

119. *The Condensation of Some Aromatic Ketones with Ethyl Succinate.*

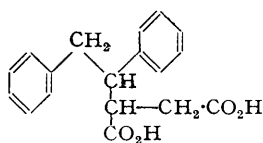
By C. L. HEWETT.

Deoxybenzoin, 2-benzoylnaphthalene, and 6-benzoyltetralin have been condensed with ethyl succinate. The acid arising from deoxybenzoin has been reduced and the two *acids* thus obtained have been cyclised to the two stereoisomeric 3 : 10-diketo-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-benzanthracenes (II). 2-Benzoylnaphthalene gave γ -phenyl- γ -naphthylitaconic acid, which was reduced to the corresponding methylsuccinic acid. 6-Benzoyltetralin gave a mixture of two *acids*, both of which were resistant to reduction.

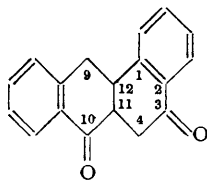
By the condensation of ethyl succinate with deoxybenzoin, Stobbe and Russwarm (*Annalen*, 1899, **308**, 157) obtained γ -phenyl- γ -benzylidenemethylsuccinic acid, but they made no attempt to reduce this to γ -phenyl- γ -benzylmethylsuccinic acid (I).

In the hope that the acid (I) could be obtained from the unsaturated acid by reduction and subsequently cyclised to 3 : 10-diketo-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-benzanthracene (II), thus providing a new route to derivatives of 1 : 2-benzanthracene, the reduction of this acid was investigated. Reduction with sodium amalgam yielded a mixture of two *acids*, of which the less soluble one (m. p. 188—189°) was isolated in a state of purity; the second *acid* was obtained from the liquors and had m. p. 122.5—123.5°, raised to 138° after

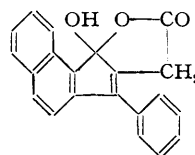
drying at 100°/0.5 mm. This acid was probably still contaminated with unsaturated acid (see below). Cyclisation of both acids gave a mixture of two neutral products, m. p. 210—211° and 132—133°, which are



(I.)



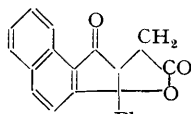
(II.)



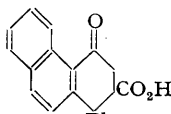
(III.)

regarded as the *diketones* (II). The higher-melting isomer was also obtained from the lower-melting isomer in an attempted Clemmensen reduction.

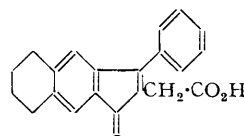
In a dissertation (Frankfurt-am-Main; 1937) * Knott has also described the reduction of γ -phenyl- γ -benzylidenemethylsuccinic acid and the ring closure of the reduced acid. He describes two reduced acids, m. p. 193° and 155°. The latter acid was obtained pure by hydrolysis of its anhydride. The two higher-melting acids would appear to be the same; the discrepancy between the m. p.'s of the two lower-melting acids may be due to contamination of the acid described in this paper with the unsaturated acid. On ring closure of his two acids, Knott obtained only the higher-melting neutral product from his higher-melting acid; from the lower-melting acid he obtained the same product together with another neutral product, m. p. 142.5°. Both of these compounds he formulates as the keto-enol, since they give monodinitrophenylhydrazones and monoximes.



(IV.)



(V.)



(VI.)

The condensation of 2-benzoylnaphthalene with ethyl succinate gave a good yield of a single *acid*, which cyclised with sulphuric acid to give a neutral product, probably the *lactone* (III) or (IV). Reduction of the unsaturated acid was effected with sodium amalgam, which was slow in action. Ring closure of the anhydride of the reduced acid gave the *keto-acid* (V).

6-Benzoyltetralin condensed with ethyl succinate to give a mixture of two unsaturated *acids* which were both resistant to reduction with sodium amalgam. One of the unsaturated acids on cyclisation with sulphuric acid gave a *keto-acid*, probably the indone (VI).

Owing to present circumstances, it is not possible to continue this investigation.

