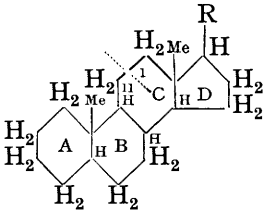
291. *Syntheses of 2-Phenylnaphthalenes.*

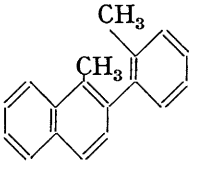
By F. S. Spring.

The present experiments were commenced prior to the publication of the synthesis of 1 : 2-*cyclo*pentenophenanthrenes (references below) with a view to the synthesis of 2-*o*-tolyl-1-methylnaphthalene (II), which it was anticipated might be identical with Diels's hydrocarbon $C_{18}H_{16}$ (Diels, Gadke, and Körding, *Annalen*, 1927, **459**, 1) obtained by the dehydrogenation of cholesterol, ergosterol, and cholic acid.

The suggested mechanism for this transformation by selenium dehydrogenation assumes a fission of the typical sterol structure (I) between carbon atoms 11 and 12 in

(I.)



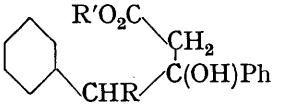


(II.)

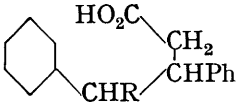
ring C, followed by elimination of the side chain R and rearrangement of ring D. Such a mechanism is somewhat analogous to that postulated by Ruzicka and Hosking (*Helv. Chim. Acta*, 1931, **14**, 210) to account for the formation of 1 : 5 : 6-trimethylnaphthalene by the dehydrogenation of tetra*cyclo*squalene.

Although recent work (Cook and Hewett, J., 1933, 1098, this vol., p. 365; Harper, Kon, and Ruzicka, *ibid.*, p. 124) shows that in all probability Diels's hydrocarbon is 3'-methyl-1 : 2-*cyclo*pentenophenanthrene, the present work is placed on record because it offers a facile method for the preparation of substituted 2-phenylnaphthalenes and other polycyclic aromatic hydrocarbons by the application of the Reformatzky reaction to deoxybenzoins, which are now readily available by the elegant method of Baker and Robinson (J., 1932, 1798).

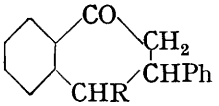
Condensation of deoxybenzoin with bromoacetic ester in the presence of zinc gave *ethyl β-hydroxy-βγ-diphenylbutyrate* (III; R = H, R′ = Et), from which on dehydration with acetic anhydride, followed by hydrolysis, β-benzylcinnamic acid, identical with that described by Ruhemann (J., 1910, **97**, 459), was produced.



(III.)



(IV.)



(V.)

Reduction of the unsaturated acid with sodium amalgam gave βγ-diphenylbutyric acid (IV; R = H). The latter acid can be obtained more conveniently and in better yield by the direct reduction of *β-hydroxy-βγ-diphenylbutyric acid* with red phosphorus and hydriodic acid. Cyclisation of (IV; R = H) was effected by means of 85% sulphuric acid (Haworth, J., 1932, 1125), 1-keto-3-phenyl-1 : 2 : 3 : 4-tetrahydronaphthalene (V; R = H) being obtained in 60% yield; v. Braun and Manz (*Annalen*, 1929, **468**, 266) prepared this ketone by treating βγ-diphenylbutyryl chloride with aluminium chloride. The ketone was reduced by Clemmensen's method, and the product dehydrogenated with selenium to give 2-phenylnaphthalene, identical with that described by Smith and Takamatsu (J., 1881, **39**, 546).

2-Phenyl-1-methylnaphthalene.—*β-Hydroxy-βγ-diphenylvaleric acid* (III; R = Me, R′ = H) was prepared by the condensation of α-phenylpropiophenone with bromoacetic ester in the presence of zinc, followed by hydrolysis of the product. This acid could not be dehydrated with boiling acetic anhydride, but on reduction with hydriodic acid and red phosphorus it readily yielded *βγ-diphenylvaleric acid*, m. p. 132°. This is not identical with the βγ-diphenylvaleric acid prepared by Meerwein (*J. pr. Chem.*, 1918, **97**, 269) by the reduction of βγ-diphenylvalerolactone with hydriodic acid and red phosphorus. Probably the two acids represent the two possible racemic varieties.

