CCCLXXII.—*Lactonic Esters derived from Phenacyl Bromide by Condensation with Ethyl Sodiomalonate and Analogous Substances.*

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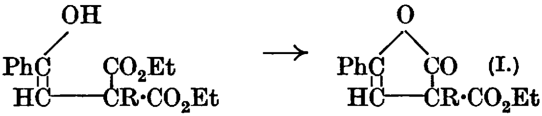
THE primary object of this work, *viz.*, the preparation of *ac*-substituted tetrahydronaphthalenes, was not achieved.

o-Benzoylbenzoic acid is readily convertible into anthraquinone. It was hoped, therefore, that phenacylmalonic ester under suitable conditions would pass into a tetrahydronaphthalene derivative. In presence of 6% aqueous potassium hydroxide, however, the reaction followed another course, the *lactone* I (R=H) being formed, which gave benzoic acid on oxidation.



(R=H, Me, Et, COMe, CH_2Ph, or $CHMe_2$.)

Lactones of type I were also formed in the reactions between phenacyl bromide and the sodio-derivatives of malonic, benzylmalonic, *iso*propylmalonic, acetylmalonic, and benzoylmalonic esters. Varying quantities of acetophenone also were produced, due to reduction of phenacyl bromide.

Phenacyl bromide, ethyl cyanoacetate, and sodium ethoxide reacting in molecular quantities in alcoholic solution gave *ethyl diphenacylcyanoacetate*, $(COPh\cdot CH_2)_2C(CN)\cdot CO_2Et$, but when dry ethyl sodiocyanoacetate (2 mols.) was heated for several hours with phenacyl bromide (1 mol.) suspended in dry benzene, a substance, m. p. 125—127°, was obtained which is believed to be the mono-substitution product. This could not be converted into a tetrahydronaphthalene derivative under a variety of conditions.

EXPERIMENTAL.

The reactions of phenacyl bromide with the following substances were examined.

With Ethyl Sodiomalonate.—The sodio-derivative (prepared from 0·7 g. of sodium and 5 c.c. of ethyl malonate) in cooled absolute alcohol (30 c.c.) was shaken vigorously with phenacyl bromide (6 g.). After 10 minutes, the mixture, now neutral, was poured into much water; by extraction with ether, ethyl phenacylmalonate was obtained as an oil (8 g.), *d* 1·2.

The crude ester was shaken in the cold with 6% potassium hydroxide solution (65 c.c.). The red, semi-solid mass that had separated after 12 hours was crystallised from rectified spirit, the *lactone* (I; R=H) of α-carbethoxy-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylic acid being obtained in colourless needles, m. p. 105° (Found: C, 67·6. $C_{13}H_{12}O_6$ requires C, 67·2%).*

By keeping the lactone (1 g.) for 12 hours in a minimum of cold alcohol saturated with dry ammonia, the corresponding *amide*, $C_{10}H_7O_2\cdot CO\cdot NH_2$, was obtained in long needles, m. p. 153—154° after crystallisation from dilute alcohol (Found: N, 7·1. $C_{11}H_9O_3N$ requires N, 6·9%).

The lactone (1 g.) was oxidised with *N*/10-sulphuric acid (50 c.c.) and *N*/10-potassium permanganate (excess) on the boiling-water bath. Ether extracted benzoic acid from the product after the usual treatment.

With Ethyl Sodiocyanoacetate.—An alcoholic solution of the reactants (1 mol. of each) was heated on the water-bath for ½ hour and then poured into water. The precipitate formed was removed after 12 hours; the filtrate gave nothing to ether. By fractionally crystallising the precipitate from 50% alcohol, *ethyl diphenacylcyanoacetate*, m. p. 141° (Found: N, 4·3. $C_{21}H_{19}O_4N$ requires N, 4·0%), was obtained together with a small quantity of a substance, m. p. 125—127°.

With Ethyl Acetylsodiomalonate.—Ethyl acetylmalonate was prepared by treating "molecular" sodium (1 atom.) with ethyl malonate in ice-cold, dry ether and warming the mixture with acetyl chloride (1·25 mols.) at 33° for an hour. The product after decomposition with a small quantity of water was shaken with ether. The dried extract was fractionated; the portion, b. p. 125—128°/17 mm., was pure acetylmalonate (yield 60%).

Ethyl acetylmalonate (4 c.c.) was added to alcoholic sodium ethoxide (0·46 g. of sodium in 25 c.c.); the mixture was treated with 4 g. of phenacyl bromide and, after a few minutes, warmed at 50—55° for ½ hour. Ether extracted from the product, diluted with water, the *lactone* (I; $R=CO\cdot CH_3$) of ethyl α-acetyl-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylic acid, which crystallised from alcohol and ether in needles, m. p. 135—136° (Found: C, 65·6. $C_{15}H_{14}O_5$ requires C, 65·7%).

As ethyl acetylmalonate is easily decomposed into ethyl acetoacetate by alkali, the compound, m. p. 119—120°, prepared from phenacyl bromide and ethyl sodioacetoacetate was compared with the preceding lactone; it depressed its m. p.

With Ethyl Sodioethylmalonate.—The reaction was carried out as

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* The humidity of the air (*ca.* 80%) made determinations of hydrogen almost impossible.

in the case of ethyl sodiomalonate. The *lactone* produced (I; R=Et) crystallised from alcohol in needles, m. p. 134—135° (Found: C, 69·3. $C_{15}H_{16}O_4$ requires C, 69·2%).

With Ethyl Sodiobenzylmalonate.—The *lactone* (I; R=CH_2Ph) obtained crystallised from alcohol in flat needles, m. p. 125° (Found: C, 73·8; H, 6·2. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

*With Ethyl Sodio*iso*propylmalonate.*—The constituents in molecular proportions were boiled in alcoholic solution on the water-bath for 1 hour. The product, on dilution with water, deposited the *lactone* (I; R=$CHMe_2$), which crystallised from alcohol in needles, m. p. 151° (Found: C, 69·7; H, 6·5. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%).

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