148. *Acenaphthene Series. Part III. Orientation of* tert.*-Butyl- and Di-*tert.*-butyl-acenaphthene, and Preparation of New Derivatives.*

By H. E. Nürsten and A. T. Peters.

The butylation of acenaphthene by means of *tert.*-butyl chloride and aluminium chloride, in carbon disulphide as a solvent, is shown to yield 2-*tert.*-butylacenaphthene and 2 : 5-di-*tert.*-butylacenaphthene.* The orientation of these hydrocarbons is based mainly on their oxidation to benzene-1 : 2 : 3 : 5-tetracarboxylic acid and provides the first instance of direct substitution of the acenaphthene nucleus in the 2-position.

The alkylacenaphthenes are degraded to the corresponding alkylnaphthalenes and thus a hydrocarbon, first described in 1884, has been identified as 2 : 7-di-*tert.*-butylnaphthalene.

New derivatives of 2-*tert.*-butyl- and of 2 : 5-di-*tert.*-butyl-acenaphthene are prepared.

The butylation of acenaphthene was first recorded in Part I of this series (Peters, *J.*, 1942, 562), where the reaction between a solution of the hydrocarbon in carbon disulphide and *tert.*-butyl chloride, in presence of aluminium chloride, was described. The separation of *tert.*-butylacenaphthene from the parent hydrocarbon and from the disubstituted product was a tedious process, but eventually the monoalkylacenaphthene was obtained in a small yield, but very pure, having m. p. 88—88·5°, whereas m. p. 73—74° had been recorded previously. Buu-Hoï and Cagniant (*Rev. sci.*, 1943, **81**, 72) gave m. p. 72° for *tert.*-butylacenaphthene, which they obtained in very poor yield from the products of a similar reaction without the use of a solvent.

Orientation of tert.*-Butylacenaphthene.*—Those substitution reactions of acenaphthene which lead to products that have been orientated (35 studies) are summarised in the table.

Acenaphthene is generally attacked in the 3-position, rarely in the 1-position, never in the 2-position, and in the 7-position only by oxidising agents. Some 2-substitution had been postulated but not proved in the case of benzylation.

From consideration of these results, the butylation of the hydrocarbon was expected to yield 3-*tert.*-butylacenaphthene, which orientation was accepted in Part I and by Buu-Hoï and Cagniant.

In the present research, the *tert.*-butylacenaphthene was converted into *tert.*-butylnaphthalic anhydride and this was decarboxylated to 2-*tert.*-butylnaphthalene either by distillation with soda–lime at ordinary or reduced pressure, or by mercuration and decomposition, followed by treatment with copper-bronze in boiling quinoline. The 2-*tert.*-butylnaphthalene was shown to be identical with that synthesised unambiguously by Bromby, Peters, and Rowe (*J.*, 1943, 144). This result indicated that the starting material had been 2(or 1)-*tert.*-butylacenaphthene. However, Tsukervanik and Terentieva (*J. Gen. Chem. Russ.*, 1937, **7**, 637) stated that 1-alkylnaphthalenes isomerise on heating to 2-alkylnaphthalenes and their statement received some support from Mayer and Schiffner (*Ber.*, 1934, **67**, 67) and from Cullinane and Chard (*Nature*, 1948, **161**, 690), although these workers employed temperatures above 400° and catalysts. The reaction might therefore be explained by 3-*tert.*-butylacenaphthene yielding 1-*tert.*-butylnaphthalene, which subsequently isomerised. No support could be found for this course of the degradation, for even when carried out under reduced pressure the reaction gave 2-*tert.*-butylnaphthalene only.

In spite of the negative results previously recorded, it was again attempted to oxidise *tert.*-butylnaphthalic anhydride, and benzene-1 : 2 : 3 : 5-tetracarboxylic acid was obtained by means of nitric acid under pressure. It was thus proved conclusively that the butylation of acenaphthene had yielded 2-*tert.*-butylacenaphthene. No rearrangement had therefore occurred in the degradation of this hydrocarbon to 2-*tert.*-butylnaphthalene.

The butylation of acenaphthene therefore presents the first example of direct 2-substitution therein. The abnormal orientation of the product is in agreement with the abnormal orientation frequently observed in the products of Friedel–Crafts alkylations in the benzene series (*e.g.*, Ador and Rilliet, *Ber.*, 1878, **11**, 1627; Kelbe, *Annalen*, 1881, **210**, 1; Pajeau, *Bull. Soc. chim.*, 1945, **12**, 637; Essner and Gossin, *ibid.*, 1884, **42**, 213; Fournier, *ibid.*, 1892, **7**, 651; Heise and Töhl, *Annalen*, 1892, **270**, 155). Moreover, naphthalene is generally attacked in

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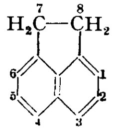
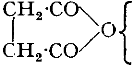
* Richter's numbering of the acenaphthene system is used in this paper. The orientation of many of these compounds amends that in Parts I and II.



the β-position in Friedel–Crafts alkylations (*e.g.*, Roux, *Bull. Soc. chim.*, 1884, **41**, 379; *Ann. Chim. Phys.*, 1887, **12**, 289).

Reagent.	Position of substitution.
HNO_3 + AcOH	3 [1,2]
Ph·CO·NO_3 or NO(OH)$(OAc)_2$	1, 3 (*ca.* 0·03% in 2) [3]
Cl_2	3 [4–7]
SO_2Cl_2	3 [7]
Br_2	3 [1,5]
I_2 and HgO	5 [5,6]
H_2SO_4 or Cl·SO_3H at 0°	3 [8,9]
H_2SO_4 at 100°	1 [8]
AcCl + $AlCl_3$	3, 1 (little) [1,10]
HOAc + HF	1 (up to 84%), 3 [10,11]
CH_2Cl·COCl + $AlCl_3$	3, 1 [12,13]
CH_2Br·COBr + $AlCl_3$	3 [14]
$CH_2(CN)$·COCl + $AlCl_3$	3 [15]
Et·COCl + $AlCl_3$	3, 1(?) [16,14]
CH_3·CH:CH·COCl + $AlCl_3$	3 [10]
 +$AlCl_3$	3 (78%), 1 (15%) [17]
+HF	1, 3 [10]
Maleic anhydride + $AlCl_3$	3 [17]
Ph·COCl + $AlCl_3$	3 [1]
CH_2Ph·COCl + $AlCl_3$	3 [18,19]
CH_2Ph·CO_2H + HF	3, 1 [19]
$C_6H_4(CO)_2O$ + $AlCl_3$	3 [1,20]
NH_2·COCl + $AlCl_3$	3 [21,12]
$(COCl)_2$	3 [22]
Phenylethyluronium chloride + $AlCl_3$	3 [23]
CNBr + $AlCl_3$	3 [24,25]
CH_2O + P_2O_5	3 [26]
$COCl_2$ + $AlCl_3$	3 [26]
HCN or H·C(NH)·N:CHCl + $AlCl_3$	3 [27,28]
H·CONMePh + $POCl_3$	3 [28]
EtBr + $AlCl_3$	3(?) [29]
CH_2PhCl + $ZnCl_2$, etc.	3, 2(?) [30–32]
PbO_2 + HOAc	7 [33]
$Pb(OAc)_4$ + HOAc at 60—70°	7 [34–37]
Cl_2 or Br_2 in sunlight	7 [38]