Cyclisation of βγ-diphenylvaleric acid (m. p. 132°) with 85% sulphuric acid yielded *4-keto-2-phenyl-1-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene* (V; R = Me), from which on reduction with amalgamated zinc and concentrated hydrochloric acid, followed by selenium dehydrogenation of the product, *2-phenyl-1-methylnaphthalene* was obtained; its pronounced fluorescence could only be reduced by sublimation (no change of m. p.). Treatment of this hydrocarbon with picric acid in alcoholic solution produced an unstable *hemipicrate*. Although distinct evidence of picrate formation was obtained with 2-phenylnaphthalene, a pure product could not be isolated.

Experimental.

Ethyl β-Hydroxy-βγ-diphenylbutyrate (III; R = H, R′ = Et).—Deoxybenzoin (30 g.) in dry benzene (100 c.c.) was warmed on the water-bath with bromoacetic ester (27 g.) and zinc filings (11 g.) until reaction set in (4 mins.). After the first vigorous reaction had subsided (15 mins.), the mixture was refluxed for a further 2 hours, and a copious crystalline mass of zinc complex had then separated. The mixture was decomposed by shaking with ice-cooled sulphuric acid (15%), and the benzene layer was separated, washed with dilute sulphuric acid, and dried. After removal of the benzene, the residual yellow oil was dissolved in 95% alcohol, from which the *ester* separated in clusters of long needles, m. p. 57—58° (Found : C, 76·0; H, 6·9. $C_{18}H_{20}O_3$ requires C, 76·1; H, 7·0%). The free *acid*, after three crystallisations from alcohol, formed colourless needles, m. p. 120° (Found : C, 75·3; H, 6·5. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%).

β-Benzylcinnamic Acid.—The ester (III; R = H, R′ = Et) (30 g.) was refluxed with acetic anhydride (100 c.c.) for 3 hours. After removal of the acetic anhydride under reduced pressure, the residual oil was hydrolysed by refluxing on a water-bath for 2 hours with a solution of potassium hydroxide (20 g.), water (100 c.c.), and ethyl alcohol (200 c.c.). The solution was acidified with dilute sulphuric acid, and the precipitated acid crystallised from alcohol, separating in long, prismatic needles, m. p. 169° (Ruhemann, *loc. cit.*, gives m. p. 168—169°) (Found : C, 80·6; H, 5·8. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·8%). The yield is only 20%, the remainder being recovered as the hydroxy-acid (III; R = H, R′ = H), m. p. 120°. The latter acid

(1 part) gave βγ-diphenylbutyric acid in 85% yield by refluxing with red phosphorus (1 part) and hydriodic acid (*d* 1·7; 8 parts) for 5 hours. After cooling, the mixture was diluted with water, and the aqueous layer decanted from the red gum. The latter was extracted with dilute potassium hydroxide solution, and filtered. The filtrate was acidified with dilute hydrochloric acid, and the precipitated acid isolated with ether. After two crystallisations from 85% ethyl alcohol, it formed colourless prisms, m. p. 95—96°, either alone or in admixture with the product obtained by the reduction of β-benzylcinnamic acid (Ruhemann, *loc. cit.*).

1-*Keto*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V; R = H).—βγ-Diphenylbutyric acid (7 g.) was heated on the water-bath for 70 minutes with concentrated sulphuric acid (21 c.c.) and water (7 c.c.), with constant stirring. The mixture was diluted with water, the oil extracted with ether, the extract washed with water and dilute alkali, and the ether removed; a yellow oil (4·0 g.) was obtained, which gave small needles from light petroleum (b. p. 40—60°), m. p. 65°, unaltered by two recrystallisations (Found: C, 86·6; H, 6·4. Calc. for $C_{16}H_{14}O$: C, 86·5; H, 6·4%). The semicarbazone separated in flakes, which after crystallisation from methyl alcohol formed colourless prisms, m. p. 211° (Found: N, 14·9. Calc. for $C_{17}H_{17}ON_3$: N, 15·1%). Braun and Manz (*loc. cit.*) give m. p.'s 65—66° and 208° for the ketone and semicarbazone respectively.

