The Constituents of High-boiling Petroleum Distillates. Part I. Preliminary Studies.

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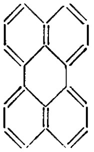
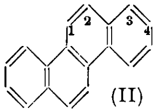
Perylene, an alkylchrysene, and two oxygen-containing compounds have been isolated from an extract of an American crude oil distillate. Several chrysene homologues with large alkyl substituents have been synthesised for comparison with the aforesaid alkylchrysene.

Very little is known about the detailed chemical composition of high-boiling petroleum fractions. It has been established that they consist largely of complex mixtures of hydrocarbons of various types, including aromatic compounds, but in only a few instances have individual components been isolated from them (compare Van Nes and Van Westen, " Aspects of the Constitution of Mineral Oils," Elsevier Publishing Co., Amsterdam, 1951). The aromatic constituents can usually be concentrated by selective extraction from the oil by means of solvents, liquid sulphur dioxide being used industrially for this purpose. We have applied chromatography to several sulphur dioxide extracts which were placed at our disposal. From one of them, prepared from an American petroleum, we have isolated four crystalline compounds. These experiments constitute exploratory work in an investigation sponsored by the Medical Research Council with a view to the identification of carcinogenic components of mineral oils. The experience gained will be applied in the systematic examination of carcinogenic fractions which have been accumulated in a carefully planned fractional distillation of three selected crude oils, each fraction having been submitted to biological test.

One of the crystalline substances isolated from the extract was a yellow substance $C_{20}H_{12}$, identified as perylene (I) by comparison with an authentic specimen and by its ultra-violet absorption spectrum (Clar, *Ber.*, 1932, **65**, 848).



(I)



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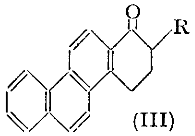


(III)

A second compound, $C_{25}H_{24}$ or $C_{26}H_{26}$, was shown by its ultra-violet absorption spectrum (Fig. 1) to be a derivative of chrysene $C_{18}H_{12}$ (II). It must therefore carry substituents totalling seven or eight carbon atoms, and incorporating a double bond or a ring. Since the compound did not absorb hydrogen in presence of palladium–charcoal and was recovered from attempted dehydrogenation with palladium-black at 300°, it seems probable that the structure includes a ring in a side chain or a five-membered ring fused to the chrysene nucleus. It has not been possible to distinguish between these alternatives.

Attempts to establish the number and orientation of substituents by degradative experiments were unsuccessful. Oxidation with sodium dichromate in acetic acid yielded a mixture of quinones which was converted into an inseparable mixture of acids by further treatment with alkaline hydrogen peroxide. Reaction with alkaline potassium permanganate and with dilute nitric acid likewise led to mixtures of acidic products. Other experiments with *N*-bromosuccinimide, lead tetra-acetate, and selenium dioxide gave no useful result.

For comparative purposes a number of chrysene derivatives with large alkyl groups was synthesised (see Table). These were generally much lower melting than the hydrocarbon from the oil, only those with the substituent at position 4 having comparable melting points. Comparison of the ultra-violet spectra of these compounds with that of the unknown hydrocarbon suggests that the latter is probably a di-, or possibly a tri-substituted chrysene. The position of the substituents is difficult to decide from the spectrum, but it seems likely that no substituent is present at positions 1, 6, 7, or 12 (compare Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3252). It is of interest that another chrysene derivative, 3-methylchrysene, has recently been isolated from a fraction of an American crude oil (Moore, Thorpe, and Mahoney, *ibid.*, 1953, **75**, 2259).

FIG. 1.

