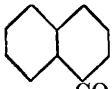
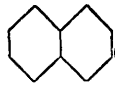
145. *Syntheses of Alkylphenanthrenes. Part I.* 1-, 2-, 3-, *and* 4-*Methylphenanthrenes.*

By Robert Downs Haworth.

The condensation of naphthalene with succinic anhydride in the presence of anhydrous aluminium chloride was first investigated by Giua (*Rend. Soc. chim. ital.*, 1912, **9**, 239), who isolated β-1-naphthoylpropionic acid (I; R = H) and β-2-naphthoylpropionic acid (II; R = H), but the only available reference to this work (*Ber.*, 1914, **47**, 2115) gives no statement of yield or the method employed in the separation of the isomerides. Borsche and Sauernheimer (*Ber.*, 1914, **47**, 1645) isolated small quantities of the second acid only from the reaction, and Krollpfeiffer and Schäfer (*Ber.*,

1923, **56**, 620) were unable to separate the acids produced. The acids (I) and (II) (R = H) have now been obtained in good yield and in approximately equal quantities by the use of nitrobenzene instead of carbon disulphide or benzene as solvent: they are identical with the acids prepared indirectly by Krollpfeiffer and Schäfer (*loc. cit.*) and by Schroeter, Müller, and Huang (*Ber.*, 1929, **62**, 645).

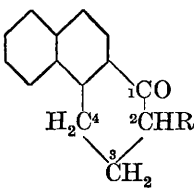
(I.) 



(II.)

The keto-acids (I) and (II) (R = H) were reduced by Clemmensen's method to the corresponding γ-naphthylbutyric acids (compare Schroeter, Müller, and Huang, *loc. cit.*), which were converted in 70—75% yields into 1-keto- and 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (III and IV; R = H), respectively, by the action of 85% sulphuric acid at 100°. This method is much more convenient and gave better results than that adopted by Schroeter, Müller, and Huang. Either cyclic ketone (III or IV; R = H) was reduced by amalgamated zinc and hydrochloric acid to 1 : 2 : 3 : 4-tetrahydrophenanthrene, which was converted into phenanthrene by dehydrogenation with selenium at 300° in 50% yield.

1-Methylphenanthrene (V) has been prepared by condensing 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (III; R = H) with methylmagnesium iodide in ethereal solution. The resulting carbinol lost water readily, yielding a mixture of hydrocarbons, which on treatment with selenium gave 1-methylphenanthrene, m. p. 118°, described previously by Pschorr (*Ber.*, 1906, **39**, 3111), whose constants for the hydrocarbon and its derivatives are slightly higher than those now recorded.



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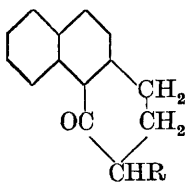

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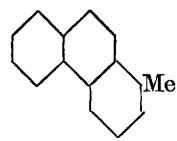

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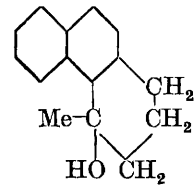


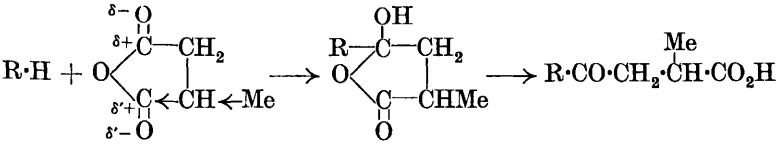
(VI.)

4-Methylphenanthrene has been prepared in a similar manner from 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene. In this case the *carbinol* (VI) was isolated as a crystalline substance, which was readily converted into a hydrocarbon mixture by the action of heat or anhydrous formic acid. When the hydrocarbon mixture was dehydrogenated with selenium, *4-methylphenanthrene*, m. p. 49—

50°, was isolated, and its *picrate*, m. p. 141°, *styphnate*, m. p. 135°, *quinone*, m. p. 187°, and *quinoxaline*, m. p. 178°, have been prepared. After this hydrocarbon had been synthesised, Radcliffe, Sherwood, and Short (J., 1931, 2293) published a synthesis of 4-methylphenanthrene, essentially similar to that outlined above, but describe the hydrocarbon as a solid, m. p. 117°, and the melting points of the picrate, styphnate, quinone, and quinoxaline are given as 125°, 144°, 187°, and 177° respectively. The divergence between the melting points of the hydrocarbon and its picrate and the agreement of those of the quinone and quinoxaline suggested that the compound, m. p. 49—50°, might be a hydrogenated phenanthrene. The analytical figures do not support this view, and prolonged treatment (24 hours) with selenium failed to affect the melting point. The work of Radcliffe, Sherwood, and Short has been repeated and the 4-methylphenanthrene obtained melted at 49—50°. Furthermore, identity was established between the intermediate products and the corresponding substances obtained as previously described.

