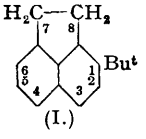
362. *Acenaphthene Series. Part V.* Preparation and Orientation of the Three Nuclear-substituted Mono-*tert.*-butylacenaphthenes. Isolation of Pure* 1-tert.*-Butylnaphthalene.*

By Eric Illingworth and Arnold T. Peters.

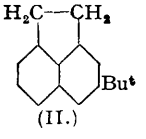
Although acenaphthene with *tert.*-butyl chloride and aluminium chloride in carbon disulphide gives 2-*tert.*-butyl- and 2 : 5-di-*tert.*-butyl-acenaphthene, use of anhydrous ferric chloride as catalyst yields surprisingly 1- and 3-*tert.*-butyl- and 1 : 6-di-*tert.*-butyl-acenaphthene. These products have been orientated by synthesis or degradation, and many new derivatives, including thioindigoid vat dyes, have been prepared.

3-*tert.*-Butylacenaphthene was converted into 4-*tert.*-butylnaphthalic anhydride and thence into 1-*tert.*-butylnaphthalene. This is the first record of the preparation of pure 1-*tert.*-butylnaphthalene, which was also synthesised from 1-tetralone by a Grignard reaction.

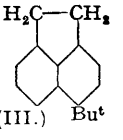
2-*tert.*-Butyl- (II) and 2 : 5-di-*tert.*-butylacenaphthene, prepared from acenaphthene by the Friedel–Crafts reaction with aluminium chloride (Peters, *J.*, 1942, 562), were orientated by Nürsten and Peters (*J.*, 1950, 729). When ferric chloride was used as catalyst, 1- (I) and 3-*tert.*-butylacenaphthene (III) were formed, the relative proportions depending on the temperature of reaction; the approximate proportions of the 1- and the 3-isomer in the total mono-*tert.*-butyl fractions formed were 45 : 55 in boiling carbon disulphide, and 83 : 17 in the same solvent at 10—15°. Some 1 : 6-di-*tert.*-butylacenaphthene was also isolated, but was difficult to obtain crystalline owing to the presence of a yellow resin.



(I.)



(II.)



(III.)

Orientation of 3-tert.*-Butylacenaphthene* (III).—This compound, which gave a *s*-trinitrobenzene complex, was oxidised by sodium dichromate in boiling acetic acid to 4-*tert.*-butylnaphthalic anhydride, from which were prepared the corresponding imide, *N*-methyl- and *N*-hydroxyethyl-imide, and 3′-keto-6′(or 7′)-*tert.*-butyl-2′-azaperinaphthano(1′ : 2′-2 : 1)benziminazole,† by methods described in previous Parts of this series. The anhydride was then converted into a *tert.*-butylnaphthalene by distillation with soda-lime, or better, by conversion through the mercuri-derivative into a mixture of 4- and 5-*tert.*-butyl-1-naphthoic acids, followed by decarboxylation by copper bronze in boiling quinoline.

* Part IV, *J.*, 1950, 2389.

† In *J.*, 1950, 729 this system was named 8′-azaphenalino(7′ : 8′-2 : 1)benziminazole. For details of the nomenclature change see *J.*, 1950, 3701.

The derived 1-*tert.*-butylnaphthalene gave a picrate which differed from that obtained from 2-*tert.*-butylnaphthalene prepared either by direct *tert.*-butylation of naphthalene or by unambiguous synthesis (cf. Bromby *et al.*, *J.*, 1943, 144). Attempted conversion of 1-*tert.*-butylnaphthalene into 1-naphthoic acid by dilute nitric acid at 180° yielded only the solid 4-nitro-derivative which was also obtained by nitric and 80% sulphuric acid at 50°. In contrast, the nitro-compound prepared from 2-*tert.*-butylnaphthalene by either of these methods could not be obtained crystalline.

Dr. N. G. Bromby (Thesis, Leeds Univ., 1941) attempted the synthesis of 1-*tert.*-butylnaphthalene by interaction of *tert.*-butylmagnesium chloride and 1-tetralone, followed by dehydration of the resulting carbinol to 1-*tert.*-butyl-3 : 4-dihydronaphthalene, which was then dehydrogenated with sulphur. The reaction was abnormal, probably owing to steric hindrance and the reducing action of *tert.*-butylmagnesium chloride. It gave naphthalene and 2-*tert.*-butylnaphthalene, with a small amount of an oil which afforded a picrate, m. p. 101·5—102·5°, which analysed correctly for a *tert.*-butylnaphthalene picrate; the m. p. (100—101·5°) of 2-*tert.*-butylnaphthalene picrate was depressed to 77—95°. Moreover, the 1-*tert.*-butylnaphthalene obtained by the present authors by degradation of 3-*tert.*-butylacenaphthene gave a picrate, m. p. 101·5—102·5°, not depressed on admixture with the synthetic product prepared from 1-tetralone. Thus the orientation of 3-*tert.*-butylacenaphthene is established.

