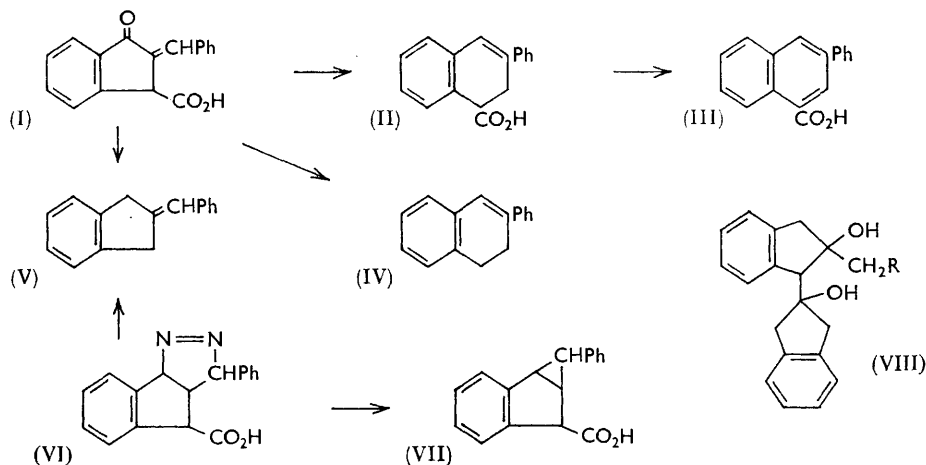


### 581. The Conversion of 2-Benzylidene-1-oxoindane-1-carboxylic Acid into 2-Phenylnaphthalene Derivatives.

By NEIL CAMPBELL and HARRY G. HELLER.

Attempts to reduce 2-benzylidene-3-oxoindane-1-carboxylic acid by the Wolff-Kishner method yielded 1,2-dihydro-3-phenylnaphthalene and its 1-carboxylic acid, and a hydrocarbon, probably 2-benzylideneindane.

FEW conversions of indane or indene derivatives into naphthalene derivatives are recorded,<sup>1</sup> and it was therefore of interest that attempted Wolff-Kishner reduction of 2-benzylidene-3-oxoindane-1-carboxylic acid (I) gave three products, two of which were naphthalene derivatives. The structure of the first, 1,2-dihydro-3-phenylnaphthalene-1-carboxylic acid (II) was established by dehydrogenation with chloranil to 3-phenylnaphthalene-1-carboxylic acid (III), and the similarity of its ultraviolet spectrum to those of 1,2-dihydro-3-phenylnaphthalene and *trans*-stilbene. Decarboxylation of the acid (III) by copper bronze in hot 4-methylquinoline yielded 2-phenylnaphthalene,<sup>2</sup> the yield being nearly quantitative in contrast to the 60% yield of naphthalene obtained from 1-naphthoic acid under the same conditions. The second product was 1,2-dihydro-3-phenylnaphthalene



(IV), whose m. p.  $52^\circ$ , rises to  $65\text{--}66^\circ$  when the substance is kept in air or is repeatedly crystallised. This is probably due to dehydrogenation to 2-phenylnaphthalene, a process which can be effected quantitatively by *N*-bromosuccinimide and accounts for the higher m. p.  $64\text{--}66^\circ$ , reported by Campbell and Kidd.<sup>2</sup> The third product, obtained in very small quantity, was a hydrocarbon, m. p.  $30^\circ$ , a plausible constitution for which is 2-benzylideneindane (V). It contains a phenyl-conjugated double bond and differs in m. p. from the isomeric 2-benzylidene.

Wolff-Kishner reduction of  $\alpha\beta$ -unsaturated ketones frequently gives either unsaturated hydrocarbons or cyclopropane derivatives through an intermediate pyrazoline<sup>3</sup> and the Huang-Minlon modification of the method yields chiefly cyclopropane derivatives.<sup>4</sup> It is therefore probable that the above transformation proceeds through the pyrazoline (VI), which loses nitrogen to give 2-benzylideneindane (V) or the cyclopropane derivative (VII), the ring strain of which is relieved by rearrangement to a dihydronaphthalene.

An attempt to prepare 2-benzylideneindane was unsuccessful since dehydration of

<sup>1</sup> Parham *et al.*, *J. Org. Chem.*, 1957, **22**, 730, 1473; Koelsch, *ibid.*, 1961, **26**, 1002.

<sup>2</sup> Campbell and Kidd, *J.*, 1954, 2154.

<sup>3</sup> Beech, Turnbull, and Wilson, *J.*, 1952, 4686; Lardelli and Jeger, *Helv. Chim. Acta*, 1949, **32**, 1817.

<sup>4</sup> Huang-Minlon, *Sci. Sinica*, 1961, **10**, 711.

