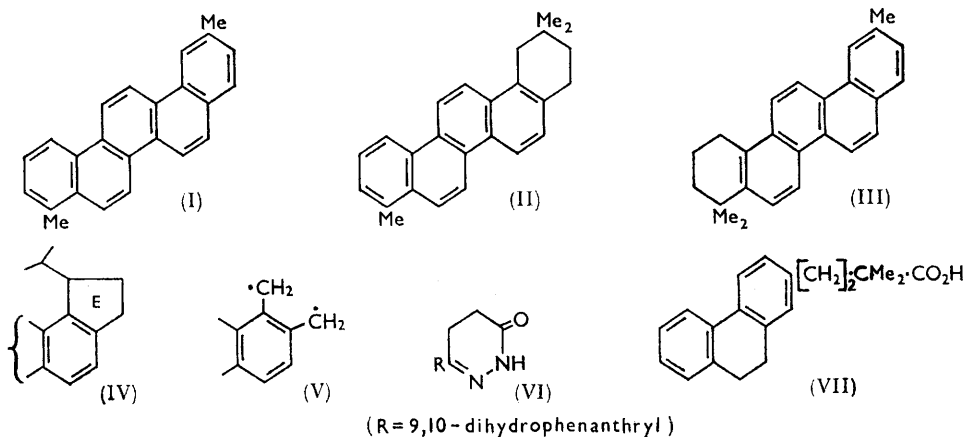


143. The Constituents of High-boiling Petroleum Distillates. Part VIII.¹ Identification of 1,2,3,4-Tetrahydro-2,2,9-trimethylpicene in an American Crude Oil.*

By W. CARRUTHERS and D. A. M. WATKINS.

A hydrocarbon previously isolated from an American crude oil has been identified by synthesis as the tetrahydropicene derivative (II) named in the title.

A HYDROCARBON isolated by Carruthers and Cook² from a fraction of an American crude oil, and shown from its ultraviolet spectrum to be a derivative of chrysene, has been identified as the tetrahydropicene derivative (II). The molecular weight, determined by mass spectroscopy, was 324, in agreement with the formula $C_{25}H_{24}$. It was resistant to dehydrogenation with palladium,² but with selenium at 350° 2,9-dimethylpicene (I) was obtained, accounting for all but one of the carbon atoms. In the infrared spectrum there were bands at 1384 and 1362 cm^{-1} , ascribable to a *gem*-dimethyl or an isopropyl group,³ and Kuhn-Roth oxidation indicated the presence of 1.9 C-methyl groups. These results pointed to structure (II) or (III), the alternative (IV) with an isopropyl substituent in a five-membered ring-E also being possible,⁴ though less likely. In favour of structure (II), the mass spectrum showed, in addition to the parent peak, a single intense fragment ion at mass-number 268, corresponding to the expected cleavage product (V),⁵ and this structure was confirmed by synthesis.



Friedel-Crafts condensation of 9,10-dihydrophenanthrene⁶ with $\alpha\alpha$ -dimethylsuccinic anhydride proceeded smoothly to give an oxo-acid, which was converted (in poor yield) into the dihydrophenanthrylbutyric acid (VII) by the Clemmensen or Huang-Minlon reaction. The main product from the Huang-Minlon reaction was a neutral crystalline substance regarded as the pyridazinone (VI);⁷ it showed strong bands in the infrared at 1670 (amide carbonyl) and 3300 cm^{-1} ($-NH-$), and by hydrolysis with ethanolic hydrogen chloride it afforded the ethyl ester of the oxo-acid. The $\alpha\alpha$ -dimethyl structure of the

* Preliminary communication, Carruthers and Watkins, *Chem. and Ind.*, 1963, 1433.

¹ Part VII, Carruthers, *J.*, 1963, 5551.

² Carruthers and Cook, *J.*, 1954, 2047.

³ Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, p. 24.

⁴ Cf. Phillips, Cimildoro, Scheiner, and Johnson, *J. Org. Chem.*, 1958, 23, 786.