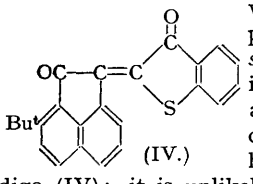
Tsukervanik and Terentieva (*J. Gen. Chem. U.S.S.R.*, 1937, **7**, 637) record that 1-alkylnaphthalenes are isomerised to 2-alkylnaphthalenes merely by heating them, but Cullinane and Chard (*Nature*, 1948, **161**, 690), who converted 1- into 2-methylnaphthalene, used alumina as catalyst at 450°, whilst Mayer and Schiffner (*Ber.*, 1934, **67**, 67) employed silica gel in a porcelain tube at 350° for the conversion of 1- into 2-alkylnaphthalenes. On refluxing 1-*tert.*-butylnaphthalene or 3-*tert.*-butylacenaphthene for 8 hours, however, we found no isomerisation; in the presence of a suitable catalyst, some migration of *tert.*-butyl occurs, and such reactions are under investigation.

For an analogous *tert.*-butylation of toluene, Buu-Hoï and Cagniant (*Bull. Soc. chim.*, 1942, **9**, 887) state that the use of aluminium chloride affords mainly *m*-*tert.*-butyltoluene, whilst ferric chloride gives mainly the *p*-isomer (cf. Baur, *Ber.*, 1891, **24**, 2833; Bialobrzeski, *Ber.*, 1897, **30**, 1773).

Controlled oxidation of 3-*tert.*-butylacenaphthene (III) with sodium dichromate and acetic acid gave 3-*tert.*-butylacenaphthenequinone, which condensed with 3-hydroxythionaphthen and its 6-ethoxy-derivative, to yield red indigoid vat dyes.

3-*tert.*-Butylacenaphthene readily afforded a crystalline monobromo-derivative with 1 or 2 mols. of bromine, whereas monobromo-2-*tert.*-butylacenaphthene could not be obtained pure and the dibromo-compound was readily isolated (*loc. cit.*).

Orientation of 1-tert.-*Butylacenaphthene.*—Oxidation of this hydrocarbon, which proceeds less readily than that of the 2- or the 3-isomeride, gave 2-*tert.*-butylnaphthalic anhydride, which was converted by soda-lime distillation into 2-*tert.*-butylnaphthalene, identical with a specimen prepared by unambiguous synthesis. Moreover, derivatives of 2-*tert.*-butylnaphthalic anhydride were shown to be isomeric with, but different from, the analogues prepared from 3- or 4-*tert.*-butylnaphthalic anhydride, but owing to the position of the *tert.*-butyl group they were obtained less readily. Further, 1-*tert.*-butylacenaphthenone, prepared by a modification of Buu-Hoï and Cagniant's method (*Rev. sci.*, 1942, **80**, 176 *), was oxidised to 2-*tert.*-butylnaphthalic anhydride, identical with that from 1-*tert.*-butylacenaphthene. Controlled oxidation of the latter afforded 1-*tert.*-butylacenaphthenequinone which condensed with 3-hydroxythionaphthen to yield an apparently homogeneous red dye, 1′-*tert.*-butyl-2 : 7′-thionaphthenacenaphthenylindigo (IV); it is unlikely that condensation occurs at the 8-position *ortho* to the *tert.*-butyl group.



(IV.)

Orientation of 1 : 6-*Di*-tert.-*butylacenaphthene.*—This hydrocarbon was much more resistant to oxidation than any of the three mono-*tert.*-butylacenaphthenes or 2 : 5-di-*tert.*-butylacenaphthene; even after 24 hours' boiling with sodium dichromate and acetic acid a mixture of di-*tert.*-butyl-acenaphthenequinone and -naphthalic anhydride resulted. Subsequent distillation with soda-lime afforded 2 : 7-di-*tert.*-butylnaphthalene identical with that prepared by direct di-*tert.*-butylation of naphthalene or by soda-lime distillation of 3 : 6-di-*tert.*-butylnaphthalic anhydride (cf. Nürsten and Peters, *loc. cit.*). This proves that the di-*tert.*-butylacenaphthene, formed from acenaphthene as above, is the 1 : 6-derivative, and this is supported

* Acknowledgment is given to Dr. Buu-Hoï, who kindly sent to us reprints of his papers in *Rev. sci*

by the relative stability of the substance to oxidising agents and by the inability of the derived 1 : 6-di-*tert.*-butylacenaphthenequinone to give a thioindigoid vat dye.

