

424. *Butylnaphthalenes and their Derivatives. Part II. Derivatives of 2-tert.-Butylnaphthalene, and the Orientation of Two Di-tert.-butylnaphthalenes.*

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*Nitro-, amino-, sulpho-, and hydroxy-*derivatives of 2-*tert.*-butylnaphthalene have been prepared, and the orientation of two di-*tert.*-butylnaphthalenes, m. p. 145—146°, and 85—90°, is examined.

THE preparation of 2-*tert.*-butylnaphthalene (I) and the determination of its orientation by oxidation and synthesis are recorded by Bromby, Peters, and Rowe (*J.*, 1943, 144). Its nitration and subsequent reduction, and sulphonation, are now described. Thus, with diacetylorthonitric acid (Pictet and Genequand, *Ber.*, 1902, **35**, 2526) at 0—5°, (I) afforded 1-*nitro-2-tert.-butylnaphthalene*, reduced by boiling aqueous-alcoholic sodium hydrosulphite (dithionite) to the corresponding *amine* (II); in ether solution the oily base gave a crystalline hydrochloride and a sulphate, it was diazotised by nitrosylsulphuric acid and converted into 1-(2-*tert.-butylnaphthalene-1-azo*)-2-*hydroxy-3-naphthoic anilide*, and with *p*-nitrobenzenediazonium chloride, it acted as coupling component to yield impure 1-amino-4-*p*-nitrobenzeneazo-2-*tert.*-butylnaphthalene.

Sulphonation of (I) with concentrated sulphuric acid at 95—100° gave 6-*tert.*-butylnaphthalene 2-sulphonic acid, isolated through the *barium* salt, and characterised as the *sulphonamide* and *S-benzylthiuronium* derivative. It was converted by alkaline fusion at 260—280° into 6-*tert.-butyl-2-naphthol* (III). A similar sulphonation of 2-ethylnaphthalene gave the 6-sulpho-derivative (Levy, *Compt. rend.*, 1936, **202**, 1679).

An isomeric *tert.*-butylnaphthol was formed by *tert.*-butylation of 2-naphthol. Thus, Diels and Stein (U.S.P. 1,788,529) and Tschitschibabin (*Bull. Soc. chim.*, 1935, **2**, 1497; *Bull. Acad. Sci. U.S.S.R.*, 1935, 951) record the preparation of a *tert.*-butyl-2-naphthol (the former authors giving m. p. 102° and the latter m. p. 113°) using aluminium chloride and phosphoric acid, respectively, as condensing agent; no orientation is given by Tschitschibabin, but the former authors suggest that the product is 4-*tert.*-butyl-2-naphthol. National Aniline Co. (U.S.P. 2,090,938) describe the interaction of 2-naphthol, *isobutyl* chloride, and zinc chloride, to give a mixture containing a *tert.*-butyl-2-naphthol, which was used without further purification as an intermediate for plastics and azo-dyes. The present authors have treated 2-naphthol with

tert.-butyl chloride in the presence of zinc chloride, aluminium chloride, and phosphoric acid, whereupon the same *tert.*-butyl-2-naphthol (IV), m. p. 119—120° (*picrate*, m. p. 142°), is formed. The sparingly soluble sodium salt of (IV) separates in colourless flakes from a 5% aqueous sodium hydroxide extract of the reaction mixture; this is a much improved method of purification. The alkali-insoluble residue, which is always formed, is the *tert.*-butyl ether, m. p. 139°, of (IV), also obtained from (IV) and *tert.*-butyl chloride in the presence of zinc chloride. The varying m. p.s of (IV) recorded by previous workers are probably due to incomplete separation by the fractional-distillation method used. Compound (IV) readily formed an *acetate*, and as a coupling component it was converted into *m*- and *p*-nitrobenzeneazo-derivatives, reduced by aqueous-alcoholic sodium hydrosulphite (dithionite) to a 1-amino-2-hydroxy-*tert.*-butylnaphthalene, which was decomposed on attempted oxidation. However, the ready formation of the above azo-derivatives excludes substitution of the *tert.*-butyl group in the 1-position, and the *tert.*-butyl group in (IV) probably occupies the 4-position, *i.e.*, in the same ring as the hydroxy-group.