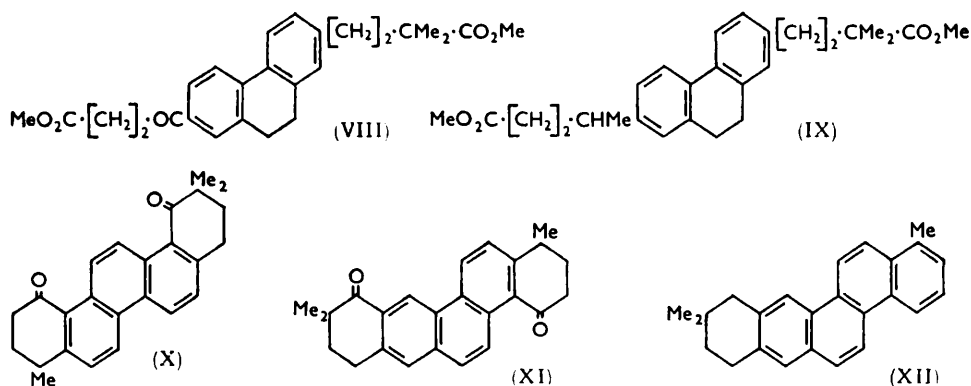
⁵ Personal communication from Dr. Bowen, Shell Research Limited.

⁶ Cf. Phillips, *J. Amer. Chem. Soc.*, 1953, 75, 3223.

⁷ Cf. Haworth, Moore, and Pauson, *J.*, 1949, 3271.

oxo-acid was based on analogy,⁸ but the poor yields obtained in the Clemmensen reaction suggested that the oxo-group might be sterically hindered and that the Friedel-Crafts product was, unexpectedly,⁶ the $\beta\beta$ -dimethyl acid. However, cyclisation of the acid (VII), followed by reduction of the carbonyl group and dehydrogenation, afforded 10-methylbenz[*a*]anthracene in good yield, thus confirming the assigned structure. Friedel-Crafts condensation of the methyl ester of acid (VII) with succinic anhydride, and esterification of the product, afforded the oxo-diester (VIII);⁶ reaction with methylmagnesium iodide and hydrogenation gave the di-ester (IX). An attempt to effect this conversion in one step by reaction of the mono-ester of (VII) with γ -valerolactone⁶ gave a mixture shown by gas chromatography to contain at least three major components. It was not further investigated.

Dehydrogenation of the di-ester (IX) with palladium, hydrolysis, and double cyclisation of the resulting phenanthrenebisbutyric acid with polyphosphoric acid afforded a mixture, from which the required product (X) and three other isomeric diketones were separated by chromatography. Wolf-Kishner reduction of the diketone (X) under forcing conditions⁹ gave the corresponding hydrocarbon whose structure was confirmed by dehydrogenation with selenium to 2,9-dimethylpicene (I), and by its infrared spectrum, which had a single strong maximum in the aromatic C-H out-of-plane deformation region at 810



cm^{-1} , similar to that in the spectrum of 1,2,7,8-tetramethylphenanthrene. On dehydrogenation of the reduced product with palladium under moderate conditions, the ring bearing the *gem*-dimethyl substituent was unaffected¹⁰ and the tetrahydrotrimethylpicene (II) was obtained in good yield. In agreement with its structure it showed typical chrysene-type ultraviolet absorption, and two bands in the infrared spectrum at 1362 and 1380 cm^{-1} due to the *gem*-dimethyl group. The infrared spectrum was identical with that of the hydrocarbon from the oil.²

A second product from the cyclisation was identified as the diketone (XI). Wolf-Kishner reduction⁹ and partial dehydrogenation with palladium gave the chrysene derivative (XII), which was converted by further dehydrogenation with selenium into 3,12-dimethylnaphth[2,1-*a*]anthracene, identified by comparison of its ultraviolet spectrum with that of the parent compound.¹¹ Two other ketones, isolated in small amount, were presumably produced by the two remaining alternative modes of cyclisation. In agreement, reduction of each by the modified Huang-Minlon procedure⁹ afforded the corresponding phenanthrene hydrocarbon, converted in each case into a derivative of benz[*a*]anthracene

⁸ Berliner, *Org. Reactions*, 1949, **5**, 245.