References.—[1] Graebe, *Annalen*, 1903, **327**, 77. [2] Rowe and Davies, *J.*, 1920, **117**, 1344. [3] Morgan and Harrison, *J. Soc. Chem. Ind.*, 1930, **49**, 413T. [4] Crompton and Cyriax, *Proc.*, 1908, **24**, 241. [5] Sachs and Mosebach, *Ber.*, 1910, **43**, 2473. [6] Crompton and Walker, *J.*, 1912, **101**, 958. [7] Dziewonski and Zakrzewska-Baranowska, *Bull. Acad. Polonaise*, 1927, *A*, 65. [8] Dziewonski and Kocwa, *ibid.*, 1926, *A*, 209; see also *ibid.*, 1927, *A*, 65; 1928, *A*, 405, 507. [9] Bogert and Conklin, *Coll. Czech. Chem. Comm.*, 1933, **5**, 187. [10] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272. [11] Mowry, Renoll, and Huber, *ibid.*, 1946, **68**, 1105. [12] G.P. 479,916; Friedlaender, **16**, i, 516. [13] Lyashchenko, Sokolova, and Zelinskii, *J. Gen. Chem. Russ.*, 1941, **11**, 1001. [14] Nightingale, Ungnade, and French, *J. Amer. Chem. Soc.*, 1945, **67**, 1262. [15] G.P., 536,652, 544,886, 547,643, 556,659; Friedlaender, **18**, i, 612, 619, 620; **19**, ii, 2179, respectively. [16] Dziewonski and Moszew, *Bull. Acad. Polonaise*, 1931, *A*, 158. [17] Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4347. [18] Päpcke, *Ber.*, 1888, **21**, 1331. [19] Fieser and Kilmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1354. [20] Peters and Rowe, *J. Soc. Dyers Col.*, 1943, **59**, 52. [21] Gattermann, *Annalen*, 1888, **244**, 29. [22] Liebermann and Zsuffa, *Ber.*, 1911, **44**, 202. [23] U.S.P. 2,072,237. [24] Karrer, Rebman, and Zeller, *Helv. Chim. Acta*, 1920, **3**, 261. [25] Grignard, Bellet, and Courtot, *Ann. Chim.*, 1915, **4**, 28. [26] Dziewonski, Kahl, Koczorowska, and Wulffsohn, *Bull. Acad. Polonaise*, 1933, *A*, 194. [27] Hinkel, Ayling, and Beynon, *J.*, 1936, 339. [28] Fieser and Jones, *J. Amer. Chem. Soc.*, 1942, **64**, 1666. [29] Mayer and Kaufmann, *Ber.*, 1920, **53**, 289. [30] Dziewonski and Rychlik, *Ber.*, 1925, **58**, 2239; Dziewonski and Leonhard, *Bull. Acad. Polonaise*, 1928, *A*, 99. [31] Lal, *J. Indian Chem. Soc.*, 1935, **12**, 616. [32] Sharma and Dutt, *ibid.*, p. 774. [33] Marquis, *Compt. rend.*, 1926, **182**, 1227. [34] Monti, *Gazzetta*, 1938, **68**, 608. [35] Fieser and Cason, *J. Amer. Chem. Soc.*, 1940, **62**, 432. [36] Brown and Yee, *ibid.*, 1945, **67**, 874. [37] Fieser and Putnam, *ibid.*, 1947, **69**, 1041. [38] Jones, *J. Soc. Chem. Ind.*, 1949, **68**, 225.

1-*tert.*-Butylacenaphthene, a liquid, b. p. 155—160°/0·8 mm., was synthesised by Buu-Hoï and Cagniant (*Rev. sci.*, 1942, **80**, 176) and was therefore quite different from the hydrocarbon under discussion.

*Orientation of Di-*tert.*-butylacenaphthene.*—By analogy with the other reactions of acenaphthene and of monosubstituted acenaphthenes, it had been assumed that the di-*tert.*-butylacenaphthene formed in the butylation of acenaphthene had the 3 : 4-structure. However, di-*tert.*-butylacenaphthene was easily oxidised by sodium dichromate in boiling acetic acid to di-*tert.*-butylnaphthalic anhydride, which by means of nitric acid under pressure was converted into benzene-1 : 2 : 3 : 5-tetracarboxylic acid. Here, as in the case of the *tert.*-butylnaphthalic anhydride, relatively high concentrations of nitric acid could be used in the oxidation, as the carbonyl groups deactivated the nucleus sufficiently to prevent nitration. The formation of benzene-1 : 2 : 3 : 5-tetracarboxylic acid proved that at least one *tert.*-butyl group of di-*tert.*-butylacenaphthene is *meta* to the acenaphthene bridge and that one such group is in each ring of the naphthalene nucleus.

Mercuration and decomposition of di-*tert.*-butylnaphthalic acid produced only one *di-*tert.*-butylnaphthoic acid*, whereas mercuration and decomposition of *tert.*-butylnaphthalic acid had produced a difficultly separable mixture of two *tert.-butylnaphthoic acids*. It was concluded that the di-*tert.*-butylacenaphthene molecule must be symmetrical, and must consequently be 2 : 5-di-*tert.*-butylacenaphthene.

This structure explained the observed *ace*-substitution in the dinitration and the postulated *ace*-substitution in dichlorination and dibromination of the hydrocarbon (see below and in Part II, Peters, *J.*, 1947, 742). The first substituent would enter the 3-position, but as the 4-position is blocked by such bulky groups in the 2-, 3-, and 5-positions, the second substituent would be forced to attack the acenaphthene bridge. *ace*-Substitution cannot be explained by the previously accepted 3 : 4-structure.

