305. *Homologues of Naphthacene. Part I. 2:6-Dimethylnaphthacene.*

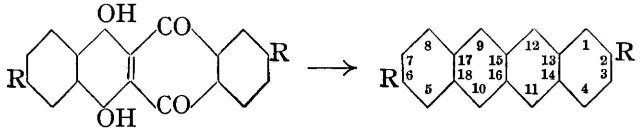
By Edward A. Coulson.

Although pure anthracene is colourless, the material derived from coal-tar oils always has a more or less intense yellow colour which cannot be removed by crystallisation. The coloured impurity, which has frequently attracted attention, was named " chrysogen " by Fritzsche (*Z. Chem.*, 1866, **2**, 139), Morton (*Chem. News*, 1872, **26**, 199), and Nickels (*ibid.*, 1880, **41**, 95), and " crackene " by Börnstein (*Ber.*, 1906, **39**, 1238). Owing to the small proportion present, its separation from commercial anthracene in quantity sufficient for detailed chemical examination is very tedious. While the work now to be described was in progress, Winterstein and Schön (*Naturwiss.*, 1934, **22**, 237) isolated a " chrysogen " whose m. p., composition, and absorption spectra showed its identity with naphthacene, a golden-orange hydrocarbon, m. p. *ca.* 335°, first prepared by Gabriel and Leupold (*Ber.*, 1898, **31**, 1272). The " chrysogens " isolated by previous workers were of lower m. p. and must therefore have contained substances other than naphthacene.

The anthracenoid hydrocarbons of low-temperature tar differ markedly from those of high-temperature tar, not only in the high proportion of various β-methyl-substituted anthracene homologues, but also in the greater proportion of coloured constituents. A direct comparison of naphthacene with coloured material separated from low-temperature tar anthracenoid hydrocarbons, of which the m. p. had slowly risen from 280° to 341° during recrystallisation, showed that, in spite of remarkable similarity in appearance, m. p., and colour reaction (moss-green) with concentrated sulphuric acid, there were significant points of difference (Morgan and Coulson, *J. Soc. Chem. Ind.*, 1934, **53**, 71T). Support was given to the view that, in this case at least, the material consisted of one or more naphthacene homologues when it was found that on oxidation it did not furnish naphthacenequinone, m. p. 295°, but an impure quinone, m. p. 220—240°.

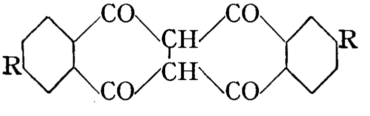
No homologues of naphthacene have yet been synthesised, and the methods used for the preparation of naphthacene itself (Deichler and Weizmann, *Ber.*, 1903, **36**, 547; Gabriel and Leupold, *Ber.*, 1898, **31**, 1272; Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 2329) are not readily adapted to the preparation of β-methyl- and 2 : 6- and 2 : 7-dimethyl-naphthacenes and the derived quinones which were initially required for comparison purposes. However, *iso*ethine diphthalide (9 : 10-dihydroxynaphthacene-11 : 12-quinone; I, R = H) can readily be reduced to naphthacene (II; R = H), and there was reason to hope that the isomeric compound 9 : 10 : 11 : 12-tetraketo-9 : 10 : 11 : 12 : 15 : 16-hexahydronaphthacene (III; R = H), prepared by Knorr and Scheidt (*Ber.*, 1894, **27**, 1167) by pyrolysis of ethyl dibenzoylsuccinate, could either be enolised to the *iso*ethine diphthalide, or under alkaline conditions reduced to naphthacene (see Barnett, " Anthracene and Anthraquinone," p. 146).

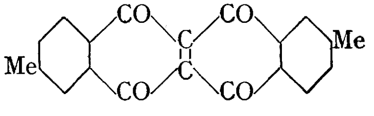
(I.)



(II.)

