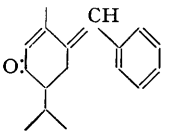
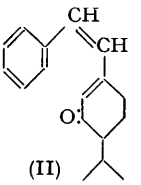
55. *Terpene Compounds. Part VIII.* The Conversion of (±)-Benzylidenepiperitone into 3-iso*Propylphenanthrene.

By J. C. Bardhan and R. N. Adhya.

(±)-7-Benzyl*iso*menthol (III), on cyclodehydration and then dehydrogenation, furnishes 3-*iso*propylphenanthrene the structure of which is placed beyond doubt by unambiguous syntheses. This proves Earl and Read's view (*J.*, 1926, 2072) as to the structure of (±)-benzylidenepiperitone (II).

Read and his co-workers (*J.*, 1921, 779; 1922, 574; 1936, 1598) found that piperitone readily condenses with benzaldehyde in the presence of sodium ethoxide giving a highly characteristic benzylidene derivative. This was also prepared by Simonsen (*J.*, 1921, 1646; cf. Wallach, *Annalen*, 1913, **397**, 216) who tentatively represented it as (I). On the other hand, Earl and Read (*J.*, 1926, 2072) preferred structure (II), since oxidation with alkaline permanganate gave α-*iso*propylglutaric acid. On reduction (±)-benzylidenepiperitone afforded a saturated alcohol (cf. Read, Smith, and Hughesdon, *J.*, 1924, 135; Read and Smith, *J.*, 1923, 2270) which was accordingly formulated as (±)-7-benzyl*iso*menthol (III), although no further proof was adduced in support of this formulation.


(I)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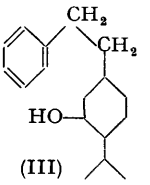
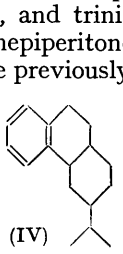
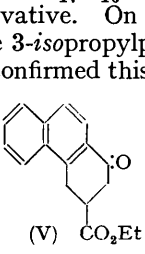
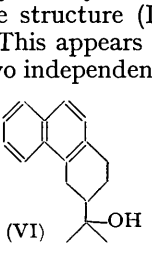

(III)

It is now found, however, that treatment of the alcohol (III) with phosphoric anhydride gives a "saturated" hydrocarbon, probably (IV), yielding on dehydrogenation with selenium at 310—320° a liquid hydrocarbon, $C_{17}H_{16}$, characterised by a crystalline picrate, styphnate, and trinitrobenzene derivative. On the basis of the structure (II) for (±)-benzylidenepiperitone this should be 3-*iso*propylphenanthrene. This appears not to have been made previously, but we have confirmed this structure by two independent syntheses.


(IV)

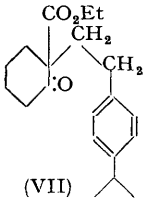

(V) CO_2Et


(VI)

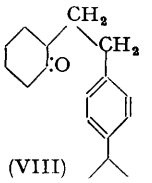
Ethyl 1:2:3:4-tetrahydro-1-oxophenanthrene-3-carboxylate (V), prepared by cyclisation of β-carboxy-γ-1-naphthylbutyric acid according to Bardhan, Nasipuri, and Adhya (*J.*, in the press), was reduced (Clemmensen–Martin) to ethyl 1 : 2 : 3 : 4-tetrahydrophenanthrene-3-carboxylate which was converted in good yield by an excess of methylmagnesium iodide into the alcohol (VI). This was dehydrated with potassium hydrogen sulphate and the product on catalytic hydrogenation followed by dehydrogenation with selenium afforded 3-*iso*propylphenanthrene.

* Part VII, *J.*, 1951, 3195.

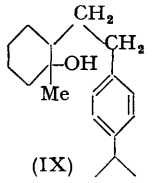
Secondly, the Grignard compound from 4-bromocumene (Jacobsen, *Ber.*, 1879, **12**, 430) with ethylene oxide gave 2-*p*-*iso*propylphenylethyl alcohol. The derived bromide, on condensation with ethyl potassio-2-oxo*cyclo*hexanecarboxylate (cf. Bardhan and Sengupta, *J.*, 1932, 2520), yielded ethyl 2-oxo-1-(2-*p*-*iso*propylphenylethyl)*cyclo*hexanecarboxylate



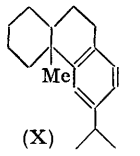
(VII)



(VIII)

