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

Allyl Ethers of Carbohydrates. I. Preparation and Polymerization of Tetra-allyl α-Methyl Glucoside

BY P. L. NICHOLS, JR., AND E. YANOVSKY

Results obtained in this Laboratory have shown that allyl ethers of complex carbohydrates such as starch and cellulose form insoluble and infusible resins when exposed to oxygen or air. In an effort to understand more clearly the nature of this insolubilization process, we prepared several allyl derivatives of simpler carbohydrates, and studied the polymerization of these compounds in the presence of air and oxygen at elevated temperatures. Treatment of this kind yielded clear and transparent polymers of the thermosetting type. This paper describes the preparation and polymerization of tetra-allyl α-methyl glucoside.

A few allyl carbohydrates such as α- and β-allyl glucosides,[2] 3-allyl glucose and its osazone,[3] α- and β-allyl galactosides,[4] and allyl cellulose[5] have been prepared. A more detailed investigation of allyl ethers of carbohydrates was made by Tomecko and Adams,[6] who prepared the allyl ethers of α-methyl glucoside, sucrose, inulin, dextrin, starch and cellulose.

Attempts to prepare tetra-allyl α-methyl glucoside following the procedure described by Tomecko and Adams were unsuccessful. Under the conditions of the experiment, the 10% alkali recommended by them hydrolyzed allyl bromide rapidly; at higher concentrations the rate of hydrolysis was reduced considerably. Fifty per cent. alkali proved to be a more satisfactory medium for this reaction.

Since complete substitution of α-methyl glucoside could not be accomplished in one etherification to prepare pure tetra-allyl α-methyl glucoside, it was necessary to treat the nearly completely substituted allyl α-methyl glucoside with sodium and the resulting alcoholate with allyl bromide. The properties of our preparations as compared with those of Tomecko and Adams are shown in Table I.

TABLE I

ANALYSES AND PHYSICAL CONSTANTS OF ALLYL α-METHYL GLUCOSIDE PREPARATIONS

		Allyl α-methyl glucoside	Tetra-allyl α-methyl glucoside	Tetra-allyl α-methyl glucoside (Tomecko and Adams)	Calcd. for $C_{19}H_{30}O_6$
Boiling point	°C.	144–145	160–162	182	...
	Mm.	0.15	1.5	1.5	
Density$^{20}_{4}$		1.0505	1.0345	1.1519	...
Refractive index n^{20}D		1.4748	1.4710	1.4836	...
Specific rotation $[\alpha]^{25}$D (8% solution in absolute alcohol)		118.6°	115.6°	116.5°	...
Molecular refraction		94.94	95.76	88.18	95.73
Carbon, %		62.34	63.92	64.13	64.38
Hydrogen, %		8.53	8.11	7.93	8.53
Free hydroxyl, %		2.28	<0.1	...	0
Allyl, %		42.8	45.95	...	46.4

The table shows the change of properties on transition from incomplete to complete substitution of methyl glucoside. The density, refractive index and specific rotation of the fully substituted compound have lower values; the molecular refraction and analytical data are nearer the theoretical figures for the tetra-allyl compound. On the basis of insufficient analytical data, it is difficult to pass judgment on the purity of the Tomecko and Adams compound. The description of their product as a thick oil suggests, however, that it might have been partly oxidized.

Under the influence of oxygen and heat, the allylated glucoside gradually polymerizes, first to a viscous liquid and finally to a colorless transparent resin. The changes in viscosity occurring during the polymerization of tetra-allyl α-methyl glucoside are shown in Table II. The gradual increase in viscosity, followed by a marked increase to the point of gelation, along with the insoluble and infusible nature of the final product, is characteristic of the formation of a three di-

TABLE II

POLYMERIZATION OF TETRA-ALLYL α-METHYL GLUCOSIDE AT 97°[a]

Time, minutes	Viscosity, seconds	Viscosity, centistokes
0	2.8	2.7
60	3.2	3.0
120	8.5	8.0
146	17.7	16.8
160	27.8	26.4
182	67.8	64.4
189	93.6	88.6
196	133.6	126.5
204	231.9	219.5
208	∞[b]	∞[b]

