89. *The Synthesis and the Physical Properties of Alkylnaphthalenes.*

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Earlier syntheses have been extended up to 1- and 2-*n*-hexadecylnaphthalene. A summary of the physical properties of 1- and 2-alkylnaphthalenes is given and the changes from aromatic to aliphatic characteristics are shown.

As now all the α- and β-mono-*n*-alkylnaphthalenes up to the hexadecylnaphthalenes have been studied in this laboratory (Morrell, Pickering, and Smith, *J. Inst. Petrol.*, 1948, **34**, 677; Bailey, Pickering, and Smith, *ibid.*, 1949, **35**, 103; Bannister and Elsner, *J.*, 1951, 1055; Anderson and Smith, *J. Inst. Petrol.*, 1952, **38**, 415) it is opportune to generalise on the methods of preparation suitable for each series and to examine the accumulated data on physical properties.

For the α-substituted naphthalenes (1-1′-naphthylalkanes), the size of the alkyl chain determines which method of preparation is the most appropriate. 1-Methylnaphthalene is obtained pure from commercial (60%) 1-methylnaphthalene by the sulphonation–desulphonation process (Coulson, *J. Soc. Chem. Ind.*, 1943, **62**, 177; Morrell, Pickering, and Smith, *loc. cit.*). Soffer and Stewart's recent observation (*J. Amer. Chem. Soc.*, 1952, **74**, 567) that the trinitrobenzene complex of 1-methylnaphthalene can be obtained pure from a mixture with the 2-compound (where the picrate method fails) should make the chloromethylnaphthalene route (Morrell, Pickering, and Smith, *ibid.*, p. 680) suitable for small quantites.

1-Ethyl- and 1-propylnaphthalene were prepared through the ketones: Friedel–Crafts reactions with acetyl or propionyl chloride yielded sufficient alkyl 1-naphthyl ketone to make practicable a separation of the picrates. By the Wurtz–Fittig reaction between 1-bromonaphthalene and 1-bromo-butane, -pentane, or -hexane reasonable yields of easily purified products were obtained. From 1-heptyl- to 1-hexadecyl-naphthalene, the condensation between 1-naphthylmagnesium bromide and the alkyl cyanide has given good results (Bannister and Elsner, *loc. cit.*; cf. Nunn and Henze, *J. Org. Chem.*, 1947,

12, 540). Condensation of α-tetralone with Grignard reagents to yield the alcohol and then the olefin was used in two cases (Bailey, Pickering, and Smith; Anderson and Smith, *locc. cit.*). Because of the possibility of freeing them completely from isomerides 1-bromonaphthalene and 1-tetralone are much-preferred starting materials. The suitability of 1-naphthaldehyde is at present being investigated.

For the β-compounds (1-2′-naphthylalkanes) the Friedel–Crafts reaction between an acid chloride and naphthalene (or tetrahydronaphthalene) in nitrobenzene was always used (Buu-Hoï and Cagniant, *Bull. Soc. chim.*, 1945, **12**, 307) as the β-ketone was then readily obtained pure and in high yield. Wherever possible the same specimen of alkyl derivative (bromide or cyanide) was used for the preparation of each of the pair of hydrocarbons, *e.g.*, *n*-tridecanonitrile with 1-naphthylmagnesium bromide for the *n*-dodecyl 1-naphthyl ketone and, after conversion into *n*-tridecanoyl chloride, with naphthalene for the 2-naphthyl ketone.

FIG. 1.

M. p.s of alkylnaphthalenes.

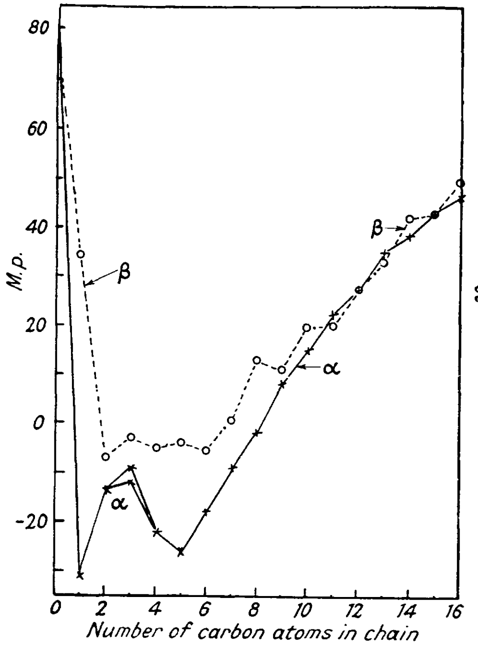
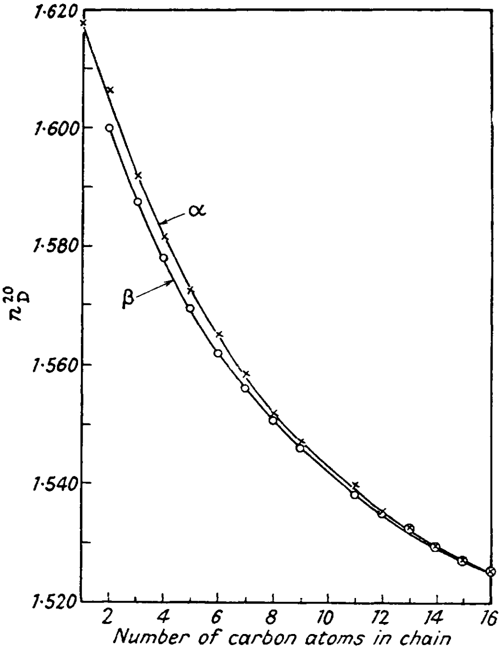