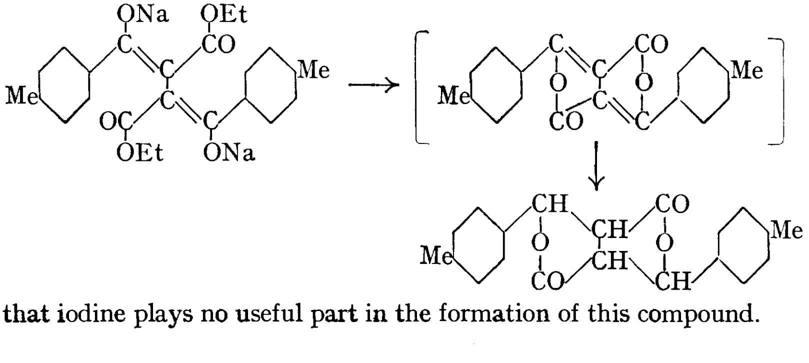
(III.)





(IV.)

With a view to the synthesis on these lines of 2 : 6-dimethylnaphthacene, 9 : 10 : 11 : 12-*tetraketo*-2 : 6-*dimethyl*-9 : 10 : 11 : 12 : 15 : 16-*hexahydronaphthacene* (III; R = CH_3) was prepared by pyrolysis of β- or γ-*ethyl di*-p-*toluoylsuccinate*. When the tetraketone (III) was treated with warm dilute alcoholic potash in an attempt at enolisation, it readily underwent decomposition, probably with ring opening, and the resinous acid product bore no resemblance to *iso*ethine diphthalide. Attempts to reduce the tetraketone to 2 : 6-dimethylnaphthacene were not successful; nor was it possible to obtain ethyl di-*p*-toluoylfumarate (with a view to prepare 2 : 6-dimethylnaphthacene-9 : 10 : 11 : 12-diquinone, IV) by treatment of ethyl di-*p*-toluoylsuccinate with sodium and iodine, for the *dilactone* of *αδ-dihydroxy-αδ-di*-p-*tolylbutane-βγ-dicarboxylic acid* (V) was the only product isolated :



(V.)

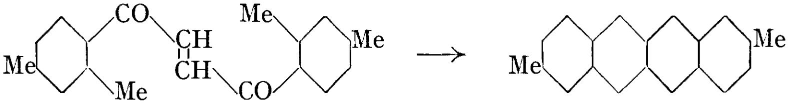
It is clear that iodine plays no useful part in the formation of this compound.

When ethyl *p*-toluoylacetate was treated with sodium and iodine, two isomeric ethyl di-*p*-toluoylsuccinates were formed. They closely resemble the β- and γ-isomerides of ethyl dibenzoylsuccinate (Knorr, *Annalen*, 1897, **293**, 74) and are therefore given a corresponding nomenclature. Both on pyrolysis yield, besides the red tetraketone (III), a yellow compound, *ethyl* 2 : 5-*ditolylfuran*-3 : 4-*dicarboxylate*.

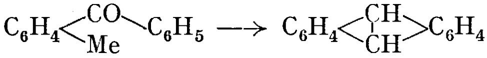
The synthesis of 2 : 6-*dimethylnaphthacene* was ultimately effected in two ways, although in the first the yield was very poor.

(I) *Pyrolysis of* αβ-*bis*-2 : 4-*dimethylbenzoylethylene*. When trans-αβ-*bis*-2 : 4-*dimethylbenzoylethylene* (VI) was heated at 315° for 5 minutes, it rapidly lost water and was transformed into a mixture containing the following five substances : 2 : 5-*di*-4′-m-*xylylfuran*, 2 : 4-dimethylacetophenone, αβ-*bis*-2 : 4-*dimethylbenzoylethane*, 2 : 4-dimethylbenzoic acid, and 2 : 6-*dimethylnaphthacene* (VII). The formation of the last-mentioned is apparently analogous to the formation of anthracene by the Elbs reaction :

(VI.)



(VII.)

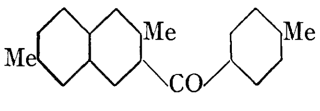


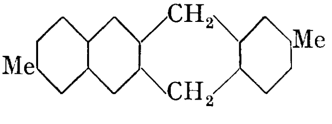
$$C_6H_4{<}^{CO}_{Me}{>}C_6H_5 \longrightarrow C_6H_4{<}^{CH}_{CH}{>}C_6H_4$$

The poorness of the yield, coupled with the preponderance of the furan, shows that *cis*-isomerisation probably occurs in the first stage of the pyrolysis. *cis*-Isomerisation of *trans*-αβ-bis-2 : 4-dimethylbenzoylethylene occurs if it is exposed to light even in the dry state, and is rapid in alcoholic solutions containing a trace of potassium hydroxide (cf. dibenzoylethylene, Paal and Schulze, *Ber.*, 1902, **35**, 168; and di-*p*-toluoylethylene, Conant and Lutz, *J. Amer. Chem. Soc.*, 1923, **45**, 1305).

