234. *The Synthesis of Hydrocarbons of High Molecular Weight. Part II. Some Di- and Tri-*n*-alkylnaphthalenes.*

By B. Bannister and B. B. Elsner.

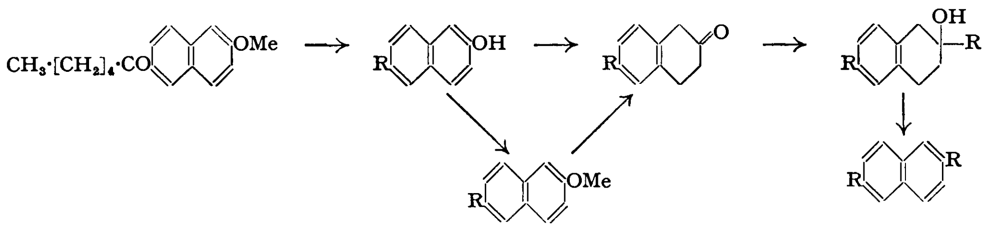
The syntheses of three di-*n*-hexylnaphthalenes and one tri-*n*-butylnaphthalene are described. 2 : 6-Di-*n*-hexylnaphthalene was prepared by the Friedel–Crafts acylation of 2-*n*-hexylnaphthalene, followed by reduction of the 6-*n*-pentyl ketone. Proof of the structure, which could not be obtained by oxidation, was achieved by an unambiguous synthesis from 2-methoxynaphthalene through 6-*n*-hexyl-2-tetralone. Acenaphthenequinone was found to react readily with *n*-pentyl-lithium to give a diol which was oxidised to the 1 : 8-diketone in good yield. Complete reduction catalytically, followed by dehydrogenation, yielded 1 : 8-di-*n*-hexylnaphthalene. 2 : 3-Di-*n*-hexylnaphthalene was obtained from tetralin by the Friedel–Crafts acylation and reduction to the 6-*n*-hexyltetralin. A second hexanoyl group was introduced by the same method and shown to occupy the 7-position by degradation to tetramethyl pyromellitate. Reduction followed by dehydrogenation gave the desired 2 : 3-di-*n*-hexylnaphthalene. A similar series of reactions was used to introduce *n*-butyl groups into the 5-, 6-, and 7-positions of tetralin, and dehydrogenation yielded 1 : 2 : 3-tri-*n*-butylnaphthalene.

(A) *Di-*n*-Hexylnaphthalenes.*—In continuation of the work reported in Part I (preceding paper), it was considered of interest to synthesise a series of di-*n*-hexylnaphthalenes.

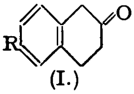
2 : 6-*Di-*n*-hexylnaphthalene.* Haworth *et al.* (*J.*, 1932, 1784, 2248) have shown in several instances that 2-methylnaphthalene is acylated in the 6-position under Friedel–Crafts conditions in nitrobenzene. This approach to a 2 : 6-derivative was therefore investigated. The Friedel–Crafts reaction with *n*-hexanoyl chloride and 2-*n*-hexylnaphthalene (Bailey, Pickering, and Smith, *J. Inst. Pet.*, 1949, **35**, 103) in nitrobenzene yielded a ketone, characterised as its 2 : 4-dinitrophenylhydrazone and semicarbazone, and later proved to be the expected 6-*n*-hexyl-2-naphthyl *n*-pentyl ketone. Reduction by the Huang-Minlon procedure gave 2 : 6-di-*n*-hexylnaphthalene.

In an attempt to prove the position of the second hexyl group by oxidation to a naphthalenedicarboxylic acid, the hydrocarbon was heated with dilute nitric acid at 190° (cf. Campbell, Soffer, and Steadman, *J. Amer. Chem. Soc.*, 1942, **64**, 425). The product appeared to be a benzenetricarboxylic acid, probably trimellitic acid. This implies that the second hexyl group has entered the other ring, and that the dihexylnaphthalene was symmetrical, *i.e.*, the 2 : 6- or the 2 : 7-compound. As an alternative approach, the oxidation of the ketone in two stages was attempted. Selenium dioxide in boiling dioxan solution gave, after treatment with alkaline hydrogen peroxide (cf. Smith *et al.*, *loc. cit.*), an acid later shown to be 6-*n*-hexyl-2-naphthoic acid. However, further oxidation of this material with dilute nitric acid at 190° resulted in the formation of the same benzenetricarboxylic acid. From attempts to oxidise the hexylnaphthalenecarboxylic acid and the dihexylnaphthalene itself with selenium dioxide at a high temperature (cf. Kacer, D.R.-P. 557,249), only starting material could be isolated.

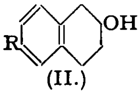
The investigation of the structure of the dihexylnaphthalene was therefore directed towards an unequivocal synthesis. A method analogous to the synthesis of 2 : 6-dimethylnaphthalene (Royer, *Ann. Chim.*, 1946, **1**, 395; *Compt. rend.*, 1946, **222**, 746) was investigated, as indicated below (R = *n*-hexyl) :



The Friedel–Crafts reaction between 2-methoxynaphthalene and *n*-hexanoyl chloride in nitrobenzene gave a good yield of a ketone, characterised as its 2 : 4-dinitrophenylhydrazone, oxime, and semicarbazone, and later shown to be 6-methoxy-2-naphthyl *n*-pentyl ketone. An attempt to oxidise this ketone with aqueous sodium hypochlorite was unsuccessful. The selenium dioxide method, however, yielded 6-methoxy-2-naphthoic acid, identical with a specimen obtained by hypochlorite oxidation of the 6-acetyl compound (Haworth and Sheldrick, *J.*, 1934, 864). Reduction of the ketone by the Huang-Minlon method was accompanied by complete demethylation, the product being 6-*n*-hexyl-2-naphthol. Since the phenol was produced, reduction to the β-tetralone was attempted by Birch's method (*J.*, 1944, 430) with sodium in liquid ammonia, ethanol being used as the proton source. From the bisulphite extract of the product, a colourless oil was obtained, shown by analysis to be 6-*n*-hexyl-2-tetralone (I). The non-ketonic residue from the bisulphite extraction contained no unchanged naphthol, and was distilled, yielding as major fraction a colourless oil, a colourless solid also being obtained but in too small a quantity for investigation. The oil was indicated by analysis and insolubility in alkali to be 6-*n*-hexyl-1 : 2 : 3 : 4-tetrahydro-2-naphthol (II). The intermediate in the reduction of the naphthol is considered to be the unconjugated dihydronaphthol (III), which, in the presence of the alkali, isomerises to the conjugated form (IV), which undergoes further reduction to the tetrahydro-stage.



