CCCCXXV.—*The Partial Esterification of Polyhydric Alcohols. Part V. The α-Structure of Alleged "β"-Monoglycerides.*

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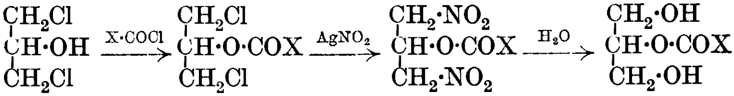
GRÜN (*Ber.*, 1910, **43**, 1288) proposed the reaction between β-monochlorohydrin and the potassium salts of acids for the preparation of β-monoglycerides,

(i) $OH{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}OH \xrightarrow{X{\cdot}CO_2K} OH{\cdot}CH_2{\cdot}CH(O{\cdot}COX){\cdot}CH_2{\cdot}OH$, and claimed to have produced these compounds independently by the reaction between esters of $\alpha\gamma$-dichlorohydrin and silver nitrite, followed by treatment with water :

(ii)



$$\begin{array}{c}CH_2Cl\\ |\\ CH{\cdot}OH\\ |\\ CH_2Cl\end{array} \xrightarrow{X{\cdot}COCl} \begin{array}{c}CH_2Cl\\ |\\ CH{\cdot}O{\cdot}COX\\ |\\ CH_2Cl\end{array} \xrightarrow{AgNO_2} \begin{array}{c}CH_2{\cdot}NO_2\\ |\\ CH{\cdot}O{\cdot}COX\\ |\\ CH_2{\cdot}NO_2\end{array} \xrightarrow{H_2O} \begin{array}{c}CH_2{\cdot}OH\\ |\\ CH{\cdot}O{\cdot}COX\\ |\\ CH_2{\cdot}OH\end{array}$$

Both these methods have now been examined : the latter gives α-compounds (compare Gilchrist and Purves, J., 1925, **127**, 2735, who, when endeavouring to prepare β-methyl glycerol, obtained the α-compound instead) and the former depends on an untrustworthy initial material.

The possibility of β-substitution in the glycerol molecule was first confirmed by proving that the *p*-nitrobenzoates of $\alpha\gamma$- and $\alpha\beta$-dibromohydrins are not identical (compare, however, Fischer, *Ber.*, 1920, **53**, 1621, and Gilchrist and Purves, *loc. cit.*, who obtained $\alpha\gamma$-derivatives when they expected to obtain $\alpha\beta$).

The preparation of the alleged " β "-monoglycerides from β-monochlorohydrin (Grün's first method) was next investigated. The instructions of Hanriot (*Ann. Chim. Phys.*, 1879, **17**, 76) were followed and a constant-boiling specimen of " β "-monochlorohydrin was obtained which had physical constants very similar to those of the α-compound. It was therefore converted into its di-*p*-nitrobenzoate. This differed from the di-*p*-nitrobenzoate of α-monochlorohydrin only in melting a few degrees lower. The depression was caused by an impurity, which could be removed by recrystallisation and was shown, by analysis of the crude mixture, to have the composition of a monochlorohydrin di-*p*-nitrobenzoate. The " β "-monochlorohydrin is, therefore, a mixture of α- and β-monochlorohydrins (compare Smith, *Z. physikal. Chem.*, 1918, **92**, 717) and no monoglyceride of undoubted structure can be obtained from it by Grün's first method of synthesis (compare Thieme, *J. pr. Chem.*, 1912, **85**, 284; Lipp and Miller, *ibid.*, 1913, **88**, 361, regarding the untrustworthy nature of the reactions between glycerol chlorohydrins and the potassium salts of acids).

For the examination of Grün's second method for synthesising " β "-monoglycerides the *p*-nitrobenzoate and 3 : 5-dinitrobenzoate of $\alpha\gamma$-dichlorohydrin were first prepared. They, however, and also $\alpha\gamma$-dibromohydrin *p*-nitrobenzoate, did not react with silver nitrite to yield monoglycerides, and thus the statement was confirmed (Grün, *loc. cit.*) that the synthesis fails with esters of such acids as benzoic or acetic acid.

Finally, Grün's actual synthesis (*loc. cit.*) was repeated, in which the laurate of $\alpha\gamma$-dichlorohydrin was heated with silver nitrite. The alleged " β "-monolaurin was isolated from the product, and its melting point confirmed. Pure α-monolaurin of undoubted structure was prepared from *iso*propylidene glycerol by Fischer's method (*Ber.*, 1920, **53**, 1600), and a mixed melting-point determination showed that it was identical with the " β "-monolaurin. Further, Grün's " β "-monopalmitin (*loc. cit.*) was similarly prepared by the action of silver nitrite on palmityl αγ-dichlorohydrin and proved identical with the α-compound prepared from *iso*propylidene glycerol (Fischer, *loc. cit.*, p. 1604).

EXPERIMENTAL.

