120. *The Constituents of High-boiling Petroleum Distillates. Part III.* Anthracene Homologues in a Kuwait Oil.*

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2 : 6- and 2 : 7-Dimethyl-, 2 : 3 : 6-trimethyl-, and 1 : 3 : 5 : 7-, 1 : 3 : 6 : 7-, and 2 : 3 : 6 : 7-tetramethyl-anthracene and four unidentified anthracene homologues have been isolated from fractions of a Kuwait mineral oil by reaction with maleic anhydride.

Very few polycyclic aromatic hydrocarbons have been detected in mineral-oil fractions. Gavat and Irimescu[1] found naphthalene homologues and phenanthrene in a Roumanian oil, and recently Moore, Thorpe, and Mahoney[2] encountered 3-methylchrysene in an American crude oil. A second chrysene derivative and perylene were found in another American crude by Carruthers and Cook,[3] while Carruthers and Douglas[4] described the isolation of three trimethylnaphthalenes from a Trinidad oil. The anthracene derivatives named in the summary have now been isolated from fractions of a Kuwait (Middle East) oil by reaction with maleic anhydride.

The sixteen 2½°-fractions employed, covering the boiling range 350—390°, were prepared in the Chemical Engineering Laboratories of the University of Birmingham by fractional distillation of the crude oil under reduced pressure and extraction of the distillates with aqueous acetone. The author is very much indebted to Professor F. Morton for carrying out these operations and supplying the resultant material for this investigation. The aromatic-enriched extracts were treated with maleic anhydride at 100°, giving small yields of alkali-soluble adducts, whose decomposition by distillation from sodium hydroxide afforded viscous oils with well-marked anthracene-type ultraviolet absorption spectra. Anthracenes crystallised from some of these oils and others were obtained by chromatography of the oils on alumina. The Table summarises the results obtained.

The well-known [5,6,7] eutectic mixture, m. p. 225—226°, of 2 : 6- and 2 : 7-dimethylanthracene separated from some of the earlier fractions. On oxidation it afforded 2 : 6- and 2 : 7-dimethylanthraquinone, identified by comparison with authentic specimens.

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* Part II, *J.*, 1955, 1847.

[1] Gavat and Irimescu, *Ber.*, 1941, **74**, 1812; 1942, **75**, 820.

[2] Moore, Thorpe, and Mahoney, *J. Amer. Chem. Soc.*, 1953, **75**, 2259.

[3] Carruthers and Cook, *J.*, 1954, 2047.

[4] Carruthers and Douglas, *J.*, 1955, 1847.

[5] Lavaux, *Compt. rend.*, 1911, **152**, 1400, and earlier references; *Ann. Chim.*, 1910, **20**, 433; **21**, 131.

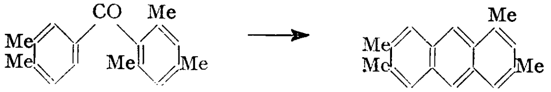
[6] Hey, *J.*, 1935, 72.

[7] Morgan and Coulson, *J.*, 1929, 2203.

Chromatography of the remaining oil from fraction 3 gave 2 : 6-dimethylanthracene. In a similar manner, 2 : 7-dimethylanthracene was obtained from fraction 4.

Several of the intermediate fractions, on being cooled, deposited 2 : 3 : 6-trimethylanthracene, which was identified by mixed m. p. and by oxidation to 2 : 3 : 6-trimethylanthraquinone.[8]

2 : 3 : 6 : 7-Tetramethylanthracene separated from the two highest-boiling fractions, and was likewise identified by mixed m. p. and by oxidation to the quinone. By chromatography of the remaining oil from these fractions the previously unknown 1 : 3 : 6 : 7-tetramethylanthracene was obtained. It was identified by comparison of its quinone with the synthetic compound,[10] and by preparation of the hydrocarbon itself by Elbs pyrolysis of 2 : 4 : 6 : 3′ : 4′-pentamethylbenzophenone. A third tetramethylanthracene, isolated from fractions 13 and 14 by chromatography, is regarded as 1 : 3 : 5 : 7-tetramethylanthracene because of the close agreement of the melting points of the hydrocarbons and of the quinones with those recorded in the literature,[11] although direct comparison has not been possible.