(I.)



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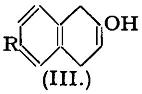

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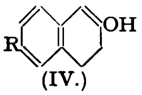


(IV.)

(R = *n*-Hexyl.)

Since the sodium–liquid ammonia reduction gave unsatisfactory results, the naphthol was methylated, and reduction of the hexylmethoxynaphthalene was carried out by Rowe and Levin's method (*J.*, 1921, **119**, 2021), xylene being used as inert solvent and ethanol as the proton source. The reduction product, a colourless oil, gave analytical data in agreement with a dihydro-derivative, and was considered to be the unconjugated 6-*n*-hexyl-1 : 4-dihydro-2-methoxynaphthalene. After hydrolysis of the enol ether, the bisulphite derivative yielded the 6-*n*-hexyl-2-tetralone (I) in 53% yield, of the same refractive index as that obtained from the sodium–liquid ammonia reduction. From the bisulphite extraction, a colourless, non-ketonic oily residue was obtained, and was indicated by analysis and reactions to be a dihydro-derivative of the hexyl-substituted ring. It is considered to be 6-*n*-hexyl-5 : 8-dihydro-2-methoxynaphthalene. The reduction product which gave analytical data consistent with the enol ether is therefore shown to be a mixture of this material and the 5 : 8-dihydro-compound.

The product of the Grignard reaction of *n*-hexylmagnesium bromide with the β-tetralone could not be purified, and the impure 2 : 6-di-*n*-hexyl-1 : 2 : 3 : 4-tetrahydro-2-naphthol was dehydrated and dehydrogenated in one stage by use of a highly active palladium–charcoal catalyst (Zelinsky and Turowa-Pollak, *Ber.*, 1925, **58**, 1295). The melting point of the product was undepressed on admixture with the di-*n*-hexylnaphthalene obtained from 2-*n*-hexylnaphthalene, thus proving the second hexyl group to occupy the 6-position. The identity of the two dihexylnaphthalenes orients also the hexanoylhexylnaphthalene and the hexylnaphthoic acid.

1 : 8-*Di*-n-*Hexylnaphthalene*. Although the problem of the synthesis of 1 : 8-dialkylnaphthalenes has attracted the attention of several workers, the only compound of this type which has been prepared is the 1 : 8-dimethyl derivative. Naphthalene-1 : 8-dicarboxylic anhydride (naphthalic anhydride) appeared to be a suitable starting material, having substituents in the required positions. The reaction between di-*n*-pentylcadmium and the anhydride, however, yielded a red gum, and only unchanged anhydride could be recovered. By using *n*-pentylmagnesium bromide, only a small quantity of acidic material, which could not be purified, was obtained, together with unchanged anhydride.

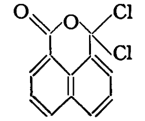
Although the anhydride shows a marked lack of reactivity, and fails completely to react under Friedel–Crafts conditions, yet the di-acid chloride is very reactive (Mason, *J.*, 1924, **125**, 2116, 2119). The interaction of di-*n*-penylcadmium and the di-acid chloride in boiling benzene led to an almost quantitative yield of anhydride after decomposition, however. Mason (*loc. cit.*) suggested the symmetrical rather than the unsymmetrical structure for the di-acid chloride, as a result of the ready diester formation. The lack of reactivity of the di-acid chloride towards the cadmium alkyl suggests the existence of the unsymmetrical form (V) under these conditions.

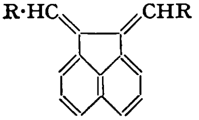
The next starting material investigated was acenaphthenequinone. By condensation of alkylmagnesium bromides with this substance, Maxim (*Bull. Soc. chim.*, 1928, **43**, 769; 1929,

45, 1137) prepared a series of 7 : 8-dialkylacenaphthene-7 : 8-diols, the yield of which decreased from 70% for the dimethyl to 30% for the di*iso*amyl compound, a large amount of unchanged quinone being recovered from the reaction with the longer-chain alkylmagnesium bromides.

In a repetition of Maxim's work on the formation of the di-*n*-propyl-diol, for which he does not record a yield, it was found that only a 9% yield could be obtained, together with 60% of unchanged quinone, and a small amount of a viscous red oil. The reaction between *n*-pentylmagnesium bromide and acenaphthenequinone was carried out by Maxim's procedure. A deep red colour rapidly developed, and decomposition of the reaction mixture led to the recovery of much unchanged quinone, together with a viscous deep red oil, which was unsaturated, and from which no pure material could be isolated. However, the red oil is considered to be impure 7 : 8-di-*n*-pentylideneacenaphthene (VI; $R = CH_3\cdot[CH_2]_3\cdot$), formed by dehydration *in situ* of the 7 : 8-di-*n*-pentyl-diol. Maxim records the formation, by the dehydration of the diols with mineral acid, of red oils which appear to be dienes of this type (see also Campbell and Gow, *J.*, 1949, 1555). The condensation of straight-chain alkylmagnesium bromides with acenaphthenequinone is therefore of little use with homologues above ethyl.