EXPERIMENTAL.

gamma-Phenyl-*gamma*-benzylmethylsuccinic Acid (I).— γ -Phenyl- γ -benzylidenemethylsuccinic acid (41 g.) (Stobbe and Russwarm, *loc. cit.*) was dissolved in water (500 c.c.) and sodium hydroxide (8.2 g.) and treated with sodium amalgam (2½%; 400 g.). After the sodium had all reacted the solution was decanted and acidified. The precipitated oil slowly set to a paste and was triturated with acetic acid, and the solid recrystallised from acetic acid. *gamma*-Phenyl-*gamma*-benzylmethylsuccinic acid (5 g.) separated in colourless needles, m. p. 188—189° (Found: C, 72.1; H, 5.9. C₁₈H₁₈O₄ requires C, 72.5; H, 6.1%). The mother-liquors on dilution with water gave a product, m. p. 83—95°, which after recrystallisation from benzene formed colourless needles, m. p. 122.5—123.5°. This isomeric *gamma*-phenyl-*gamma*-benzylmethylsuccinic acid after drying at 100°/0.5 mm. had m. p. 138° (Found: C, 73.1; H, 5.9%).

3:10-Diketo-3:4:9:10:11:12-hexahydro-1:2-benzanthracene (II).—The higher-melting acid (5 g.) was dissolved in concentrated sulphuric acid (25 c.c.) and heated on the water-bath for 1 minute, cooled, and poured on ice. The product was extracted with ether, filtered from a sparingly soluble crystalline solid, and the ethereal solution, after washing with sodium carbonate solution, dried and evaporated. The residue was dissolved in hot methyl alcohol, filtered from a further amount of sparingly soluble crystals, and allowed to crystallise. The *diketone* (II), probably the *cis*-isomer separated in colourless plates (0.2 g.), m. p. 132—133° (Found: C, 82.6; H, 5.9. C₁₈H₁₄O₂ requires C, 82.4; H, 5.4%). The sparingly soluble fractions were boiled with dilute sodium carbonate solution, washed with water, and crystallised from benzene; the other isomer (probably *trans*) of the *diketone* then separated in colourless plates (0.5 g.), m. p. 210—211° (Found: C, 82.2; H, 5.4%). Cyclisation of the lower-melting acid (10 g.) with concentrated sulphuric acid (25 c.c.) on the water-bath for 2 minutes gave the higher-melting ketone (0.1 g.), m. p. 209—210°, but the product was mainly the lower-melting isomer (3.3 g.), m. p. 132—133°.

The lower-melting diketone (1.8 g.) was boiled with amalgamated zinc (6 g.), water (8 c.c.), concentrated hydrochloric acid (4 c.c.), and toluene (2.5 c.c.) for 5 hours. The product on crystallisation from benzene had m. p. 209—210°, not depressed by the higher-melting diketone.

gamma-Phenyl-*gamma*-naphthylitaconic Acid.—2-Benzoylnaphthalene (105 g.), prepared by dehydrogenation of 6-benzoyltetralin with sulphur (Scharwin, *Ber.*, 1902, **35**, 2513; Barbot, *Bull. Soc. chim.*, 1930, **47**, 1318), and ethyl succinate (105 g.) were added to a suspension of sodium ethoxide (prepared from 21 g. of sodium, 42 g. of ethyl alcohol, and 200 c.c. of ether) and heated on the water-bath for 1 hour. Water (500 c.c.) was then added, and the aqueous layer separated; hydrolysis was completed by boiling the aqueous layer with sodium hydroxide (50 g.). After acidification the crude acid was dissolved in sodium carbonate solution and filtered (charcoal), and the sodium salt salted out. The acid obtained by

* A copy of this dissertation was sent to Professor J. W. Cook after the experiments now recorded had been completed.

decomposition of the sodium salt was dissolved in benzene; after 1 day γ -phenyl- γ -naphthylitaconic acid (97 g.) separated, which after crystallisation from benzene-toluene formed colourless micro-crystals, m. p. 173.5—174.5° (Found: C, 75.5; H, 5.0. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.85%). It separated from aqueous acetic acid in colourless plates, m. p. 154—158°. The dimethyl ester prepared from the acid and diazomethane, separated from methyl alcohol in colourless plates, m. p. 94—95° (Found: C, 76.2; H, 5.75. $C_{23}H_{20}O_4$ requires C, 76.65; H, 5.6%).

Cyclisation. The foregoing acid (5 g.) was dissolved in concentrated sulphuric acid (50 c.c.) and after 20 minutes at the ordinary temperature was poured on ice. The solid lactone (III or IV) was collected, washed free from colouring matter with sodium carbonate solution, and crystallised from a large amount of methyl alcohol, forming colourless needles (1.5 g.), m. p. 166.5—167.5° (Found: C, 79.7; H, 4.6. $C_{21}H_{14}O_3$ requires C, 80.2; H, 4.5%). Its formulation as a lactone is based on the fact that it is insoluble in sodium carbonate solution, but slowly dissolves in boiling alcoholic sodium hydroxide, from which it is precipitated by acids but not by water.