⁹ Barton, Ives, and Thomas, *J.*, 1955, 2056.

¹⁰ Cf. Plattner, in "Newer Methods of Preparative Organic Chemistry," Interscience, New York and London, 1948, p. 21 *et seq.*

¹¹ Clar and Lombardi, *Ber.*, 1932, **65**, 1411.

by partial dehydrogenation with palladium. There was insufficient material to identify the isomers completely.

The structure of the hydrocarbon (II) strongly suggests that it is derived from an isoprenoid precursor, possibly a triterpenoid; chrysene derivatives have been detected among the products of selenium dehydrogenation of some triterpenoids.¹² Other polyisoprenoids have recently been found in petroleum fractions¹³ and their occurrence further supports the view that part at least of crude petroleum oils is of biological origin.¹⁴ A number of aromatic hydrocarbons which are thought to be derived from triterpenes by partial dehydrogenation have recently been isolated from Bohemian brown coal.¹⁵ One of these, C₂₅H₂₄, m. p. 251°, has been shown to be identical with one hydrocarbon by direct comparison (mixed m. p. and infrared spectra) with a specimen supplied by Professor Šorm, who reports that he has independently arrived at the same structure for the compound.

EXPERIMENTAL

M. p.s were determined on a Kofler block. Ultraviolet spectra were recorded with a Unicam S.P. 700 spectrophotometer, for solutions in 95% ethanol unless otherwise stated. Light petroleum had b. p. 60—80°.

Dehydrogenation of the Hydrocarbon from Oil.—A mixture of the hydrocarbon (70 mg.) and selenium (140 mg.) was heated at 350° under nitrogen in a sealed tube for 24 hr. The product (68 mg.), extracted with hot benzene, was chromatographed on alumina and gave 2,9-dimethylpicene (I) as plates, m. p. 301—304° (from benzene), not depressed when mixed with an authentic specimen, m. p. 303—305° (Found: C, 94.0; H, 5.85. Calc. for C₂₄H₁₈: C, 93.7; H, 6.3%), λ_{max.} (in chloroform) 261, 278, 289, 306, 319, 334, 360, 378 mμ (log ε 4.77, 4.85, 4.99, 4.58, 4.27, 4.36, 3.03, 3.00). Oxidation of the 2,9-dimethylpicene (38 mg.) with chromium trioxide (40 mg.) in acetic acid, and purification of the product on alumina, afforded the quinone, m. p. 245—250° (decomp.) [lit.,¹⁶ 252—255° (decomp.)]. With concentrated sulphuric acid it gave a deep blue colour, rapidly developing a greenish tinge.

Condensation of 9,10-Dihydrophenanthrene with αα-Dimethylsuccinic Anhydride.—A solution of 9,10-dihydrophenanthrene (115 g.) in nitrobenzene (100 c.c.) was added gradually to a cooled (ice-bath) solution of αα-dimethylsuccinic anhydride (68 g.) and aluminium chloride (143 g.) in nitrobenzene (500 c.c.). Next morning, ice and hydrochloric acid were added and nitrobenzene was removed in steam. The recovered *oxo-acid* crystallised from benzene as plates, m. p. 174—176° (91 g.) (Found: C, 77.9; H, 6.7. C₂₀H₂₀O₃ requires C, 77.9; H, 6.5%), λ_{max.} (235), 294, 298, 310, 316 mμ [log ε (3.93), 4.39, 4.39, 4.36, 4.34]. Concentration of the mother-liquors afforded a second crop (30 g.), m. p. 170—174°.