Melting points are compared in the attached Table. Although those of 2- and 4-*tert.*-butylnaphthalic anhydride and their analogous derivatives are almost identical, depressions in m. p. of 25—30° are observed in each case.

Position of Bu^t group :	1	2	3
tert.-Butylacenaphthene	65—66°	88—88·5	101·5—102°
Do., picrate	93—95	121—123	Not formed
Do., trinitrobenzene complex	118—119	149—150	87—88
tert.-Butylacenaphthenequinone	152—154·5	156—159	138—139
tert.-Butyl-2 : 7'-thionaphthacenaphthenylindigo	260—262	300—301	186—188

Position of Bu^t group :	2	3	4
tert.-Butylnaphthalic anhydride	163—164°	204—205°	165—166°
tert.-Butylnaphthalimide	201—202	256	208·5—210·5
tert.-Butyl-*N*-methylnaphthalimide	132—133	173	132—133
tert.-Butylnaphthalene, by degradation	2-; picrate, 100—101·5°	2-; picrate, 100—101·5°	1-; picrate, 101·5—102·5°

The migration of *tert.*-butyl groups in this series of compounds, by the action of catalysts, is being investigated. It is noteworthy that 2 : 5-di-*tert.*-butylacenaphthene is an excellent insulating material of convenient melting point (162°), *e.g.*, for thermo-couple joints.

Experimental.

Micro-analyses were carried out by Drs. Weiler and Strauss, of Oxford.

3-tert.-*Butylacenaphthene* (III).—Anhydrous ferric chloride (66 g., 0·2 mol.) was added to a stirred solution of acenaphthene (308 g., 1 mol.) in carbon disulphide (800 c.c.) at 40°. *tert.*-Butyl chloride (240 c.c., 1·1 mols.) was then introduced during 30 minutes, with vigorous stirring; an efficient condensing system is essential, as the hydrogen chloride liberated tends to carry away *tert.*-butyl chloride. After 4 hours' refluxing the mixture was filtered (charcoal), the carbon disulphide distilled off, and the reddish-brown oil fractionated (24" column; steam-jacketed condenser to eliminate loss by sublimation and to prevent blockage), to give unchanged acenaphthene (80 g.), b. p. 270°/760 mm., a mixture (11 g.), b. p. 270—319°, and *tert.*-butylacenaphthenes (125 g.), b. p. 319—321°; the resinous residue, b. p. >360°, was distilled at 15 mm. and yielded 102 g. of a pale yellow glass, b. p. 190—200°. The main fraction (125 g.) solidified and was crystallised repeatedly from absolute alcohol to give large, colourless, prismatic needles, m. p. 101·5—102°, of 3-tert.-*butylacenaphthene* (46 g.) (Found : C, 91·5; H, 8·3. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). On admixture with the 2- (m. p. 88—88·5°) or 1-isomer (m. p. 65—66°), the m. p. was depressed to 58° or 50°, respectively.

From the mother-liquors, a little pure 1-*tert.*-butylacenaphthene (2 g.) was isolated, and a mixture (A) (56 g.), m. p. 48—52° (Found : C, 91·1; H, 8·7%), of isomers, which could not be purified by fractional crystallisation. 3-*tert.*-Butylacenaphthene did not give a picrate, but in absolute alcohol afforded a s-*trinitrobenzene* complex, which crystallised from the same solvent in deep orange needles, m. p. 87—88° (Found : C, 62·7; H, 5·3; N, 9·8. $C_{16}H_{18},C_6H_3O_6N_3$ requires C, 62·4; H, 5·0; N, 9·9%).

The above pale yellow glass (102 g.) was crystallised several times from acetic acid and then alcohol, to yield colourless, prismatic needles, m. p. 135—136·5°, b. p. 358—360°/758 mm., of 1 : 6-*di*-tert.-*butylacenaphthene* (60 g.) (Found : C, 90·4; H, 9·8. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%). On admixture with 2 : 5-di-*tert.*-butylacenaphthene (m. p. 162—163°), the m. p. was depressed to 112°. In absolute alcohol, it gave a *picrate*, which crystallised from absolute alcohol in scarlet needles, m. p. 169—170° (Found : C, 63·2; H, 5·9; N, 8·3. $C_{20}H_{26},C_6H_3O_7N_3$ requires C, 63·0; H, 5·9; N, 8·5%), and a s-*trinitrobenzene* complex, silky orange needles (from absolute alcohol), m. p. 194—195·5° (Found : C, 64·9; H, 5·9; N, 8·6. $C_{20}H_{26},C_6H_3O_6N_3$ requires C, 65·1; H, 5·85; N, 8·8%). On admixture with 2 : 5-di-*tert.*-butylacenaphthene picrate, m. p. 165—165·5°, the m. p. of the 1 : 6-isomer was depressed to 135—140°.