(II) *Pyrolysis of* 3-p-*toluoyl*-2 : 6-*dimethylnaphthalene*. The usual product of pyrolysis of an *o*-methylbenzophenone is the anthracene (by loss of water, see above), but Elbs has noted the formation of an anthraquinone (by aerial oxidation), and the formation of an anthrone (loss of hydrogen) has been observed in rare cases. When 3-p-*toluoyl*-2 : 6-*dimethylnaphthalene* (VIII) is pyrolysed, much charring occurs, but two products may be isolated, 2 : 6-dimethylnaphthacene (VII) and 2 : 6-*dimethyl*-9 : 10-*dihydronaphthacene* (IX). The latter is dehydrogenated by heating, alone, or better with selenium, to the former, and both on oxidation yield 2 : 6-*dimethylnaphthacene*-9 : 10-*quinone*.

(VIII.)





(IX.)

The formation of a dihydride in an Elbs pyrolysis has previously been noted by Clar and John (*Ber.*, 1929, **62**, 3021), who obtained 2 : 3 : 6 : 7-dibenzdihydroanthracene from 4 : 6-dibenzoyl-*m*-xylene. The unexpected degree of unsaturation thus shown by *linear* four- and five-ring systems in their ready formation of dihydrides is probably not unconnected with their deep colour.

The 3-*p*-toluoyl-2 : 6-dimethylnaphthalene (VIII) required for this synthesis was obtained from 3 : 7-dimethyl-β-naphthol, which was converted by the Bucherer reaction into 3 : 7-*dimethyl*-β-*naphthylamine*. This base was diazotised and yielded by Sandmeyer's process 3 : 7-*dimethyl*-β-*naphthonitrile*, which was saponified, and the resulting *acid* transformed by thionyl chloride into 3 : 7-*dimethyl*-β-*naphthoyl chloride*. The acyl chloride condensed with toluene, in presence of aluminium chloride, to yield the required ketone.

EXPERIMENTAL.

p-Toluic acid is best prepared in quantity by hypobromite oxidation of *p*-methylacetophenone. Bromine (135 c.c.) was dissolved in an ice-cold solution of 265 g. of sodium hydroxide in 1700 c.c. of water, and added in portions to a cooled well-shaken mixture of 111 g. of *p*-methylacetophenone and 111 g. of water until no further decolorisation occurred. The mixture was treated with sulphur dioxide, the heavy colourless oil (bromoform and carbon tetrabromide) removed, and pure *p*-toluic acid (83 g.), m. p. 179—181°, precipitated by acidification of the aqueous liquid.

p-*Toluoyl Bromide.*—*p*-Toluic acid (109 g.) was boiled with 275 g. of phosphorus tribromide during ½ hour, and the crude acyl bromide decanted and fractionated in a vacuum, yielding 111·5 g. of p-*toluoyl bromide*, b. p. 173°/113 mm., as a colourless heavy oil (Found : Br, 40·4. C_8H_7OBr requires Br, 40·2%).

Ethyl p-*Toluoylacetate.*—To the cold ethereal suspension of ethyl sodioacetoacetate prepared from 12 g. of powdered sodium and 69 g. of ethyl acetoacetate in about 400 c.c. of cold ether, an ethereal solution of 82 g. of *p*-toluoyl chloride was added in small portions with shaking during 2 hours, followed by a cold solution of 12 g. of sodium in 120 g. of absolute alcohol; the whole was left over-night at 0°, and the yellow sodio-derivative of ethyl *p*-toluoylacetoacetate which crystallised was added to a solution of 63 g. of ammonium chloride in 255 c.c. of water at 40° containing 22·5 c.c. of aqueous ammonia (*d* 0·880). After 15 minutes' shaking at this temperature, ethyl *p*-toluoylacetate separated; it was taken up in ether, washed with dilute sodium carbonate solution and water, recovered, and distilled in a vacuum; yield, 46·5 g. having b. p. 133°/2 mm. (42%).