γ-(9,10-Dihydro-2-phenanthryl)-αα-dimethylbutyric Acid (VII).—(a) A solution of the *oxo-acid* (13 g.), sodium hydroxide (13 g.), and 99% hydrazine hydrate (16 c.c.) in diethylene glycol (200 c.c.) was boiled for 2 hr., and heating was then continued for 3 hr. at 200°. The cooled solution was diluted with water, extracted with benzene to recover a precipitated neutral product (9.4 g.), and acidified. The *product* (3.6 g.) formed needles from benzene—light petroleum, m. p. 105—107° (Found: C, 81.6; H, 7.3. C₂₀H₂₂O₂ requires C, 81.6; H, 7.5%), λ_{max.} 270, 299, 323 mμ (log ε 4.20, 3.58, 2.68%). The *methyl ester*, prepared with methanol and hydrogen chloride, had b. p. 180°(air bath)/0.5 mm. (Found: C, 82.0; H, 7.9. C₂₁H₂₄O₂ requires C, 81.8; H, 7.8%), λ_{max.} 276, 308 mμ (log ε 4.24, 3.69), ν_{max.} 1730 cm⁻¹. The neutral product was chromatographed on alumina and crystallised from benzene and from ethanol, giving the *dihydropyridazinone* (VI) as needles, m. p. 185° (Found: C, 78.6; H, 6.4; N, 9.7%; M, 294. C₂₀H₂₀N₂O requires C, 78.9; H, 6.6; N, 9.2%; M, 304), λ_{max.} 244, (312), 327 mμ

¹² Ruzicka, Brungger, Egli, Ehman, Furter, and Hösli, *Helv. Chim. Acta*, 1932, **15**, 431; Jacobs and Isler, *J. Biol. Chem.*, 1937, **119**, 155; Ruzicka, Rey, and Muhr, *Helv. Chim. Acta*, 1944, **27**, 472.

¹³ Barton, Carruthers, and Overton, *J.*, 1956, 788; Dean and Whitehead, *Tetrahedron Letters*, 1961, No. 21, 768; Bendoraitis, Brown, and Hepner, *Analyt. Chem.*, 1962, **34**, 49.

¹⁴ See, e.g., Sir Robert Robinson, *Catalyst*, 1961, **6**, 41; *Nature*, 1963, **199**, 113; Martin, Winters, and Williams, *Nature*, 1963, **199**, 110.

¹⁵ Jarolím, Streibl, Horák, and Šorm, *Chem. and Ind.*, 1958, 1142; Jarolím, Hejno, and Šorm, International Symposium on the Chemistry of Natural Products, Brussels, 1962, Abstracts, p. 524; Jarolím, Streibl, Hejno, and Šorm, *Coll. Czech. Chem. Comm.*, 1961, **26**, 451.

¹⁶ Wieland, Hartman, and Dietrich, *Annalen*, 1936, **522**, 206.

[log ϵ 2.83, (3.46), 3.5]. Hydrolysis with hydrogen chloride in ethanol for 12 hr. on the water-bath afforded the oily oxo-ester (ν_{\max} 1740, 1690 cm^{-1}), converted with potassium hydroxide in aqueous ethylene glycol into the oxo-acid, m. p. and mixed m. p. 173—174°.

(b) A mixture of the oxo-acid (91 g.), amalgamated zinc (160 g.), hydrochloric acid (300 c.c.), water (70 c.c.), toluene (150 c.c.), and acetic acid (100 c.c.) was boiled for 72 hr. The product was crystallised from benzene–light petroleum (1 : 1; \sim 500 c.c.). The first crop was mainly the oxo-acid, m. p. 160—170° (63 g.); concentration of the mother-liquors and fractional crystallisation of the residue then gave the butyric acid (VII) (16 g.), m. p. 105° alone or mixed with the product from the Huang-Minlon reduction. Separation was more conveniently effected by esterification of the material from the mother liquors with methanol and hydrogen chloride, followed by chromatography of the mixed esters on alumina and graded elution of the esters with light petroleum–benzene mixtures.

Cyclisation of γ -(9,10-Dihydro-2-phenanthryl)- α -dimethylbutyric Acid.—The acid (790 mg.) and phosphorus pentachloride (690 mg.) in benzene (15 c.c.) were kept at room temperature for 1 hr., then warmed on the water-bath for 5 min. The resulting solution was cooled to 0° and a solution of stannic chloride (6 c.c.) in benzene (30 c.c.) was added. After 1 hr. ice was added and the ketone (560 mg.) was chromatographed on alumina. It crystallised from hexane as plates, m. p. 113—114° (Found: C, 87.0; H, 7.3. $\text{C}_{20}\text{H}_{20}\text{O}$ requires C, 86.9; H, 7.3%), λ_{\max} 253, (273), 290, 320, 323 $\text{m}\mu$ [log ϵ 4.56, (4.29), 3.94, 3.23, 3.23], ν_{\max} (Nujol) 1660 cm^{-1} .