γ -Phenyl- γ -naphthylmethylsuccinic Acid.—The foregoing acid (45 g.) was dissolved in water (450 c.c.) and sodium hydroxide (11.7 g.) and treated with sodium amalgam (2½%; 900 g.) on a water-bath. After all the sodium had reacted the solution was decanted, filtered (charcoal), and sodium chloride added. The sodium salt which separated was decomposed with dilute hydrochloric acid, and the free acid extracted with ether. After removal of the ether the residue was crystallised from acetic acid (charcoal) and then benzene-light petroleum; the acid (35 g.) then separated as a snow-white powder, m. p. 130—131° (Found: C, 75.15; H, 5.7. $C_{21}H_{14}O_3$ requires C, 75.4; H, 5.4%).

4-Keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-phenanthroic Acid (V).—The reduced acid (35 g.) was refluxed with acetyl chloride (35 g.) and after removal of the acetic acid and excess of acetyl chloride the crude anhydride was dissolved in nitrobenzene (350 c.c.). Aluminium chloride (35 g.) was added with ice-cooling and after 20 hours at 0° the product was decomposed with ice, and the nitrobenzene distilled with steam. The residue was extracted with sodium carbonate solution, filtered, and acidified; the resulting keto-acid (16.3 g.) crystallised from acetic acid in colourless needles, m. p. 243—245° after sintering at 240° (Found: C, 79.25; H, 5.3. $C_{21}H_{16}O_3$ requires C, 79.7; H, 5.1%). It was converted into a gum on attempted Clemmensen reduction.

γ -Phenyl- γ -(6-tetralyl)itaconic Acid.—6-Benzoyltetralin (Scharwin, *loc. cit.*) (90 g.), ethyl succinate (90 g.), and ether (90 c.c.) were added to sodium ethoxide (prepared from 18 g. of sodium, 36 g. of ethyl alcohol, and 180 c.c. of ether), and the whole heated on the water-bath for 2½ hours, the alcohol and ether being allowed to distil off. Water (500 c.c.) and sodium hydroxide (50 g.) were then added, and the solution boiled for 1½ hours and acidified. The precipitated oil was dissolved in water (500 c.c.) and potassium hydroxide (60 g.) and boiled for a further 8 hours. The hot solution was saturated with potassium carbonate, and the potassium salt which separated on cooling crystallised from water and decomposed with dilute acid; the pure acid (30 g.) crystallised from acetic acid in fine colourless plates, m. p. 183—185° (Found: C, 74.6; H, 6.0. $C_{21}H_{20}O_4$ requires C, 74.95; H, 6.0%). The liquors of the potassium salt were acidified, and the sticky acid extracted with benzene. After standing for several days at 0° a new acid (43 g.) separated, which after recrystallisation from toluene formed a colourless microcrystalline powder, m. p. 188—189° (Found: C, 75.4; H, 6.2%). A mixture of the two acids had m. p. 169—175°.

Cyclisation. A solution of the acid, m. p. 183—185° (5 g.), in concentrated sulphuric acid (25 c.c.) was stirred for 1 minute at the ordinary temperature and then poured on ice. The solid was collected, reprecipitated from its filtered solution in sodium carbonate solution, and crystallised from acetic acid. The keto-acid (2.4 g.) formed red needles, m. p. 165—166° (Found: C, 79.0; H, 5.7. $C_{21}H_{18}O_3$ requires C, 79.2; H, 5.7%). From its colour and by analogy with the cyclisation of other diarylitaconic acids (Stobbe and Vieweg, *Ber.*, 1902, 35, 637) this compound is probably the indone (VI).

Reduction. In a typical experiment, the acid, m. p. 188—189° (45 g.), was dissolved in water (400 c.c.) and sodium hydroxide (9.6 g.), and sodium amalgam (2½%; 600 g.) added. After heating on the water-bath for 4 hours and standing at the ordinary temperature for 20 hours, the solution was filtered (charcoal) and acidified. The oily acid was extracted with ether, the ether evaporated, and the residue crystallised from benzene. The product had m. p. 100—160°, indicating that some reduction had taken place.

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