A New Synthesis of Chrysene.

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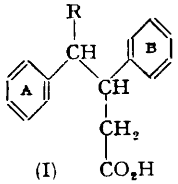
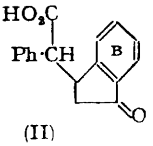
Cyclisation of γ-cyano-$\beta\gamma$-diphenylbutyric acid (I; R = CN) yields the amide (III; R = $CO{\cdot}NH_2$) of 1 : 2 : 3 : 4-tetrahydro-4-oxo-2-phenyl-1-naphthoic acid. Hence by standard methods *trans*-1 : 2 : 3 : 4-tetrahydro-2-phenyl-1-naphthylacetic acid (V; R = $CH_2{\cdot}CO_2H$) and *trans*-1 : 2 : 7 : 8 : 15 : 16-hexahydro-2-oxochrysene (VI) are synthesised and converted into chrysene.

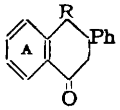
THE preponderant formation of an indanone derivative (II) in preference to the tetralone (III; R = CO_2H) during cyclisation of $\alpha\beta$-diphenylglutaric acid (I; R = CO_2H) has been attributed to deactivation of ring A in (I) by the nearer carboxyl group (R) (Badger, Campbell, and Cook, *J.*, 1949, 1084). Similar retarding effects have also been noted in cyclisations of α-arylglutaric acids (Hey and Nagdy, *J.*, 1953, 1894) whereas the related γ-aryl-γ-cyanopimelic acids are readily cyclised without apparent retardation by the cyano-group (*idem, J.*, 1954, 1204). It was therefore of interest to examine the behaviour of γ-cyano-$\beta\gamma$-diphenylbutyric acid (I; R = CN). This compound resisted cyclisation by hydrogen fluoride but afforded the tetralone derivative (III; R = $CO{\cdot}NH_2$), together with some $\alpha\beta$-diphenylglutarimide, when treated with polyphosphoric acid.



(I)



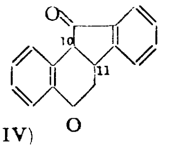
(II)



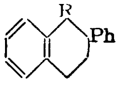
(III)

The formation of an amide from a nitrile under treatment with polyphosphoric acid is frequently observed (cf. Snyder and Elston, *J. Amer. Chem. Soc.*, 1954, **76**, 3039) and the tetralone structure (III; R = $CO{\cdot}NH_2$) assigned to the present compound is fully confirmed by the behaviour of the carboxylic acid which is obtained by hydrolysis. This acid (III; R = CO_2H) was converted into 2-phenylnaphthalene by reduction and dehydrogenation with simultaneous decarboxylation. It was also cyclised to the dione (IV) and this by dehydrogenation afforded the known 3-hydroxy-1 : 2-benzofluorenone. Moreover the availability of (III; R = CO_2H) opens the way to a synthesis of chrysene, which has now been accomplished and should be applicable to a number of chrysene derivatives.

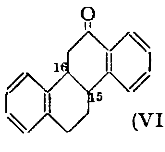
Clemmensen reduction of the acid (III; R = CO_2H) yielded 1-carboxy-2-phenyltetralin (V; R = CO_2H) and this was converted into the homo-acid (V; R = $CH_2{\cdot}CO_2H$) by Newman and Beal's modification of the Arndt–Eistert reaction (*J. Amer. Chem. Soc.*, 1950, **72**, 5163). This homo-acid and the hexahydro-oxochrysene (VI) which is obtained from it by cyclisation differ markedly from the respective, known isomers of *cis*-structure (Newman, *ibid.*, 1938, **60**, 2947). That they are the hitherto unknown *trans*-compounds is confirmed by reduction of the ketone (VI) to a hexahydrochrysene which corresponds with the known *trans*-isomer in m. p. (Ramage and Robinson, *J.*, 1933, 607) and in ultraviolet absorption spectrum (Askew, *J.*, 1935, 512). Dehydrogenation of this hexahydrochrysene, effected as described by Ramage and Robinson (*loc. cit.*), afforded chrysene.



(IV)



(V)



(VI)

EXPERIMENTAL

α-(3-*Oxoindan*-1-*yl*)-α-*phenylacetic Acid*.—This acid (II), m. p. and mixed m. p. 153—154° (Badger, Campbell, and Cook, *loc. cit.*), was isolated in poor yield from cyclisation of αβ-diphenylglutaric acid (0·4 g.) by polyphosphoric acid (from 2 c.c. of syrupy phosphoric acid and 5 g. of phosphoric anhydride) at 100° (2—3 hr.). The glutaric acid was recovered after attempted cyclisation by hydrogen fluoride in which it appeared to be insoluble.