5,6,8,9,10,11-Hexahydro-10,10-dimethylbenz[a]anthracene.—The above ketone (800 mg.), amalgamated zinc (5 g.), hydrochloric acid (25 c.c.), acetic acid (10 c.c.), and toluene (6 c.c.) were boiled for 72 hr. The cooled mixture was extracted with benzene, and the recovered neutral gum in light petroleum was filtered through alumina. The hexahydro-compound formed plates, m. p. 88° (from hexane) (Found: C, 91.7; H, 8.4. $\text{C}_{20}\text{H}_{22}$ requires C, 91.5; H, 8.45%), λ_{\max} 266, (272), (294), 303 $\text{m}\mu$ [log ϵ 4.28, (4.25), (3.83), 3.87].

This compound (200 mg.) was dehydrogenated with selenium (500 mg.) at 340° for 20 hr. The product was chromatographed on alumina, and afforded 10-methylbenz[a]anthracene (160 mg.) m. p. and mixed m. p. 180—182° (lit.,¹⁷ 181°), λ_{\max} 227, 256, 266, 276, 286, 298, (315), 323, 331, 336, 344, 352, 361, 370, 382 $\text{m}\mu$ (log ϵ 4.46, 4.54, 4.58, 4.83, 4.94, 4.99, (3.69), 3.78, 3.78, 3.82, 3.73, 3.66, 3.40, 2.92, 3.04). Oxidation with chromium trioxide in acetic acid gave 10-methylbenz[a]anthracene-7,12-dione as fine yellow needles, m. p. 163—164° (lit.,¹⁷ 164—166°).

Condensation of Methyl- γ -(9,10-Dihydro-2-phenanthryl)- α -dimethylbutyrate with Succinic Anhydride.—A solution of the ester (VII) (39 g.) in nitrobenzene (70 c.c.) was added to a solution of succinic anhydride (15.2 g.) and aluminium chloride (41 g.) in nitrobenzene (130 c.c.). Next morning, ice and hydrochloric acid were added and the nitrobenzene was removed with steam. The oxo-acid (40 g.) crystallised from ethanol–benzene as plates, m. p. 145—147° (Found: C, 73.5; H, 6.95. $\text{C}_{25}\text{H}_{28}\text{O}_5$ requires C, 73.5; H, 6.9%). The methyl ester (VIII), prepared with methanol and hydrogen chloride, formed plates from methanol–benzene, m. p. 80—81° (Found: C, 74.2; H, 7.1. $\text{C}_{26}\text{H}_{30}\text{O}_5$ requires C, 73.9; H, 7.2%); λ_{\max} 306—328 $\text{m}\mu$ (log ϵ 4.36), ν_{\max} (Nujol), 1660, 1720 cm^{-1} .

Reaction of the Oxo-di-ester with Methylmagnesium Iodide.—A solution prepared from magnesium (1.5 g.) and methyl iodide (9.1 g.) in ether (200 c.c.) was added dropwise to a stirred solution of the foregoing oxo-di-ester (VIII) (18 g.) in benzene (150 c.c.). The mixture was boiled for 4 hr., decomposed with dilute sulphuric acid, and the organic layer separated and extracted with aqueous sodium carbonate. Acidification of the extract gave the unsaturated acid (11.8 g.), m. p. 113—116° (Found: C, 76.7; H, 7.5. $\text{C}_{26}\text{H}_{30}\text{O}_4$ requires C, 76.8; H, 7.4%), λ_{\max} 286, (313) $\text{m}\mu$ (log ϵ 4.45, 4.44), ν_{\max} (Nujol) 1700, 1740 cm^{-1} . The dimethyl ester, prepared with diazomethane, had b. p. 270°(air bath)/0.5 mm. (Found: C, 77.35; H, 7.85. $\text{C}_{27}\text{H}_{32}\text{O}_4$ requires C, 77.1; H, 7.7%), λ_{\max} 290, (313) $\text{m}\mu$ [log ϵ 4.38, (4.21)], ν_{\max} 1740 cm^{-1} .