Chromatography of the oily portions of fractions 10 and 12 afforded small amounts of three other hydrocarbons, $C_{17}H_{16}$ or $C_{18}H_{18}$ (see Table). The anthracenic structure of these compounds was shown by their ultraviolet absorption spectra, but their m. p.s and those of the corresponding quinones do not correspond with those recorded for any C_{17} or C_{18} anthracene or its quinone, and the compounds have not been identified.

Fraction	Yield *	B. p.†	Products
1	0·9	350—352·5°	Eutectic mixture of 2 : 6- and 2 : 7-dimethylanthracene
2	0·9	352·5—355	,, ,, ,,
3	0·8	355—357·5	Eutectic mixture and 2 : 6-dimethylanthracene
4	0·5	357·5—360	2 : 7-Dimethylanthracene
5	0·9	360—362·5	2 : 3 : 6-Trimethylanthracene
6	1·6	362·5—365	—
7	0·9	365—367·5	2 : 3 : 6-Trimethylanthracene
8	1·0	367·5—370	,,
9	0·9	370—372·5	—
10	0·5	372·5—375	2 : 3 : 6-Trimethylanthracene; hydrocarbon, m. p. 108—110°; hydrocarbon, m. p. 224—225°
11	0·8	375—377·5	2 : 3 : 6-Trimethylanthracene
12	0·9	377·5—380	2 : 3 : 6-Trimethylanthracene; hydrocarbon, m. p. 224—225°; hydrocarbon, m. p. 169—170
13	1·0	380—382·5	1 : 3 : 5 : 7-Tetramethylanthracene
14	1·1	382·5—385	,,
15	0·9	385—387·5	1 : 3 : 6 : 7- and 2 : 3 : 6 : 7-Tetramethylanthracene
16	1·4	387·5—390	,,

* Yield of maleic anhydride extract, as percentage of distillate fraction.

† These are the equivalent b. p.s at atmospheric pressure of the original distillates. The actual distillations were carried out under reduced pressures.

An unknown tetramethylanthracene, m. p. 67—69°, was obtained from the combined fractions 14 and 15 by crystallisation of molecular complexes. The large bathochromic shift of 13—15 mμ in the ultraviolet absorption spectrum of this compound suggests the presence of a substituent in one of the *meso*-positions.[12]

EXPERIMENTAL

Melting points were determined on a Kofler hot stage. Ultraviolet absorption spectra were measured in 95% ethanol on a " Unicam " spectrophotometer.

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[8] Morgan and Coulson, *J.*, 1929, 2551.

[9] *Idem, J.*, 1931, 2323; Barnett, Goodway, and Watson, *Ber.*, 1933, **66**, 1876; Hey, ref. 6; *J.*, 1938, 1847.

[10] Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 1679.

[11] Seer, *Monatsh.*, 1912, **33**, 33; Scholl, Meyer, and Keller, *Annalen*, 1934, **513**, 295.

[12] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951.

Reaction with Maleic Anhydride.—The starting materials were dark thick oils at ordinary temperatures. A Kuwait (Middle East) oil was first roughly distilled under reduced pressure, and a fraction boiling above 340° carefully refractionated by using a Stedman type column at 2—3 cm. pressure. Fractions were taken every 2½° and distillation was discontinued when there was evidence of cracking (b. p. 390°). Aromatic extracts were prepared from the distillates in approximately 20% yield by treatment with 5% aqueous acetone in a countercurrent spinning-disc solvent-extraction unit.

In a typical experiment, the extract, after being washed with dilute hydrochloric acid and sodium hydroxide, was stirred at 100° with maleic anhydride (1/10 part) for 5—6 hr. A slight excess of sodium hydroxide solution (20%) was cautiously added to the cooled mixture, and the whole stirred at 60° for some time. The sodium salt of the adduct often separated as a dark tar at the interface of the two layers, and was carefully separated, along with the aqueous solution, and dissolved in warm water. The oil was washed several times with warm water and the combined aqueous solutions thoroughly extracted with benzene and acidified. The gummy adduct was taken up in benzene, washed with water, recovered, and decomposed by distillation from sodium hydroxide, affording, generally, an orange-red viscous oil at 180—200°/0·2 mm.

