much more slowly.

TABLE III

GELATION TIMES FOR COMPLETELY SUBSTITUTED ALLYL AND METHALLYL ETHERS AT 97°

Polyhydric alcohol	Gelation time, minutes Allyl	Methallyl
Mannitol	220	553
Sorbitol	240	455
Glycerol	207	937
Pentaerythritol	188	510
Dipentaerythritol	290	360
Sucrose (approx. heptasubstituted)	207	395
With 0.2% cobalt (added as cobalt naphthenate) as catalyst		
Sorbitol	85	95
Pentaerythritol	87	140

As in the case of allyl ethers, polymerization of methallyl ethers was not catalyzed by small quantities of benzoyl peroxide. Even 5% of benzoyl peroxide gave only a slight increase in viscosity. Both allyl and methallyl ethers, however, gel readily when larger amounts of benzoyl peroxide (15% or more) are gradually added to the ethers heated at 97°.

It is believed that the oxidation of methallyl ethers proceeds according to the tentative mechanism outlined in one of the previous articles.[2] As additional evidence for the scheme suggested, the fact can be cited that a positive test for epoxide[7] was obtained during the oxidation of both allyl and methallyl ethers. Oxygen was passed through methallyl mannitol and allyl pentaerythritol for seven hours at 80°. Analyses showed in the former 0.75% peroxide (iodimetric determination) and 0.28% epoxide; in the latter there were 1.60% peroxide and 0.25% epoxide.

Experimental

Methallylation of Polyhydric Alcohols.—Step I: Methallyl bromide and 50% alkali were used in the manner described in a previous article[3] on allyl ethers to give partially etherified products.

Step II: Complete etherification was effected by reaction with sodium to form the alcoholate and further treatment of the alcoholate with methallyl bromide.[3]

Methallyl D-Mannitol.—Forty-two grams of mannitol (m. p., 165–166° uncor.) was partially etherified to give 75 g. of a main fraction boiling between 170 and 180° at 0.8 mm. Analyses showed that this product had 59.1% methallyl and 4.7% free hydroxyl, corresponding to 4.3 and 4.8 methallyl groups per mannitol molecule, respectively. In general the hydroxyl values gave slightly higher degrees of substitution. The yield was 79% of the theoretical yield for a product containing 4.3 methallyl groups. Treatment of the product by Step II gave a 54% yield of hexamethallyl mannitol boiling at 173–174° at 0.8 mm. This step was repeated to obtain a slightly purer product. The properties of this final product and other completely substituted methallyl ethers whose preparation is described below are given in Table IV.

Methallyl D-Sorbitol.—Forty-two grams of D-sorbitol gave 86 g. of partially methallylated sorbitol (4.8 groups) boiling at 189–193° at 0.9 mm. The yield was 85%. based on the product obtained. A repetition of the first step gave a 79% yield of a product containing 5.4 ether groups. Hexamethallyl D-sorbitol was prepared by step II.

Methallyl Pentaerythritol.—Sixty grams of pentaerythritol treated by Step I gave an 80% yield of a product containing 3.0 methallyl groups distilling between 135 and 140° at 0.8 mm. Another treatment by Step I gave an 85% yield of a product containing 3.3 groups. Step II gave tetramethallyl pentaerythritol.

Methallyl Dipentaerythritol.—By Step I, 52 g. of dipentaerythritol gave a 63% yield of a product containing 4.6 methallyl groups distilling between 200 and 205° at 0.8 mm. Treating the product according to Step I by using four times the required amount of methallyl bromide and alkali gave a 74% yield of a material containing 5.4 methallyl groups. By Step II, a 57% yield of hexamethallyl dipentaerythritol was obtained.

Methallyl Sucrose.—By Step I, 52 g. of sucrose gave a 70% yield of a product containing 6.3 methallyl groups. Treating the product according to Step I but using three and ten times the amount of methallyl bromide required to complete the etherification resulted in a product containing 7.5 methallyl groups. Since the product could not be distilled at 0.3 mm.. it was purified by washing an ether solution of it with water and removing volatile materials under diminished pressure. The resulting product contained 54.5% methallyl (calcd. for subst. 7.5, 55.25%) and had the following properties: $n^{20}\text{D}$ 1.4835; d^{20}_{4} 1.0303; $[\alpha]^{25}\text{D}$ +42.1.

Methallyl Glycerol.—For the preparation of methallyl glycerol. addition of 50% sodium hydroxide dropwise to a mixture of glycerol and methallyl bromide proved more satisfactory. By this modification of Step I, it was possible to obtain a 33% yield of partially methallylated glycerol containing 2.8 methallyl groups.

The product was heated with excess sodium for one hour at 100° and then distilled off under diminished pressure, giving a 64% yield of trimethallyl glycerol.

Methallyl Ethylene Glycol.—When treated according to the procedure described for glycerol. 85 g. of ethylene glycol gave a 34% yield of a product containing 1.9 methallyl groups and distilling in the range 48–50° at

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[7] Nicolet and Poulter, THIS JOURNAL, 52, 1186 (1930).