1 : 2 : 3 : 4-*Tetrahydro*-4-*oxo*-2-*phenyl*-1-*naphthamide* (III; $R = \mathrm{CO{\cdot}NH_2}$).—γ-Cyano-βγ-diphenylbutyric acid (2 g.) (Helmkamp, Tanghe, and Plati, *J. Amer. Chem. Soc.*, 1940, **62**, 3217) was heated for 2 hr. with polyphosphoric acid (from 10 c.c. of phosphoric acid and 25 g. of phosphoric anhydride) at 100°. The cooled mixture was treated with crushed ice and the resultant solid, after being washed with dilute sodium carbonate, was separated into a neutral and an acidic component by fractional crystallisation from acetic acid or, better, by treatment with cold dilute sodium hydroxide solution. The acidic component, which was also the less soluble in acetic acid, was identified by m. p. and mixed m. p. 226—227° (from acetic acid), and by its infrared spectrum, as αβ-diphenylglutarimide (Found: C, 76·8; H, 5·7; N, 5·4. Calc. for $\mathrm{C_{17}H_{15}O_2N}$: C, 76·95; H, 5·7; N, 5·3%) for which Barr and Cook (*J.*, 1945, 440) record m. p. 221—223°. The neutral component afforded 1 : 2 : 3 : 4-*tetrahydro*-4-*oxo*-2-*phenyl*-1-*naphthamide* as needles, m. p. 200—201° (from acetic acid) (Found: C, 77·0; H, 6·0; N, 5·3. $\mathrm{C_{17}H_{15}O_2N}$ requires C, 76·95; H, 5·7; N, 5·3%). Light absorption in EtOH: max. at 248 and 291 mμ (log ε 4·05 and 3·23 respectively). The naphthamide was characterised as the 2 : 4-*dinitrophenylhydrazone*, m. p. 277—279° (decomp.) (from acetic acid) (Found: C, 62·3; H, 4·5; N, 15·6. $\mathrm{C_{23}H_{19}O_5N_5}$ requires C, 62·0; H, 4·3; N, 15·7%).

1 : 2 : 3 : 4-*Tetrahydro*-4-*oxo*-2-*phenyl*-1-*naphthoic acid* (III; $R = \mathrm{CO_2H}$) was obtained as colourless needles, m. p. 151—152° [from benzene–light petroleum (b. p. 60—80°)] when the amide (III; $R = \mathrm{CO{\cdot}NH_2}$) (2 g.) was heated (3 hr.) with 5N-sodium hydroxide (25 c.c.) and ethanol (5 c.c.) and the resultant solution was acidified (Found: C, 76·7; H, 5·6. $\mathrm{C_{17}H_{14}O_3}$ requires C, 76·7; H, 5·3%). It formed a 2 : 4-*dinitrophenylhydrazone*, m. p. 240—242° (decomp.) (from ethanol) (Found: C, 61·7; H, 3·85; N, 12·8. $\mathrm{C_{23}H_{18}O_6N_4}$ requires C, 61·9; H, 4·0; N, 12·55%).

3 : 4 : 10 : 11-*Tetrahydro*-3-*oxo*-1 : 2-*benzofluorenone* (IV) was formed when the foregoing acid (III; $R = \mathrm{CO_2H}$) was cyclised by polyphosphoric acid (40 min. at 100°). It was obtained as needles, m. p. 148—150° (from methanol) (Found: C, 82·0; H, 5·15. $\mathrm{C_{17}H_{12}O_2}$ requires C, 82·2; H, 4·85%). When heated under reflux (5—10 min.) in nitrobenzene containing a crystal of iodine, it afforded 3-hydroxy-1 : 2-benzofluorenone which was identified by m. p. and mixed m. p. 303—307° (decomp.), and by its infrared spectrum.