FIG. 2.

n_D^{20} of alkylnaphthalenes.



In most cases previous work left no doubt as to the structure of the ketone or hydrocarbon synthesised, but in some compounds the orientation of the side-chain was established by oxidation. For example, ethyl 1-naphthyl ketone, oxidised with selenium dioxide in dioxan, gave a crude 1 : 2-diketone which, on treatment with alkaline hydrogen peroxide solution, yielded 1-naphthoic acid (Morrell, Pickering, and Smith, *loc. cit.*). This method has been applied also to *n*-amyl 2-naphthyl ketone (Bailey, Pickering, and Smith, *loc. cit.*) and to 1 : 4-di-(5 : 6 : 7 : 8-tetrahydro-2-naphthoyl)butane (Bannister and Elsner, *loc. cit.*).

A satisfactory method of orientating the side-chains of the hydrocarbons by oxidation to 1- or 2-naphthoic acid was developed for 2-*n*-butylnaphthalene. The action of *N*-bromosuccinimide, followed by alkali, on 2-butylnaphthalene gave an olefin which was readily oxidised with permanganate in acetone to 2-naphthoic acid (Pickering and Smith, *Rec. Trav. chim.*, 1950, **69**, 535; cf. Buu-Hoï and Lecocq, *J.*, 1946, 830).

After the intermediates had been carefully purified they were converted into the hydrocarbons which were fractionally distilled, and then crystallised to constant m. p. and refractive index. (Owing to the difficulty of measuring refractive indices at 30—50° accuracy beyond the third place of decimals is not claimed in the values recorded.)

From an inspection of atomic models of the alkylnaphthalenes it appears that the 2-naphthyl isomerides should be less dense than the 1-isomerides, if a freely rotating methylene chain is assumed. In Table 1 the densities recorded all agree with this view. The 2-alkylnaphthalenes have also the lower refractive indices.

Besides this interesting difference between 1- and 2-substituted naphthalenes there is also the gradual change of physical properties (in both the series) with increasing length of paraffin chain. Plotting the refractive index (or the density) against the number of carbon atoms in the paraffin chain gives a smooth curve showing, with increasing molecular weight, a gradual approach to aliphatic values (see Fig. 2): the denser, more highly refracting, aromatic hydrocarbon is changing to the lighter, less refracting, aliphatic type.

For the first six pairs of homologues (1- and 2-isomerides) the boiling points could be measured at atmospheric pressures. The measurements, all made on the same day by distillation from the same apparatus, show that 1-methyl- and 1-ethyl-naphthalene have higher boiling points than the 2-isomerides, but that 2-propyl-, 2-butyl-, 2-pentyl-, and 2-hexyl-naphthalene are higher-boiling than the 1-isomerides. This crossing of the b. p.–C_n curves at C_3 is surprising (Bailey, Pickering, and Smith, *loc. cit.*). Higher in the series the boiling points listed (Table 1) are recorded during distillation *in vacuo* and are not sufficiently accurate to allow comparison.

TABLE 1.

	1-Alkylnaphthalene				2-Alkylnaphthalene			
Alkyl	B. p./mm.†	M. p.	n_D^{20}	d_4^{20}	B. p./mm.†	M. p.	n_D^{20}	d_4^{20}
Methyl	244·5°	−31°	1·6174	1·020	241°	34·2°	—	—
Ethyl	259	−13·5	1·6062	1·008	258	−7	1·5999	0·992
Propyl	272·5	−12, −9	1·5923	0·990	273·5	−3	1·5872	0·977
Butyl	289	−22	1·5811	0·977	292	−5	1·5776	0·966
Pentyl	307	−26	1·5728	0·966	310	−4	1·5694	0·956
Hexyl	322	−18	1·5652	0·958	323·5	−5·5	1·5621	0·948
Heptyl	141/0·5	−9	1·5583	0·9500	146/0·5	0·6	1·5565	0·9407
Octyl *	170/4	−2	1·5510	—	—	13	1·5511	—
Nonyl	138/0·05	8	1·5472	0·9367	139/0·08	11	1·5460	0·9304
Decyl *	200/4	15	1·5448	—	—	19·6	1·5440	—
Undecyl	145/0·01	22·4	1·5394	0·9280	151/0·01	20	1·5383	0·9220
Dodecyl	193/0·5	27·5	1·5348	—	—	27·0	1·5344	0·918
Tridecyl	198/0·5	35	1·5328	—	195/0·5	33	1·5325	—
Tetradecyl ...	204/0·7	38·5	1·5298	—	195/0·15	42	1·5296	—
Pentadecyl ...	213/0·5	43	1·5273	—	220/0·5	43	1·5271	—
Hexadecyl ...	223/0·5	46·5	1·5251	—	210/0·05	49·5	1·5249	—