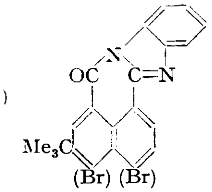
Derivatives of 2-tert.-*Butylacenaphthene and* 2 : 5-*Di*-tert.-*butylacenaphthene.*—Several new derivatives of 2-*tert.*-butylacenaphthene were prepared. From the facts that two *mononitro*-2-tert.-*butylacenaphthenes* were isolated and that *bromo*-2-tert.-*butylacenaphthene* was only obtained in an impure condition even after repeated crystallisation, it can be deduced that in the 2-*tert.*-butylacenaphthene molecule two positions are approximately equally reactive. These are probably the 3 : 4-positions. If, as was done in the case of bromination, the reaction is carried to the di-substituted stage, one product only is obtained in a satisfactory yield and almost immediately in a pure state.

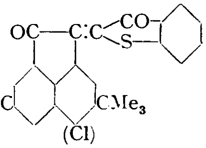
The reaction of *dibromo*-3-tert.-*butylnaphthalic anhydride* with methylamine was of interest, for not only was the compound converted into its *N*-methylimide, but, also, even under mild conditions, one of the bromine atoms was replaced by a methylamino-group. Under similar conditions, ammonia only gave the *imide* and left the bromine atoms unaffected. *o*-Phenylenediamine yielded the yellow *dibromo*-9′-*keto*-2′(or 5′)-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′ : 2 : 1)-*benziminazole* (I).

From the general rules of substitution and from those of acenaphthene substitution, it can be assumed that the 3-position of 2 : 5-di-*tert.*-butylacenaphthene is the most reactive. The nomenclature of the many derivatives recorded in Part II must therefore be amended accordingly, the *tert.*-butyl groups being at positions 2 and 5, and the nitro- or bromo-group at 3.

Some further derivatives have now been prepared. Although 2 : 5-di-*tert.*-butylacenaphthene would not react with chlorine in chloroform solution, reaction proceeded smoothly in carbon tetrachloride. 3-*Chloro*-2 : 5-*di*-tert.-*butylacenaphthene* was also prepared, but less satisfactorily, by means of sulphuryl chloride in chloroform solution. The chloro-compound was oxidised, and in addition to the naphthalic anhydride derivative, some quinone was formed, as shown by its ability to condense with 3-hydroxythionaphthen to give the red 3′(or 4′)-*chloro*-2′ : 5′-*di*-tert.-*butyl*-2 : 7′-*thionaphthenacenaphthenylindigo* (II). The 4-*chloro*-3 : 6-*di*-tert.-*butylnaphthalic anhydride* yielded *imides* and also the canary-yellow 3′(or 4′)-*chloro*-9′-*keto*-2′ : 5′-*di*-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′-2 : 1)*benziminazole.*

(I.)





(II.)

The hydrocarbon reacted with 2 mols. of chlorine to give a *dichloro*-2 : 5-*di*-tert.-*butylacenaphthene.* As this compound lost much of its chlorine content upon oxidation, it can be assumed that the second chlorine atom had entered one of the *ace*-positions (cf. dinitro-2 : 5-di-*tert.*-butylacenaphthene; Part II).

2 : 7-*Di*-tert.-*butylnaphthalene.*—Two di-*tert.*-butylnaphthalenes have often been isolated; Gump (*J. Amer. Chem. Soc.*, 1931, **53**, 380) first recognised them as such, but Wegscheider (*Monatsh.*, 1884, **5**, 236) was the first to prepare them. One, m. p. 146—147°, will not form a picrate; the other (recorded m. p.s varying between 80° and 95°) gives a picrate, m. p 157—158°. Tsukervanik and Terentieva (*loc. cit.*) are alone in recording m. p. 132°, picrate, m. p. 99°, for a di-*tert.*-butylnaphthalene.

Contractor, Peters, and Rowe (*J.*, 1949, 1993) obtained the above two hydrocarbons by the action of *tert.*-butyl chloride and aluminium chloride on 2-*tert.*-butylnaphthalene, which had been orientated by Bromby *et al.* (*loc. cit.*), thus showing that one *tert.*-butyl group in each of these hydrocarbons must be in a β-position. They also oxidised the lower-melting isomer by means of potassium permanganate to an acid, the composition of which corresponded to that of a mono-*tert.*-butylphthalonic acid. They therefore concluded that the lower-melting isomer contained the *tert.*-butyl groups in different rings.

Price, Shafer, Huber, and Bernstein (*J. Org. Chem.*, 1942, **7**, 517) decomposed the picrate, m. p. 156—156·5°, to obtain a hydrocarbon, m. p. 80—82°, raised by repeated recrystallisation to 103—104°. A mixture consisting of 2 parts of this recrystallised product, m. p. 103—104°, and 1 part of the di-*tert.*-butylnaphthalene, m. p. 145—146°, melted at 80—82° and was identical with the hydrocarbon, m. p. 80—82°, obtained by decomposition of the picrate, m. p. 156—156·5°. The picrate was thus composed of 2 mols. of di-*tert.*-butylnaphthalene, m. p. 103—104°, 1 mol. of di-*tert.*-butylnaphthalene, m. p. 145—146°, and 2 mols. of picric acid, which constitution was supported by the analyses obtained.

In the present research, a specimen of the picrate, m. p. 157—158°, was analysed, and its constitution agreed with that given by the above authors. It was decomposed, and the hydrocarbon obtained was repeatedly crystallised from alcohol to give colourless, silky needles, m. p. 102—103°. These needles were converted into a *picrate*, an egg-yolk-coloured powder, m. p. 145—146°, not previously prepared. This picrate was dissolved in dry alcohol and the required amount of the di-*tert.*-butylnaphthalene, m. p. 145—146°, dissolved in the same solvent, was added. The mixture was boiled and, on cooling, the orange needles of the picrate, m. p. 157—158°, separated. They gave analyses agreeing with the formula given by Price *et al.* and they showed no depression of m. p. on admixture of the starting material.

Decarboxylation of 3 : 6-di-*tert.*-butylnaphthalic anhydride by soda–lime distillation, by copper-bronze in boiling quinoline, or by mercuration and decomposition, followed by copper-bronze in boiling quinoline, yielded the di-*tert.*-butylnaphthalene, m. p. 102·5—103·5° (picrate, m. p. 145—145·5°). This hydrocarbon is therefore 2 : 7-*di-*tert.*-butylnaphthalene*, which formula satisfies the requirements laid down by Contractor *et al.*

The research is being extended to show whether other Friedel–Crafts alkylations of acenaphthene yield 2-substituted derivatives, whether alkylating agents other than alkyl halide and aluminium chloride yield differently orientated products, and what action aluminium chloride has on alkylacenaphthenes.

