76. *Polycyclic Aromatic Hydrocarbons. Part XXX. Synthesis of Chrysenols.*

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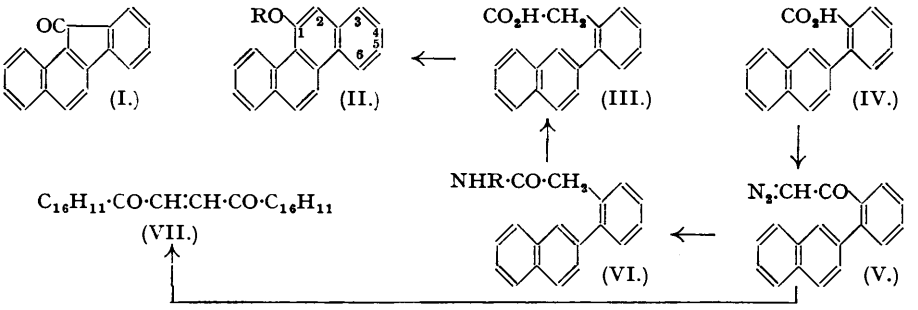
Four new monohydroxychrysenes have been synthesised, so that all six possible isomerides are now known. The *diazo-ketone* formed from α-chrysenic acid (IV) was used for the synthesis of 1-*chrysenol* (II), and was also found to undergo cyclisation to 2-chrysenol under the influence of sulphuric acid in acetic acid. The Reformatsky reaction between the readily accessible methyl γ-bromocrotonate and 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene has enabled 3-*chrysenol* to be conveniently synthesised, and 4-*chrysenol* was prepared by modification of the Pschorr phenanthrene synthesis. 6-*Chrysenol* was obtained by dehydrogenation of the known 6-keto-3 : 4 : 5 : 6-tetrahydrochrysene (X).

When polycyclic aromatic hydrocarbons are introduced into the animal body (mice, rats, rabbits) by various routes (orally or by subcutaneous or intraperitoneal injection), they become hydroxylated and eliminated. Evidence has been adduced that the compound so formed in rats and mice from the carcinogenic hydrocarbon, 3 : 4-benzpyrene, is a monohydroxy-derivative (Chalmers and Crowfoot, *Biochem. J.*, 1941, **35**, 1270), probably the 8-hydroxy-compound (Berenblum *et al.*, *Cancer Res.*, 1943, **3**, 151). As part of a systematic study of the metabolism of polycyclic aromatic hydrocarbons, one of us (R. S.) is engaged, in collaboration with Dr. I. Berenblum, in an investigation of the biochemical oxidation of chrysene. To facilitate identification of the products, and also because some monomethoxy-derivatives of polycyclic aromatic hydrocarbons strongly inhibit the growth of tumours (20th *Annual Report of the British Empire Cancer Campaign*, 1943, 20), it was decided to prepare all the six monohydroxychrysenes which are theoretically possible. Two of these have been described previously, and the other four have now been synthesised, together with their methyl ethers.

Ring-enlargement of cyclic ketones by means of diazomethane has been applied to fluorenone by Schultz, Schultz, and Cochran (*J. Amer. Chem. Soc.*, 1940, **62**, 2902), who obtained 9-methoxyphenanthrene as the principal product. By this reaction 1 : 2-benzfluorenone ("chrysene ketone," I) might conceivably have been converted into 1-methoxychrysene (II; R = Me). Although ring-enlargement did take place with diazomethane, most of the ketone (I) did not react, and the only pure product isolated was the known 2-methoxychrysene (Newman and Cathcart, *J. Org. Chem.*, 1940, **5**, 618). 1-*Chrysenol* (II; R = H) was, however, obtained, as its *acetate*, by zinc chloride–acetic anhydride dehydration of 2-(2′-*naphthyl*)*phenylacetic*

acid (III), which was prepared from α-chrysenic acid (IV) by the Arndt–Eistert reaction. α-Chrysenic acid is formed by fusion of 1 : 2-chrysaquinone with alkali and lead dioxide, and the structure (IV) assigned to it by Graebe and Hönigsberger (*Annalen*, 1900, **311**, 257) has been confirmed by Hey and Lawton (J., 1940, 380).