[a] The reaction was conducted and the viscosity measured in a modified Ostwald pipet through which oxygen was passed at a uniform rate. [b] During this measurement the material gelled in the tube. A control experiment in an atmsophere of carbon dioxide remained unchanged.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Bourquelot and Bridel, *Compt. rend.*, **155**, 437 (1912); Bourquelot, Hérissey and Bridel, *ibid.*, **156**, 1493 (1913); Fischer and Strauss, *Ber.*, **45**, 2467 (1912); Fischer, *Z. physiol. Chem.*, **108**, 3 (1919); Olive, *Bull. soc. chim.*, **13**, 254 (1931); Helferich and Gerdeler, *Ber.*, **73B**, 532 (1940).

[3] Freudenberg, Hochstetter and Engels, *Ber.*, **58B**, 666 (1925).

[4] Bourquelot and Bridel, *Compt. rend.*, **156**, 1104 (1913); Pacsu and Ticharich, *Ber.*, **62B**, 3008 (1929).

[5] Sakurada, *Z. angew. Chem.*, **42**, 549 (1929); Haller and Heckendorn, *Helv. Chim. Acta*, **24**, 85 (1941).

[6] Tomecko and Adams, THIS JOURNAL, **45**, 2698 (1923).

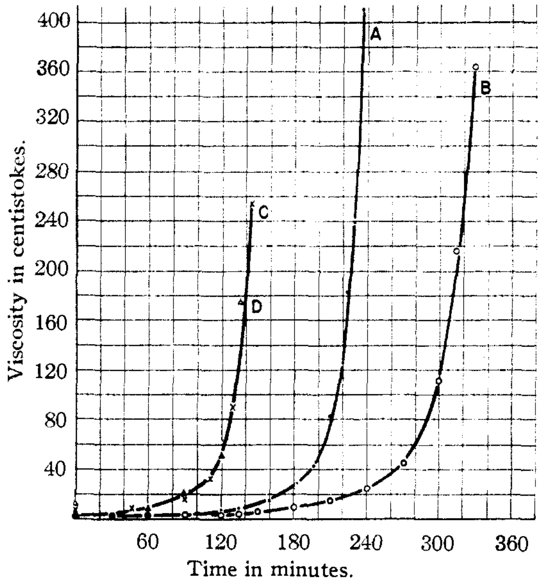

Fig. 1.—Polymerization of allyl methyl glucoside (3.5 allyl groups): A, ●, at 97°, oxygen 26 l. per hour; B, O, at 97°, oxygen 7.5 l. per hour; C, X, at 97°, oxygen 7.5 l. per hr. + Co naphthenate; D, Δ, at 116.5°, oxygen, 7.5 l. per hour.

mensional network.[7] Figure 1 shows the change in viscosity for allyl α-methyl glucoside (with an allyl content corresponding to 3.5 allyl groups per glucoside molecule) under various conditions. Curves A and B show the influence of the rate of flow of oxygen. Curves D and C show the influence of temperature and the addition of a catalyst on the polymerization of the glucoside. The gelation points for these curves are: A, 270 min., B, 390 min., C, 185 min., D, 170 min.

As compared with oxygen, benzoyl peroxide, an efficient catalyst for the vinyl type of polymerization, is relatively ineffective with allyl α-methyl glucoside. To test the effect of benzoyl peroxide two 10-g. portions of allyl α-methyl glucoside (with an allyl content corresponding to 3.5 allyl groups per glucoside molecule) were mixed with 0.1- and 0.2-g. portions of benzoyl peroxide, respectively. The two samples and a control were heated at 100° for sixteen hours. The viscosities (in centistokes) at 25° were 113 for the control, 163 for the sample containing 1% benzoyl peroxide, and 257 for the sample containing 2% benzoyl peroxide. Another sample of the same allyl α-methyl glucoside containing 1% benzoyl peroxide when heated at 180° for ninety-six hours remained fluid and solvent-soluble, although it darkened and the viscosity increased.

