

white, stable liquid of a sharp taste and disagreeable odor, and is slightly soluble in water;  $d_{20}^{20}$  1.0401;  $n_D^{20}$  1.4528.

*Anal.* Calcd. for  $C_6H_{16}O_3$ : C, 62.74; H, 9.37. Found: C, 62.50, 62.35; H, 9.50, 9.46.

### Summary

$\alpha$ -Methyl- $\gamma$ -tetrahydro-2-furylpropylmagnesium bromide is obtainable in excellent yields from the corresponding bromide which is accessible, in turn, from furfural. This organomagnesium halide is one of the unusually small number of the furan type so far reported, and probably the first to be obtained by a direct reaction. It has been characterized by appropriate derivatives.

AMES, IOWA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY, AT WASHINGTON SQUARE COLLEGE]

## CRYSTALLINE MONOMETHYLDIETHYLMERCAPTOGLUCOSE

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The author has had occasion to prepare pentamethyldiethylmercaptoglucose using Fischer's<sup>1</sup> method for the formation of diethylmercaptoglucose and a combination of Haworth<sup>2</sup> and Freudenberg's methods for the methylation process as described by Levene and Meyer.<sup>3</sup>

In some experiments, instead of following Levene and Meyer's procedure, which favors the formation of the polymethylated product, the following method was adopted. The dimethyl sulfate, three times the required amount, was placed in a three-necked flask; the flask was provided with an efficient stirrer, a reflux condenser and a large separatory funnel; the diethylmercaptoglucose was suspended in the sodium hydroxide, which was placed in the separatory funnel, and thence was allowed to flow into the flask gradually. The temperature was kept at 67°.

The methylated product was extracted by ether. After the ether was evaporated the remaining brown sirup which was supposed to contain the polymethylated product was very little in quantity. From the brown sirup, however, a crystalline substance was obtained which was recrystallized from absolute alcohol and gave a melting point of 156°. These crystals were kept for future reference.

Besides these crystals it was observed that during the ether extraction a solid substance was going into suspension in the ether layer. From this solid substance some unmethylated mercaptoglucose was extracted by boiling ether. The residue had a melting point between 155 and 160°.

<sup>1</sup> E. Fischer, *Ber.*, **27**, 673 (1894).

<sup>2</sup> W. N. Haworth, *J. Chem. Soc.*, **107**, 11 (1915).

<sup>3</sup> Levene and Meyer, *J. Biol. Chem.*, **67**, 176 (1926).

It had an appearance similar to the unmethylated product, but a different melting point. At this point it was decided to subject this substance to further methylation.

These crystals as well as more diethylmercaptoglucose were further subjected to methylation. This time the procedure described by Levene and Meyer was followed. The results with respect to the polymethylated diethylmercaptoglucose were more satisfactory, but the yield was smaller than that of Levene and Meyer. On account of this, the water layer after the ether extraction of the polymethylated product was placed aside for later investigation. After some days it was observed that a precipitate was formed which was not soluble in water. This substance was dissolved in chloroform and alcohol and left to stand overnight. In the alcohol layer were formed thin silky fibrous crystals which were recrystallized three times from absolute alcohol and gave a melting point of 156–157°. The results of micro analysis of this substance are given later.

The ether extract which contained the polymethylated diethylmercaptoglucose had dissolved some of the above substance. On evaporation of the ether and distillation of the polymethylated mercaptoglucose under reduced pressure, a substance remained in the distilling flask which always charred at higher temperature. This residue before charring was dissolved in chloroform and from the dark oily liquid after long standing crystals were obtained which were recrystallized from hot alcohol and gave a melting point of 152°; on further recrystallization they gave a melting point of 156–157°.

The analyses for carbon, hydrogen, sulfur, ethyl and methyl radicals were made according to F. Pregl's micro analytical methods at the Rockefeller Institute for Medical Research by Mr. D. Rigakos. The results are indicated in the following Table.

TABLE I

ANALYTICAL DATA FOR MONOMETHYLDIETHYLMERCAPTOGLUCOSE						
Sample, mg.	Weighed, mg.		Calculated for	%	Found, %	
3.630	AgI	8.440	1 Me, 2 Et	24.35	24.13	
3.350	BaSO <sub>4</sub>	5.195	S	21.28	21.30	
4.450	{	H <sub>2</sub> O	3.30	H	8.05	8.28
		CO <sub>2</sub>	7.185	C	43.97	44.03
4.930	{	H <sub>2</sub> O	3.615	H	8.05	8.20
		CO <sub>2</sub>	7.920	C	43.97	43.81

These results indicate that the partially methylated diethylmercaptoglucose is the monomethyl derivative.

The author wishes to express his thanks to Professor W. C. MacTavish of New York University at Washington Square College and to Professor John M. Nelson of Columbia University for their constant interest in his research. The author is indebted to Mr. Rigakos for the analytical part of this work.

### Summary

Monomethyldiethylmercaptoglucose has been isolated as a by-product from the preparation of pentamethyldiethylglucose.

NEW YORK CITY

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### NOTE

**The Use of Aryl Esters for the Preparation of Amides and Derivatives of Urea.**—During my investigations with Professor W. A. Noyes concerning optically active diazo compounds, the preparation of N-substituted acid amides was frequently necessary in order to separate certain stereoisomeric amines. They were also required as intermediate products in obtaining the diazo compounds. These preparations have been accomplished, usually, by condensation of the ethyl esters of the organic acids concerned with the amine by means of refluxing for several hours. In this condensation it has been observed that in general the esters of phenol or substituted phenols react more rapidly and at lower temperatures than the corresponding ethyl esters. Occasionally a considerable development of heat was noticed. Isolated examples of this behavior may be found in the literature. Diphenyl carbonate has been recommended as especially adapted for the preparation of urea, since it reacts very readily with ammonia even at water-bath temperature.<sup>1</sup> The corresponding ethyl ester reacts only by heating at 180° for a long time in a sealed tube.<sup>2</sup>

It has been recorded in the literature that guaiacol carbonate behaves with ammonia and amines in the same manner as diphenyl carbonate, forming urea or its N-substituted derivatives, instantly.<sup>3</sup> Dr. Noller, in this Laboratory, has recently prepared diphenylcarbazide (C<sub>6</sub>H<sub>5</sub>NH-NH)<sub>2</sub>CO, from phenylhydrazine and guaiacol carbonate.<sup>4</sup>

It has now been found that diphenyl carbonate reacts as readily with aniline, bornylamine and other amines as it does with ammonia. A mixture of bornylamine and diphenyl carbonate melts with an evolution of heat. By warming on the water-bath the reaction will be finished after five to ten minutes, with solidification. In the use of diethyl carbonate no action could be obtained even by heating to 180° in a sealed tube for four hours.

It has also been found that diphenyl oxalate shows a behavior very similar to the diphenyl and guaiacol carbonates, being much more reactive than the diethyl ester. Bornylamine and diphenyl oxalate react at 80° within a few minutes, forming dibornylamide, while the reaction with diethyl-oxalate requires refluxing for three to four hours. Also, the formation of

<sup>1</sup> Hentschel, *Ber.*, **17**, 1286 (1884).

<sup>2</sup> Natanson, *Ann.*, **98**, 289 (1856).

<sup>3</sup> Cazeneuve, *Bull. soc. chim.*, [3] **15**, 714 (1896).

<sup>4</sup> Private communication.