x-*Bromo*-3-tert.-*butylacenaphthene*.—Bromine (1·3 c.c., 1·1 mols.) in chloroform (50 c.c.) was added to a solution of 3-*tert.*-butylacenaphthene (5 g., 1 mol.) in the same solvent (50 c.c.) during 20 minutes, at room temperature. Decolorisation was rapid, and after 1 hour at room temperature alcohol (100 c.c.) was added and the mixture concentrated to 100 c.c., crystallisation then beginning. The *bromo*-derivative crystallised from alcohol–chloroform in colourless needles, m. p. 178—179° (3·1 g., 57%) (Found : C, 66·3; H, 5·7; Br, 27·5. $C_{16}H_{17}Br$ requires C, 66·4; H, 5·9; Br, 27·7%). This bromination differs from that of 2-*tert.*-butylacenaphthene in that the use of 2 mols. of bromine in the above reaction affords solely the same monobromo-derivative.

3-tert.-*Butylacenaphthenequinone*.—Powdered sodium dichromate (45 g.) was added, all at once, with vigorous stirring, to a solution of 3-*tert.*-butylacenaphthene (15 g.) in acetic acid (400 c.c.) at 95°. After 6 minutes, when the vigorous reaction had subsided, the mixture was added to ice-water (600 g.) and set aside for 4 hours. The solid was collected, washed with water, and repeatedly extracted with 5% aqueous sodium carbonate at 80° to remove 4-*tert.*-butylnaphthalic anhydride (2 g., 12%). The insoluble residue was then extracted with sodium metabisulphite (50 g.) in boiling water (500 c.c.), and the extract acidified with hydrochloric acid, and boiled; on cooling, the resulting precipitate was

collected, washed with boiling 5% aqueous sodium carbonate, and crystallised from alcohol in orange-yellow needles, m. p. 138—139°, of 3-tert.-*butylacenaphthenequinone* (3·5 g., 20% of pure quinone) (Found : C, 80·5; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%).

3'- + 4'-tert.-*Butyl*-2 : 7'-*thionaphthenacenaphthenylindigo*.—Freshly prepared 3-hydroxythionaphthen in acetic–hydrochloric acid (5 : 1) was added to a hot solution of 3-*tert.*-butylacenaphthenequinone in acetic acid; a scarlet colour developed immediately and, after 2 minutes' boiling and addition of a little water and cooling, the red precipitate was collected and crystallised several times from acetic acid in deep red prisms, m. p. 186—188°, of the thioindigoid vat *dye* (Found : C, 77·7; H, 4·9; S, 8·4. $C_{24}H_{18}O_2S$ requires C, 77·8; H, 4·9; S, 8·65%). It dissolves in cold concentrated sulphuric acid with a green colour, becoming pink on dilution. No separation could be effected by fractional crystallisation or chromatography, but it is probable that this relatively low-melting dye, which is more soluble in organic solvents than the 1'- or 2'-isomeride, is a mixture of isomers.

3'- + 4'-tert.-*Butyl*-6-*ethoxy*-2 : 7'-*thionaphthenacenaphthenylindigo*.—In similar manner, 6-ethoxy-3-hydroxythionaphthen gave the *dye* in red needles, m. p. 165—167° (shrinks from 163°) (Found : C, 75·4; H, 5·3. $C_{26}H_{22}O_3S$ requires C, 75·4; H, 5·6%), soluble in sulphuric acid with a Bordeaux colour, becoming pink on dilution.

4-tert.-*Butylnaphthalic Anhydride*.—Sodium dichromate (45 g.) was added to a solution of 3-*tert.*-butylacenaphthene (15 g.) in boiling acetic acid (400 c.c.), and the mixture refluxed for 5 hours. On addition of the mixture to ice-water (600 g.), the resulting precipitate was collected and extracted repeatedly with boiling 5% aqueous sodium carbonate. Acidification of the alkaline extracts gave the *anhydride*, which crystallised from alcohol in needles, m. p. 165—166° (16·5 g., 92%) (Found : C, 75·8; H, 5·3. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

