[CONTRIBUTION FROM VICTORIA UNIVERSITY COLLEGE]

Glycol Esters of Dibasic Acids. The Di-β-hydroxyethyl Esters[1]

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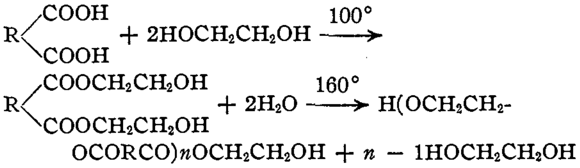
Previous investigators have amply demonstrated that in a reaction between glycol and a dibasic acid the type of compound formed varies with the nature of the acid and with the experimental conditions. Certain possible compounds such as the di-β-hydroxyethyl esters, with the exception of the succinate obtained in an approximately pure state by Carothers and Dorough,[2] have not yet been described. The possible reactions between glycol and a dibasic acid may be enumerated as follows: (1) cyclic ester formation;[3,4] (2) formation of di-β-hydroxyethyl esters; (3) polyester formation;[5] (4) acid ester formation.[2]

Since dibasic acids react with excess alcohol to form diethyl esters, it is reasonable to suppose that under analogous conditions glycol would yield di-β-hydroxyethyl esters. Actually, as shown in the present investigation, the esterification of succinic, glutaric, adipic and sebacic acids with excess glycol at 100° results in the formation of the corresponding di-β-hydroxyethyl esters. The sebacate is a solid (m. p. 46°), sparingly soluble in glycol and water, but dissolving readily in alcohol, chloroform and ether. The remaining esters are liquids soluble in hydroxylic solvents but insoluble in chloroform and ether. These esters on warming to 160° slowly polymerize. The stages of the reaction may be represented as



$$\mathrm{R}\begin{cases}\mathrm{COOH}\\ \mathrm{COOH}\end{cases} + \mathrm{2HOCH_2CH_2OH} \xrightarrow{100^\circ} \mathrm{R}\begin{cases}\mathrm{COOCH_2CH_2OH}\\ \mathrm{COOCH_2CH_2OH}\end{cases} + \mathrm{2H_2O} \xrightarrow{160^\circ} \mathrm{H(OCH_2CH_2\text{-}OCORCO)}_n\mathrm{OCH_2CH_2OH} + n - \mathrm{1HOCH_2CH_2OH}$$

The final products on heating to 260° are the polyesters, which with the exception of the glutarate have been described by Carothers and Arvin.[5] Ethylene glutarate is a viscous liquid which conforms to the usual properties of the polyesters, being insoluble in ether, water and glycol but soluble in chloroform, benzene and acetone.

Attempts to prepare di-β-hydroxyethyl oxalate and di-β-hydroxyethyl malonate by this method gave, respectively, formic and acetic esters. It is probable in the case of the formic ester that the reaction is analogous to the well-known reaction between glycerol and oxalic acid, which Chattaway[6] has shown to take place through the decomposition of an unstable monoxalate. It is probable also that the interaction of malonic acid with excess glycol proceeds through the decomposition of an unstable glycol malonate, since under these conditions malonic acid esterified nearly ten times as rapidly as acetic acid.

The analysis of a carefully evaporated reaction mixture of succinic acid and excess glycol showed the formation of the di-β-hydroxyethyl ester at 100° to be nearly quantitative. With the exception of the solid sebacate no attempts were made to purify the di-β-hydroxyethyl esters, since they reverted rapidly to the corresponding polyester when distilled under reduced pressure. The acetyl derivatives, however, were sufficiently stable to be purified. In the case of glutaric, adipic and sebacic acids more than 80% of the theoretical yield of the di-β-acetoxyethyl ester was obtained. The relatively low yield of the succinate is probably due to decomposition during distillation as the higher boiling point fractions contained considerable quantities of succinic anhydride.

The di-β-acetoxyethyl esters, with the exception of the sebacate, which melts at 25°, are liquids. They are faint smelling compounds soluble in benzene, chloroform, ether and alcohol, but insoluble in water. At 5 mm. pressure they can be purified by distillation; at higher pressures they tend to break down to form polyesters. The relative stability and volatility of the di-β-acetoxyethyl esters as compared with the corresponding di-β-hydroxyethyl esters shows that the tendency to remove acetic acid from the molecule is considerably less than the tendency to remove water from the parent substance. This increased stability resulting from the acetylation of the molecule has also been noted by Lycan and Adams,[7] who found that although ω-hydroxy-

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(2) Carothers and Dorough, THIS JOURNAL, **52**, 711 (1930).