EXPERIMENTAL.

(M.p.s are corrected. Micro-analyses were carried out by Drs. Weiler and Strauss, Oxford.)

2-tert.-*Butylacenaphthene*.—A mixture of acenaphthene (308 g., 1 mol.), carbon disulphide (750 c.c.), and aluminium chloride (54 g., 0·2 mol.) was stirred at room temperature and *tert.*-butyl chloride (218 c.c., 1 mol.) was added dropwise during one hour. Stirring was continued at room temperature for 3 hours, and the whole then heated under reflux for 2 hours. After standing overnight, the carbon disulphide solution was poured off and there remained a mixture of granular and tarry complex, which consisted mainly of di-*tert.*-butylacenaphthene and aluminium chloride. The carbon disulphide solution was filtered through charcoal, solvent removed, and the residue distilled at 765 mm. (269 g., 64%). The fractions, b. p. 290—335°, were redistilled at 7 mm., and the part, b. p. 160—174° (66 g., 16%), collected. This was recrystallised twice from acetic acid and then from methyl alcohol, giving colourless plates, m. p. 88—88·5° (Found : C, 91·35; H, 8·6. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%) (Part I : m. p. 73—74° for supposed 3-isomers). The distillation under reduced pressure proved difficult but was indispensable, because fractional distillation at ordinary pressure and fractional crystallisation from a variety of solvents (ethyl alcohol, methyl alcohol, 2-ethoxyethanol, and acetic acid) failed to separate the *tert.*-butylacenaphthene from acenaphthene and di-*tert.*-butylacenaphthene. The difficulty was that the distillates solidified very readily and that the substances involved sublimed easily; the apparatus therefore often became obstructed, yet any rise in pressure caused by such a blockage upset the separation, which can only be controlled by the temperature of distillation.

The above experiment was the best of the many carried out under various conditions. Nitrobenzene, used instead of carbon disulphide, proved unsuccessful as a solvent. On redistillation, the *tert.*-butylacenaphthene distilled at 130—140°/1 mm.

The *picrate* separated in clusters of orange, microcrystalline needles, m. p. 121—123° (Found : C, 60·4; H, 4·8; N, 10·0. $C_{16}H_{18},C_6H_3O_7N_3$ requires C, 60·1; H, 4·8; N, 9·6%). A styphnate could not be prepared.

The 1 : 3 : 5-*trinitrobenzene* complex was obtained as a yellow, microcrystalline powder, m. p. 149—150°, softening at 145° (Found : N, 10·3. $C_{16}H_{18},C_6H_3O_6N_3$ requires N, 9·9%).

Reaction between 3-Bromoacenaphthene and tert.*-Butyl Chloride,* tert.*-Butyl Bromide, or* n*-Butyl Bromide in Presence of Sodium.*—To a solution of 3-bromoacenaphthene (10 g.) and *tert.*-butyl chloride (6 c.c., 1·25 mols.) in sodium-dried ether (50 c.c.) was added finely-divided sodium (1·5 g., 1·5 mols.), and the whole was heated under reflux for 3 hours. From the products, only 3-bromoacenaphthene could be isolated. A similar experiment with *tert.*-butyl bromide also afforded only unchanged bromoacenaphthene.

n-Butyl bromide and 3-bromoacenaphthene reacted spontaneously under conditions similar to the above, and after 2 hours' refluxing only acenaphthene, m. p. and mixed m. p. 93—94°, was isolated (cf. reaction between 3-bromoacenaphthene and *n*-butylmagnesium bromide; Kharasch, Sayles, and Fields, *J. Amer. Chem. Soc.*, 1944, **66**, 481).

3-tert.-*Butylnaphthalic Anhydride.*—This was prepared by oxidation of 2-*tert.*-butylacenaphthene essentially as described in Part I, but on about a double scale; it had m. p. 203—204° (yield 56%), raised by recrystallisation from acetic acid to 204—205°, depressed to below 180° on admixture with 3 : 6-di-*tert.*-butylnaphthalic anhydride, m. p. 211—212°. In Part II, m. p. 201—202° was recorded for the supposed 4-isomer.

N-(2-*Hydroxyethyl*)-3-tert.-*butylnaphthalimide.*—To a solution of 3-*tert.*-butylnaphthalic anhydride in boiling alcohol was added an excess of aqueous ethanolamine. The solution was kept at the boil for

15 minutes and then allowed to cool. Colourless, silky needles separated and were recrystallised from absolute alcohol; m. p. 167—168° (Found : C, 72·7; H, 6·4; N, 4·6. $C_{18}H_{19}O_3N$ requires C, 72·7; H, 6·4; N, 4·7%).

Oxidation of 3-tert.-*Butylnaphthalic anhydride*.—(*a*) *With potassium permanganate.* Potassium permanganate (10 g.) was added to a solution of 3-*tert.*-butylnaphthalic anhydride (2 g.) in boiling 2·5% aqueous sodium hydroxide (100 c.c.), and the whole left on a steam-bath for 3 days; it was then almost decolorised. A little alcohol was added to destroy any excess of permanganate and the manganese dioxide was filtered off. The filtrate was acidified and extracted with ether. The ether was removed from the extract and the residue was stirred with ligroin; a solid separated which was extracted with ligroin–chloroform and left a white powder, m. p. 207—208° (decomp.; shrinking from 200°) (Found : C, 56·0; H, 4·6. $C_{14}H_{14}O_7$ requires C, 57·15; H, 4·8%). It was impossible to crystallise this acid. Its *trimethyl* ester, prepared by means of diazomethane, after repeated crystallisation from aqueous methyl alcohol, formed beautiful, colourless needles, m. p. 127—129° (Found : C, 60·45, 60·6; H, 6·1, 5·8. $C_{17}H_{20}O_7$ requires C, 60·7; H, 6·0%). The acid is therefore probably 4-tert.-*butyl*-2 : 6-*dicarboxybenzoylformic acid* [cf. Graebe and Bossel, *Annalen*, 1896, **290**, 206; Randall, Benger, and Groocock, *Proc. Roy. Soc.*, 1938, *A*, **165**, 432, who obtained 2 : 6-dicarboxybenzoylformic acid by alkaline permanganate oxidation of naphthalic anhydride and of acenaphthene, acenaphthenequinone, and 3-(*o*-carboxybenzoyl)acenaphthene, respectively].

