

**110.** *Acenaphthene Series. Part I. Mono- and Di-tert.-butyl-acenaphthene, -acenaphthenequinone, and -naphthalic Anhydride, and their Derivatives.*

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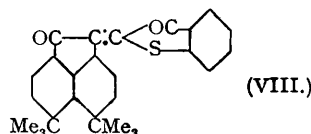
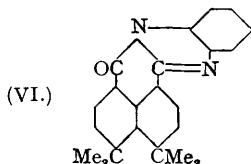
3-*tert.-Butylacenaphthene* (I), prepared by the Friedel-Crafts reaction from acenaphthene, is oxidised to 4-*tert.-butyl-naphthalic anhydride* (III), which condenses with *o*-phenylenediamine to yield 9'-*keio*-3'(or 4')-*tert.-butyl-8'-azaphenalino-(7' : 8' : 2 : 3)-ψ-indole* (as VI). Controlled oxidation of (I) affords (III) and 12% of 3-*tert.-butylacenaphthenequinone* (IV). 3 : 4-*Di-tert.-butylacenaphthene* (II) is oxidised to 4 : 5-*di-tert.-butyl-naphthalic anhydride* (V), or to a double compound (VII) of the anhydride (V) and 3 : 4-*di-tert.-butylacenaphthenequinone*, from which the pure quinone is liberated by the novel method of repeated extraction with 10% aqueous sodium carbonate at 170° under pressure. Many derivatives are prepared; *e.g.*, 3' : 4'-*di-tert.-*

*butyl-1 : 7'-thionaphthenacenaphthenylindigo* (VIII), which dyes cotton magenta-red from an alkaline hydro-sulphite vat.

THE object of this research was to obtain oriented higher alkyl derivatives of acenaphthene, acenaphthenequinone, and naphthalic anhydride, and to investigate their use as intermediates for vat dyes.

3-*tert.*-Butyl-(I) and 3 : 4-*di-tert.*-butyl-acenaphthene (II) are prepared from acenaphthene (1 mol.) and *tert.*-butyl chloride (1 and 1.8 mols., respectively) in carbon disulphide, only 0.2 mol. of aluminium chloride being used. In preparing (II), small amounts of (I) are always formed, but the use of relatively larger amounts of *tert.*-butyl chloride produces more resinous material. 3-*tert.*-Butylacenaphthene is oxidised by sodium dichromate in acetic acid to 4-*tert.*-butyl-naphthalic anhydride (III), which affords an *imide*, *N*-methylimide, and *phenylhydrazide*, and condenses with *o*-phenylenediamine in acetic acid to yield 9'-*keto-3'*(or 4')-*tert.*-butyl-8'-azaphenalino-(7' : 8' : 2 : 3)- $\psi$ -indole (as VI). A carefully controlled oxidation of (I) affords (III) together with 12% of 3-*tert.*-butylacenaphthenequinone (IV), which condenses with 2-hydroxythionaphthen in a mixture of acetic and hydrochloric acids (5 : 1) to give the brilliant scarlet 3' (or 4')-*tert.*-butyl-1 : 7'-thionaphthenacenaphthenylindigo; this stains cotton pink from a difficultly formed alkaline hydrosulphite vat. Unlike acenaphthenequinone, (IV) is only sparingly soluble in boiling aqueous sodium bisulphite, and even after extraction with boiling aqueous sodium carbonate in an open vessel or under pressure at 150°, followed by fractional crystallisation, and then chromatographic analysis, complete purification was not effected.

3 : 4-*Di-tert.*-butylacenaphthene (II) is oxidised to 4 : 5-*di-tert.*-butyl-naphthalic anhydride (V), which yields an *imide*, *N*-methylimide, and 9'-*keto-3'* : 4'-*di-tert.*-butyl-8'-azaphenalino-(7' : 8' : 2 : 3)- $\psi$ -indole (VI). An unusual product resulted from a carefully controlled oxidation of (II) with sodium dichromate and acetic acid at 95—105° for 15 minutes; after separation of the anhydride (V), the residue crystallised in golden-yellow needles, m. p. 186°, of a double compound (VII) of equimolecular proportions of 3 : 4-*di-tert.*-butylacenaphthenequinone and 4 : 5-*di-tert.*-butyl-naphthalic anhydride, unchanged by crystallisation from nitrobenzene, pyridine or quinoline, or by chromatographic analysis. The pure *quinone* is obtained with difficulty after several extractions of (VII) with 10% aqueous sodium carbonate at 170° in a sealed tube, and is reconvertible into (VII). Quantitative experiments were carried out by condensing (VII) with phenylhydrazine; 3 : 4-*di-tert.*-butylacenaphthenequinonediphenylhydrazone was then separated from the *phenylhydrazide* of (V). Similarly, condensation of (VII) with 2-hydroxythionaphthen caused reaction with the 3 : 4-*di-tert.*-butylacenaphthenequinone to give 3' : 4'-*di-tert.*-butyl-1 : 7'-thionaphthenacenaphthenylindigo (VIII) and the unreacted anhydride (V) was recovered. Compound (VIII) dyes cotton magenta-red from an orange-brown alkaline hydrosulphite vat, and 5-*ethoxy-3'* : 4'-*di-tert.*-butyl-1 : 7'-thionaphthenacenaphthenylindigo dyes cotton reddish-orange from a yellow vat.