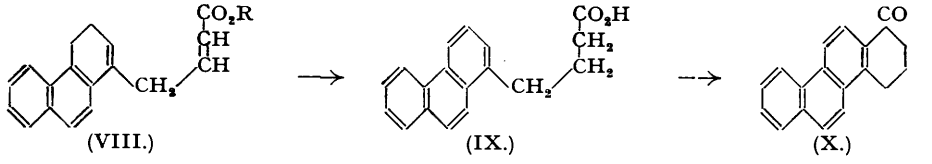
The conditions for the preparation of the chloride of α-chrysenic acid were somewhat critical, as it passed very easily into 1 : 2-benzfluorenone (I). 2-(2′-ω-*Diazoacetyl*)*phenylnaphthalene* (V), obtained by the action of diazomethane on the chloride of (IV), was converted in the normal way into the ***amide*** (VI; R = H) of the homo-acid (III). This amide was cyclised by sulphuric acid in boiling acetic anhydride to 1-***acetamidochrysene***, oxidised by sodium dichromate in boiling acetic acid to 1 : 2-chrysaquinone.



Addition of the diazo-ketone (V) to a 10% solution of sulphuric acid in acetic acid led to the elimination of nitrogen with formation of 2-chrysenol. This type of cyclisation by decomposition of a diazo-ketone has not hitherto been observed. Possibly the chrysenol is formed directly by rearrangement of the free radical formed by loss of nitrogen, or there may be formed as an intermediate the hydroxymethyl ketone or an ester of this (compare Langenbeck and Baehren, *Ber.*, 1936, **69**, 514; Eistert, *ibid.*, p. 1074). The diazo-ketone (V) was also decomposed with evolution of nitrogen when it was heated with methanol. Analysis of the crystalline ***product*** suggested that it had structure (VII), formed by union of two bivalent carbon radicals.

Mosettig and Duvall (*J. Amer. Chem. Soc.*, 1937, **59**, 367) found a very satisfactory method for the preparation of 1- and 4-phenanthrols in the action of palladium-black, in a suitable boiling inert solvent, on the corresponding 1- and 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrenes. This same type of method has been used for the preparation of 5-chrysenol from a 5-ketohexahydrochrysene (Wilds and Shunk, *ibid.*, 1943, **65**, 469), and we have extended it to the preparation of 3- and 6-*chrysenols* by palladium dehydrogenation of the known 3- and 6-keto-3 : 4 : 5 : 6-tetrahydrochrysenes. The 6-keto-compound was prepared by Fieser and Johnson's method (*ibid.*, 1939, **61**, 1647), but an improved method was worked out for 3-keto-3 : 4 : 5 : 6-tetrahydrochrysene (X), as the existing methods of Hoch (*Compt. rend.*, 1938, **207**, 921) and Bachmann and Struve (*J. Org. Chem.*, 1940, **5**, 423) are cumbersome and involve many stages.

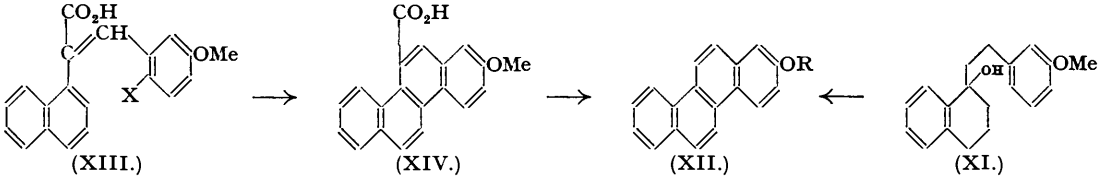
For this new synthesis of (X) advantage was taken of the excellent technique of Ziegler *et al.* (*Annalen*, 1943, **551**, 80) for the preparation of methyl γ-bromocrotonate, and of the significant observation of Ziegler, Schumann, and Winkelmann (*ibid.*, p. 120) that this bromo-ester gives very satisfactory results in the Reformatsky reaction. Methyl γ-bromocrotonate condensed smoothly with zinc and 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene to give, after distillation, the unsaturated *ester* (VIII; R = Me). This was isomerised by palladium-black at 280—300° to the methyl ester of γ-1-phenanthrylbutyric acid (IX), which was cyclised by anhydrous hydrogen fluoride (compare Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272) to give the tetracyclic ketone (X) in almost theoretical yield. The final dehydrogenation to 3-chrysenol was effected



by palladium-black in boiling α-methylnaphthalene. This simple procedure for the synthesis of hydroaromatic fused-ring systems has many possible applications, and the method is being further developed in these laboratories.