Failure of benzoyl peroxide to polymerize completely allyl α-methyl glucoside is apparently due to the fact that an appreciable amount of oxygen is required for this process. The actual amount of oxygen combined was measured in the following manner: A sample of pure tetra-allyl α-methyl glucoside was heated at 97° while a constant stream of oxygen was passed through it. After three and one-half hours, analysis showed 59.9% carbon and 7.5% hydrogen; after five and one-half hours (which is past the gelation point) the composition was 58.5% carbon and 7.2% hydrogen. Taking into consideration that the formula for tetra-allyl α-methyl glucoside is $C_{19}H_{30}O_6$ (mol. wt. 354.43), it is possible to calculate the number of oxygen atoms (x) combined during the oxidation from the equation[8]

$$x = \frac{12.01 \cdot 19 \cdot 100 - 354.43 \cdot C}{16 \cdot C}$$

where C is the carbon percentage at any given time during the polymerization. Substituting the above carbon values gives 1.7 oxygen atoms for three and one-half hours and 2.2 for five and one-half hours.

At present the manner in which the oxygen is combined in the gelled material is not quite clear. Tests during polymerization showed the presence of peroxides.

Experimental

Preparation of Allyl α-Methyl Glucoside.—500 grams of α-methyl glucoside (m. p. 165–166°, uncor.) was suspended in 890 cc. of allyl bromide in a 5-liter 3-neck flask equipped with condenser, dropping funnel and stirrer. The reaction mixture was maintained at the reflux temperature of allyl bromide (70–75°); 790 cc. of 52% sodium hydroxide was added to the well-stirred reaction mixture dropwise over a period of three and one-half hours. The reaction was allowed to proceed for an additional one and one-half hours. Unreacted allyl bromide and by-products of the reaction, such as allyl ether and allyl alcohol, were removed by steam distillation after the addition of approximately 1.5 liters of water. The oily layer was extracted with two 300-cc. portions of ether. The ether layer was dried with anhydrous sodium sulfate. Distillation from an ordinary Claisen flask in an atmosphere of carbon dioxide yielded from 500 to 540 g. (55–59.0% of theoretical) of a main fraction (I) boiling at 155–160° at 1 mm. This was redistilled through a Vigreux fractionating column fitted with a Whitmore and Lux type still head.[9] The main fraction (II) boiled at 144–145° at 0.14 mm. of mercury. Yields ranged from 403 to 428 g. (44 to 47% of theoretical).

Further Allylation of Allyl α-Methyl Glucoside.—150 grams of fraction II was placed in a 250-cc. flask equipped with a condenser, dropping funnel and glass stirrer; 12.7 g. of metallic sodium was added, and for five hours the reaction mixture was heated between 105 and 110° while it was stirred sufficiently to form small droplets of molten sodium. The temperature of the reaction mixture was then lowered to 80–85°, and 46 cc. of allyl bromide was added slowly dropwise. This reaction mixture was heated for an additional two hours. Sufficient ethanol was added to insure the complete removal of free sodium, and the contents of the flasks were poured into 250 cc. of water; 200 cc. of ether was used to extract allyl glucoside, and the ether layer was washed free of alkali and dried with anhydrous sodium sulfate. After ether was removed at atmospheric pressure, the allyl glucoside was distilled *in*

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(7) Carothers, *Trans. Faraday Soc.*, **32**, 39 (1936); Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941).

(8) This equation is strictly correct only if no losses of volatile material occur during the polymerization. Actual experiments have shown that there is approximately 1 per cent. loss which, on the assumption that the material lost contained 50 per cent. carbon, would give a correction in the second decimal place for x.

(9) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

vacuo from a Claisen flask, carbon dioxide instead of air being bubbled through the flask. After a small forerun, which was discarded, 142.0 g. of pure tetra-allyl α-methyl glucoside distilled.

Unsaturation in allyl derivatives was determined by the Wijs method. Wijs solution was prepared as recommended by Kemp and Mueller.[10]

Free hydroxyl was determined by acetylating with pyridine-acetic anhydride (3:1) mixture and titrating the uncombined acetyl by a method to be published shortly by W. L. Porter, C. L. Ogg and C. O. Willits of this Laboratory.

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Summary

The preparation and properties of tetra-allyl α-methyl glucoside are described. Polymerization of this compound in the presence of oxygen is discussed.

