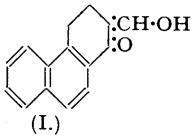
97. *Polycyclic Aromatic Hydrocarbons. Part XXXI. Some Nitrogenous Analogues of Chrysene, Pyrene and* 3 : 4-*Benzphenanthrene.*

By J. W. Cook and W. H. S. Thomson.

1- and 4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene have been used as the starting points in syntheses of 6-*azachrysene* (IV), 1-*azapyrene* (VI; R = H), 5-*methyl*-4 : 6-*diazachrysene*, 3 : 4-*benz*-5-*azaphenanthrene* (V), 3 : 4-*benz*-5 : 7-*diazaphenanthrene* (X; R = H), and some of their homologues and derivatives. In pyrimidine ring synthesis it was found that condensation of acetamidine with 2-chloromethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene readily took place, but failed with the corresponding 2-hydroxymethylene compound.

In view of the inhibitory action on tumour growth of many carcinogenic polycyclic aromatic hydrocarbons attention has been devoted to the synthesis for biological test of many derivatives of these compounds (compare Badger and Cook, J., 1939, 802; 1940, 409; Cook and Preston, J., 1944, 553). The marked growth-inhibitory action of certain polycyclic compounds containing nitrogen atoms in the ring system (see 20th *Annual Report of the British Empire Cancer Campaign*, 1943, p. 19) suggested the examination of more compounds of this type, and we have investigated the synthesis of nitrogenous compounds related to chrysene and 3 : 4-benzphenanthrene. Some homologues of these two hydrocarbons have carcinogenic properties, but on the whole they are much less potent than derivatives of 1 : 2-benzanthracene, and it is this consideration which has led to our selection of the former types of ring-system. Nitrogenous analogues of all three types have been described by other workers (*e.g.*, Borsche *et al.*, *Annalen*, 1937, **532**, 127, 146; 1942, **550**, 160; Mosettig and Krueger, *J. Org. Chem.*, 1938, **3**, 317; Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1940, **62**, 1640).

2-*Hydroxymethylene*-1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (I) condensed smoothly with cyanoacetamide (compare Sen-Gupta, J., 1915, **107**, 1347) to give 5-*hydroxy*-4-*cyano*-1 : 2-*dihydro*-6-*azachrysene* (II), or the tautomeric lactam. This was hydrolysed by hydrochloric acid at 150° to the corresponding *hydroxy-acid*, which was decarboxylated by heat to 5-*hydroxy*-1 : 2-*dihydro*-6-*azachrysene* (III; X = OH).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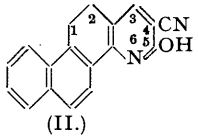
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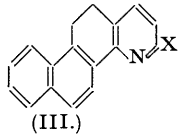
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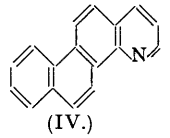
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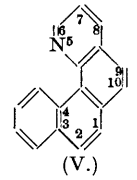
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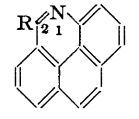
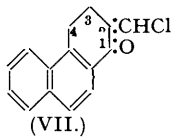

(VI.)

Treatment of the hydroxy-compound (III; X = OH) with phosphorus pentachloride led, in small yield, to a *chloro*-compound, m. p. 179°, in which dehydrogenation had occurred as well as replacement of hydroxyl. With phosphorus oxychloride, however, 5-*chloro*-1 : 2-*dihydro*-6-*azachrysene* (III; X = Cl), m. p. 115°, was readily formed, and this was converted by palladium-black, in boiling tetralin, into 6-*azachrysene* (IV). In the condensation of (I) with cyanoacetamide an *iso*quinoline rather than a quinoline derivative could arise (compare Basu, *J. Indian Chem. Soc.*, 1931, **8**, 119; Basu and Banerjee, *Annalen*, 1935, **516**, 243). That the products are correctly formulated, nevertheless, was shown by the alternative synthesis of 6-azachrysene from 1-aminophenanthrene by the Skraup reaction. 4-Aminophenanthrene was similarly converted into 3 : 4-*benz*-5-*azaphenanthrene* (V).