(V.)





(VI.)

Wittig *et al.* (see, *e.g.*, Wittig, " Newer Methods of Preparative Organic Chemistry," 1948 edn., p. 521; Wicks, *Interchem. Rev.*, 1946, **6**, 69) have found that, although certain diketones give glycols in poor yield, or not at all, with organomagnesium compounds, yet organolithium derivatives give excellent yields of the glycols. The interaction of *n*-pentyl-lithium and acenaphthenequinone proved to be successful. On the addition of the solid quinone to the ethereal pentyl-lithium solution, a vigorous reaction developed. The colourless solid, obtained after decomposition, was shown by analysis and reactions to be the required 7 : 8-di-*n*-pentylacenaphthene-7 : 8-diol. No isomeric diol could be obtained from the reaction mixture, but a small quantity of a red oil was obtained from the ethereal mother-liquors of the dipentyl-diol. No purification of this material could be effected, but from its colour and rapid decolorisation of aqueous potassium permanganate, it is considered to be the impure dipentylideneacenaphthene (VI), also formed as the sole product isolated from the corresponding Grignard reaction. The failure to form an adduct of this compound with maleic anhydride is probably due to the steric hindrance of the pentylidene groups (see Campbell and Gow, *loc. cit.*).

The glycol fission was achieved by the use of lead tetra-acetate. The oxidation gave only a 34% yield of 1 : 8-di-*n*-hexanoylnaphthalene when carried out in glacial acetic acid, much unchanged diol being recovered. In benzene solution, however, the yield of pure diketone was 80%. A solution of the diketone gave a red colour with 2 : 4-dinitrophenylhydrazine sulphate, but no solid derivative could be isolated. Similarly, no conversion into the perinaphthinden-1-one could be achieved with piperidine as catalyst (cf. Criegee *et al.*, *Annalen*, 1933, **507**, 176). In view of our inability (see Part I) to obtain derivatives of the *n*-alkyl 1-naphthyl ketones, it is not surprising that the 1 : 8-diketone is also unreactive. The presence of the carbonyl groups in the molecule was proved by the infra-red spectrum, which showed a strong absorption band at 1685 ν.

As with the *n*-alkyl 1-naphthyl ketones, this lack of reactivity again gave rise to the problem of the conversion of the carbonyl into methylene groups. Hydrogenation under high temperature and pressure with copper chromite as catalyst, successful in the former case, gave a product containing oxygen, and with a high percentage of hydrogen, suggesting the partial reduction of the naphthalene nucleus. A similar result was obtained by using Hartung's palladium–charcoal catalyst with a glacial acetic acid solution of the ketone at 80° under 3 atm. (cf. Hornung and Reisner, *J. Amer. Chem. Soc.*, 1949, **71**, 1870; Ju, Shen, and Wood, *J. Inst. Petrol.*, 1940, **26**, 514). Since it seemed to be impossible to reduce the diketone without causing partial reduction of the nucleus simultaneously, it was decided to hydrogenate the molecule by using Raney nickel as catalyst at a high temperature and pressure. Repeated treatment yielded 1 : 8-di-*n*-hexyldecahydronaphthalene. Dehydrogenation of the latter, by the aid of a highly active palladium–charcoal catalyst, was accomplished in moderate yield, giving 1 : 8-di-*n*-hexylnaphthalene.

2 : 3-*Di*-n-*hexylnaphthalene*. The best route to certain di- and poly-alkylnaphthalenes, in which the substituents are in the same ring, starts from tetralin (cf. Scharwin, *Ber.*, 1902, **35**,

2511; Fleischer and Siefert, *Ber.*, 1920, **53**, 1255; Smith and Lo, *J. Amer. Chem. Soc.*, 1948, **70**, 2209). *n*-Pentyl 5 : 6 : 7 : 8-tetrahydro-2-naphthyl ketone was prepared by the Friedel–Crafts reaction, *n*-hexanoyl chloride being used in nitrobenzene solution. Reduction to the 6-*n*-hexyltetralin was achieved by means of both the Huang-Minlon method, and catalytically, by means of copper chromite. Re-acylation of this hydrocarbon with *n*-hexanoyl chloride gave a ketone, subsequently shown to be 3-*n*-hexyl-5 : 6 : 7 : 8-tetrahydro-2-naphthyl *n*-pentyl ketone, although no ketonic derivatives could be obtained. The positions of the substituents were proved by oxidation with dilute nitric acid at 190° (cf. Smith and Lo, *loc. cit.*). The solid product obtained from the aqueous solution was methylated with diazomethane, and a mixed m. p. with an authentic specimen showed it to be tetramethyl pyromellitate. The ketone was reduced by means of high temperature and pressure hydrogenation in the presence of copper chromite, and the 6 : 7-di-*n*-hexyltetralin dehydrogenated in good yield over a palladium–charcoal catalyst to 2 : 3-di-*n*-hexylnaphthalene. After the completion of this work, both 6-*n*-hexyl- and 6 : 7-di-*n*-hexyl-tetralins were reported by Hart and his co-workers (*J. Amer. Chem. Soc.*, 1948, **70**, 3731; 1950, **72**, 1249). The refractive indices they record agree with ours.

