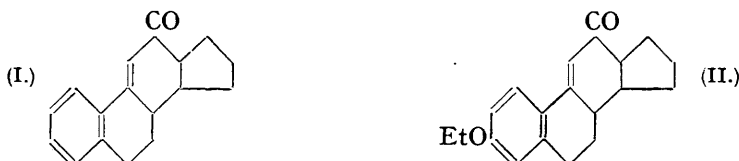


175. *Experiments on the Synthesis of Substances Related to the Sterols.*
 Part XIII. *Hydrocyclopentanophenanthrene Derivatives.*

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THE condensation of sodio- α -tetralone with acetylcyclopentene (Rapson and Robinson, J., 1935, 1287) does not proceed so smoothly as with acetylcyclohexene (preceding paper) and only one of the products has been isolated in a crystalline condition; there is a considerable uncrystallisable fraction which has not yet been fully investigated.

Ketotetrahydrocyclopentanophenanthrene (I) has been reduced to a saturated *alcohol*



(*phenylurethane*), and the latter oxidised to a saturated *ketone*. The unsaturated ketone has also been reduced by the Wolff-Kishner method with formation of a *tetrahydro-1:2-cyclopentanophenanthrene*.

6-Ethoxy- α -tetralone and acetylcyclopentene were condensed under the usual conditions with the formation of (II).

EXPERIMENTAL.

1-Acetylcyclopentene (cf. Rapson and Robinson, *loc. cit.*).—By maintaining the temperature below -15° during the addition of the *cyclopentene* and acetyl chloride the yield was increased to 50%. A longer period of heating with dimethylaniline at 180° gave a much purer product, b. p. $72-74^{\circ}/12$ mm. (Found: C, 76.4; H, 8.9. Calc. for $C_7H_{10}O$: C, 76.4; H, 9.0%). Attempts to add the elements of hydrogen chloride and hydrogen bromide to acetylcyclopentene

were only partly successful; the products decomposed on distillation and clear-cut fractions were not obtainable in adequate amount.

3-Keto-3 : 9 : 10 : 11-tetrahydro-1 : 2-cyclopentanophenanthrene (I).— α -Tetralone (10 g.) (Hock and Susemihl, *Ber.*, 1933, **66**, 61), finely powdered sodamide (3 g.), and dry ether (140 c.c.) were refluxed with stirring in a current of dry oxygen-free hydrogen for 5 hours; the sodio-derivative had then separated as a pale yellow precipitate. Acetylcyclopentene (8 g.) was added to the hot reaction mixture and stirring and refluxing were continued for 1 hour. The sodio-derivative disappeared and the solution darkened. After 12 hours the mixture was kept in the ice-chest for a further 24 hours; the product then crystallised. Dilute sulphuric acid was added, and the crude product (3 g.) collected. The substance crystallised from alcohol in colourless needles, m. p. 169—170° (Found : C, 85.6; H, 7.5. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%). From the ethereal layer there was obtained a viscous liquid (5 g.), b. p. 170—190°/0.065 mm. (mostly at 180—187°), and an alcoholic solution of this deposited only 0.5 g. of the above unsaturated ketone, m. p. 170°. The *oxime* separated from alcohol in glistening prisms, m. p. 235.5° (decomp.) (Found : C, 80.7; H, 7.2; N, 5.8. $C_{17}H_{18}ON$ requires C, 80.6; H, 7.5; N, 5.5%).

3-Hydroxy-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-cyclopentanophenanthrene.—Ketotetrahydrocyclopentanophenanthrene (0.5 g.), methyl alcohol (50 c.c.), and a 2% palladised strontium carbonate catalyst (2 g.) were shaken together in hydrogen for 10 hours, and the filtered solution evaporated. The residue crystallised from aqueous alcohol in fine colourless needles, m. p. 106° (yield, 60%) (Found : C, 83.5; H, 9.2. $C_{17}H_{22}O$ requires C, 84.3; H, 9.0%). The low value for carbon is difficult to explain, but it could not be remedied. The *phenylurethane* was therefore prepared in order to confirm the composition of the substance. The alcohol (0.1 g.) and phenyl isocyanate (0.05 g.) were heated together at 100° for 30 minutes. The derivative separated on the addition of light petroleum; it crystallised from alcohol in prisms, m. p. 175° (Found : C, 79.9; H, 7.6. $C_{24}H_{27}O_2N$ requires C, 79.8; H, 7.5%). The product of reduction of ketotetrahydrocyclopentanophenanthrene with sodium and alcohol was an uncrystallisable viscous liquid.