* Bannister and Elsner, *loc. cit.*

† 760 mm. unless otherwise stated.

TABLE 2. n-*Alkyl naphthyl ketones.*

C atoms in alkyl (Me = 1)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
M. p., 1-naphthyl:	10°	—	—	—	−12°	—	−3°	−8°	10°	—	26°	28°	39°	41°	46°
,, , 2-naphthyl:	53°	59°	53°	54°	68°	60°	58°	57°	52°	47°	47°	51°	55°	61°	62°

Melting points, being properties of the solid state, show less regularity (Fig. 1). After the initial drop from naphthalene (m. p. 80°) to 1- (m. p. −31°) and 2-methylnaphthalene (+34°; cf. benzene 5·5°, and toluene −91°) there is a surprisingly small variation up to the hexylnaphthalenes. Thereafter the aliphatic character begins to assert itself and the two series show rising melting points fitting on " mildly zig-zag curves " which cross and re-cross. It is well known that for nearly all naphthalene derivatives the 2-substituted isomeride is higher-melting (often 50° higher) than the 1-isomeride. With the *n*-alkylnaphthalenes the rule applies up to the decanes; but the undecylnaphthalenes, with more " aliphatic " than " aromatic " carbon atoms provide the first instance of a lower-melting 2-isomeride (1-, m. p. 22°; 2-, m. p. 20°).

Data on the melting points of *n*-alkyl naphthyl ketones are not complete, but the values listed in Table 2 (taken from the naphthalene literature already referred to) give m. p–C_n curves similar to those for the hydrocarbons. There is a maximum difference between the

1- and the 2-isomeride when the side-chain has 6 carbon atoms. After the dodecanoylnaphthalenes the m. p. curves are close and approximately parallel.

The infra-red and ultra-violet spectra of the two series of hydrocarbons have been measured in several laboratories and recorded earlier. Data now given are for only those hydrocarbons described in this paper.

Bailey, Pickering, and Smith (*loc. cit.*) pointed out that the alkylnaphthalenes formed complexes with the usual polynitroaromatic compounds only up to the hexylnaphthalenes. But even the *s*-trinitrobenzene complexes of the hexylnaphthalenes decomposed near their m. p.s; the picrates and styphnates could not be isolated.

Alkyl 2-naphthyl ketones form the usual ketonic derivatives (semicarbazones, oximes, etc.) though with decreasing activity as the length of the paraffin chain increases. From the first two or three *n*-alkyl 1-naphthyl ketones derivatives can be obtained slowly and with difficulty: higher ketones fail to give ketonic reactions except under extreme conditions.

EXPERIMENTAL

Attention to the prescribed detail is essential for the yields and purities recorded.

1-*Tridecylnaphthalene* (1-1′-*Naphthyltridecane*).—*Dodecan*-1-*ol*. Commercial dodecyl alcohol (m. p. 23°) gave on distillation at 140—145°/12 mm. 5 fractions, ranging from m. p. 22·8°, n_{D}^{25} 1·4404, to m. p. 23·5°, n_{D}^{25} 1·4409; the residue melted at 22·9°. Crystallisation of the purer fractions from acetone gave a final product of f. p. 23·90°, m. p. 23·95°, n_{D}^{25} 1·4410. Verkade and Coops (*Rec. Trav. chim.*, 1927, **46**, 903) give f. p. 23·8°, b. p. 130·3°/7 mm. 1-Bromododecane (90% yield by the procedure of *Org. Synth.*, Coll. Vol. I, 1941, pp. 29, 35) had b. p. 150—152°/18 mm., and n_{D}^{20} 1·4580—1·4584, n_{D}^{25} 1·4560—1·4564, throughout the distillation. Heston, Hennethy, and Smyth (*J. Amer. Chem. Soc.*, 1950, **72**, 2071) give n_{D}^{25} 1·45637.