4-Acylamidophenanthrenes were readily dehydrated by phosphoric oxide in boiling xylene to 1-*azapyrene* and its derivatives (VI; R = H, Me or Ph). The parent compound (VI; R = H) should be identical with thebenidine, obtained by Vongerichten (*Ber.*, 1901, **34**, 767) by distillation of the alkaloid thebenine with zinc dust. The m. p. of our synthetic product (157—159°) is somewhat higher than that given by Vongerichten for his base (m. p. 144—148°), but this does not exclude their identity. This synthesis of azapyrenes is analogous to the method used by Morgan and Walls (J., 1931, 2447) to obtain phenanthridines.

Condensation of the hydroxymethylene ketone (I) with acetamidine to give a pyrimidine derivative could not be brought about. Under the conditions used, the ketone underwent auto-oxidation to 1-*hydroxy*-2-*phenanthraldehyde*. The corresponding *chloromethylene ketone* (VII) readily condensed with acetamidine in presence of sodium ethoxide to give 5-*methyl*-1 : 2-*dihydro*-4 : 6-*diazachrysene* (VIII), which was dehydrogenated by heating with palladium to 5-*methyl*-4 : 6-*diazachrysene*. By similar reactions, using formamidine and acetamidine, 3-*chloromethylene*-4-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (IX) was converted into 3 : 4-*benz*-5 : 7-*diazaphenanthrene* (X; R = H) and 6-*methyl*-3 : 4-*benz*-5 : 7-*diazaphenanthrene* (X; R = Me).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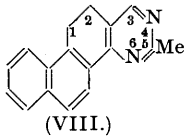
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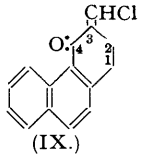
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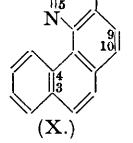
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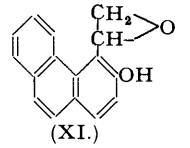
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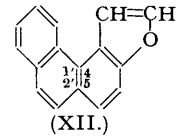
(XII.)

One of the difficulties of Windaus's structure for colchicine (*Annalen*, 1924, **439**, 59) is concerned with the behaviour of colchiceine, which reacts as a hydroxymethylene ketone rather than in the tautomeric aromatic *o*-hydroxy-aldehyde form. Simple hydroxy-aldehydes of the type of salicylaldehyde do not show this behaviour, and it seemed of interest to examine an *o*-hydroxy-aldehyde of the phenanthrene series. An attempt was made to methylate 3-hydroxy-4-phenanthraldehyde with diazomethane, in order to determine whether the resulting ether were derived from the hydroxy-aldehyde form or the hydroxymethylene ketone form. The product of this reaction appeared still to contain a phenolic hydroxyl group but did not react with 2 : 4-dinitrophenylhydrazine; it is regarded as the *oxide* (XI), with which structure the analytical figures are in good agreement (compare Arndt, Eistert, and Ender, *Ber.*, 1928, **61**, 1118; 1929, **62**, 44). When heated with alcoholic hydrogen chloride, this oxide lost a molecule of water and passed into an alkali-insoluble compound which did not react with 2 : 4-dinitrophenylhydrazine. This compound is believed to be 4 : 5-(1′ : 2′-*naphtha*)*coumarone* (**XII**).

Experimental.

2-Hydroxymethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (I).—Sodium wire (7·5 g.), followed by ethyl formate (27 c.c.), was added to a cold solution of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (60 g.) (Haworth, J., 1932, 1125) in dry toluene (300 c.c.). Reaction set in, and a brown solid separated. After being kept overnight, the paste was treated with water. The aqueous solution, separated from the toluene layer, was washed with ether and acidified with dilute sulphuric acid. This precipitated an oil which soon became a sandy brown solid. After crystallisation from methanol (charcoal), *2-hydroxymethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene* (I) formed straw-coloured crystals (45 g.), m. p. 84—85°, giving an intense green colour with ferric chloride in methanol (Found : C, 80·2; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%). The *methyl ether*, prepared from the hydroxymethylene compound and ethereal diazomethane, formed colourless plates (from methanol), m. p. 96—97° (Found : C, 80·5; H. 6·0. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

2-Chloromethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (VII).—Thionyl chloride (6 g.) was added to finely powdered 2-hydroxymethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (6·7 g.). Violent effervescence ensued, and the solution was kept for an hour at room temperature. The deep red solution was then poured into ice-cold 2N-sodium hydroxide (500 c.c.), and after 2 hours the solid was collected, washed and dried. The crude chloro-compound was extracted (Soxhlet) with light petroleum, and the material recovered from the extract was recrystallised from ethanol and then light petroleum (yield, 5·5 g.). The *chloro-ketone* (VII) crystallised from hexane in agglomerates of thick colourless plates, m. p. 106—107° (Found : C, 74·3; H, 4·5. $C_{15}H_{11}OCl$ requires C, 74·2; H, 4·5%).