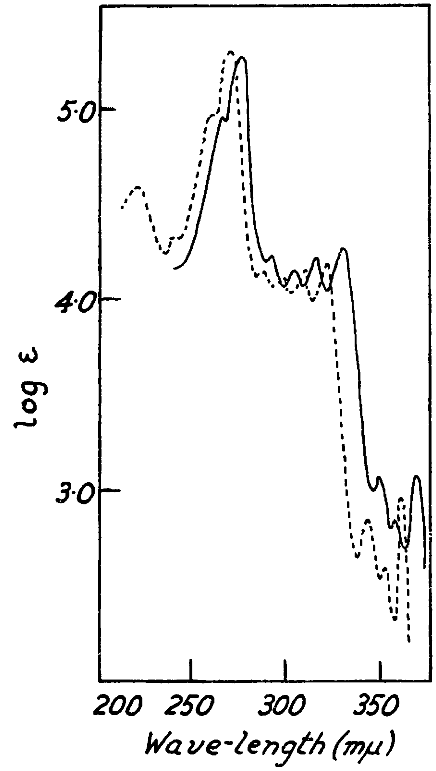
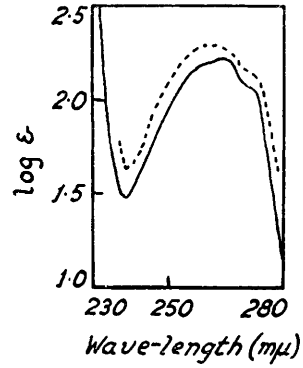


FIG. 1. *Ultra-violet absorption spectrum of hydrocarbon from mineral oil* (———) *and of chrysene* (– – – –) *in* 95% *ethanol.*

FIG. 2. *Ultra-violet absorption spectrum of compound from oil* (———) *and of* 1 : 2 : 3 : 4-*tetrahydro*-5-*methylnaphthalene* (– – – –) (Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," John Wiley & Sons, New York, 1951).



Compound	M. p.		Ultra-violet absorption maxima (mμ) *								
Chrysene	256°	λ	258	267	282	293	305	319	343	351	360
		log ε	4·96	5·20	4·09	4·09	4·13	4·13	2·81	2·51	2·81
Hydrocarbon from oil	247	λ	265	274	—	301	314	327·5	348·5	354	367
		log ε	4·87	5·09	—	4·09	4·17	4·17	2·82	2·62	2·83
2-*n*-Heptylchrysene	83—84	λ	261	270·5	—	299	311·5	326	347	—	365
		log ε	4·86	5·10	—	4·01	4·15	4·15	3·03	—	2·92
3-*n*-Heptylchrysene	127	λ	261	270·5	—	299	311	325	346	352·5	364
		log ε	4·93	5·15	—	4·08	4·17	4·14	2·87	2·65	2·75
4-*n*-Heptylchrysene	174	λ	261	271	(285)	296	308	321	345	352	363
		log ε	4·91	5·19	(4·21)	4·17	4·12	4·07	2·68	2·51	2·51
4-*cyclo*Hexylmethylchrysene	203—204	λ	262	271·5	—	(296)	308	321	345·5	353	363
		log ε	4·76	5·03	—	(4·17)	4·04	3·96	2·54	2·40	2·24
5-*n*-Heptylchrysene	91	λ	262	271	(285)	296·5	308·5	322	347	355	364
		log ε	4·84	5·08	(4·14)	4·07	4·09	4·09	2·88	2·55	2·88
5-*cyclo*Hexylmethylchrysene	138—139	λ	261·5	271	—	297	309	322	346·5	354	364
		log ε	4·96	5·20	—	4·09	4·11	4·11	3·86	2·55	2·77
3-*n*-Hexyl-4-methylchrysene	141	λ	263·5	272·5	—	300	313	325·5	347	354	365
		log ε	4·84	5·08	—	4·08	4·09	4·05	2·85	2·61	2·57

* Figures in parentheses indicate inflexions.

Another compound, isolated in very small amount, had the molecular formula $C_{20}H_{28}O$, $C_{21}H_{30}O$, or $C_{22}H_{32}O$. It was unaffected by hot dilute acid or alkali, and did not react with 2 : 4-dinitrophenylhydrazine sulphate in ethanol, or with *p*-nitrobenzoyl chloride. It did not decolorise bromine in carbon tetrachloride, but micro-hydrogenation with platinum in acetic acid showed the presence of three double bonds. These are attributed to the presence of a benzene ring, and this view is supported by the ultra-violet absorption spectrum (Fig. 2) which is similar to that of typical alkylbenzenes. The compound was recovered from attempted dehydrogenation with palladium at 300°. The absence of hydroxyl and carbonyl functions was confirmed by the infra-red spectrum, which showed no absorption in the characteristic carbonyl- and hydroxyl-stretching regions. The evidence available suggests a tetracyclic structure, one of the rings being benzenoid and the others alicyclic. The oxygen is probably present as an ether grouping, but an attempt to demonstrate this by treatment with hydriodic acid yielded a gummy product.