The possibility of synthesising 2- and 3-alkylphenanthrenes from 1-keto- and 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene has been examined. The cyclic ketones (III and IV; R = H) condense with ethyl oxalate in the presence of potassium ethoxide, yielding *ethyl* 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate* and *ethyl* 4-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-3-*glyoxylate*, respectively, as bright yellow, crystalline compounds. Attempts to convert these into the desired β-ketonic esters by the action of heat has so far proved unsuccessful. When, however, ethyl 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-glyoxylate was treated with methyl iodide and potassium methoxide, and the neutral product distilled, 1-*keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (III; R = Me) was isolated. The hydrolysis of the glyoxylate side chain under these circumstances is analogous to the action of potassium methoxide on disubstituted acetoacetic esters (Dieckmann, *Ber.*, 1900, **33**, 2670). The yield of (III; R = Me) was very small and the reaction between naphthalene and methylsuccinic anhydride was therefore investigated. Two acids were separated by crystallisation from glacial acetic acid. On oxidation with warm sodium hypobromite the less soluble acid, m. p. 166°, gave β-naphthoic acid and the more soluble acid, m. p. 124°, gave α-naphthoic acid. That the two acids are β-2-*naphthoyl*- and β-1-*naphthoyl*-iso*butyric acid* (II and I; R = Me), respectively, and not the alternatively possible derivatives of *n*-butyric acid, has been determined by independent syntheses. β-Naphthyl chloromethyl ketone (Schroeter, Müller, and Huang, *loc. cit.*) was condensed with ethyl sodiomethyl-

malonate in benzene solution; the product, after hydrolysis and heating at 180°, gave an acid, m. p. 166°, identical with the less soluble acid (II; R = Me). In a similar manner α-naphthyl chloromethyl ketone was converted into an acid, m. p. 124°, identical with the more soluble acid (I; R = Me). In the condensation of methylsuccinic anhydride with naphthalene, the greater reactivity of the carbonyl group adjacent to the methylene group is apparent, and a similar behaviour is observed in the reaction of methylsuccinic anhydride with benzene (Oppenheim, *Ber.*, 1901, **34**, 4228; Mayer and Stamm, *ibid.*, 1923, **56**, 1424). The reaction being assumed to depend upon addition to kationoid carbon, an explanation follows from considerations of the electron-repelling effect of the methyl group, which would reduce the reactivity of the carbon of the β-carbonyl group (δ + is greater than δ′ +).



β-1-Naphthoyl*iso*butyric acid was reduced by Clemmensen's method to *γ-1-naphthyl-α-methylbutyric acid*, which was converted into 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (III; R = Me) by the action of sulphuric acid. This ketone was reduced and the product dehydrogenated to yield 2-methylphenanthrene, m. p. 55—56°, identical with the hydrocarbon prepared by Klinckhard (*Annalen*, 1911, **379**, 375). In a similar manner β-2-naphthoyl*iso*-butyric acid was converted into *γ-2-naphthyl-α-methylbutyric acid*, 4-*keto*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV; R = Me), and 3-methylphenanthrene, m. p. 63°, which was identical with the hydrocarbon obtained by Pschorr (*loc. cit.*).

The condensation of succinic anhydride with substituted naphthalenes is being investigated.

EXPERIMENTAL.

General Methods.—The Clemmensen reduction processes were carried out as follows: The keto-compound (1 part), amalgamated zinc (5 parts), and concentrated hydrochloric acid (5 vols.) were boiled gently for 12 hours, the mixture was then diluted with water, and the product isolated by ether extraction or filtration. In the case of keto-acids, the reduction product was usually contaminated with zinc salts and was purified by dissolving it in sodium carbonate solution and acidifying the filtered solution.

For the conversion of the *γ*-naphthylbutyric acids into ketotetrahydrophenanthrenes, the finely powdered acid (1 part) was added

gradually with stirring to a mixture of concentrated sulphuric acid (3 vols.) and water (1 vol.) and after 1 hour's heating on the water-bath the red solution was cooled, diluted with water, and extracted with ether. The extract was washed with water, which removed traces of coloured sulphonation product, then with dilute ammonia solution, and dried with anhydrous potassium carbonate, the solvent

60—80°); the 1-naphthyl-acid melted at 106—107° and the 2-naphthyl-acid at 94—95° (S., M., and H., *loc. cit.*, give 106° and 95° respectively).

1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (III; R = H) separated from chloroform–light petroleum in colourless plates, m. p. 95—96°, and 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (IV; R = H) from methyl alcohol in needles, m. p. 69°.

