

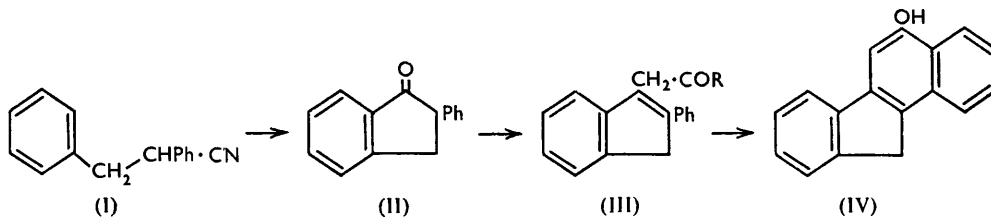
745. *A New Synthesis of 3-Hydroxy-1 : 2-benzofluorene.*

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Convenient methods for the preparation of 2-phenylindanone and 3-hydroxy-1 : 2-benzofluorene are described.

THE preparation of 2-phenylindanone from  $\alpha\beta$ -diphenylpropionic acid<sup>1</sup> and deoxybenzoin<sup>2</sup> has been described. We find it may advantageously be obtained by condensing benzyl chloride with the sodium derivative of benzyl cyanide to give  $\alpha\gamma$ -diphenylpropionitrile (I). Hydrolysis of this to the acid, followed by ring-closure, gives 2-phenylindanone (II) in an over-all yield of 30%.

3-Hydroxy(or 3-acetoxy)-1 : 2-benzofluorene has been prepared by reduction of the fluorenone.<sup>3</sup> It can also be readily prepared by treating 2-phenylindanone with ethyl bromoacetate and zinc, to give the ester (III; R = OEt) which after hydrolysis and conversion into the acid chloride is cyclised to 3-hydroxy-1 : 2-benzofluorene (IV). The



structure of the product was thus established, for not only does ring-closure occur preferentially to give a six-membered ring, but also ring-closure on the aromatic nucleus of the indanone ring would give a sterically improbable product with two five-membered rings annealed to one another and to the benzene ring.<sup>4</sup> The structure was confirmed by identity with that of the reduction product of 3-hydroxy-1 : 2-benzofluorenone<sup>5</sup> kindly supplied by Dr. J. D. Loudon.

The dehydration of the Reformatsky product may yield either the ester (III) or the isomer with an *exo*-double bond. Although elimination reactions of 5-membered rings favour the formation of an *exo*- rather than an *endo*-double bond<sup>6</sup> we favour formula (III) since the substance forms a colourless ureide with carbobis-*p*-dimethylaminophenylimide.<sup>7</sup> This is in harmony with Linstead's finding that at equilibrium *cyclopentenylacetic acid*

<sup>1</sup> Von Auwers and Auffenberg, *Ber.*, 1919, **52**, 108.

<sup>2</sup> Plattner, Sandrin, and Wyss, *Helv. Chim. Acta*, 1946, **29**, 1604.

<sup>3</sup> Cook and Preston, *J.*, 1944, 553; Badger, Campbell, and Cook, *J.*, 1949, 1084; Gross and Lankelma, *J. Amer. Chem. Soc.*, 1951, **73**, 3439.

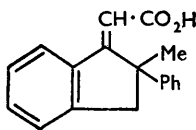
<sup>4</sup> See, e.g., Cook and Hunter, *J.*, 1952, 3168.

<sup>5</sup> Jarrett and Loudon, *J.*, 1955, 4052.

<sup>6</sup> Brown, Brewster, and Shechter, *J. Amer. Chem. Soc.*, 1954, **76**, 467.

<sup>7</sup> Zetsche, *Ber.*, 1939, **72**, 1599.

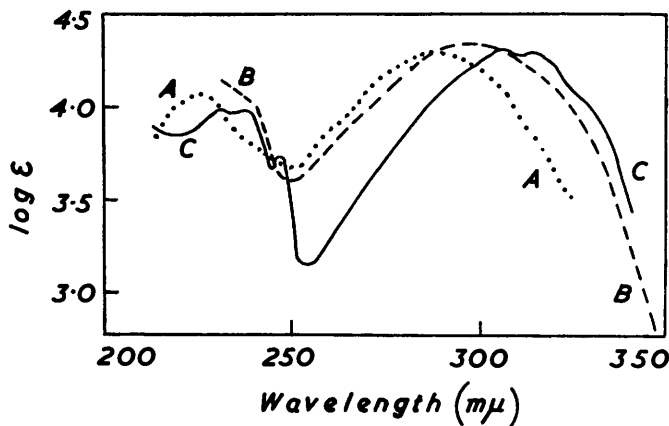
contains 96% of the  $\beta\gamma$ -isomer.<sup>8</sup> Our structure (III) was confirmed by the general similarity of the absorption spectrum of the acid to those of 2-phenylindene<sup>9</sup> and *trans*-stilbene<sup>10</sup> (see Figure). The preferential formation of an *endo*-double bond may be attributed in part to the conjugation of this bond with two phenyl nuclei. It is perhaps cogent that in the equilibrium  $\text{Ph}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{H} \rightleftharpoons \text{Ph}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  the second acid with its phenyl nuclei conjugated through the ethylenic linkage occurs to the extent of 83%.<sup>11</sup>