1 : 2 : 3 : 4-*Tetrahydro*-2-*phenyl*-1-*naphthoic Acid* (V; $R = \mathrm{CO_2H}$).—The keto-acid (III; $R = \mathrm{CO_2H}$) (2 g.), amalgamated zinc (5 g.), water (3 c.c.), concentrated hydrochloric acid (7 c.c.), and toluene (4 c.c.) were briskly heated under reflux for 50 hr., concentrated hydrochloric acid (2 c.c.) being added every 10 hr. The organic layer, combined with an ethereal extract of the aqueous layer, afforded after recovery 1 : 2 : 3 : 4-*tetrahydro*-2-*phenyl*-1-*naphthoic acid* as needles, m. p. 143—144° (from acetic acid) (Found: C, 81·0; H, 6·3. $\mathrm{C_{17}H_{16}O_2}$ requires C, 80·9; H, 6·4%). By reaction with thionyl chloride in benzene the acid afforded the acid chloride and thence, by treatment with ammonia, the corresponding *amide* of m. p. 183—184° (from benzene) (Found: C, 81·05; H, 6·9. $\mathrm{C_{17}H_{17}ON}$ requires C, 81·2; H, 6·8%).

In one experiment the reducing mixture after 36 hr. was inadvertently evaporated to dryness and heated at 200—300° for 3—4 hr. Recovery in benzene, chromatography in benzene on alumina, and sublimation afforded 2-phenylnaphthalene, identified by its infrared spectrum, and by m. p. 100—101°, alone or in admixture with an authentic sample for which we thank Dr. N. Campbell.

trans-1 : 2 : 3 : 4-*Tetrahydro*-2-*phenyl*-1-*naphthylacetic Acid* (V; $R = \mathrm{CH_2{\cdot}CO_2H}$).—The foregoing acid chloride, prepared from 4 g. of the acid (V; $R = \mathrm{CO_2H}$), reacted with ethereal diazomethane to form a crystalline diazo-ketone. To a solution of this diazo-ketone in anhydrous methanol (55 c.c.) there was added, at 20° during 2 hr., a portion (3·8 g.) of a filtered solution prepared from silver benzoate (1 g.) and triethylamine (9·1 g.). The mixture was then heated under reflux for 2 hr. and, after treatment with charcoal, was concentrated *in vacuo*. The gummy product was hydrolysed with 5N-potassium hydroxide (25 c.c.) containing a little ethanol. Acidification of the filtered solution gave trans-1 : 2 : 3 : 4-*tetrahydro*-2-*phenyl*-1-*naphthylacetic acid* as colourless prisms, m. p. 136—137° (from acetonitrile) (Found: C, 80·9; H, 6·6. $\mathrm{C_{18}H_{18}O_2}$ requires C, 80·9; H, 6·8%).

trans-1 : 2 : 7 : 8 : 15 : 16-*Hexahydro-2-oxochrysene* (VI) was obtained as neutral product when the foregoing acid (V; R = $CH_2\cdot CO_2H$) was heated with polyphosphoric acid at 120—130° for 3—4 hr. It formed colourless rhombs, m. p. 118° (from light petroleum, b. p. 60—80°) (Found : C, 86·9; H, 6·3. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). Light absorption in EtOH : max. at 253 and 294 mμ (log ε 4·12 and 3·34 respectively). It was characterised as the *semicarbazone*, m. p. 237—239° (decomp.) (from acetic acid) (Found : C, 74·65; H, 6·1; N, 13·5. $C_{19}H_{19}ON_3$ requires C, 74·7; H, 6·3; N, 13·75%). For the *cis*-isomer Newman (*loc. cit.*) records m. p. 75·8—76·8°, and semicarbazone, m. p. 255—258° (decomp.).

trans-1 : 2 : 7 : 8 : 15 : 16-*Hexahydrochrysene*.—The chrysenone (VI) was reduced (24 hr.) as described for the preparation of the tetralin (V; R = CO_2H). The resultant hexahydrochrysene, after chromatography in light petroleum (b. p. 60—80°) on alumina, had m. p. 112—114° (from light petroleum, b. p. 40—60°) (Found : C, 92·25; H, 7·4. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). Light absorption in EtOH : max. at 266 and 274 mμ (log ε 3·19 and 3·01 respectively). Ramage and Robinson (*loc. cit.*) record m. p. 115°, and by their procedure the present specimen was dehydrogenated to chrysene which was identified by m. p. and mixed m. p. 248—250°, and by its infrared spectrum.

We are indebted to Dr. G. Eglinton for helpful discussion of infrared absorption spectra. Microanalyses were carried out by Mr. J. M. L. Cameron and Miss M. W. Christie : measurements of absorption spectra were made by Mr. G. Milmine.

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