The fourth compound also appeared to be largely non-aromatic. Elementary analysis could not distinguish between the formulæ $C_{27}H_{42}O_2$, $C_{28}H_{44}O_2$, $C_{29}H_{46}O_2$, and $C_{30}H_{48}O_2$. It was unchanged by boiling dilute aqueous or alcoholic acid or alkali, and did not react with 2 : 4-dinitrophenylhydrazine sulphate or with 3 : 5-dinitrobenzoyl chloride. The infra-red spectrum showed no hydroxyl absorption but, surprisingly, exhibited a very distinct band at a typical carbonyl frequency (1756 ± 5 cm.$^{-1}$), attributable to carbonyl in a ring or to an ester or, less likely, a carboxyl group (compare Jones, Williams, Whallon, and Dobriner, *J. Amer. Chem. Soc.*, 1948, **70**, 2024). None of these groups could be detected by chemical means. Carbonyl, if present, must be highly hindered, for the compound did not react with hydroxylamine even in boiling diethylene glycol. Attempts to dehydrogenate the compound with palladium or selenium at 300° were unsuccessful. At higher temperatures with selenium the substance was decomposed but no aromatic compound could be isolated from the product. Attempted reduction with phosphorus and hydriodic acid led to resinous products.

The alkylchrysenes listed in the Table were prepared by standard methods. Reaction of 3 : 4 : 5 : 6-tetrahydro-3-oxochrysene (III; R = H) (Bachmann and Struve, *J. Org. Chem.*, 1940, **5**, 416) with *n*-heptylmagnesium bromide yielded a tertiary alcohol and hence, by heating with palladium, 3-*n*-heptylchrysene (cf. *idem, ibid.*, 1939, **4**, 456). 3-*n*-Hexyl-4-methylchrysene was similarly obtained from 3 : 4 : 5 : 6-tetrahydro-4-methyl-3-oxochrysene (III; R = Me) and *n*-hexylmagnesium bromide. The other hydrocarbons were obtained by Clemmensen reduction of the corresponding ketones prepared from chrysene by Friedel–Crafts reaction with *n*-heptanoyl and *cyclo*hexanecarbonyl chloride (compare Carruthers, *J.*, 1953, 3486). Thus reaction of chrysene with *n*-heptanoyl chloride and aluminium chloride in nitrobenzene gave a mixture of products from which 4- and 5-*n*-heptanoylchrysenes were isolated; 2-*n*-heptanoylchrysene was obtained when the reaction was conducted in methylene chloride. The orientation of these ketones was confirmed by oxidation to the known chrysenecarboxylic acids, and is similar to that obtaining in the Friedel–Crafts acetylation of chrysene (Carruthers, *loc. cit.*). 4- and 5- *cyclo*Hexanecarbonylchrysenes similarly resulted from reaction of chrysene with aluminium chloride and *cyclo*hexanecarbonyl chloride in nitrobenzene solution. They were converted into the chrysenecarboxylic acids, and thus orientated, by reduction with lithium aluminium hydride, dehydration of the resulting alcohols by means of potassium hydrogen sulphate, and oxidation of the products with potassium permanganate in acetone.

EXPERIMENTAL

Absorption spectra were determined in 95% ethanol with a " Unicam " spectrophotometer. Unless otherwise stated, " light petroleum " refers to the fraction of b. p. 60—80°.

Chromatography of the Extract.—The extract was a dark, very viscous oil at ordinary temperatures, prepared commercially by treatment of a lubricating-oil fraction of a West Baumont, U.S.A., crude with liquid sulphur dioxide. It was supplied by Manchester Oil Refinery and had been found by Dr. D. L. Woodhouse, of the University of Birmingham, to be non-carcinogenic. The material was distilled at 220—240°/$4{\cdot}7 \times 10^{-3}$ mm. (air-bath temp.), yielding a viscous orange-red distillate.

In a typical experiment the distillate (30 g.) was chromatographed on alumina (800 g.) from solution in light petroleum (b. p. 40—60°; 300 c.c.). The column was eluted with light petroleum (b. p. 40—60°) until no more material came through (2 l.). Evaporation of the eluate yielded a nearly colourless oil (20 g.). Development was continued with benzene–light petroleum (1 : 1; 250 c.c.), benzene–light petroleum (3 : 1; 500 c.c.), and benzene (250 c.c.), and the eluate collected in fractions of 50 c.c. Concentration of these afforded dark gums, some of which yielded crystalline compounds as described below.