2-Aminomethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene was formed when dry ammonia was passed into a solution of 2-hydroxymethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (5 g.) in chloroform (50 c.c.). After 4 hours the precipitate was collected and recrystallised from benzene, forming tufts of red needles, m. p. 147—149° (Found : C, 80·9; H, 5·6. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8%).

3-Hydroxymethylene-4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (7·3 g.) was obtained from 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (10 g.) (Haworth, *loc. cit.*) in the manner described above for the 1-keto-compound. It formed lemon-yellow tablets (from light petroleum), m. p. 39—41° (Found : C, 80·25; H, 5·5. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%), and reacted with ethereal diazomethane to give the *methyl ether*; this crystallised from acetone in thick straw-coloured rods, m. p. 110—112° (Found : C, 80·7; H, 5·8. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%).

3-Chloromethylene-4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (15 g.) was prepared from the hydroxymethylene ketone (17·7 g.) and thionyl chloride (18 g.) as described above for its isomeride, except that the reaction was completed by heating on the water-bath (½ hour). The chloro-compound (IX) crystallised from light petroleum as long greenish-white plates, m. p. 94—96° (Found : C, 74·3; H, 4·5. $C_{15}H_{11}OCl$ requires C, 74·2; H, 4·5%).

5-Hydroxy-4-cyano-1 : 2-dihydro-6-azachrysene (II).—A solution of cyanoacetamide (3·4 g.) in water (25 c.c.) and then piperidine (1·5 c.c.) were added to a solution of 2-hydroxymethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (9 g.) in aqueous ethanol (250 to 500 c.c.), and the mixture kept at 40° for 100 hours. The brown powder which had separated was collected, more piperidine (1·5 c.c.) was added to the filtrate, after concentration, and this was heated at 40° for a further 100 hours. The product which separated was added to the first portion and recrystallised four times from acetic acid (charcoal). The *cyano*-compound (II) formed yellow microscopic needles, m. p. 364—366° (Found : C, 67·6; H, 5·0. $C_{18}H_{12}ON_2,2C_2H_4O_2$ requires C, 67·4; H, 5·1%).