Attempted oxidation of the *tert.*-butyl groups to carboxyl in compounds (III) and (V) by chromic acid, alkaline permanganate or hydrogen peroxide, or dilute nitric acid, under various conditions, yielded either unchanged material or resins. There is little doubt that the stated orientations for the *tert.*-butylacenaphthenes are correct, by analogy with the ethyl analogues (Mayer and Kaufmann, *Ber.*, 1920, 53, 289), and this is supported by the known reactivity of positions 3 and 4 in acenaphthene; e.g., 3-acetyl- and -propionyl-, and 3 : 4-diacetyl- and -dipropionyl-acenaphthene are obtained by the Friedel-Crafts reaction (Dziewonski and collaborators, *Bull. Acad. Polonaise*, 1931, A, 232, 242).

#### EXPERIMENTAL.

The m. p.'s are corrected. Microanalyses were carried out by Dr. G. Weiler and Dr. F. B. Strauss, of Oxford.

3-*tert.*-Butylacenaphthene.—Anhydrous aluminium chloride (13.4 g.; 0.2 mol.) was added during 1 hour to a well-stirred mixture of acenaphthene (77 g.; 1 mol.) and *tert.*-butyl chloride (46.25 g.; 1 mol.) in dry carbon disulphide, the mixture refluxed for 2 hours, and ice-water (400 g.) and concentrated hydrochloric acid (60 c.c.) then added. The solvent layer was separated, the aqueous layer extracted with carbon disulphide, the combined extracts dried (sodium sulphate), and the solvent removed. The residue was distilled and the fraction, b. p. 310—325°, was recrystallised from aqueous alcohol, 3-*tert.*-butylacenaphthene separating in colourless prisms, m. p. 73—74°, b. p. 170—174°/7 mm. (yield, 56 g.; 53.3%) (Found : C, 91.4; H, 8.6.  $C_{16}H_{18}$  requires C, 91.4; H, 8.6%). It is accompanied by unchanged acenaphthene and some *di-tert.*-butylacenaphthene; traces of the latter are difficult to remove and successive distillation and fractional crystallisation are necessary to obtain a pure specimen.

The *picrate* separated in orange-red needles, m. p. 86—90° (Found : N, 9.8.  $C_{16}H_{18}, C_6H_3O_7N_3$  requires N, 9.6%), readily decomposed on heating with organic solvents.

4-*tert.*-Butyl-naphthalic Anhydride.—Sodium dichromate (45 g.) was added to a solution of 3-*tert.*-butylacenaphthene (15 g.) in acetic acid (400 c.c.), and the mixture refluxed for 40 minutes. After addition to ice-water (600 g.), the precipitate was collected and extracted repeatedly with boiling 15% aqueous sodium carbonate; the cooled, charcoaled, combined extracts were acidified, and the precipitate refluxed with acetic acid for 10 minutes. The *anhydride* crystallised from dilute acetic acid in colourless needles, m. p. 201—202° (yield, 13 g.; 71.7%) (Found : C, 75.6; H, 5.4.  $C_{16}H_{14}O_3$  requires C, 75.6; H, 5.5%).

