The Constituents of High-boiling Petroleum Distillates. Part II. Trimethylnaphthalenes in a Trinidad Oil.*

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1 : 2 : 5-, 1 : 2 : 7-, and 2 : 3 : 6-Trimethylnaphthalene and a hydrocarbon considered to be an unknown ethylmethylnaphthalene have been isolated from a fraction of a Trinidad crude oil.

THE presence of naphthalene homologues in mineral oil fractions has been demonstrated by several groups of workers. Thus, 1- and 2-methylnaphthalene and seven of the ten dimethylnaphthalenes have been isolated from oils from various sources (see, for example, Sachanen, " The Chemical Constituents of Petroleum," Reinhold Publ. Corp., New York, 1945; Gavat and Irimescu, *Ber.*, 1941, **74**, 1812; Easterfield and McClelland, *J. Soc. Chem.*

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Ind., 1923, **42**, 936). Trimethylnaphthalenes (including the 2 : 3 : 6-isomer) were first unequivocally identified in a fraction from a Roumanian crude oil by Gavat and Irimescu (*Ber.*, 1942, **75**, 820) although other investigators had previously obtained them in an impure form (Markownikoff, *Annalen*, 1886, **234**, 89; Coscuig, *Petroleum Ztg.*, 1938, **34**, No. 20, 1). We have isolated the three trimethylnaphthalenes mentioned in the summary and what is probably an ethylmethylnaphthalene from a fraction of a Trinidad crude oil.

This fraction, of boiling range 267—278°, was prepared by fractional distillation of the crude oil under reduced pressure in the Chemical Engineering Laboratories of the University of Birmingham, and we are greatly indebted to Professor F. Morton for carrying out the fractionation and supplying us with the material for our investigation. The naphthalene components of the fraction were concentrated by selective extraction with furfuraldehyde (Kemp, Hamilton, and Gross, *Ind. Eng. Chem.*, 1948, **40**, 220) and reaction of the resulting aromatic-enriched extract with picric acid in ethanol. The bright red crystalline picrate obtained, on treatment with alkali, yielded an oil consisting very largely of naphthalene derivatives as shown by the ultraviolet absorption spectrum. When this material was cooled, 2 : 3 : 6-trimethylnaphthalene separated in considerable quantity and was identified by analysis, ultraviolet absorption, and oxidation with chromic acid in acetic acid to the known 2 : 3 : 6- and 2 : 6 : 7-trimethyl-1 : 4-naphthaquinone (Kruber, *Ber.*, 1939, **72**, 1972). Its abundance in our material is noteworthy. The total yield of crude hydrocarbon was 14% of the naphthalene concentrate or nearly 1% of the original distillate.

The remaining unsolidified portion of the picrate-forming material was fractionally distilled under reduced pressure, and the fractions were converted into their crystalline picrates and styphnates. By fractional crystallisation of these complexes two other trimethylnaphthalenes, a solid of m. p. 31° and a liquid, were isolated in small yield. These were identified as 1 : 2 : 5- and 1 : 2 : 7-trimethylnaphthalene respectively by comparison of the styphnates and picrates with authentic specimens. There was also obtained a small amount of another liquid hydrocarbon regarded as an unknown ethylmethylnaphthalene. Elementary analysis of the compound and its ultraviolet absorption show that it is a naphthalene hydrocarbon $C_{13}H_{14}$, but the melting points of the picrate (120—121°) and styphnate (131—133°) do not correspond with those recorded for the corresponding derivatives of any of the trimethyl-, propyl-, or *iso*propyl-naphthalenes, or of the known ethylmethylnaphthalenes. With the small amount of hydrocarbon available attempts to obtain further evidence of its structure by oxidation experiments were unsuccessful.

