233. *The Synthesis of Hydrocarbons of High Molecular Weight. Part I. Monoalkylnaphthalenes.*

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The synthesis of a series of alkylnaphthalenes with side chains containing 8, 10, 12, and 18 carbon atoms is described. The 1-2′-naphthylalkanes were prepared by the reduction of the corresponding *n*-alkyl 2-naphthyl ketones, obtained by Friedel–Crafts acylation of naphthalene. Some 2′-naphthylalkanes with chains branched on the carbon atom α to the nucleus were obtained by the Grignard reaction on suitable ketones prepared as above. Three methods of synthesis of the *n*-alkyl 1-naphthyl ketones were investigated: the reaction between (i) di-1-naphthylcadmium and acyl chlorides, (ii) 1-naphthonitrile and alkylmagnesium halides, and (iii) alkyl cyanides and 1-naphthylmagnesium bromide, the last of which gave the highest yields increasing as the chain length increased. Catalytic reduction of these ketones yielded the corresponding 1-1′-naphthylalkanes. 1 : 6-Di-2′-naphthylhexane was obtained from the diketone resulting from the Friedel–Crafts reaction between tetralin and polymeric adipic anhydride.

The synthesis of a series of hydrocarbons of high molecular weight has been undertaken with the object of determining their physical constants, which should be of value in establishing some relation between the structure of these compounds and their chemical and physical properties. In this paper, the syntheses are recorded; the correlation between structure and properties will be published elsewhere.

(A) 1-2′-*Naphthylalkanes with Side Chains containing* 8, 10, 12, *and* 18 *Carbon Atoms.*—Since it was desired to synthesise alkylnaphthalenes of considerable chain length, methods useful for the preparation of lower members were not applicable in this case (cf. Smith *et al.*, *J. Inst. Pet.*, 1949, **35**, 103). Direct alkylation by the Friedel–Crafts reaction is well known to cause isomerisation, however, even under mild conditions.

The acylation of naphthalene has been used extensively in the present work, since the reduction of the ketones obtained forms a convenient method of synthesis of the alkylnaphthalenes. The somewhat conflicting results concerning the ratio of 1- to 2-ketones when different solvents are used are discussed by Smith *et al.* (*loc. cit.*). Buu-Hoï and Cagniant (*Bull. Soc. chim.*, 1945, **12**, 307) showed that high yields of ketones resulted from the Friedel–Crafts reaction with higher fatty acid chlorides, nitrobenzene being used as solvent. However, the position of the acyl group was merely assumed from analogy with the lower members: this assumption has been verified for those ketones used as intermediates in the present work. Of interest in this connection is the observation that the proportion of 1-isomer formed in carbon disulphide solution decreases with an increase in the chain length of the acyl group. In acetylation the reaction yields approximately 50% of the 1-isomer; the hexoylation of naphthalene in carbon disulphide solution yielded an appreciable amount of the 1-isomer, although the proportion of 1- to 2-isomer is much less than with the acetylation. In confirmation of this decrease, Seidel and Engelfried (*Ber.*, 1936, **69**, 2567) record the formation of only about 20% of 1-stearoylnaphthalene in the mixture of ketones formed in this solvent.

2-Naphthyl *n*-nonyl, *n*-undecyl, and *n*-heptadecyl ketones were prepared in yields of 50—70% by the method of Buu-Hoï and Cagniant (*loc. cit.*), the yield being improved by the use of aluminium chloride in a molecular proportion of 1 : 1. The purification of the 2-ketones from the small amount of the 1-isomers presented few difficulties since the former have higher m. p.s and are less soluble in organic solvents. The ketones were characterised as their 2 : 4-dinitrophenylhydrazones and azines. Proof of the structure of the ketones was obtained by selenium dioxide oxidation to 2-naphthoic acid (Smith *et al.*, *loc. cit.*). In order to determine the best method of reduction of the higher members of this series of ketones, the Clemmensen reduction and the Huang-Minlon reaction were investigated. The former was successful in all cases, although the yields decreased from approximately 56% with the *n*-heptyl ketone to 33% with the *n*-heptadecyl ketone, even with up to 18 hours' heating under reflux. We found that the Huang-Minlon reaction conditions applicable to the lower ketones gave poor results with the higher members; in view of this, the initial hydrazone formation was investigated. Each of the prepared ketones, in boiling ethanol and with an excess of hydrazine hydrate, gave the azine, $C_{10}H_7{\cdot}C(C_nH_{2n+1}){:}N{\cdot}N{:}C(C_nH_{2n+1}){\cdot}C_{10}H_7$, and no hydrazone could be isolated.