Eutectic Mixture of 2 : 6- *and* 2 : 7-*Dimethylanthracene.*—A solution of the adduct-forming material (2·6 g.) from fraction 1 in light petroleum (b. p. 60—80°) deposited crystals at −10°. After chromatography on alumina in light petroleum (b. p. 60—80°) and crystallisation from ethanol–benzene, the eutectic mixture was obtained as plates (25 mg.), m. p. 225—227° (Found : C, 93·2; H, 6·9. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). More of this substance was isolated in the same way from the two succeeding fractions, and by chromatography of the remaining oily part of the present fraction.

Oxidation of the hydrocarbon with chromic acid in acetic acid, and chromatography of the crude product on alumina in benzene afforded yellow crystals, m. p. 225—237°. Repeated crystallisation from benzene–ethanol yielded 2 : 6-dimethylanthraquinone, m. p. and mixed m. p. 241—242° (Found : C, 81·5; H, 5·2. Calc. for $C_{16}H_{12}O_2$: C, 81·3; H, 5·1%). The mother liquors afforded a small amount of pale yellow crystals, m. p. 176—180°; when mixed with 2 : 7-dimethylanthraquinone of m. p. 168—169° the m. p. was 170—175°. (This experiment was carried out by Mr. A. G. Douglas, B.Sc.)

2 : 6-*Dimethylanthracene.*—After removal of a small amount of eutectic mixture, the oily adduct-forming material from fraction 3 (3·0 g.) was chromatographed on alumina (140 g.), light petroleum (b. p. 40—60°; later b. p. 60—80°), mixtures of the latter and benzene, and finally benzene being used as eluants. Several of the fractions obtained gave crystals at −10° from some of which 2 : 6-dimethylanthracene was obtained by further chromatography and crystallisation from benzene as nearly colourless blades, m. p. 237—240° (lit., 250° corr.). Oxidation with chromic acid afforded 2 : 6-dimethylanthraquinone as pale yellow needles, m. p. 235° (from ethanol–benzene) not depressed when mixed with an authentic specimen (m. p. 239—240°).

2 : 7-*Dimethylanthracene.*—A solution of the " anthracene fraction " from distillate 4 (3·8 g.), in light petroleum (b. p. 40—60°) was chilled to −70°, and the solid which separated (100 mg.) crystallised from benzene–ethanol. 2 : 7-Dimethylanthracene was obtained as nearly colourless blades, m. p. 235° alone or mixed with an authentic specimen (Found : C, 93·2; H, 6·8%). Light absorption : $\lambda_{max.}$ 256·5 (infl. 327), 343, 360, 379·5 mμ [log ε 5·22, (3·23), 3·62, 3·72, 3·60]. Oxidation with chromic acid afforded 2 : 7-dimethylanthraquinone as pale yellow needles (from methanol), m. p. and mixed m. p. 163—165°.

2 : 3 : 6-*Trimethylanthracene.*—This hydrocarbon separated from several of the intermediate anthracene fractions (see Table) when their solutions in light petroleum (b. p. 40—60°) were kept at −10°. After purification by chromatography on alumina, it crystallised from benzene–ethanol in nearly colourless blades (50 mg.), m. p. 244—245° (Found : C, 93·0; H, 7·1. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). Light absorption : $\lambda_{max.}$ 258, (infl. 313), (infl. 325), 342·5, 359·5, 380 mμ [log ε 5·34, (3·18), (3·44), 3·65, 3·77, 3·68]. The m. p. of a mixture with an authentic specimen (m. p. 252—253°) was 245—246°. The quinone formed pale yellow needles (from ethanol–benzene), m. p. 236—237° alone or mixed with 2 : 3 : 6-trimethylanthraquinone.