For the synthesis of 4-*chrysenol* (XII; R = H) two methods have been examined. One of these, based on the work of Cook and Hewett (J., 1933, 1098; 1934, 365) and of Ruzicka and Hösli (*Helv. Chim. Acta*, 1934, **17**, 470), involved the condensation of β-*m*-methoxyphenylethylmagnesium chloride with α-tetralone, followed by dehydration of the crude carbinol (XI) so formed, and then treatment with aluminium chloride in boiling carbon disulphide solution. This gave a mixture of products from which 4-***methoxychrysene*** (XII; R = Me) was isolated in very small yield. By-products of the Grignard condensation were 1 : 1′-dihydroxy-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydro-1 : 1′-dinaphthyl and its dehydration product 3 : 4 : 3′ : 4′-tetrahydro-1 : 1′-dinaphthyl, the former arising from the reducing action of the Grignard solution on α-tetralone (com-

pare Schroeter, *Ber.*, 1925, **58**, 716; Barnett and Lawrence, J., 1935, 1107). A much more satisfactory method of synthesis of 4-chrysenol was found in a suitable adaptation of the Pschorr phenanthrene synthesis (compare Weitzenböck and Lieb, *Monatsh.*, 1912, **33**, 549). To this end, sodium 1-naphthylacetate was condensed with 2-nitro-5-methoxybenzaldehyde to give a *nitro-acid* (XIII; X = NO_2), which was reduced to the *amino-acid* (XIII; X = NH_2). The diazo-compound prepared from this was cyclised to *4-methoxychrysene-1-carboxylic acid* (XIV) and this was decarboxylated to 4-methoxychrysene, from which 4-chrysenol was obtained by demethylation.



(XIII.) (XIV.) (XII.) (XI.)

All six chrysenols were characterised by the preparation oftheir methyl ethers, their acetates, and their molecular *compounds* with 2 : 7-dinitroanthraquinone.

Experimental.

2-Methoxychrysene from 1 : 2-*Benzfluorenone* (I).—Ethereal diazomethane, in large excess, was added slowly to a stirred suspension of chrysene ketone (2·3 g.), prepared from chrysaquinone (Bamberger and Burgdorf, *Ber.*, 1890, **23**, 2433), in ether (5 c.c.) and methanol (10 c.c.). After being kept at room temperature overnight, the solution was evaporated, the residue dissolved in light petroleum, and its solution passed through a column of alumina. Five bands were visible in ultra-violet light. The lowest band (colourless, with a violet fluorescence), when eluted with light petroleum and the eluate concentrated, gave crystals of 2-methoxychrysene which, after recrystallisation from benzene–light petroleum, had m. p. 126—127°, alone or mixed with 2-methoxychrysene prepared from chrysene by sulphonation and caustic fusion, with methylation of the chrysenol (U.S.P. 2,032,505; Newman and Cathcart, *loc. cit.*). Identification was completed by preparation from both samples of the same picrate, m. p. and mixed m. p. 165—166°. The molecular *compound* with 2 : 7-dinitroanthraquinone had m. p. 230—231° (from xylene) (Found : C, 71·5; H, 3·9; N, 4·8. $C_{33}H_{20}O_7N_2$ requires C, 71·2; H, 3·6; N, 5·0%).

The yellow band above the colourless band in the chromatogram contained most of the 1 : 2-benzfluorenone unchanged. The coloured bands above this were not examined.

2-(2′-ω-Diazoacetyl)phenylnaphthalene (V).—α-Chrysenic acid (IV) was prepared from 1 : 2-chrysaquinone by the method of Graebe and Hönigsberger (*loc. cit.*) and separated from the more soluble β-chrysenic acid by crystallisation from aqueous acetic acid. It crystallised from benzene in colourless prisms, m. p. 189—190°. For conversion into the chloride, a mixture of the finely powdered α-chrysenic acid (1 g.), pure dry benzene (2 c.c.), and thionyl chloride (2 c.c.) was heated at 40—50° until solution was complete (30—45 mins.). The excess of thionyl chloride and the benzene were removed by evaporation under reduced pressure, and in order to remove the last traces of thionyl chloride the residue was twice evaporated with dry benzene under reduced pressure. If α-chrysenic acid and thionyl chloride were heated together under reflux, or kept at room temperature until solution was complete (several hours), the sole product was 1 : 2-benzfluorenone (I).

A solution of the oily chloride, prepared as described from α-chrysenic acid (1 g.), in pure dry benzene (5 c.c.) was added dropwise to ethereal diazomethane (100 c.c.), prepared from *N*-nitroso-*N*-methylurea (5 g.) (*Organic Syntheses*, 1935, **15**, 3). The solution was kept until evolution of gas ceased (several hours or overnight), and the ether and excess of diazomethane were distilled under slightly reduced pressure. The resulting benzene solution deposited long, pale yellow needles of 2-(2′-ω-*diazoacetyl*)*phenylnaphthalene*, m. p. 131—131·5° with gas evolution (Found : C, 79·6; H, 4·6; N, 10·2. $C_{18}H_{12}ON_2$ requires C, 79·4; H, 4·4; N, 10·3%).