(*b*) *With nitric acid.* 3-*tert.*-Butylnaphthalic anhydride (0·5 g.), concentrated nitric acid (3 c.c.), and water (2 c.c.) were heated in a sealed tube to 200—220° for 24 hours. The solution was evaporated until solid began to separate and then allowed to cool. The solid was collected, and dried at 100° and then *in vacuo* over phosphoric oxide and sodium hydroxide, to give a white powder, m. p. 249—255° (decomp.), and at 240° as the anhydride (Found : C, 46·3, 46·2; H, 2·2, 2·3. Calc. for $C_{10}H_6O_8$: C, 47·25; H, 2·4%). An aqueous solution of the acid gave, on standing, a white precipitate with barium chloride solution, a reaction not given by benzene-1 : 2 : 3 : 4-tetracarboxylic acid.

The acid (0·25 g.) was covered with ether (10 c.c.), and diazomethane solution (from nitrosomethylurethane, 3 c.c.) was added. Vigorous frothing occurred and after 30 minutes the solid was filtered off; it was an almost colourless nitrogen-containing powder, which shrank a little below 300°, but on further heating it turned yellow and eventually gave off a gas and charred with a little explosion. The filtrate was evaporated to dryness, and the solid crystallised three times from methyl alcohol to give colourless needles, m. p. 106—107°, depressed to 90—93° on admixture of tetramethyl benzene-1 : 2 : 3 : 4-tetracarboxylate (Found : C, 52·9, 53·0; H, 4·5, 4·3. Calc. for $C_{14}H_{14}O_8$: C, 54·2; H, 4·5%).

The product of oxidation with nitric acid was therefore mainly benzene-1 : 2 : 3 : 5-tetracarboxylic acid (cf. Bamford and Simonsen, *J.*, 1910, **97**, 1904; Smith and Byrkit, *J. Amer. Chem. Soc.*, 1933, **55**, 4305). The impurities are probably due to products arising from attack on the nucleus carrying the *tert.*-butyl group.

tert.-*Butyl*-1-*naphthoic Acids* (cf. method of mercuration : Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, 1929, **51**, 1835; Davies, Heilbron, and Irving, *J.*, 1932, 2715).—Finely-ground 3-*tert.*-butylnaphthalic anhydride (10 g.) was dissolved in water (500 c.c.) containing sodium hydroxide (6·3 g., 4 mols.) by refluxing for some time, a large flask (2 l.) being used in order to avoid frothing over in the later stage. A boiling solution of mercuric oxide (8·6 g., 1 mol.) in a mixture of acetic acid (13 c.c.) and water (37 c.c.) was added, and the slightly red mixture, which was acid to litmus, was refluxed for 98 hours, during which the precipitate became a pure white. It was filtered off, washed, and refluxed with concentrated hydrochloric acid (100 c.c.) and water (200 c.c.) for 2 hours. A lump of solid was formed and this was dissolved in much alcohol. The solution was filtered from a finely-divided white solid, which was insoluble in sodium hydroxide solution and did not melt below 300°. The alcoholic solution was filtered (charcoal) and evaporated to approximately 50 c.c. It was allowed to cool and the precipitate collected. The tert.-*butyl*-1-*naphthoic acid* (1·5 g.) crystallised from alcohol in colourless, irregular crystals, m. p. 167—169° (with previous sintering), unaltered by recrystallisation (Found : C, 79·4; H, 7·2. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0%).

The residues were evaporated to dryness, yielding a cream-coloured powder, m. p. 110—150° (4·4 g.), which had a distinct odour of 2-*tert.*-butylnaphthalene. Fractional crystallisation from aqueous methyl alcohol, with rejection of the least soluble portions, gave some colourless plates and rods, m. p. 124—127°, of an isomeric tert.-*butyl*-1-*naphthoic acid* (Found : C, 78·9; H, 7·1%).

2-tert.-*Butylnaphthalene*.—(*a*) *From* tert.-*butylnaphthalic anhydride.* 3-*tert.*-Butylnaphthalic anhydride (5 g.) was distilled with soda-lime, giving a small yield of a colourless oil, b. p. 270° (uncorr.), which was converted into a picrate, m. p. 98—99°, not depressed on admixture of authentic 2-*tert.*-butylnaphthalene picrate (Found : C, 57·65; H, 4·7; N, 10·0. Calc. for $C_{14}H_{16},C_6H_3O_7N_3$: C, 58·1; H, 4·6; N, 10·2%). When the experiment was repeated under reduced pressure (*ca.* 20 mm.), a mixture of unchanged anhydride and an oil was obtained. The latter, b. p. 275°, gave 2-*tert.*-butylnaphthalene picrate, m. p. and mixed m. p. 98—99°.

(*b*) *From the* tert.-*butyl*-1-*naphthoic acids.* The crude acids (7 g.) (see above) were boiled with quinoline (20 c.c.) and copper-bronze (2·5 g.) (Sheppard, Winslow, and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2083) and the mixture was distilled with steam after acidification with hydrochloric acid. Ether extraction of the distillate and evaporation of the ether gave a colourless oil (2 g., 39%). The picrate, m. p. 99—100°, prepared from it, showed no depression of m. p. on admixture with authentic 2-*tert.*-butylnaphthalene picrate (Found : C, 58·2; H, 4·6; N, 10·2%).

Bromo-2-tert.-*butylacenaphthene*.—To a solution of 2-*tert.*-butylacenaphthene (5 g.) in cold carbon tetrachloride (50 c.c.) was added slowly and with shaking a solution of bromine (1·3 c.c., 1·1 mols.) in the same solvent (50 c.c.). The mixture was kept with occasional shaking for 1 hour, much hydrogen bromide being evolved. The carbon tetrachloride was gradually replaced by absolute alcohol, and the solution allowed to cool. Tars were obtained and these were crystallised to give three fractions, each of which gave, on repeated crystallisation from alcohol, colourless needles, m. p. 145° (Found : C, 68·2; H, 6·75; Br, 26·05. $C_{16}H_{17}Br$ requires C, 66·4; H, 5·9; Br, 27·7%). The *bromo*-2-tert.-*butylacenaphthene* obtained was therefore impure.

