Summary

The *p*-bromobenzenesulfonyl derivatives of several common amines have been characterized. These compounds are useful for the identification of amines.

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THE ALLYL ETHERS OF VARIOUS CARBOHYDRATES

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Some of the most important developments in the chemistry of carbohydrates during the past fifteen years have been through the use of the alkyl ether derivatives. The original method of alkylation, as developed by Irvine[2] and his co-workers, was by means of silver oxide and alkyl iodides. More recently, an improvement has been made upon this procedure by Haworth[3] who has used methyl and ethyl sulfates in place of the alkyl iodides; with these reagents aqueous alkaline solutions or suspensions are employed and the preparation of the ethers is thus rendered very simple. Of especial interest may be mentioned that the ethers of the disaccharides have been used in the determination of the structure of the disaccharides; the ethers of cellulose apparently are of commercial importance and consequently their preparation by this same process has engaged the attention of many investigators. In spite of the general interest and importance of the ethers of the carbohydrates, no other ethers than the methyl and ethyl derivatives have been prepared until very recently. Gomberg and Buchler[4] made the benzyl derivatives of a variety of carbohydrates, following the same procedure as with the alkyl sulfates; this was possible due to the great reactivity of the chlorine in the benzyl chloride. In that paper a review of the previous articles discussing alkylation was given. Since that time many patents[5] have appeared on the

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[1] This communication is an abstract of a portion of a thesis submitted by C. G. Tomecko in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Purdie and Irvine, *J. Chem. Soc.*, **83**, 1021 (1903).

[3] Haworth, *ibid.*, **107**, 8 (1915).

[4] Gomberg and Buchler, THIS JOURNAL, **43**, 1904 (1921). See also U. S. pat., 1,451,331; *C. A.*, **17**, 2505 (1923).

[5] Lilienfeld, Brit. pat. 163,016, 163,017, 163,018 [*C. A.*, **15**, 3207 (1921)]; Can. pat. 220,831 [*C. A.*, **16**, 2989 (1922)]; Brit. pat. 177,810 [*C. A.*, **16**, 3206 (1922)]; Brit. pat. 181,392, 181,393, 181,395 [*C. A.*, **16**, 3758 (1922)]; Can. pat. 222,377 [*C. A.*, **16**, 4087 (1922)]; U. S. pat. 1,441,889 [*C. A.*, **17**, 1141 (1923)]. Young, Brit. pat. 184,825 [*C. A.*, **17**, 878 (1923)]. Clancy, U. S. pat. 1,439,293 [*C. A.*, **17**, 879 (1923)]. Seel, U. S. pat. 1,437,820, 1,437,821 [*C. A.*, **17**, 879 (1923)]. Dreyfuss, Brit. pat. 187,639 [*C. A.*, **17**, 1141 (1923)].

methylation and ethylation of cellulose, as well as numerous scientific papers involving the methylation[6] or ethylation of a variety of different carbohydrates.

From a practical standpoint the methyl and ethyl ethers are at present the only types which are of particular interest, but from a theoretical standpoint the preparation and study of other types of ethers should lead to important results. An investigation was undertaken in this Laboratory to prepare such ethers of the carbohydrates as contain in the ether groups other active groups through which new types of carbohydrate compounds may be prepared and studied. Such new ethers may be formed by allowing active halogen compounds to react with an alkaline solution or suspension of the carbohydrate; of these may be mentioned the first two that have been studied, allyl bromide and chloro-acetic acid.

This preliminary communication describes work on the allylation of carbohydrates with allyl bromide and sodium hydroxide. Owing to the great reactivity of the bromine, the introduction of the allyl group is extremely simple and good yields of products are obtained. The number of ether groups introduced corresponds to the number of benzyl groups introduced by benzyl chloride and sodium hydroxide.

The products resemble in physical properties the corresponding methyl and ethyl derivatives. The tetra-allyl-α-methyl glucoside is a high-boiling, viscous liquid that can be distilled under diminished pressure without decomposition. Penta-allyl sucrose is a viscous oil that cannot be distilled without decomposition. Mono-allyl inulin, mono-allyl potato starch, mono-allyl corn starch, mono-allyl dextrin and allylated cellulose are practically white, amorphous substances that were purified by solution in various organic solvents and then reprecipitation with ether. They give rather indefinite decomposition points. Various derivatives of the new allyl ethers are now being studied.

No record of the preparation of allyl ethers of carbohydrates has previously appeared. The only allyl derivatives of the carbohydrates which have been mentioned are the allyl glucosides prepared by Fischer[7] and Bourquelot.[8]

Experimental Part

One molecular equivalent of carbohydrate was dissolved or suspended in 10% sodium hydroxide containing an excess of alkali (2 to 2.5 mo-

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[6] Denham and Woodhouse, *J. Chem. Soc.*, **119**, 77 (1921). Karrer and Nagelli, *Helvetica Chim. Acta*, **4**, 185 (1921). Karrer and Lang, *ibid.*, **4**, 249 (1921). Irvine, Steele and Shannon, *J. Chem. Soc.*, **121**, 1060 (1922). Irvine and Hirst, *ibid.*, **121**, 1213 (1922). Irvine and Patterson, *ibid.*, **121**, 2696 (1922). Heuser and Neunstein, *Cellulosechemie*, **3**, 101 (1922). Haworth and Linnell, *J. Chem. Soc.*, **123**, 294 (1923). Haworth and Mitchell, *ibid.*, **123**, 301 (1923). Irvine and Hirst, *ibid.*, **123**, 518 (1923).

[7] Fischer, *Ber.*, **45**, 2467 (1912).

