

### CXI.— *$\alpha$ -Monosodium Glyceroxide : Its Structure and Application.*

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UP to the present the general methods of attempted identification of the structure of monoglycerides have depended either on the action of glyceryl chlorohydrins on the salts of fatty acids or on the esterification of the fatty acids with the chlorohydrins and the subsequent exchange of the halogen atoms for hydroxyl groups (*Annual Reports*, 1920, **17**, 58). Fischer has shown these methods to be untrustworthy (*Ber.*, 1920, **53**, [B], 1621), and there has now been published an alternative and trustworthy method based on

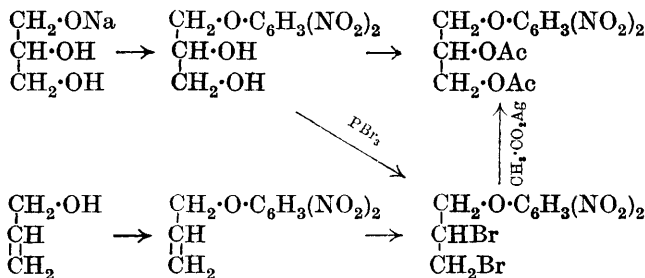
the constitution of "acetone glycerol" (Fischer, Bergmann, and Barwind, *Ber.*, 1920, **53**, [B], 1589).

The present authors found it necessary to determine the exact constitution of certain monoglycerides in the course of a larger investigation on the preparation of oxazines, but in view of the current interest in this problem it is felt desirable that these experiments should now be communicated separately, since they embody an independent and quite different method of preparation of  $\alpha$ -mono-derivatives of glycerol of undoubted purity.

Willgerodt (*Ber.*, 1879, **12**, 766) condensed glycerol, in the presence of potassium hydroxide, with 1-chloro-2:4-dinitrobenzene, then called " $\alpha$ -dinitrochlorobenzol," whence he named the product "monoalphanitrophenylglycerinäther," the letter of identification, however, being used apparently without reference to the position of substitution in the glyceryl radicle, a terminology which would seem to be largely responsible for this ether subsequently remaining in the literature, without proof, as definitely an  $\alpha$ -ether of glycerol.

Löbisch and Loos (*Monatsh.*, 1881, **2**, 782, 842) prepared both the mono- and di-sodium derivatives of glycerol, no attempt being made to prove the constitution of either compound. Letts (*Ber.*, 1872, **5**, 159) also prepared the mono-sodium derivative, removing the accompanying molecule of alcohol of crystallisation by heating the crystalline product in a current of hydrogen, and Nef (*Annalen*, 1904, **335**, 285), whilst working on the dissociation of this substance, obtained indirect evidence that it was probably the  $\alpha$ -compound.

In the present work, this derivative has been prepared in large quantity, quite free from alcohol, by warming the precipitated powder in an evacuated flask. The product was then condensed with 1-chloro-2:4-dinitrobenzene to give an ether of necessarily the same constitution as that of the sodium derivative, and this constitution has been successfully determined by proof of the identity of its diacetyl derivative with that obtained from the 2:4-dinitrophenyl ether of allyl alcohol, and confirmed by the identity of the dibromides obtained from the glyceryl and the allyl ethers respectively.



## EXPERIMENTAL.

 *$\alpha$ -Monosodium Glyceroxide,  $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{ONa}$ .*

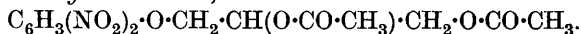
Twenty-three grams of sodium (1 mol.) were dissolved in 350 c.c. of absolute alcohol, and to this was cautiously added slightly less than one molecular proportion of glycerol. The addition of each portion caused a violent action and the precipitation of a white, crystalline solid, which was filtered rapidly and washed with alcohol and then with ether. The yield, calculated as  $\text{C}_3\text{H}_7\text{O}_3\text{Na}, \text{C}_2\text{H}_5\cdot\text{OH}$ , was nearly theoretical (Found:  $\text{Na}=14.22$ ;  $\text{C}_2\text{H}_5\cdot\text{OH}=28.5$ .  $\text{C}_3\text{H}_7\text{O}_3\text{Na}, \text{C}_2\text{H}_5\cdot\text{OH}$  requires  $\text{Na}=14.37$ ;  $\text{C}_2\text{H}_5\cdot\text{OH}=28.7$  per cent.).