Hydrogenation of the Unsaturated Di-ester.—The unsaturated di-ester (10.2 g.) was hydrogenated in methanol solution with 10% palladised charcoal (1 g.). The saturated di-ester (IX) (9.3 g.) had b. p. 260—270°(air bath)/0.8 mm. (Found: C, 77.2; H, 7.95. $\text{C}_{27}\text{H}_{34}\text{O}_4$ requires C, 76.7; H, 8.1%), λ_{\max} 276, (303) $\text{m}\mu$ (log ϵ 4.20, 3.90), ν_{\max} 1740, 1385, 1365 cm^{-1} .

Dehydrogenation.—The saturated di-ester (9.8 g.) was heated with 10% palladised charcoal (1 g.) at 240° in an atmosphere of nitrogen. The temperature was raised slowly to 280° and after 45 min. the product was extracted with benzene and filtered through alumina. The

¹⁷ Bachman and Chemarda, *J. Org. Chem.*, 1941, 6, 36.

728 *The Constituents of High-boiling Petroleum Distillates. Part VIII.*

phenanthrenebisbutyric ester (8.6 g.) was obtained as an oil, b. p. 260°(air bath)/0.5 mm. (Found: C, 77.5; H, 7.65. $C_{27}H_{32}O_4$ requires C, 77.1; H, 7.7%), λ_{max} (223), 256, 281, 289, 299, 321, 329, 336, 344, 352 $m\mu$ [$\log \epsilon$ (4.20), 4.70, 4.18, 4.04, 3.80, 3.36, 3.28, 2.37, 2.17, 2.00]. Hydrolysis of the ester (8.9 g.) with potassium hydroxide (6.5 g.) in water (16 c.c.) and ethylene glycol (80 c.c.) for 10 hr. gave the corresponding acid (6.3 g.) as needles, m. p. 187—189° (from benzene-methanol) (Found: C, 76.3; H, 7.3. $C_{25}H_{28}O_4$ requires C, 76.5; H, 7.2%).

Cyclisation with Polyphosphoric Acid.—The phenanthrenebisbutyric acid (3.9 g.) and polyphosphoric acid (125 c.c.) were heated, with stirring, at 70—75° for 70 hr. The cooled solution was poured into water and extracted with ether, the extract washed (Na_2CO_3 and water) and dried, and the ether evaporated. The semi-solid product (3.2 g.) was chromatographed on alumina (grade II); graded elution with light petroleum-benzene mixtures, followed when necessary by re-chromatography, gave four crystalline ketones eluted in order as follows.

(i) 3,4,5,6,10,11,12,13-Octahydro-3,12,12-trimethylnaphth[2,1-a]anthracene-6,13-dione (XI) (600 mg.; crude) formed pale yellow blades, m. p. 178—179° (from ethanol-benzene) (Found: C, 84.3; H, 6.5. $C_{25}H_{24}O_2$ requires C, 84.2; H, 6.8%), λ_{max} (236), 250, 258, 268, 321, 333, 358, 378 $m\mu$ [$\log \epsilon$ (4.58), 4.55, 4.63, 4.58, 4.29, 4.27, 3.69, 3.63].