Ethyl 1-*Keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate and Ethyl* 4-*Keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-3-*glyoxylate*.—Ethyl oxalate (1·4 g.) was added to a solution of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (2 g.) and potassium ethoxide (from 0·4 g. of potassium) in ether (40 c.c.). A yellow solid rapidly separated and after 12 hours water was added and the aqueous layer acidified with dilute hydrochloric acid. The yellow solid was collected and crystallised from methyl alcohol; *ethyl* 1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate* separated in yellow needles (2 g.), m. p. 84—85° (Found: C, 72·8; H, 5·5. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·5%). 4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene was converted in a similar manner into *ethyl* 4-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-3-*glyoxylate*, which crystallised from methyl alcohol in bright yellow plates, m. p. 73—74° (Found: C, 72·8; H, 5·6%). Attempts to distil these esters under diminished pressure caused profound decomposition.

1-*Methylphenanthrene* (V).—1-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (4 g.) was condensed with methylmagnesium iodide (from magnesium, 0·5 g., and methyl iodide, 3 g.) in ethereal solution (40 c.c.), the mixture finally being gently boiled for 1 hour. The product was decomposed with dilute sulphuric acid, the ethereal layer separated and dried with anhydrous potassium carbonate, and the solvent removed. The semi-solid residue (A) yielded a *picrate* in hot methyl-alcoholic solution, from which it separated in scarlet needles, m. p. 127—128°, which gave analytical figures in agreement with the loss of a molecule of water from the carbinol (Found: C, 59·4; H, 4·1. $C_{21}H_{17}O_7N_3$ requires C, 59·6; H, 4·1%). The semi-solid residue (A) was completely dehydrated to an oil, either by warming on the water-bath with formic acid or by distillation at 0·3 mm. The product (4 g.), heated with selenium, yielded 1-methylphenanthrene, which crystallised from alcohol in colourless plates (2 g.), m. p. 118° (Found: C, 93·7; H, 6·3. Calc. for $C_{15}H_{12}$: C, 93·75; H, 6·25%). The picrate melted at 135—136° (Found: C, 59·6; H, 3·7. Calc. for $C_{21}H_{15}O_7N_3$: C, 59·9; H, 3·6%), the styphnate at 149—150°, the quinone at 191°, and the quinoxaline at 177°. Pschorr (*loc. cit.*) gives 123°, 139°, and 196° (corr.) for hydrocarbon, picrate, and quinone respectively.

4 - *Methylphenanthrene.* — 4 - Keto - 1 : 2 : 3 : 4 - tetrahydrophenanthrene (4 g.) was condensed with methylmagnesium iodide as described above. After removal of the ether, the product, which solidified, was crystallised from light petroleum (b. p. 60—80°), from which 4-*hydroxy*-4-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (VI) separated in rectangular plates, m. p. 111—112° (Found : C, 84·7; H, 7·6. $C_{15}H_{16}O$ requires C, 84·9; H, 7·6%). In cold methyl-alcoholic solution the carbinol was converted into a *picrate*; bright yellow needles, m. p. 96—98° (Found : C, 57·0; H, 4·6. $C_{21}H_{19}O_8N_3$ requires C, 57·1; H, 4·4%). This picrate regenerated the carbinol (VI) on treatment with cold ammonia solution, but continued heating at 100° resulted in dehydration and the crystals became scarlet. Further, when the carbinol (VI) was mixed with picric acid in hot methyl alcohol, dehydration occurred and a *picrate*, m. p. 110°, separated in scarlet plates (Found : C, 59·6; H, 4·3. $C_{21}H_{17}O_7N_3$ requires C, 59·6; H, 4·1%). This picrate gave an oily hydrocarbon on treatment with ammonia. The carbinol (VI) was dehydrated by warming on the water-bath with formic acid, and the product (4 g.) distilled at 0·3 mm. and dehydrogenated with selenium. 4-*Methylphenanthrene*, which crystallised from alcohol in colourless plates, m. p. 49—50°, was obtained (Found : C, 93·6; H, 6·2. $C_{15}H_{12}$ requires C, 93·75; H, 6·25%). The *picrate* separated from methyl alcohol in slender orange needles, m. p. 140—141° (Found : C, 59·7; H, 3·8. $C_{21}H_{15}O_7N_3$ requires C, 59·9; H, 3·6%). The styphnate, m. p. 135°, separated from alcohol in orange needles. The *quinone* crystallised from alcohol in orange plates, m. p. 187° (Found : C, 80·8; H, 4·7. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%). The *quinoxaline* derivative crystallised from alcohol in pale yellow needles, m. p. 178° (Found : C, 84·6; H, 4·9. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8%).