Transformations of 2-(2′-ω-*Diazoacetyl*)*phenylnaphthalene* (V).—(*a*) When the solid diazo-ketone was added at room temperature to a 10% solution of concentrated sulphuric acid in acetic acid, gas and heat were liberated, and on pouring the solution into water 2-chrysenol was precipitated; it was identified by direct comparison with an authentic sample. If the acetic acid used as solvent for this reaction was replaced by acetic anhydride, the product was 2-acetoxychrysene (Newman, *J. Amer. Chem. Soc.*, 1938, **60**, 2949).

(*b*) When a suspension of the diazo-ketone in methanol was heated on the water-bath, solution took place with evolution of gas. The *product* formed long, almost colourless needles (probably VII), m. p. 245° (decomp.) (Found : C, 88·2; H, 4·9. $C_{36}H_{24}O_2$ requires C, 88·4; H, 4·9%).

(*c*) When 20% aqueous ammonia was used for attempted conversion of the diazo-ketone into the amide of the homo-acid, as in the examples of Walker (J., 1940, 1304), the diazo-ketone was recovered unchanged. With more dilute ammonia solution the rearrangement was satisfactorily accomplished. A 10% solution of ammonia (20 c.c.) and a 10% solution of silver nitrate (3 c.c.) were added to a solution in dioxan (50 c.c.) of the crude diazo-ketone (from 3 g. of α-chrysenic acid). The mixture was heated on the water-bath, and in a few minutes gas was evolved and the yellow solution became brown and opaque. After ½ hour's heating the hot solution was filtered, and the amide which crystallised on cooling was purified by passing its solution in benzene through a short column of alumina. 2-(2′-*Naphthyl*)-*phenylacetamide* (VI; R = H) formed white needles (1·7 g.) (from benzene), m. p. 162—163° (Found : C, 82·6; H, 5·7; N, 5·4. $C_{18}H_{15}ON$ requires C, 82·8; H, 5·7; N, 5·4%). Hydrolysis with boiling methanolic potash (50 c.c. of 55% aqueous potash and 50 c.c. of methanol) for 4—5 hours gave 2-(2′-*naphthyl*)*phenylacetic acid* (III) (1·6 g.), which crystallised from aqueous methanol in colourless needles, m. p. 123—124° (Found : C, 82·3; H, 5·3. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·3%).

1-*Acetamidochrysene*.—A solution of the amide (VI; R = H) in 20% sulphuric acid in acetic anhydride was boiled for 2 hours, and the product purified by chromatographic adsorption on alumina. A fluorescent compound, obtained in small yield, was found to be 1-*acetamidochrysene*. It formed fine, colourless needles (from benzene–light petroleum), m. p. 249—250° (Found : C, 84·4; H, 5·3; N, 5·0. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3; N, 4·9%), and was oxidised by sodium dichromate in boiling acetic acid (1 hour) to 1 : 2-chrysaquinone, m. p. 232—234° (after chromatographic purification), identified by direct comparison with a specimen prepared from chrysene (Graebe and Hönigsberger, *loc. cit.*, p. 262). From another experiment, in which the amide was treated with 20% sulphuric acid in acetic anhydride at room temperature overnight and then at 60° for an hour, there was isolated, in addition to acetamidochrysene, the *acetyl-amide*

(VI; R = Ac). This formed colourless, rhombic crystals (from methanol), m. p. 122—123° (Found: C, 79·2; H, 5·8; N, 4·3. $C_{20}H_{17}O_2N$ requires C, 79·3; H, 5·65; N, 4·6%).

A fruitless attempt was made to convert 1-acetamidochrysene into 1-chrysenol by heating it in a sealed tube with 10% sulphuric acid (6 hours at 215—225° or 19 hours at 200—210°). 2-Aminochrysene was hydrolysed in this way to 2-chrysenol by Newman and Cathcart (*loc. cit.*).

1-*Chrysenol* (II; R = H).—A solution of 2-(2′-naphthyl)phenylacetic acid (100 mg.) in acetic acid (1 c.c.) and acetic anhydride (1 c.c.) together with a trace of zinc chloride was boiled under reflux for an hour (compare Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1028; Newman, *ibid.*, 1938, **60**, 2950). The cooled solution was poured into water, giving a resinous precipitate which soon solidified. After being dried, this was separated by fractional crystallisation from light petroleum into the more soluble 1-*acetoxychrysene*, which formed colourless needles (from methanol), m. p. 147—148° (Found: C, 83·7; H, 4·8. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%), and a smaller amount of a less soluble *compound*, which crystallised from benzene in colourless rods, m. p. 209—211° (with evolution of gas). This compound, which was obtained consistently by this cyclisation, may be 1-*acetoxy*-2-*acetylchrysene*, formed from the 1-acetate by a Fries rearrangement with reacetylation of the hydroxy-ketone (Found: C, 80·3; H, 4·7. $C_{22}H_{16}O_3$ requires C, 80·45; H, 4·9%). Its m. p. was greatly depressed by admixture with 1-chrysenol, and it dissolved in alcoholic alkali to give a yellow solution which remained clear on dilution.