5-Hydroxy-1 : 2-dihydro-6-azachrysene-4-carboxylic Acid.—The cyano-compound (II) (0·5 g.) was heated in a sealed tube at 150° for 3 hours with hydrochloric acid (*d* 1·19; 10 c.c.). The resulting *acid* formed soft fine yellow needles, m. p. 324—325° (from ethylene glycol monomethyl ether), soluble in sodium carbonate solution (Found : C, 74·5; H, 4·5; N, 5·55. $C_{18}H_{13}O_3N$ requires C, 74·2; H, 4·5; N, 4·8%). Ethereal diazomethane converted this acid into the alkali-insoluble *methyl 5-methoxy-1 : 2-dihydro-6-azachrysene-4-carboxylate*, colourless needles, m. p. 118—120° (from ethanol) (Found : C, 75·5; H, 5·25; N, 4·5. $C_{20}H_{17}O_3N$ requires C, 75·2; H, 5·3; N, 4·4%). The acid was decarboxylated by heating for 10 minutes at 340—350°. The product was sublimed at 200°/0·2 mm., and the sublimate was crystallised from methanol, giving a small amount of sparingly soluble, pale yellow leaflets, m. p. 344—345°, probably 5-hydroxy-6-azachrysene (see below), and a larger amount of *5-hydroxy-1 : 2-dihydro-6-azachrysene* (III; X = OH), which was obtained more conveniently in 90% yield from the cyano-compound (II) by heating with fuming hydrochloric acid in a sealed tube at 170—180° for 4 hours. This dihydro-compound formed long yellow prisms (from methanol), m. p. 275—276° (Found : C, 82·4; H, 5·0; N, 5·8. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3; N, 5·7%). It dissolved in hot sodium hydroxide solution (but not in carbonate), and the solution, when cooled, deposited colourless leaflets of the sodium salt, m. p. 526—528°. The sodium salt (0·25 g.), when heated at 100° for 1½ hours with methyl sulphate (5 c.c.), gave a water-insoluble *compound*, which crystallised from acetone in greenish-yellow rhombs, m. p. 211—212° (Found : C, 60·3; H, 4·4; N, 4·4%). The nature of this compound, which contained sulphur, has not been investigated further. The hydroxy-compound was recovered unchanged when its sodium salt was heated with methyl iodide in ethanol, and attempted methylation with diazomethane in ether–dioxan was likewise unsuccessful. *5-Acetoxy-1 : 2-dihydro-6-azachrysene* (III; X = O·COMe), prepared from the hydroxy-compound (0·25 g.) by heating on the water-bath (½ hour) with acetic anhydride (0·2 g.) in pyridine (5 c.c.), crystallised from ethanol in colourless needles, m. p. 145—147°, having a violet or blue fluorescence (Found : C, 78·8; H, 5·2; N, 5·0. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 5·2%). *5-Benzoyloxy-1 : 2-dihydro-6-azachrysene* (III; X = O·COPh), prepared from hydroxy-compound and benzoyl chloride by the Schotten–Baumann method, formed short colourless needles (from ethanol), m. p. 209—210° (Found : C, 81·95; H, 4·7; N, 4·2. $C_{24}H_{17}O_2N$ requires C, 82·1; H, 4·8; N, 4·0%).

5-Hydroxy-6-azachrysene was obtained in good yield from its dihydride (III; X = OH) (0·2 g.) by heating with palladium-black (20 mg.), first at 290—300° for an hour and then at 350° for 1¼ hours. The volume of hydrogen liberated corresponded with loss of one molecule from the substance. The product crystallised from ethanol in almost colourless needles, m. p. 355—365° (decomp.) (Found : C, 84·0; H, 4·4; N, 5·5. $C_{17}H_{11}ON$ requires C, 83·3; H, 4·5; N, 5·7%). Its *acetate*, prepared with acetic anhydride in pyridine at 100°, formed colourless silky needles (from ethanol), m. p. 149—151° (Found : C, 79·4; H, 4·3. $C_{19}H_{13}O_2N$ requires C, 79·4; H, 4·5%).

5-Chloro-6-azachrysene. A mixture of the hydroxy-compound (III; X = OH) (1 g.), phosphorus pentachloride (1 g.), and chlorobenzene (60 c.c.) was heated in an oil-bath at 150° for 3½ hours. The solvent and phosphorus oxychloride were removed under reduced pressure, the last traces being eliminated by a second evaporation after addition of benzene. Fractional crystallisation of the residue from acetic acid gave 5-chloro-6-azachrysene (0·2 g.) as colourless leaflets, m. p. 179—180°, and the more soluble 5-hydroxy-6-azachrysene (0·2 g.), m. p. 362—364° (decomp.), formed by dehydrogenation without replacement of hydroxyl (Found : C, 83·6; H, 4·5; N, 5·6%). This sample did not depress the m. p. of the specimen prepared as described in the preceding paragraph.

5-Chloro-1 : 2-dihydro-6-azachrysene (III; X = Cl).—A mixture of the hydroxy-compound (III; X = OH) (2·7 g.) and phosphorus oxychloride (11 c.c.) was heated in a sealed tube at 175° for 7 hours. After cooling, the contents of the tube were poured on ice, and the solid product was collected and recrystallised from aqueous acetic acid (yield, 2·1 g.). The *chloro*-compound (III; X = Cl) formed large colourless plates, m. p. 115—116° (Found : C, 77·0; H, 4·4; N, 5·1. $C_{17}H_{12}NCl$ requires C, 76·85; H, 4·5; N, 5·3%).

