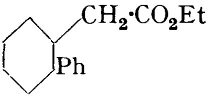
71. *Syntheses in the Phenanthrene Series. Part III.*

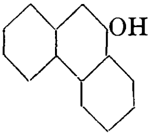
9-Hydroxyphenanthrene.

By I. R. SHERWOOD, W. F. SHORT, and J. WOODCOCK.

IN this communication we describe a synthesis of 9-hydroxyphenanthrene by an extension of the method employed for the synthesis of members of the diphenyl series (Sherwood, Short, and Stansfield, J., 1932, 1832); we hope to employ it as a model for other syntheses in the phenanthrene group.* 2-Phenyl*cyclo*hexanone (Lévy and Sfiras, *Bull. Soc. chim.*, 1931, **49**, 1834) was condensed with ethyl bromoacetate by the Reformatsky method, and the product dehydrogenated by sulphur to *ethyl diphenylyl-2-acetate* (I). By the action of concentrated sulphuric acid, this ester was converted into 9-hydroxyphenanthrene (II).

(I.)





(II.)

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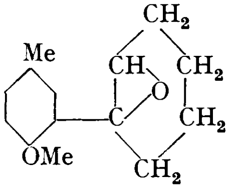
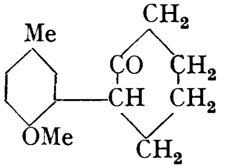
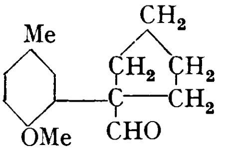
* Subsequent to the completion of our experiments, similar phenanthrene and hydrophenanthrene syntheses involving the building of the central nucleus were described by Chatterjee (*J. Indian Chem. Soc.*, 1935, **12**, 591) and Cook, Hewett, and Lawrence (this vol., p. 71).

Similarly, the Grignard compound of 3-bromo-*p*-tolyl methyl ether and *cyclo*hexanone afforded 1-(4′-methoxy-*m*-tolyl)*cyclo*hexanol, which was successively dehydrated to 1-(4′-*methoxy*-m-*tolyl*)-Δ^1-cyclo*hexene* and oxidised to the oxide (III). When the oxide was heated with zinc chloride, isomerisation to 2-(4′-methoxy-*m*-tolyl)*cyclo*hexanone (IV) occurred. The semicarbazone melted at 199—200° and since the isomerisation product did not possess reducing properties the isomeric *cyclo*pentane aldehyde (V) was presumably not formed in this instance.


(III.)


(IV.)


(V.)

The ketone (IV) could not be brought into reaction with ethyl bromoacetate and zinc or with ethyl cyanoacetate under any of the standard conditions and alternative methods for introducing the carbon atoms for building up the central nucleus of the phenanthrene ring system are being sought.

EXPERIMENTAL.

2-*Phenyl*cyclo*hexanone*.—1-Phenyl*cyclo*hexanol (Sabatier and Mailhe, *Compt. rend.*, 1904, **138**, 1321) was dehydrated to 1-phenyl-Δ^1-*cyclo*hexene, b. p. 136—139°/20 mm., by heating at 150—160° for 1 hour with an equal weight of potassium hydrogen sulphate. The unsaturated hydrocarbon was oxidised to 1-phenyl*cyclo*hexane 1 : 2-oxide, b. p. 120°/10 mm., as described by Nametkin and Iwanov (*Ber.*, 1923, **56**, 1805) and then converted into a mixture of 2-phenyl*cyclo*hexanone, m. p. 62°, and 1-phenyl*cyclo*pentane-1-aldehyde by heating with zinc chloride (Lévy and Sfiras, *loc. cit.*).

Ethyl Diphenylyl-2-*acetate*.—The Reformatsky reaction between 2-phenyl*cyclo*hexanone (20 g.), ethyl bromoacetate (21·1 g.), and zinc needles (7·5 g.) was carried out in benzene solution (150 c.c.), and the resulting semi-solid mixture of hydroxy and unsaturated esters (12·6 g.), b. p. 155—166°/5 mm., was dehydrogenated by heating at 180—240° for 4 hours with sulphur (2 atoms). Distillation of the product yielded *ethyl diphenylyl*-2-*acetate* (5·9 g.), b. p. 154—155°/4 mm. (Found : C, 80·1; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

9-*Hydroxyphenanthrene*.—The preceding ester was added gradually with stirring to 85% sulphuric acid, warmed slowly, and heated on the water-bath for 1 hour. The dark solution was cooled, diluted with water, and extracted with ether. The extract was washed with water and dried over magnesium sulphate, the solvent removed, and the residue distilled. The fraction, b. p. 216—225°/5 mm., was converted into the picrate, m. p. 183° after recrystallisation from alcohol (lit., 183°; 185°). Decomposition of the picrate with ammonia afforded 9-hydroxyphenanthrene, m. p. 150—151°, from which the methyl ether, m. p. 97—98°, was prepared. Oxidation of the methyl ether with chromic anhydride in acetic acid solution yielded phenanthraquinone, m. p. 203—204°, identified by conversion into the quinoxaline, m. p. and mixed m. p. 218—219°.

1-(4′-*Methoxy*-m-*tolyl*)-Δ^1-cyclo*hexene*.—Dropwise addition of bromine (1 mol.) to a solution of *p*-tolyl methyl ether (1 mol.) in glacial acetic acid (8 mols.) in presence of iron powder (½ g.), with stirring and cooling in water, afforded 3-bromo-*p*-tolyl methyl ether, b. p. 124—125°/20 mm., in 60% yield. The yield of 1-(4′-methoxy-*m*-tolyl)*cyclo*hexanol, m. p. 77°, obtained by the reaction between the Grignard compound of this ether and *cyclo*hexanone (Sherwood, Short, and Stansfield, *loc. cit.*) was raised to 45% when the experiment was performed on a larger scale. Dehydration of the carbinol (54 g.) with potassium hydrogen sulphate at 150—160° (1 hour) or by boiling for 1 hour with 130 g. of 100% formic acid gave an 80% yield of 1-(4′-*methoxy*-m-*tolyl*)-Δ^1-cyclo*hexene*, b. p. 163°/20 mm. (Found : C, 83·1; H, 9·0. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). Saturation of a cold acetic acid solution of the unsaturated compound with dry hydrogen bromide produced a white unstable solid which fumed in air. After cautious recrystallisation from acetic acid this melted at 58—60° (decomp.) (Found, by titration with alcoholic potash : Br, 26·2. $C_{14}H_{19}OBr$ requires Br, 28·3%).

2-(4′-*Methoxy*-m-*tolyl*)cyclo*hexanone*.—Oxidation of the unsaturated compound with perbenzoic acid in chloroform solution was complete in 24 hours at 0°. The chloroform solution was repeatedly washed with aqueous sodium carbonate and water, dried over magnesium sulphate, and distilled. The main fraction boiled at 170—200°/26 mm., but there was always a small fraction, b. p. 200—220°/26 mm., containing benzoic acid. The crude oxide was heated to 180° with a fragment of zinc chloride, and the temperature allowed to fall to 150° during 1 hour. Distillation afforded a fraction, b. p. 160—170°/10 mm., which gave a *semicarbazone*, m. p. 199—200° after recrystallisation from methyl alcohol (Found : N, 15·3. $C_{15}H_{11}O_2N_3$ requires N, 15·85%).

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