Tridecanonitrile. The bromide (157 g.; n_{D}^{25} 1·4563), potassium cyanide (60 g.; AnalaR), water (70 c.c.), and ethanol (160 c.c.) were heated under reflux for 6 hours. After addition of more potassium cyanide (20 g.), water (30 c.c.), and ethanol (30 c.c.) the mixture was further heated for 48 hours to complete the reaction: the resulting crude nitrile (114 g., 92%) was free from halogen. After distillation at 120°/1 mm. the colourless product crystallised from ethanol at −30° and then melted at +9·6° (thermometer in the liquid) and boiled at 113°/0·2 mm.; n_{D}^{20} was 1·4388. All the nitrile was systematically crystallised to yield a stock of pure tridecanonitrile, m. p. 9·65°. This substance has not previously been described as a solid. The liquid boils at 275°/760 mm. (Lutz, *Ber.*, 1886, **19**, 1438). Daragan (*Bull. Soc. chim. Belg.*, 1935, **44**, 597) gives n_{D}^{20} 1·43867.

n-*Dodecyl* 1-*naphthyl ketone*. Bromonaphthalene (m. p. 5°), crystallised from ethanol at −18°, yielded a product of m. p. 6·15° (thermometer in the liquid). Recrystallisation gave pure 1-bromonaphthalene, m. p. 6·17°. Jones and Lapworth (*J.*, 1914, **105**, 1804) give m. p. 6·2°.

To a solution of 1-naphthylmagnesium bromide (from magnesium, 5·34 g., 0·22 g.-atom; 1-bromonaphthalene, 41·4 g., 0·20 mole; ether, 90 c.c.) was added with stirring tridecanonitrile (31 g., 0·16 mole; m. p. 9·65°) in ether (60 c.c.) during 1 hour while the mixture was refluxing on a hot-plate; heating was continued for 18 hours. There resulted a clear, brown solution and a little unchanged magnesium. After decomposition with water and acid the mixture yielded 4 g. of naphthalene and then 47 g. of a fraction (92%), b. p. 210—220°/0·1 mm., m. p. 26—27°. This *ketone* crystallised easily from acetone at −10°. Systematic crystallisation gave 42·5 g. (82%, calc. on the nitrile) of pure ketone, m. p. 29·25° (thermometer in the liquid), 30—31° (capillary tube), $n_{\mathrm{D}}^{34\cdot5}$ 1·5367, $n_{\mathrm{D}}^{29\cdot5}$ 1·5386, d*n*/d*t* 38 × 10^{-5}, n_{D}^{20} (calc.) 1·5422 (Found: C, 85·2; H, 10·1. $C_{23}H_{32}O$ requires C, 85·2; H, 9·9%). In common with other ketones of this type the substance failed to form carbonyl derivatives.

1-*Tridecylnaphthalene*. The ketone (31·9 g.; m. p. 29·2°) and copper chromite catalyst (8 g.) were stirred with hydrogen (max. pressure 160 atms.) at 200—230° for 4 hours and then for 15 minutes at 250°. After cooling and separation from the catalyst with the aid of ether the reduction product (27 g., 90%) boiled at 170—180°/0·05 mm. and had n_{D}^{20} 1·5028. This low refractive index indicated nuclear reduction, and the specimen was therefore dehydrogenated by heating it with palladium–charcoal (9 g. of hydrocarbon to 0·5 g. of catalyst). Evolution of hydrogen began at 200° and the temperature was gradually raised to 280° during 4 hours. In the presence of a slow stream of nitrogen the melt was heated for 10 minutes to 300°. The product (8·3 g.; b. p. 185°/0·1 mm.) froze at 33·2° and crystallised from acetone (50 c.c.) in icewater, melting at 34·5° (capillary tube); it had $n_{\mathrm{D}}^{29\cdot5}$ 1·5293, n_{D}^{20} (calc.) 1·5329. After being stirred with sodium at 170—200° for ½ hour in nitrogen, and then crystallised from acetone it had m. p. 34·5—35°, $n_{\mathrm{D}}^{29\cdot5}$ 1·5291 (Found: C, 88·8; H, 11·1. Calc. for $C_{23}H_{34}$: C, 89·0; H, 11·0%). Luther and Wächter (*Ber.*, 1949, **82**, 161) give n_{D}^{20} 1·5226 for their (liquid) specimen. An earlier preparation of the hydrocarbon had given n_{D}^{49} 1·5218, $n_{\mathrm{D}}^{39\cdot5}$ 1·5255, $n_{\mathrm{D}}^{29\cdot5}$ 1·5293, so d*n*/d*t* = 38 × 10^{-5}, and, for the pure specimen above, n_{D}^{20} (calc.) 1·5328.

2-*Tridecylnaphthalene*.—n-*Dodecyl* 2′-*naphthyl ketone*. *n*-Tridecanonitrile (49 g.; m. p. 9·65°), potassium hydroxide (40 g.), water (40 c.c.), and ethanol (200 c.c.), when heated for 48 hours under reflux, yielded 53 g. of solid acid. Fractional distillation (with a short column) at 120—128°/0·01 mm. gave 6 g. of m. p. 40·3°, 25 g. of m. p. 41·5°, and 20 g. of m. p. 41·7°. Systematic crystallisation from light petroleum (b. p. 40—60°) brought all fractions to m. p. 41·65—41·70° and, from the mother-liquor, unchanged nitrile was recovered. Garner, Madden, and Rushbrooke (*J.*, 1926, 2491) give f. p. 41·1°.