(ii) A diketone (250 mg.; crude), forming pale yellow blades in ethanol-benzene, m. p. 199—200° (Found: C, 84.3; H, 6.9. Calc. for $C_{25}H_{24}O_2$: C, 84.2; H, 6.8%), λ_{max} 260, 268, (310), 328, 342, (362), 384 $m\mu$ [$\log \epsilon$ 4.80, 4.76, (4.11), 4.28, 4.29, (3.71), 3.20]. Reduction of this product (170 mg.) with sodium (0.1 g.) and hydrazine in diethylene glycol (10 c.c.)⁹ gave the corresponding hydrocarbon (80 mg.) as blades, m. p. 130—131° (Found: C, 91.3; H, 8.65. Calc. for $C_{25}H_{28}$: C, 91.4; H, 8.6%), λ_{max} 261, 279, (286), (298), 305, 326, 342.5, 351 $m\mu$ [$\log \epsilon$ 4.86, 4.52, (4.46), (4.29), 4.14, 2.70, 2.63, 2.55]. A portion, with 10% palladised charcoal at 240° for $\frac{1}{2}$ hr., was converted into a benz[a]anthracene derivative forming plates in ethanol, which melted at 168°, resolidified, and melted at 188° (Found: C, 92.3; H, 7.2. Calc. for $C_{25}H_{24}$: C, 92.5; H, 7.5%), λ_{max} (258), 266, 276, 286, 296, 319, 333, 347, 364 $m\mu$ [$\log \epsilon$ 4.24, 4.34, 4.50, 4.76, 4.83, 3.60, 3.77, 3.81, 3.68]; further dehydrogenation of this material with selenium afforded a small amount of a product which could not be purified.

(iii) Continued elution afforded 1,2,3,4,9,10,11,12-octahydro-2,2,9-trimethylpicene-1,12-dione (X) (800 mg.) as pale yellow blades (from ethanol-benzene), m. p. 160—162° (Found: C, 84.3; H, 6.8. $C_{25}H_{24}O_2$ requires C, 84.2; H, 6.8%), λ_{max} 227, (256), 264, 313, (333), (370) $m\mu$ [$\log \epsilon$ 4.56, (4.53), 4.62, 4.25, (4.46), (3.45)].

(iv) A fourth diketone (400 mg.; crude) formed plates, m. p. 200—202° (from ethanol-benzene) (Found: C, 84.2; H, 6.8. Calc. for $C_{25}H_{24}O_2$: C, 84.2; H, 6.8%), λ_{max} 262, 270, (313), 330, 342, (364), 385 $m\mu$ [$\log \epsilon$ 4.69, 4.65, (4.00), 4.18, 4.19, 3.58, 3.24]. Reduction of this product (130 mg.) with sodium (0.1 g.) and hydrazine in diethylene glycol (10 c.c.)⁹ afforded the hydrocarbon as needles (70 mg.), m. p. 166—167° (from ethanol-benzene) (Found: C, 91.9; H, 8.4. Calc. for $C_{25}H_{28}$: C, 91.4; H, 8.6%), λ_{max} 263, 283.5, (294), 308, 325, 340, 357 $m\mu$ [$\log \epsilon$ 4.71, 4.27, (4.09), 4.09, 3.25, 3.00, 2.98]. Dehydrogenation of this hydrocarbon (45 mg.) with 10% palladised charcoal at 240° for 1 hr. gave a benz[a]anthracene derivative as plates (12 mg.), m. p. 225—226° (from ethanol-benzene) (Found: C, 92.4; H, 7.5. Calc. for $C_{25}H_{24}$: C, 92.5; H, 7.5%), λ_{max} 248, 257, 266, 276, 286, 297, 325, 340, 355, 373 $m\mu$ ($\log \epsilon$ 4.42, 4.50, 4.53, 4.63, 4.82, 4.82, 3.75, 3.76, 3.92, 3.82). Dehydrogenation with selenium at 360° gave a minute amount of a product with a well defined naphth[2,1-a]anthracene ultraviolet spectrum [λ_{max} (in benzene) 282, 291, 307, 348, 366, 373, 386, 397, 434 $m\mu$ ($\log \epsilon$ 4.28, 4.44, 4.12, 3.35, 3.34, 3.34, 3.22, 3.16, 2.59)], but there was insufficient pure material for analysis.

