

246. A Synthesis of 1-Naphthol-2 : 4-dicarboxylic Acid.

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CLAISEN (*Annalen*, 1897, **297**, 88) has shown that ethyl ethoxymethylenemalonate readily condenses with ethyl sodiomalonate to give ethyl $\alpha\gamma$ -dicarbethoxyglutaconate. In an investigation on the synthesis of α -phenylglutaconic acid (to be published later) by the condensation of ethyl phenylacetate and ethyl ethoxymethylenemalonate in presence of sodium ethoxide, it was found that, if the conditions of the experiment were altered, instead of ethyl γ -carbethoxy- α -phenylglutaconate (I), ethyl 1-naphthol-2 : 4-dicarboxylate (II) was produced.



The first product of the reaction was certainly (I), for its hydrolysis gave phenylglutaconic acid. But when the crude product was distilled under reduced pressure, decomposition set in after removal of the excess of ethyl phenylacetate and ethyl ethoxymethylenemalonate and the residue consisted of (II). When the condensation was carried out first in the cold and then at 150° , the product was (II), for on hydrolysis it gave 1-naphthol-2 : 4-dicarboxylic acid.

The ring closure must have taken place during heating. It bears a close resemblance to the production of α -naphthol by the elimination of water from γ -phenylisocrotonic acid (Fittig and Erdmann, *Ber.*, 1883, 16, 43). Auwers and Moller (*J. pr. Chem.*, 1925, 109, 146) have shown that ethyl β -phenylethylacetoacetate is readily cyclised by sulphuric acid at -15° to 1-methyl-3:4-dihydro- β -naphthoic acid.

1-Naphthol-2:4-dicarboxylic acid, when heated with soda-lime, gave α -naphthol. It coupled readily with *p*-nitrobenzenediazonium chloride and two products were isolated; one, m. p. 242° , corresponds to the 4-*p*-nitrobenzeneazo- α -naphthol-2-carboxylic acid of Hewitt and Mitchell (*J.*, 1907, 91, 1260), and the other, m. p. 262° , may be the isomeric 2-*p*-nitrobenzeneazo- α -naphthol-4-carboxylic acid. According to Heller (*Ber.*, 1912, 45, 675) 4-hydroxy-1-naphthoic acid, on coupling with benzenediazonium chloride, gives benzeneazo- α -naphthol, the carboxyl group being eliminated. With benzenediazonium chloride, 1-naphthol-2:4-dicarboxylic acid gave a benzeneazo- α -hydroxynaphthoic acid, m. p. 212° . Here again it appears that 2-benzeneazo- α -naphthol-4-carboxylic acid is formed by the elimination of the carboxyl group in the 2-position, for 4-benzeneazo- α -naphthol-2-carboxylic acid melts at 194° (Grandmougin, *Ber.*, 1906, 39, 3610). The author does not press this point, especially in view of Heller's work, and the constitutions of these compounds have still to be elucidated.

The condensation of ethyl ethoxymethylenemalonate with other compounds containing reactive methylene groups is being studied.

EXPERIMENTAL.

Ethyl 1-Naphthol-2:4-dicarboxylate (II).—To an ice-cold solution of sodium (5 g.) in absolute alcohol (70 c.c.), ethyl phenylacetate (36 g.) was added slowly, followed by ethyl ethoxymethylenemalonate (43 g.; Claisen, *loc. cit.*). Next day the alcohol (50 c.c.) was distilled under reduced pressure and the residue was heated at 150° for 2 hours, cooled, dissolved in water, and acidified with 2*N*-sulphuric acid (100 c.c.) in the cold. The separated oil was extracted in benzene, dried over anhydrous magnesium sulphate, and recovered [54 g., containing 35% of the ester (II) calculated from the amount of the acid formed by hydrolysis]. On distillation under reduced pressure, unchanged ethyl phenylacetate and ethyl ethoxymethylenemalonate ($120-170^\circ/8$ mm.; temp. of bath, $200-220^\circ$; wt. 12.5 g.) were obtained; the distillation was then stopped, as decomposition set in. When the residue (33 g.) was cooled, a solid separated, which was crystallised from alcohol; yield, 12 g.; m. p. 98° (Found: C, 66.4; H, 5.5. $C_{16}H_{16}O_5$ requires C, 66.7; H, 5.55%). The ester gave a green coloration with ferric chloride. The residual liquor contained 50% of the ester (II) and was utilised for the preparation of the acid.

1-Naphthol-2:4-dicarboxylic Acid.—The ester (II) (5 g.) was boiled with caustic potash (4 g. in 10 c.c. of water and 20 c.c. of alcohol) for 3 hours. The alcohol was then distilled off, and the residue diluted with water and acidified. The solid acid was collected, dissolved in sodium bicarbonate solution, and recovered (3.8 g.). It separated from alcohol in microscopic crystals, m. p. 304° (decomp.), which in alcoholic solution showed a blue fluorescence and gave a green coloration with ferric chloride (Found: C, 62.0; H, 3.55. $C_{12}H_8O_5$ requires C, 62.1; H, 3.5%).

A mixture of the acid (1 g.) and soda-lime (6 g.) was heated, and the distillate caught in caustic soda solution. Saturation with carbon dioxide precipitated α -naphthol, m. p. and mixed m. p. $93-94^\circ$.

4-p-Nitrobenzeneazo- α -naphthol-2-carboxylic Acid.—1-Naphthol-2:4-dicarboxylic acid (1 g.) was dissolved in sodium bicarbonate (3 g.) solution and coupled with *p*-nitrobenzenediazonium chloride prepared from *p*-nitroaniline (0.6 g.), sodium nitrite (0.4 g.), and concentrated hydrochloric acid (2 c.c.). The precipitated azo-compound was crystallised from nitrobenzene. The first crop melted at 242° (Found: N, 12.7. Calc. for $C_{17}H_{11}O_5N_3$: N, 12.5%), and the second crop at 262° (Found: N, 12.25%), both with decomposition. Hewitt and Mitchell (*loc. cit.*) give m. p. 242° for 4-*p*-nitrobenzeneazo- α -naphthol-2-carboxylic acid. Both substances gave deep blue solutions in caustic soda.

1-Methoxynaphthalene-2:4-dicarboxylic Acid.—1-Naphthol-2:4-dicarboxylic acid (1 g.) was methylated with methyl sulphate (1.5 g.) and caustic soda, and the product worked up in the usual way. It formed crystals from dilute alcohol, m. p. 252° (decomp.) (Found: C, 63.1; H, 4.05. $C_{13}H_{10}O_5$ requires C, 63.4; H, 4.1%).

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The *amide*, m. p. 198° (decomp.) (Found : N, 11.2. $C_{13}H_{12}O_3N_2$ requires N, 11.5%), and the *anilide*, m. p. 262° (decomp.) (Found : N, 7.2. $C_{25}H_{20}O_3N_2$ requires N, 7.1%), were crystallised from dilute alcohol.

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