6-*Azachrysene* (IV).—(*a*) A solution of 5-chloro-6-azachrysene (0·2 g.), m. p. 179°, in boiling tetralin (25 c.c.) was boiled under reflux for 19 hours with palladium-black (20 mg.). Hydrogen chloride was slowly evolved. The filtered solution was evaporated under reduced pressure, the residue re-evaporated with benzene, and the residual brown oil triturated with light petroleum; it then crystallised. The *picrate* of 6-azachrysene, prepared from this material in ethanol, formed fine yellow needles, m. p. 256—258° (from ethanol) (Found: C, 60·4; H, 2·9; N, 12·2. $C_{17}H_{11}N,C_6H_3O_7N_3$ requires C, 60·3; H, 3·1; N, 12·2%). The free base was obtained from the pure picrate by boiling with dilute aqueous ammonia. After recrystallisation from aqueous acetone and then hexane, 6-*azachrysene* (IV) formed stout colourless prisms, m. p. 137—138° (Found: C, 89·3; H, 4·6; N, 6·1. $C_{17}H_{11}N$ requires C, 89·1; H, 4·8; N, 6·1%).

(*b*) 5-Chloro-1 : 2-dihydro-6-azachrysene (2·1 g.) was similarly converted into 6-azachrysene by palladium-black in boiling tetralin. The free base (1·2 g.) obtained from the purified picrate was identical with that obtained as described under (*a*). The completely aromatic character of this compound was confirmed by the fact that it did not evolve hydrogen when heated with palladium-black at 300°.

(*c*) 1-Aminophenanthrene was prepared from the oxime of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene by Schroeter's method, the procedure used being essentially that of Langenbeck and Weissenborn (*Ber.*, 1939, **72**, 726). Concentrated sulphuric acid (1 c.c.) was added, with stirring, to a mixture of 1-aminophenanthrene (1 g.), crystalline ferrous sulphate (0·2 g.), glycerol (2 g.), and nitrobenzene (1 c.c.), and the whole was heated first at 145° in an oil-bath for an hour and then over a free flame for 2 hours. The product was freed from nitrobenzene by steam-distillation, and the filtered solution boiled with charcoal. The solution (about 150 c.c.) was then poured into saturated brine (500 c.c.); this precipitated the hydrochloride of the base as a brown solid, which was collected and treated with aqueous ammonia. The crude base was purified through its picrate, which melted at 258—260° alone or mixed with the picrate as described under (*a*). The regenerated base had m. p. 137—139°, in agreement with the figure given above for 6-azachrysene.

3 : 4-*Benz*-5-*azaphenanthrene* (V).—4-Aminophenanthrene was prepared by the following modification of the method of Langenbeck and Weissenborn (*loc. cit.*) : Dry hydrogen chloride was passed for 3 hours through a solution, heated on the water-bath, of the oxime, m. p. 171—173° (compare Schroeter, Müller, and Huang, *Ber.*, 1929, **62**, 658) of 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (5·2 g.) in acetic acid (25 c.c.) and acetic anhydride (3 c.c.). After cooling, with continued passage of hydrogen chloride, the precipitate, which separated only after vigorous scratching, was collected, washed with ether, and dissolved in hot water (400 c.c.) containing a little hydrochloric acid. Addition of ammonia to the cold filtered solution precipitated 4-aminophenanthrene (0·7 g.). This melted at 63—64°, in agreement with Krueger and Mosettig (*J. Org. Chem.*, 1938, **3**, 340) but not in agreement with Langenbeck and Weissenborn (*loc. cit.*) or with Schmidt (*Ber.*, 1911, **44**, 1502; 1922, **55**, 1194).

A mixture of 4-aminophenanthrene (1 g.), sodium *m*-nitrobenzenesulphonate (2 g.), concentrated sulphuric acid (2·5 c.c.), water (2·5 c.c.), and glycerol (1·5 c.c.) was boiled under reflux for 2¾ hours. The dark red solution was poured into water (100 c.c.), boiled with charcoal, and filtered. Addition of ammonia gave a dark precipitate, which after crystallisation from light petroleum and then aqueous methanol had m. p. 93—94° (yield, 0·25 g.). The base was purified through its hydrochloride, precipitated by passing hydrogen chloride into a solution of the base in benzene. This salt was dissolved in water, and the base was precipitated with ammonia and crystallised from methanol. 3 : 4-*Benz*-5-*azaphenanthrene* (V) formed colourless rectangular plates, m. p. 95—96° (Found: C, 89·0; H, 5·0; N, 6·1. $C_{17}H_{11}N$ requires C, 89·1; H, 4·8; N, 6·1%), and gave a *picrate*, small yellow plates (from methanol), m. p. 200—201° (Found: C, 60·1; H, 3·3. $C_{17}H_{11}N,C_6H_3O_7N_3$ requires C, 60·3; H, 3·1%).