1,2,3,4-Tetrahydro-2,2,9-trimethylpicene.—The diketone (X) (400 mg.) was reduced with sodium (0.2 g.) and anhydrous hydrazine in diethylene glycol (10 c.c.) as described by Barton, Ives, and Thomas.⁹ Chromatography of the product on alumina afforded the octahydro-trimethylpicene (320 mg.) as needles, m. p. 158—161° (Found: C, 91.1; H, 8.7. $C_{25}H_{28}$ requires C, 91.4; H, 8.6%), λ_{max} 230, 256, 265, 285, 296, 310, (327), 342, 357 $m\mu$ [$\log \epsilon$ 4.41, 4.76, 4.84, 4.26, 4.24, 4.30, (3.10), 3.03, 2.87]. Dehydrogenation of this product (280 mg.) with 10% palladised charcoal (70 mg.) at 240° for 45 min. gave 1,2,3,4-tetrahydro-2,2,9-trimethylpicene (230 mg.) as plates, m. p. 247—249° alone or mixed with the hydrocarbon A from mineral oil⁸ (Found: C, 92.5; H, 7.6. Calc. for $C_{25}H_{24}$: C, 92.5; H, 7.5%), λ_{max} 227, 233, 265, 275, (289), 303, 316, 331, 351, (357), 368 $m\mu$ [$\log \epsilon$ 4.53, 4.53, 4.84, 5.30, (4.30), 4.26, 4.27, 3.28, 3.24, 3.06, 3.15]. The 2,4,7-trinitrofluorenone complex formed orange-red needles, m. p. 259—260° undepressed on admixture with the complex of the hydrocarbon from oil.

Dehydrogenation with selenium at 360° for 18 hr. gave, after chromatography on alumina, plates (from benzene), m. p. 289—300° undepressed when mixed with 2,9-dimethylpicene (m. p. 303—304°), λ_{max} . (in CHCl_3) 262, 280, 290, 308, 323, 336, 362, 382 μ ($\log \epsilon$ 4.63, 4.74, 4.97, 4.41, 4.19, 4.26, 2.96, 2.92).

3,12-Dimethylnaphth[2,1-a]anthracene.—The diketone (XI) (500 mg.) was converted into the *octahydrotrimethylnaphth[2,1-a]anthracene* by the method described above; chromatography on alumina and crystallisation from ethanol-benzene gave blades, m. p. 157—159° (220 mg.) (Found: C, 91.3; H, 8.55. $\text{C}_{25}\text{H}_{28}$ requires C, 91.4; H, 8.6%). Dehydrogenation of the hydrocarbon (70 mg.) with 10% palladised charcoal at 240° for 1 hr. gave 10,11,12,13-tetrahydro-3,12-trimethylnaphth[2,1-a]anthracene (50 mg.) as needles, m. p. 176° (from ethanol-benzene) (Found: C, 92.3; H, 7.3. $\text{C}_{25}\text{H}_{24}$ requires C, 92.5; H, 7.5%), λ_{max} . (227), 235, (250), 269, 278, (292), 305, 311, 321, 333, 351, (357), 370 μ [$\log \epsilon$ (4.50), 4.55, (4.26), 5.09, 5.18, (4.12), 4.08, 4.08, 4.09, 4.04, 2.80, 2.75, 2.58]. Further dehydrogenation of this compound (200 mg.) with selenium (50 mg.) at 340—350° for 18 hr., and chromatography of the product on alumina, gave 3,12-dimethylnaphth[2,1-a]anthracene (20 mg.) as needles, m. p. 308—310° (from benzene) (Found: C, 94.0; H, 6.6. $\text{C}_{24}\text{H}_{18}$ requires C, 94.1; H, 5.9%), λ_{max} . (in benzene) 294, 314, 339, (348), 357, 368, 378, (384), 400 μ [$\log \epsilon$ 5.24, 4.81, 3.96, (3.96), 3.97, 4.02, (3.92), 3.81].

We are indebted to Professor D. H. R. Barton, F.R.S., who first suggested to us the structure of the hydrocarbon from the oil, and to Sir James Cook, F.R.S., for his interest.

MEDICAL RESEARCH COUNCIL, CARCINOGENIC SUBSTANCES RESEARCH UNIT,
UNIVERSITY OF EXETER.

[Received, August 7th, 1963.]