[8] Bourquelot, *Compt. rend.*, **155**, 437 (1912); **156**, 1493 (1913).

lecular equivalents). This mixture was heated on a water-bath and stirred mechanically while an excess of allyl bromide was dropped in slowly. It was generally advisable to heat the reaction mixture on a water-bath for about an hour after all the bromide had been added. The reaction mixture was then steam distilled to remove any allyl alcohol or excess of allyl bromide, the oily or gummy reaction product washed with water and purified. The yields, properties and methods of purification are described under the individual substances.

All analyses were made on the solids after drying in a vacuum at 110° for 24 hours. It was found that two or three of the allylated compounds did not give analyses as close to the calculated values as might be expected. In these cases duplicate analyses were carried out on subsequent reprecipitations and in every instance gave check results with those analyses which are reported. This led to the conclusion that certain of the mono-allyl derivatives were contaminated, perhaps with small amounts of higher allylated compounds which had very similar properties to the mono-allyl derivatives and were not removed by the precipitations.

None of the solids prepared had a definite melting or decomposition point. Since melting points were reported for the benzylated compounds[4] two or three of these were made in this Laboratory and the effect of temperature determined. The points mentioned by these authors as melting points are unquestionably points of decomposition resembling closely the type of decomposition found for the allylated compounds. The "melting points" reported for the benzyl compounds are actually the points where the various materials start to shrink.

Tetra-allyl-α-methyl Glucoside.—From 100 g. of α-methyl glucoside, 249 g. of allyl bromide and 124 g. of sodium hydroxide, there was obtained 83 g. of purified tetra-allyl-α-methyl glucoside boiling at 182° (1.5 mm.); n_D^{18}, 1.4836; d_{20}^{20}, 1.1519; $[\alpha]_D^{30}$, 116.5° (in absolute alcohol). It is a thick, colorless oil, insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.1503: CO_2, 0.3160; H_2O, 0.1070. Calc. for $C_{19}H_{30}O_4$: C, 64.41, H, 8.47. Found: C, 64.13; H, 7.93.

Penta-allyl Sucrose.—From 100 g. of sucrose, 340 g. of allyl bromide and 141 g. of sodium hydroxide there was produced 118 g. of the penta-allyl derivative. The crude reaction product was taken up in chloroform, filtered and the chloroform evaporated. There was thus formed a practically colorless, thick oil which could not be distilled under diminished pressure without decomposition. It was insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.4710: CO_2, 1.0232; H_2O, 0.3056. Calc. for $C_{27}H_{42}O_{11}$: C, 59.59; H, 7.74. Found: C, 59.21; H, 7.58.

Mono-allyl Dextrin.—From 25 g. of dextrin, 100 g. of allyl bromide and 75 g. of sodium hydroxide there was obtained 16 g. of allylated dextrin. The crude product formed a gummy mass. This was purified by dissolving it in chloroform and precipitating with ether. After a number of such treatments a practically white, amorphous solid was obtained, shrinking at 155–165° and gradually decomposing at about 240–250°.

Analyses. Subs., 0.3876: CO_2, 0.7334; H_2O, 0.2260. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 51.41; H, 6.43.

Mono-allyl Inulin.—From 10 g. of inulin, 100 g. of allyl bromide and 75 g. of sodium hydroxide there was obtained about 5 g. of gummy product. When this was treated with a limited amount of cold alcohol, it dissolved and was then reprecipitated with ether. Care must be taken not to add too much alcohol as such an excess also causes precipitation. Further purification was effected by dissolving the material in glacial acetic acid and reprecipitating it with ether. There was thus produced 3 g. of nearly white product, shrinking at 150–155° and decomposing at 205–210°.

Analyses. Subs., 0.3014: CO_2, 0.5330; H_2O, 0.1898. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 48.22; H, 7.00.

Mono-allyl Potato Starch.—From 10 g. of potato starch, 85 g. of allyl bromide and 50 g. of potassium hydroxide, a gummy product was produced. This was dissolved in alcohol as described under allyl inulin and reprecipitated with ether, then twice dissolved in glacial acetic acid and reprecipitated with ether. The final product was practically white and weighed 10 g. It shrank at 160–165° and decomposed without melting at about 260–270°.

Analyses. Subs., 0.3470: CO_2, 0.6318; H_2O, 0.2054. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 49.64, H, 6.55.

Mono-allyl Corn Starch.—From 10 g. of corn starch, 110 g. of allyl bromide and 75 g. of potassium hydroxide there was obtained a gummy product which was purified like the mono-allyl potato starch. A practically white, amorphous product resulted which weighed 12 g. It became brown at about 250–265° but did not shrink or melt.

Analyses. Subs., 0.3447: CO_2, 0.5699; H_2O, 0.1853. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 50.41; H, 6.70.

Allylated Cellulose.—Pure filter paper was hydrated by dissolving it in cuprammonium hydroxide and precipitating in the usual way. From 10 g. of this precipitated cellulose, 85 g. of allyl bromide and 65 g. of potassium hydroxide there was obtained a residue which was treated with several portions of cuprammonium hydroxide. The material that remained undissolved was carefully dried and analyzed.

Analyses. Subs., 0.3852: CO_2, 0.6313; H_2O, 0.2211. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 45.15; H, 6.44.

The product was obviously impure as shown by the analysis, but this was unquestionably due to the fact that no solvent for crystallization was found.

Summary

Several different types of carbohydrates have been treated in aqueous alkaline solution or suspension with allyl bromide. Under these conditions allyl derivatives of these carbohydrates are produced.

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