1-*Azapyrene* (VI; R = H).—4-*Formamidophenanthrene* was prepared from 4-aminophenanthrene (1·9 g.) and 98—100% formic acid (0·5 g.) by heating on the water-bath for 2 hours. The solid mass was ground under acidulated water and recrystallised from ethanol, forming long, colourless, silky needles, m. p. 208—210° (Found: C, 81·4; H, 4·9; N, 6·2. $C_{15}H_{11}ON$ requires C, 81·45; H, 5·0; N, 6·3%). For dehydration, a solution of this formyl compound (1·8 g.) in purified xylene (250 c.c.) was heated for ½ hour in an oil-bath at 160° with phosphoric oxide (6 g.). The residue which remained after decantation of the xylene solution was dissolved in water, the aqueous solution freed from traces of xylene by boiling, and the base precipitated by ammonia. It was purified through its *picrate*, m. p. 250—253° after softening (from acetic acid) (Found: C, 58·5; H, 2·7; N, 13·0. $C_{15}H_9N,C_6H_3O_7N_3$ requires C, 58·3; H, 2·8; N, 13·0%), and the base regenerated by treatment with ammonia. 1-*Azapyrene* (VI; R = H) (0·55 g.) formed colourless needles, m. p. 157—159° (Found: C, 88·6; H, 4·5; N, 6·8. $C_{15}H_9N$ requires C, 88·7; H, 4·4; N, 6·9%).

2-*Methyl*-1-*azapyrene* (VI; R = Me).—4-Acetamidophenanthrene was prepared by acetylating the amine with acetic anhydride in pyridine. It had m. p. 198—200° (from benzene–light petroleum) (Krueger and Mosettig, *loc. cit.*, give m. p. 196—197°). Cyclisation with phosphoric oxide was carried out as described for the formamido-compound. 2-*Methyl*-1-*azapyrene* (VI; R = Me) was purified through its *picrate*, orange-yellow needles, m. p. 240—241° (from ethanol) (Found: C, 59·3; H, 3·2; N, 12·7. $C_{16}H_{11}N,C_6H_3O_7N_3$ requires C, 59·2; H, 3·1; N, 12·6%), and then formed colourless, thick, rhombic tablets (from hexane), m. p. 139—141° (yield, 0·65 g. from 1·5 g. of 4-acetamidophenanthrene) (Found: C, 88·7; H, 5·0; N, 6·4. $C_{16}H_{11}N$ requires C, 88·5; H, 5·1; N, 6·45%).

2-*Phenyl*-1-*azapyrene* (VI; R = Ph).—4-Benzamidophenanthrene was prepared from 4-aminophenanthrene by treatment with benzoyl chloride in pyridine. It crystallised from benzene–light petroleum in tufts of colourless needles, m. p. 216—218°, in agreement with Krueger and Mosettig (*loc. cit.*). From the mother-liquors was isolated 4-*dibenzoylaminophenanthrene* in thick colourless crystals, m. p. 190—192° (Found: C, 83·9; H, 4·9; N, 3·6. $C_{28}H_{19}O_2N$ requires C, 83·8; H, 4·7; N, 3·5%). Cyclisation of 4-benzamidophenanthrene with phosphoric oxide was effected as described for the formamido-compound. 2-*Phenyl*-1-*azapyrene* (VI; R = Ph) formed colourless silky needles (from ethanol), m. p. 143—144° (Found: C, 90·5; H, 4·7; N, 5·0. $C_{21}H_{13}N$ requires C, 90·3; H, 4·7; N, 5·0%), and gave a *picrate* which formed golden-yellow blades (from ethanol), m. p. 256—258° (Found: N, 10·9. $C_{21}H_{13}N,C_6H_3O_7N_3$ requires N, 11·0%).