β- *and* γ-*Ethyl Di*-p-*toluoylsuccinates.*—Iodine (28·7 g.) was added in portions with shaking to a cooled ethereal suspension of the sodio-derivative of ethyl *p*-toluoylacetate formed from 5·2 g. of powdered sodium and 46·5 g. of the ester. The ethereal solution was washed with dilute sulphurous acid and water. A portion of the product separated, and the remainder was obtained, after evaporation of the ether, as a resinous mass which crystallised slowly and incompletely. The less soluble portion, obtained by fractional crystallisation from alcohol and benzene, formed rosettes of colourless, elongated, rhombic plates (10·5 g.), m. p. 145° (Found: C, 70·3; H, 6·4. $C_{24}H_{26}O_6$ requires C, 70·3; H, 6·3%). It is distinguished as β-*ethyl di*-p-*toluoylsuccinate* because of its correspondence to Knorr's β-ethyl dibenzoylsuccinate (*loc. cit.*). The more soluble part of the product slowly crystallised in contact with benzene and furnished the γ-*isomeride* in tufts of colourless rhombs, m. p. 82—83°, when fractionally crystallised from this solvent (Found : C, 70·3, 70·6; H, 6·5, 6·6%).

When 1·0 g. of either the β- or the γ-isomeride was boiled during ½ hour with a dilute alcoholic solution of sodium hydroxide, it was converted into αβ-di-*p*-toluoylethane, which crystallised on cooling in colourless needles, m. p. 161° (Found : C, 81·1; H, 7·0. Calc. for $C_{18}H_{18}O_2$: C, 81·2; H, 6·8%). Conant and Lutz (*loc. cit.*) give m. p. 159°. A solution of αβ-di-*p*-toluoylethane in acetic acid containing a few drops of concentrated hydrochloric acid was boiled during ¼ hour and yielded 2 : 5-*ditolylfuran*, which crystallised on cooling in colourless, hexagonal, curled spangles, m. p. 166° (Found : C, 87·0; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%).

Pyrolysis of β- *and* γ-*Ethyl Di*-p-*toluoylsuccinates.*—Both isomeric esters were heated rapidly in 0·5 g. portions at 320° for 5 minutes. The product was cooled, and extracted with boiling alcohol. From 16 g. of the β-isomeride, 2·5 g. of 9 : 10 : 11 : 12-*tetraketo*-2 : 6-*dimethyl*-9 : 10 : 11 : 12 : 15 : 16-*hexahydronaphthacene* (III; $R = CH_3$), which is only slightly soluble in boiling alcohol, were obtained; purified by recrystallisation from acetic acid, it formed red needles, m. p. 320° (Found : C, 75·4; H, 4·6. $C_{20}H_{14}O_4$ requires C, 75·5; H, 4·4%). Its solutions have a brilliant green fluorescence and it dissolves in cold concentrated sulphuric acid with development of a deep purple colour.

The alcoholic washings of the pyrolytic product were concentrated and cooled, whereupon 3·0 g. of *ethyl* 2 : 5-*ditolylfuran*-3 : 4-*dicarboxylate* separated; recrystallised from alcohol, this formed large, straw-coloured, elongated prisms, m. p. 118° (Found : C, 73·3, 73·3; H, 6·3, 6·4. $C_{24}H_{24}O_5$ requires C, 73·5; H, 6·1%). The ester was saponified by refluxing for ¼ hour with aqueous-alcoholic caustic potash to yield the *acid*, which separated on acidification and, recrystallised from acetic acid, formed pale yellow needles, m. p. 264° (decomp.) (Found : C, 71·6; H, 4·8. $C_{20}H_{16}O_5$ requires C, 71·4; H, 4·8%).

Reactions of 9 : 10 : 11 : 12-*Tetraketo*-2 : 6-*dimethyl*-9 : 10 : 11 : 12 : 15 : 16-*hexahydronaphthacene.*—(1) *Attempted reduction.* The tetraketone was not vatted with zinc dust and ammonia solution, and was unaffected by Clemmensen methods of reduction, but when a solution in boiling acetic acid was treated with hydrochloric acid and amalgamated zinc, it decomposed into soluble resinous products which could not be crystallised. The tetraketone was heated with selenium at 280° but was unchanged; at higher temperatures it sublimed.