*Glycerol α-Monochlorohydrin Di-*p*-nitrobenzoate.*—A mixture of α-monochlorohydrin (b. p. 135°/32 mm.; supplied by British Drug Houses) (2·2 g.) and 5·6 g. of quinoline was dissolved in 5 c.c. of dry chloroform, and 7·48 g. of *p*-nitrobenzoyl chloride, dissolved in 10—15 c.c. of dry chloroform, were added slowly with cooling. After 24 hours, ether was added and the mixture was shaken with water, dilute sulphuric acid, sodium bicarbonate solution, and again with water. The ethereal extract was dried over fused sodium sulphate, and the solvent removed. The residual oil (yield, quantitative) solidified and was then washed with alcohol and acetone and crystallised from ligroin–acetone, needles, m. p. 107—108°, being obtained (Found: C, 50·5; H, 3·6. $C_{17}H_{13}O_8N_2Cl$ requires C, 49·95; H, 3·2%).

" Glycerol β-monochlorohydrin di-*p*-nitrobenzoate " was prepared in exactly the same way from the alleged β-monochlorohydrin obtained by Hanriot's method (*loc. cit.*). The di-*p*-nitrobenzoate crystallised from ligroin–acetone in needles resembling those described above but melting indefinitely at 100—104°. (A mixture of the two specimens melted at a slightly higher temperature.) After several recrystallisations from ligroin–acetone, however, α-monochlorohydrin di-*p*-nitrobenzoate was obtained which, alone or mixed with an authentic specimen, melted at 107—108°.

The impurity in the crude product of m. p. 100—104° was proved to be an isomeride by analysis of the latter (Found : C, 50·4; H, 3·5. Calc. : C, 49·95; H, 3·2%). By continued fractional crystallisation, a substance, m. p. 121—122°, was isolated; this lowered the m. p. of α-monochlorohydrin di-*p*-nitrobenzoate and was probably the true β-isomeride, but the quantity obtained was too small for accurate analysis (Found : C, 51·8; H, 3·8%).

Glycerol αγ-Dichlorohydrin p*-Nitrobenzoate* (compare Conant and Quayle, *J. Amer. Chem. Soc.*, 1923, **45**, 2771).—αγ-Dichlorohydrin (b. p. 175—177°; 5·16 g.) was treated with quinoline (5·6 g.) and *p*-nitrobenzoyl chloride (7·48 g.) in dry chloroform (15—20 c.c.);

the ester, isolated from the product in the usual manner, was quite pure and melted at 59—60° (yield, quantitative).

Glycerol $\alpha\gamma$-dichlorohydrin 3 : 5-*dinitrobenzoate* was prepared by the same method, 8·8 g. of 3 : 5-dinitrobenzoyl chloride being used in place of *p*-nitrobenzoyl chloride. The product crystallised from alcohol in needles, m. p. 129° (yield, quantitative) (Found : Cl, 21·5. $C_{10}H_8O_6N_2Cl_2$ requires Cl, 22·0%).

Glycerol $\alpha\gamma$-dibromohydrin p-*nitrobenzoate* was obtained in almost quantitative yield from 4·58 g. of $\alpha\gamma$-dibromohydrin (Aschan, *Ber.*, 1888, **21**, 2890), 3·93 g. of *p*-nitrobenzoyl chloride, 3 g. of quinoline, and 15 c.c. of dry chloroform. It crystallised from alcohol in needles, m. p. 77—78° (Found : C, 33·0; H, 2·7. $C_{10}H_9O_4NBr_2$ requires C, 32·7; H, 2·5%). This compound is obviously not identical with the *p*-nitrobenzoate of $\alpha\beta$-dibromohydrin (preceding paper).

Preparation of the Alleged " β "-*Monolaurin*.—This compound was prepared by Grün's method (*Ber.*, 1910, **43**, 1289). The lauryl $\alpha\gamma$-dichlorohydrin obtained boiled at 155—160°/1 mm. and the " β "-monolaurin melted at 61·5—62°. The lauryl $\alpha\gamma$-dichlorohydrin was alternatively prepared by the method described above for the *p*-nitrobenzoate. It then occurred as a solid, m. p. 3°.

Preparation of α-Monolaurin.—This compound was prepared from *iso*propylidene glycerol by Fischer's method (*Ber.*, 1920, **53**, 1600). The lauryl *iso*propylidene glycerol obtained, b. p. 155—156°/1 mm., was hydrolysed to α-monolaurin by cold hydrochloric acid in the way he described (*loc. cit.*). After recrystallisation from ether–ligroin solution this melted at 62°, and at 61·5—62° when mixed with the alleged " β "-monolaurin (m. p. 61·5—62°).

Preparation of the Alleged " β "-*Monopalmitin*.—This compound was also prepared by Grün's method (*ibid.*, 1290). The palmityl $\alpha\gamma$-dichlorohydrin crystallised from alcohol, m. p. 34° (compare Whitby, this vol., p. 1460), and the " β "-monopalmitin melted at 74—75°.

Preparation of α-Monopalmitin.—This compound was prepared from *iso*propylidene glycerol by the method of Fischer (*loc. cit.*, p. 1604), and crystallised from ligroin (b. p. 60—80°) in plates which melted at 74—75° alone or mixed with the alleged " β " monopalmitin.

The authors wish to express their indebtedness to the Chemical Society for a grant which has partly defrayed expenses incurred in this work, and also to the Department of Scientific and Industrial Research for a maintenance grant which enabled one of them to take part in it.

KING'S COLLEGE, LONDON, W.C. 2. [*Received, October 4th*, 1926.]