Dibromo-2-tert.-*butylacenaphthene*.—Bromine (1·9 c.c., 2 mols.), dissolved in chloroform (40 c.c.), was added slowly and with shaking to a solution of 2-*tert*.-butylacenaphthene (4 g.) in the same solvent (50 c.c.). The mixture was kept with occasional shaking for 3 hours and then a portion of the chloroform was replaced by absolute alcohol. On cooling, *dibromo*-2-tert.-*butylacenaphthene* (4·2 g., 60%) was deposited and recrystallised from absolute alcohol–chloroform in colourless pillars, m. p. 185—185·5° (Found : C, 52·6; H, 4·5; Br, 43·5. $C_{16}H_{16}Br_2$ requires C, 52·2; H, 4·35; Br, 43·5%). It did not form a picrate in alcoholic solution.

Dibromo-3-tert.-*butylnaphthalic Anhydride*.—To a solution of dibromo-2-*tert*.-butylacenaphthene (2 g.) in boiling acetic acid (100 c.c.), sodium dichromate (8 g.) was added gradually and the solution was heated under reflux for 4 hours, then poured into water; after standing, the colourless precipitate was filtered off and extracted with boiling 5% aqueous sodium carbonate. The extract was acidified, and the resulting solid crystallised from acetic acid containing a little acetic anhydride in colourless, silky needles and plates, m. p. 218—219° (Found : C, 46·95; H, 2·9; Br, 39·5. $C_{16}H_{12}O_3Br_2$ requires C, 46·6; H, 2·9; Br, 38·8%), both forms separating simultaneously; this phenomenon was also noticed with 3 : 6-di-*tert*.-butylnaphthalic anhydride.

Derivatives of Dibromo-3-tert.-*butylnaphthalic Anhydride*.—On being heated under reflux with excess of aqueous ammonia (*d* 0·88), an alcoholic solution of the anhydride gave *dibromo*-3-tert.-*butylnaphthalimide*, which crystallised from absolute alcohol in very pale yellow plates, m. p. 294—295° (Found : N, 3·4; Br, 38·3. $C_{16}H_{13}O_2NBr_2$ requires N, 3·4; Br, 38·9%). On using 33% aqueous methylamine instead of ammonia in a similar reaction, there were obtaind lemon-coloured needles, m. p. 301—302° (Found : N, 6·35; Br, 22·2. $C_{18}H_{19}O_2N_2Br$ requires N, 7·5; Br, 21·3%. $C_{17}H_{15}O_2NBr_2$ requires N, 3·3; Br, 37·6%). In the reaction with methylamine, therefore, not only was the *N*-methylimide formed, but one bromine atom had been replaced to a large extent by a methylamino-group. The anhydride (0·5 g.) and *o*-phenylenediamine (0·15 g.), refluxed in acetic acid for 15 minutes, afforded *dibromo*-9′-*keto*-2′(or 5′)-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′-2 : 1)*benziminazole*, which crystallised from acetic acid in yellow needles, m. p. 250—251° (Found: N, 5·7; Br, 33·4. $C_{22}H_{16}ON_2Br_2$ requires N, 5·8; Br, 33·1%).

Nitro-2-tert.-*butylacenaphthenes*.—To a cold solution of 2-*tert*.-butylacenaphthene (5 g.) in acetic acid (200 c.c.) was added nitric acid (1·65 c.c., 1·1 mols.) dissolved in acetic acid (50 c.c.); the solution, which turned yellow, was kept for 1 hour, then evaporated to small bulk. On cooling, a yellow semi-crystalline precipitate separated and this was crystallised three times from absolute alcohol, yielding yellow plates, m. p. 158—159° (0·4 g.) (Found : C, 75·1; H, 6·5; N, 5·7. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%). From the mother-liquor was obtained by repeated crystallisation from alcohol a very small quantity of yellow needles, m. p. 208—210°, with previous softening (Found : N, 5·9%). Two isomeric *nitro*-2-tert.-*butylacenaphthenes* were therefore formed in the nitration of the hydrocarbon.

Nitro-3-tert.-*butylnaphthalic Anhydride*.—Oxidation of the nitro-2-*tert*.-butylacenaphthene, m. p. 158—159° (0·4 g.), with sodium dichromate (2 g.) in boiling acetic acid (30 c.c.) for 3 hours yielded, by the usual procedure, some yellow crystalline masses and plates, m. p. 194—195°, of *nitro*-3-tert.-*butylnaphthalic anhydride* (Found : C, 64·6; H, 4·6; N, 4·6. $C_{16}H_{13}O_5N$ requires C, 64·2; H, 4·35; N, 4·7%).

2 : 5-*Di*-tert.-*butylacenaphthene* (cf. Part I).—This was prepared essentially as described formerly for the supposed 3 : 4-isomer, but on a four-fold scale; it formed colourless needles, m. p. 162·5—163·5° (Part I, 162—163°). There remained in the flask a fluorescent, orange tar, which on cooling set to a glass, b. p. *ca*. 220°/0·5 mm. (Found : H, 8·3. Calc. for $C_{24}H_{34}$: H, 10·6%). This analysis does not support Buu-Hoï and Cagniant's suggestion (*loc. cit.*) that this consisted of tri-*tert*.-butylacenaphthene. The glass may be of the nature of the yellow-green, fluorescent oil obtained by Niggemann (*Chem. Zentr.*, 1919, II, 584) by boiling acenaphthene with aluminium chloride.

The picrate had m. p. 165—165·5° (Part I, 164°). The 1 : 3 : 5-trinitrobenzene complex was obtained in orange rosettes of needles, m. p. 205—206°, from absolute alcohol (Found: N, 8·75. Calc. for $C_{20}H_{26},C_6H_3O_6N_3$: N, 8·8%).

3 : 6-*Di*-tert.-*butylnaphthalic anhydride* (cf. Part I).—The hydrocarbon was oxidised as before to this anhydride; m. p. 211—212° (211° in Part I for supposed 4 : 5-isomer).

N-(2-*Hydroxyethyl*)-3 : 6-*di*-tert.-*butylnaphthalimide*.—To a solution of the anhydride (1 g.) in boiling alcohol (60 c.c.) was added an excess of aqueous ethanolamine and the whole was heated on the steam-bath for 10 minutes. The *naphthalimide*, which separated on cooling, crystallised from alcohol in silky, colourless needles (0·8 g.), m. p. 248° (Found : C, 75·0; H, 7·6; N, 4·4. $C_{22}H_{27}O_3N$ requires C, 74·8; H, 7·65; N, 4·0%).