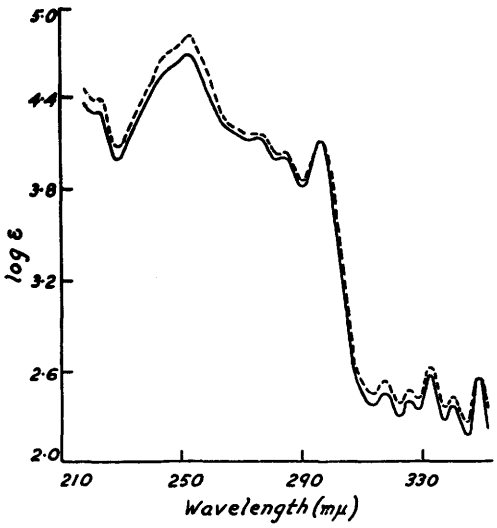


(IX)



(X)

(VII). This, on alkaline hydrolysis and decarboxylation (cf. Kon, *J.*, 1933, 1082), gave 2-(2-*p*-*iso*propylphenylethyl)*cyclo*hexanone (VIII), yielding the alcohol (IX) with methylmagnesium iodide. This was cyclised with phosphoric anhydride to the hydrocarbon (X) which on dehydrogenation with selenium yielded 3-*iso*propylphenanthrene.



Ultraviolet absorption of 3-iso*propylphenanthrene* (——, *synthetic*; – – – – *from piperitone*).

The synthetic hydrocarbon was identified by its b. p. and ultraviolet absorption (see Figure) and as the picrate, styphnate, and trinitrobenzene derivative with the corresponding compound prepared from (±)-benzylidenepiperitone (II).

Cyclodehydration of the substituted *cyclo*hexanol (III), which obviously proceeds through the corresponding olefin (cf. Fieser and Fieser, " Natural Products Related to Phenanthrene," Rheinhold, New York, 3rd edn., 1949, p. 91), is somewhat remarkable since hitherto only the derivatives of 2- and 1-phenethyl*cyclo*hexanol (Bardhan and Sengupta, *loc. cit.*; Bogert, *Science*, 1933, **77**, 289; Perlman, Davidson, and Bogert, *J. Org. Chem.*, 1936, **1**, 288; Cook and Hewett, *J.*, 1933, 1098) have been found to give derivatives of octahydrophenanthrene on cyclodehydration, although, according to Roblin, Davidson, and Bogert (*J. Amer. Chem. Soc.*, 1935, **57**, 151) the analogous cyclisation of 5-phenylpentanol leads to 1-methyltetralin in high yield.

Experimental

(±)-7-*Benzyliso*menthol (III).—(−)-Piperitone, b. p. 98—100°/10 mm. (Messrs. Schimmel and Co.), was converted successively into (±)-benzylidenepiperitone, b. p. 195—197°/5 mm., (±)-7-benzyl*iso*menthone, b. p. 163—164°/3 mm., and (±)-7-benzyl*iso*menthol, b. p. 168—169°/4 mm., as described by Read and his co-workers (*locc. cit.*).

Cyclodehydration and Dehydrogenation (with B. K. GANGULI).—As a result of a large number of experiments the following procedure was adopted which gave reproducible results. The foregoing alcohol (6 g.) was heated under reflux with phosphoric anhydride (12 g.) at 170—180° for 6 hr., then cooled. Powdered ice was added, the solution extracted with ether, and the ethereal solution washed with water, dried, and evaporated. The residual oil was again heated with phosphoric anhydride (12 g.) at 170—180° for 6 hr. at 135—140°/5 mm. for 30 min., and then gradually to 170—180°, whereupon, a liquid (5 g.) distilled which on redistillation over sodium gave a colourless oil (4·6 g.), b. p. 135—140°/5 mm. The hydrocarbon, which could not be obtained sufficiently pure for analysis, was heated with selenium (9·2 g.) at 315—320° for 20 hr. The product (3·8 g.), isolated in the usual way, on distillation over sodium had b. p. 168—170°/4 mm. and gave a picrate, m. p. 95—100°, which after four crystallisations from absolute ethanol had m. p. 127—128°. The mother-liquors from this crystallisation yielded an oil which was not further examined.

3-iso*Propylphenanthrene*.—The pure *hydrocarbon* regenerated from the above picrate, on distillation, finally over sodium, formed a colourless liquid with a faint blue fluorescence and had b. p. 173°/5 mm. (Found : C, 92·6; H, 7·3. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%). The *picrate* prepared from the pure hydrocarbon formed orange yellow needles, m. p. 128—129° (Found : C, 61·3; H, 4·3. $C_{17}H_{16},C_6H_3O_7N_3$ requires C, 61·5; H, 4·2%), and when pure was of the usual bright appearance. The *styphnate*, bright yellow needles from ethanol, had m. p. 142—143° (Found : C, 58·9; H, 4·1. $C_{17}H_{16},C_6H_3O_8N_3$ requires C, 59·3; H, 4·1%). The *trinitrobenzene* derivative formed yellow needles (from ethanol), m. p. 138—139° (Found : C, 63·4; H, 4·4. $C_{17}H_{16},C_6H_3O_6N_3$ requires C, 63·7; H, 4·4%).

