135. *Derivatives of the Aliphatic Glycols. Part IV.*

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Convenient methods are described for the preparation of dodeca-, tetradeca- and hexadeca-methylene glycols, and *octadecamethylene glycol* has been isolated for the first time. The monochlorohydrins of these glycols have been prepared and are of importance for synthetic purposes.

UNSYMMETRICAL derivatives have been described of the glycols with from 4 to 10 carbon atoms (J., 1927, 472; 1929, 268; 1931, 1697), and the series of chlorohydrins was completed by the isolation of that from hexamethylene glycol (Bennett and Turner, this vol., p. 813). For synthetic purposes in another connexion higher members of this series were needed, and we now describe the preparation by convenient methods of the normal glycols of 12, 14, 16 and 18 carbon atoms and their chlorohydrins. The preparations are in all cases improved, and *octadecamethylene glycol* and the chlorohydrins are now isolated for the first time. A simplified method for obtaining azelaic acid from oleic acid has been used and is shown to be applicable to the analogous preparation of brassylic acid from erucic acid. In applying the Kolbe–Brown electrosynthesis to the production of some of the dicarboxylic acids, required for conversion into the glycols, we have found that the use of methyl-alcoholic, instead of aqueous, solutions is a great improvement on the original method.

EXPERIMENTAL.

Preparation of the Dicarboxylic Esters required.—Decamethylenedicarboxylic ester was synthesised from decamethylene dibromide. In preparing the latter from decamethylene glycol (compare Chuit, *Helv. Chim. Acta*, 1926, **9**, 264) poor yields were obtained owing to the formation of quantities of material of high molecular weight in which intermolecular ether bonds had been formed. After various trials a satisfactory preparation was made as follows (compare Carothers, *J. Amer. Chem. Soc.*, 1930, **52**, 5287): the glycol (43·5 g.) was vigorously stirred at 90—95° while dry hydrogen bromide was passed for 2 hours. The temperature was then raised to 130—135°, and the gas passed for a further 6 hours. The material now solidified on cooling. It was taken up in a little benzene, the water separated, and the solution distilled. After a second distillation the product was a white solid, m. p. 28°, b. p. 167°/10 mm. (Found: Br, 53·6. Calc.: Br, 53·3%) (yield, 91% of the calculated).

When the dibromide was converted into dinitrile, and the latter hydrolysed without purification, *n*-decane-1 : 10-dicarboxylic acid was obtained in 90% yield. It was esterified.

Dodecanedicarboxylic ester, m. p. 27°, was made from decamethylene dibromide by the malonic ester method (yield, 56%).

Azelaic acid was prepared conveniently as follows: oleic acid (240 c.c.) in glacial acetic acid (1600 c.c.) was oxidised in a 7-l. flask by standing with hydrogen peroxide (400 c.c. of 100 vols.) for a week with frequent shaking; solid dihydroxystearic acid separated after a few days. The mixture was heated on the steam-bath until the peroxide reaction with iodide was slight (1 day) and then vigorously stirred hot with chromic acid mixture (500 g. of sodium dichromate, 2·5 l. of water, and 750 c.c. of sulphuric acid). After 6 hours the pelargonic acid was removed in a current of steam (12 hours), the bulk being at the same time reduced to about 2 l. When the mixture was cooled, a cake of crude azelaic acid (110 g.) was formed. The acid, crystallised from benzene–light petroleum, had m. p. 102—104° (Found: equiv., 94·2. Calc.: equiv., 94·1). Yield, 50 g. or 35%.

The corresponding process applied to erucic acid (72 g.) with one quarter of the above quantities of reagents gave brassylic acid, m. p. 109° (Found: equiv., 122·8. Calc.: equiv., 122·1). Yield, 24 g. or 41%.

n-Tetradecane-1 : 14-dicarboxylic ester, m. p. 35—36°, was prepared by the electrolysis of ethyl sodium azelate in methyl-alcoholic solution (0·3 mol. in 600 c.c. of alcohol) at 50—60° (compare Ruzicka and Stoll, *Helv. Chim. Acta*, 1933, **16**, 493). The anode of platinum (5 × 5 cm.) was situated between a pair of slightly larger iron cathodes, kept at about 4 mm. distance by glass riders. The current was about 3 amps., voltage 30—60 (yield, 45%). Some interchange of ethyl and methyl groups may have taken place, but this was no disadvantage.

n-Hexadecane-1 : 16-dicarboxylic ester, m. p. 48°, was obtained in the corresponding way from ethyl sodium sebacate.

Preparation of the Glycols.—The reduction of the esters to the glycols was carried out as described in Part III (*loc. cit.*). Kahlbaum's 99·8% alcohol gave only 30% yields. Alcohol dried by the method of Smith (J., 1927, 1288) gave the best results, but alcohol which had stood for several months over quicklime was almost as good. The higher glycols were best isolated as follows: the products from five batches (⅓ mole in all) were submitted to steam-distillation to remove alcohol, cooled somewhat, and shaken with benzene (500 c.c.) mixed with a little of the alcoholic distillate (100 c.c.), and the extract separated hot. Two further extractions were made (each with 300 c.c. of benzene and 100 c.c. of the alcoholic distillate). The combined extracts were boiled and washed with hot water. If a stable emulsion formed, the whole was acidified with concentrated hydrochloric acid and the benzene extract was washed with hot sodium carbonate solution and then with water. The benzene solution was then concentrated to about 300 c.c., and the glycol allowed to crystallise. With glycols of less than 10 carbon atoms the same method may be used, but the solution should be evaporated and distilled. The following average yields were obtained: decamethylene glycol, m. p. 73°, 67%; dodecamethylene glycol, m. p. 83·5—84·5°, 75%; hexadecamethylene glycol, m. p. 87—88°, 87%; *octadecamethylene glycol*, crystallising from benzene in colourless needles, m. p. 97—98° (Found: C, 75·5; H, 13·2. $C_{18}H_{38}O_2$ requires C, 75·4; H, 13·4%) (yield, 66%).