*Derivatives.* On refluxing with excess of aqueous ammonia (*d* 0.88) and a little alcohol for 20 minutes, the *anhydride* afforded 4-*tert.*-butyl-naphthalimide, which crystallised from methyl alcohol in colourless needles, m. p. 256° (Found :

C, 76.1; H, 6.0; N, 6.0.  $C_{16}H_{15}O_2N$  requires C, 75.9; H, 5.9; N, 5.5%. 33% Aqueous methylamine similarly yielded the *N*-methylimide, which crystallised from alcohol in colourless silky needles, m. p. 173° (Found: N, 5.4.  $C_{17}H_{17}O_2N$  requires N, 5.2%). The phenylhydrazide crystallised from aqueous acetic acid in yellow prisms, m. p. 187—188° (Found: N, 8.0.  $C_{22}H_{20}O_2N_2$  requires N, 8.1%). The anhydride (1 mol.) and *o*-phenylenediamine (1.4 mols.), refluxed in acetic acid for 10 minutes, afforded 9'-*keto*-3' (or 4')-*tert*-butyl-8'-azaphenalino-(7' : 8' : 2 : 3)- $\psi$ -indole, which separated from aqueous acetic acid in greenish-yellow prismatic needles, m. p. 194—195° (Found: C, 81.0; H, 5.3; N, 8.8.  $C_{22}H_{19}ON_2$  requires C, 81.0; H, 5.5; N, 8.6%), soluble in alcohol or acetic anhydride with a yellow colour and slight green fluorescence, and in cold concentrated sulphuric acid with an orange colour. The usual intense fluorescence, due to naphthaflorescein formation, was observed when the fusion mixture of the anhydride, resorcinol, and zinc chloride was added to dilute ammonia solution.

3-*tert*-butylacenaphthenequinone.—Sodium dichromate (45 g.) was added all at once to a solution of specially purified 3-*tert*-butylacenaphthene (15 g.) in acetic acid (400 c.c.) at 95°, and the mixture heated to 105°; the reaction was then allowed to proceed without external heating until it subsided (7 minutes). Ice-water (600 g.) was added, and the yellow precipitate (A) (14.5 g.) washed with warm water and extracted seven times with boiling 15% aqueous sodium carbonate (500 c.c.) for 20 minutes; the combined extracts were acidified and the colourless precipitate was boiled with acetic acid and crystallised to give 4-*tert*-butyl-naphthalic anhydride, m. p. and mixed m. p. 201—202° (yield; 5.5 g.; 30.3%). The residue was fractionally crystallised from aqueous alcohol, and the fractions tested by condensing with 2-hydroxythionaphthen. The resulting yellow needles, rich in quinone, were extracted repeatedly with boiling 15% aqueous sodium carbonate, and the residue was crystallised repeatedly from aqueous acetic acid and finally from aqueous alcohol, forming pale yellow needles, m. p. ca. 156—159°, of 3-*tert*-butylacenaphthenequinone (yield, 1.6 g.; 9.4%) (Found: C, 80.8; H, 5.8.  $C_{16}H_{14}O_2$  requires C, 80.7; H, 5.9%).

Condensation of product (A) (0.87 g.) with freshly prepared 2-hydroxythionaphthen (0.7 g.) in a mixture of acetic and hydrochloric acids (5 : 1) yielded 3-*tert*-butyl-1 : 7-*thionaphthenacenaphthenylindigo* [0.19 g., equivalent to 14% of 3-*tert*-butylacenaphthenequinone in the product (A)], which separated from acetic acid in brilliant scarlet prismatic needles, m. p. 300—301° (Found: C, 78.3; H, 5.4; S, 8.2.  $C_{24}H_{18}O_2S$  requires C, 77.8; H, 4.9; S, 8.65%). It dissolved in cold concentrated sulphuric acid with a deep bluish-green colour, becoming bluish-red on dilution.

3 : 4-*Di-tert*-butylacenaphthene.—This was prepared in the same way as the 3-*tert*-butyl compound, 83.3 g. (1.8 mols.) of *tert*-butyl chloride being used. The residue was distilled, and the fraction, b. p. 335—365°/760 mm., collected, leaving a resin which, if not removed, hindered subsequent crystallisation. 3 : 4-*Di-tert*-butylacenaphthene crystallised from alcohol in colourless plates or more slowly in colourless prismatic needles, or from acetic acid in long, colourless, prismatic needles, m. p. 162—163°, b. p. 358—360°/758 mm. (yield, 87 g.; 72.7%, calc. on *tert*-butyl chloride) (Found: C, 90.2; H, 9.6.  $C_{20}H_{26}$  requires C, 90.2; H, 9.8%), soluble in cold benzene, acetone, chloroform, light petroleum or ether. It afforded a red micro-crystalline *picrate*, m. p. 164° (Found: N, 8.75.  $C_{20}H_{26}C_6H_3O_7N_3$  requires N, 8.5%), decomposed in hot dry alcohol, chloroform, or light petroleum.