Although di-*tert.*-butylnaphthalenes have been described in the literature, their orientations have not been determined. Gump (*J. Amer. Chem. Soc.*, 1931, **53**, 380) isolated two di-*tert.*-butylnaphthalenes, m. p. 82—83° and 145—146°, which Wegscheider (*Monatsh.*, 1884, **5**, 236) had suggested were 1 : 1- and 1 : 2-dinaphthyls. Fieser and Price (*J. Amer. Chem. Soc.*, 1936, **58**, 1841) recorded m. p. 86—90° for the isomer of lower m. p., whilst Tsukervanik and Terentieva (*J. Gen. Chem. Russia*, 1937, **7**, 637) stated that *tert.*-butyl alcohol, naphthalene, and aluminium chloride gave a di-*tert.*-butylnaphthalene, m. p. 132° (*picrate*, m. p. 99°), and Calcott (*J. Amer. Chem. Soc.*, 1939, **61**, 1010), using hydrofluoric acid as condensing agent, obtained a derivative of m. p. 143°. Price and collaborators (*J. Org. Chem.*, 1942, **7**, 517) recorded m. p.s of 80—82° and 145—146° for the two di-*tert.*-butylnaphthalenes, and stated that repeated crystallisation of the former raised its m. p. to 103—104°. The present authors have worked for several years on these derivatives, and substantiate the experimental work of Price *et al.* Di-*tert.*-butylnaphthalene, m. p. 145—146°, does not form a *picrate* and can be readily separated from the more soluble isomer; the latter, when regenerated from its *picrate*, has m. p. 85—90°, and in this regenerated product the possibility of the presence of a closely-related isomer (*e.g.*, 2 : 6 and 2 : 7) is not overlooked.

The determination of the orientation of the two isomers has now been attempted; previous attempts by Price *et al.* (*loc. cit.*) by nitric acid oxidation failed. The well-known stability of the *tert.*-butyl group to oxidising agents (*cf.* Bromby *et al.*, *loc. cit.*, naphthalene series; Peters, *J.*, 1942, 562, acenaphthene series) is a vital factor in oxidation experiments. One of the *tert.*-butyl groups in both di-*tert.*-butylnaphthalenes must be in the β -position, as the same mixture results by *tert.*-butylating naphthalene and 2-*tert.*-butylnaphthalene.

Chromic acid oxidation of the di-*tert.*-butylnaphthalene, m. p. 145—146°, afforded a steam-volatile di-*tert.*-butyl-1 : 4-naphthaquinone, m. p. 83°, which (*a*) gave a *phenylhydrazone*, probably possessing the *p*-hydroxyazo-structure (*cf.* Linke *et al.*, *Ber.*, 1884, **17**, 3026), (*b*) was convertible into 1 : 4-diacetoxydi-*tert.*-butylnaphthalene (V), m. p. 132—133°, and (*c*) was oxidised by boiling aqueous permanganate, followed by alkaline hydrogen peroxide, to an acid agreeing in analysis with the data required for a di-*tert.*-butylphthalic acid. This suggests that both *tert.*-butyl groups are in the same ring in the di-*tert.*-butylnaphthalene, m. p. 145—146°, which is possibly the 1 : 3-derivative.

The di-*tert.*-butylnaphthalene, m. p. 85—90°, gave a difficultly steam-volatile quinone, which (*a*) afforded a *phenylhydrazone*, differing from that obtained similarly from the other isomer, (*b*) was converted by reductive acetylation into a diacetoxy-derivative, m. p. 114—120°, which on repeated crystallisation gave colourless needles, m. p. 132—133°, not depressed on admixture with (V) (this anomalous behaviour is not clear), and (*c*) was oxidised by permanganate to give a low yield of an acid, the analysis of which suggested a mono-*tert.*-butylphthalonic acid. Thus, the *tert.*-butyl groups are probably in different rings in the di-*tert.*-butylnaphthalene, m. p. 85—90°, which is probably the 2 : 6-derivative. However, as this was possibly a mixture of isomers, the results are not regarded as conclusive. We regard the isomer, m. p. 85—90°, as a compound in which the *tert.*-butyl groups are certainly in different rings.

EXPERIMENTAL.

