140. *Acenaphthene Series. Part II. Bromo-, Nitro-, and Amino-derivatives of* 3 : 4-*Di*-tert.-*butylacenaphthene, and some Brominated Thioindigoid Dyes. Novel* ace*Substitution.*

By Arnold T. Peters.

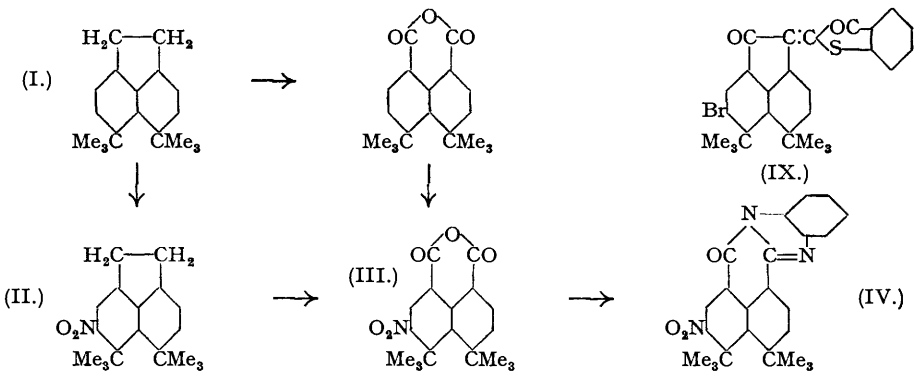
Nitration of 3 : 4-di-*tert.*-butylacenaphthene (I) gives 2-*nitro*- (II) and then 2 : (?)7-*dinitro*-3 : 4-*di*-tert.-*butylacenaphthene* (V), both of which are oxidised to the colourless 3-*nitro*-4 : 5-*di*-tert.-*butylnaphthalic anhydride* (III). No trace of a dinitro-4 : 5-di-*tert.*-butylnaphthalic anhydride is detected by oxidising (V), and the orientation of (III) is supported by its preparation from 4 : 5-di-*tert.*-butylnaphthalic anhydride. Although the presence of the nitro-group in the acenaphthene derivatives inhibits acenaphthenequinone formation, bromine substitution does not. Thus, restricted oxidation of 2-*bromo*-3 : 4-*di*-tert.-*butylacenaphthene* (VI) gives 16% of 2-*bromo*-3 : 4-*di*-tert.-*butylacenaphthenequinone* (VIII), from which the scarlet 2′(or 5′)-*bromo*-3′ : 4′-*di*-tert.-*butyl*-1 : 7′-*thionaphthenacenaphthenylindigo* (IX) and analogous vat *dyes* are prepared. Further oxidation of (VI) or (VIII) yields 3-*bromo*-4 : 5-*di*-tert.-*butylnaphthalic anhydride* (VII), which condenses with *o*-phenylenediamine to give the bright canary-yellow 2′(or 5′)-*bromo*-9′-*keto*-3′ : 4′-*di*-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′ : 2 : 3)-*ψ*-*indole*.

3-*tert.*-Butyl- and 3 : 4-di-*tert.*-butyl-acenaphthene (I) were obtained by the direct *tert.*-butylation of acenaphthene, and several new thioindigoid vat dyes were prepared (Part I; *J.*, 1942, 562); the preparation and properties of nitro-, amino-, and bromo-derivatives of (I) are now examined.

With 1·2 mols. of nitric acid (*d* 1·5) or its equivalent of diacetylorthonitric acid, (I) gave 2-*nitro*-3 : 4-*di*-tert.-*butylacenaphthene* (II). On restricted oxidation with sodium dichromate and acetic acid at 105°, under conditions whereby the unnitrated analogue gave 3 : 4-di-*tert.*-butylacenaphthenequinone, (II) gave no quinone, and no product was detected which condensed with 2-hydroxythionaphthen to give a thionaphthenacenaphthenylindigo dye. This is parallel to the case of 3-nitroacenaphthene, from which 3-nitroacenaphthenequinone could not be obtained by a variety of methods of oxidation (cf. Graebe and Briones, *Annalen*, 1903, **327**, 80; Morgan and Harrison, *J. Soc. Chem. Ind.*, 1930, **49**, 413 T). The sole oxidation product of (II) isolated was the colourless 3-*nitro*-4 : 5-*di*-tert.-*butylnaphthalic anhydride* (III), which gave an *imide* and a N-*methylimide*, condensed with *o*-phenylenediamine in acetic acid to yield 2′(or 5′)-*nitro*-9′-*keto*-3′ : 4′-*di*-tert.-*butyl*-8′-*azaphenalino* (7′ : 8′ : 2 : 3)-*ψ*-*indole* (IV), and showed the expected formation of a naphthafluorescein on fusion with resorcinol, and of a colouring matter of the rhodamine type with *m*-diethylaminophenol.