The alcohol of crystallisation was removed from this compound by heating it for five hours at  $100^\circ$  and 25 mm. pressure, a modification of this method being used in the estimation of the alcohol in the original compound. The percentage of sodium was estimated in the alcohol-free glyceroxide obtained in this way (Found:  $\text{Na}=19.94$ .  $\text{C}_3\text{H}_7\text{O}_3\text{Na}$  requires  $\text{Na}=20.17$  per cent.).

*Glycerol  $\alpha$ -2 : 4-Dinitrophenyl Ether,*  
 $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ .

Molecular proportions of  $\alpha$ -monosodium glyceroxide (11.4 grams) and 1-chloro-2 : 4-dinitrobenzene (20.25 grams) were dissolved in 104 c.c. and 206 c.c. of glycerol respectively. When these solutions had cooled to about  $100^\circ$ , the chlorodinitrobenzene solution was poured into that of the glyceroxide, which immediately assumed a cherry-red colour. The mixture was heated almost to boiling for twenty minutes, and was then poured into 1180 c.c. of water, the precipitated material being redissolved by boiling. After keeping for twenty-four hours, the mass of yellow crystals was filtered off and washed with light petroleum (b. p.  $40$ — $60^\circ$ ), the yield being 90 per cent. of the theoretical.

This ether is, when pure, colourless, and it crystallises from water, benzene, and tetrachloroethane. It is soluble in ether, alcohol, and acetone, and in alkaline solution is deep red; but it becomes colourless on the addition of a slight excess of acid. It melts at  $85^\circ$  (compare Willgerodt for an ether of unknown constitution, m. p.  $83^\circ$ ; *Ber.*, 1879, **12**, 769).

*The Diacetyl Derivative,*

—The glycerol ether was heated under reflux for two to three hours with five parts of acetic anhydride and one part of anhydrous sodium acetate. The oil, obtained by pouring the mixture into

water, dissolved on boiling, and on cooling reappeared as a colourless, crystalline substance. It crystallises from water and from alcohol, and melts at 106–107° (Found :  $\text{CH}_3\cdot\text{CO}=25\cdot12$ ,  $25\cdot13$ .  $\text{C}_{13}\text{H}_{14}\text{O}_9\text{N}_2$  requires  $\text{CH}_3\cdot\text{CO}=25\cdot15$  per cent.).

### 2 : 4-Dinitrophenyl Allyl Ether.

This compound was prepared by a method similar to that used by Willgerodt (*loc. cit.*), who distilled off the excess of allyl alcohol after condensation had taken place. It has been found that this procedure leads in most cases to charring, and in one instance an explosion occurred. Instead, therefore, of distilling off all the allyl alcohol, some 80 per cent. only was removed in this way, the residue being poured into a 5 per cent. solution of sodium chloride and extracted with ether. The fibrous mass obtained after the removal of the ether crystallised from alcohol in long, colourless needles, m. p. 46°.

Several unsuccessful attempts were made to oxidise this substance directly to the corresponding dihydroxy-compound, and this method of identifying the structure of these substances was ultimately abandoned, attention being directed towards the diacetyl and dibromo-derivatives.

