393. *Synthetic Experiments in the Naphthalene and the Phenanthrene Series.*

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IT has been shown (J., 1935, 1061) that the condensation of ethyl phenylacetate and ethyl ethoxymethylenemalonate in the presence of sodium ethoxide leads to either ethyl γ-carbethoxy-α-phenylglutaconate or ethyl 1-naphthol-2 : 4-dicarboxylate.* The investigation has now been extended to include halogen-substituted phenylacetates. By the condensation of ethyl *p*-chloro- or *p*-bromo-phenylacetate and ethyl ethoxymethylenemalonate at 150° *ethyl 7-chloro-* or *7-bromo-1-naphthol-2 : 4-dicarboxylate* was obtained; from the former condensation product, α-p-*chlorophenylglutaconic acid* also was isolated.

* 1-Naphthol-2 : 4-dicarboxylic acid, described by the author as a new compound, was first prepared by the Society of Chemical Industry in Basle (B.P. 195,513).

Decarboxylation of the halogenonaphtholdicarboxylic acids could not be satisfactorily effected.

From the condensation product of ethyl 1-naphthylacetate and ethyl ethoxymethylenemalonate, 1-*phenanthrol*-2 : 4-*dicarboxylic* and α-1-*naphthylglutaconic acids* were obtained. The yield of the former acid was very poor compared with those of the naphtholdicarboxylic acids.

Experimental.

Ethyl 7-*Bromo*-1-*naphthol*-2 : 4-*dicarboxylate*.—To an ice-cold solution of sodium (2·3 g.) in absolute alcohol (50 c.c.), ethyl *p*-bromophenylacetate (0·1 mol.) was added, followed by ethyl ethoxymethylenemalonate (0·1 mol.). Next day, the mixture was heated at 145—155° for 4 hours, the alcohol removed, and the residue dissolved in water. The solution was acidified with hydrochloric acid and extracted with ether, and the extract washed with water, dried (magnesium sulphate), and evaporated. The residue gave a distillate, b.p. below 145°/8 mm. (10 g., mostly unchanged esters), and then began to decompose. It (25 g.) was therefore cooled and stirred with alcohol; the solid obtained (4·1 g.) was removed from the oil by filtration and crystallised from alcohol, forming needles, m. p. 105° (Found : Br, 21·4. $C_{16}H_{15}O_5Br$ requires Br, 21·8%), giving a brown colour with ferric chloride.

The oil remaining after removal of the solid ester was heated with potassium hydroxide (20 g.) in alcohol (150 c.c.) on the water-bath for 3 hours, and the 7-*bromo*-1-*naphthol*-2 : 4-*dicarboxylic acid* worked up in the usual way. After repeated solution in aqueous sodium bicarbonate and reprecipitation it was crystallised from aqueous alcohol; yield 4 g., m. p. 299° (decomp.) (Found : Br, 26·15; equiv. 150. $C_{12}H_7O_5Br$ requires Br, 25·7%; equiv., 155). The acid was also obtained in quantitative yield by the hydrolysis of the pure ester. On methylation it furnished 7-*bromo*-1-*methoxynaphthalene*-2 : 4-*dicarboxylic acid*, m. p. 261° after crystallisation from benzene–alcohol (Found : Br, 24·15. $C_{13}H_9O_5Br$ requires Br, 24·6%), the *dianilide* of which had m. p. 260° (Found : Br, 16·8. $C_{25}H_{19}O_3N_2Br$ requires Br, 16·8%).

7-Bromo-1-naphthol-2 : 4-dicarboxylic acid (0·2 g.) was boiled with quinoline (3 c.c.) for 2 hours in an atmosphere of nitrogen, and the quinoline removed by hydrochloric acid. A solution of the residue in aqueous sodium hydroxide, on saturation with carbon dioxide, gave a small quantity of a solid, m. p. 103°, which developed a purple colour with ferric chloride (7-bromo-1-naphthol has m. p. 105—106°; Fuson, *J. Amer. Chem. Soc.*, 1925, **47**, 516).