Chrysene Derivative.—Several of the early benzene–light petroleum fractions (4—7) deposited small amounts of a yellow solid when triturated with light petroleum (b. p. 40—60°) at 0°. This was collected (40 mg.) and purified by crystallisation of its molecular complex with 2 : 4 : 7-trinitrofluorenone, from which it was recovered by treatment with stannous chloride in boiling acetic acid. It crystallised from benzene in colourless plates, m. p. 247—248° (Found: C, 92·4; 92·6; H, 7·6, 7·4. Calc. for $C_{25}H_{24}$: C, 92·6; H, 7·4%. Calc. for $C_{26}H_{26}$: C, 92·3; H, 7·7%). Ultra-violet absorption data are recorded in the Table. The 2 : 4 : 7-trinitrofluorenone complex formed fine brick-red needles from toluene, m. p. 258—259° (Found: C, 71·2; H, 4·5; N, 6·5. Calc. for $C_{38}H_{29}O_7N_3$: C, 71·4; H, 4·5; N, 6·6%. Calc. for $C_{39}H_{31}O_7N_3$: C, 71·7; H, 4·8; N, 6·4%). The 2 : 7-dinitroanthraquinone complex gave fine, bright red needles from benzene, m. p. 260° (decomp.) (Found: C, 75·4; H, 5·0; N, 4·6. Calc. for $C_{39}H_{30}O_6N_2$: C, 75·2; H, 4·8; N, 4·5%. Calc. for $C_{40}H_{32}O_6N_2$: C, 75·5; H, 5·0; N, 4·4%).

Perylene.—The gums from which the above hydrocarbon had been obtained, accumulated from a number of chromatograms, were collected (26 g.) and chromatographed on alumina in benzene solution. Fifteen arbitrary fractions of 30 c.c. were collected. Evaporation yielded gums, some of which deposited crystals of the above hydrocarbon (300 mg.) after some time. From several of the fractions immediately following, a yellow compound (64 mg.) was obtained on trituration with light petroleum. After further purification by repeated chromatography on alumina in benzene, and by crystallisation of its molecular complex with *s*-trinitrobenzene, it formed golden-yellow plates (from benzene), m. p. 268—269° alone or mixed with synthetic perylene (Found: C, 94·9; H, 4·8. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·8%). Light absorption in ethanol: $\lambda_{\text{max.}}$ 245, 252, 263, 286, 291, 300, 323, 328, 338, 367, 387, 408, 436 mμ. With concentrated sulphuric acid the hydrocarbon gave a transient green followed by a stable purple colour. The picrate formed brown needles (from benzene), m. p. 219—222° not lowered on admixture with perylene monopicrate (Brass and Tingler, *Ber.*, 1931, **64**, 1650). The *s*-trinitrobenzene complex crystallised from benzene in deep red needles, m. p. 244°. The *s*-trinitrobenzene complex of perylene is described by Hertel and Bergck (*Z. physikal. Chem.*, 1936, **33**, *B*, 324) as black needles, m. p. 276°. However, a sample prepared from pure perylene in benzene formed deep red needles, m. p. 246°, and was identical with the compound described above (mixed m. p.) (Found: C, 67·3; H, 3·3; N, 9·3. Calc. for $C_{26}H_{15}O_6N_3$: C, 67·1; H, 3·2; N, 9·0%).

The Oxygen-containing Compounds.—The gums recovered from the later benzene–light petroleum and benzene eluates of the chromatograms sometimes deposited crystals after a long time. These were collected and separately crystallised. By this means two homogeneous compounds were obtained. (*a*) One was readily purified by crystallisation from benzene, from which it crystallised in colourless plates, m. p. 252—253° (170 mg. from several experiments). Halogens, nitrogen, and sulphur were absent (Found: C, 84·5, 84·2; H, 10·3, 10·2. Calc. for $C_{20}H_{28}O$: C, 84·5; H, 9·9%. Calc. for $C_{21}H_{30}O$: C, 84·6; H, 10·1%. Calc. for $C_{22}H_{32}O$: C, 84·6; H, 10·3%). (*b*) The other compound was more difficult to purify. The crude material (670 mg.) was crystallised several times from acetic acid and from benzene, and then formed colourless needles, m. p. 290—300° depending on the rate of heating. Careful chromatography of this material on alumina in benzene, followed by sublimation at 300°/20 mm., afforded crystals with the same properties. By repeated crystallisation from benzene, colourless needles were obtained which melted at 330° (decomp.) (bath preheated to 300°). Sulphur, halogens, and nitrogen were absent [Found: C, 81·8, 81·6; H, 10·7, 10·8%; *M* (Rast), 370. Calc. for $C_{27}H_{42}O_2$: C, 81·4; H, 10·6%; *M*, 398. Calc. for $C_{28}H_{44}O_2$: C, 81·6; H, 10·7%. Calc. for $C_{29}H_{46}O_2$: C, 81·7; H, 10·8%. Calc. for $C_{30}H_{48}O_2$: C, 81·9; H, 10·9%].