When 3 hours' heating was allowed for hydrazone formation in the presence of a large excess of hydrazine hydrate, followed by 12 hours' heating under reflux, however, high yields of hydrocarbons were obtained, identical with the products from the Clemmensen reduction. No azine, or unsaturated compound formed by the elimination of nitrogen at the high temperatures involved, was found, although some unchanged ketone could be detected.

None of the 2-alkylnaphthalenes prepared gave complexes with picric acid, styphnic acid, or *s*-trinitrobenzene. Two of these hydrocarbons are recorded in the literature. Petrov and Andreev (*J. Gen. Chem. U.S.S.R.*, 1942, **12**, 95) claimed the synthesis of 1-2′-naphthyloctane by the Friedel–Crafts alkylation of naphthalene in *cyclo*hexane solution in the cold to minimise the isomerisation of the *n*-octyl chain. From the quoted physical constants, however, it is evident that extensive isomerisation did occur. Mikeska (*J. Org. Chem.*, 1937, **2**, 499) reported the synthesis of 1-2′-naphthyloctadecane by the Friedel–Crafts reaction in carbon disulphide solution, but since he stated that no attempt was made to separate the isomeric ketones, the hydrocarbon was certainly a mixture of 1- and 2-naphthyloctadecanes. After the completion of this work, Hart and Robinson (*J. Amer. Chem. Soc.*, 1948, **70**, 3731) described the synthesis of 1-2′-naphthyl-butane, -pentane, and -decane by the general method of Smith and Lo (*ibid.*, p. 2209). Neither refractive index nor melting point is in agreement with the values obtained in the present work. The values quoted by Hart and Robinson, being considerably lower, would suggest that the final stage of their preparation, that of dehydrogenation, was incomplete. These authors record the m. p. of the picrates of all of their hydrocarbons, but state that none was analysed. Not even the *s*-trinitrobenzene complex of 1-2′-naphthyldecane could be obtained in the present investigation, and Smith *et al.* (*loc. cit.*) state that no picrate formation occurred with the pentane derivative. Luther and Wächter (*Ber.*, 1949, **82**, 161) describe the synthesis of 1-2′-naphthyloctane by a method identical with that of Hart and Robinson; although the refractive indices they record agree with ours, yet the m. p. they give is much lower than that obtained by us.

(B) *2′-Naphthylalkanes with Branched Side Chains.*—The readily obtainable *n*-alkyl 2-naphthyl ketones were used as starting materials. 2-Naphthyl *n*-propyl ketone with *n*-butylmagnesium bromide yielded 4-2′-naphthyloctan-4-ol. The same ketone, by reaction with *n*-hexylmagnesium bromide, gave 4-2′-naphthyldecan-4-ol. In a similar manner, 6-2′-naphthyldodecan-6-ol was prepared from 2-naphthyl *n*-pentyl ketone and *n*-hexylmagnesium bromide. The same ketone afforded with ethylmagnesium chloride 3-2′-naphthyloctan-3-ol. In some cases, the crude carbinol contained some of the corresponding olefin.

Carbinol and carbinol–olefin mixture were dehydrated with anhydrous copper sulphate, and the olefins hydrogenated with Raney nickel as catalyst at 4 atm. and room temperature, giving 3-2′-naphthyloctane, 4-2′-naphthyl-octane, -decane, and -dodecane, and 6-2′-naphthyldodecane.

No complexes with picric acid, styphnic acid, or *s*-trinitrobenzene could be obtained from these hydrocarbons. On attempted crystallisation at low temperature, all of them set to glasses at about −60°.

(C) 1-1′-*Naphthylalkanes.*—In view of the decreasing yields obtained by Nunn and Henze (*J. Org. Chem.*, 1947, **12**, 540) in the preparation of the lower members of the alkyl 1-naphthyl ketones as the series was ascended, and the poor yields reported by Smith *et al.* in similar reactions, the synthesis of the higher 1-naphthyl ketones by a new approach, using di-1-naphthylcadmium, was investigated. With this reagent, *n*-heptyl 1-naphthyl ketone was obtained from *n*-octanoyl chloride in 60% yield, and the *n*-nonyl ketone in 56% yield from *n*-decanoyl chloride. This decrease in yield was also apparent in the case of the further two members of the series, 1-naphthyl *n*-undecyl and *n*-heptadecyl ketones being obtained in yields of 50% and 40%, respectively. The last two ketones are recorded in the literature (Ryan and Nolan, *Proc. Roy. Irish Acad.*, 1912, **30**, *B*, 1; Ralston and Christensen, *Ind. Eng. Chem.*, 1937, **29**, 194; Turkiewicz, *Ber.*, 1940, **73**, 861; Mikeska *et al.*, *J. Org. Chem.*, 1937, **2**, 499; Seidel and Engelfried *Ber.*, 1936, **69**, 2567), but the constants quoted differ from those in this work.

