47. *The Constituents of High-boiling Petroleum Distillates. Part IV.*[1] *Some Polycyclic Aromatic Hydrocarbons in a Kuwait Oil.*

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1 : 8-Dimethylphenanthrene, 1 : 2 : 8-trimethylphenanthrene, 1 : 2-benzofluorene, 8-methyl-1 : 2-benzofluorene, and 1-methylpyrene have been isolated from a Kuwait oil.

THE isolation of a number of anthracene homologues from fractions of a Kuwait mineral oil by reaction with maleic anhydride was described in Part III.[1] In experiments designed to concentrate the carcinogenic constituents of the oil, the unchanged materials recovered from this treatment were treated with picric acid in ethanol, and the oils regenerated from the crystalline picrates were chromatographed on alumina and collected in fractions formed by elution with light petroleum, benzene, and methanol. By further chromatography of some of these benzene eluates the compounds named in the summary have now been isolated. They were identified by elementary analyses, preparation of derivatives, and ultraviolet absorption measurements, and the structure was confirmed in each case by comparison with authentic material.

In addition, another hydrocarbon, m. p. 198—199°, was obtained which has not been fully identified. Elementary analysis supports the molecular formulæ $C_{17}H_{18}$ and $C_{18}H_{20}$ and it appears from its ultraviolet absorption spectrum to be a derivative of fluorene.

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[1] Part III, *J.*, 1956, 603.

Because of the small amount available we were not able to carry out any degradative experiments. A number of sulphur-containing compounds which were also obtained will be described later.

The isolation of these compounds adds interestingly to the number of polycyclic aromatic hydrocarbon types which have been found in mineral oils. Phenanthrene itself was obtained from a Roumanian oil by Gavat and Irimescu,[2] but as far as we are aware no hydrocarbon of the fluorene, benzofluorene, or pyrene type has been detected previously. It may be significant that 1 : 2 : 8-trimethylphenanthrene is known as a major product of dehydrogenation of tetracyclic triterpenoids, and of many diterpenoids.

EXPERIMENTAL

Ultraviolet absorption spectra were measured in 95% ethanol, on a " Unicam " spectrophotometer. M. p.s were determined on a Kofler hot stage.

Formation of Picrates and Chromatography of Picrate-forming Oils.—The preparation of the fractions used in this work is described in Part III.[1]

The materials recovered from the reaction with maleic anhydride (Part III) were washed with water, and the ten 2½° fractions boiling above 365°, as well as the fraction of b. p. 357½—360°, were severally treated with picric acid (⅛ part) in boiling ethanol (5—6 parts). When the resulting deep red solutions were cooled the picrate generally separated as an orange-red powder; this separation took place with increasing difficulty, however, with increasing b. p. of the fractions. The filtrate was re-treated with picric acid (⅒ part) and this process was repeated until largely picric acid separated when the solution was cooled to 0°. The total crude picrates from each fraction were decomposed by washing their benzene solutions with aqueous sodium hydroxide, and the recovered dark oils adsorbed on alumina (10 parts). The columns were eluted successively with light petroleum (b. p. 60—80°), benzene, and methanol, in each case until no more material was recovered. The petroleum eluates were collected in two portions, a refractive index of 1·5000 being the point of separation, so that in all, four fractions were obtained. Details are given in the Table.

B. p. of original distillate	Picrate-forming material		Chromatography eluates (g.)			
	wt. (g.)	% of aromatic extract	light petroleum $n_D < 1{\cdot}5000$	light petroleum $n_D > 1{\cdot}5000$	benzene	methanol
357½—360°	285	30	60	195	16·1	9·3
365 —367½°	164	39	60	77	19	9·4
367½—370°	243	30	103	103	25	9·4
370 —372½°	153	27	63	90	9·6	6
372½—375°	188	22	33	120	24	13
375 —377½°	98	52	—	—	—	—
377½—380°	243	19	33	193	—	17·5
380 —382½°	245	31	54	157	22	15
382½—385°	260	28	80	131	27	21
385 —387½°	180	22	42	102	20	13
387½—390°	159	30	39	80	30	10

Further experiments described here are concerned only with the benzene eluates. Results obtained with the light petroleum and methanol fractions will be reported later.