2-*Phenylnaphthalene*.—The ketone (V; R = H) (3 g.) was gently boiled for 15 hours with amalgamated zinc (15 g.) and concentrated hydrochloric acid (25 c.c.). The product was isolated with ether, and dehydrogenated by heating with selenium (2·5 g.) for 24 hours; during the process the crystalline sublimate was thrice melted down. The product was extracted with dry ether, and distilled from sodium at 12 mm.; the green fluorescent oil obtained rapidly solidified to a crystalline mass, which recrystallised from alcohol as colourless plates, m. p. 98°. Sublimation of this material gave 2-phenylnaphthalene, m. p. 101°, in large colourless plates with a delicate blue fluorescence (Breuer and Zincke, *Ber.*, 1878, **11**, 1403, give m. p. 101—101·5°) (Found: C, 94·0; H, 6·1. Calc. for $C_{16}H_{12}$: C, 94·1; H, 5·9%).

β-*Hydroxy*-βγ-*diphenylvaleric Acid* (III; R = Me, R′ = H).—A mixture af α-phenylpropiophenone (Meyer and Oelkers, *Ber.*, 1888, **21**, 1295) (20 g.), bromoacetic ester (17 g.), zinc needles (6·5 g.), and dry benzene (100 c.c.) was heated on the water-bath for 2½ hours. The green solution was decomposed by shaking with ice-cooled 15% sulphuric acid; ether was added to facilitate the separation of the benzene, and the upper layer washed with dilute sulphuric acid and dried (sodium sulphate). After removal of the solvent, the residual oil was hydrolysed by 3 hours' refluxing with alcoholic potassium hydroxide (300 c.c. of 20%), the resulting solution acidified with dilute sulphuric acid, and the product ether-extracted. The residual colourless oil obtained after removal of the ether was dissolved in light petroleum (b. p. 60—80°), and set aside for 12 hours at 0°. The *hydroxy-acid* was collected and twice recrystallised from the same solvent, separating in fine needles of constant m. p. 178° (Found: C, 75·7; H, 6·5. $C_{17}H_{18}O_3$ requires C, 75·6; H, 6·6%).

βγ-*Diphenylvaleric Acid* (IV; R = Me).—The above hydroxy-acid was reduced with red phosphorus and hydriodic acid in exactly the manner described above. After three crystallisations from light petroleum (b. p. 60—80°), the *acid* formed beautiful small needles, m. p. 132° (yield, 80%) (Found: C, 80·4; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%).

4-*Keto*-2-*phenyl*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (V; R = Me).—βγ-Diphenylvaleric acid (10 g.) was warmed on the water-bath for 70 minutes with concentrated sulphuric acid (31 c.c.) and water (10 c.c.). The product was worked up as previously described, the neutral portion rapidly solidifying to a crystalline mass, which separated from light petroleum (b. p. 40—60°) in plates, and from dilute methyl alcohol in needles, m. p. 68° (Found: C, 86·7; H, 6·9. $C_{17}H_{16}O$ requires C, 86·5; H, 6·8%). The *semicarbazone* separated from methyl alcohol in colourless prisms, m. p. 221° (Found: N, 13·9. $C_{18}H_{19}ON_3$ requires N, 14·3%).

2-*Phenyl*-1-*methylnaphthalene*.—The ketone (V; R = Me) (3·5 g.) was refluxed for 18 hours with concentrated hydrochloric acid (24 c.c.) and amalgamated zinc (15 g.). The product was isolated with ether, and dehydrogenated by heating with selenium (3 g.) for 30 hours at 320°, the crystalline sublimate being repeatedly melted down. The product was extracted with ether and filtered from unchanged selenium. Removal of the ether and distillation of the residue over sodium at 13 mm. gave a clear, highly fluorescing oil which solidified on standing overnight in the refrigerator. Recrystallisation (charcoal) from absolute alcohol gave long green needles, m. p. 84°, with a very pronounced purple fluorescence, which persisted after repeated recrystallisations. Sublimation, however, gave 2-*phenyl*-1-*methylnaphthalene* in colourless plates, m. p. 84° (Found: C, 93·8; H, 6·5; *M*, 210. $C_{17}H_{14}$ requires C, 93·6; H, 6·4%; *M*, 218). The *hemipicrate*, prepared in warm alcoholic solution, separated in orange-coloured plates,

m. p. 83° (Found : N, 6·4, 6·3. $C_{17}H_{14},\frac{1}{2}C_6H_3O_7N_3$ requires N, 6·3%). On recrystallisation this readily decomposed into its components.

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