(V)

2-Methyl-2-phenylindanylidenecetic acid (V) was prepared for comparison of its spectrum with that of our acid (III; R = OH), but it was not obtained in sufficient quantity to ensure that it was spectroscopically pure. With Zetsche's reagent in ether it gave a yellow solution.

Absorption spectra of (A) 2-phenylindanylidenecetic acid, (B) *trans*-stilbene, and (C) 2-phenylindene.



#### EXPERIMENTAL

M. p.s were determined on the Kofler block.

**2-Phenylindanone.**—Freshly distilled benzyl cyanide (170 g.) was added during 1 hr. to powdered sodium (33 g.) and dry ether (600 ml.) under nitrogen. The mixture was boiled and stirred until all the sodium dissolved (*ca.* 2 hr.), then cooled to room temperature, and to it was added, during 30 min. with vigorous stirring, freshly distilled benzyl chloride (85 g.). The solution was stirred overnight, the ether boiled off, and dry benzene (600 ml.) added. The mixture was boiled for 2 hr., then cooled, and dilute hydrochloric acid added. The benzene layer was washed with aqueous sodium carbonate, water, and saturated aqueous sodium chloride, and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent and distillation yielded  $\alpha\beta$ -diphenylpropionitrile (63%), b. p. 138—145°/0.4—0.5 mm.

The nitrile (88 g.) was boiled for 10 hr. with trimethylene glycol (250 ml.), sodium hydroxide (35 g.), and water (80 ml.) and poured into water. Unchanged nitrile was removed in benzene; and the alkaline solution with hydrochloric acid gave  $\alpha\beta$ -diphenylpropionic acid (88%), m. p. 95° after two crystallisations from light petroleum (b. p. 60—80°). The acid (50 g.) was converted by phosphorus pentachloride into the acid chloride, which was added in benzene dropwise to a stirred cooled suspension of aluminium chloride (38 g.) in dry benzene (500 ml.; "AnalaR"). The mixture was stirred for 3 hr. at room temperature, ether (100 ml.) was added, and the complex decomposed by aqueous hydrochloric acid (1:1). The organic layer was washed with sodium carbonate solution, water, and saturated sodium chloride solution, and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent and distillation gave 2-phenylindanone (67%), b. p. 145—155°/0.4—0.5 mm., m. p. 78° after crystallisation from light petroleum (b. p. 60—80°).

<sup>8</sup> Linstead, J., 1928, 2343; 1930, 1603.

<sup>9</sup> Wiegand and Merkel, *Annalen*, 1942, 550, 175.

<sup>10</sup> Arends, *Ber.*, 1931, 64, 1936.

<sup>11</sup> Phalnikar and Nargund, *J. Univ. Bombay*, 1939, 8, III, 184.

**3-Hydroxy-1 : 2-benzofluorene.**—2-Phenylindanone (23 g.), benzene (50 ml.), ethyl bromoacetate (25 g.), and iodine (trace) were added to amalgamated zinc wool (20 g.) in dry benzene (150 ml.) and dry ether (150 ml.). The mixture was heated to start the reaction and when this was complete heating was resumed (4 hr.), more bromo-ester ( $2 \times 10$  g.) and amalgamated zinc ( $5 \times 4$  g.) being added at intervals. The colourless addition product was decomposed by a little ethanol and acetic acid, the solution poured into acetic acid and water (1 : 1), and the organic layer separated, washed with water, and dilute ammonia, and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was removed and the residue dehydrated by a crystal of iodine at  $200^\circ/100$  mm. during 30 min. Distillation yielded ethyl 2-phenylindanylacetate, b. p.  $168\text{--}178^\circ/0.6$  mm., which was hydrolysed when boiled for 2 hr. with potassium hydroxide (7 g.), ethanol (50 ml.), and water (50 ml.) to pale-yellow 2-phenylindanylacetic acid (21.2 g., crude), m. p.  $144^\circ$  [after crystallisation from benzene-light petroleum (b. p.  $60\text{--}80^\circ$ )] (Found : C, 81.4; H, 5.6.  $\text{C}_{17}\text{H}_{14}\text{O}_2$  requires C, 81.6; H, 5.6%). The acid in ether with a slight excess of carbobis-*p*-dimethylaminophenyl-imide deposited overnight the colourless *ureide*, m. p.  $245^\circ$  after sintering at  $198^\circ$  (Found : C, 76.4; H, 6.5; N, 10.8.  $\text{C}_{34}\text{H}_{34}\text{O}_2\text{N}_4$  requires C, 76.9; H, 6.5; N, 10.6%).