Ethyl 7-*Chloro*-1-*naphthol*-2 : 4-*dicarboxylate*.—Ethyl *p*-chlorophenylacetate (0·1 mol.) was condensed with ethyl ethoxymethylenemalonate (0·1 mol.) in the presence of sodium ethoxide under the conditions above described. Distillation of the crude ester under diminished pressure furnished a fraction (A), 15 g., b.p. below 142°/2 mm. (mainly unchanged esters), a fraction (B), 3·9 g., b.p. 142—192°/2 mm. (mainly at 192°), and a residue (C), 14 g., which began to decompose. (C), when cooled and stirred with alcohol, gave a solid, which was removed and crystallised from alcohol; m. p. 102—103° (2·5 g.). It gave a reddish-purple colour with ferric chloride (Found : Cl, 10·5. $C_{16}H_{15}O_5Cl$ requires Cl, 11·0%).

The oily mother-liquor (8·7 g.) from (C) was hydrolysed with potassium hydroxide (7·5 g.) in aqueous alcohol (40 c.c.), and the product worked up in the usual way. 7-*Chloro*-1-*naphthol*-2 : 4-*dicarboxylic acid* (2 g.), crystallised from aqueous alcohol, had m. p. 294° (Found : Cl, 12·9; equiv., 136·7. $C_{12}H_7O_5Cl$ requires Cl, 13·3%; equiv., 133·25). On methylation it gave 7-*chloro*-1-*methoxynaphthalene*-2 : 4-*dicarboxylic acid*, m. p. 228° after crystallisation from aqueous alcohol (Found : Cl, 12·2. $C_{13}H_9O_5Cl$ requires Cl, 12·65%), the *dianilide* of which had m. p. 215° (Found : Cl, 8·2. $C_{25}H_{19}O_3N_2Cl$ requires Cl, 8·25%).

α-p-*Chlorophenylglutaconic acid*. The fraction (B) (3·9 g.) was hydrolysed with aqueous alcoholic potassium hydroxide (5 g. in 30 c.c.); from the product, an *acid* (2·7 g.), crystallising from aqueous alcohol in needles, m. p. 175°, was obtained (Found : Cl, 14·8; equiv., 119·3. $C_{11}H_9O_4Cl$ requires Cl, 14·7%; equiv., 120·75).

1-*Phenanthrol*-2 : 4-*dicarboxylic Acid*.—Ethyl 1-naphthylacetate (0·1 mol.) was condensed with ethyl ethoxymethylenemalonate and the crude ester obtained was distilled under reduced pressure. Two fractions were collected, (A), 12 g., b. p. below 170°/3·5 mm. (mainly unchanged esters), and (B), 6 g., b. p. 170—120°/3·5 mm. The residue (14 g.), on hydrolysis with potassium hydroxide, gave an *acid* (1·5 g.), m. p. 304° after crystallisation from aqueous alcohol (Found : C, 68·2; H, 4·05. $C_{16}H_{10}O_5$ requires C, 68·15; H, 3·55%). This acid on methylation gave 1-*methoxyphenanthrene*-2 : 4-*dicarboxylic acid*, m. p. 228° after crystallisation from aqueous alcohol (Found : C, 69·1; H, 4·6. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·05%).

The decarboxylation of 1-phenanthrol-2 : 4-dicarboxylic acid with quinoline and copper-bronze gave a very small amount of a phenolic product. This was methylated, yielding a solid, m. p. 86—89°, which could not be further purified owing to the very small amount available. 1-Methoxyphenanthrene has m. p. 105° (Pschorr, Wolfes, and Buckow, *Ber.*, 1900, **33**, 170).

α-1-*Naphthylglutaconic acid.* Fraction (B), after hydrolysis with potassium hydroxide, gave the above *acid*, m. p. 171° after crystallisation from aqueous alcohol (Found : C, 70·1; H, 5·0; equiv., 129·3. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7; equiv., 128).

The author thanks Professor D. H. Peacock for his help and the University of Rangoon for a grant.

UNIVERSITY COLLEGE, RANGOON, BURMA. [*Received, October 26th*, 1936.]