(2) *Action of alkali.* When a few drops of 50% sodium hydroxide solution were added to a suspension of the tetraketone in boiling alcohol, the ketone rapidly dissolved to a yellow solution. On cooling, dilution, and acidification, a yellow, gummy, acid substance separated, which was

fairly soluble in hot water but could not be crystallised and bore no resemblance to *iso*ethine diphthalide (ruby needles, m. p. 346—347°).

Action of Sodium and Iodine upon β-*Ethyl Di*-p-*toluoylsuccinate.*—To 0·9 g. of powdered sodium, suspended in boiling ether, were added 8·0 g. of β-ethyl di-*p*-toluoylsuccinate, which slowly dissolved to a yellow solution. (The sodio-derivative of ethyl α-acetylsuccinate is soluble in ether, and probably the sodium forms a chelate ring in this type of compound; see Isbell, Wojcik, and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 3678.) Iodine (5·0 g.) was added in portions to the cold ethereal solution, which was finally washed with dilute sulphurous acid and water and concentrated; a colourless crystalline compound (2·0 g.) which separated was recrystallised from benzene–petrol (b. p. 40—60°) and formed rhombs, m. p. 228—229° (Found: C, 74·6, 74·3; H, 5·5, 5·6. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). This compound is apparently the *dilactone* of *αδ-dihydroxy-αδ-di*-p-*tolylbutane-βγ-dicarboxylic acid* (V).

trans-*αβ-Bis-2 : 4-dimethylbenzoylethylene* (VI).—Fumaric acid did not react with thionyl chloride, but after the acid (100 g.) had been treated with 360 g. of phosphorus pentachloride (Kekulé, *Annalen*, Suppl. **2**, 86), 58·7 g. of fumaryl chloride, b. p. 157—162°, were isolated by fractional distillation.

To 170 g. of powdered aluminium chloride, covered with carbon disulphide, were added first *m*-xylene (212 g.) and then a solution of 53 g. of fumaryl chloride in carbon disulphide. After standing for 2 days in the cold, the mixture was poured on ice. The bulk of the trans-*αβ-bis-2 : 4-dimethylbenzoylethylene* separated; a smaller amount was recovered from the excess of *m*-xylene after concentration to small volume. The compound crystallised from acetic acid, in which it is rather easily soluble, or alcohol, in large, elongated, straw-coloured prisms (74 g.), m. p. 129—130° (Found: C, 82·3; H, 7·1. $C_{20}H_{20}O_2$ requires C, 82·2; H, 6·9%). Oddy (*J. Amer. Chem. Soc.*, 1923, **45**, 2159) described the preparation of this compound in poor yield, but gave no analysis and erroneously called it " di-(2 : 4-xylyl)ethylene."

In acetic acid it rapidly added bromine, yielding *αβ-dibromo-αβ-bis-2 : 4-dimethylbenzoylethane*, colourless needles from alcohol, m. p. 146° (decomp.) (Found: C, 52·7; H, 4·8; Br, 35·6. $C_{20}H_{20}O_2Br_2$ requires C, 53·1; H, 4·4; Br, 35·4%). When reduced with zinc dust in boiling acetic acid, it furnished *αβ-bis-2 : 4-dimethylbenzoylethane*, colourless flat prisms or plates from acetic acid or alcohol, m. p. 131—132° (Found: C, 81·4; H, 7·6. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%). The ethane was boiled for a short time with a mixture of acetic and hydrochloric acids, and quantitatively yielded 2 : *5-di-4′*-m-*xylylfuran*, which crystallised from petrol (b. p. 40—60°) in colourless needles, m. p. 95—96° (Found: C, 86·9; H, 7·2. $C_{20}H_{20}O$ requires C, 86·9; H, 7·2%).

On exposure to sunlight, the yellow *trans*-αβ-bis-2 : 4-dimethylbenzoylethylene became coated with the colourless gummy *cis*-isomeride. The same transformation also occurred when the *trans*-isomeride was dissolved in boiling acetic acid containing a few drops of concentrated hydrochloric acid, or in boiling alcohol containing a few drops of 50% aqueous potash. The *cis*-isomeride separated as a low-melting crystalline solid on cooling and dilution, but could not be freed from the yellow *trans*-isomeride into which it appeared to revert slowly when recrystallised. On reduction, the *cis*-isomeride yielded αβ-bis-2 : 4-dimethylbenzoylethane quantitatively.