(B) 1 : 2 : 3-*Tri*-n-*butylnaphthalene.*—In order to obtain a trisubstituted naphthalene of the same molecular weight, the corresponding series of reactions was used to introduce *n*-butyl groups. *n*-Propyl 5 : 6 : 7 : 8-tetrahydro-2-naphthyl ketone was obtained in good yield by Barbot's method (*Bull. Soc. chim.*, 1930, **47**, 1314). The Huang-Minlon reduction, followed by re-acylation, gave 3-*n*-butyl-5 : 6 : 7 : 8-tetrahydro-2-naphthyl *n*-propyl ketone, the structure of which was proved by the method employed for the hexanoylhexyltetralin above. Clemmensen and catalytic reduction, with copper chromite, afforded the 6 : 7-di-*n*-butyltetralin in good yield, and of refractive index in agreement with that later recorded by Hart *et al.* (*loc. cit.*). The Friedel–Crafts reaction with *n*-butyryl chloride in carbon disulphide solution gave a moderate yield of a ketone, which must be the 5-derivative, since the 5- and the 8-position in the dibutyltetralin are equivalent. No ketonic derivatives of this ketone could be prepared. The high temperature and pressure reduction of this material using copper chromite gave the 5 : 6 : 7-tri-*n*-butyltetralin together with some unchanged ketone. More drastic conditions gave the 1 : 2 : 3-tri-*n*-butyldecalin. The tetralin was dehydrogenated to 1 : 2 : 3-tri-*n*-butylnaphthalene as in the previous case.

EXPERIMENTAL.

2 : 6-*Di*-n-*hexylnaphthalene.*—6-n-*Hexyl-2-naphthyl* n-*pentyl ketone.* 2-*n*-Hexylnaphthalene was prepared by the method of Smith *et al.* (*loc. cit.*). The *n*-hexyl chain was shown to be unaffected by anhydrous aluminium chloride under Friedel–Crafts conditions by recovering unchanged material from a solution of the two in nitrobenzene. The hydrocarbon (53 g., 1 mol.) in dry nitrobenzene (200 c.c.) containing *n*-hexanoyl chloride (40 g., 1·2 mols.) was treated with anhydrous aluminium chloride (40 g., 1·2 mols.) in the cold, and the product isolated in the normal manner (see preceding paper). The crude material, b. p. 255—257°/12 mm., crystallised from ethanol in plates (56 g., 72%), m. p. 55°, later shown to be 6-n-*hexyl-2-naphthyl* n-*pentyl ketone* (Found : C, 85·2; H, 9·6. $C_{22}H_{30}O$ requires C, 85·2; H, 9·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in elongated orange prisms, m. p. 159° (Found : C, 69·0; H, 6·9; N, 11·6. $C_{28}H_{34}O_4N_4$ requires C, 68·6; H, 6·9; N, 11·4%), and the *semicarbazone* from ethanol in plates, m. p. 142° (Found : C, 75·1; H, 9·0; N, 11·0. $C_{23}H_{33}ON_3$ requires C, 75·2; H, 9·0; N, 11·4%).

2 : 6-*Di*-n-*hexylnaphthalene.* The ketone (30 g.) was reduced by the normal Huang-Minlon procedure, sodium (7·5 g.) in diethylene glycol (180 c.c.), and hydrazine hydrate (20 c.c.; 90%) being used. Isolation of the product with benzene gave a colourless oil, b. p. 207—208°/1 mm. Crystallisation from ethanol at 0° gave 2 : 6-*di*-n-*hexylnaphthalene* in prisms, m. p. 36·5—37° (Found : C, 89·1; H, 10·9. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%).

Oxidation of 2 : 6-*di*-n-*hexylnaphthalene.* The hydrocarbon (0·1 g.) was heated in a sealed tube at 190° for 20 hours with nitric acid (1·8 c.c.; *d* 1·42) and water (3·6 c.c.). Evaporation of the solution from three such oxidations gave a colourless solid (0·2 g.), m. p. 210—215°, which crystallised from water in needles, m. p. 214—216°. The analysis agrees with that of a benzenetricarboxylic acid (Found : C, 51·1; H, 3·1. Calc. for $C_9H_6O_6$: C, 51·4; H, 2·9%). A suspension of the acid in ether was treated with ethereal diazomethane. Removal of the solvent gave an oil which could not be obtained crystalline (trimellitic acid has m. p. 216°; its trimethyl ester, m. p. −13°).

Oxidation of 6-n-*hexyl-2-naphthyl* n-*pentyl ketone.* The ketone (5·0 g.) was oxidised with selenium dioxide (4·2 g.) in boiling dioxan (50 c.c.), and the crude product treated with alkaline hydrogen peroxide. Crystallisation of the acidic product from light petroleum (b. p. 80—100°) and then from acetic acid yielded prisms (0·6 g.; m. p. 141°) of a substance later shown to be 6-n-*hexyl-2-naphthoic acid* (Found : C, 79·5; H, 7·6. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%). Further oxidation of this acid with dilute nitric acid at 190° resulted in formation of the benzenetricarboxylic acid described above.

From attempts to oxidise the hexylnaphthalenecarboxylic acid and the dihexylnaphthalene with selenium dioxide in boiling nitrobenzene, only unchanged material could be isolated.

6-*Methoxy*-2-*naphthyl* n-*pentyl ketone*. 2-Methoxynaphthalene (79·0 g., 1 mol.) and *n*-hexanoyl chloride (81·0 g., 1·2 mols.) in dry nitrobenzene (320 c.c.) were treated at 0° with anhydrous aluminium chloride (87·0 g., 1·3 mols.). Isolation of the product in the usual manner gave the crude material, b. p. 203—205°/1·9 mm. Crystallisation from light petroleum (b. p. 40—60°) gave 78·9 g. (62%) of a substance later shown to be 6-*methoxy*-2-*naphthyl* n-*pentyl ketone* as plates, m. p. 65° (Found : C, 79·9; H, 7·8. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate as dark red needles, m. p. 195° (Found : N, 12·9. $C_{23}H_{24}O_5N_4$ requires N, 12·8%). From ethanol, the *semicarbazone* crystallised in prisms, m. p. 174° (Found : N, 13·4. $C_{18}H_{23}O_2N_3$ requires N, 13·4%), and the *oxime* in needles, m. p. 100° (Found : C, 75·4; H, 7·9. $C_{17}H_{21}O_2N$ requires C, 75·3; H, 7·8%).