The acid chloride, obtained in 80% yield by the action of purified thionyl chloride (2 mols. : 1 mol. of acid), boiled at 175°/30 mm., 156—158°/11 mm.

To a solution of pure naphthalene (6·3 g., 1·5 mols.) and tridecanoyl chloride (8·9 g., 1 mol.) in dry, distilled nitrobenzene, powdered aluminium chloride (5·5 g., 1·1 mols.) was gradually added during 0·5 hour, with stirring at <0°. After a further 0·5 hour's stirring the red mixture was left at 20° for 22 hours. Working up in the usual way (excess of naphthalene distilled over with the nitrobenzene) gave a yellow *ketone*, 210—220°/0·2 mm., f. p. 51° (11·7 g., 95%; 91% in another experiment). Crystallisation of 21·7 g. from alcohol and then from acetone gave 15·3 g. of m. p. 54° (capillary tube) (Found: C, 85·2; H, 9·8%). On evaporation of the mother-liquors 3 crops of crystals were obtained, all melting below 30° and containing, presumably, some of the isomeric 1′-naphthyl ketone, a little of which is formed even when nitrobenzene is used as the solvent for the Friedel–Crafts reaction. Ketone of m. p. 54° yielded a 2 : 4-*dinitrophenylhydrazone* (orange-red needles from ethyl acetate), m. p. 122° (Found: N, 11·1. $C_{29}H_{36}O_4N_4$ requires N, 11·3%).

Following the procedure of Huang-Minlon (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) the ketone (12 g.) in 2-2′-hydroxyethoxyethanol (30 c.c.) was added to a solution of sodium (3·0 g.) in this glycol (30 c.c.) and hydrazine hydrate (6·0 c.c. of 90%). After the mixture had been heated for 6 hours the condenser was removed and steam allowed to escape. When the temperature of the liquid reached 230° an air-condenser was fitted and refluxing continued for 18 hours. After an oil, b. p. 90—190°/0·1 mm. and smelling of burnt sugar, had distilled, the main product, b. p. 190—195°/0·1 mm., was obtained as a yellow oil (10·0 g., 87%). When the colour had been removed by passage in light petroleum through alumina, the recovered hydrocarbon was crystallised from acetone to the constant m. p. 33° and $n_{\mathrm{D}}^{29\cdot5}$ 1·5290 (supercooled), n_{D}^{20} (calc.) 1·5326.

A second, similar preparation gave a product (after treatment with alumina) of m. p. 27—30° with a high refractive index, n_{D}^{27} 1·5325, n_{D}^{20} (calc.) 1·5353, and setting to a soft, curdy mass. It seemed that unchanged ketone was present. Fractional distillation, with rejection of the higher-boiling fractions, followed by heating with sodium at 150—200°, gave a product of m. p. 32—33°, $n_{\mathrm{D}}^{24\cdot7}$ 1·5313, n_{D}^{20} (calc.) 1·5332. Crystallisation from acetone gave a *hydrocarbon* of m. p. 32·5—33, $n_{\mathrm{D}}^{29\cdot5}$ 1·5289, n_{D}^{20} (calc.) 1·5325, unchanged by further treatment with sodium and recrystallisation (Found: C, 88·8; H, 10·8. $C_{23}H_{34}$ requires C, 89·0; H 11·0%).

1-*Alkylnaphthalenes*.—These were all obtained in 80—90% yield by reduction of the ketones with copper chromite and hydrogen at 200—250°/150—200 atm., followed by dehydrogenation of the products as described in the preparation of 1-tridecylnaphthalene, and were crystallised from acetone to constant m. p.: 1-Dodecylnaphthalene, b. p. 193°/0·5 mm., m. p. 27·5° (capillary tube), n_{D}^{20} 1·5348 (super-cooled), n_{D}^{49} 1·5235, $n_{\mathrm{D}}^{39\cdot5}$ 1·5272, $n_{\mathrm{D}}^{29\cdot5}$ 1·5309, d*n*/d*t* 38 × 10^{-5}, n_{D}^{20} (calc.) 1·5346 (Buu-Hoï and Cagniant, *loc. cit.*, give m. p. 26·5°); 1-*tetradecylnaphthalene*, b. p. 204/0·7 mm., needles, m. p. 38·5°, d*n*/d*t* 39 × 10^{-5}, $n_{\mathrm{D}}^{40\cdot2}$ 1·5220, n_{D}^{20} (calc.) 1·5298 (Found: C, 88·9; H, 11·3. $C_{24}H_{36}$ requires C, 88·9; H, 11·1%); 1-*pentadecylnaphthalene*, b. p. 213°/0·5 mm., m. p. 42·5—43°, $n_{\mathrm{D}}^{49\cdot5}$ 1·5157, $n_{\mathrm{D}}^{39\cdot5}$ 1·5197, d*n*/d*t* 40 × 10^{-5}, n_{D}^{20} (calc.) 1·5273 (Found: C, 88·7; H, 11·2. $C_{25}H_{38}$ requires C, 88·8; H, 11·2%); 1-hexadecylnaphthalene, b. p. 223°/0·5 mm., m. p. 46—47° (Luther and Wächter, *loc. cit.*, give m. p. 37°), $n_{\mathrm{D}}^{49\cdot5}$ 1·5139, $n_{\mathrm{D}}^{39\cdot5}$ 1·5177, d*n*/d*t* 38 × 10^{-5}, n_{D}^{20} (calc.) 1·5251 (Found: C, 88·6; H, 11·4. Calc. for $C_{26}H_{40}$: C, 88·6; H, 11·4%).