1 : 3 : 5 : 7-*Tetramethylanthracene.*—This was obtained by chromatography of fractions 13 and 14 by the general method outlined above. The crude material (100 mg.) was purified by chromatography and crystallisation from ethanol–benzene, and gave the pure hydrocarbon as needles, m. p. 164—165° (20 mg.) (lit., m. p. 163—164°) (Found : C, 92·2; H, 7·4. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). Light absorption : $\lambda_{max.}$ 253, 261, (infl. 320), (infl. 330), 339, 353, 368, 387 mμ [log ε 4·95, 5·29, (3·33), (3·46), 3·58, 3·70, 3·73, 3·73]. The quinone was obtained

from benzene–ethanol as yellow needles, m. p. 238—239° (lit., m. p. 237°) (Found : C, 81·8; H, 5·9. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%). The picrate formed dark purple needles (from ethanol–benzene), m. p. 189—190° (lit., m. p. 189—190°).

1 : 3 : 6 : 7- *and* 2 : 3 : 6 : 7-*Tetramethylanthracene.*—Light petroleum (b. p. 60—80°) solutions of fractions 15 and 16 deposited small amounts of a yellow substance at $-10°$. This was purified by chromatography on alumina and crystallisation from ethanol–benzene, affording 2 : 3 : 6 : 7-tetramethylanthracene as fluffy yellow needles (6 mg.), m. p. 292—293° alone or mixed with an authentic specimen (Found : C, 92·5; H, 7·7%). Light absorption : $\lambda_{\max.}$ (in *cyclo*hexane) 252, 261, 275·5, 294, (infl. 314), 328, 343, 360, 380 mμ [log ε 4·87, 5·37, 4·17, 3·16, (3·16), 3·45, 3·65, 3·78, 3·68]. (The maxima at 275·5 and 294 are spurious and indicate the presence of some persistent impurity.) Oxidation of the hydrocarbon with chromic acid afforded 2 : 3 : 6 : 7-tetramethylanthraquinone as nearly colourless needles, m. p. 317—320° (from benzene) not depressed when mixed with authentic material.

Chromatography on alumina of the remaining oils of fractions 15 and 16 produced crystalline fractions from which by further chromatography and crystallisation from benzene–ethanol 1 : 3 : 6 : 7-*tetramethylanthracene* was obtained as pale yellow plates, m. p. 131—132° (Found : C, 92·3; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Light absorption : $\lambda_{\max.}$ 253, 261, (infl. 330), 344, 362, 383 mμ [log ε 4·99, 5·30, (3·51), 3·69, 3·81, 3·71]. Oxidation with chromic acid gave 1 : 3 : 6 : 7-tetramethylanthraquinone as pale yellow needles, m. p. and mixed m. p. 198—199° (Found : C, 81·8; H, 6·3. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%).

Unidentified Anthracene Homologues.—Chromatography on alumina (350 g.) of the anthracene fraction 10 (5·0 g.) by the general method outlined above yielded three products. (i) 2 : 3 : 6-Trimethylanthracene, m. p. 248—250°, was identified by mixed m. p. (ii) A *substance* which, after further chromatography and crystallisation from methanol–benzene, formed blades (10 mg.), m. p. 108—110° (Found : C, 92·2; H, 7·5. $C_{17}H_{16}$ requires C, 92·7; H, 7·3. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Light absorption : $\lambda_{\max.}$ 258, (infl. 317), 329, 344, 361, 381 mμ [log ε 5·03, (3·17), 3·43, 3·66, 3·81, 3·73]. Its *quinone* crystallised from benzene–ethanol in pale yellow needles, m. p. 193—194° (Found : C, 81·9; H, 5·9. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). The m. p. was depressed when the compound was mixed with 1 : 2 : 3-trimethylanthraquinone (m. p. 187—188°), prepared as described by Baddeley, Holt, and Makar.[13] (iii) The third hydrocarbon formed pale yellow blades, m. p. 224—225° (10 mg.), from ethanol–benzene (Found : C, 92·5; H, 7·4%). Light absorption : $\lambda_{\max.}$ 258, 331, 347, 367, (infl. 381), 386 mμ [log ε 5·08, 3·49, 3·80, 4·04, (3·81), 3·90]. Its quinone separated from ethanol–benzene in fine yellow needles, m. p. 225—226°, and depressed the m. p. of the hydrocarbon.