### 2 : 4-Dinitrophenyl $\beta\gamma$ -Dibromopropyl Ether,



Three grams of 2 : 4-dinitrophenyl allyl ether were dissolved in 10 c.c. of chloroform, and a solution of rather more than the theoretical amount of bromine (2·26 grams) in 10 c.c. of the same solvent was added. The chloroform was distilled off and the residue heated on a water-bath until the excess of bromine had volatilised. The solid thus obtained crystallised in small, hard plates with a silvery lustre, m. p. 110°. The yield was quantitative (Found :  $\text{Br}=41\cdot76$ .  $\text{C}_9\text{H}_8\text{O}_5\text{N}_2\text{Br}_2$  requires  $\text{Br}=41\cdot67$  per cent.).

### Action of Silver Acetate on 2 : 4-Dinitrophenyl $\beta\gamma$ -Dibromopropyl Ether.

Many attempts were made, in various solvents, to replace the bromine in this compound by acetyl radicles, but only in glacial acetic acid solution were any signs of success apparent. The silver acetate used was freshly prepared and analysed in order to check its purity.

Five grams (1 mol.) of pure silver acetate were suspended in

glacial acetic acid, and to it was added a solution of 3.6 grams (1 mol.) of the dibromide in the same solvent. The mixture was heated under reflux for four hours, and the silver bromide was then filtered off and washed several times with water. The washings and the filtrate were combined, diluted with water, neutralised with sodium carbonate, and extracted with ether. The solid extracted in this way was a mixture of the required diacetyl compound and unchanged dibromide. By extraction with water and repeated crystallisation from alcohol, a substance was obtained which melted at 104—105°. Further crystallisation had no effect on the melting point, but a mixture with the diacetyl derivative of glycerol  $\alpha$ -2 : 4-dinitrophenyl ether melted at 105—106°.

M. p. of the diacetyl derivative of the glycerol ether ...	106—107°
M. p. of the diacetyl derivative of the allyl ether .....	104—105°
M. p. of the mixed substances .....	105—106°

The diacetyl derivative obtained indirectly from the allyl ether, therefore, was not perfectly pure, but it was obviously identical with that produced by acetylating the glycerol ether. Since, in the allyl ether, the 2 : 4-dinitrophenyl radicle must be joined to a terminal carbon atom, it follows that the glycerol ether and the sodium derivative are both  $\alpha$ -compounds. This conclusion has been definitely confirmed by the identity of the corresponding dibromides in the following manner.

*Action of Phosphorus Tribromide on Glycerol  $\alpha$ -2 : 4-Dinitrophenyl Ether.*

This substance was warmed gently for an hour with phosphorus tribromide, and when no further evolution of gas occurred the mixture was poured into water. The solid substance obtained after keeping for several days was washed, first with sodium carbonate solution and then with water. After crystallisation from alcohol, the following series of melting points was obtained :

M. p. of this product .....	110°
M. p. of the dibromide of the allyl ether .....	110°
M. p. of the mixed substances .....	110°

The identity of these melting points affords an independent proof of the structure of the monosodium glyceroxide and of the dinitrophenyl ether derived from it.

The constitution of the  $\alpha$ -monosodium derivative being now proved, it is thus possible to prepare mono-substituted products of glycerol by treating this sodium compound with acid chlorides or

compounds of a similar nature, as has been done in the case of the dinitrophenyl ether described above. A typical example of mono-acyl preparations (glycerides) is that of the benzoyl ester, the constitution of which as an  $\alpha$ -derivative has been proved by the following representative experiment.

Equimolecular proportions of  $\alpha$ -monosodium glyceroxide and benzoyl chloride were placed in dry benzene and kept for twenty-four hours. The mixture was then heated for a few minutes and filtered. The benzoyl glyceride was obtained as a viscous oil, which crystallised after being subjected to a freezing mixture of ice and salt for two days (Found:  $C_6H_5 \cdot CO = 53.60$ .  $C_{10}H_{14}O_4$  requires  $C_6H_5 \cdot CO = 53.56$  per cent.).

The authors wish to take this opportunity of expressing their thanks to Professor Smiles for the interest he has taken in this work.

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