4- *and* 5-n-*Heptanoylchrysene.*—A suspension of finely powdered chrysene (9 g.) in nitrobenzene (50 c.c.) was added with stirring to an ice-cold solution of aluminium chloride (6 g.) and *n*-heptanoyl chloride (6·7 g.) in nitrobenzene (30 c.c.). After 1 hr. the temperature was raised to 35—40° for 5 hr. Next morning, ice and hydrochloric acid were added, and nitrobenzene was removed in steam. The product (9 g.) was collected and extracted with boiling ethanol (4 × 100 c.c.), and the residue (6 g.) distilled at 210°/10^{-2} mm. The distillate was chromatographed on alumina in benzene solution. After removal of chrysene (0·8 g.) a ketonic product was recovered. This was dissolved in carbon tetrachloride (100 c.c.), and the solution set aside. The crystals (1·4 g.) which separated were crystallised further from carbon tetrachloride and from benzene, 4-n-*heptanoylchrysene* (0·4 g.) being obtained as colourless needles which collapsed to an opaque liquid at 187° and finally melted at 198—199°. Repeated crystallisation of this material from different solvents, and careful chromatography on alumina did not lead to any sharper definition of the m. p. (Found : C, 87·9; H, 7·2. $C_{25}H_{24}O$ requires C, 88·2; H, 7·1%). Oxidation with potassium hypoiodite in aqueous dioxan (Fuson and Tulloch, *J. Amer. Chem. Soc.*, 1934, **56**, 1638) afforded chrysene-4-carboxylic acid, m. p. 317—318° (decomp.); the methyl ester formed pale yellow plates in benzene, m. p. 218—220° alone or mixed with an authentic specimen.

The carbon tetrachloride mother-liquors were concentrated to 30 c.c. After removal of some 4-*n*-heptanoylchrysene (0·2 g.) the solution was set aside at 0° for several days. The crystals (1·2 g.) which separated were collected. Crystallisation from benzene–ethanol afforded 5-n-*heptanoylchrysene* as colourless needles, m. p. 96—97° (Found : C, 88·0; H, 7·0%). Oxidation of this compound as described above gave chrysene-5-carboxylic acid, m. p. 295° (decomp.); methyl ester, m. p. 147—148° alone or mixed with an authentic specimen.

2-n-*Heptanoylchrysene*.—Chrysene (4 g.) was added to a stirred ice-cold solution of aluminium chloride (2·9 g.) and *n*-heptanoyl chloride (3 g.) in methylene chloride (30 c.c.). Next morning stirring was continued for 2 hr. at 35—40°. Ice and hydrochloric acid were added, and methylene chloride distilled off. The dark gum was dissolved in benzene, a small amount of insoluble material filtered off, and the solution chromatographed on alumina. Elution with benzene–light petroleum (1 : 1) removed first some chrysene (0·5 g.), then a yellow gum (2·6 g.) which crystallised on trituration with ethanol. Crystallisation from ethanol gave colourless needles of 2-n-*heptanoylchrysene*, m. p. 66° (Found: C, 88·0; H, 7·1%). Oxidation of this ketone by the method of Arnold and Rondesvedt (*J. Amer. Chem. Soc.*, 1945, **67**, 1265) with selenium dioxide followed by alkaline hydrogen peroxide yielded chrysene-2-carboxylic acid, m. p. 300° (decomp.) (methyl ester, m. p. 141—142° not reduced when mixed with an authentic specimen).