A chloronaphthafluorescein was prepared from 4-chloronaphthalic anhydride by Dziewoński and Zakrzewskwa-Barnaowska (*Bull. intern. Acad. Polonaise*, 1926, *A*, 209) and Tanaka and Morikawa (*J. Chem. Soc. Japan*, 1930, **51**, 121), and Ferrario and Weber (*Arch. sci. phys. nat.*,

1908, **25**, 517) prepared rhodamine derivatives from naphthalic anhydride and *m*-diethyl- and -dimethyl-aminophenol, respectively.



With excess of nitric acid (*d* 1·5) at 95—100°, even in presence of 25% fuming sulphuric acid, **4** : 5-di-*tert.*-butylnaphthalic anhydride could be mononitrated only, and the nitration product was identical with (III). This supports the constitution of (III) and thence of (II), as the dicarboxylic anhydride group directs the nitro-group into the 3-position even when the **4** : 5-positions of naphthalic anhydride are free (cf. Anselm and Zuckmayer, *Ber.*, 1899, **32**, 3283; Graebe and Briones, *loc. cit.*; Mihăilescu and Stoepoe, *Bull. Acad. Sci. Roumaine*, 1923, **8**, 102). Careful further nitration of (II) with nitric acid (*d* 1·5) in acetic acid at $< 60°$ afforded (probably) 2 : 7-*dinitro*-3 : 4-*di*-tert.-*butylacenaphthene* (V), which on oxidation gave the unexpected result of a 75% yield of the mononitro-anhydride (III). Analyses confirmed that no trace of a dinitronaphthalic anhydride was formed at any stage. This lends strong support to the view that the second substituted nitro-group enters the 7-position, although no such novel nitro-substitution has been recorded previously in the acenaphthene series. An alleged acenaphthene-7-sulphonic acid was described by Kalle and Co. (G.P. 248,994), who sulphonated acenaphthene with chlorosulphonic acid, and favoured this constitution because of its conversion by alkaline fusion into acenaphthylene. However, Dziewoński and Stolyhwo (*Ber.*, 1924, **57**, 1531) showed that oxidation of the sulphonic acid gave 2-sulphonaphthalene-1 : 8-dicarboxylic acid, thus indicating that the sulphonic group occupies the 1-position in the acenaphthene nucleus. Side-chain nitration is recorded in the naphthalene series; *e.g.*, Robinson and Turner (*J.*, 1932, 2015) prepared 4-methyl-1-nitromethylnaphthalene, which was oxidised to naphthalene-1 : 4-dicarboxylic acid.

The nitro-derivative (II) is reduced best by aqueous-alcoholic sodium hydrosulphite to yield 2-*amino*-3 : 4-*di*-tert.-*butylacenaphthene*, which is diazotisable with difficulty, in hydrochloric acid or nitrosylsulphuric acid, with much resin formation, but yields an *azo*-β-*naphthol* derivative.

Direct amination in the acenaphthene series does not appear to have been attempted. Under a variety of conditions, 1 mol. of acenaphthene reacted vigorously with 1·3 mols. of hydroxylamine hydrochloride and 2·2 mols. of aluminium chloride, but only a trace of amine was formed, detected by formation of the azo-β-naphthol derivative; 3 : 4-di-*tert.*-butylacenaphthene gave no identifiable base. It was, however, confirmed that a similar amination of benzene or toluene gave 5 to 6% yields of aniline or mixed toluidines, respectively (cf. Graebe, *Ber.*, 1901, **34**, 1778).