Pyrolysis of trans-*αβ-Bis-2 : 4-dimethylbenzoylethylene.*—The yellow isomeride was heated in 2·0 g. portions at 315° for 5 minutes and the product was distilled and collected in two fractions boiling below and above 280°. When the first was cooled, a mixture of 2 : 4-dimethylbenzoic acid, m. p. 128°, and αβ-bis-2 : 4-dimethylbenzoylethane, m. p. 131—132°, crystallised; these constituents were separated and identified by mixed m. p. determinations with authentic specimens. The oily residue was fractionally distilled and yielded 2 : 4-dimethylacetophenone, b. p. 228°, which was identified by its quantitative oxidation with sodium hypobromite solution to 2 : 4-dimethylbenzoic acid. The less volatile part of the pyrolytic product was diluted with ether and shaken with sodium carbonate solution to remove 2 : 4-dimethylbenzoic acid. The ether was evaporated and left a deep red oil containing a small amount of 2 : 6-dimethylnaphthacene, which slowly separated and was crystallised from acetic acid; it was identical with a specimen made from 3-*p*-toluoyl-2 : 6-dimethylnaphthalene (see below). The remaining oil was mixed with an equal volume of petrol (b. p. 40—60°) and cooled to — 70°, whereupon crystals of slightly pink (due to traces of 2 : 6-dimethylnaphthacene) but otherwise pure 2 : 5-di-4′-*m*-xylylfuran separated, identical with a specimen made as above.

3 : *7-Dimethyl-β-naphthylamine.*—A poor yield of the base was obtained when dry sodium 3 : 7-dimethylnaphthalene-β-sulphonate (Weissgerber and Kruber, *Ber.*, 1919, **52**, 340) was heated at 200° for 2 hours with sodamide in naphthalene. 3 : 7-Dimethyl-β-naphthol (Weissgerber and Kruber, *loc. cit.*) (52 g.) was heated at 200° during 6 hours with 40 g. of ammonium

sulphite and 400 c.c. of ammonia solution (*d* 0·880) in an autoclave. The product was boiled with dilute sodium hydroxide solution, cooled, and thoroughly extracted with ether. From the ethereal extract, on shaking with 10% hydrochloric acid, 52·0 g. (83% of the theoretical yield) of the crude hydrochloride were precipitated, and 9·0 g. of the naphthol were recovered. The *base*, liberated by digesting the hydrochloride with warm dilute caustic soda solution, crystallised from petroleum (b. p. 60—80°) in colourless needles, m. p. 129°, readily soluble in benzene or alcohol (Found : C, 84·0; H, 7·7. $C_{12}H_{13}N$ requires C, 84·2; H, 7·6%). The *hydrochloride* forms minute colourless flakes, which darken at 200° and melt (decomp.) at 275° (Found : Cl, 17·0. $C_{12}H_{13}N,HCl$ requires Cl, 17·1%). The *acetyl* derivative, m. p. 231°, is dimorphic, separating from alcohol in voluminous tufts of colourless needles, which change slowly into colourless compact rhombs (Found : C, 78·9; H, 7·2. $C_{14}H_{15}ON$ requires C, 78·9; H, 7·0%).

3 : 7-*Dimethyl*-β-*naphthonitrile*.—The base (16·5 g.), suspended in 25 c.c. of concentrated hydrochloric acid and 80 c.c. of water, was treated at 0—5° with 8·0 g. of sodium nitrite, and the diazo-solution mixed with cold potassium cuprocyanide solution (34 g. of potassium cyanide, 30 g. of copper sulphate, and 200 c.c. of water). The first-formed, thick, yellow-brown precipitate gradually decomposed with effervescence on warming to 100°, leaving a suspension of the crude *nitrile* (11·0 g.); when purified by sublimation and crystallisation from alcohol, this formed colourless flakes with a satiny sheen, m. p. 160° (Found : C, 86·3; H, 6·3. $C_{13}H_{11}N$ requires C, 86·2; H, 6·1%).