As an alternative method of synthesis of these ketones, the Grignard reaction was investigated. In the preparation of *n*-heptyl 1-naphthyl ketone from 1-naphthonitrile and *n*-heptylmagnesium bromide, the general procedure of Nunn and Henze (*loc. cit.*) and of Radcliffe, Sherwood, and Short (*J.*, 1931, 2293) was followed. Radcliffe *et al.* give no details concerning the isolation of the ketones, and Nunn and Henze state that all the ketones were isolated by extracting the organic layer of the reaction product, after decomposition with aqueous ammonium chloride, by means of dilute sulphuric acid, and hydrolysing the ketimine by boiling the acid solution. In the present instance, this procedure yielded no ketone whatsoever. When the toluene layer was heated under reflux with 10N-sulphuric acid and the resulting organic layer was treated in the normal way, the pure ketone was obtained in 50% yield, the melting point and refractive index being in agreement with the values obtained from the di-1-naphthylcadmium reaction. The yield is considerably higher than that expected from Nunn and Henze's results, and it would appear that their yields are not indicative of the extent of reaction.

The alternative Grignard method (condensation of 1-naphthylmagnesium bromide with the alkyl cyanide) has been described in certain cases by Ralston and Christensen (*loc. cit.*) and Turkiewicz (*loc. cit.*), who record high yields of ketones. By this method, ketones in yields increasing from 76 to 80% as the chain length increased have been obtained in this work. Similarly, no ketimine could be extracted from the reaction product.

All attempts to prepare the 2 : 4-dinitrophenylhydrazones, semicarbazones and phenylsemicarbazones resulted in formation of oils, the only indication of reaction being the reddish colour produced with 2 : 4-dinitrophenylhydrazine sulphate solution. This lack of reactivity of the 1-naphthyl ketones has been noted by Ryan and Nolan and by Smith *et al.* in the case of 1-naphthyl *n*-heptadecyl and pentyl ketones, respectively, the latter authors proving the presence of the carbonyl group by the infra-red spectrum. In the present work, the presence of the carbonyl group in *n*-heptyl 1-naphthyl ketone was shown by the infra-red spectrum band at 1698 ν. In view of this lack of reactivity of the series of ketones, the failure of chemical methods of reduction was not surprising. However, by catalytic reduction with copper chromite at a high temperature and pressure, 1-1′-naphthyl-octane, -decane, -dodecane, and -octadecane were obtained in excellent yield. Luther and Wächter (*loc. cit.*) have prepared the 1-naphthyloctane from 1-tetralone by the Grignard synthesis, but their value of the refractive index does not agree with ours.

None of the hydrocarbons formed complexes with picric or styphnic acids, or with *s*-trinitrobenzene.

(D) 1 : 6-*Di-2′-Naphthylhexane*.—To prepare a dinaphthyl hydrocarbon of comparable molecular weight, with the nuclei occupying positions at the ends of the aliphatic chain, the Friedel–Crafts reaction between polymeric adipic anhydride and tetralin was used. When the reaction was conducted in carbon disulphide solution, decomposition of the product led to an intractable tar, together with a small amount of adipic acid. Steam-distillation of the tar yielded unchanged tetralin, which was shown to contain 6-acetyltetralin, isolated as its 2 : 4-dinitrophenylhydrazone. The Friedel–Crafts reaction was repeated with benzene as solvent, and yielded a keto-acid and a diketone, later proved to be δ-(5 : 6 : 7 : 8-tetrahydro-2-naphthoyl)-valeric acid and 1 : 4-di-(5 : 6 : 7 : 8-tetrahydro-2-naphthoyl)butane, respectively. Both these substances were characterised as their 2 : 4-dinitrophenylhydrazones. The products were obtained in 30% yield, and in the proportion required by theory for the breaking of the –OC•O•CO– groups in both of the two possible ways. The recovered excess of tetralin again contained the 6-acetyl derivative. The formation of this material may be explained by the reaction of the terminal acetyl groups formed on the polymeric adipic anhydride when acetic anhydride is used as the dehydrating agent (Hill and Carothers, *J. Amer. Chem. Soc.*, 1932, **54**, 1569). 1 : 6-Di-(5 : 6 : 7 : 8-tetrahydro-2-naphthyl)hexane was obtained from the 1 : 6-diketone by the Huang-Minlon reaction, and catalytic dehydrogenation gave 1 : 6-di-2′-naphthylhexane in good yield. Although no complex with picric acid could be obtained, the hydrocarbon was characterised as its mono-*s*-trinitrobenzene complex.

EXPERIMENTAL.

(M. p.s are uncorrected. Analyses are by Mr. F. C. Hall and Drs. Weiler and Strauss, Oxford.)