4 : 5-*Di-tert*-butyl-naphthalic Anhydride.—Sodium dichromate (40 g.) was added during 15 minutes to a solution of 3 : 4-*di-tert*-butylacenaphthene (10 g.) in acetic acid (300 c.c.) at 110°, and the mixture refluxed for 1 hour. After addition to ice-water (500 g.), the almost colourless precipitate was collected and washed with water. 4 : 5-*Di-tert*-butyl-naphthalic anhydride crystallised from acetic acid or alcohol in colourless fine needles, or in rhombohedra, m. p. 211°, both forms often separating simultaneously (Found: C, 77.4; H, 6.95.  $C_{20}H_{22}O_3$  requires C, 77.4; H, 7.1%).

*Derivatives.* 4 : 5-*Di-tert*-butyl-naphthalimide crystallised from alcohol in colourless needles, m. p. 240° (Found: N, 4.6.  $C_{20}H_{22}O_2N$  requires N, 4.5%), the *N*-methylimide in long colourless needles, m. p. 231—232° (Found: C, 78.4; H, 7.6; N, 4.2.  $C_{21}H_{25}O_2N$  requires C, 78.0; H, 7.7; N, 4.3%), which gave a violet fluorescence in alcohols, the phenylhydrazide in pale yellow prisms, m. p. 246° (Found: C, 78.0; H, 6.8; N, 7.0.  $C_{26}H_{28}O_2N_2$  requires C, 78.0; H, 7.0; N, 7.0%), and the oxime in colourless prisms, m. p. 180° (Found: N, 4.2.  $C_{20}H_{23}O_3N$  requires N, 4.3%). 9'-*Keto*-3' : 4'-*di-tert*-butyl-8'-azaphenalino (7' : 8' : 2 : 3)- $\psi$ -indole (VI), prepared similarly to the mono-*tert*-butyl compound (see above), crystallised from acetic acid in greenish-yellow prismatic needles, m. p. 278—279° (Found: C, 81.7; H, 6.5; N, 7.7.  $C_{26}H_{26}ON_2$  requires C, 81.7; H, 6.8; N, 7.3%), which dissolved in alcohol with a yellow colour and a green fluorescence; a similar but less marked fluorescence appeared in acetic anhydride, from which solvent the product could be recrystallised unchanged. It dissolved in cold concentrated sulphuric acid with an orange colour. 4 : 5-*Di-tert*-butyl-naphthalic anhydride is recovered unchanged on melting with *p*-nitroaniline, or on boiling with a solution of 2-hydroxythionaphthen in aqueous alcohol containing potassium carbonate or in a mixture of acetic and hydrochloric acids (5 : 1).

*Double Compound of 3 : 4-*Di-tert*-butylacenaphthenequinone and 4 : 5-*Di-tert*-butyl-naphthalic Anhydride.* Preparation of 3 : 4-*Di-tert*-butylacenaphthenequinone.—The oxidation of 3 : 4-*di-tert*-butylacenaphthene (15 g.) with sodium dichromate was carried out similarly to that of the 3-*tert*-butyl compound. The sodium carbonate extracts of the yellow solid (13 g.) obtained gave on acidification an almost colourless solid, which crystallised from acetic acid in almost colourless, fine needles or rhombohedra of 4 : 5-*di-tert*-butyl-naphthalic anhydride (4 g.). The residue from the alkali extractions was extracted with 15% aqueous sodium bisulphite (300 c.c.) on the water-bath for 20 minutes, and the extract boiled with dilute sulphuric acid for 20 minutes to yield a yellow solid (B, 0.3 g.), m. p. 186°. The insoluble residue, recrystallised from acetic acid, formed large, yellow, prismatic needles, or, from alcohol, long silky needles, of constant m. p. 186°, identical with (B). The compound appeared homogeneous under the microscope, and is a double compound of equimolecular proportions of 3 : 4-*di-tert*-butylacenaphthenequinone and 4 : 5-*di-tert*-butyl-naphthalic anhydride (Found: C, 79.4, 79.6; H, 7.3, 7.3.  $C_{20}H_{22}O_2, C_{20}H_{22}O_3$  requires C, 79.5; H, 7.3%). The m. p. was not depressed by either the pure quinone or the anhydride. After chromatographic analysis (alumina; light petroleum or benzene) the compound still had m. p. and mixed m. p. 186° (Found: C, 79.4; H, 7.2%). It dissolved in warm alcoholic potassium hydroxide with a green colour, with partial decomposition of the quinone. The quinone could not be separated *via* the hydrazone or oxime, but after the double compound (1 g.) had been extracted three times with 10% aqueous sodium carbonate in a sealed tube at 170° for 3 hours, the insoluble residue crystallised from alcohol in yellow silky needles (0.3 g.), m. p. 213—214°, of 3 : 4-*di-tert*-butylacenaphthenequinone (mixed m. p. with 4 : 5-*di-tert*-butyl-naphthalic anhydride 182—186°) (Found: C, 81.7; H, 7.2.  $C_{20}H_{22}O_2$  requires C, 81.6; H, 7.5%). A mixture of equimolecular proportions of the quinone and the anhydride on crystallisation from alcohol gave yellow needles, m. p. and mixed m. p. with the double compound 185—186°.