Attempted Condensation of 2-*Hydroxymethylene*-1-*keto*-1 : 2 : 3 : 4-*tetrahydrophenanthrene with Acetamidine.*—A solution of the hydroxymethylene ketone (2·5 g.) in ethanol (30 c.c.) was added to a solution of sodium ethoxide (from 225 mg. of sodium and 5 c.c. of ethanol), and the mixture added to a solution of acetamidine hydrochloride (1·05 g.) in ethanol (20 c.c.). After being kept at room temperature for 5 days, the brown solution was poured into water (1 l.). After a month the suspended solid was collected, dried, and extracted (Soxhlet) with light petroleum. The extract gave red needles, which on repeated crystallisation from light petroleum were transformed into yellow plates, m. p. 125—127°, consisting of 1-*hydroxy*-2-*phenanthraldehyde* (Found: C, 80·9; H, 4·4. $C_{15}H_{10}O_2$ requires C, 81·0; H, 4·5%). The substance, which did not contain nitrogen, was soluble in sodium hydroxide solution, and with hydroxylamine hydrochloride in pyridine at 100° gave an *oxime*, crystallising from light petroleum in fawn needles, m. p. 188—189° (Found: C, 76·6; H, 4·6; N, 6·0. $C_{15}H_{11}O_2N$ requires C, 76·0; H, 4·6; N, 5·9%). When this reaction was attempted by heating the reactants at 100° for 2 hours and then keeping at room temperature in the absence of air, a small amount of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene was isolated.

5-*Methyl*-1 : 2-*dihydro*-4 : 6-*diazachrysene* (VIII).—Acetamidine hydrochloride (1·9 g.) was added to a solution of

2-chloromethylene-1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (VII) (4·85 g.) in ethanol (80 c.c.), followed by a solution of sodium ethoxide (from 1·4 g. of sodium in 40 c.c. of ethanol). Sodium chloride was precipitated and the solution became deep red; it was heated on the water-bath for 1½ hours, kept overnight, concentrated to half its volume under reduced pressure, and then poured into dilute hydrochloric acid (2½ l.). The heated solution was clarified with charcoal, cooled, and made alkaline with ammonia. After standing overnight, the colourless precipitate of the *pyrimidine* derivative (VIII) was collected (3 g.) and recrystallised from light petroleum, and then hexane. It formed thin colourless blades, m. p. 142—143° (Found: C, 83·0; H, 5·7; N, 11·2. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7; N, 11·4%), and gave a yellow, microcrystalline *picrate* (from ethanol), m. p. 225—227° (decomp.) (Found: C, 58·2; H, 3·8; N, 14·9. $C_{17}H_{14}N_2,C_6H_3O_7N_3$ requires C, 58·1; H, 3·6; N, 14·7%).

This dihydro-compound (0·5 g.) was rapidly dehydrogenated by palladium-black (50 mg.) at 200—250° to *5-methyl-4 : 6-diazachrysene* (0·25 g.), which formed pale greenish-yellow leaflets (from ethanol), m. p. 196—197°, soluble in cold dilute hydrochloric acid (Found: C, 83·4; H, 4·8; N, 11·5. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·9; N, 11·5%). Its *picrate* formed orange prisms (from ethanol), m. p. 230—231° (decomp.) (Found: C, 58·3; H, 3·1; N, 14·9. $C_{17}H_{12}N_2,C_6H_3O_7N_3$ requires C, 58·3; H, 3·2; N, 14·8%).

9 : 10-Dihydro-3 : 4-benz-5 : 7-diazaphenanthrene.—Formamidine hydrochloride (Pinner, *Ber.*, 1883, **16**, 352, 1647) (1·6 g.) and then sodium ethoxide (from 1·4 g. of sodium in 40 c.c of ethanol) were added to a solution of 3-chloromethylene-4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (IX) (4·85 g.) in ethanol (80 c.c.). The red solution was heated on the water-bath for 1½ hours, then kept at room temperature overnight, and the product isolated as in the case of the analogous pyrimidine derivative already described. The crude base was an oil, which was purified by passing its solution in benzene through a column of alumina. The purified *9 : 10-dihydro-3 : 4-benz-5 : 7-diazaphenanthrene* (2·8 g.) formed colourless prisms (from light petroleum), m. p. 70—71° (Found: C, 82·9; H, 5·4; N, 12·2. $C_{16}H_{12}N_2$ requires C, 82·75; H, 5·2; N, 12·1%). Its *picrate* crystallised from ethanol in deep yellow prisms, m. p. 238—239° (decomp.) (Found: C, 57·4; H, 3·1. $C_{16}H_{12}N_2,C_6H_3O_7N_3$ requires C, 57·3; H, 3·25%).