3-Keto-3 : 4 : 9 : 10 : 11 : 12-hexahydro-1 : 2-cyclopentanophenanthrene.—A solution of chromic acid (0.07 g.) in glacial acetic acid (2 c.c.) was gradually added to the above-described alcohol (0.25 g.) in glacial acetic acid (3 c.c.) with cooling and stirring. After 12 hours at room temperature, water was added. The *product* (yield, 75%) crystallised from aqueous alcohol in short colourless needles, m. p. 115—116.5° (Found : C, 84.8; H, 8.5. $C_{17}H_{20}O$ requires C, 85.0; H, 8.3%). The *semicarbazone* was only slowly formed in hot alcoholic solution. It separated from aqueous methyl alcohol in small plates, m. p. 191—192° (Found : C, 72.6; H, 7.5; N, 13.9. $C_{18}H_{23}ON_3$ requires C, 72.7; H, 7.7; N, 14.1%).

Under similar conditions of oxidation 3-hydroxy-7-methoxyhexahydrocyclopentanophenanthrene (Rapson and Robinson, *loc. cit.*) was largely recovered unchanged.

3 : 9 : 10 : 11-Tetrahydro-1 : 2-cyclopentanophenanthrene.—The semicarbazone of 3-keto-3 : 9 : 10 : 11-tetrahydro-1 : 2-cyclopentanophenanthrene (2 g.) was heated in a sealed tube at 170° with alcoholic sodium ethoxide (1.6 g. sodium, 25 c.c. alcohol) for 17 hours. The *product* was isolated by means of ether and heated with sodium for 1 hour at 150°; it then distilled from sodium as a clear liquid, b. p. 164—165°/3 mm. (Found : C, 91.2; H, 9.0. $C_{17}H_{20}$ requires C, 91.1; H, 8.9%).

3 : 4 : 9 : 10 : 11 : 12-Hexahydrocyclopentanophenanthrene.—A mixture of ketohexahydrocyclopentanophenanthrene (2 g.), amalgamated zinc (20 g.), and concentrated hydrochloric acid (10 c.c.), was refluxed for 24 hours. The *hydrocarbon* was isolated, heated for $\frac{1}{2}$ hour with sodium at 150°, and distilled; b. p. 201°/16 mm. (Found : C, 90.6; H, 9.6. $C_{17}H_{22}$ requires C, 90.3; H, 9.7%).

1 : 2-cyclopentanophenanthrene.—Dehydrogenation of 3-hydroxy-3 : 4 : 9 : 10 : 11 : 12-hexahydrocyclopentanophenanthrene by means of palladised charcoal at 330° for 17 hours afforded a small amount of material, m. p. 152° after sublimation in a vacuum and crystallisation from alcohol. The nearly colourless leaflets may have consisted of a polymorphic form of the hydrocarbon, but the quantity was too small for further examination.

Hydroxyhexahydrocyclopentanophenanthrene (0.5 g.), mixed with selenium powder (2.5 g.), was heated (bath at 310—320°) for 15 hours, any sublimate being returned to the melt. The powdered mass was extracted with alcohol, and the greenish-blue fluorescent solution concentrated. The material that separated was further purified by crystallisation from alcohol, adsorption on and elution from alumina, and crystallisation from light petroleum (b. p. 40—50°). The colourless needles had m. p. 135°, alone or mixed with an authentic specimen supplied by Dr. G. A. R. Kon, to whom we are very grateful.

3-Keto-7-ethoxy-3 : 9 : 10 : 11-tetrahydro-1 : 2-cyclopentanophenanthrene (II).—The sodio-derivative of 6-ethoxy- α -tetralone (Part X; this vol., p. 756) (9.5 g.) was prepared in boiling ethereal solution (100 c.c.) by means of powdered sodamide (2 g.) during 4 hours; air was displaced by nitrogen during this operation. Acetylcyclopentene (7 g., containing a little chlorine) was then added, and the mixture refluxed for 7 hours (nitrogen). A crystalline precipitate (5.3 g.) was collected after cooling, neutralisation with dilute hydrochloric acid, and keeping in the ice-chest. The *substance* crystallised from ethyl alcohol, in which it was sparingly soluble, in prismatic needles, m. p. 154—156° (Found : C, 80.6, 80.7; H, 7.8, 8.0; EtO, 16.2. $C_{19}H_{22}O_2$ requires C, 80.8; H, 7.8; EtO, 16.0%). No pure substance, other than a small further quantity of the main product, could be isolated from the ethereal mother-liquor by crystallisation, but, on distillation, ethoxytetralone was recovered (3 g.) and an oil of the approximate composition $C_{18}H_{22}O_2$ was also obtained (1.6 g.).

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