n-*Alkyl* 1-*Naphthyl Ketones*.—These were prepared by methods similar to that for *n*-dodecyl 1-naphthyl ketone: 1-naphthyl undecyl ketone, b. p. 190°/1 mm., m. p. 26° [from 1-naphthylmagnesium bromide and pure dodecanonitrile, n_{D}^{20} 1·4360 (from dodecanoic acid, m. p. 43°);

Bannister and Elsner, *loc. cit.*, give, for the ketone, b. p. 234—236°/6 mm., m. p. 26·8°]; 1-*naphthyl* n-*tridecyl ketone*, b. p. 243°/1 mm., m. p. 39° [from myristonitrile, m. p. 19°, n_D^{20} 1·4411 (Daragan, *loc. cit.*, gives n_D^{20} 1·44126 for the nitrile; Dorinson and Ralston, *J. Amer. Chem. Soc.*, 1944, **66**, 361, give n_D^{20} 1·4410, m. p. 19·25°)] (Found : C, 85·1; H, 10·1. $C_{24}H_{34}O$ requires C, 85·2; H, 10·1%) ; 1-naphthyl *n*-pentadecyl ketone [from palmitonitrile, m. p. 31° (from palmitic acid, m. p. 63°) (Dorinson and Ralston, *loc. cit.*, give m. p. 31·40° for the nitrile)], b. p. 257°/1 mm., m. p. 48° (Found : C, 85·5; H, 10·4. Calc. for $C_{26}H_{38}O$: C, 85·2; H, 10·4%) (Ryan and Nolan, *Proc. Roy. Irish Acad.*, 1913, **30**, *B*, 1, give m. p. 48°).

1-*Naphthyl* n-*tetradecyl ketone*. Tetradecyl alcohol, m. p. 38°, was converted into the bromide, b. p. 167—169°/18 mm., n_D^{20} 1·4575, and this into the nitrile, b. p. 112°/0·5 mm., n_D^{25} 1·4413. Dorinson and Ralston (*loc. cit.*) give n_D^{25} 1·4413 for pentadecanonitrile. With 1-naphthylmagnesium bromide the nitrile yielded the *ketone*, b. p. 250°/1 mm., m. p. 41° (Found : C, 85·1; H, 10·3. $C_{25}H_{36}O$ requires C, 85·2; H, 10·2%).

2-*Alkylnaphthalenes*.—2-Dodecylnaphthalene was kindly supplied by Dr. S. L. Langedijk of the Koninklijke/Shell-Laboratorium, Amsterdam. The remaining 2-alkylnaphthalenes were prepared as follows :

2-*Tetradecylnaphthalene*. Purified tetrahydronaphthalene, tetradecanoyl chloride (from myristic acid, m. p. 54°), nitrobenzene, and aluminium chloride gave 2-(5 : 6 : 7 : 8-tetrahydronaphthyl) *n*-tridecyl ketone, b. p. 225°/0·5 mm., which, crystallised from acetone, melted at 36° (Kölbel and Fritsch, *Brennstoff-Chemie*, 1949, **30**, 73, give m. p. 36·5—36·8°). The 2 : 4-*dinitrophenylhydrazone*, red plates from alcohol, melted at 97° (Found : N, 10·6. $C_{30}H_{42}O_4N_4$ requires N, 10·7%). The crude product from the Huang-Minlon reduction was dehydrogenated (Pd–C at 280°) to give the alkylnaphthalene, b. p. 195°/0·15 mm. Crystallised twice from acetone it melted at 41·5—42·5° (Found : C, 88·8; H, 11·2. Calc. for $C_{24}H_{36}$: C, 88·9; H, 11·1%). Kölbel and Fritsch (*loc. cit.*) give m. p. 21·5°.