1 : 8-*Dimethylphenanthrene and the Unknown Fluorene Derivative.*—The benzene eluate obtained from the picrate of the fraction, b. p. 357½—360°, was evaporated and the gum (16 g.), in light petroleum (b. p. 40—60°), was adsorbed on alumina (500 g.). Elution was started with light petroleum (b. p. 40—60°) and continued with light petroleum (b. p. 60—80°) alone and later with increasing proportions of benzene, and completed with benzene. Evaporation of the 42 eluates yielded oils some of which crystallised spontaneously and others when triturated with light petroleum at −10°. Fractions 18—20, eluted with light petroleum–benzene (4 : 1), afforded a solid (70 mg.) which, after one crystallisation from ethanol–benzene, melted about 190°. After purification through its *s*-trinitrobenzene complex, this yielded 1 : 8-dimethylphenanthrene as plates (from ethanol–benzene), m. p. 190—191° alone or mixed with a specimen kindly supplied by Professor F. E. King (Found: C, 92·8; H, 7·0. Calc. for $C_{16}H_{14}$: C,

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[2] Gavat and Irimescu, *Ber.*, 1942, **75**, 820.

93·2; H, 6·8%). Light absorption : $\lambda_{max.}$ 225, 252, 258·5, 282, 293, 305, 336, 345, 352 mμ (log ε 4·33, 4·72, 4·81, 4·05, 4·18, 4·26, 2·56, 2·39, 2·31). The *s*-trinitrobenzene complex crystallised from ethanol–benzene as yellow needles, m. p. 170—171° (lit. 173—174°) (Found : N, 9·7. Calc. for $C_{16}H_{14},C_6H_3O_6N_3$: N, 10·0%).

Later benzene eluates of this chromatogram deposited small amounts of another crystalline substance, m. p. about 190°. This was purified through its bright red 2 : 4 : 7-trinitrofluorenone *complex*, m. p. 240° (from benzene) (Found : C, 67·1; H, 4·1. $C_{17}H_{18},C_{13}H_5O_7N_3$ requires C, 67·0; H, 4·3. $C_{18}H_{16},C_{13}H_5O_7N_3$ requires C, 67·5; H, 4·6%). The parent *fluorene*, recovered from the complex by chromatography on alumina, formed needles (from ethanol–benzene), m. p. 198—199° (Found : C, 91·3; H, 8·3. $C_{17}H_{18}$ requires C, 91·8; H, 8·2. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%). Light absorption : $\lambda_{max.}$ 225, (infl. 257), 263, 272, (infl. 283), 294, (infl. 299), 305·5 mμ [log ε 4·38; (4·25), 4·38, 4·44, (4·26), 3·91, (3·76), 3·92].[3] This hydrocarbon was also isolated, in the same way, from the fraction of b. p. 370—372½°.

1 : 2 : 8-*Trimethylphenanthrene and* 1 : 2-*Benzofluorene*.—Chromatography of the picrate-forming part of the fraction, b. p. 372½—375°, afforded a benzene eluate which partly solidified. The solid (1·7 g.) was crystallised from ethanol–benzene, giving plates of 1 : 2 : 8-trimethylphenanthrene, m. p. 141—143° not depressed when mixed with authentic material for which we are indebted to Professor F. E. King (Found : C, 92·7; H, 7·2. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). Light absorption : $\lambda_{max.}$ 215, (infl. 246), 254, 262, 283, 294, 306, 326, 337·5 mμ [log ε 4·57, (4·49), 4·69, 4·77, 4·10, 4·11, 4·20, 2·57, 2·56].[4] The picrate formed orange needles, m. p. 167° (lit. 165°) (Found : N, 9·7. Calc. for $C_{17}H_{16},C_6H_3O_7N_3$: N, 9·3%). The *s*-trinitrobenzene complex gave yellow needles, m. p. 187—190° (lit. 188—190°).