3 : 4-Benz-5 : 7-diazaphenanthrene.—The dihydro-compound (1·8 g.) was heated at 200° for 4 hours with palladium-black (0·2 g.) in an atmosphere of carbon dioxide. The product was purified by crystallisation from light petroleum and then ethanol (charcoal), then sublimation at 140°/0·3 mm., and finally crystallisation from ethanol, and then hexane. *3 : 4-Benz-5 : 7-diazaphenanthrene* (X; R = H) formed small colourless rhombs, m. p. 155—156° (Found: C, 83·3; H, 4·5; N, 12·2. $C_{16}H_{10}N_2$ requires C, 83·5; H, 4·35; N, 12·2%). Its *picrate*, prepared in ethanol, formed fine yellow needles, m. p. 255—258° (decomp.) (Found: C, 57·5; H, 2·9. $C_{16}H_{10}N_2,C_6H_3O_7N_3$ requires C, 57·5; H, 2·8%).

6-Methyl-9 : 10-dihydro-3 : 4-benz-5 : 7-diazaphenanthrene was prepared from 3-chloromethylene-4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (4·85 g.) and acetamidine hydrochloride (1·9 g.) as described for 5-methyl-1 : 2-dihydro-4 : 6-diazachrysene. It crystallised from hexane or light petroleum in thick colourless prisms, m. p. 102—103° (Found: C, 83·0; H, 5·6; N, 11·35. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7; N, 11·4%), and gave a *picrate* which formed fine yellow needles (from ethanol), m. p. 216—217° (decomp.) (Found: C, 58·3; H, 3·6; N, 14·8. $C_{17}H_{14}N_2,C_6H_3O_7N_3$ requires C, 58·1; H, 3·6; N, 14·7%).

Dehydrogenation to *6-methyl-3 : 4-benz-5 : 7-diazaphenanthrene* (X; R = Me) with palladium-black at 200° (4 hours) in an atmosphere of carbon dioxide was carried out in the usual way. The product, obtained in good yield, formed long, white, silky needles (from hexane), m. p. 133—134° (Found: C, 83·5; H, 5·0; N, 11·5. $C_{17}H_{12}N_2$ requires C, 83·6; H, 4·9; N, 11·5%). This base gave a yellow *picrate*, m. p. 217—219° (decomp.) (Found: C, 58·3; H, 3·4; N, 14·8. $C_{17}H_{12}N_2,C_6H_3O_7N_3$ requires C, 58·3; H, 3·2; N, 14·8%).

Action of Diazomethane on 3-Hydroxy-4-phenanthraldehyde.—A solution of diazomethane (from 4 g. of nitrosomethylurea) in ether (50 c.c.) was added to a solution of 3-hydroxy-4-phenanthraldehyde (Smith, J., 1916, **109**, 568) (1·6 g.) in ether (25 c.c.), and the mixture kept at room temperature for 3 days. The gum obtained by evaporation was treated for several hours with boiling light petroleum and the dark coloured solid which remained was collected, rapidly washed with a little cold benzene, and recrystallised three times from benzene–light petroleum (charcoal). *3-Hydroxy-4-phenanthrylethylene oxide* (XI) formed colourless narrow blades, m. p. 152—153° (Found: C, 81·6; H, 4·95. $C_{16}H_{12}O_2$ requires C, 81·4; H, 5·1%). A solution of this oxide (50 mg.) in ethanol (3·5 c.c.), concentrated hydrochloric acid (1 c.c.), and water (2 c.c.) was boiled for 2 hours. After cooling, the solution was kept overnight and the colourless plates which crystallised were sublimed at 95°/3 mm. *4 : 5-(1′ : 2′-Naphtha)coumarone* (XII) formed a colourless, microcrystalline powder, m. p. 114—115° (Found: C, 87·7; H, 4·4. $C_{16}H_{10}O$ requires C, 88·0; H, 4·6%).

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