Nitric Acid Oxidation of 3 : 6-*Di*-tert.-*butylnaphthalic Anhydride*.—A mixture of the anhydride (0·75 g.), water (2 c.c.), and concentrated nitric acid (4 c.c.) was heated in a sealed tube at 160—180° for 24 hours. Two such experiments yielded a few insoluble pale yellow plates, m. p. up to 170°, which were filtered off. The filtrate was evaporated to dryness, yielding a white powder, which under the microscope appeared as masses of tiny crystals. These melted at 252—254°, shrinking a little before this temperature was reached and giving an opaque liquid which decomposed at 256—257°. On cooling, the liquid solidified immediately and on reheating was clear again by 237°. The powder was extremely soluble in water and an aqueous solution gave, on standing, a white, microcrystalline precipitate with barium chloride solution. The powder was benzene-1 : 2 : 3 : 5-tetracarboxylic acid (Found : C, 47·0; H, 2·4. Calc. for $C_{10}H_6O_8$: C, 47·2; H, 2·4%). The tetramethyl ester was prepared by means of diazomethane in ethereal solution and, after crystallising twice from methyl alcohol, formed rosettes of colourless plates, m. p. 109—110° (Found : C, 53·95; H, 4·3. Calc. for $C_{14}H_{14}O_8$: C, 54·2; H, 4·5%).

In another experiment under the same conditions but with 1·0 g. of anhydride, the solution was not evaporated to dryness, but was allowed to crystallise when it had been reduced to small bulk. Rosettes of needles were obtained and these, crystallised from water, softened at 180°, and melted at 195—198° (Found : C, 54·6; H, 5·6. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%); when dissolved in water they gave an immediate precipitate with barium chloride solution. The analysis approximated to that of a tert.-*butylbenzenetricarboxylic acid*. It can be concluded with certainty that the naphthalene ring had been oxidised before the butyl group was attacked.

3-*Chloro*-2 : 5-*di*-tert.-*butylacenaphthene*.—To a cold solution of 2 : 5-di-*tert*.-butylacenaphthene (10 g.) in carbon tetrachloride (50 c.c.) was slowly added with frequent shaking during 30 minutes a solution of chlorine (3 g., 1·1 mols.) in the same solvent (50 c.c.); the solution was then kept with occasional shaking for 1 hour. Most, but not all, of the carbon tetrachloride was then evaporated off, and the remainder gradually replaced by absolute alcohol. On cooling, slightly yellow needles (7·8 g., 69%), m. p. 118—119°, separated. By repeated crystallisation from absolute alcohol, 3-*chloro*-2 : 5-*di*-tert.-*butylacenaphthene* was obtained as colourless rods, m. p. 124—125° (Found : C, 80·2; H, 8·4; Cl, 12·2. $C_{20}H_{25}Cl$ requires C, 79·9; H, 8·4; Cl, 11·8%). In chloroform solution, or in hot acetic acid, there was no reaction between chlorine and the hydrocarbon.

Alternatively, sulphuryl chloride (3·1 c.c., 1 mol.) was added to a solution of 2 : 5-di-*tert*.-butylacenaphthene (10 g.) in chloroform (50 c.c.); after reaction had subsided, the mixture was heated under reflux for 2 hours, then poured into absolute alcohol, and the whole partly concentrated, then cooled. Impure 3-chloro-2 : 5-di-*tert*.-butylacenaphthene (7 g., 62%) crystallised out in yellow rods, m. p. 118—119°. This product was not as pure as that obtained above; from the most insoluble portion some orange needles, m. p. 299—300° (Found : Cl, 5·4%), were isolated.

3-*Chloro*-2 : 5-*di*-tert.-*butylacenaphthene picrate* was obtained from alcoholic solution as red needles, m. p. 151—152° (Found : N, 7·9; Cl, 7·4. $C_{20}H_{25}Cl,C_6H_3O_7N_3$ requires N, 7·9; Cl, 6·7%).

4-*Chloro*-3 : 6-*di*-tert.-*butylnaphthalic Anhydride*.—3-Chloro-2 : 5-di-*tert*.-butylacenaphthene (3·5 g.) was dissolved in boiling acetic acid (150 c.c.), and sodium dichromate (12 g.) added gradually. The whole was refluxed for 2 hours, poured on ice–water, and filtered off after standing. The pale yellow powder (3·3 g., 82%) thus obtained was crystallised once from acetic acid and once from absolute alcohol, yielding colourless, irregular plates of the *anhydride*, m. p. 170·5—171° (Found : C, 69·8; H, 5·8; Cl, 10·9. $C_{20}H_{21}O_3Cl$ requires C, 69·7; H, 6·1; Cl, 10·3%).

The *naphthalimide* crystallised from absolute alcohol in colourless needles, m. p. 294° (Found : C, 70·3; H, 6·8; N, 4·2; Cl, 9·7. $C_{20}H_{22}O_2NCl$ requires C, 69·9; H, 6·4; N, 4·1; Cl, 10·3%). The N-*methylimide* separated from alcoholic solution in colourless needles, m. p. 265° (Found : N, 4·2. $C_{21}H_{24}O_2NCl$ requires N, 3·9%). 3′(or 4′)-*Chloro*-9′-*keto*-2′ : 5′-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′ : 2 : 1)-*benziminazole* crystallised from acetic acid in canary-yellow rods, m. p. 270—272° (Found : N, 7·2. $C_{26}H_{25}ON_2Cl$ requires N, 6·7%).

3′(or 4′)-*Chloro*-2′ : 5′-*di*-tert.-*butyl*-2 : 7′-*thionaphthenacenaphthenylindigo*.—To a solution of 3-chloro-2 : 5-di-*tert*.-butylacenaphthene (3 g.) in boiling acetic acid (50 c.c.) was added all at once roughly ground sodium dichromate (10 g.), and the mixture was stirred and kept gently boiling for 4 minutes after the reaction had subsided. It was poured on ice–water and filtered. The solid (3 g.) was extracted 6 times with boiling 5% aqueous sodium carbonate (1 l.). Acidification of the combined extracts yielded 4-chloro-3 : 6-di-*tert*.-butylnaphthalic anhydride (1·5 g.). The insoluble, straw-coloured residue, m. p. 135—138° (1·3 g.), was condensed with 2-hydroxythianaphthen by boiling in acetic acid–hydrochloric acid (10 : 1) for 5 minutes to yield a thioindigoid *dye*, which crystallised from acetic acid in bright red needles, m. p. 269—270° (0·4 g.) (Found : Cl, 7·5; S, 7·0. $C_{28}H_{25}O_2ClS$ requires Cl, 7·7; S, 6·95%). This was equivalent to the presence of 0·3 g. of 3-chloro-2 : 5-di-*tert*.-butylacenaphthenequinone, which was thus formed in 9% yield in the above reaction.