Synthesis of 3-iso*Propylphenanthrene*.—*Method* (*a*). Ethyl 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene-3-carboxylate (Bardhan, Nasipuri, and Adhya, *loc. cit.*) (10 g.), amalgamated zinc (50 g.), water (10 ml.), acetic acid (2 ml.), concentrated hydrochloric acid (40 ml.), and toluene (25 ml.) were refluxed for 48 hr., concentrated hydrochloric acid (10 ml.) being added every 12 hr. After cooling, the toluene layer was washed with water, dried, and evaporated. The residue was esterified with ethanolic hydrogen chloride (33 ml.; 3%) for 12 hr. The product, isolated in the usual way, was distilled, giving fractions (*a*) b. p. 195—198°/4 mm. (5·8 g.) and (*b*) b. p. 198—210°/4 mm. (3·1 g.). Fraction (*a*), on hydrolysis with ethanolic potassium hydroxide (40 ml.; 10%), afforded 1 : 2 : 3 : 4-*tetrahydrophenanthrene-3-carboxylic acid*, plates (from ethanol; charcoal), m. p. 205—206° (Found : C, 79·8; H, 6·2. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%). The corresponding *ethyl ester* was a pale yellow liquid, b. p. 195—198°/4 mm. (Found : C, 80·3; H, 7·0. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%). Fraction (*b*) on hydrolysis as above yielded a solid mixture (m. p. 196—197°) from which 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene-3-carboxylic acid, m. p. 218°, and 1 : 2 : 3 : 4-tetrahydrophenanthrene-3-carboxylic acid, m. p. 205—206°, were isolated with the aid of semicarbazide acetate.

A solution of the preceding ester (5 g.) in dry ether (5 ml.) was gradually introduced into methylmagnesium iodide (magnesium, 2·9 g.; ether, 25 ml.; and methyl iodide, 8·5 ml.), cooled to −10°, and the whole was kept overnight, then refluxed for 5 hr., decomposed with ice and dilute hydrochloric acid, and extracted with ether. The ethereal solution was washed with aqueous sodium hydrogen sulphite and water, dried, and evaporated. The crude alcohol, m. p. 90—92° (6 g.), was boiled with potassium hydroxide (2 g.) in water (5 ml.) and ethanol (30 ml.) for 1 hr. The solution was diluted with water and repeatedly extracted with ether, the ethereal extract washed with water and dried, and the solvent removed. The residual oil (5·1 g.) was then heated with freshly fused and powdered potassium hydrogen sulphate (10·5 g.) at 150° for 1 hr. After cooling, the mixture was mixed with water and extracted with ether, and the ethereal solution washed, dried, and distilled, finally over sodium, giving an almost colourless liquid (4·4 g.), b. p. 189—190°/4 mm. This was dissolved in ethanol (10 ml.) and shaken in an atmosphere of hydrogen with palladous chloride (0·1 g.), gum arabic (0·1 g.), and water (2 ml.) until a little more than 1 mol. of hydrogen had been absorbed. The product was worked up in the usual manner and distilled; almost the whole amount (4·0 g.) boiled constantly at 173°/4 mm. This was heated with selenium (8 g.) at 315—320° for 24 hr. 3-*iso*Propylphenanthrene (3·6 g.), thus obtained, readily yielded a picrate as orange yellow needles, m. p. 131—132° (Found : C, 61·3; H, 4·3%), a styphnate, yellow needles, m. p. 142—143° (Found : C, 58·9; H, 4·1%), and a trinitrobenzene derivative, yellow needles, m. p. 138—139° (Found : C, 63·4; H, 4·4%). The pure hydrocarbon regenerated from its picrate formed a colourless oil, b. p. 173°/5 mm., which exhibited a weak blue fluorescence (Found : C, 92·6; H, 7·3%).