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(10) Kemp and Mueller, *Ind. Eng. Chem., Anal. Ed.*, **6**, 52 (1934).

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The Dehydration of the Lower Aliphatic Alcohols in the Presence of Dilute Aqueous Solutions of Acids and Salts

BY V. N. IPATIEFF AND G. S. MONROE

In a previous investigation pertaining to the solubilities of various gases in aqueous alcoholic solutions, the observation was made that one of the alcohols employed underwent dehydration to the olefin. The magnitude of the reaction was so great that a systematic study of the lower aliphatic alcohols seemed justified on the grounds that a catalyst of unknown nature was probably present.

Alumina, as is generally known, is one of the best catalysts for the dehydration of alcohols[1] and can give good yields in the presence of small amounts of water. Other catalysts for the dehydration of alcohols have been described in the literature.

The dehydration of unsaturated alcohols (especially those with a secondary or tertiary hydroxyl group) with potassium acid sulfate, oxalic acid, or acetic anhydride has been discussed by Kyriakides.[2] Hibbert used iodine for the dehydration of the tertiary amyl alcohol to trimethylethylene, and also obtained tetrahydrobenzene from cyclohexanol with the same catalyst.[3] Volkow, using methyl iodide as a catalyst for the dehydration of monohydric alcohols, concluded that complete dehydration occurred with secondary and tertiary alcohols, while primary alcohols gave ethers.[4] Reppe and Trieschmann employed ammonium chloride, oxalic acid, or phosphoric acid in dilute 1,4-butylene glycol for dehydration to tetrahydrofuran.[5] The dehydration of alcohols of the terpene series with dilute aqueous salt solutions has been reported by Ipatieff and Pines.[6]

The present investigation of the dehydration of the lower aliphatic alcohols in the presence of dilute aqueous solutions of acids and salts began with the unexpected formation of isobutylene from tertiary butyl alcohol when heated with an equal weight of water at 200° in a rotating autoclave without any added catalyst. Repetition of the experiment gave the same results, over 80% of the alcohol going to the olefin. Further investigation revealed that the walls of the supposedly clean autoclave were contaminated with nickel chloride. When the experiment was repeated in another bomb with clean walls only 2% of the alcohol was dehydrated.

In the study of secondary butyl alcohol at 230°, no dehydration of the alcohol occurred in the presence of water alone or anhydrous hydrochloric acid. When dilute aqueous solutions of hydrochloric acid were employed in concentrations of 1.0% down to 0.02%, almost 84% of the alcohol underwent dehydration, about 81% to butenes and about 3% to polymer. The catalytic effect of the solution was still apparent when the concentration was reduced to 0.002%. In this case about 13% of the alcohol was dehydrated.

Dilute solutions of other strong acids, such as sulfuric, arsenic pentoxide (in the presence of water) or the salts of strong acids that dissolve or hydrolyze in water to give an acid reaction, such as potassium hydrogen sulfate or ferric chloride, likewise caused dehydration. Aqueous solutions of weak acids, such as carbon dioxide (in the presence of water), or acetic, had only a slight catalytic effect.

The fact that no olefin was produced from the alcohol in the presence of water alone or of anhydrous hydrochloric acid, while dilute aqueous hydrochloric acid solutions catalyzed the dehydration of about 84% of the alcohol to the olefin, indicates that the acid solution was the catalyzing agent. The low yields of olefins ob-

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(1) V. N. Ipatieff, *Ber.*, **34**, 3579 (1901); **36**, 1990 (1903).

(2) L. P. Kyriakides, THIS JOURNAL, **36**, 985 (1914).

(3) H. Hibbert, *ibid.*, **37**, 1748 (1915).

(4) A. Volkow, *J. Russ. Phys.-Chem. Soc.* **21**, 333 (1889); *J. Chem. Soc. Abs.*, **58**, 354 (1890).

(5) W. Reppe and H. G. Trieschmann (to General Aniline and Film Corp.) U. S. Patent 2,251,835 (August 5, 1941).

(6) V. N. Ipatieff and H. Pines, THIS JOURNAL, **66**, 816 (1944).