2-*Bromo*-3 : 4-*di*-tert.-*butylacenaphthene* (VI) was readily prepared in 83% yield by brominating 3 : 4-di-*tert.*-butylacenaphthene in chloroform, but care was necessary in order to obtain a specimen free from a trace of product which gives a persistent intense blue fluorescence in alcohols or acetic acid. The bromo-compound (VI) was unaffected by heating with excess of aqueous ammonia (*d* 0·88) in a sealed tube at 150°, and the nuclear position of the bromine atom was confirmed by oxidation of (VI) with sodium dichromate in acetic acid to the colourless *3-bromo*-4 : 5-*di*-tert.-*butylnaphthalic anhydride* (VII), which gives the naphthafluorescein reaction but does not condense with 2-hydroxythionaphthen. The anhydride (VII) gave *imides* and condensed with *o*-phenylenediamine to form the bright canary-yellow 2′(or 5′)-*bromo*-9′-*keto*-3′ : 4′-*di*-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′ : 2 : 3)-ψ-*indole*. The anhydride (VII) could not be prepared directly from **4** : 5-di-*tert.*-butylnaphthalic anhydride, which was unchanged by

the action of bromine alone or in chloroform or nitrobenzene at various temperatures, by excess of bromine and a little acetic acid at 150° in a sealed tube for 4 hours, or by excess of bromine in 10% fuming sulphuric acid at 100—120°. Francesconi and Bargellini (*Gazzetta*, 1902, **32**, 73) brominated naphthalic anhydride in fuming sulphuric acid.

The nitro-compound (II) could not be brominated, but further bromination of 2-bromo-3 : 4-di-*tert.*-butylacenaphthene in chloroform or carbon disulphide gave the 2 : *x*-*dibromo*-derivative; oxidation caused some loss of bromine and much resin formation, but orientation of the second bromine atom was not established, as the oxidation product gave inconsistent analytical data.

Unlike the nitro-group, nuclear-substituted bromine does not have an inhibiting effect on acenaphthenequinone formation. Mild oxidation converts 3-bromoacenaphthene into 3-bromoacenaphthenequinone (cf. Graebe and Guinsbourg, *Annalen*, 1903, **327**, 85; Guha, *J.*, 1931, 583). Restricted oxidation of 2-bromo-3 : 4-di-*tert.*-butylacenaphthene with sodium dichromate and acetic acid, and repeated extraction of the anhydride (VII) from the product with boiling aqueous sodium carbonate, gave 16% of 2-*bromo*-3 : 4-*di*-tert.-*butylacenaphthene-quinone* (VIII), from which small amounts of (VII) are difficult to remove. The use of ammonium dichromate has no advantage over sodium dichromate in this reaction (Daschevskii and Karischin, *Org. Chem. Ind. U.S.S.R.*, 1936, **1**, 729, claim a yield of 71·1% of acenaphthenequinone from acenaphthene). When (VI) was oxidised for 40 minutes, mixed crystals of (VII) and (VIII) were obtained, a similar phenomenon occurring in the oxidation of 3 : 4-di-*tert.*-butylacenaphthene (*loc. cit.*); mixed crystals of acenaphthenequinone and naphthalic anhydride are recorded by Kiprianov and Dashevskii (*J. Appl. Chem. Russia*, 1934, **7**, 944), who state that prolonged alkali extraction is necessary to obtain the quinone reasonably pure. Condensation of the quinone (VIII) with 2-hydroxythionaphthen was best effected in a mixture of acetic and hydrochloric acid (8 : 1) rather than by the alcoholic-alkali method recorded in G.P. 205,377 (Basler Chem. Fabrik in Basel). The resulting scarlet 2′(or 5′)-*bromo*-3′ : 4′-*di*-tert.-*butyl*-1 : 7′-*thionaphthenacenaphthenylindigo* (IX) shows no improvement in dyeing properties compared with the unbrominated analogue, and dyes cotton pink from a difficulty-formed bluish-violet alkaline hydrosulphite vat. Similar thioindigoid vat *dyes* were prepared by condensing the quinone (VIII) with 5-ethoxy- and 5-chloro-3-methyl-2-hydroxythionaphthen, severally.

Experimental.