(A) 1-2′-*Naphthylalkanes*.—n-*Alkyl 2-naphthyl ketones*. *n*-Heptyl 2-naphthyl ketone was prepared by the general method of Buu-Hoï and Cagniant (*loc. cit.*), finely powdered anhydrous aluminium chloride (80 g., 1·1 mols.) being added in portions (10 g.) to a stirred solution of naphthalene (64 g., 1 mol.) and *n*-octanoyl chloride (90 g., 1·1 mols.) in dry nitrobenzene (270 c.c.), cooled to –5°. The complex was decomposed next morning by ice and concentrated hydrochloric acid, and the nitrobenzene removed from the washed and dried (Na_2SO_4) solution by distillation *in vacuo*. The crude ketone was distilled, redistilled (b. p. 219—221°/10 mm.), and crystallised twice from ethanol, the pure material being obtained as plates, m. p. 56—57°, in 50% yield (63 g.). Buu-Hoï gives m. p. 56°. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate as orange-red plates, m. p. 163° (Found : C, 66·4; H, 6·0. $C_{24}H_{26}O_4N_4$ requires C, 66·4; H, 6·0%). The *ketazine*, obtained by refluxing an aqueous solution of hydrazine sulphate (4 mols.) containing excess of sodium acetate with the ketone (1 mol.) in ethanol for 1 hour, crystallised from ethanol in yellow prisms, m. p. 70° (Found : N, 5·6. $C_{36}H_{44}N_2$ requires N, 5·6%).

The following ketones and their derivatives were prepared by the above methods. 2-Naphthyl *n*-nonyl ketone, 54% yield, plates, m. p. 52—53° (Buu-Hoï gives 52°); 2 : 4-*dinitrophenylhydrazone*, red plates, m. p. 139° (Found : N, 12·3. $C_{26}H_{30}O_4N_4$ requires N, 12·1%); *ketazine*, yellow prisms, m. p. 68—69° (Found : N, 5·3. $C_{40}H_{52}N_2$ requires N, 5·0%). 2-Naphthyl *n*-undecyl ketone, 60% yield, elongated prisms, m. p. 48° (Buu-Hoï gives 48°); 2 : 4-*dinitrophenylhydrazone*, orange-red plates, m. p. 119—120° (Found : C, 68·5; H, 6·8. $C_{28}H_{34}O_4N_4$ requires C, 68·6; H, 6·9%); *ketazine*, long yellow prisms, m. p. 76° (Found : N, 4·3. $C_{44}H_{60}N_2$ requires N, 4·5%). *n*-Heptadecyl 2-naphthyl ketone, 74% yield, amorphous solid, m. p. 66° (Buu-Hoï gives 66°); 2 : 4-*dinitrophenylhydrazone*, red plates, m. p. 118° (Found : N, 10·0. $C_{34}H_{46}O_4N_4$ requires N, 9·8%); *ketazine*, yellow prisms, m. p. 55° (Found : N, 3·5. $C_{56}H_{84}N_2$ requires N, 3·6%).

Degradation of n-*alkyl 2-naphthyl ketones to 2-naphthoic acid.* The method of Smith *et al.* (*loc. cit.*) using selenium dioxide and a dioxan solution of the ketone was adopted. The acidic material so obtained was crystallised from aqueous ethanol, and melted at 183—184°, undepressed by admixture with 2-naphthoic acid. The yield of acid obtained decreased from 30% with the *n*-heptyl ketone to 15% with the *n*-heptadecyl ketone.

1-2′-*Naphthylalkanes.* (*a*) Clemmensen method. The ketone (20 g.) was added to a mixture of amalgamated granulated zinc (100 g.), concentrated hydrochloric acid (100 c.c.), and water (75 c.c.), and the mixture heated under reflux for 18 hours, additional acid (90 c.c.) being added every 6 hours. The cold reaction mixture was decanted from the zinc, which was washed with warm benzene. The hydrocarbon was extracted from the aqueous layer with benzene, and the combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent followed by distillation gave the crude hydrocarbon, which was purified by distillation over sodium, followed by crystallisation from acetone or ethanol at −60° in the case of the lower members. In the reduction of the *n*-heptadecyl ketone, the method was modified by passing a continuous stream of hydrogen chloride through the reaction mixture during refluxing, and using toluene as an immiscible solvent. 1-2′-Naphthyloctane (56% yield) a colourless solid from acetone, had m. p. 13°, n_D^{20} 1·5511 (Found : C, 89·8; H, 10·0. Calc. for $C_{18}H_{24}$: C, 90·0; H, 10·0%). Luther and Wächter (*loc. cit.*) give m. p. −3·3°, n_D^{20} 1·55106; Petrov and Andreev (*loc. cit.*) give m. p. −45°, n_D^{20} 1·5510. 1-2′-Naphthyldecane, 54% yield, m. p. 19·5—19·6° (from ethanol), n_D^{20} 1·5440 (Found : C, 89·6; H, 10·2. Calc. for $C_{20}H_{28}$: C, 89·6; H, 10·4%). Hart and Robinson (*loc. cit.*) give m. p. 13°, n_D^{20} 1·5394. 1-(2′-*Naphthyl*)*dodecane*, 50% yield, m. p. 26° (from ethanol), n_D^{30} 1·5339 (Found : C, 89·2; H, 10·7. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%). 1-2′-*Naphthyloctadecane*, 33% yield, m. p. 54° (from ethanol) (Found : C, 88·4; H, 11·5. $C_{28}H_{44}$ requires C, 88·4; H, 11·6%).