2-benzylindan-2-ol yielded only 2-benzylindene, whose structure followed from its formation of a Grignard reagent on reaction with ethylmagnesium bromide.<sup>5</sup> In the preparation of the benzylindanol by the interaction of indan-2-one and benzylmagnesium chloride, according to the conditions of the experiment other products included 1-(2-hydroxyindan-2-yl)indan-2-one, m. p. 145°,<sup>6</sup> 1-2'-indanylideneindan-2-one, and a substance, m. p. 160°, with a strong hydroxyl band (3400 cm.<sup>-1</sup>) but no carbonyl band, that is probably the compound (VIII; R = Ph) formed from the hydroxyindanylidan-2-one and the Grignard reagent. The product obtained by Koelsch and Johnson<sup>7</sup> by interaction of indan-2-one and methylmagnesium bromide is probably a compound of this type (VIII; R = H).

#### EXPERIMENTAL

*2-Benzylidene-3-oxoindane-1-carboxylic Acid.*—3-Oxoindane-1-carboxylic acid, m. p. 83—84°, was prepared (48% yield) by cyclisation of phenylsuccinyl chloride by aluminium chloride in nitrobenzene.<sup>8</sup> The keto-acid (17.6 g., 0.1 mole) and benzaldehyde (15.8 g., 0.15 mole) in ethanol (40 c.c.) were treated with 10% (w/v) ethanolic potassium hydroxide until the yellow solution became green. The mixture was boiled for 5 min. and on acidification with dilute hydrochloric acid gave *2-benzylidene-3-oxoindane-1-carboxylic acid* (17.5 g., crude), which crystallised from benzene in prisms, m. p. 169—170° (Found: C, 77.1; H, 4.5. C<sub>17</sub>H<sub>12</sub>O<sub>3</sub> requires C, 77.3; H, 4.5%); its ultraviolet spectrum [ $\lambda_{\max}$ , 225, 323 m $\mu$  (log  $\epsilon$  4.14, 4.36),  $\lambda_{\min}$ , 250 m $\mu$  (log  $\epsilon$  3.69)] resembled those of 2-benzylideneindan-1-one [ $\lambda_{\max}$ , 225, 325 m $\mu$  (log  $\epsilon$  4.13, 4.31),  $\lambda_{\min}$ , 255 m $\mu$  (log  $\epsilon$  3.84)] and  $\omega$ -benzylideneacetophenone [ $\lambda_{\max}$ , 225, 300 m $\mu$  (log  $\epsilon$  4.05, 4.35),  $\lambda_{\min}$ , 240 m $\mu$  (log  $\epsilon$  3.65)].

Hydrogenation in ethanol with hydrogen and palladium on barium sulphate gave *2-benzyl-3-oxoindane-1-carboxylic acid*, needles, m. p. 114—115° (from benzene—light petroleum) (Found: C, 76.8; H, 5.3. C<sub>17</sub>H<sub>14</sub>O<sub>3</sub> requires C, 76.8; H, 5.3%),  $\lambda_{\max}$ , 245, 293 m $\mu$  (log  $\epsilon$  4.17, 3.44),  $\lambda_{\min}$ , 270 m $\mu$  (log  $\epsilon$  3.075); this spectrum was similar to those of 2-benzylidane-1-one [ $\lambda_{\max}$ , 240, 283 m $\mu$  (log  $\epsilon$  4.25, 3.52),  $\lambda_{\min}$ , 260 m $\mu$  (log  $\epsilon$  3.06)] and  $\omega$ -benzylacetophenone [ $\lambda_{\max}$ , 240, 278 m $\mu$  (log  $\epsilon$  4.18, 2.97) and  $\lambda_{\min}$ , 260 m $\mu$  (log  $\epsilon$  2.90)].

*Wolff-Kishner Reduction of 2-Benzylidene-3-oxoindane-1-carboxylic Acid.*—The keto-acid (7.92 g.), potassium hydroxide (6 g.), 99% hydrazine hydrate (4 c.c.), and ethylene glycol (40 c.c.) were gradually heated to 180° during 1 hr. and then boiled for 1½ hr. at 195—200° after the water produced and the hydrazine hydrate had been distilled off. The mixture was poured into water, and the resulting oil extracted with benzene and washed with 10% sodium hydroxide and then with water. The dried extract (Na<sub>2</sub>SO<sub>4</sub>) was evaporated and the residual oil was fractionally distilled, to give an oil (3.8 g.) which yielded 1,2-dihydro-3-phenylnaphthalene, plates (from methanol), m. p. 52° (Found: C, 92.9; H, 6.6. Calc. for C<sub>16</sub>H<sub>14</sub>: C, 93.2; H, 6.8%),  $\lambda_{\max}$ , 230 and 305 m $\mu$  (log  $\epsilon$  4.09, 4.32),  $\lambda_{\min}$ , 250 m $\mu$  (log  $\epsilon$  3.13). Repeated crystallisation from ethanol raised the m. p. to 58°, giving a mixed m. p. of 58—60° with a sample,<sup>2</sup> m. p. 65—66°, which had been kept in a stoppered bottle for several years. Both samples, m. p. 58° and 65—66°, gave a trinitrobenzene derivative, m. p. 110—111°, while dehydrogenation of the first-named sample (0.69 g.) by boiling it for 15 min. with *N*-bromosuccinimide (0.6 g.) in carbon tetrachloride (20 c.c.) gave 2-phenylnaphthalene (70%), m. p. and mixed m. p. 99°, after two crystallisations from methanol.