Oxidation of 6-*methoxy*-2-*naphthyl* n-*pentyl ketone*. No acidic material could be isolated from the attempted oxidation of the ketone by heating with aqueous sodium hypochlorite for 8 hours. However, from the ketone (3·0 g.) and selenium dioxide (2·6 g.) in boiling dioxan (50 c.c.) for 8 hours, followed by treatment with alkaline hydrogen peroxide, an acid was isolated, which separated from ethanol in needles, m. p. 197—198°, after purification by heating the alcoholic solution with kieselguhr. No depression resulted on admixture with an authentic specimen of 6-methoxy-2-naphthoic acid prepared by the alkaline hypochlorite oxidation of 6-methoxy-2-naphthyl methyl ketone (Haworth and Sheldrick, *J.*, 1934, 864).

6-n-*Hexyl*-2-*naphthol*. The methoxynaphthyl ketone (30·0 g.) was reduced by the usual Huang-Minlon procedure, sodium (7·5 g.), diethylene glycol (210 c.c.), and hydrazine hydrate (15 c.c.; 90%) being used. After 9 hours at 220°, the red upper layer of hydrazone had completely disappeared. Benzene extraction of the cooled and diluted reaction mixture failed to yield a product, showing that complete hydrolysis of the methoxyl group had occurred. From the benzene extract of the solution after acidification with hydrochloric acid, a yellow oil was obtained, which solidified on cooling. Two crystallisations from light petroleum (b. p. 80—100°) yielded 6-n-*hexyl*-2-*naphthol* in large plates, m. p. 101° (20·3 g., 76%) (Found : C, 84·3; H, 8·9. $C_{16}H_{20}O$ requires C, 84·2; H, 8·8%). The *phenylurethane*, prepared by heating the naphthol and phenyl *iso*cyanate on the water-bath for 3 hours, separated from light petroleum (b. p. 100—120°) in plates, m. p. 135—136° (Found : C, 79·7; H, 7·3; N, 4·4. $C_{23}H_{25}O_2N$ requires C, 79·5; H, 7·2; N, 4·0%).

Reduction of 6-n-*hexyl*-2-*naphthol*. A solution of the naphthol (4·0 g., 1 mol.) in ethanol (4·1 c.c., 2 mols.) was added cautiously to liquid ammonia (200 c.c.). To the stirred solution, sodium (1·8 g., 2·2 atoms) was added slowly. At the end of the addition, the ammonia was allowed to evaporate, and water (100 c.c.) added to the white residue. The resultant gummy blue material was rapidly acidified with concentrated hydrochloric acid, and the oil extracted with ether. Removal of the solvent from the washed and dried solution gave a red oil, which was shaken for 4 hours with a saturated aqueous solution of sodium hydrogen sulphite. The microcrystalline bisulphite compound was then removed at the pump, washed with ether, and decomposed by warming it for ½ hour on the water-bath with dilute hydrochloric acid. The oil which separated was isolated by means of ether, and distilled in a bulb apparatus. A colourless oil (1·0 g.) distilled at 184—185° (bath-temp.)/1 mm., and redistilled at 187°/1 mm. This compound, m. p. −2° to −1°, n_D^{20} 1·5249, was shown to be 6-n-*hexyl*-2-*tetralone*. The pure ketone was obtained in 20% yield (0·8 g.) (Found : C, 83·7; H, 9·5. $C_{16}H_{22}O$ requires C, 83·5; H, 9·6%). No crystalline derivatives of this ketone could be obtained with 2 : 4-dinitrophenylhydrazine sulphate, semicarbazide hydrochloride, or 4-phenylsemicarbazide. A solution in ethanol gave the characteristic " tetralone blue " colour with aqueous alkali, however.

The ethereal solution of the non-ketonic reduction product was extracted with alkali, but no phenolic material was present. Removal of the solvent gave a red oil, from which two fractions were collected on bulb distillation : (i) a pale yellow oil, b. p. 200°/1·6 mm., and (ii) a colourless oil, b. p. 205°/1·6 mm., which solidified on cooling. The first fraction was redistilled, b. p. 185—187°/1 mm., and is considered to be 6-n-*hexyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthol* (1·0 g., 25%) (Found : C, 82·7; H, 10·0. $C_{16}H_{24}O$ requires C, 82·8; H, 10·3%). The solid (0·5 g.) was shown to be non-ketonic : repeated crystallisation gave needles, m. p. 80—87°, and no further purification could be effected.

Reduction of 6-n-*hexyl*-2-*methoxynaphthalene*. The hexylnaphthol was methylated in 74% yield by using methyl sulphate and 66% aqueous potassium hydroxide in acetone. 6-n-*Hexyl*-2-*methoxynaphthalene* crystallised from ethanol in plates, m. p. 56° (Found : C, 84·5; H, 9·3. $C_{17}H_{22}O$ requires C, 84·3; H, 9·1%). A solution of the methoxy-compound (20·0 g., 1 mol.) in dry xylene (350 c.c.) containing sodium (9·5 g., 2·5 equivs.) was heated to boiling and stirred vigorously. Dry ethanol (24 c.c., 2·5 equivs.) was then added through the condenser as rapidly as possible. At the end of the reaction, ethanol (2·5 c.c.) was added to remove any sodium, and the reaction mixture cooled. Water (400 c.c.) was then added, and the xylene layer removed. Fractionation of the washed and dried solution gave a colourless mobile oil, b. p. 168—171°/1 mm., n_D^{20} 1·5416. The oil gave a 2 : 4-dinitrophenylhydrazone colour reaction, and a " tetralone blue " colour after treatment with mineral acid, and appeared to be 6-*n*-hexyl-1 : 4-dihydro-2-methoxynaphthalene (Found : C, 83·6; H, 10·0. $C_{17}H_{24}O$ requires C, 83·6; H, 9·8%).