Hydrolysis of the crude 1-acetoxychrysene by brief boiling with methanolic potash, followed by distillation of the methanol and acidification of the diluted concentrate, gave 1-*chrysenol* (II; R = H), which, after sublimation in a high vacuum and crystallisation from light petroleum, formed colourless needles, m. p. 208—209° (in an evacuated sealed tube), which became coloured on standing in air (Found: C, 88·35; H, 5·3. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%). Oxidation with sodium dichromate in boiling acetic acid, gave 1 : 2-chrysaquinone, m. p. 235—236°. The *methyl ether*, prepared from the phenol by 6 hours' boiling with excess of methyl iodide and sodium methoxide in methanol, formed long colourless needles (from benzene–light petroleum), m. p. 142—143° (Found: C, 88·1; H, 5·5; OMe, 12·7. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4; OMe, 12·0%). The *complex* of 1-methoxychrysene with 2 : 7-dinitroanthraquinone (prepared in xylene) formed long, thin, crimson rods, m. p. 220—221° (Found: C, 71·1; H, 3·7. $C_{33}H_{20}O_7N_2$ requires C, 71·2; H, 3·6%). The *benzoate* of 1-chrysenol, prepared with benzoyl chloride and aqueous alkali, formed colourless needles (from light petroleum), m. p. 171—172° (Found: C, 86·0; H, 4·6. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%).

1 : 2-*Diacetoxychrysene*.—This was obtained by 2 hours' boiling with zinc dust of a solution of 1 : 2-chrysaquinone (0·75 g.) in pyridine (10 c.c.) and acetic anhydride (2 c.c.). It formed colourless crystals (from benzene), m. p. 193—194° (Found: C, 76·6; H, 4·6. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). The compound, m. p. 225—228°, prepared by Knesch (D.R.-P., 151,981) and regarded by him as 1 : 2-diacetoxychrysene must therefore have some other structure. 1 : 2-*Dimethoxychrysene*, prepared by reductive methylation of chrysaquinone, had m. p. 129—130° (Found: C, 83·1; H, 5·4. $C_{20}H_{16}O_2$ requires C, 83·3; H, 5·6%).

5-*Chrysenol*.—This was prepared by the method of Wilds and Shunk (*loc. cit.*) except that the dehydrogenation of the ketohexahydrochrysene with palladium was carried out in boiling α-methylnaphthalene. The chrysenol was formed in good yield in 20 hours, whereas Wilds and Shunk found that 3 days were required in boiling xylene. The *complex* of 5-methoxychrysene with 2 : 7-dinitroanthraquinone had m. p. 268—270° (from xylene) (Found: C, 71·4; H, 3·7. $C_{33}H_{20}O_7N_2$ requires C, 71·2; H, 3·6%).

6-*Chrysenol*.—A solution of 6-keto-3 : 4 : 5 : 6-tetrahydrochrysene (Fieser and Johnson, *loc. cit.*) (1 g.) in mesitylene (10 c.c.) was boiled with palladium-black (0·1 g.) for 20 hours. The filtered solution deposited, on cooling, cream-coloured rosettes of 6-*chrysenol* (0·8 g.) which, after sublimation at 140°/0·2 mm. and crystallisation from benzene–light petroleum, formed almost colourless crystals, m. p. 152—153° (Found: C, 88·4; H, 5·1. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%). Its *methyl ether*, prepared as described for the 1-isomeride, formed short, cream-coloured needles (from methanol), m. p. 102—103° (Found: C, 88·4; H, 5·6; OMe, 12·5. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4; OMe, 12·0%), and gave a *complex* with 2 : 7-dinitroanthraquinone as orange-red crystals, m. p. 232—234° (Found: C, 71·3; H, 3·6. $C_{33}H_{20}O_7N_2$ requires C, 71·2; H, 3·6%). 6-*Acetoxychrysene*, prepared from the phenol by refluxing with acetic anhydride and pyridine, was sublimed in a vacuum; it then crystallised from light petroleum in colourless needles, m. p. 155—156° (Found: C, 84·1; H, 5·1. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