*Derivatives of 3 : 4-*Di-tert*-butylacenaphthenequinone.*—These were most conveniently prepared from the double compound, m. p. 186°, which had been recrystallised until the m. p. was constant for three successive crystallisations.

The compound (VII) (0.25 g.) in 90% aqueous acetic acid (7 c.c.) was refluxed with phenylhydrazine (0.3 g.) in the same solvent (5 c.c.) for 10 minutes. After cooling to 50°, the orange crystals were collected and recrystallised from acetic acid, forming orange-red needles, m. p. 240—242°, of 3 : 4-*di-tert*-butylacenaphthenequinone di-phenylhydrazone (yield, 0.11 g.; 56%) (Found: C, 79.8; H, 7.5; N, 11.7.  $C_{32}H_{34}N_4$  requires C, 80.4; H, 7.2; N, 11.8%). The mother-liquors yielded pale yellow prisms, m. p. and mixed m. p. with the phenylhydrazide of 4 : 5-*di-tert*-butyl-naphthalic anhydride, 246° (yield, 0.09 g.; 53%); 0.1 g. of a mixture, m. p. 200°, of the hydrazone and the hydrazide was also obtained, and the m. p. was not depressed on admixture with a synthetic mixture.

An analytical specimen of 3' : 4'-di-tert.-butyl-1 : 7'-thionaphthenacenaphthenylindigo (VIII), prepared by condensation of (VII) and 2-hydroxythionaphthen in a mixture of acetic and hydrochloric acids (5 : 1), crystallised from acetic acid in bluish-red prismatic needles, m. p. 260—262° (Found : C, 78.7; H, 6.1; S, 7.2.  $C_{28}H_{26}O_2S$  requires C, 78.9; H, 6.1; S, 7.5%). 2-Hydroxythionaphthen and its analogues are slightly decomposed in aqueous-alcoholic alkali, though the latter medium is useful in preparing large amounts of dye. The dye dissolves in cold concentrated sulphuric acid with a deep green colour, becoming wine-red on dilution.

5-Ethoxy-3' : 4'-di-tert.-butyl-1 : 7'-thionaphthenacenaphthenylindigo crystallised from acetic acid in fine orange-red needles, m. p. 262—265° (Found : C, 76.1; H, 6.1; S, 6.5.  $C_{30}H_{30}O_3S$  requires C, 76.6; H, 6.4; S, 6.8%), which dissolved in cold concentrated sulphuric acid with a brownish-violet colour, becoming salmon-coloured on dilution.

3 : 4-Di-tert.-butylacenaphthenequinone-p-nitrophenylhydrazone crystallised from acetic acid in orange prismatic needles, m. p. 285—287° (Found : C, 72.8; H, 6.1; N, 10.1.  $C_{28}H_{27}O_3N_3$  requires C, 72.7; H, 6.3; N, 9.8%). The 2 : 4-dinitrophenylhydrazone crystallised in deep orange needles, m. p. 324° (Found : C, 65.7; H, 5.6; N, 11.7.  $C_{26}H_{26}O_5N_4$  requires C, 65.8; H, 5.5; N, 11.8%). converted by refluxing with excess of 2 : 4-dinitrophenylhydrazine in acetic acid for 2 hours into the bis-2 : 4-dinitrophenylhydrazone, which separated in orange-red prisms, m. p. 320° (Found : N, 16.3.  $C_{32}H_{30}O_8N_8$  requires N, 17.1%).

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