Preparation of the Chlorohydrins.—The method used by Bennett and Mosses for some of the lower glycols (Part III, *loc. cit.*), of heating the glycol with concentrated hydrochloric acid and continuously extracting the product with light petroleum, was found to be of diminished efficiency when applied to dodecamethylene glycol owing to its lower solubility in the acid on the one hand and to its marked solubility in the extracting solvent on the other. The latter was therefore collected as it ran off (the removal of water and hydrochloric acid being here omitted), decanted when cold from the glycol which had crystallised, shaken with potassium carbonate, and evaporated in a vacuum: 20 g. of the glycol thus gave a 50% yield of crude chlorohydrin and 5 g. of recovered glycol. The product was distilled, and crystallised from light petroleum, 12-*chlorododecyl alcohol* being obtained in colourless crystals, m. p. 28°, b. p. 134°/1 mm. (Found: Cl, 16·3. $C_{12}H_{25}OCl$ requires Cl, 16·1%). The *phenylurethane* formed colourless needles, m. p. 66°, from petroleum (Found: C, 67·3; H, 9·0; N, 4·3; Cl, 10·4. $C_{19}H_{30}O_2NCl$ requires C, 67·1; H, 8·9; N, 4·1; Cl, 10·4%).

A similar process, in which recovered glycol was returned to the reaction mixture, was applied to tetradecamethylene glycol and gave a smaller (32%) yield of 14-*chlorotetradecyl alcohol*, colourless crystals, m. p. 37—38°, b. p. 156—160°/4 mm. (Found: Cl, 14·1. $C_{14}H_{29}OCl$ requires Cl, 14·3%). This formed a *phenylurethane*, which crystallised in colourless leaflets, m. p. 68°, from light petroleum (Found: C, 68·4; H, 9·1; N, 3·9; Cl, 9·4. $C_{21}H_{34}O_2NCl$ requires C, 68·5; H, 9·3; N, 3·8; Cl, 9·6%).

A more satisfactory way of converting this and the two higher glycols into their chlorohydrins was found in an application of the reaction of Darzens (*Compt. rend.*, 1911, **152**, 1314). To the glycol (0·1 mol.) with dimethylaniline (8 c.c.) in benzene (250 c.c.), thionyl chloride (3 c.c.) was carefully added, and the mixture boiled for 2 hours. The benzene was evaporated, and the concentrate heated for 3 hours with 400 c.c. of 2N-50% alcoholic hydrochloric acid to hydrolyse any sulphite present. The liquid was then twice extracted with hot benzene (100 c.c.), and the extracts washed with hot dilute hydrochloric acid. The benzene was again evaporated, and the residue boiled out twice with light petroleum (200 c.c. of b. p. 60—80°). The solution, when cold, was filtered from glycol which had crystallised, and this was put through the whole process again. The combined solutions were evaporated, and the residue taken up in light petroleum (300 c.c. of b. p. 40—60°) and left overnight to deposit the last traces of glycol. The solution was again evaporated, and the residue dissolved in methyl alcohol (200 c.c.). Crystals of the dichloride separated and were removed by filtration. The material was recovered by evaporation once more, and crystallised several times from light petroleum (b. p. 40—60°). The yield of chlorotetradecyl alcohol obtained by this process was 12 g. or 43% of the calculated yield without allowance for glycol finally recovered.

The solid by-product was recrystallised several times from methyl alcohol, 1 : 14-*dichlorotetradecane* being obtained in colourless crystals, m. p. 40° (Found: Cl, 26·3. $C_{14}H_{28}Cl_2$ requires Cl, 26·5%). The corresponding dibromide, m. p. 50·4°, was isolated by Chuit (*loc. cit.*).

Hexadecamethylene glycol (25·8 g.), subjected to this thionyl chloride process, furnished the chlorohydrin (16·5 g., or 60%) together with the dichloride (2·5 g.) and some recovered glycol (1·5 g.). After several crystallisations from light petroleum 16-*chlorohexadecyl alcohol* formed colourless crystals, m. p. 43° (Found: Cl, 12·6. $C_{16}H_{33}OCl$ requires Cl, 12·8%). The dichloride was recrystallised several times from methyl alcohol: 1 : 16-*dichlorohexadecane* was thus isolated in colourless crystals, m. p. 47° (Found: Cl, 23·6. $C_{16}H_{32}Cl_2$ requires Cl, 24·0%).

From octadecamethylene glycol (28·6 g.) by the same process there was obtained the chlorohydrin (15 g., or 50%) together with the dichloride (2 g.) and recovered glycol (1 g.). 18-*Chloro-octadecyl alcohol* forms colourless crystals, m. p. 53—54·5° (Found: Cl, 11·5. $C_{18}H_{37}OCl$ requires Cl, 11·6%). The *phenylurethane*, after crystallisation successively from alcohol and light petroleum, formed colourless leaflets, m. p. 77° (Found: C, 70·8; H, 10·0; N, 3·4; Cl, 8·3. $C_{25}H_{42}O_2NCl$ requires C, 70·8; H, 10·0; N, 3·3; Cl, 8·4%). After several crystallisations from methyl and ethyl alcohols 1 : 18-*dichloro-octadecane* was isolated in colourless crystals, m. p. 54° (Found: Cl, 21·8. $C_{18}H_{36}Cl_2$ requires Cl, 21·9%).

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