M. ps. are corrected. Micro-analyses were carried out by Dr. G. Weiler and Dr. F. B. Strauss, of Oxford.

2-*Nitro*-3 : 4-*di*-tert.-*butylacenaphthene* (II).—(*a*) Nitric acid (*d* 1·5; 2·3 g., 1·2 mols.) was added to 3 : 4-di-*tert.*-butylacenaphthene (8 g.; 1 mol.) in acetic acid (40 c.c.) at room temperature, and the mixture heated gradually during 10 minutes to 60°. On cooling, the *mononitro*-derivative separated; it crystallised from alcohols, acetic acid, or acetic anhydride, in yellow prismatic needles, m. p. 144° (7·8 g.; 83·3%) (Found: C, 77·1; H, 8·0; N, 4·6. $C_{20}H_{25}O_2N$ requires C, 77·2; H, 8·0; N, 4·5%). No isomeride was found in the mother-liquors. Potassium nitrate and sulphuric acid were unsatisfactory for nitration, there being much frothing and charring.

(*b*) Diacetylorthonitric acid (Pictet and Genequand, *Ber.*, 1902, **35**, 2526) (9·6 g.; 8·2 c.c., equivalent to 1·3 mols. of HNO_3) was added all at once to a stirred mixture of finely-powdered 3 : 4-di-*tert.*-butylacenaphthene (10·4 g.; 1 mol.) suspended in acetic anhydride (25 c.c.) at 0°; a clear solution was formed, from which yellow needles separated progressively (8·5 g.; 76·6%).

2 : (?)7-*Dinitro*-3 : 4-*di*-tert.-*butylacenaphthene* (V).—Nitric acid (d 1·5; 2·3 g., 1·1 mols.) in acetic acid (5 c.c.) was added during 5 minutes to a solution of 2-nitro-3 : 4-di-*tert.*-butylacenaphthene, m. p. 144° (10 g., 1 mol.), in acetic acid (40 c.c.) at 40°; after the mixture had been heated slowly to 60° and kept at this temperature for 15 minutes, and then cooled, the *dinitro*-compound separated; it crystallised from acetic acid in pale yellow needles, m. p. 198° (decomp.) (8 g.; 70·2%) (Found: C, 67·5; H, 6·9; N, 8·0. $C_{20}H_{24}O_4N_2$ requires C, 67·4; H, 6·7; N, 7·9%). To avoid resin formation, the reaction temperature must not exceed 60°. The dinitro-compound was unchanged on boiling with aqueous sodium carbonate or ammonia, or with dilute mineral acids, but became resinous with hot aqueous or alcoholic alkali hydroxides; it could not be converted into the mononitro-derivative (II).

2-*Amino*-3 : 4-*di*-tert.-*butylacenaphthene*.—The 2-nitro-compound (II) (7 g.) was refluxed with a solution of sodium hydrosulphite (20 g.) in water (80 c.c.) and alcohol (30 c.c.) for 3 hours. After removal of the alcohol, the *base* separated in pale yellow leaflets, which crystallised from aqueous alcohol containing a trace of hydrosulphite in almost colourless prisms, m. p. 153° (5·2 g.; 83·5%) (Found: C, 84·9; H, 9·6; N, 5·2. $C_{20}H_{27}N$ requires C, 85·4; H, 9·6; N, 5·0%), which become brown in air. With concentrated hydrochloric acid, the hydrochloride was obtained in colourless needles, m. p. 220°. The *acetyl* derivative crystallised from alcohol in colourless needles, m. p. 257—258° (Found: N, 4·2. $C_{22}H_{29}ON$ requires N, 4·3%). The *phthalanil* separated from acetic acid in colourless prisms, m. p. 292—293° (Found: C, 81·7; H, 7·2. $C_{28}H_{29}O_2N$ requires C, 81·75; H, 7·05%). The *azo*-β-*naphthol* derivative, obtained in only low yield, crystallised from aqueous acetic acid in minute, dark brown needles, m. p. 175° (Found: C, 81·8; H, 7·1; N, 6·0. $C_{30}H_{32}ON_2$ requires C, 82·6; H, 7·3; N, 6·4%), which dissolved in cold concentrated sulphuric acid with a bluish-green colour.