(3) Bischoff and Walden, *Ber.*, **27**, 2939 (1894).

(4) Carothers and Van Natta, THIS JOURNAL, **52**, 314 (1930).

(5) Carothers and Arvin, *ibid.*, **51**, 2560 (1929).

(6) Chattaway, *J. Chem. Soc.*, **105**, 151 (1914).

(7) Lycan and Adams, THIS JOURNAL, **51**, 3450 (1929).

decanoic acid is not volatile at any temperature owing to polymerization, the acetyl derivative may be distilled under reduced pressure without decomposition.

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Experimental

The general method of preparation of the di-β-hydroxyethyl ester was to esterify 0.05 gram mole of the dibasic acid with 0.5 gram mole of glycol at 100°. The excess glycol was then removed under reduced pressure by heating the mixture in an oil-bath at 130–140° for a period of one to two hours. From the crude di-β-hydroxyethyl esters the corresponding acetyl derivatives were obtained by acetylation with excess acetic anhydride and purified by distillation under reduced pressure. Acetylation with excess acetyl chloride proceeded irregularly with the formation of some chlorinated ester.

The velocity of esterification at 90° was measured on a 0.45 gram mole solution of the acid in freshly distilled anhydrous glycol using standard $N/20$ baryta to follow the reaction. In the case of oxalic acid, the baryta rapidly hydrolyzed the glycol ester, necessitating the use of $N/20$ ammonia with brom thymol blue as indicator. Since the retarding effect of the water formed during esterification was small, the velocity constants were taken as the mean of the first three determinations. The following values for K_2 (bimolecular, time in minutes) were obtained: oxalic 0.160; malonic 0.020; succinic 0.0017; sebacic 0.0006; acetic 0.0021.

Di-β-hydroxyethyl Succinate.—Obtained in nearly theoretical yield (compare Carothers and Dorough[2]).

Anal. Calcd. for $C_8H_{14}O_6$: sap. equiv., 103. Found: sap. equiv., 104.

On warming for three hours to 160° at 5 mm. some glycol distilled over and upon the addition of one volume of water 18% of the theoretical yield of polyester gradually precipitated out.

Diacetyl Derivative.—B. p. 196° at 5 mm.; yield 40%.

Anal. Calcd. for $C_{12}H_{18}O_8$: sap. equiv., 72.5; $2CH_3COO$, 40.7. Found: sap. equiv., 72.7; $2CH_3COO$, 40.4.

Di-β-acetoxyethyl Glutarate.—B. p. 198° at 5 mm.; yield 92%.

Anal. Calcd. for $C_{13}H_{20}O_8$: sap. equiv., 76.0; $2CH_3COO$, 38.8. Found: sap. equiv., 75.9; $2CH_3COO$, 38.4.

Di-β-acetoxyethyl Adipate.—B. p. 210° at 5 mm.; yield 87%.

Anal. Calcd. for $C_{14}H_{22}O_8$: sap. equiv., 79.5; $2CH_3COO$, 37.1. Found: sap. equiv., 79.45; $2CH_3COO$, 37.2.

Di-β-hydroxyethyl Sebacate.—This was prepared according to the general method except that the temperature was increased to 110–115° in order to hasten the reaction. The reaction mixture was taken up with benzene and washed with dilute sodium carbonate and finally twice with water. The benzene layer was evaporated and the residue after repeated recrystallization from ether gave two slightly soluble fractions of m. p. 68–69°, m. p. 61–64°, and a main fraction of m. p. 46°, crystallizing from ether in microscopic clusters of needles, yield 81%.

Anal. Calcd. for $C_{14}H_{26}O_6$: sap. equiv., 145. Found: sap. equiv., 147.

Diacetyl Derivative.—B. p. 242° at 5 mm.; m. p. 25.5°

Anal. Calcd. for $C_{18}H_{30}O_8$: sap. equiv., 93.5; $2CH_3COO$, 31.6. Found: sap. equiv., 92.7; $2CH_3COO$, 32.1.

Summary

1. Oxalic and malonic acids when esterified with excess glycol at 100° yield, respectively, formic and acetic esters.

2. Succinic, glutaric, adipic and sebacic acids react with excess glycol at 100° to form di-β-hydroxyethyl esters.

3. The di-β-hydroxyethyl esters on heating to 160° slowly polymerize.

4. Acetylation of the di-β-hydroxyethyl esters with excess acetic anhydride produces di-β-acetoxyethyl esters which can be distilled under reduced pressure.

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