3 : 7-*Dimethyl*-β-*naphthoic Acid*.—A poor yield of the acid was obtained when equal weights of potassium cyanide and sodium 3 : 7-dimethylnaphthalene-β-sulphonate were heated under a water-pump vacuum and the resulting sublimate, containing the nitrile, was saponified. The nitrile, prepared as above from 16·5 g. of the base, was saponified by heating with 50% potassium hydroxide solution and alcohol for 24 hours. The mixture was diluted with water, and the filtered liquid acidified, whereupon 12 g. of the *acid* (yield, 62% of theoretical from base) were precipitated. It separated from aqueous acetic acid in colourless needles, m. p. 228° (Found : C, 77·8; H, 6·2. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%). When the acid (21·0 g.) was boiled with 60 g. of thionyl chloride for 3 hours, it yielded 3 : 7-*dimethyl*-β-*naphthoyl chloride*, which was purified by distillation in a vacuum; it (23 g.) boiled at 182—185°/6 mm. and set on cooling to cream flakes, m. p. 79° (Found : Cl, 16·5. $C_{13}H_{11}OCl$ requires Cl, 16·3%). The acid chloride reacts with aniline to give 3 : 7-*dimethyl*-β-*naphthanilide*, colourless flattened prisms with pearly lustre, from alcohol, m. p. 238° (Found : C, 82·6; H, 6·4. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2%).

3-p-*Toluoyl*-2 : 6-*dimethylnaphthalene* (VIII).—To powdered aluminium chloride (11·0 g.), covered with dry toluene and warmed to 40—50°, 11·0 g. of 3 : 7-dimethyl-β-naphthoyl chloride, dissolved in 20 c.c. of toluene, were slowly added. The reaction mixture, after standing overnight, was poured on ice, whereupon the *ketone* (6·0 g.) crystallised from the excess of toluene; recrystallised from alcohol, it formed cream-coloured elongated plates or leaflets, m. p. 168° (Found : C, 87·4; H, 6·7. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%). Part of the reaction product remained dissolved in the excess of toluene, and was recovered as a thick viscid oil which charred when heated at 400° and yielded no sublimable pyrolytic products.

Pyrolysis of 3-p-*Toluoyl*-2 : 6-*dimethylnaphthalene*.—When the ketone was heated at 360—400° for 4 hours, it gradually lost water and yielded a sublimate containing two substances, which were separated by fractional crystallisation from acetic acid. The less soluble, 2 : 6-*dimethylnaphthacene* (0·1 g.), formed golden-orange flakes, m. p. 365° (if heated slowly, it darkens, partly sublimes, and melts at 350—360°) (Found : * C, 93·1; H, 6·5. $C_{20}H_{16}$ requires C, 93·7; H, 6·3%). This hydrocarbon, which is sparingly soluble in the common solvents, yielding orange solutions with marked green fluorescence, is soluble in cold concentrated sulphuric acid, but is precipitated when the deep moss-green solution is diluted with water.

The second substance, 2 : 6-*dimethyl*-9 : 10-*dihydronaphthacene* (1·5 g.) (Found : * C, 93·0; H, 7·3. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%), is freely soluble in acetic acid, less soluble in alcohol, and crystallises in pale yellow flakes, m. p. 217°. It does not dissolve in nor develop a coloration with cold concentrated sulphuric acid. When heated with selenium for 2 hours at 230°, it loses hydrogen to give 2 : 6-dimethylnaphthacene, which sublimes at 350°.

2 : 6-*Dimethylnaphthacene*-9 : 10-*quinone*.—2 : 6-Dimethylnaphthacene (0·1 g.) was dissolved in boiling acetic acid, and chromic anhydride (0·13 g.) added in portions. The *quinone* was precipitated on dilution with water and, after being warmed with dilute sodium carbonate solution, was crystallised from acetic acid, in which it was moderately easily soluble, forming yellow flakes, m. p. 249° (decomp.) (Found : C, 83·5; H, 5·0. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%). In another preparation, 0·14 g. of 2 : 6-dimethyl-9 : 10-dihydronaphthacene was oxidised with

0·2 g. of chromic anhydride. The deep reddish-purple colour of the solution of the quinone in cold concentrated sulphuric acid fades on dilution, and the quinone is finally precipitated.

Thanks are due to Dr. J. J. Fox of the Government Laboratory for the micro-analyses marked with an asterisk, and to Professor G. T. Morgan, O.B.E., F.R.S., Director of Chemical Research, for his interest and advice and for permission to publish these results.

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