4-tert.-*Butylnaphthalimide*, prepared in aqueous alcohol, crystallised from alcohol in prismatic needles, m. p. 208·5—210·5° (Found : C, 75·8; H, 5·6; N, 5·4. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%); the N-*methylimide* crystallised from alcohol in prismatic needles, m. p. 132—133° (Found : C, 76·4; H, 6·1; N, 5·2. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·3; N, 5·2%); and the N-2-*hydroxyethylimide* formed needles, m. p. 127—128° (Found : C, 72·8; H, 6·6; N, 4·3. $C_{18}H_{19}O_3N$ requires C, 72·7; H, 6·4; N, 4·7%). When the anhydride (1 mol.) and *o*-phenylenediamine (1·4 mols.) were boiled in acetic acid for 10 minutes and diluted with a little water, canary-yellow needles of 3'-*keto*-6'(+7')-tert.-*butyl*-2'-*azaperinaphthano*(1' : 2'-2 : 1)*benziminazole* separated (Found : C, 81·1; H, 5·6; N, 8·6. $C_{22}H_{18}ON_2$ requires C, 81·0; H, 5·5; N, 8·6%). The m. p. rose progressively on crystallisation from 188—194° to 220—221°, probably owing to the presence of the 6'- and 7'-*tert.*-butyl isomers. In alcohol solution, there was a strong green fluorescence.

x-Bromo-3-*tert.*-butylacenaphthene (2 g.) was oxidised in the usual way to x-*bromo*-4-tert.-*butylnaphthalic anhydride* (2 g.; 87%), which crystallised from acetic acid in colourless prismatic needles, m. p. 236—237° (Found : C, 57·5; H, 4·1; Br, 24·0. $C_{16}H_{13}O_3Br$ requires C, 57·6; H, 3·9; Br, 24·1%).

4- + 5-tert.-*Butyl*-1-*naphthoic Acid* (method : Leuch *et al.*, *J. Amer. Chem. Soc.*, 1929, **51**, 1835).—4-*tert.*-Butylnaphthalic anhydride (10 g.) was dissolved in boiling water (500 c.c.) containing sodium hydroxide (6·3 g.) in a large flask (much frothing), and a solution of mercuric oxide (8·6 g.) in acetic acid (14 c.c.) and water (37 c.c.) was added. A precipitate was formed immediately, and the suspension, which was just acid to litmus, was refluxed for 98 hours, with intermittent stirring. The solid mercuri-derivative was collected and hydrolysed by refluxing with hydrochloric acid (100 c.c.) and water (200 c.c.) for 2 hours. The resulting light brown solid (7·4 g.) coagulated and was collected and crystallised from alcohol in almost colourless needles, m. p. 130—139°, probably of mixed *tert.*-butyl-1-naphthoic acids.

1-tert.-*Butylnaphthalene*.—(*a*) The mixed *tert.*-butyl-1-naphthoic acids were refluxed with quinoline (20 c.c.) and copper bronze (2·5 g.) for 15 minutes and the mixture was then added to an excess of dilute hydrochloric acid. Distillation with steam, followed by extraction of the distillate with ether, gave 1-tert.-*butylnaphthalene* as an almost colourless oil (5 g., 70% calc. on anhydride), b. p. 90—95°/0·8—1 mm. (Found : C, 91·3; H, 8·2. $C_{14}H_{16}$ requires C, 91·5; H, 8·5%). The derived *picrate* crystallised from absolute alcohol in needles, m. p. 101·5—102·5° (Found : C, 58·0; H, 4·5; N, 10·2. $C_{14}H_{16},C_6H_3O_7N_3$ requires C, 58·1; H, 4·6; N, 10·2%), which depressed the m. p. (100—101·5°) of 2-*tert.*-butylnaphthalene picrate to 80—95°.

(*b*) 4-*tert.*-Butylnaphthalic anhydride (4 g.) was thoroughly ground with soda-lime and the mixture was distilled; the distillate was distilled with steam and gave, as above, 1-*tert.*-butylnaphthalene (1·5 g., 52%), b. p. 100°/2 mm. The picrate (Found : C, 58·0; H, 4·6; N, 10·0%) was identical with that obtained by method (*a*).

Attempted oxidation of 1-*tert.*-butylnaphthalene (0·5 g.) by 5% aqueous nitric acid (14 or 18 c.c.) at 160—180° for 20 hours gave no alkali-soluble naphthoic acid, but yielded a thick yellow oil; dissolution in ether, removal of solvent, and treatment with alcohol gave pale yellow needles, m. p. 91—92·5° (in both cases) (Found : C, 73·7; H, 6·7; N, 6·1. $C_{14}H_{15}O_2N$ requires C, 73·3; H, 6·55; N, 6·1%), of 4-*nitro*-1-tert.-*butylnaphthalene*. Under similar conditions, 2-*tert.*-butylnaphthalene gave oils, from which no solid product was isolable.

1-*tert.*-Butylnaphthalene was refluxed for 8 hours, at b. p. 272°, but an examination of the resulting picrate showed that no conversion into the 2-isomer had occurred. Similarly, 2- and 3-*tert.*-butylacenaphthene were unchanged.