γ-1-(3 : 4-*Dihydrophenanthryl*)*crotonic acid* (VIII; R = H).—Zinc wool (10 g.) was amalgamated by heating with a little dry mercuric chloride in pure dry benzene (40 c.c.) (Hoch, *Bull. Soc. chim.*, 1938, **5**, 274). While the mixture was still warm, 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (Haworth, J., 1932, 1125) (14·9 g.) and methyl γ-bromocrotonate (Ziegler *et al.*, *loc. cit.*) (22·4 g.) were added. Reaction set in immediately, and proceeded without external heat. When its violence had subsided, the whole was heated on the water-bath for ½ hour, and then decomposed with ice and hydrochloric acid. Ether and more benzene were added, and the extract was washed with sodium carbonate solution and water, and dried (sodium sulphate). The solvents were evaporated off, and the residue distilled at 1 mm. The first fraction, to 220°, was largely unreacted ketone (6·5 g.). The main fraction had b. p. about 240° (10 g.) and was a yellow, viscous oil consisting chiefly of the ester (VIII; R = Me). The *acid* (VIII; R = H), obtained by hydrolysis with alcoholic potash, formed yellowish plates (from benzene), m. p. 237—239° (decomp.), and its solution in chloroform decolorised bromine immediately (Found: C, 81·65; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The *methyl* ester, obtained from the pure acid by means of ethereal diazomethane, crystallised from light petroleum in rosettes of almost colourless needles, m. p. 97—98° (Found: C, 82·2; H, 6·8. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

γ-1-*Phenanthrylbutyric acid* (IX).—(*a*) The foregoing crystalline ester (200 mg.) was heated with palladium-black (20 mg.) for an hour at 250—280° in an atmosphere of carbon dioxide. The product, which did not crystallise, was hydrolysed with alcoholic alkali. The resulting acid, after purification, had m. p. 152—154° and was identical with that described in the next paragraph.

(*b*) The crude distilled ester from the Reformatsky reaction (8 g.) was heated at 280—300° for 3 hours with palladium-black (0·25 g.) in an atmosphere of carbon dioxide. The acid (6·6 g.) obtained by hydrolysis of the product with alcoholic alkali was recrystallised from alcohol, sublimed at 0·2 mm., and finally crystallised from benzene. The resulting γ-1-phenanthrylbutyric acid had m. p. 155—156° (Bachmann and Struve, *loc. cit.*, give 154·5—155·5°) (Found: C, 81·9; H, 6·1. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%)

3-*Keto*-3 : 4 : 5 : 6-*tetrahydrochrysene* (X).—The acid (IX) (2 g.) was added to anhydrous hydrogen fluoride (20 c.c.) in a platinum crucible which was kept covered for 3—4 hours with occasional stirring. The hydrogen fluoride was then allowed to evaporate, and the residual solid was washed with dilute sodium carbonate solution and dried. The ketone (X) (1·9 g.) was sublimed in a vacuum and recrystallised from benzene, forming colourless leaflets, m. p. 227—228° (Bachmann and Struve give 228—229°) (Found: C, 87·65; H, 5·8. Calc. for $C_{18}H_{14}O$: C, 87·8; H, 5·7%).

3-*Chrysenol*.—Dehydrogenation of the ketone (X) (0·75 g.) by palladium-black (80 mg.) in boiling α-methylnaphthalene (nitrogen atmosphere) to 3-chrysenol (0·55 g.) was complete in 30 hours. When mesitylene was used as the solvent, only a trace of the phenol was obtained in 60 hours. This chrysenol, sublimed at 170—190°/0·2 mm. and recrystallised from benzene, formed colourless leaflets, m. p. 281—283° (in an evacuated sealed tube) (Found: C, 88·3; H, 5·0. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%). Its *methyl ether*, prepared by 6 hours' boiling with methyl iodide and sodium

methoxide in methanol, formed colourless, lustrous leaflets (from benzene–light petroleum), m. p. 167—168° (Found: C, 88·5; H, 5·35; OMe, 12·5. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4; OMe, 12·0%), and gave a *complex* with 2 : 7-dinitroanthraquinone, m. p. 283—284·5° (from xylene) (Found: C, 71·2; H, 3·6. $C_{33}H_{20}O_7N_2$ requires C, 71·2; H, 3·6%). 3-*Acetoxychrysene*, prepared from the phenol and acetic anhydride in pyridine (2 hours at 100°), formed colourless needles (from benzene), m. p. 235—236° (Found: C, 83·8; H, 5·1. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