3-*Nitro*-4 : 5-*di*-tert.-*butylnaphthalic Anhydride* (III).—(*a*) Sodium dichromate (35 g.) was added

during 30 minutes to a solution of 2-nitro-3 : 4-di-*tert.*-butylacenaphthene (10 g.) in acetic acid (250 c.c.) at 110°, and the mixture refluxed for a further 3 hours. On addition of ice-water, an almost colourless precipitate separated; it was collected, washed with warm water, and crystallised from acetic acid; colourless prisms, m. p. 183° (8·7 g.; 76·3%) (Found: C, 67·6; H, 5·9; N, 3·9. $C_{20}H_{21}O_5N$ requires C, 67·6; H, 5·9; N, 3·9%). 3-*Nitro*-4 : 5-*di*-tert.-*butylnaphthalic anhydride* is moderately soluble in boiling 15% aqueous sodium carbonate. On fusion with resorcinol and zinc chloride, and addition to dilute aqueous ammonia, the anhydride gives a pale yellow solution with a strong green fluorescence, owing to naphthafluorescein formation. (III) was recovered unchanged on heating with nitric acid (*d* 1·5) in absence or presence of 25% fuming sulphuric acid at 95—100° for 1 hour.

(*b*) Pure 2 : (?)7-dinitro-3 : 4-di-*tert.*-butylacenaphthene (10 g.) was oxidised with sodium dichromate (40 g.) in boiling acetic acid (400 c.c.) for 5 hours to give colourless prisms, m. p. and mixed m. p. with the product from (*a*), 183° (7·5 g.; 75%) (Found: N, 4·0%).

(*c*) Finely ground 4 : 5-di-*tert.*-butylnaphthalic anhydride (5 g.) was warmed to 50° with excess of nitric acid (*d* 1·5; 8 g.) and then kept at room temperature for 2 hours. After dilution, the solid was collected and crystallised from acetic acid; colourless needles, m. p. 183° (4·1 g.; 71·7%), identical with those obtained by methods (*a*) and (*b*).

Derivatives of 3-*Nitro*-4 : 5-*di*-tert.-*butylnaphthalic Anhydride*.—On being refluxed with excess of aqueous ammonia (*d* 0·88) and a little alcohol for 1 hour, the anhydride gave 3-*nitro*-4 : 5-*di*-tert.-*butylnaphthalimide*, which crystallised from acetic acid in colourless prisms, or from alcohol in colourless needles, m. p. 288—289° (Found: C, 67·7; H, 6·3; N, 7·7. $C_{20}H_{22}O_4N_2$ requires C, 67·8; H, 6·2; N, 7·9%), also obtained from 4 : 5-di-*tert.*-butylnaphthalimide (cf. *J.*, 1942, 562) and excess of nitric acid (*d* 1·5) at 40° for 10 minutes. The corresponding N-*methylimide*, prepared by boiling the anhydride in methyl alcohol with excess of 33% aqueous methylamine for 1 hour, crystallised from acetic acid in colourless prisms, m. p. 260° (Found: C, 68·2; H, 6·4; N, 7·6. $C_{21}H_{24}O_4N_2$ requires C, 68·5; H, 6·5; N, 7·6%). The 2 : 4-*dinitrophenylhydrazide* crystallised from acetic acid in pale yellow needles, m. p. 308—309° (Found: C, 58·7; H, 4·7. $C_{26}H_{25}O_8N_5$ requires C, 58·3; H, 4·7%). The anhydride (1 mol.) and *o*-phenylenediamine (1·4 mols.), refluxed in acetic acid for 15 minutes, afforded 2′(or 5′)-*nitro*-9′-*keto*-3′ : 4′-*di*-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′ : 2 : 3)-*ψ*-*indole* (IV), which crystallised from acetic acid or alcohol in bright yellow needles, m. p. 266—267° (Found: C, 72·6; H, 6·0; N, 9·7. $C_{26}H_{25}O_3N_3$ requires C, 73·1; H, 5·85; N, 9·8%).