2-*Pentadecylnaphthalene*. Pentadecanonitrile, n_D^{25} 1·4413, was hydrolysed to pentadecanoic acid, m. p. 53—54° (lit., m. p. 53—54°). The acid chloride, b. p. 151°/5 mm., condensed with naphthalene in nitrobenzene in presence of aluminium chloride, yielded 2-*naphthyl tetradecyl ketone*, b. p. 230°/1 mm., m. p. 61° (from acetone) (Found : C, 85·0; H, 10·1. $C_{25}H_{36}O$ requires C, 85·2; H, 10·2%). The 2 : 4-*dinitrophenylhydrazone*, red needles from ethyl acetate, melted at 120—121° (Found : N, 10·2. $C_{31}H_{40}O_4N_4$ requires N, 10·5%). By Huang-Minlon reduction,

Infra-red spectra (15—6 μ).

1-Alkylnaphthalenes.
Frequency (cm.$^{-1}$) : liquid

$C_{22}H_{32}$	$C_{23}H_{34}$	$C_{24}H_{36}$	$C_{25}H_{38}$	$C_{26}H_{40}$	
691	690	691	691	690	w
721	721	721	721	721	s
729	729	729	729	729	sh
777	777	777	777	777	vs
792	792	792	792	792	vs
858	858	857	857	857	m
889	889	—	—	—	w
900	900	—	—	—	w
948	948	947	948	947	m
966	966	966	966	965	m
1016	1017	1015	1015	1016	m
1025	1026	1025	1026	1026	sh
1080	1080	1079	1078	1080	m
1116	1116	1117	1116	1115	w
1123	1123	1123	1122	1125	w
1144	1145	1142	1142	1142	w
1166	1166	1164	1165	1164	m
1217	1217	1217	1217	1218	w
1241	1242	1240	1239	1239	w
1260	1262	1260	1261	1260	m
1300	1300	1300	1300	1300	w
1358	1358	1358	1358	1358	w
1376	1376	1376	1376	1376	m
1396	1396	1396	1396	1396	m
1466	1466	1466	1466	1466	s
1508	1508	1508	1508	1508	m
1600	1600	1600	1600	1600	m

2-Alkylnaphthalenes.
Frequency (cm.$^{-1}$) : liquid

$C_{22}H_{32}$	$C_{23}H_{34}$	$C_{24}H_{36}$	$C_{25}H_{38}$	$C_{26}H_{40}$	
720	720	720	720	720	s
744	744	744	744	744	vs
815	815	815	813	813	vs
853	854	853	852	852	s
890	890	890	890	889	s
945	946	946	945	945	m
957	958	958	957	959	m
1018	1020	1019	1019	1019	m
1127	1127	1127	1127	1128	m
1145	1144	1145	1144	1142	w
1155	1156	1156	1154	1154	w
1169	1171	1171	1171	1171	w
1210	1212	1210	1210	1210	w
1243	1243	1240	1240	1241	w
1270	1270	1268	1269	1269	m
1304	1304	1304	1304	1304	w
1370	1370	1365	1365	1365	m
1466	1466	1466	1466	1466	s
1508	1508	1508	1508	1508	m
1605	1605	1610	1608	1610	m
1635	1635	1635	1635	1635	m

s = Strong; vs = very strong; m = medium; w = weak; sh = shoulder.

at 240° for 16 hours, the ketone yielded a *hydrocarbon*, b. p. 220°/0·5 mm. Three crystallisations from acetone gave a product of sharp m. p. 43° (Found : C, 88·6; H, 11·1. $C_{25}H_{38}$ requires C, 88·8; H, 11·2%).

2-Hexadecylnaphthalene. (*a*) *n*-Pentadecyl 2-(5 : 6 : 7 : 8-tetrahydronaphthyl) ketone was prepared from tetrahydronaphthalene, palmitoyl chloride (from palmitic acid, m. p. 63°), nitrobenzene, and aluminium chloride. The fraction of the product boiling at 235—240°/0·1 mm., after two crystallisations from acetone, melted at 44° (Fernholtz, Ansbacher, and MacPhillamy, *J. Amer. Chem. Soc.*, 1940, **62**, 430, give m. p. 44—45°). The 2 : 4-*dinitrophenylhydrazone*, red plates from alcohol, melted at 95—96° (Found : N, 10·1. $C_{32}H_{40}O_4N_4$ requires N, 10·2%).

By the Huang-Minlon reduction (4 hours at 160° and 20 hours at 230°) the crude hydrocarbon, b. p. 203°/0·5 mm., was obtained. It was dehydrogenated with palladium–charcoal (2 hours at 280°) and the product distilled at 200°/1 mm. Crystallisation from acetone yielded plates, m. p. 49·5° (Found : C, 88·5; H, 11·4. Calc. for $C_{26}H_{40}$: C, 88·6; H, 11·4%). Fernholtz, Ansbacher, and MacPhillamy (*loc. cit.*) give m. p. 45—46°; Kölbel and Fritsch (*loc. cit.*) give m. p. 35°.