In a second experiment the oil was fractionally distilled, giving two main fractions, b. p. 126—128°/0.5 mm. and 134—142°/0.5 mm., the second yielding impure 1,2-dihydro-3-phenylnaphthalene. The first fraction (2.17 g.) in ethanol with trinitrobenzene (2 g.) gave 2.3 g. of the adduct of 1,2-dihydro-3-phenylnaphthalene, m. p. and mixed m. p. 110—111°. The ethanolic filtrate was evaporated, giving an oil which was chromatographed in light petroleum on alumina. Development with light petroleum gave a fraction which was shown by infrared spectroscopy to be free from trinitrobenzene and was distilled in a vacuum. The distillate crystallised from ethanol as prisms, m. p. 30°, probably *2-benzylideneindane* (Found: C, 93.1; H, 6.7. C<sub>16</sub>H<sub>14</sub> requires C, 93.15; H, 6.85%),  $\lambda_{\max}$ , 253 m $\mu$  (log  $\epsilon$  4.06) and  $\lambda_{\min}$ , 230 m $\mu$  (log  $\epsilon$  3.71).

<sup>5</sup> Courtot, *Ann. Chim. (France)*, 1915, **4**, 58.

<sup>6</sup> Schroth and Treibs, *Annalen*, 1961, **639**, 214.

<sup>7</sup> Koelsch and Johnson, *J. Amer. Chem. Soc.*, 1943, **65**, 567.

<sup>8</sup> Vargha, Horvath, Nogradi, and Gyermek, *Acta Chim. Acad. Hung.*, 1954, **5**, 116.

In one experiment, the aqueous alkaline washings were treated with concentrated hydrochloric acid, giving 1,2-dihydro-3-phenylnaphthalene-1-carboxylic acid, needles (from aqueous ethanol), m. p. 128—130° (Found: C, 81.4; H, 5.4.  $C_{17}H_{14}O_2$  requires C, 81.6; H, 5.6%),  $\lambda_{max}$ . 235, 305  $m\mu$  ( $\log \epsilon$  4.305, 4.37),  $\lambda_{min}$ . 264  $m\mu$  ( $\log \epsilon$  3.88). The spectrum resembles that of impure 1,2-dihydro-3-phenylnaphthalene, m. p. 58—59°, more closely than that of the pure hydrocarbon, m. p. 52°, and this may indicate that the sample contains some dehydrogenated acid.<sup>9</sup> Dehydrogenation of the acid by chloranil in boiling xylene gave 3-phenyl-1-naphthoic acid, needles (from aqueous ethanol), m. p. 222—224° (Found: C, 81.8; H, 4.8. Calc. for  $C_{17}H_{12}O_2$ : C, 82.2; H, 4.9%), identical with a sample obtained from the alkaline extract of another experiment. The acid (0.25 g.), when boiled in 4-methylquinoline (5 c.c.) with copper bronze for 5 hr., gave 2-phenylnaphthalene (0.20 g.), m. p. and mixed m. p. 99°.

*2-Benzylindene*.—Indan-2-one (23 g.) in ether (200 c.c.) was added to benzylmagnesium chloride in ether, to give as the main product 1-(2-hydroxyindan-2-yl)-indan-2-one, m. p. 145°, which with formic acid yielded 1-2'-indanylideneindan-2-one, m. p. 173—175°. In a second experiment indan-2-one (23 g.) in ether (500 c.c.) was added during 4 hr. to benzylmagnesium chloride at 0°. Working up in the usual manner gave a gum, which was dissolved in light petroleum and cooled by acetone-solid carbon dioxide. The resulting gum, on solidification and crystallisation from light petroleum, gave 2-benzylindan-2-ol (6.9 g.), m. p. 82° (Found: C, 86.5; H, 7.2.  $C_{16}H_{16}O$  requires 85.7; H, 7.2%). The combined filtrates were chromatographed on alumina and developed with light petroleum (b. p. 60—80°). The first fraction with an intense violet fluorescence gave on evaporation a solid, part of which dissolved in a limited volume of light petroleum leaving an insoluble residue. The filtrate when cooled to 0° gave 2-hydroxy-2-benzylindane (2.6 g.), m. p. 80°, while the residue when crystallised from ethanol yielded 2-benzyl-1-(2-hydroxyindan-2-yl)-indan-2-ol (VIII; R = Ph), (Found: C, 84.5; H, 6.5.  $C_{25}H_{24}O_2$  requires C, 84.2; H, 6.8%). A later chromatographic fraction gave 1-2'-indanylideneindan-2-one, m. p. 173—175°. Dehydration of the benzylindanol with formic acid yielded 2-benzylindene, m. p. 48° (Found: C, 92.8; H, 6.8.  $C_{16}H_{14}$  requires C, 93.2; H, 6.8%),  $\lambda_{max}$ . 259  $m\mu$  ( $\log \epsilon$  4.15),  $\lambda_{min}$ . 236  $m\mu$  ( $\log \epsilon$  3.71).

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DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH.

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