2-*Bromo*-3 : 4-*di*-tert.-*butylacenaphthene* (VI).—Bromine (7·7 g.; 1·2 mols.) in chloroform (20 c.c.) was added during 5 minutes to a stirred solution of 3 : 4-di-*tert.*-butylacenaphthene (10·6 g.) in chloroform (100 c.c.) at room temperature. Hydrogen bromide was evolved, and after 1 hour the mixture was refluxed for 10 minutes; most of the chloroform was then removed, but care must be taken to add alcohol before all the chloroform is distilled, otherwise a trace of yellowish-green colouring matter with a very strong blue fluorescence in organic solvents, is formed, which is extremely difficult to remove on subsequent crystallisation. When pure, the *monobromo*-compound separated from alcohol in colourless prismatic needles, m. p. 137—138° (11·4 g.; 83·2%) (Found: C, 70·0; H, 7·5; Br, 22·6. $C_{20}H_{25}Br$ requires C, 69·6; H, 7·2; Br, 23·2%), which show no fluorescence in alcohols or acetic acid. A little soluble resin was also formed, but no isomeride was isolable. The bromo-derivative was unchanged on boiling with alcoholic picric acid, or on boiling with excess of aqueous ammonia (*d* 0·88) in a sealed tube at 150° for 4 hours. A resin only was obtained on attempted preparation from 2-amino-3 : 4-di-*tert.*-butylacenaphthene by the diazo-reaction, or on attempted nitration under various conditions.

2 : x-*Dibromo*-3 : 4-*di*-tert.-*butylacenaphthene*.—Bromine (2·8 g.; 1·2 mols.) in chloroform (15 c.c.) was added to a well-stirred solution of 2-bromo-3 : 4-di-*tert.*-butylacenaphthene, m. p. 137—138° (5 g., 1 mol.), in chloroform (60 c.c.) during 20 minutes. The mixture was stirred at room temperature for a further hour and then refluxed for 20 minutes, and most of the chloroform was removed; addition of alcohol precipitated a yellow resinous mass which solidified when kept at 0° for 12 hours. No fluorescence was noticed in alcohol (cf. the monobromo-derivative). Dissolution of the product in *tert.*-butyl alcohol at 50°, followed by careful dilution with water and standing for 48 hours gave cream needles, m. p. 110—120°, which crystallised from aqueous acetic acid in colourless prisms, m. p. 126°, of the *dibromo*-compound (3·6 g.; 58·5%) (Found: C, 56·6; H, 5·7; Br, 37·8. $C_{20}H_{24}Br_2$ requires C, 56·6; H, 5·7; Br, 37·7%). No higher brominated derivative could be isolated by treating 3 : 4-di-*tert.*-butylacenaphthene or its monobromo- or dibromo-derivative with excess of bromine in chloroform or carbon disulphide, the sole products formed being the above dibromo-compound and an intractable tar. Oxidation of the dibromo-compound with sodium dichromate and acetic acid under various conditions gave a resin and a low yield of alkali-soluble product which crystallised from aqueous acetic acid in pale yellow needles, m. p. varying between 155° and 175° (Found in these different specimens: Br, 21·5, 24·3, 27·5%).

2-*Bromo*-3 : 4-*di*-tert.-*butylacenaphthenequinone* (VIII) *and* 3-*Bromo*-4 : 5-*di*-tert.-*butylnaphthalic Anhydride* (VII).—(*a*) 2-Bromo-3 : 4-di-*tert.*-butylacenaphthene (10 g.) was refluxed with sodium dichromate (40 g.) in acetic acid (200 c.c.). After 40 minutes, addition to water gave a solid (10 g.) which was extracted twice with boiling 15% aqueous sodium carbonate and crystallised five times from aqueous acetic acid to give pale yellow prismatic needles (4 g.), m. p. 152—153° (Found: C, 63·6; H, 5·8; Br, 21·2. $C_{20}H_{21}O_2Br$,$C_{20}H_{21}O_3Br$ requires C, 63·0; H, 5·5; Br, 21·0%), which were probably mixed crystals of (VII) and (VIII), as condensation with 2-hydroxythionaphthen gave a red thioindigoid dye.

(*b*) When the reaction, as in (*a*), was extended by refluxing for 6 hours, and the resulting resinous solid extracted twelve successive times with boiling 15% aqueous sodium carbonate (1 l.), the combined extracts on acidification gave 3-*bromo*-4 : 5-*di*-tert.-*butylnaphthalic anhydride* (VII), which crystallised from aqueous acetic acid and then alcohol in colourless glistening leaflets, m. p. 184—185° (5·7 g.; 50·5%) (Found: C, 62·3; H, 5·5; Br, 20·6. $C_{20}H_{21}O_3Br$ requires C, 61·7; H, 5·4; Br, 20·6%). This colourless anhydride does not react with 2-hydroxythionaphthen, but gives the naphthafluorescein reaction on fusion with resorcinol and zinc chloride.