Condensation of α-Tetralone with β-m-Methoxyphenylethylmagnesium Chloride.—*β-m*-Methoxyphenylethyl alcohol (from *m*-bromoanisylmagnesium bromide and ethylene oxide; Shoesmith and Connor, J., 1927, 2333) was converted into the chloride by treatment with dimethylaniline and thionyl chloride (compare Cook and Hewett, J., 1933, 1107). The Grignard solution prepared from this chloride (17 g.), magnesium turnings (3 g.), activated with iodine, and anhydrous ether (85 c.c.) was treated at 0° with α-tetralone (17 g.) in dry ether (20 c.c.). After being kept overnight, the mixture was worked up in the usual manner, and the product distilled. After removal of lower-boiling material (unchanged chloride and tetralone) a solution of the residual oil in ether was set aside overnight and deposited a small amount of 1 : 1′-dihydroxy-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-octahydro-1 : 1′-dinaphthyl, which formed colourless prisms, m. p. 191·5—192·5°, alone or in admixture with a specimen prepared by reduction of α-tetralone by Weidlich's procedure (*Ber.*, 1938, **71**, 1206; compare Schroeter, *loc. cit.*, and Barnett and Lawrence, *loc. cit.*) (Found: C, 81·6; H, 7·3. Calc. for $C_{20}H_{22}O_2$: C, 81·6; H, 7·5%). The ethereal solution from which this diol had been separated was distilled, the principal fraction, which did not crystallise, having b. p. 175—185°/0·5 mm. (10 g.). The highest-boiling fraction (b. p. 200°/0·5 mm.) gave crystals of 3 : 4 : 3′ : 4′-tetrahydro-1 : 1′-dinaphthyl, which had m. p. 140—141° (from ethanol), alone or mixed with an authentic specimen (Found: C, 92·6; H, 7·1. Calc. for $C_{20}H_{18}$: C, 93·0; H, 7·0%).

Dehydration and Cyclisation of the Carbinol (XI).—A mixture of the crude liquid carbinol fraction, b. p. 175—185°/0·5 mm. (see preceding paragraph), and potassium hydrogen sulphate (2 parts) was heated at 170° for an hour, and the product distilled (b. p. 160—170°/0·5 mm.). A mixture of this (2·5 g.) with anhydrous aluminium chloride (2·5 g.) and carbon disulphide (25 c.c.) was heated on the water-bath for 3 hours. After decomposition with ice and hydrochloric acid and washing with dilute sodium hydroxide solution, the solvent was removed, and the residue, dissolved in benzene–light petroleum, was adsorbed on a column of alumina. A colourless fluorescent lower band was eluted with benzene and gave crystals of 4-methoxychrysene, m. p. 245—247°, of which the complex with 2 : 7-dinitroanthraquinone had m. p. *ca.* 250° (see below). More of this methoxy-compound was obtained by methylating with methyl sulphate the alkaline washings referred to above, but the total amount was only a few mg. and the method was not investigated further.

2-*Nitro*-5-*methoxy*-α-1′-*naphthylcinnamic Acid* (XIII; X = NO_2).—A mixture of sodium 1-naphthylacetate (20·8 g.) (obtained crystalline by addition of sodium ethoxide to an ethanolic solution of the acid), 2-nitro-5-methoxybenzaldehyde (Mason, J., 1925, **127**, 1195) (18·1 g.), zinc chloride (2 g.), and acetic anhydride (180 g.) was heated in an oil-bath at 120—130° for 4 hours. The acetic anhydride was decomposed with water. The reddish, resinous material which separated was triturated with ether, which left undissolved a pink solid (20·4 g.). This, after several crystallisations from toluene–ethanol (charcoal), gave cream-coloured, rhombic crystals of the *nitro-acid* (XIII; X = NO_2), m. p. 218·5—219·5° (Found: C, 68·9; H, 4·4; N, 4·3. $C_{20}H_{15}O_5N$ requires C, 68·8; H, 4·3; N, 4·0%). The ethereal extract of the crude acid was mixed with ethanol; the solution then slowly deposited crystals which, after recrystallisation from alcohol, formed dark red needles, m. p. 160—161° (Found: C, 75·6; H, 4·3; N, 5·2%). The structure of this *compound*, which was insoluble in sodium carbonate solution, has not been investigated.

2-*Amino*-5-*methoxy*-α-1′-*naphthylcinnamic Acid* (XIII; X = NH_2).—A 40% solution of ferrous sulphate (250 c.c.) was added to a solution of the nitro-acid (10 g.) in 15% aqueous ammonia (250 c.c.), the mixture heated for 2 hours on the water-bath, filtered from iron hydroxides, and the precipitate extracted repeatedly with hot 1% aqueous ammonia. The combined filtrate and extracts were acidified with acetic acid, and the precipitated *amino-acid* (XIII; X = NH_2) (7·5 g.) was recrystallised from ethanol. A sample for analysis was purified through its hydrochloride, m. p. 246—247° (decomp.), which was sparingly soluble in cold water, and then formed colourless needles (from ethanol), m. p. 220—221° (decomp.) (Found: C, 75·6; H, 5·45; N, 4·5. $C_{20}H_{17}O_3N$ requires C, 75·2; H, 5·3; N, 4·4%).