Preparation of 2-tert.-Butylnaphthalene and the Two Di-tert.-butylnaphthalenes (*cf.* Bromby *et al.*, *loc. cit.*).—The method of isolation of the mixed *tert.*-butylnaphthalenes was modified. The reaction mixture was cooled in an ice-salt mixture, filtered, and the filtrate distilled with steam until the last traces of naphthalene were removed; the dried oil was then fractionally distilled to give 2-*tert.*-butylnaphthalene, b. p. 128°/6 mm., and almost equal amounts of two di-*tert.*-butylnaphthalenes, m. p.

145—146°, and m. p. 85—90°. The latter formed a picrate, orange needles, m. p. 157—158°, decomposed by 5% aqueous sodium hydroxide to the hydrocarbon, m. p. 85—90°; repeated crystallisation of the latter from alcohol gave a product, m. p. 102—103°. The same mixture of di-*tert.*-butylnaphthalenes resulted from the *tert.*-butylation of authentic 2-*tert.*-butylnaphthalene.

1-Nitro-2-*tert.*-butylnaphthalene.—Diacetylorthonitric acid (38 g., 33 c.c., 1.25 mols.) was added to a well-stirred mixture of 2-*tert.*-butylnaphthalene (30 g.; 1 mol.) and acetic anhydride (30 c.c.) at 0—5° during one hour. After being left overnight at room temperature, the mixture was added to ice and extracted with ether and the ether extract was washed well with aqueous sodium carbonate and water until free from acid, and dried (Na₂SO₄). After removal of the ether, the residue was distilled, giving the *nitro*-compound as a colourless oil, b. p. 250°/85 mm. (22.8 g.; 60%), which on being kept became reddish-brown (Found: C, 74.0; H, 6.6; N, 6.5. C₁₄H₁₅O₂N requires C, 73.3; H, 6.55; N, 6.1%). Numerous attempts at further nitration gave only a resinous polynitro-derivative, and no crystalline derivative of definite m. p. could be characterised.

1-Amino-2-*tert.*-butylnaphthalene (II).—The above mononitro-compound (40 g.) was suspended in alcohol (300 c.c.) and the mixture refluxed gently during the addition (2 hours) of sodium hydrosulphite (dithionite) (160 g.) in water (350 c.c.). The mixture was diluted with water and extracted with ether yielding an oil, which when distilled gave the *amine* (II) as a reddish-brown oil, b. p. 238—242°/85 mm. (13.5 g.; 41%) (Found: C, 84.0; H, 9.0; N, 7.0. C₁₄H₁₇N requires C, 84.4; H, 8.5; N, 7.0%). Attempted preparation of the acetyl and toluene-*p*-sulphonyl derivatives gave sticky solids. The hydrochloride and sulphate, which were sticky when obtained from aqueous solution, were obtained in colourless crystals when a solution of the base in dry ether was treated with dry hydrogen chloride and monohydrate, respectively. Attempted oxidation of the amine with chromic acid gave only resins.

1-(2-*tert.*-Butylnaphthalene-1-azo)-2-hydroxy-3-naphthamide.—A solution of the amine (II) (3 g.) in acetic acid (30 c.c.) was added to nitrosylsulphuric acid at 5° and the mixture poured on ice and filtered; the clear filtrate was coupled with Naphthol AS to give the *azo*-derivative (4 g.), which crystallised from acetic acid in lustrous greenish-violet prisms, decomp. 145—150° (Found: C, 77.8; H, 5.4; N, 8.5. C₂₃H₂₇O₃N₃ requires C, 78.6; H, 5.7; N, 8.9%), which gave a blue solution in cold concentrated sulphuric acid.

1-Amino-4-*p*-nitrobenzeneazo-2-*tert.*-butylnaphthalene.—Diazotised *p*-nitroaniline (1.5 g.) was added to a solution of the amine (II) (1.5 g.) in alcohol (100 c.c.) at room temperature. After 15 minutes, sodium acetate was added and the residue of *azo*-dye separated from aqueous acetic acid as an amorphous powder, m. p. 146—150° (Found: N, 18.2. C₂₀H₂₀O₃N₄ requires N, 16.4%).