(*b*) [By R. J. RALLINGS]. *2-Naphthyl* n-*pentadecyl ketone*. Pure palmitic acid, f. p. 62·6° (Smith, *J.*, 1931, 803), was converted into the acid chloride which was not distilled (it melted at 12°). With naphthalene and aluminium chloride in nitrobenzene the acid chloride gave the crude ketone, m. p. 56—59° (70%). Distillation at 240—245°/0·05 mm., followed by crystallisation from alcohol and then acetone, gave the pure ketone, m. p. 62—62·5° (Found : C, 85·1; H, 10·5. Calc. for $C_{26}H_{38}O$: C, 85·2; H, 10·4%). Buu-Hoï and Cagniant (*loc. cit.*) give m. p. 56°. The semicarbazone melted at 105° (Buu-Hoï and Cagniant, *loc. cit.*, give m. p. 97°) (Found : N, 9·7. Calc. for $C_{27}H_{41}ON_3$: N, 9·9%), and the 2 : 4-*dinitrophenylhydrazone*, red needles from alcohol or ethyl acetate, at 117—118° (Found : N, 10·0. $C_{32}H_{42}O_4N_4$ requires N, 10·2%). Hydrolysis of the semicarbazone gave back the ketone, m. p. 62—62·5°, and oxidation of the ketone with selenium dioxide followed by hydrogen peroxide (Morrell, Pickering, and Smith, *loc. cit.*) gave 2-naphthoic acid, m. p. and mixed m. p. 184°.

The pure semicarbazone, heated with sodium ethoxide in ethanol for 20 hours at 220°, gave the hydrocarbon, b. p. 200—210°/0·05 mm., m. p. 45—46° (85%). Crystallised from acetone it reached the constant m. p. 49·5°, as in the preparation (*a*) (Found : C, 88·8; H, 11·4%).

Infra-red Spectra.—These were recorded by Mrs. M. Broomfield, Physical Chemistry Group,

1-*Alkylnaphthalenes.*

Dodecyl		Tridecyl		Tetradecyl		Pentadecyl		Hexadecyl	
λ	log ε	λ	log. ε	λ	log ε	λ	log ε	λ	log ε
2618	3·63	2621	3·71	2617	3·57	2621	3·60	2618	2·97
2717	3·82	2715	3·94	2717	3·84	2718	3·83	2715	3·24
2783	3·81	2790	3·94	—	—	2785	3·84	—	—
2828	3·91	2831	4·03	2825	3·92	2826	3·93	2829	3·33
2891	3·73	2891	3·84	2885	3·72	2890	3·72	2893	3·14
2941	3·73	2941	3·84	2941	3·74	2940	3·73	2942	3·14
3037	2·96	3033	2·86	3038	2·99	3041	2·94	3040	2·91
3078	2·67	3078	2·58	3079	2·60	3071	2·68	3077	2·63
3098	2·60	3100	2·53	3108	2·55	3095	2·58	3102	2·59
3146	2·65	3141	2·58	3147	2·59	3142	2·65	3142	2·63
3182	2·13	3182	2·07	3185	2·10	3188	1·55	3186	1·15
3238	1·57	3248	1·57	3235	1·50	—	—	3239	0·54

2-*Alkylnaphthalenes.*

Dodecyl		Tridecyl		Tetradecyl		Pentadecyl		Hexadecyl	
λ	log ε	λ	log ε	λ	log ε	λ	log ε	λ	log ε
2561	3·52	2554	3·58	2559	3·76	2561	3·57	2561	3·62
2657	3·64	2654	2·72	2655	3·92	2654	3·70	2653	3·76
2757	3·70	2761	3·76	2758	3·96	2756	3·73	2765	3·81
2865	3·53	2868	3·60	2868	3·81	2868	3·56	2868	3·65
2972	2·66	—	—	—	—	2975	2·79	2980	2·77
3050	2·68	3059	2·58	3051	2·77	3048	2·79	3049	2·74
3094	2·38	3094	2·43	3092	2·51	3098	2·48	3094	2·45
3116	2·41	3117	2·47	3117	2·40	3117	2·52	3117	2·48
3146	2·25	3146	2·30	3146	2·39	3146	2·35	3146	2·39
3192	2·66	3193	2·66	3195	2·77	3195	2·79	3196	2·74
3248	1·61	3239	0·57	3252	1·67	3245	1·86	3242	1·72

Imperial Chemical Industries Limited, Billingham Division, on a Hilger D.209 Spectrometer (used on a single beam) with a prism of rock-salt. The comments by Anderson and Smith (*J. Inst. Petrol.*, 1952, **38**, 145) on the spectra of the lower naphthylalkanes apply here also. The two types of substitution (α- or β-) in the naphthalene nucleus can readily be distinguished.

Ultra-violet Spectra.—These were measured in *iso*octane solution by Mrs. M. Mikiewicz, Physical Chemistry Group, Imperial Chemical Industries Limited, Billingham Division, and are very similar to the spectra of the lower naphthylalkanes (see Anderson *et al.*, *loc. cit.*).

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