4-*Methoxychrysene*-1-*carboxylic Acid* (XIV).—A 5% solution of sodium nitrite (17 c.c.) was added to a solution of the amino-acid (XIII; X = NH_2) (5 g.) in 8% sulphuric acid (250 c.c.). The solution was kept overnight at room temperature, during which a voluminous yellowish precipitate separated. This was dissolved by addition of ethanol (250 c.c.), the solution made just alkaline with sodium carbonate (the total volume of solution being 1 l.), and then heated at 50° for 1—2 hours. When reaction was complete, nitrogen evolution ceased and the solution no longer gave a colour with alkaline β-naphthol. The precipitate obtained by acidification was recrystallised from methanol (yield, 1·2 g.) and then several times from benzene and methanol. 4-*Methoxychrysene*-1-*carboxylic acid* (XIV) formed long, pinkish needles, m. p. 244—245° (Found: C, 79·3; H, 4·5. $C_{20}H_{14}O_3$ requires C, 79·4; H, 4·6%). Its crystalline chloride, prepared by the action of thionyl chloride at 40°, reacted with boiling methanol to give the *methyl* ester, which crystallised from methanol in almost colourless needles, m. p. 172—173° (Found: C, 79·8; H, 5·0; OMe, 19·9. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1; OMe, 19·6%).

4-*Methoxychrysene*.—Decarboxylation of the acid (XIV) (1 g.) with copper chromite (0·25 g.) in pure quinoline (14 c.c.) at 230—250° (bath temp.) was complete in 4 hours. A solution of the neutral product in tetrachloroethane was purified by passage through a column of alumina. On concentration, 4-*methoxychrysene* (0·75 g.) crystallised and formed colourless leaflets (from benzene), m. p. 250—251° (Found: C, 88·65; H, 5·5; OMe, 11·8. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4; OMe, 12·0%). Its scarlet *complex* with 2 : 7-dinitroanthraquinone had m. p. 240—241° (from xylene) (Found: C, 71·2; H, 3·7. $C_{33}H_{20}O_7N_2$ requires C, 71·2; H, 3·6%).

4-*Chrysenol*.—A solution of the methoxy-compound (250 mg.) in acetic acid (10 c.c.) and hydrobromic acid (*d*, 1·7; 7 c.c.) was boiled for 2 hours, poured into water, the precipitate dissolved in dilute sodium hydroxide, and the filtered solution acidified. The resulting 4-*chrysenol* was sublimed in a high vacuum and recrystallised from benzene, forming pinkish needles, m. p. 273—275° (in an evacuated sealed tube) (Found: C, 88·4; H, 5·0. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%). The *acetate*, obtained from this chrysenol by brief boiling with acetic anhydride and a little pyridine, formed almost colourless needles (from benzene), m. p. 229—230° (Found: C, 84·25; H, 4·9. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

4-*Methoxy*-1 : 2-*chrysaquinone*.—A solution of the acid (XIV) (0·1 g.) and sodium dichromate (0·6 g.) in acetic acid (7 c.c.) was boiled for an hour and poured into water. The precipitate, dissolved in benzene, was adsorbed on a column of alumina. On developing the chromatogram with benzene there were obtained (*a*) a dark band at the top of the column, (*b*) a red band below this, and (*c*) the least strongly adsorbed band which fluoresced strongly in ultra-violet light. The red band (*b*) was eluted with chloroform, and the chromatography repeated. The material so purified gave deep red, rhombic needles, m. p. 233—234° (from benzene), of 4-*methoxy*-1 : 2-*chrysaquinone* (Found: C, 79·0; H, 4·3. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·2%).

The band (*c*), when eluted, gave long, yellowish crystals, m. p. 236—238°, which, after sublimation in a high vacuum and crystallisation from benzene, had m. p. 239—240°, depressed strongly by admixture with the red 1 : 2-quinone. Analysis suggested that this was an isomeric *quinone*, possibly 4-methoxy-3 : 6-chrysaquinone, although this structure

does not readily accommodate the fact that decarboxylation had occurred during oxidation (Found: C, 79·3; H, 4·1. $C_{19}H_{12}O_3$ requires C, 79·2; H, 4·2%).

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