3 : 7(or 8)-*Dichloro*-2 : 5-*di*-tert.-*butylacenaphthene*.—2 : 5-Di-*tert*.-butylacenaphthene (5 g.) was dissolved in carbon tetrachloride (50 c.c.) and, during 30 minutes, a solution of chlorine (2·7 g., 2 mols.) in the same solvent (50 c.c.) was added with shaking. The solution was kept for another 30 minutes, and some of the carbon tetrachloride was then evaporated and the remainder gradually replaced by absolute alcohol. On cooling, there separated an oil, which on repeated crystallisation from absolute alcohol yielded colourless needles, m. p. 139—141° (0·5 g., 8%) (Found : C, 71·5; H, 6·9; Cl, 21·1. $C_{20}H_{24}Cl_2$ requires C, 71·6; H, 7·2; Cl, 21·2%).

Oxidation of the *dichloro*-compound with sodium dichromate in acetic acid solution gave a small quantity of solid, which crystallised from aqueous alcohol in small irregular plates, m. p. 170—172°, not depressed on admixture of authentic 4-chloro-3 : 6-di-*tert*.-butylnaphthalic anhydride (Found : C, 68·9; H, 5·7; Cl, 11·8. Calc. for $C_{20}H_{21}O_3Cl$: C, 69·7; H, 6·1; Cl, 10·3%). These results suggested that the second chlorine atom had entered the di-*tert*.-butylacenaphthene molecule in one of the *ace*-positions.

3 : 6-*Di*-tert.-*butyl*-1-*naphthoic Acid*.—Finely-powdered 3 : 6-di-*tert*.-butylnaphthalic anhydride (13 g.) was boiled with a solution of sodium hydroxide (10 g.) in water (500 c.c.) but only partly dissolved. A hot solution of mercuric oxide (9·1 g.) in a mixture of acetic acid (10 c.c.) and water (30 c.c.) was added. A reddish precipitate formed and the whole was heated under reflux for 80 hours in a 2-l. flask. The precipitate gradually became white; it was filtered off; some globules of mercury had formed. The solid was boiled with dilute hydrochloric acid for 2 hours and filtered off. The insoluble material was dissolved in acetic acid, and the solution filtered from a white substance, m. p. >300°, and allowed to cool. 3 : 6-*Di*-tert.-*butyl*-1-*naphthoic acid* (5 g., 42%) separated, and two recrystallisations from acetic acid, in which it is very soluble, gave small clusters of crystals, m. p. 197—198° (Found : C, 80·3; H, 8·4. $C_{19}H_{24}O_2$ requires C, 80·3; H, 8·45%). A second crop (3·7 g., 31%) was obtained and from it crude di-*tert*.-butylnaphthoic acid and crude di-*tert*.-butylnaphthalic anhydride could be isolated.

Derivatives of 3 : 6-*di*-tert.-*butyl*-1-*naphthoic acid*. From absolute alcohol, the *amide* was obtained as colourless, microcrystalline needles, m. p. 212—213° (Found : N, 5·05. $C_{19}H_{25}ON$ requires N, 4·95%), and the p-*toluidide* as colourless, irregular plates, m. p. 221·5—222·5° (Found : N, 3·35. $C_{26}H_{31}ON$ requires N, 3·75%).

2 : 7-*Di*-tert.-*butylnaphthalene*.—*From* 3 : 6-*di*-tert.-*butylnaphthalic anhydride*. Soda–lime distillation of 3 : 6-di-*tert*.-butylnaphthalic anhydride (5 g.) yielded, on crystallisation from aqueous alcohol, colourless needles, m. p. 102—103° (0·5 g.). Refluxing the anhydride (5 g.) with quinoline (10 c.c.) and copper-bronze (2·5 g.) for 50 minutes and steam-distilling the product from an acid solution gave a substance, m. p. 103—104° (0·3 g.). From the residues was recovered crude anhydride (3·8 g.).

From 3 : 6-*di*-tert.-*butyl*-1-*naphthoic acid.* The acid (1 g.) was refluxed in quinoline (2 c.c.) in the presence of copper-bronze (0·5 g.) for 30 minutes and the whole was poured into excess of dilute hydrochloric acid. Distillation with steam yielded a solid, m. p. 102—103° (0·45 g.).

The products of the above experiments were crystallised together from alcohol, giving colourless, silky needles, m. p. 102·5—103·5° (Found: C, 90·1; H, 9·85. $C_{18}H_{24}$ requires C, 90·0; H, 10·0%), of 2 : 7-*di*-tert.-*butylnaphthalene.* The *picrate,* prepared in alcoholic solution, was obtained as yellow, microscopic crystals, m. p. 145—145·5° (Found : C, 61·4; H, 5·8; N, 9·05. $C_{18}H_{24},C_6H_3O_7N_3$ requires C, 61·4; H, 5·8; N. 8·95%).

From naphthalene. The di-*tert.*-butylnaphthalene picrate, m. p. 157—158°, was prepared by the method of Bromby *et al.* (*loc. cit.*) (Found : C, 67·7; H, 6·7; N, 6·6. Calc. for $C_{66}H_{78}O_{14}N_6$: C, 67·2; H, 6·65; N, 7·15%). It was decomposed with 5% aqueous sodium hydroxide and the hydrocarbon, m. p. 82—85°, obtained was repeatedly crystallised from alcohol to give colourless, silky needles, m. p. 102—103°, not depressed on admixture with the 2 : 7-di-*tert.*-butylnaphthalene prepared as above.

To a boiling solution of this compound (0·3 g.) in dry alcohol (1·5 c.c.) was added a solution of picric acid (0·3 g.) in the same solvent (1·5 c.c). The colour deepened to orange and, after a few seconds' boiling, the mixture was allowed to cool. There separated an egg-yolk-coloured compound, m. p. 145—146° (0·5 g.), not depressed on admixture with the 2 : 7-di-*tert.*-butylnaphthalene picrate prepared as above.

To a solution of the picrate (0·5 g.) in boiling dry alcohol (5 c.c.) was added di-*tert.*-butylnaphthalene, m. p. 145—146° (0·15 g), dissolved in the same solvent (3 c.c.). The mixture was boiled for a few seconds and allowed to cool, whereupon orange needles (0·55 g.) crystallised out; m. p. 157—158°, not depressed on admixture with the picrate, m. p. 157—158°, used as the starting material (Found: C, 67·5; H, 6·6; N, 7·35. Calc. for $C_{66}H_{78}O_{14}N_6$: C, 67·2; H, 6·65; N, 7·15%).

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