Synthesis of 1-tert.-*Butylnaphthalene*.—1-Tetralone (prep. : Martin and Fieser, *Org. Synth.*, 1935, **15**, 77) (51·1 g., 0·35 mol.) in dry ether (150 c.c.) was added during 20 minutes to a cold ethereal solution (520 c.c.) of *tert.*-butylmagnesium chloride, prepared from magnesium (61 g.) and *tert.*-butyl chloride (227 g.) in ether (1100 c.c.) (evaluated by titration by Gilman's method, *J. Amer. Chem. Soc.*, 1923, **45**,

150). The mixture was refluxed for 2 hours and kept overnight; a mixture of sulphuric acid (25 c.c.) and water (200 c.c.) was added and the resulting precipitate dissolved on shaking. The ethereal layer was collected, washed with water, and dried (Na_2SO_4); removal of ether gave a straw-coloured liquid (57 g.) of the carbinol. This was refluxed with acetic anhydride (300 c.c.) for 4 hours and set aside at room temperature overnight, and then hot water (300 c.c.) was added to decompose excess of acetic anhydride, and the solution neutralised with aqueous sodium carbonate. On ether-extraction, a dark oil (42 g.) resulted, which was distilled and fractionated at 8 mm. to give oils, b. p. 80—100° (8·5 g.), 100—110° (9·3 g.), 110—130° (2·7 g.), and a tarry residue. The three fractions were combined and treated with semicarbazide hydrochloride (15 g.) and sodium acetate (10·7 g.) in boiling alcohol (150 c.c.) and water (150 c.c.) for 15 minutes; water (700 c.c.) was added, and the suspension extracted with ligroin (b. p. 60—80°). The 1-tetralone semicarbazone (total yield, 4·8 g., corresponding to 3·5 g. of 1-tetralone) suspended in the ligroin was filtered off, and the ligroin distilled off, yielding an oil, which was separated into fractions *X*, b. p. up to 100°/5 mm., and *Y*, b. p. 104—106°/5 mm. Fraction *X* (2·8 g.) was heated with sulphur (1·2 g.) at 220—230° for 3 hours, and steam-distillation of the resulting oil gave mainly naphthalene (1·5 g.). Fraction *Y* (8·9 g.) was heated with sulphur (3·5 g.) for 3·5 hours, the temperature being raised slowly to 225—235°; the resulting dark liquid was distilled with steam from 100 c.c. of 20% aqueous sodium carbonate. Naphthalene distilled first, followed by an oil (3·7 g.), b. p. 268—276°/754 mm., separated into fractions, b. p. 270—274° and 274—276°. The former was shown to be mainly 2-*tert.*-butylnaphthalene by oxidation with chromic and acetic acid to 2-*tert.*-butyl-1 : 4-naphthaquinone, m. p. and mixed m. p. 76—77°, whilst the latter fraction was converted in absolute alcohol into a picrate, m. p. 80—95°; fractionation of this picrate from absolute alcohol gave two picrates, *viz.*, (i) 1-*tert.*-butylnaphthalene picrate, pale yellow needles, m. p. 101—102·5° (Found : C, 58·5; H, 4·6; N, 10·7. $C_{14}H_{16},C_6H_3O_7N_3$ requires C, 58·1; H, 4·6; N, 10·2%), which did not depress the m. p. of the product obtained from 4-*tert.*-butylnaphthalic anhydride, and (ii) 2-*tert.*-butylnaphthalene picrate, yellow needles, m. p. 100—101·5°, not depressed on admixture with an authentic specimen, but which depressed the m. p. of the 1-isomer to 77—95°.

1-tert.-*Butylacenaphthene* (I).—This was prepared in a manner similar to that given for the 3-isomer, but the reaction temperature was kept at 10—15°. The resulting product was fractionated to give acenaphthene (84 g.), b. p. 270°, a mixture (9 g.), b. p. 270—319°, mono-*tert.*-butylacenaphthenes (106 g.), b. p. 319—321°, and a residue which afforded di-*tert.*-butylacenaphthenes (114 g.), b. p. 205—230°/7 mm. Fractional crystallisation of the monobutyl fraction from absolute alcohol gave pure 1-tert.-*butylacenaphthene* (28 g.), m. p. 65—66° (Found : C, 91·3; H, 8·4. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%), the 3-isomer (0·7 g.), and a mixture (*B*) (61 g.), m. p. 48—52° (Found : C, 91·3; H, 8·7%), not depressed in m. p. on admixture with (*A*) in the analogous experiment described above. Buu-Hoï and Cagniant (*Rev. sci.*, 1942, **80**, 176) record a *tert.*-butylacenaphthene, an oil, b. p. 155—160°/0·8 mm., considered by them to be the 1-isomer.