TABLE IV

METHALLYL ETHERS

Compounds	Boiling point °C.	Mm.	Formula	$n^{20}D$	d^{20}_4	Molecular refraction Calcd.	Molecular refraction Found	Methallyl, % Calcd.	Methallyl, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Hexamethallyl-D-mannitol[a]	173–174	0.8	$C_{30}H_{50}O_6$	1.4713	0.9537	147.80	148.58	65.2	64.6	71.1	71.5	10.0	10.2
Hexamethallyl-D-sorbitol[b]	165–167	.3	$C_{30}H_{50}O_6$	1.4703	.9528	147.80	148.45	65.2	64.4	71.1	71.1	10.0	9.9
Trimethallyl glycerol	94– 96	.5	$C_{15}H_{26}O_3$	1.4532	.9142	75.00	75.23	65.0	64.5	70.8	70.9	10.3	10.0
Dimethallyl ethylene glycol	48– 50	.4	$C_{10}H_{18}O_2$	1.4383	.8779	50.73	50.93	64.7	64.1	70.6	70.6	10.7	10.6
Tetramethallyl pentaerythritol	128–129	.3	$C_{21}H_{36}O_4$	1.4621	.9285	103.88	104.15	62.5	62.1	71.6	71.4	10.3	10.1
Hexamethallyl dipentaerythritol	183–185	.3	$C_{34}H_{58}O_7$	1.4682	.9561	167.11	168.34	57.1	56.4	70.6	70.3	10.1	10.1

[a] $[\alpha]^{25}D$ of an 8% solution in absolute alcohol, +15.7°. [b] $[\alpha]^{25}D$ of an 8% solution in absolute alcohol, +5.9°.

0.4 mm. Step II gave a 70% yield of dimethallyl ethylene glycol.

Methallyl Starch.—Thirty-four grams of air-dried potato starch was treated with three times the stoichiometrically equivalent quantities of methallyl bromide and 50% alkali with 150 ml. of methyl ethyl ketone as solvent. The reaction mixture was stirred at 85° for ten hours. It was then steam distilled, and the resulting gummy material kneaded with water until free of alkali. The yield was 30 g. of methallyl starch containing 43.7% methallyl, or 2.25 methallyl groups, per glucose unit. This material was gummy while wet but soon became dry and crumbly. Thin films of the product polymerized to an insoluble infusible state in the same manner as allyl starch.[8]

Allyl Dipentaerythritol.—By Step I, 200 g. of dipentaerythritol gave a 59% yield of a partially allylated product containing 4.6 allyl groups and distilling at 174° at 0.3 mm.

Step II gave a 67% yield of hexaallyldipentaerythritol, boiling point 184–186° at 1 mm., $n^{20}D$ 1.4679, d^{20}_4 0.9777, molecular refraction, 140.03 (calcd. 140.20); allyl 49.9% (calcd. for $C_{28}H_{46}O_7$, 49.8%); carbon, 68.1% (calcd. 68.0%); hydrogen, 9.3% (calcd. 9.3%).

Isolation of Methacrolein as a By-product of Oxidation of Methallyl Ethers.—Methacrolein was isolated and identified essentially in the same manner as described for isolation of acrolein.[3] The pungent liquid which distilled off during oxidation of methallyl sorbitol at 97° was collected in the trap cooled with solid carbon dioxide in acetone. The 2,4-dinitrophenylhydrazone was prepared, and after two recrystallizations from xylene melted at 205.5–206° (reported in literature[9] 206.0–206.5). When this material was mixed with authentic methacrolein-2,4-dinitrophenylhydrazone, there was no depression in the melting point.

Preparation of Methallyl Bromide.—One mole of methallyl chloride and 1.5 moles of sodium bromide were heated with 360 ml. of absolute methanol for ten hours at reflux temperature. After filtration and removal of methanol by washing with water, the methallyl bromide was recovered by fractionation. The average yield of four preparations was 31%, as compared with 15 to 20% obtained by Tamele, Ott, Marple and Hearne.[10]

Unsaturation was determined as described in the second article of this series.[3] The method of Ogg, Porter and Willits[11] was used for determination of free hydroxyl.

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Summary

Eight new methallyl ethers of polyhydroxy compounds have been prepared. Their rates of oxygen absorption are higher than those for corresponding allyl ethers and they absorb more oxygen at the gelation point. Comparative gelation times for allyl and methallyl ethers have been determined. The mechanism of oxidation of methallyl ethers appears to be similar to that described for allyl ethers.

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(8) Nichols, Hamilton, Smith and Yanovsky, *Ind. Eng. Chem.*, **37**, 201 (1945).

(9) Shriner and Sharp, THIS JOURNAL, **62**, 2245 (1940).

(10) Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

(11) Ogg, Porter and Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945).

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Chemical Interactions of Amino Compounds and Sugars. I(1)

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In the processing of many foodstuffs the products often develop undesirable colors. Much of this coloring or "browning" has been ascribed to the reaction between the carbohydrates and proteins present, or, more specifically, to the reaction between reducing sugars and amino acids. This decomposition reaction, in its final stages, has been termed the Maillard[3] reaction. Attempts to determine the nature of the interaction between amino acids and sugars are numerous and many techniques have been employed. The principal investigative tools used have been polarimetry,[4] cryoscopy,[5] colorimetry,[3b] potentiometry[6] and chemical analysis, the latter including

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(2) Research Foundation Associate, The Ohio State University, Project 238.

(3) (a) L.-C. Maillard, *Compt. rend.*, **154**, 66 (1912); (b) *Ann. chim.*, [9] **5**, 258 (1916).

(4) C. Neuberg and Maria Kobel, *Biochem. Z.*, **162**, 496 (1925); *ibid.*, **174**, 464 (1926); H. v. Euler and K. Josephson, *Z. physiol. Chem.*, **153**, 1 (1926).

(5) H. v. Euler, E. Brunius and K. Josephson, *Z. physiol. Chem.*, **155**, 259 (1926); H. v. Euler and E. Brunius, *Ber.*, **59B**, 1581 (1926); *Ann.*, **467**, 201 (1928).

(6) M. Frankel and A. Katchalsky, *Biochem. J.*, **31**, 1595 (1937).