(*b*) Huang-Minlon method. The ketone (10 g.) was added to a solution of sodium (2·5 g.) in diethylene glycol (70 c.c.), together with hydrazine hydrate (5 c.c. of 90%). After 3 hours' heating under reflux to form hydrazone, the temperature of the reaction mixture was raised to 220°, and heating then continued for a further 12 hours, during which the upper layer of hydrazone changed from orange-red to almost colourless, with a pale blue-purple fluorescence. After cooling, the mixture was acidified with dilute hydrochloric acid, and extracted with benzene. After removal of the solvent from the washed and dried solution, the crude product was purified by the method described under (*a*). The pure products, which were identical with the materials described above, were obtained in the following yields: 1-2′-naphthyloctane, 75%; -decane, 74%; -dodecane, 75%; -octadecane, 71%.

(B) *Branched-chain 2′-Naphthylalkanes.*—These hydrocarbons were all prepared by the same method, given in detail for one only.

4-2′-*Naphthyloctan*-4-*ol.* 2-Naphthyl *n*-propyl ketone (Smith *et al.*, *loc. cit.*; 25 g., 0·5 mol.) in dry ether (150 c.c.) was added slowly to a stirred solution of *n*-butylmagnesium bromide (1·1 mols.; from *n*-butyl bromide 42 g., magnesium 6·7 g., and dry ether 125 c.c.). After being left overnight at room temperature, the reaction mixture was cooled in an ice–water bath, and decomposed by careful addition of sulphuric acid (20%). The separated ethereal layer was washed, dried (Na_2SO_4), and fractionated, giving 4-2′-*naphthyloctan*-4-*ol*, b. p. 138—139°/0·4 mm., n_D^{20} 1·5692, in 74% yield (23·5 g.) (Found : C, 84·3; H, 9·3. $C_{18}H_{24}O$ requires C, 84·4; H, 9·4%).

4-2′-*Naphthyloct*-3- *and* -4-*ene.* The carbinol (20 g.) was heated with anhydrous copper sulphate (2 g.) in an oil-bath at 175° for 1 hour. The cooled mixture was extracted with ether, and fractionation of the extract yielded the *octenes* as a colourless oil, b. p. 130—131°/0·5 mm., n_D^{20} 1·5857 (85% yield, 15·8 g.) (Found : C, 91·1; H, 9·3. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%).

4-2′-*Naphthyloctane.* The olefin (14 g.) in ethanol (25 c.c.) was hydrogenated with Raney nickel under Burgess–Parr conditions, with an initial hydrogen pressure of 31·5 lb./sq. in., the theoretical volume of hydrogen being absorbed in 1 hour. Fractionation of the product gave 4-2′-*naphthyloctane*, b. p. 116°/0·3 mm., n_D^{20} 1·5559 (Found : C, 90·0; H, 10·1. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%).