Method (*b*). A solution of ethylene oxide (25 g.) in dry ether (50 ml.) was gradually added to an ice-cold solution of the Grignard reagent prepared from magnesium (5·4 g.), 4-bromocumene

(Jacobsen, *loc. cit.*) (44·7 g.), and dry ether (70 ml.). The product which set to a semisolid mass was set aside overnight in the cold, excess of ether distilled off at 60°, and the residue decomposed by ice and dilute hydrochloric acid. 2-p-iso*Propylphenylethyl alcohol*, isolated with ether, was a colourless oil (18·5 g.), b. p. 136—140°/13 mm. (Found : C, 80·3; H, 9·7. $C_{11}H_{16}O$ requires C, 80·5; H, 9·7%). This alcohol (18·2 g.) was added dropwise to phosphorus tribromide (5·2 ml.), the mixture heated on the steam-bath for 1·5 hr. and then poured into ice, and the oil collected in ether. 2-p-iso*Propylphenylethyl bromide* (21 g.) had b. p. 127—130°/13 mm. (Found : Br, 34·9. $C_{11}H_{15}Br$ requires Br, 35·2%). Finely divided potassium (6·8 g.) was kept under xylene (100 ml.), and ethyl 2-oxo*cyclo*hexanecarboxylate (Kotz and Michels, *Annalen*, **1906, 350**, 204) (29·7 g.) gradually introduced with cooling and occasional swirling. The clear solution which resulted was mixed with 2-*p-iso*propylphenylethyl bromide (39·7 g.), and the whole heated at 152—157° for 40 hr. After cooling, water was added and the xylene layer separated, dried, and distilled. *Ethyl* 2-*oxo*-1-(2-p-iso*propylphenylethyl*)cyclo*hexanecarboxylate* (VII) was a pale yellow oil (32·3 g.), b. p. 191—193°/4 mm. (Found : C, 75·7; H, 8·9. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·8%). It gave no colour with ethanolic ferric chloride. This keto-ester (16 g.) was boiled with potassium hydroxide (10 g.), water (10 ml.), and ethanol (18 ml.) for 1 hr. After removal of the excess of ethanol, the solution was acidified and extracted with ether, and the ethereal solution dried (Na_2SO_4) and evaporated. The residual oily acid (14·6 g.) was heated with barium hydroxide (2 g.) at 315° until no more liquid distilled over. 2-(2-p-iso*Propylphenylethyl*)cyclo*hexanone* (VIII) (6·7 g.), recovered from the aqueous distillate, formed an almost colourless liquid, b. p. 157—160°/4 mm. (Found : C, 83·4; H, 9·9. $C_{17}H_{24}O$ requires C, 83·6; H, 9·8%). The *semicarbazone* crystallised from aqueous ethanol in prisms, m. p. 132—133° (Found : C, 71·3; H, 8·8. $C_{18}H_{27}ON_3$ requires C, 71·7; H, 8·9%). The above ketone (6·2 g.) in dry ether (5 ml.) was allowed to react with methylmagnesium iodide (magnesium, 0·8 g.; methyl iodide, 2·3 ml.; dry ether, 20 ml.) in the usual way, and finally heated for 1 hr. 1-*Methyl*-2-(2-p-iso*propylphenylethyl*)cyclo*hexanol* (IX) (6·2 g.) was thus obtained as a viscous oil, b. p. 160°/3 mm. (Found : C, 82·9; H, 10·6. $C_{18}H_{28}O$ requires C, 83·1; H, 10·8%). The alcohol (5·8 g.) was heated with phosphoric anhydride (12·4 g.) under the standard conditions (cf. Bardhan and Sengupta, *loc. cit.*). The product was extracted with light petroleum (b. p. 60—80°), and the petroleum solution washed with 85% sulphuric acid and water, dried, and distilled, finally over sodium, giving 1 : 2 : 3 : 4 : 9 : 10 : 13 : 14-*octahydro*-13-*methyl*-3-iso*propylphenanthrene* (X) (4·3 g.) as a colourless liquid having a characteristic bluish green fluorescence, b. p. 136—137°/4 mm. (Found : C, 89·1; H, 10·6. $C_{18}H_{26}$ requires C, 89·2; H, 10·7%). This (4·0 g.) was heated with selenium (8 g.) at 320—325° for 26 hr. and the product worked up in the usual way. On distillation over sodium, 3-*iso*propylphenanthrene (2·6 g.) had b. p. 165—170°/3 mm., and showed no tendency to solidify. The picrate, after four crystallisations from absolute ethanol, had m. p. 128—129° (Found : C, 61·3; H, 4·3%), indistinguishable from the corresponding derivative prepared from (±)-7-benzyl*iso*menthol as described above.

The ultra-violet absorption spectra were measured in purified ethanol with a Beckman spectrophotometer, model DU, and we express our indebtedness to Dr. (Miss) K. Rohatgi for much valuable assistance.

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