β-2- *and* β-1-*Naphthoylisobutyric Acids* (II and I; R = Me).—A mixture of naphthalene (20 g.) and methylsuccinic anhydride (10 g.) was added to a solution of aluminium chloride (24 g.) in nitrobenzene (50 c.c.) and after 24 hours the products were isolated as described on p. 1129; 5·8 g. of the acid (II; R = Me) and 6·0 g. of the acid (I; R = Me) were obtained. β-2-*Naphthoylisobutyric acid* separated from hot glacial acetic acid or hot methyl alcohol in colourless plates, m. p. 165—166° (Found : C, 74·0; H, 6·0. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%).

β-Naphthyl chloromethyl ketone was condensed with ethyl sodiomethylmalonate (1·25 mols.) in boiling benzene solution, the mixture decomposed with water and dried, the benzene removed, and the residual oil hydrolysed by warming with a slight excess of methyl-alcoholic potassium hydroxide. The product was diluted

with water, the alcohol removed, and the residue acidified and extracted with ether. The extract was dried, the solvent removed, the residue heated at 180°, until evolution of carbon dioxide ceased, and then crystallised from acetic acid; the 2-naphthoyl-acid separated in colourless plates, m. p. 165—166°, identical with the above.

β-1-*Naphthoyl*isobutyric *acid* separated from methyl alcohol in colourless needles, m. p. 123—124° (Found: C, 74·1; H, 5·7%).

γ-2-*Naphthyl*-α-*methylbutyric acid*, prepared in 75% yield from the 2-naphthoyl acid by the Clemmensen process, crystallised from light petroleum (b. p. 60—80°) in rosettes of needles, m. p. 85—86° (Found: C, 78·7; H, 7·0. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%).

γ-1-*Naphthyl*-α-*methylbutyric acid*, prepared similarly, crystallised from light petroleum–ether in colourless prisms, m. p. 90° (Found: C, 78·6; H, 7·2%).

1-*Keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (III; R = Me). —(a) Ethyl 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-glyoxylate (2 g.) was heated with potassium methoxide (from 0·4 g. of potassium) and methyl iodide (2 g.) in methyl-alcoholic solution (25 c.c.) for 6 hours. After dilution with water, the solution was extracted with ether, and the extract washed with dilute sodium hydroxide solution, dried, and distilled at 0·3 mm. The distillate (0·25 g.), which solidified on cooling, was crystallised from ether–light petroleum (b. p. 40—60°).

(b) γ-1-Naphthyl-α-methylbutyric acid, cyclised in the usual way with 85% sulphuric acid, gave the ketone in 70% yield.

1-*Keto*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, prepared by either method (a) or (b), crystallised in rhombic plates, m. p. 75—76° (Found: C, 85·8; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%). The picrate crystallised from methyl alcohol in yellow nodules, m. p. 104°, and the semicarbazone from alcohol in small needles, m. p. 250—252°.

4-*Keto*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IV; R = Me), prepared in 70% yield by the action of sulphuric acid on γ-2-naphthyl-α-methylbutyric acid, crystallised from ether–light petroleum (b. p. 40—60°) in colourless plates, m. p. 64—65° (Found: C, 85·7; H, 6·5%).

3-Methylphenanthrene, prepared by reducing the ketone (IV; R = Me) with amalgamated zinc and dehydrogenating the product with selenium, crystallised from concentrated alcoholic solutions in colourless needles and from more dilute solutions in stout prisms, either form melting at 62—63° (Found: C, 94·0; H, 6·2. Calc. for $C_{15}H_{12}$: C, 93·7; H, 6·2%). The picrate crystallised from alcohol in bright yellow needles, m. p. 137—138° (Found: C, 59·5;

H, 3·6. Calc. for $C_{21}H_{15}O_7N_3$: C, 59·9; H, 3·6%), the *quinone* from alcohol in orange plates, m. p. 205—206° (Found: C, 80·7; H, 4·8. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%), and the *quinoxaline* derivative from glacial acetic acid in pale yellow needles, m. p. 207—208° (Found: C, 85·8; H, 5·0. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8%). Pschorr (*loc. cit.*) gives m. p. 65° and 141° for the hydrocarbon and picrate respectively.

2-Methylphenanthrene, prepared similarly from the ketone (III; R = Me), crystallised from alcohol in colourless needles, m. p. 55—56° (Klinckhard, *loc. cit.*, gives 52—53°) (Found: C, 93·8; H, 6·2%). The *picrate* crystallised from methyl alcohol in yellow needles, m. p. 118—119° (Found: C, 59·6; H, 3·7. $C_{21}H_{15}O_7N_3$ requires C, 59·9; H, 3·6%), the *quinone* from alcohol in large orange plates, m. p. 147—148° (Found: C, 80·7; H, 4·8. $C_{15}H_{10}O_2$ requires C, 81·1; H, 4·5%), and the *quinoxaline* derivative from alcohol in long, pale yellow needles, m. p. 186—188° (Found: C, 85·4; H, 5·1. $C_{21}H_{14}N_2$ requires C, 85·7; H, 4·8%).

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