CCXXVI.—*Derivatives of the Aliphatic Glycols. Part III.*

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The preparation of unsymmetrical derivatives of the lower glycols (J., 1927, 472; 1929, 268) has now been extended to the glycols with six to ten carbon atoms.

The chloroacetin of hexamethylene glycol is readily obtained by the action of acetyl chloride on the glycol. From the higher glycols the chlorohydrins have been prepared by heating them with hydrochloric acid in presence of petroleum under conditions such as to remove the product continuously as it is formed. The isolation of decamethylene chlorohydrin was recorded by Alberti and Smieciuszewski (*Monatsh.*, 1903, **24**, 618; 1906, **27**, 411), but we found it difficult to obtain the substance pure by the method they describe. The hepta-, nona-, and deca-methylene chlorohydrins were purified by crystallisation from petroleum at a low temperature; they melt at 10—11°, 28°, and 10—11° respectively. All the chlorohydrins were characterised by the preparation of their phenylurethanes.

These derivatives of the glycols have been applied to the preparation of a series of ω-hydroxyalkyl sulphides, $Ph{\cdot}S{\cdot}[CH_2]_n{\cdot}OH$ ($n=6$—10), and from each the corresponding chlorosulphide was also obtained.

EXPERIMENTAL.

Preparation of the Glycols.—The improved yields in the reduction of the dibasic esters must be attributed to details of technique. The alcohol used was kept in a closed vessel over quicklime for several months and was syphoned out for use. Careful drying of the alcohol and exclusion of moisture from the apparatus are well-recognised precautions in such reductions, but the preparation of the sodium was found to be an equally important factor. The metal was cut and weighed under dry xylene, the surface layer being completely removed; it was then quickly transferred (without drying) to the flask, and the alcoholic solution of the ester at once added.

Heptamethylene glycol, for example, was prepared as follows. A solution of methyl pimelate (0·1 mol.) in absolute alcohol (300 c.c.) was quickly run down the condenser (1″ copper tube, 3′ long, water-jacketed) on to sodium (30 g., cut as described) in a 1 litre Pyrex flask. When the temperature had risen sufficiently, the sodium was dispersed by vigorous shaking. After the initial reaction had subsided (30 mins.), the mixture was heated at 130° for ½ hour and, after addition of water (10 c.c.), boiled for a further 20 minutes to bring all into solution and hydrolyse any remaining ester. The flask was then cooled, and concentrated hydrochloric acid (160 g.) added down the condenser. The mixture was cooled, the sodium chloride removed, and the filtrate kept with potassium carbonate (150 g.) to free it from water and acid. The alcoholic solution was again filtered from the solid, and the latter twice extracted with boiling alcohol. The combined solutions were then distilled, salts being removed if necessary towards the end of the process by addition of acetone, filtration, and evaporation. The residue from two reductions was distilled under diminished pressure, yielding the glycol, b. p. 151°/14 mm., m. p. 18° (average yield from 4 reductions, 72%).

The yields of other glycols, obtained in repeated preparations, were: tetramethylene glycol, b. p. 134°/18 mm., from ethyl succinate, 62%; hexamethylene glycol, b. p. 145—149°/17 mm., from methyl adipate, 56%; octamethylene glycol, b. p. 167—168°/18 mm., m. p. 63°, from methyl suberate, 77%; nonamethylene glycol, b. p. 162—167°/13 mm., m. p. 46°, from methyl azelate, 65%; decamethylene glycol, m. p. 74·5° (not distilled but crystallised from benzene), 85%. These yields are better than those recorded by other workers (Bouveault and Blanc, *Compt. rend.*, 1903, **137**, 129, 329; Scheuble and Loebel, *Monatsh.*, 1904, **25**, 345, 1085; Franke, *ibid.*, 1929, **54**, 577).

Preparation of the Chlorohydrins.—Alberti and Smiecuiszewski's method (*loc. cit.*) for obtaining the chlorohydrin from decamethylene glycol by heating with concentrated hydrochloric acid tended with the lower glycols to yield the corresponding dichloride. The reaction with hydrochloric acid was therefore carried out in a flask kept at 95°, petroleum (b. p. 90—120°), introduced by a dropping-funnel the tip of which reached the bottom of the vessel, being continuously passed up through the reaction mixture. The petroleum removed the chlorohydrin as it was formed, collected on the surface, and overflowed down a side-tube through a condenser and a drying tube containing potassium carbonate. The residue from the evaporation of this solution was fractionated under diminished pressure with the aid of a glass spiral column. The glycol chlorohydrin was thus obtained in a sufficiently pure condition for synthetic purposes, but it usually contained a small amount of the dichloride which could not be completely removed by repeated fractionation. The pure substances were obtained in three cases by crystallising them at low temperatures.

Derivatives of Hexamethylene Glycol.—The glycol was heated for 6 hours at 100° in a sealed tube with acetyl chloride (1·2 mols.), the two being allowed to mix only after sealing. A small amount of dichlorohexane and hexamethylene diacetate having been removed by fractionation, *ζ-chlorohexyl acetate* was obtained as a colourless liquid of pleasant odour, b. p. 113—116°/17 mm. (yield, 43%). The substance has $d_{4^\circ}^{20^\circ}$ 1·0371, $n_{\mathrm{D}}^{20^\circ}$ 1·44163, whence $[R_L]_{\mathrm{D}}$ 45·50 (calc., 45·54) (Found : Cl, 19·3. $C_8H_{15}O_2Cl$ requires Cl, 19·8%).

A mixture of the chloroacetin with an excess of thiophenol and aqueous sodium hydroxide was heated for 3 hours; it was then acidified with acetic acid, and steam passed through it. The oily product solidified on cooling; the *phenyl ζ-hydroxyhexyl sulphide* thus obtained crystallised from light petroleum in colourless plates, m. p. 43° (yield, 85%) (Found : S, 14·8. $C_{12}H_{18}OS$ requires S, 15·2%).