4- *and* 5-cyclo*Hexanecarbonylchrysene*.—Finely powdered chrysene (11 g.) with nitrobenzene (20 c.c.) was added to a stirred solution of aluminium chloride (7·5 g.) and *cyclo*hexanecarbonyl chloride (8·4 g.) in nitrobenzene (30 c.c.) at 0°. After 1½ hr. the temperature was raised to 35—40° for 4 hr. Next morning, ice and hydrochloric acid were added, and nitrobenzene was removed in steam. The solid residue was powdered, washed, dried, and extracted with boiling carbon tetrachloride (100 c.c.), and the solution set aside. The solid which separated was combined with the insoluble residue, and the whole chromatographed in benzene on alumina. After removal of chrysene (0·3 g.), 4-cyclo*hexanecarbonylchrysene* (1·3 g.) was recovered, and crystallised from benzene in colourless needles, m. p. 211—212° (Found: C, 88·8; H, 6·7. $C_{25}H_{22}O$ requires C, 88·8; H, 6·6%). The carbon tetrachloride mother-liquors were concentrated to 20 c.c. and set aside at 0° for several days. The dark solid (7·9 g.) was collected and chromatographed in benzene on alumina to remove chrysene (0·5 g.) as described above. The recovered ketonic product was crystallised from carbon tetrachloride (30 c.c.). After removal of some of the 4-isomer (0·6 g.), 5-cyclo*hexanecarbonylchrysene* (2·9 g.) was obtained. It formed colourless blades, m. p. 168—169°, from benzene-*cyclo*hexane (Found : C, 88·7; H, 6·4%).

Treatment of the 4-isomer (150 mg.) with excess of lithium aluminium hydride in ether afforded an alcohol, m. p. 220—221°. This was dehydrated with potassium hydrogen sulphate (100 mg.) at 160° for ½ hr. The resulting olefin was purified by chromatography on alumina, and formed colourless crystals, m..p. 94—197°. It was oxidised with potassium permanganate (0·5 g.) in acetone (50 c.c.) at 20° for 12 hr. After evaporation of acetone, and removal of manganese dioxide with aqueous sulphurous acid, a product was obtained which yielded an acid (15 mg.) on extraction with dilute alkali. The acid was converted directly into the methyl ester with diazomethane. Crystallisation from methanol (charcoal) gave crystals of methyl chrysene-4-carboxylate, m. p. 214—215°, identified by comparison with an authentic specimen.

Methyl chrysene-5-carboxylate, m. p. 144—145°, was similarly obtained from 5-*cyclo*hexanecarbonylchrysene, *via* the olefin, m. p. 114—117°.

2-n-*Heptylchrysene*.—A mixture of 2-*n*-heptanoylchrysene (0·5 g.), amalgamated zinc (5 g.), toluene (2 c.c.), ethanol (2 c.c.), and concentrated hydrochloric acid (15 c.c.) was boiled for 24 hr. The oily product was chromatographed on alumina in light petroleum, and afforded 2-n-*heptylchrysene* (0·3 g.) as colourless needles, m. p. 83—84° (from *cyclo*hexane) (Found: C, 91·8; H, 7·9. $C_{25}H_{26}$ requires C, 92·0; H, 8·0%). The *s*-trinitrobenzene *complex* formed deep yellow needles, m. p. 125°, from ethanol (Found : N, 8·0. $C_{31}H_{29}O_6N_3$ requires N, 7·8%).

3-n-*Heptylchrysene*.—To a solution prepared from *n*-heptyl bromide (2 g.) and magnesium (0·35 g.) in ether (10 c.c.) was added 3 : 4 : 5 : 6-tetrahydro-3-oxochrysene (0·4 g.) (Bachmann and Struve, *J. Org. Chem.*, 1940, **5**, 416) in benzene (10 c.c.), and the mixture refluxed for an hour. Next morning the complex was decomposed with dilute sulphuric acid and the oily product obtained was heated at 180°/15 mm. for a short time to remove some high-boiling liquid. The resulting solid was heated with palladium black (50 mg.) at 280—290° for an hour in an atmosphere of carbon dioxide. The product was extracted with benzene, and purified by chromatography on alumina, and by sublimation at 200°/0·5 mm. 3-n-*Heptylchrysene* (360 mg.) was obtained as colourless needles, m. p. 127° (from ethanol) (Found : C, 91·9; H, 8·1%). The 2 : 4 : 7-trinitrofluorenone complex formed brick-red micro-crystals (from benzene), m. p. 175°, but could not be obtained free from the fluorenone (Found : N, 7·3. Calc. for $C_{38}H_{31}O_7N_3$: N, 6·5%). The picrate, and the complexes with *s*-trinitrobenzene and 2 : 7-dinitroanthraquinone, showed more pronounced dissociation on crystallisation.