The oil (18·5 g.) was dissolved in ethanol (250 c.c.) containing aqueous hydrochloric acid (50 c.c.; 10%), and warmed on the water-bath for 20 minutes. A pale red oil was isolated by means of ether, and was shaken with saturated sodium hydrogen sulphite solution. The bisulphite compound was decomposed as described above, and purification of the product gave the hexyl-β-tetralone in 53% yield (9·2 g.), identical with the material obtained from the hexylnaphthol.

From the ethereal washings of the bisulphite compound, an oil was isolated, which distilled at 169—170°/1 mm., n_D^{20} 1·5359 (4·9 g., 24%); it was non-ketonic, and is considered to be 6-n-*hexyl*-5 : 8-*dihydro*-2-*methoxynaphthalene* (Found : C, 83·6; H, 9·8. $C_{17}H_{24}O$ requires C, 83·6; H, 9·8%).

2 : 6-*Di*-n-*hexylnaphthalene*. The tetralone (6·0 g., 1 mol.) was added in ether to an excess of *n*-hexylmagnesium bromide at room temperature, and the reaction mixture then heated under reflux for 12 hours. Decomposition and isolation of the product in the normal manner, followed by distillation, gave a fore-run of ketone, and the b. p. then rose steadily from 158° to 179°/0·1 mm. This crude carbinol (1·7 g.) was heated at 240° with a palladium–charcoal catalyst (0·2 g.; 30%) (Zelinsky and Turowa-Pollak, *Ber.*, 1925, **58**, 1295), with a slow stream of carbon dioxide passing over the surface. A vigorous reaction occurred in the first few minutes, after which the temperature was raised to 260° for 1½ hours, and finally to 300° for 10 minutes. The product was isolated with the aid of acetone: distillation gave a colurless oil, b. p. 200—230°/1·4 mm., which crystallised on cooling. Recrystallisation from chilled ethanol gave 2 : 6-di-*n*-hexylnaphthalene, colourless plates, m. p. 36°, undepressed on admixture with the hydrocarbon obtained from 2-*n*-hexylnaphthalene.

1 : 8-*Di*-n-*hexylnaphthalene*. The reactions of naphthalene-1 : 8-dicarboxylic anhydride (Graebe and Gfeller, *Ber.*, 1892, **25**, 653) with di-*n*-pentylcadmium and with *n*-pentylmagnesium bromide, and of the dicarboxyl dichloride with di-*n*-pentylcadmium proved useless for the present investigation (see p. 1062).

Reactions of Acenaphthenequinone.—*n*-Pentylmagnesium bromide (1 mol.; from *n*-pentyl bromide, 16·6 g.) was stirred vigorously at room temperature, and finely powdered acenaphthenequinone (5 g., 0·5 mol.) was added slowly. The solution rapidly became deep red, and heat was evolved. The mixture was then heated under reflux for 4 hours, kept overnight, and worked up by Maxim's general method (*loc. cit.*). Unchanged quinone (2·3 g.) was recovered from the orange ethereal solution, which, on removal of solvent, gave a deep red oil, from which no pure material could be isolated, but which reacted rapidly with cold aqueous permanganate. This oil is probably impure 7 : 8-di-*n*-pentylideneacenaphthene. A modification using an excess of Grignard reagent, and the temperature being kept at 0° throughout the reaction, gave an 82% recovery of quinone, together with a small quantity of the red oil. A repetition of the reaction with *n*-propylmagnesium bromide (Maxim, *loc. cit.*) gave a 9% yield of the di-*n*-propyl-diol, m. p. 171° (Maxim, m. p. 173°), together with much unchanged quinone and an unsaturated red oil.

7 : 8-*Di*-n-*pentylacenaphthene*-7 : 8-*diol*. Lithium metal (25·0 g., 2·2 atoms) was hammered under liquid paraffin into thin foil, which was cut into strips and dropped through a rapid stream of dry, oxygen-free nitrogen into dry ether (700 c.c.). *n*-Pentyl chloride (174 g., 1 mol.) in dry ether (300 c.c.) was added until reaction began; stirring was then commenced, and the addition regulated so as to maintain gentle reflux, the nitrogen stream being continued. The mixture was then heated under reflux for 2 hours. After cooling, the ethereal pentyl-lithium was transferred to a second flask under nitrogen pressure, being filtered from unchanged lithium and the bulk of lithium chloride by passing it through an inverted filter funnel covered with fine muslin. The residual solid was washed three times with ether, and the combined ethereal solutions were cooled in an efficient freezing mixture and stirred under nitrogen. Acenaphthenequinone (50·0 g., 0·5 mol.) was finely powdered and added in small portions to this solution. A vigorous reaction resulted, and the solution developed a red-purple colour. After the addition, the mixture was stirred at room temperature for 2 hours. Next day, the lithium complex was decomposed by careful addition of water to the stirred and cooled solution. The white solid (20·9 g.; m. p. 148—150°) which separated at this stage was removed at the pump and washed with ether. The combined ethereal solutions, after being washed and dried ($MgSO_4$), gave a light brown solid on removal of the solvent. Trituration with light petroleum (b. p. 40—60°) gave a white solid (45·1 g.; m. p. 147—148°, undepressed on admixture with that obtained above). The combined solids were crystallised from benzene and then light petroleum (b. p. 100—120°), giving 7 : 8-*di*-n-*pentylacenaphthene*-7 : 8-*diol* (58·0 g., 65%) as needles, m. p. 150° (Found: C, 80·9; H, 9·2. $C_{22}H_{30}O_2$ requires C, 81·0; H, 9·2%).

From the light petroleum washings of the crude diol, a viscous red oil (15·7 g.) was obtained. Although no pure material could be isolated, it reacted rapidly with aqueous permanganate, and appeared to be the impure di-*n*-pentylideneacenaphthene.