When the remaining oily part of the benzene eluate was chromatographed carefully on alumina as described above, many of the fractions obtained on elution with benzene–light petroleum afforded further quantities of 1 : 2 : 8-trimethylphenanthrene. Later eluates gave fractions from which solid was precipitated in light petroleum at −10°. This was collected and purified by further chromatography on alumina; the pure material crystallised from ethanol in needles, m. p. 187—188°, and was identified as 1 : 2-benzofluorene by mixed m. p. with a specimen kindly provided by Professor Milton Orchin. Light absorption : $\lambda_{max.}$ 253, 258, 262·5, 293, 303, 314, 327·5, 343·5 mμ (log ε 4·74, 4·61, 4·96, 4·16, 4·12, 4·05, 3·24, 3·01). The bis-*s*-trinitrobenzene complex formed yellow plates, m. p. 143—144° alone or mixed with authentic material (Found : C, 53·95; H, 2·9. Calc. for $C_{17}H_{12},2C_6H_3O_6N_3$: C, 54·2; H, 2·8%).

1 : 2 : 8-Trimethylphenanthrene was also obtained from the fraction, b. p. 377½—380°.

8-*Methyl*-1 : 2-*benzofluorene*.—This was isolated from the fraction, b. p. 387½—390°. The crude benzene eluate obtained from the picrate-forming part of this fraction (see Table) was rechromatographed on alumina as described above. Some of the fractions obtained near the end of the chromatogram, benzene being used as eluant, crystallised spontaneously. The collected crystals were recrystallised from methanol and then converted into the *s*-trinitrobenzene complex. After repeated crystallisation from ethanol the bis-*s*-trinitrobenzene complex of 8-methyl-1 : 2-benzofluorene was obtained as orange-yellow plates, m. p. 147—149° alone or mixed with an authentic specimen (Found : C, 55·3; H, 3·0. Calc. for $C_{18}H_{14},2C_6H_3O_6N_3$: C, 54·9; H, 3·1%). The hydrocarbon (40 mg.) recovered from the pure complex on alumina, formed blades (from ethanol–benzene), m. p. 125—126° not depressed when mixed with the synthetic compound kindly provided by Dr. M. E. Gross[5] (Found : C, 94·0; H, 6·3. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%). Light absorption : $\lambda_{max.}$ 255, 265, (infl. 295), 303, 315, 327, 343 mμ [log ε 4·48, 4·60, (3·73), 3·79, 3·72, 2·92, 2·55].

Oxidation of the hydrocarbon with sodium dichromate in acetic acid afforded 8-*methyl*-1 : 2-*benzofluorenone* as golden-yellow plates, m. p. 165° (from methanol) (Found : C, 88·4; H, 5·3. $C_{18}H_{12}O$ requires C, 88·7; H, 4·95%).

1-*Methylpyrene*.—This hydrocarbon was obtained from the fractions, b. p. 380—382½° and 382½—385°. The benzene eluates (see Table) were reconverted into their picrates which were recrystallised several times from benzene before the recovered oils (about 2 g.) were chromatographed on alumina. In each case a crude mixture of pyrene derivatives which proved very difficult to purify was eluted with light petroleum (b. p. 40—60°). By repeated chromatography on alumina and by crystallisation of molecular complexes, cubes were eventually

[3] Askew, *J.*, 1935, 512.

[4] *Idem, ibid.*, p. 509.

[5] Gross and Lankelma, *J. Amer. Chem. Soc.*, 1951, **73**, 3439.

obtained, having m. p. 145—147° (from *cyclo*hexane) alone or mixed with 1-methylpyrene. (We thank Professor O. Kruber for a gift of this hydrocarbon.) There was insufficient for analysis, but the pyrene structure was confirmed by the ultraviolet light absorption.[6] $\lambda_{\text{max.}}$ 234, 243, (infl. 253), 265, 276, (infl. 297), 308, 322, 338, 373 mμ [log ε 4·74, 4·97, (4·27), 4·50, 4·72, (3·87), 4·18, 4·51, 4·67, 2·20]. The 2 : 4 : 7-trinitrofluorenone complex formed red-brown needles, m. p. 222—224° [(lit. 230° (corr.)]. The picrate had m. p. 225—233° (decomp.) [lit. 226—227°; 229—232° (decomp.)].

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[6] Cook and Hewett, *J.*, 1934, 365; Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, **152**, 299.