1 : 2 : 7-Trimethylnaphthalene has not previously been isolated from a mineral oil. Gavat and Irimescu (*loc. cit.*) claim to have obtained the 1 : 2 : 5-isomer from a Roumanian petroleum, but their identification appears open to doubt. They isolated a hydrocarbon, f. p. —5°, and assigned to it the structure of 1 : 2 : 5-trimethylnaphthalene because its picrate had the correct m. p. for this (142—143°). Two other trimethylnaphthalenes (1 : 2 : 3- and 1 : 3 : 7-), however, have picrates melting at almost the same temperature and are lower-melting than the 1 : 2 : 5-isomer which has m. p. 33·5° (Harvey, Heilbron, and Kam, *J.*, 1926, 3136; Ruzicka and Ehman, *Helv. Chim. Acta*, 1932, **15**, 140; Kruber, *Ber.*, 1939, **72**, 1972; Hewett, *J.*, 1940, 293).

Attempted fractional sulphonation of the remainder of the naphthalene concentrate, as applied by Kruber to coal tar fractions (see, for example, *Ber.*, 1939, **72**, 1972; 1940, **73**, 1174), was unsuccessful. Much tar was produced and a crystalline sulphonic acid was not obtained. Similar failure attended an attempt to isolate fluorene hydrocarbons from the non-picrate-forming part of the furfuraldehyde extract, through the 9-carboxylic acids by reaction with sodium at 100° and subsequent carboxylation. No acidic product was formed.

EXPERIMENTAL

Preparation of Naphthalene Concentrate.—The Trinidad distillate was a dark yellow mobile oil, b. p. 266·8—278·2°, n_D^{20} 1·5059. It constituted the fraction which ranged from 62·3 to 70·3% of the crude oil distilled. This material (10 l.) was extracted in batches (500 c.c.) by shaking with furfuraldehyde (1 l.) at room temperature for 5—6 hr. The undissolved material from the first extraction was re-treated in the same way. Furfuraldehyde was removed on the steam-bath under reduced pressure and the dark residue distilled as a yellow oil at 110—120°/0·8 mm. (Total yield, 3400 c.c.; n_D^{20} 1·5529.) The aldehyde-insoluble oil was nearly colourless (n_D^{20} 1·4775). The distillate was treated in portions (400 c.c.) with picric acid (250 g.) in ethanol (1 l.). The red picrate was collected and the mother-liquors were repeatedly treated with picric acid (40 g.) until no more picrate separated. The later crops of picrate were contaminated with picric acid. The picrate obtained in this way from the whole of the extract was decomposed by washing its benzene solution with dilute aqueous ammonia and yielded the naphthalene concentrate as a dark oil (490 g.). This had typical naphthalene ultraviolet absorption ($\lambda_{max.}$ 270—280, 325 mμ; log $E^{1\%}_{1\,cm.}$ 2·36, 1·22). From the intensity at 275 mμ it was estimated that the fraction contained 89% of naphthalene compounds.

2 : 3 : 6-*Trimethylnaphthalene*.—When the oil so obtained was kept at −10° for several hours a colourless solid separated (40 g.); it crystallised from ethanol, giving 2 : 3 : 6-trimethylnaphthalene (20 g.) as plates, m. p. 100° (lit., 102°) (Found : C, 91·9; H, 8·4. Calc. for $C_{13}H_{14}$: C, 91·8; H, 8·2%), $\lambda_{max.}$ 228, 270—275, 306 (infl. 314), 320 [log ε 5·05, 3·67, 2·76, (2·56), 2·85]. The picrate formed orange needles, m. p. 126—127° (lit., 130°), and the styphnate pale yellow needles, m. p. 165° (lit., 165°). Further quantities of the hydrocarbon were obtained from the oily filtrate in ethanol (1 l.) at −70° : the crude solid (30 g.; m. p. 93°) afforded pure 2 : 3 : 6-trimethylnaphthalene, m. p. 100° on crystallisation from ethanol. Fractional crystallisation of the styphnate prepared from the mother-liquors of these crystallisations did not afford any other hydrocarbon.

The hydrocarbon, oxidised as described by Kruber (*loc. cit.*), afforded 2 : 3 : 6-, m. p. 100—101° (lit., 103°) (Found : C, 78·1; H, 6·3. Calc. for $C_{13}H_{12}O_2$: C, 78·0; H, 6·0%), and 2 : 6 : 7-trimethyl-1 : 4-naphthaquinone, m. p. 73—74° (lit., 72°) (Found : C, 78·3; H, 6·0%).