In a similar manner, the following 2′-naphthyl derivatives were prepared. 4-2′-*Naphthyldecan*-4-*ol*, from the *n*-propyl ketone and *n*-hexylmagnesium bromide in 85% yield; b. p. 136°/0·4 mm., n_D^{20} 1·5590 (Found : C, 84·7; H, 9·7. $C_{20}H_{28}O$ requires C, 84·5; H, 9·9%). 4-2′-*Naphthyldec*-3- and -4-*ene*, 87% yield, b. p. 150—151°/0·8 mm., n_D^{20} 1·5720 (Found : C, 90·5; H, 9·6. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%). 4-2′-*Naphthyldecane*, 94% yield, b. p. 150°/1 mm., n_D^{20} 1·5457 (Found : C, 89·9; H, 10·3. $C_{20}H_{28}$ requires C, 89·6; H, 10·4%). 4-2′-*Naphthyldodec*-3- and -4-*enes*, 66% overall yield from the *n*-propyl ketone and *n*-octylmagnesium bromide; b. p. 178°/1 mm., n_D^{20} 1·5592 (Found : C, 89·8; H, 10·1. $C_{22}H_{30}$ requires C, 89·8; H, 10·2%). 4-2′-*Naphthyldodecane*, 96% yield, b. p. 183°/1 mm., n_D^{20} 1·5371 (Found : C, 89·4; H, 10·7. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%). 6-2′-*Naphthyldodecan*-6-*ol*, 85% yield from the *n*-pentyl ketone and *n*-hexylmagnesium bromide; b. p. 150°/0·1 mm., n_D^{20} 1·5479 (Found : C, 84·4; H, 10·3. $C_{22}H_{32}O$ requires C, 84·6; H, 10·3%). [The *n*-pentyl ketone was prepared from *n*-hexanoyl chloride in nitrobenzene in 60% yield; in carbon disulphide the yield was only 47%, and the crude ketone contained an appreciable amount of the 1-isomer (cf. Smith *et al.*, *loc. cit.*).] 6-2′-*Naphthyldodec*-5- and -6-*enes*, 77·6% yield, b. p. 166—168°/1 mm., n_{D}^{20} 1·5602 (Found : C, 89·8; H, 10·2. $C_{22}H_{30}$ requires C, 89·8; H, 10·2%). 6-2′-*Naphthyldodecane*, 82% yield, b. p. 240—242°/2 mm., n_{D}^{20} 1·5399 (Found : C, 89·4; H, 10·5. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%). 3-2′-*Naphthyloct*-3- and -4-*enes*, 63% overall yield from the *n*-pentyl ketone and ethylmagnesium chloride; b. p. 170°/1 mm., n_{D}^{20} 1·5809 (Found : C, 90·9; H, 9·3. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%). 3-2′-*Naphthyloctane*, 92% yield, b. p. 156—157°/1 mm., n_{D}^{20} 1·5580 (Found : C, 89·9; H, 10·0. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%). None of these branched-chain derivatives could be obtained crystalline.

(C) 1-1′-*Naphthylalkanes.*—n-*Alkyl* 1-*naphthyl ketones.* (*a*) By use of di-1-naphthylcadmium. Di-1-naphthylcadmium was obtained in benzene solution from purified 1-bromonaphthalene (Jones and Lapworth, *loc. cit.*) (30 g.), magnesium (3·5 g.), and dry ether (75 c.c.), dry benzene (75 c.c.) being added to the stirred and heated solution of the Grignard reagent, followed by finely powdered anhydrous cadmium chloride (13·4 g., 1 equiv.). The exchange reaction was complete in about 20 minutes, as determined by Gilman and Schulze's colour reaction (*J. Amer. Chem. Soc.*, 1925, **47**, 2002). The ether was then removed by distillation, and a further quantity (125 c.c.) of dry benzene added. *n*-Octanoyl chloride (19 g., 0·8 mol.) in benzene (60 c.c.) was added in one portion, and stirring and heating were continued for 4 hours. When cool, the product was decomposed with dilute sulphuric acid in the normal way, and the washed and dried benzene extract fractionated. n-*Heptyl* 1-*naphthyl ketone*, b. p. 184°/2 mm., n_{D}^{20} 1·5661, m. p. −4° to −3°, was obtained in 60% yield (18 g.) by purification on an alumina column, benzene being used as solvent, followed by redistillation (Found : C, 85·0; H, 8·6. $C_{18}H_{22}O$ requires C, 85·1; H, 8·7%). The following ketones were similarly obtained.

1-*Naphthyl* n-*nonyl ketone*, 70% yield, from *n*-decanoyl chloride; m. p. 10° (from chilled acetone), n_{D}^{20} 1·5570, b. p. 190°/2 mm. (Found : C, 85·1; H, 9·1. $C_{20}H_{26}O$ requires C, 85·1; H, 9·2%). 1-Naphthyl *n*-undecyl ketone, 50% yield, from *n*-dodecanoyl chloride; m. p. 26·8° (thermometer in the melt) [from light petroleum (b. p. 100—120°)], b. p. 234—235°/6 mm., n_{D}^{30} 1·5430 (Found : C, 85·3; H, 9·4. Calc. for $C_{22}H_{30}O$: C, 85·2; H, 9·7%); Ralston and Christensen (*loc. cit.*) record b. p. 240—245°/5 mm., and Turkiewicz (*loc. cit.*) records $n_{\mathrm{D}}^{26 \cdot 5}$ 1·5438. *n*-Heptadecyl 1-naphthyl ketone : 40% yield from stearoyl chloride; m. p. 57° [from light petroleum (b. p. 60—80°)] (Found : C, 85·4; H, 10·5. Calc. for $C_{28}H_{42}O$: C, 85·3; H, 10·7%). Seidel and Engelfried (*Ber.*, 1936, **69**, 2567) record m. p. 52—54·5°, Ryan and Nolan (*loc. cit.*), m. p. 53—54°, and Ralston and Christensen (*loc. cit.*) m. p. 53—54°. No ketonic derivatives of these ketones could be prepared.