Ring-closure of the acid by polyphosphoric acid or sulphuric acid was unsuccessful, but was achieved by the inverse Friedel-Crafts reaction on the acid chloride. The acid (1 g.) and phosphorus pentachloride gave the acid chloride, which, dissolved in benzene (50 ml.; "AnalaR"), was added during  $\frac{1}{2}$  hr. dropwise to an ice-cooled, stirred suspension of finely powdered aluminium chloride (0.7 g.) in benzene (500 ml.; "AnalaR"). The ice-bath was removed and the mixture stirred until the temperature reached  $20^\circ$  (ca.  $1\frac{1}{2}$  hr.), then cooled and treated with ether (50 ml.) and hydrochloric acid (1 : 1 v/v). The yellow organic layer was washed with sodium carbonate solution, water, and saturated sodium chloride solution, and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent gave 3-hydroxy-1 : 2-benzofluorene (42%), m. p.  $215\text{--}223^\circ$  (decomp.) depending on the rate of heating (lit.,  $219^\circ$ ), which yielded an acetyl derivative, m. p.  $159\text{--}160^\circ$  (lit.,  $155\text{--}156^\circ$ ), and with dimethyl sulphate and alkali gave the *methyl ether*, colourless needles, m. p.  $142\text{--}143^\circ$  (Found : C, 87.2; H, 5.7.  $\text{C}_{18}\text{H}_{14}\text{O}$  requires C, 87.8; H, 5.7%).

**2-Methyl-2-phenylindanylidenecetic Acid.**—A crystal of an iron salt was added to sodium (0.37 g.) in liquid ammonia (100 ml.) and the mixture kept for 1 hr. Dry benzene (50 ml.) was added dropwise to remove the liquid ammonia; a further 150 ml. of benzene were added and nitrogen passed through the flask. 2-Phenylindanone (3 g.) in benzene (20 ml.) was added to the stirred suspension of sodamide, and the mixture boiled for 3 hr., cooled to  $40^\circ$ , and treated dropwise with methyl iodide (10 g.) in benzene (20 ml.). The mixture was again boiled for 3 hr., then cooled and decomposed by dilute hydrochloric acid. The organic layer was washed with aqueous sodium hydrogen sulphite and sodium carbonate, then with water, and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent gave 2-methyl-2-phenylindanone (44%), m. p.  $110\text{--}111^\circ$  after crystallisation from light petroleum (b. p.  $60\text{--}80^\circ$ ) (Found : C, 86.5; H, 6.4.  $\text{C}_{16}\text{H}_{14}\text{O}$  requires C, 86.5; H, 6.4%).

This indanone (1 g.) in benzene (20 ml.) and dry ether (20 ml.) was treated with ethyl bromoacetate (2.5 g.) and amalgamated zinc (2 g.) as described above. The product was dehydrated by iodine at  $210^\circ/100$  mm. The resulting oil in benzene was washed with aqueous sodium hydrogen sulphite, aqueous sodium carbonate, and water, and dried, and the solution evaporated. The residue was hydrolysed for 1 hr. with potassium hydroxide (0.5 g.) in boiling water (10 ml.) and ethanol (10 ml.). Acidification afforded 2-methyl-2-phenylindanylidenecetic acid (34%), m. p.  $175\text{--}176^\circ$  (rapid heating) after crystallisation from benzene-light petroleum (b. p.  $60\text{--}80^\circ$ ) (Found : C, 82.2; H, 6.2.  $\text{C}_{18}\text{H}_{16}\text{O}_2$  requires C, 81.8; H, 6.1%).

**Spectroscopic Measurements.**—The ultraviolet spectra were measured by means of a Unicam SP.500 Spectrophotometer with cyclohexane as solvent. 2-Phenylindanylacetic acid,  $\lambda_{\text{max}}$ , 227 and 288  $\text{m}\mu$  ( $\log \epsilon$  4.03 and 4.27 respectively), and  $\lambda_{\text{min}}$ , 248  $\text{m}\mu$  ( $\log \epsilon$  3.63). 2-Phenylindene,  $\lambda_{\text{max}}$ , 230, 237, 246, 306, and 314  $\text{m}\mu$  ( $\log \epsilon$  4.08, 4.08, 3.84, 4.28, and 4.28 respectively).

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