1 : 2 : 5- *and* 1 : 2 : 7-*Trimethylnaphthalene*.—The oil remaining after removal of 2 : 3 : 6-trimethylnaphthalene was fractionally distilled under reduced pressure in a column (24 in.) packed with glass helices and surrounded by an electrically heated jacket. Thirty fractions, each of about 12 g., were collected in the boiling range 80—92°/0·5 mm. These quantities were too small for successful fractional crystallisation of molecular complexes. Fractions with similar refractive indexes were accordingly recombined to give eleven larger blends.

The picrate from blended fractions 3 and 4 (25 g.; b. p. 81°/0·5 mm.; n_D^{20} 1·5740) after several crystallisations from benzene was decomposed on alumina and the recovered oil (5 g.) converted into the styphnate. Repeated crystallisation of this from ethanol raised the m. p. of the yellow needles to 154—155°, not depressed when mixed with the styphnate of 1 : 2 : 7-trimethylnaphthalene (lit., m. p. 159°). Decomposition of the pure styphnate on alumina yielded 1 : 2 : 7-trimethylnaphthalene (50 gm.), b. p. 90°/0·2 mm. (air-bath temp.) (Found : C, 91·5; H, 8·1%), $\lambda_{max.}$ 230·5, 280—285, 320, 326 mμ (log ε 5·0, 3·74, 2·56, 2·36). The picrate formed orange-red needles (from ethanol), m. p. and mixed m. p. 127—128° (lit., 129—131°) (Found : C, 56·9; H, 4·4. Calc. for $C_{13}H_{14},C_6H_3O_7N_3$: C, 57·1; H, 4·4%).

1 : 2 : 5-Trimethylnaphthalene was obtained from fractions 23—29. In a typical experiment the picrate from the blend of fractions 23—25 (35·4 g.; b. p. 88—89°/0·5 mm.; n_D^{20} 1·6052) was crystallised twice from benzene and the oil (2·0 g.) recovered from the orange-red needles kept at −70° in ethanol solution. Scratching caused crystallisation. Further quantities were obtained from the mother-liquors. The crystals (500 mg.) were crystallised from methanol, 1 : 2 : 5-trimethylnaphthalene being obtained as colourless needles, m. p. 30—31° (lit., 33·5°) (Found : C, 91·7; H, 8·2%), $\lambda_{max.}$ 230, 275, 288 (infl. 295, 307, 311), 321 mμ [log ε 5·07, 3·78, 3·84, (3·72), (3·12), (2·92), 3·04]. The picrate formed orange-red needles, m. p. 138° (lit., 139—142°), and the styphnate orange needles or plates, m. p. and mixed m. p. 127—129° (lit., 131°) (Found : C, 55·1; H, 4·3. Calc. for $C_{13}H_{14},C_6H_3O_8N_3$: C, 54·9; H, 4·1%).

Ethylmethylnaphthalene.—Fractions 8 and 9 were combined (26·4 g.; b. p. 84°/0·5 mm.; n_D^{20} 1·5940); the picrate was crystallised several times from benzene and the recovered oil (5·6 g.) converted into the styphnate. By repeated crystallisation from ethanol yellow needles of constant m. p. 131—133° were obtained. The hydrocarbon (80 mg.) recovered on decomposition of the styphnate crystallised at −10° but melted again at room temperature. It distilled as a colourless oil at 90°/0·3 mm. (air-bath temp.) (Found : C, 91·6; H, 8·2%), $\lambda_{max.}$ 230·5, 275, 284, (infl. 292), 320 mμ [log ε, 4·9, 3·68, 3·72, (3·26), 2·53]. The picrate formed orange-red needles (from ethanol), m. p. 119—120° (Found : N, 10·7. Calc. for $C_{13}H_{14},C_6H_3O_7N_3$: N, 10·5%). The styphnate crystallised from ethanol in yellow needles, m. p. 131—133°, depressed to 122—125° when mixed with 1 : 2 : 5-trimethylnaphthalene styphnate (Found : N, 10·1. Calc. for $C_{13}H_{14},C_6H_3O_8N_3$: N, 10·1%).

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