Both (*A*) and (*B*) were shown by oxidation (see later) to contain approximately 25% of 3- and 75% of 1-*tert.*-butylacenaphthene. 1-tert.-*Butylacenaphthene picrate* crystallised from absolute alcohol in orange-red needles, m. p. 93—95° (Found : C, 60·2; H, 4·9; N, 9·3. $C_{16}H_{18},C_6H_3O_7N_3$ requires C, 60·1; H, 4·8; N, 9·6%), and a *s-trinitrobenzene* complex, golden-orange needles (from alcohol), m. p. 118—119° (Found : C, 63·0; H, 4·9; N, 10·1. $C_{16}H_{18},C_6H_3O_6N_3$ requires C, 62·4; H, 5·0; N, 9·9%).

The di-*tert.*-butylacenaphthene fraction above gave the 1 : 6-isomer (57 g.), m. p. and mixed m. p. 135—136·5°.

1-tert.-*Butylacenaphthenequinone.*—Sodium dichromate (15 g.) was added all at once to 1-*tert.*-butylacenaphthene (5 g.) in acetic acid (140 c.c.) at 95°, reaction being vigorous and the mixture boiling. After 7 minutes, when reaction had subsided, the mixture was added to ice-water (200 g.) and the resulting solid extracted repeatedly with boiling 5% aqueous sodium carbonate to remove anhydride. The residue was extracted with aqueous sodium metabisulphite and gave 1-tert.-*butylacenaphthene-quinone* (0·8 g.), golden-yellow prisms (from alcohol), m. p. 152—154·5° (Found : C, 80·1; H, 5·9. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%). On admixture with the 3-isomeride, m. p. 138—139°, the m. p. was depressed to 111—117°.

1′-tert.-*Butyl*-2 : 7′-*thionaphthenacenaphthenylindigo.*—Prepared in similar manner to the 3′-analogue, the vat *dye* crystallised from toluene in large greenish-black (reflected light) or deep bluish-red (transmitted light) prisms, m. p. 260—262° (Found : C, 77·8; H, 4·7; S, 8·5. $C_{24}H_{18}O_2S$ requires C, 77·8; H, 4·9; S, 8·65%). It dissolves in concentrated sulphuric acid with a green colour, becoming pink on dilution.

2-tert.-*Butylnaphthalic Anhydride.*—Oxidation of 1-*tert.*-butylacenaphthene (15 g.), as for the 4-isomer, is incomplete after 8 hours, much acenaphthenequinone derivative being unoxidised. The *anhydride*, purified through aqueous sodium carbonate, crystallised from acetic acid in needles, m. p. 163—164° (9·4 g., 52%) (Found : C, 75·5; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%), which depressed the m. p. of the 4-isomer to 130—135°. It was identical with a synthetic specimen (see later).

2-tert.-*Butylnaphthalimide*, prismatic needles (from alcohol), m. p. 201—202°, was prepared by heating the anhydride with aqueous ammonia (*d* 0·88) and alcohol (1 : 1) at 100° (in a sealed tube; essential) for 6 hours (Found : C, 76·3; H, 6·3; N, 5·2. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5%). The corresponding N-*methylimide*, prepared in an analogous manner, crystallised from aqueous alcohol in needles, m. p. 132—133° (Found : C, 76·4; H, 6·2; N, 5·1. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%). Each of these derivatives depressed the m. p. of the respective 4-*tert.*-butyl analogues.

2-tert.-*Butylnaphthalene.*—2-*tert.*-Butylnaphthalic anhydide (5 g.) was distilled with excess of soda-lime, to give 2-*tert.*-butylnaphthalene (2 g.), b. p. 100°/1·8 mm., which yielded a picrate, yellow needles (from absolute alcohol), m. p. 100—101°, not depressed on admixture with an authentic specimen, but depressed to 78—92° on admixture with 1-*tert.*-butylnaphthalene picrate.

Synthesis of 2-tert.-*Butylnaphthalic Anhydride* (cf. Buu-Hoï and Cagniant, *loc. cit.*; Backmann and Sheehan, *J. Amer. Chem. Soc.*, 1941, **63**, 2599, who prepared the ethyl analogue).—Modified methods were used. Pure 2-*tert.*-butylnaphthalene (30 g.), b. p. 102—103°/2 mm. (Bromby *et al.*, *loc. cit.*), was mixed with hydrochloric acid (28 c.c.), acetic acid (24 c.c.), paraformaldehyde (9 g.), and phosphoric acid (14 c.c.) and stirred vigorously at 80—85° for 6 hours. The resulting upper layer was washed twice with water, then with aqueous sodium carbonate, then water, and dissolved in ether (it is important to dry this over potassium carbonate to remove acid and water; otherwise decomposition occurs on distillation). 2-tert.-*Butyl*-1-*chloromethylnaphthalene* (13·5 g.) distilled at 118—126°/0·5 mm. (Found: Cl, 15·6. $C_{15}H_{17}Cl$ requires Cl, 15·3%).

