TRANSFORMATIONS OF DIETHYL MONO- AND DI(β-CHLOROALLYL)MALONATES

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In the reaction between γ-chloro-δ-hydroxy-γ-valerolactone and potassium phthalimide in dimethylformamide, γ-phthalimido-δ-hydroxy-γ-valerolactone is formed, alkaline hydrolysis of which gives δ-hydroxylevulinic acid. It is shown that oxidation of di(β-chloroallyl)malonic acid with hydrogen peroxide in acetic acid gives the dilactone of bis(δ-hydroxy-γ-chloro-γ-hydroxy)malonic acid.

The present paper reports the transformations of diethyl mono- and di(β-chloroallyl)malonates (I and II). These were obtained simultaneously from the reaction between 2,3-dichloro-1-propene and diethyl malonate in the presence of sodium ethoxide in ethanol [1]. From **II**, 5,5-di(β-chloroallyl)barbituric and -thiobarbituric acids were obtained [2,3]. I and II were subjected to hydrolysis and decarboxylation, giving mono- and di(β-chloroallyl)malonic and di(β-chloroallyl)acetic acids. Oxidation of β-chloroallylacetic acid with hydrogen peroxide in acetic acid gave γ-chloro-δ-hydroxy-γ-valerolactone [4], which reacted with potassium phthalimide in dimethylformamide to give γ-phthalimido-δ-hydroxy-γ-valerolactone.

EXPERIMENTAL

Diethyl mono- and di(β-chloroallyl)malonates (I and II). [1]. Best results were obtained using the following proportions: 170 ml of absolute alcohol, 15 g of sodium methoxide, 96 g of diethyl malonate and 66 g of 2,3-dichloro-1-propene. Yield 36% for **I** and 32% for **II.** n_D^{20} 1.4759, d_4^{20} 1.1743. Found, %: Cl 22.97; MR_D 74.34. Calculated for $C_{13}H_{18}Cl_2O_4$, %: Cl 22.54; MR_D 74.20.

5,5-Di(β-chloroallyl)barbituric acid (V). To a hot alkoxide solution from 10 ml of alcohol and 0.8 g sodium was added 1.4 g of dry urea and 6.8 g of **II** in 10 ml of absolute alcohol. The mixture was boiled for 10 hr, the alcohol was evaporated, and the oily residue dissolved in water and acidified to Congo Red with HCl. Yellow crystals separated which were recrystallized from aqueous alcohol using activated charcoal. Yield 54%, mp 195° C. Found, %: Cl 25.47; N 10.11. Calculated for $C_{10}H_{10}Cl_2N_2O_3$, %: Cl 25.63; 10.49.

5,5-Di(β-chloroallyl)thiobarbituric acid (VI). To a solution of 1 g of sodium in 15 ml of absolute alcohol was added 3 g of dry thiourea in 15 ml of absolute alcohol. The mixture was boiled for 10 hr and worked up as above. Yield 51%, mp 186° C. Found, %: N 9.5. Calculated for $C_{10}H_{10}Cl_2N_2O_2S$, %: N 9.0.

Di(β-chloroallyl)malonic acid (III). To a hot solution of 14.4 g (0.36 mole) of sodium hydroxide in 20 ml of water was slowly added 37 g (0.12 mole) of **II.** The mixture was heated on a steam bath for 4 hr, 100 ml of water was added, then washed with ether and acidified with HCl. The oil layer was separated from the aqueous, phase, which was then extracted with ether. The combined nonaqueous layers were dried over $MgSO_4$ and the ether evaporated off, giving 23 g (76%) of a crystalline product with mp 146° C (from benzene). Found, %: Cl 28.06. Calculated for $C_9H_{10}Cl_2O_4$, %: Cl 28.01.

Oxidation of III. To a solution of 10 g of **III** in 50 ml of acetic acid was added slowly, with mechanical stirring, 5.37 g of 29% hydrogen peroxide. The mixture was heated 24 hr at 60° C, the acetic acid was distilled off, and the residue was distilled under vacuum. Yield 6.16 g (54.7%) of the dilactone VII, bp 163–170° C (1 mm), mp 110–112° C. Found, %: Cl 24.4. Calculated for $C_9H_{10}Cl_2O_6$, %: Cl 24.9.

Di(β-chloroallyl)acetic acid (VIII). Di(β-chloroallyl)acetic acid was obtained by the decarboxylation of **III** at 110–120° C with simultaneous distillation of the product at 114–120° C (1 mm). Yield 9.8 g (96.2%), mp 56° C (from petroleum ether). Found, %: Cl 33.62; MR_D 49.51. Calculated for $C_8H_{10}Cl_2O_2$, %: Cl 34.13%; MR_D 49.20.

γ-Phthalimido-δ-hydroxy-γ-valerolactone (IV). To 4.3 g (0.0232 mole) of potassium phthalimide in 20 ml of dimethylformamide was added dropwise, with mechanical stirring, 3.5 g (0.0252 mole) of γ-chloro-δ-hydroxy-γ-valerolactone in 10 ml of dimethylformamide. The mixture was heated at 150° C for 2 hr, the KCl was filtered off, and the dimethylformamide was distilled off under vacuum. The residual crystals were dissolved in acetone, and the mixture was treated several times with cold ether to remove phthalimide. Yield 4 g of IV, mp 200° C. Found, %: N 5.3. Calculated for $C_{13}H_{11}NO_5$, %: N 6.00.

Alkaline hydrolysis of IV. 7.5 g of **IV** was added to a solution of 3.4 g of sodium hydroxide in 5 ml of water and the mixture was heated for 4 hr, then 30 ml of water was added. The solution was washed with ether and acidified with HCl; an oil layer separated from the aqueous, which was then extracted several times with ether. The combined ethereal extracts and oil layer were dried over Na_2SO_4 and the ether was evaporated. Yield 4 g of δ-hydroxylevulinic acid, mp 101° C. Identified as the 2,4-dinitrophenylhydrazone, mp 104° C. Found, %: N 17.59. Calculated for $C_{11}H_{12}N_4O_7$, %: 17.94.

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