(*c*) Sodium dichromate (45 g.) was added all at once to 2-bromo-3 : 4-di-*tert.*-butylacenaphthene (15 g.) in acetic acid (200 c.c.) at 110°, and the reaction allowed to proceed without external heat for 10

minutes. Ice–water was added and the precipitate (15·5 g.) was extracted seven times with boiling 15% aqueous sodium carbonate; acidification gave the above anhydride (VII) (6·5 g.; 38·6%). The insoluble residue (*A*) was chromatographed, using alumina and benzene, with no further apparent separation except for the removal of a little resin, and finally it was crystallised from aqueous acetic acid in pale yellow needles, m. p. 162—163°, mainly of the quinone (VIII) (2·6 g.; 16%) (Found : C, 63·6; H, 5·6; Br, 21·2. $C_{20}H_{21}O_2Br$ requires C, 64·3; H, 5·6; Br, 21·45%), but still containing a little of the anhydride (VII).

Derivatives of 3-*Bromo*-4 : 5-di-*tert.*-*butylnaphthalic Anhydride*.—The *naphthalimide* crystallised from aqueous acetic acid in colourless, glistening needles, m. p. 314—315° (Found : N, 3·7; Br, 20·3. $C_{20}H_{22}O_2NBr$ requires N, 3·6; Br, 20·6%). The N-*methylimide* separated from aqueous alcohol in colourless, asbestos-like needles, m. p. 218—220° (Found : N, 3·3; Br, 20·0. $C_{21}H_{24}O_2NBr$ requires N, 3·5; Br, 19·9%). 2′(or 5′)-*Bromo*-9′-*keto*-3′ : 4′-*di*-tert.-*butyl*-8′-*azaphenalino*(7′ : 8′ : 2 : 3)-*ψ*-*indole* crystallised from much acetic acid in canary-yellow needles, m. p. 280—283° (Found : N, 5·7; Br, 17·7. $C_{26}H_{25}ON_2Br$ requires N, 6·1; Br, 17·35%).

Derivatives of 2-*Bromo*-3 : 4-*di*-tert.-*butylacenaphthenequinone*.—Condensation of the above oxidation product (*A*) with freshly prepared colourless 2-hydroxythionaphthen in a mixture of acetic and hydrochloric acid (8 : 1), after boiling for 5 minutes, gave 2′(or 5′)-*bromo*-3′ : 4′-*di*-tert.-*butyl*-1 : 7′-*thionaphthenacenaphthenylindigo* (IX), which was purified by boiling with alcohol and crystallisation of the insoluble residue from acetic acid; scarlet prisms, m. p. 274—275° (Found : C, 65·7; H, 4·9; S, 6·2. $C_{28}H_{25}O_2BrS$ requires C, 66·5; H, 4·95; S, 6·3%), which dissolve in cold concentrated sulphuric acid with a bluish-green colour and form a bluish-violet vat with aqueous-alcoholic sodium hydrosulphite. 2′(or 5′)-*Bromo*-5-*ethoxy*-3′ : 4′-*di*-tert.-*butyl*-1 : 7′-*thionaphthenacenaphthenylindigo* crystallised from acetic acid in red prisms, m. p. 236—238° (Found : Br, 14·5; S, 6·2. $C_{30}H_{29}O_3BrS$ requires Br, 14·6; S, 5·8%), which dissolve in concentrated sulphuric acid with a greenish-brown colour and form a brownish-violet vat with hydrosulphite. The 5-*chloro*-3-*methyl* analogue of (IX) crystallised from acetic acid in orange-red prisms, m. p. 340—343° (Found : S, 6·1; 5·037 mg. gave 3·07 mg. of AgCl + AgBr, $C_{29}H_{26}O_2ClBrS$ requires S, 5·8; AgCl + AgBr, 3·02 mg.), soluble in concentrated sulphuric acid with a brown colour and forming a brownish-violet hydrosulphite vat.

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