1 : 8-*Di*-n-*hexanoylnaphthalene*. The diol (16·8 g., 1 mol.) in dry benzene (400 c.c.) was shaken at room temperature with lead tetra-acetate (23 g., 1 mol.) for 4 hours, then warmed on the water-bath for ½ hour, and poured into a large volume of water. Removal of the solvent from the washed and dried benzene layer yielded a colourless oil, which solidified on cooling. Crystallisation from benzene gave plates, m. p. 86·0—86·5° (13·4 g., 80%) (Found: C, 81·3; H, 8·4. $C_{22}H_{28}O_2$ requires C, 81·5; H, 8·6%). When the reaction was carried out in glacial acetic acid, *ca.* 30% of unchanged diol was recovered. The crude diketone could only be purified by adsorption on alumina and elution with light petroleum (b. p. 60—80°). The pure diketone was obtained in 34% yield.

A solution of the diketone in methanol gave a red colour with 2 : 4-dinitrophenylhydrazine sulphate, but no solid derivative could be obtained. Also, no perinaphthindenone could be obtained by heating the diketone in piperidine solution. The strong infra-red absorption band at 1685 ν proved the presence of the carbonyl group, however.

1 : 8-*Di*-n-*hexyldecahydronaphthalene*. Copper chromite being used as catalyst, and with high temperature and pressure, hydrogenation of the diketone yielded a material shown by analysis to contain oxygen and too high a percentage of hydrogen for a naphthalene derivative. Similar results were obtained by using Hartung's palladised charcoal in acetic acid at 65° (cf. Hornung and Reisner, *loc. cit.*; Ju, Shen, and Wood, *loc. cit.*).

The diketone (18·5 g.) was hydrogenated with Raney nickel in the absence of solvent under an initial hydrogen pressure of 120 atm. The temperature was raised to 250°, and kept thereat for 4 hours. After cooling, additional catalyst was added, and the hydrogenation continued. After a repetition with a third amount of catalyst, the product was isolated by means of ether, and distillation, followed by redistillation over sodium, gave 1 : 8-*di*-n-*hexyldecahydronaphthalene*, b. p. 160—162°/1 mm., n_D^{20} 1·4783 (14·3 g., 80%) (Found : C, 86·3; H, 13·4. $C_{22}H_{42}$ requires C, 86·3; H, 13·7%).

1 : 8-*Di*-n-*hexylnaphthalene*. The dihexyldecalin (11·5 g.) was heated with 30% palladised charcoal in a metal-bath at 310° for 5 hours under a stream of nitrogen, vigorous hydrogen evolution occurring initially. The temperature was then raised to 330°, and kept thereat for an additional 2 hours. Isolation by means of ether gave an oil, b. p. 170—175°/3 mm. From its refractive index (1·5163) it appeared to be a tetrahydro-derivative, and so was dehydrogenated again as before. Isolation with ether followed by fractionation gave 1 : 8-*di*-n-*hexylnaphthalene*, b. p. 198—200°/3 mm., n_D^{20} 1·5531, m. p. −9° to −8° (Found : C, 89·0; H, 11·0. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%).

2 : 3-*Di*-n-*hexylnaphthalene*.—n-*Pentyl* 5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl ketone*. The Friedel–Crafts reaction was conducted in the normal manner, tetralin (132 g., 1 mol.), *n*-hexanoyl chloride (148 g., 1·1 mols.), and aluminium chloride (148 g., 1·1 mols.) being used in dry nitrobenzene (540 c.c.) at 0°. The *ketone* was obtained as a colourless oil (153·6 g., 67%), b. p. 198—199°/13 mm., n_D^{20} 1·5366, m. p. 3° (Found : C, 83·8; H, 9·6. $C_{16}H_{22}O$ requires C, 83·5; H, 9·6%). Its 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in dark red needles, m. p. 170° (Found : C, 64·6; H, 6·4. $C_{22}H_{26}O_4N_4$ requires C, 64·4; H, 6·3%), and its *semicarbazone* crystallised from ethanol in prisms, m. p. 159° (Found : C, 71·3; H, 8·7. $C_{17}H_{25}ON_3$ requires C, 71·1; H, 8·7%).

6-n-*Hexyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The ketone (60 g.) in diethylene glycol (350 c.c.), containing sodium (15 g.) and hydrazine hydrate (30 c.c.; 90%), was treated under the normal Huang-Minlon conditions. Redistillation of the crude product, isolated by means of benzene, gave 6-*n*-hexyl-1 : 2 : 3 : 4-tetrahydronaphthalene (48·3 g., 86%) as a colourless oil, b. p. 160°/10 mm., n_D^{20} 1·5182 (Found : C, 88·6; H, 11·2. Calc. for $C_{16}H_{24}$: C, 88·9; H, 11·1%). Catalytic reduction by means of copper chromite at 210° and an initial hydrogen pressure of 80 atm. gave the same product in 82% yield. Hart *et al.* (*loc. cit.*) report n_D^{20} 1·5177.

3-n-*Hexyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl* n-*pentyl ketone*. As with 2-*n*-hexylnaphthalene, the side chain was shown to be unaffected by aluminium chloride. The 6-*n*-hexyltetralin (77·8 g.) was acylated under the normal conditions, *n*-hexanoyl chloride (53·5 g.), anhydrous aluminium chloride (53·0 g.), and nitrobenzene (200 c.c.) being used. Purification of the crude product yielded the *ketone* as a colourless oil (84 g., 74%), b. p. 198—200°/2·5 mm., n_D^{20} 1·5196 (Found : C, 83·9; H, 11·0. $C_{22}H_{34}O$ requires C, 84·1; H, 10·8%). No solid derivatives of this ketone could be obtained.