The hydrocarbon, m. p. 224—225°, was also obtained by chromatography of fraction 12, and accompanied another substance which, after further chromatography, gave blades, m. p. 169—170°, from ethanol–benzene (30 mg.) (Found : C, 92·5; H, 7·4%). Light absorption : $\lambda_{\max.}$ 260, 333, 348·5, 366, 385 mμ [log ε 5·17, 3·40, 3·63, 3·74, 3·62]. Oxidation with chromic acid afforded a quinone as pale yellow needles, m. p. 169—170° (Found : C, 81·7; H, 5·6%); reduction of the quinone with zinc and acetic acid regenerated the hydrocarbon, thus showing the absence of *meso*-substituents.

Attempts to obtain crystalline hydrocarbons from some of the gummy chromatogram fractions by codistillation with ethylene glycol, as described by Farthing,[14] were unsuccessful.

Crystallisation of Molecular Complexes.—The benzene and light petroleum–benzene eluates of fractions 14 and 15 were combined, and the oil (5·6 g.) treated with picric acid (6 g.) in ethanol. The dark purple picrate was crystallised three times from benzene–ethanol, decomposed on alumina, and the recovered oil converted into its *s*-trinitrobenzene complex. After repeated crystallisation from benzene, the red needles (m. p. about 159°) were decomposed with stannous chloride in acetic acid. The recovered oil was chromatographed on alumina in light petroleum (b. p. 60—80°) and afforded a pale yellow oil (100 mg.) which crystallised at $-10°$. Crystallisation from methanol gave pale yellow blades, m. p. 67—69° (Found : C, 92·4; H, 7·4. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Light absorption : $\lambda_{\max.}$ 253, 261, (infl. 335), 352, 370, 390 mμ [log ε 4·91, 5·23, (3·44), 3·70, 3·83, 3·77]. The *s-trinitrobenzene complex* formed bright red needles, m. p. 167—168°, from methanol–benzene (Found : C, 64·7; H, 4·9. $C_{18}H_{18},C_6H_3O_6N_3$ requires C, 64·4; H, 4·7%). The picrate crystallised from ethanol in brown needles, m. p. 157—159°.

2 : 4 : 6 : 3′ : 4′-*Pentamethylbenzophenone.*—A solution of aluminium chloride (30 g.) and 3 : 4-dimethylbenzoyl chloride (36·5 g.) in methylene chloride (200 c.c.) was added to one of

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[13] Baddeley, Holt, and Makar, *J.*, 1952, 2415.

[14] Farthing, *J.*, 1953, 3261.

mesitylene (26 g.) in methylene chloride (200 c.c.), cooled in ice water. After ½ hr. at room temperature the orange-red solution was poured on ice, and the methylene chloride layer washed (sodium hydroxide solution and water), dried, and evaporated. The *ketone* was crystallised from light petroleum (b. p. 40—60°) and from methanol, and formed rhombs, m. p. 86—87° (32 g.) (Found : C, 85·7 ; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7 ; H, 8·0%).

Elbs Pyrolysis.—The ketone (5·0 g.) was heated at 340° in a metal-bath for 8 hr. The dark semi-solid product was chromatographed on alumina in benzene–light petroleum (b. p. 60—80°) (1 : 4). This removed most of the colour, and afforded a yellow gum (2·7 g.) and, later, a solid (0·5 g.). The latter crystallised from benzene in plates, m. p. 250—252° alone or mixed with 2 : 3 : 6-trimethylanthracene (Found : C, 93·0; H, 7·0. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). The oil solidified and after several crystallisations from ethanol formed needles, m. p. 129—130° (400 mg.). This material was further purified by oxidation to the quinone (m. p. and mixed m. p. with 1 : 3 : 6 : 7-tetramethylanthraquinone, 196—197°), and reduction of the latter by the two-stage method of Badger and Cook.[15] 1 : 3 : 6 : 7-*Tetramethylanthracene* was obtained as prismatic needles (120 mg.), m. p. 130° (from benzene–ethanol) (Found : C, 92·1; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Light absorption : $\lambda_{max.}$ 251, 260, (infl. 330), 345, 362, 383 mμ [log ε 4·98, 5·33, (3·42), 3·66, 3·76, 3·65]. The m. p. of a mixture with the hydrocarbon from the oil was 130—131°.

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[15] Badger and Cook, *J.*, 1939, 802.