To the hydroxy-sulphide (3 g.), dissolved in diethylaniline (3 c.c.), thionyl chloride (1·25 c.c. in an equal volume of carbon tetrachloride) was added at 60°, and the mixture heated on the steam-bath for 45 minutes. Water was added and the carbon tetrachloride extract was washed twice with concentrated hydrochloric acid, once with aqueous sodium carbonate, once with water, dried over sodium sulphate, and evaporated under reduced pressure at 100°. *Phenyl ζ-chlorohexyl sulphide* was thus obtained as a brown oil which could not be distilled without decomposition but solidified in a freezing mixture and then melted at 7—8° (Found : Cl, 15·4. $C_{12}H_{17}ClS$ requires Cl, 15·5%).

Derivatives of Heptamethylene Glycol.—By the action of hydrochloric acid under the conditions described above, *η-chloroheptyl alcohol* was obtained, b. p. 150°/20 mm. (yield, 43%). It was freed from a trace of the dichloride by crystallisation from light petroleum and had m. p. 10—11° (Found : Cl, 23·4. $C_7H_{15}OCl$ requires Cl, 23·55%). The liquid has $d_{4^\circ}^{25^\circ}$ 0·9998, $n_{\mathrm{D}}^{25^\circ}$ 1·45367, whence $[R_L]_{\mathrm{D}}$ 41·43 (calc., 41·0). The *phenylurethane* crystallised from petroleum or dilute alcohol in colourless needles, m. p. 76° (Found : N, 5·2. $C_{14}H_{20}O_2NCl$ requires N, 5·2%).

Condensation of chloroheptyl alcohol with sodium thiophenoxide yielded *phenyl η-hydroxyheptyl sulphide*, crystallising from petroleum in flat needles, m. p. 49° (Found : S, 14·0. $C_{13}H_{20}OS$ requires S, 14·3%).

The hydroxy-sulphide reacted with thionyl chloride as described above and *phenyl η-chloroheptyl sulphide* was isolated, after solution in light petroleum, cooling, filtration and evaporation, as a brown oil (Found : Cl, 14·1. $C_{13}H_{19}ClS$ requires Cl, 14·6%).

Derivatives of Octamethylene Glycol.—The chlorohydrin *θ-chloro-octyl alcohol* was obtained (yield, 80%) in a slightly impure condition, b. p. 125—140°/18 mm. (Found : Cl, 22·8. $C_8H_{17}OCl$ requires Cl, 21·6%). The *phenylurethane* formed colourless needles, m. p. 77°, from aqueous alcohol (Found : N, 4·9. $C_{15}H_{22}O_2NCl$ requires N, 4·9%).

Condensation with sodium thiophenoxide yielded *phenyl θ-hydroxy-octyl sulphide*, which crystallised from light petroleum in colourless plates, m. p. 55° (Found : S, 13·3. $C_{14}H_{22}OS$ requires S, 13·4%).

Thionyl chloride reacted with the latter substance to give *phenyl θ-chloro-octyl sulphide* as a brown oil solidifying in a freezing mixture. After crystallisation from aqueous alcohol at a low temperature the substance had m. p. 16° (Found : Cl, 13·7. $C_{14}H_{21}ClS$ requires Cl, 13·8%).

Derivatives of Nonamethylene Glycol.—The crude *ι-chlorononyl alcohol* (obtained in weight equal to that of the glycol used) was fractionated, two-thirds of it boiling at 140—145°/20 mm. This solidified and, crystallised from light petroleum, had m. p. 28° (Found : Cl, 20·0. $C_9H_{19}OCl$ requires Cl, 19·9%). The *phenylurethane*, crystallised from dilute alcohol, had m. p. 67° (Found : N, 4·7. $C_{16}H_{24}O_2NCl$ requires N, 4·7%).

Phenyl ι-hydroxynonyl sulphide, obtained by condensation of the foregoing chlorohydrin with thiophenol, was crystallised from light petroleum and had m. p. 60° (Found : S, 12·5. $C_{15}H_{24}OS$ requires S, 12·7%). The action on it of thionyl chloride furnished *phenyl ι-chlorononyl sulphide*, which had m. p. 5° after crystallisation from aqueous alcohol at low temperatures (Found : Cl, 13·5; $C_{15}H_{23}ClS$ requires Cl, 13·1%).

Derivatives of Decamethylene Glycol.—The chlorohydrin partially purified by fractional distillation solidified in a freezing mixture, and the solid *κ-chlorodecyl alcohol* was crystallised from petroleum at a low temperature; m. p. 10—11° (Found : Cl, 18·7. $C_{10}H_{21}OCl$ requires Cl, 18·5%). The liquid has $d^{25°}_{4°}$ 0·9630, $n^{25°}_{D}$ 1·45796, whence $[R_L]_D$ 54·5 (calc., 54·9). The *phenylurethane* separated from aqueous alcohol in colourless needles, m. p. 72° (Found : N, 4·4. $C_{17}H_{26}O_2NCl$ requires N, 4·5%).

Condensation of the chlorohydrin with thiophenol yielded *phenyl ϰ-hydroxydecyl sulphide*, which crystallised from light petroleum in colourless needles, m. p. 66·5° (Found : S, 12·1. $C_{16}H_{26}OS$ requires S, 12·0%). The action of thionyl chloride on the latter furnished *phenyl ϰ-chlorodecyl sulphide*, which solidified, and after crystallisation from ethyl alcohol had m. p. 27·5° (Found : Cl, 12·1. $C_{16}H_{25}ClS$ requires Cl, 12·4%).

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