The chloromethyl derivative (18 g.), acetone (180 c.c.), potassium cyanide (17 g.), and water (56 c.c.) were stirred and boiled under reflux for 24 hours. The acetone was removed and the nitrile extracted with ether, isolated, and boiled with hydrochloric acid (60 c.c.), acetic acid (150 c.c.), and water (15 c.c.) for 24 hours. After addition of the mixture to water, the resulting oil was extracted with ether, and the ethereal extract shaken with 10% aqueous sodium hydroxide; the alkali extract was acidified; the resulting oil was extracted with ether, the solvent removed, and the oil distilled, to give a pale brown glass of 2-*tert.*-butyl-1-naphthylacetic acid (10 g.). This was converted by thionyl chloride (+ a little pyridine) in dry ether into the acid chloride, and cyclisation was effected by aluminium chloride (15 g.) in dry benzene (250 c.c.) at 0—5° for 2 hours. 1-*tert.*-Butylacenaphthenone crystallised from alcohol in colourless, prismatic needles, m. p. 91·5—92° (Buu-Hoï and Cagniant give m. p. 92°).

Oxidation of 1 g. with sodium dichromate (3·5 g.) in boiling acetic acid (35 c.c.) for 5 hours gave 2-*tert.*-butylnaphthalic anhydride (1 g., 88%), m. p. and mixed m. p. with that prepared above, 163—164°. Confirmation of this constitution was afforded by preparing the imide, m. p. 201—202°, and *N*-methylimide, m. p. 132—133°, neither of which was depressed in m. p. on admixture with the products already prepared from 1-*tert.*-butylacenaphthene.

Oxidation of Mixed tert.-*Butylacenaphthenes* (A) *and* (B).—(*A*) (10 g.) was oxidised as usual to the mixed *tert.*-butylnaphthalic anhydrides; the first extraction of crude product by boiling 5% aqueous sodium carbonate gave the more soluble 4-*tert.*-butylnaphthalic anhydride (2·2 g.), m. p. and mixed m. p. 165—166°, and three subsequent similar extractions afforded mainly the 2-butylanhydride (2·6 g.), (allowance was made for solubility in dilute hydrochloric acid: 0·18 g. in 1200 c.c.), m. p. and mixed m. p. 163—164°; the insoluble residue was shown to be 1-*tert.*-butylacenaphthenequinone (4·2 g.), but, as expected, no 3-isomeride was isolated. By this means, it is shown that (*A*) and (*B*) (which gave similar results) contain approx. 25% of 3- and 75% of 1-*tert.*-butylacenaphthene.

1 : 6-*Di*-tert.-*butylacenaphthenequinone*.—When oxidised in similar manner to that used for preparing other quinones, 1 : 6-di-*tert.*-butylacenaphthene (15 g.) gave the corresponding *acenaphthenequinone* (4·1 g.), which was purified by chromatography (alumina–benzene), and crystallised from alcohol in yellow needles, m. p. 147—148·5° (Found: C, 81·9; H, 7·4. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%). It would not form a thioindigoid dye when boiled with 3-hydroxythionaphthen in acetic and hydrochloric acids.

When oxidation was prolonged (24 hours), and excess of sodium dichromate (75 g.) was used, 1 : 6-di-*tert.*-butylacenaphthene (15 g.) gave a mixture (15 g.) of the above quinone and 2 : 7-di-*tert.*-butylnaphthalic anhydride; extraction with aqueous sodium carbonate or metabisulphite, crystallisation, or chromatography, did not effect a separation; the mixture, pale yellow crystals, m. p. 127—131°, was used in the following experiment.

2 : 7-*Di*-tert.-*butylnaphthalene*.—The mixture of anhydride and quinone was distilled with soda-lime to yield a solid, which was distilled with steam. The solid part of the distillate crystallised from aqueous alcohol in colourless needles, m. p. 103°, identical with 2 : 7-di-*tert.*-butylnaphthalene prepared from naphthalene or from 3 : 6-di-*tert.*-butylnaphthalic anhydride. Confirmation of this orientation was obtained by conversion into the picrate, yellow needles, m. p. and mixed m. p. 145—146°, and into the complex picrate, orange needles, m. p. 157—158° (cf. Nürsten and Peters, *loc. cit.*).

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