3-n-*Hexyl*-4-*methylchrysene*.—A solution of 3 : 4 : 5 : 6-tetrahydro-4-methyl-3-oxochrysene (Bachmann and Struve, *loc. cit.*) (130 mg.) in benzene (10 c.c.) was added to a solution prepared from *n*-hexyl bromide (1·5 g.) and magnesium (0·27 g.) in ether (6 c.c.), and the mixture boiled for ½ hr. Next morning, dilute sulphuric acid was added, and the product recovered in the usual way. Some high-boiling liquid was distilled off at 180°/0·5 mm., and the residue heated with palladium–charcoal (30% ; 300 mg.) at 290—300° for an hour in an atmosphere of carbon dioxide. The product (100 mg.) was purified by chromatography on alumina in benzene. 3-n-*Hexyl*-4-*methylchrysene* was obtained as colourless plates, from m. p. 141°, ethanol–benzene (Found : C, 91·8; H, 7·9%). The molecular complexes with *s*-trinitrobenzene, 2 : 7-dinitroanthraquinone, and 2 : 4 : 7-trinitrofluorenone dissociated on crystallisation; the last formed orange-red microcrystals (from benzene), m. p. 208° (Found : N, 7·4%).

4-n-*Heptylchrysene*.—A mixture of 4-*n*-heptanoylchrysene (400 mg.), amalgamated zinc (8 g.), toluene (2 c.c.), acetic acid (2 c.c.), and hydrochloric acid (10 c.c.) was boiled for 30 hr. The product was purified by chromatography on alumina in benzene–light petroleum (1 : 10), and 4-n-*heptylchrysene* (75 mg.) obtained as colourless plates, m. p. 174° (from ethanol–benzene) (Found : C, 92·0; H, 8·1%). The 2 : 7-dinitroanthraquinone complex formed bright red crystals, m. p. 222°, but dissociated on crystallisation. The 2 : 4 : 7-trinitrofluorenone and *s*-trinitrobenzene complexes behaved likewise.

5-n-*Heptylchrysene*.—This was prepared from 5-*n*-heptanoylchrysene (400 mg.) as described for the 4-isomer. After purification by chromatography, 5-n-*heptylchrysene* (300 mg.) crystallised from ethanol in colourless plates, m. p. 91° (Found : C, 91·9; H, 7·9%). The *s*-trinitrobenzene *complex* crystallised in yellow needles, m. p. 102—103° (from ethanol) (Found : N, 7·7. $C_{31}H_{29}O_6N_3$ requires N, 7·8%).

4-cyclo*Hexylmethylchrysene*.—4-*cyclo*Hexanecarbonylchrysene (150 mg.), amalgamated zinc (2 g.), acetic acid (2 c.c.), toluene (2 c.c.), and concentrated hydrochloric acid (10 c.c.) were boiled together for 40 hr. The product (110 mg.) was purified by chromatography on alumina in light petroleum. 4-cyclo*Hexylmethylchrysene* crystallised from *cyclo*hexane–benzene (1 : 1) in colourless plates, m. p. 203—204° (Found : C, 92·5; H, 7·6. $C_{25}H_{24}$ requires C, 92·6; H, 7·5%). The 2 : 7-dinitroanthraquinone *complex* gave bright red plates (from benzene), m. p. 243° (Found : N, 4·5. $C_{39}H_{30}O_6N_2$ requires N, 4·5%).

5-cyclo*Hexylmethylchrysene*.—This was prepared from 5-*cyclo*hexanecarbonylchrysene (200 mg.) as was the 4-isomer. After purification by chromatography in light petroleum on alumina, it formed colourless needles, from *cyclo*hexane, m. p. 138—139° (Found : C, 92·5; H, 7·5%). The *s*-trinitrobenzene *complex* formed yellow needles (from ethanol), m. p. 166° (Found : N, 8·0. $C_{31}H_{27}O_6N_3$ requires N, 7·8%).

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