(*b*) By use of 1-naphthonitrile (cf. Nunn and Henze, *loc. cit.*). The nitrile (30·6 g., 1 mol.) in dry toluene (300 c.c.) was added slowly to a stirred solution of *n*-heptylmagnesium bromide [1 mol., from magnesium (5·0 g.), *n*-heptyl bromide (39·4 g.), and dry ether (250 c.c.)]. The ether was then removed by distillation, more toluene (80 c.c.) being added. After 12 hours' refluxing, the cooled reaction mixture was decomposed by addition of saturated ammonium chloride solution containing chipped ice. The separated aqueous layer was extracted with ether, and the ether and toluene layers were combined. Extraction of this organic solution with 2N-sulphuric acid (3 × 150 c.c.) gave a colourless solution, from which no material could be isolated after 3 hours' heating under reflux. The ether was therefore removed from the ether–toluene extract, and the residual solution heated under reflux for 2 hours with 10N-sulphuric acid (100 c.c.). Removal of the toluene from the washed and dried solution, followed by fractionation of the dark residue, gave a pale yellow oil, b. p. 188°/4 mm. Crystallisation from acetone at −60° gave *n*-heptyl 1-naphthyl ketone (50%), identical with that obtained by method (*a*).

(*c*) By use of 1-bromonaphthalene (cf. Ralston and Christensen, *loc. cit.*; Turkiewicz, *loc. cit.*). 1-Naphthylmagnesium bromide [1 mol.; from purified 1-bromonaphthalene (50·5 g.) and magnesium (5·0 g.)] was stirred and heated under reflux, *n*-octanonitrile (38·3 g., 1 mol.) added slowly, and the heating and stirring continued for a further 6 hours. Decomposition in the normal manner with dilute sulphuric acid yielded an acid layer from which no ketone could be obtained. From the washed and dried ethereal solution, however, *n*-heptyl 1-naphthyl ketone was obtained in 76% yield. The homologous ketones were obtained in a similar manner : *n*-nonyl (70% from *n*-decanonitrile); *n*-undecyl (76% from *n*-dodecanonitrile); and *n*-heptadecyl (80% from stearonitrile).

1-1′-*Naphthylalkanes.* *n*-Heptyl 1-naphthyl ketone (33·8 g.) was placed in a tilting hydrogenator with copper chromite (5 g.) under an initial hydrogen pressure of 100 atm. The temperature was kept at 205° for 3 hours, and the hydrogenator allowed to cool, refilled to 100 atm., and the heating continued for a further 6 hours. After cooling, the product was isolated by means of ether. On distillation, a major fraction collected at 171—174°/6 mm. Redistillation over sodium, followed by crystallisation from acetone at −50°, gave 1-1′-naphthyloctane (25·6 g., 80%), m. p. −2°, b. p. 170°/4 mm., n_{D}^{20} 1·5510 (Found : C, 90·0; H, 10·1. Calc. for $C_{18}H_{24}$: C, 90·0; H, 10·0%). Luther and Wächter record n_{D}^{20} 1·55322.

In a similar manner, the following hydrocarbons were obtained : 1-1′-*Naphthyldecane*, 86% yield, m. p. 15° (from acetone at −50°), b. p. 200°/4 mm., n_{D}^{20} 1·5448 (Found : C, 89·5; H, 10·4. $C_{20}H_{28}$ requires C, 89·6; H, 10·4%). 1-1′-*Naphthyldodecane*, 81·5% yield, needles (from acetone at 0°), m. p. 26·5°, b. p. 209°/4 mm., n_{D}^{30} 1·5310 (Found : C, 89·0; H, 10·7. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%). 1-1′-*Naphthyloctadecane*, 83% yield, elongated plates (from ethanol), m. p. 53·5°, b. p. 169—171°/0·5 mm. (Found : C, 88·3; H, 11·7. $C_{28}H_{44}$ requires C, 88·4; H, 11·6%); mixed m. p. with 1-2′-naphthyloctadecane 45—47°.

(D) 1 : 6-*Di-2′-naphthylhexane.*—*Polymeric adipic anhydride–tetralin reaction.* Finely powdered anhydrous aluminium chloride (70 g., 1·4 mols.) was added in small portions to a vigorously stirred solution of redistilled tetralin (50 g., 1 mol.) and the polymeric anhydride (27·3 g., 1·1 mols.; prepared by the method of Plant and Tomlinson, *J.*, 1935, 253) in dry, thiophen-free benzene (300 c.c.). After the addition, the mixture was heated under reflux for 3 hours, and the complex decomposed in the normal manner. The white solid (8 g.) which separated at this stage was adipic acid. The separated benzene layer was washed and dried (Na_2SO_4), the solvent removed at 100°/20 mm., and the unchanged tetralin at 1 mm. The recovered tetralin gave a red precipitate with 2 : 4-dinitrophenylhydrazine. This derivative separated from dioxan as dark red prisms, m. p. 227—228°, and a mixed m. p. with an authentic specimen prepared from 6-acetyltetralin (Scharwin, *Ber.*, 1902, **35**, 2511) showed this to be 6-*acetyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* 2 : 4-*dinitrophenylhydrazone* (Found: C, 61·2; H, 5·0; N, 15·5. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%). (When the reaction was carried out with carbon disulphide as solvent, only adipic acid and this derivative could be isolated from the reaction mixture.)