Following the method of Smith and Lo (*loc. cit.*), the ketone (4 drops) was heated with nitric acid (1·8 c.c.; *d* 1·42) and water (3·6 c.c.) at 190—200° for 20 hours. The colourless solid (0·2 g.) obtained on evaporation of three such oxidations was suspended in ether and esterified with diazomethane (from 2·0 g. of *N*-nitrosomethylurea). Two crystallisations from methanol yielded plates, m. p. 141°, undepressed on admixture with tetramethyl pyromellitate.

6 : 7-*Di*-n-*hexyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The ketone (38·4 g.) was hydrogenated under an initial hydrogen pressure of 195 atm. by using copper chromite as catalyst and a final temperature of 195° for 6 hours. Isolation by means of ether gave the product as a colourless oil (28·2 g., 77%), b. p. 191—192°/4 mm., n_D^{20} 1·5090, m. p. 4—5°. Clemmensen reduction gave the same material in 54% yield (Found : C, 88·1; H, 11·8. Calc. for $C_{22}H_{36}$: C, 88·0; H, 12·0%). Hart *et al.* (*loc. cit.*) report n_D^{20} 1·5090 for this hydrocarbon.

2 : 3-*Di*-n-*hexylnaphthalene*. The dihexyltetralin (20·6 g.) was heated with 10% of its weight of 10% palladised charcoal (Diels and Gädke, *Ber.*, 1925, **58**, 1231) at 260° for 3 hours in a stream of nitrogen. The evolution of hydrogen was vigorous at first. The temperature was then raised slowly at 300° and kept thereat until the evolution of hydrogen ceased (*ca.* 2 hours). Isolation of the product with the aid of ether gave 2 : 3-*di*-n-*hexylnaphthalene* as a colourless oil, m. p. 10°, after crystallisation from acetone at −40°, b. p. 202°/4 mm., n_D^{20} 1·5430 (Found : C, 89·2; H, 10·9. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%).

1 : 2 : 3-*Tri*-n-*butylnaphthalene*.—6-n-*Butyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. *n*-Propyl 5 : 6 : 7 : 8-tetrahydro-2-naphthyl ketone was prepared in 65% yield by Barbot's method (*Bull. Soc. chim.*, 1930, **47**, 1314), but with nitrobenzene as solvent. It was obtained as a colourless oil, b. p. 177—178°/15 mm., n_D^{20} 1·5472, n_D^{23} 1·5459, m. p. +1°. Barbot gives n_D^{23} 1·5460. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark red plates, m. p. 195—196° (Found : C, 62·5; H, 5·8. $C_{20}H_{22}O_4N_4$ requires C, 62·8; H, 5·8%). Huang-Minlon reduction of the ketone gave the hydrocarbon as a colourless liquid, b. p. 141°/15 mm., n_D^{20} 1·5228, in 80% yield (Found : C, 89·2; H, 10·8. Calc. for $C_{14}H_{20}$: C, 89·4; H, 10·6%). After the completion of this work, Hart and Robinson (*J. Amer. Chem. Soc.*, 1948, **70**, 3731) reported n_D^{20} 1·5234 for this hydrocarbon.

3-n-*Butyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthyl* n-*propyl ketone*. Friedel–Crafts conditions were again shown not to isomerise the side chain. Acylation by the normal procedure gave this *ketone* in 66% yield as a colourless oil, b. p. 153—154°/1 mm., n_D^{20} 1·5302 (Found : C, 83·7; H, 10·3. $C_{18}H_{26}O$ requires C, 83·7; H, 10·1%). The structure was proved by degradation to tetramethyl pyromellitate, by the method described for the corresponding hexanoylhexyltetralin. The red 2 : 4-dinitrophenylhydrazone, deposited from methanol on long storage at 0°, could not be purified for analysis.

6 : 7-Di-*n*-butyl-1 : 2 : 3 : 4-tetrahydronaphthalene was obtained as a colourless oil, b. p. 160—161°/1 mm., n_D^{20} 1·5174, in 70% yield (Found : C, 88·5; H, 11·5. Calc. for $C_{18}H_{28}$: C, 88·6; H, 11·5%) by the copper chromite reduction of the ketone. Hart and Robinson (*loc. cit.*) record n_D^{20} 1·5172.

2 : 3-*Di*-n-*butyl*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthyl* n-*propyl ketone*. The dibutyltetralin was acylated in 51% yield by the normal method, carbon disulphide being used as solvent. The *ketone* was obtained as a colourless oil, b. p. 190°/4 mm., n_D^{20} 1·5189 (Found : C, 83·9; H, 10·8. $C_{22}H_{34}O$ requires C, 84·1; H, 10·8%); no derivatives could be obtained.

5 : 6 : 7-*Tri*-n-*butyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. Catalytic reduction with copper chromite, at, initially, 110 atm., followed by heating at 200° for 6 hours, gave incompletely reduced material. Repeated

hydrogenation at 240° eventually gave the ***hydrocarbon*** as a colourless oil, b. p. 171—172°/2 mm., n_D^{20} 1·5160, in 57% yield (Found : C, 88·2; H, 12·0. $C_{22}H_{36}$ requires C, 88·0; H, 12·0%). Use of a higher temperature and pressure (140 atm. initially, and then at 300°) gave 1 : 2 : 3-***tri*-n-*butyldecalin***, b. p. 162—164°/2 mm., n_D^{20} 1·4860 (Found : C, 86·3; H, 13·7. $C_{22}H_{42}$ requires C, 86·3; H, 13·7%). 1 : 2 : 3-***Tri*-n-*butylnaphthalene*** was obtained in 70% yield by the catalytic dehydrogenation of the tributyltetralin under the conditions described for 2 : 3-di-*n*-hexylnaphthalene. The colourless oil, b. p. 199—200°/3 mm., n_D^{20} 1·5437, could not be obtained crystalline (Found : C, 89·1; H, 11·1. $C_{22}H_{32}$ requires C, 89·2; H, 10·8%).

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