The viscous residue after the removal of the solvent crystallised on trituration with acetone, giving 34 g. of solid. This was shaken in the cold with aqueous sodium carbonate (2N.) for 2 hours, and then filtered. Acidification of the alkaline filtrate with concentrated hydrochloric acid yielded a brown gum, which solidified on stirring. Two crystallisations from benzene yielded slender prisms (18 g.), m. p. 92°. Analysis and degradation showed this to be δ-(5 : 6 : 7 : 8-*tetrahydro*-2-*naphthoyl*)*valeric acid* (Found: C, 73·7; H, 7·6. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%); its 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in deep red prisms, m. p. 144° (Found: N, 12·4. $C_{22}H_{24}O_6N_4$ requires N, 12·7%).

The alkali-insoluble material from the separation was crystallised twice from ethanol, yielding long prismatic needles (12·5 g.), m. p. 91—92° (depressed to 73—75° by admixture with the keto-acid). Analysis and degradation showed this to be 1 : 4-*di*-(5 : 6 : 7 : 8-*tetrahydro*-2-*naphthoyl*)*butane* (Found: C, 83·6; H, 7·8. $C_{26}H_{30}O_2$ requires C, 83·4; H, 8·0%). The *bis*-2 : 4-*dinitrophenylhydrazone* (dark red needles from *cyclo*hexanone) melted at 264° (decomp.) (Found: C, 62·1; H, 5·4. $C_{38}H_{38}O_8N_8$ requires C, 62·1; H, 5·2%).

The diketone was oxidised with selenium dioxide, and the crude product treated with alkaline hydrogen peroxide by the method described under the 2-naphthyl ketones. The resulting tetrahydronaphthoic acid melted at 153° after crystallisation from ethanol (lit., m. p. of 5 : 6 : 7 : 8-tetrahydronaphthalene-2-carboxylic acid, 154°). Dehydrogenation with palladised charcoal at 280° for 4 hours in a stream of hydrogen yielded 2-naphthoic acid. The structure of the keto-acid was proved by degradation to this acid in a similar manner.

1 : 6-*Di*-(5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl*)*hexane*. The diketone (31·5 g.) was reduced by the normal Huang-Minlon procedure, sodium (14·0 g.), diethylene glycol (360 c.c.), and hydrazine hydrate (40 c.c. of 90%) being used. Distillation of the washed and dried benzene extract yielded a major fraction, b. p. 250—255°/0·5 mm., which was redistilled over sodium. The *hexane* (19·9 g., 69%) crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 47·5° (Found: C, 90·1; H, 9·6. $C_{26}H_{34}$ requires C, 90·2; H, 9·8%).

1 : 6-*Di*-2′-*naphthylhexane*. The ditetralylhexane (15·6 g.) was heated with 10% of its weight of palladised charcoal (Diels and Gädke, *Ber.*, 1925, **58**, 1231) at 260° for 3 hours in a stream of dry, oxygen-free nitrogen. Hydrogen was evolved vigorously at first, and the temperature was raised slowly to 300° for 2 hours whereafter this evolution ceased. The solid obtained on cooling was isolated by extracting it several times with hot benzene. Crystallisation from light petroleum (b. p. 100—120°) gave 1 : 6-*di*-2′-*naphthylhexane* in plates, m. p. 102° (11·7 g., 77%) (Found: C, 92·3; H, 7·5. $C_{26}H_{26}$ requires C, 92·3; H, 7·7%).

A mixture of molecular proportions of the hydrocarbon and picric acid in hot ethanol or benzene yielded a solid, m. p. 96—103°, from which only picric acid could be isolated on attempted purification. However, a solution of the hydrocarbon (0·5 g.) and *s*-trinitrobenzene (0·5 g.) in hot ethanol (20 c.c.) deposited a pale yellow solid on cooling. Crystallisation from the same solvent yielded the trinitrobenzene *complex* in pale yellow needles, m. p. 143—145° (Found: C, 71·2; H, 5·4; N, 7·1. $C_{26}H_{26},C_6H_3O_6N_3$ requires C, 69·7; H, 5·3; N, 7·6%).

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