6-*tert.*-Butylnaphthalene-2-sulphonic Acid.—2-*tert.*-Butylnaphthalene (54 g.) and concentrated sulphuric acid (45 g.) were heated at 95—100° for 7 hours, the mixture was then kept overnight at room temperature and poured into ice-water. Unchanged 2-*tert.*-butylnaphthalene was removed by extraction with ether, and the aqueous solution treated with barium carbonate and the *barium* salt of the sulphonic acid isolated (Found: C, 48.6; H, 4.9; S, 8.9. C₂₈H₃₀O₆S₂Ba₂·2H₂O requires C, 48.05; H, 4.9; S, 9.15%). Potassium sulphate converted this into the *potassium* salt (Found: S, 10.7. C₁₄H₁₅O₂SK requires S, 10.6%), which with excess of phosphorus pentachloride afforded the acid chloride as a sticky mass (solidifies at -15°), and thence the *sulphonamide*, colourless prisms (from aqueous alcohol), m. p. 201—202° (Found: C, 63.9; H, 6.3; N, 5.5; S, 12.7. C₁₄H₁₇O₂NS requires C, 63.9; H, 6.5; N, 5.3; S, 12.2%). The *S*-benzylthiuronium derivative crystallised from alcohol in colourless prisms, m. p. 210—211° (Found: C, 61.6; H, 6.2; N, 5.9; S, 15.3. C₂₂H₂₆O₃N₂S₂ requires C, 61.4; H, 6.05; N, 6.0; S, 15.0%).

6-*tert.*-Butyl-2-naphthol (III).—The powdered potassium salt (20 g.) above was added to a stirred melt of sodium hydroxide (50 g.) and water (3 c.c.) at 230°. After the temperature had been slowly raised to 260° (30 minutes) and then to 280°, the melt was kept at this temperature for 40 minutes. The resulting oily layer was separated and extracted with dilute sodium hydroxide solution. The alkaline extract was acidified and extracted with ether, the ether extract dried (Na₂SO₄), and the residue distilled to give the *naphthol* as a pale yellow oil, b. p. 239—241°/160 mm. (Found: C, 83.3; H, 7.5. C₁₄H₁₆O requires C, 84.0; H, 8.0%).

4(?)*tert.*-Butyl-2-naphthol (IV).—(a) 2-Naphthol (50 g.), light petroleum (b. p. 60—80°) (150 c.c.), and anhydrous zinc chloride (15 g.) were stirred at room temperature during the addition of *tert.*-butyl chloride (50 g.). The mixture was gradually heated to 70° (oil-bath) and kept at this temperature for one hour, and then at 70—95° for 4 hours. After removal of excess of *tert.*-butyl chloride and light petroleum, the residue was boiled with 5% aqueous sodium hydroxide (1200 c.c.) and filtered; on cooling, the filtrate deposited colourless flakes of the sodium salt of a *tert.*-butyl-2-naphthol, converted by hydrochloric acid into 4(?)*tert.*-butyl-2-naphthol (IV) (21 g.), which crystallised from light petroleum in colourless plates, m. p. 119—120° (Found: C, 83.9; H, 7.9. Calc. for C₁₄H₁₆O: C, 84.0; H, 8.0%). The residue (30 g.) insoluble in sodium hydroxide was crystallised from light petroleum, and 2-*tert.*-butoxy-4(?)*tert.*-butylnaphthalene separated in colourless needles, m. p. 138—139° (Found: C, 84.3; H, 9.5. C₁₈H₂₄O requires C, 84.3; H, 9.4%). The ether could be prepared directly from the naphthol (IV) by further *tert.*-butylation in presence of zinc chloride.

The *picrate* of (IV) crystallised from alcohol in orange needles, m. p. 142° (Found: C, 55.9; H, 4.2; N, 9.8. C₂₀H₁₉O₃N₃ requires C, 55.9; H, 4.4; N, 9.8%). The *acetate* of (IV) separated from alcohol in colourless needles, m. p. 64° (Found: C, 79.8; H, 7.8. C₁₆H₁₈O requires C, 79.3; H, 7.4%). Coupling of *m*-nitrobenzenediazonium chloride to (IV) in aqueous-alcoholic sodium hydroxide gave the *m*-nitrobenzeneazo-derivative, which crystallised from acetic acid in orange-red needles, m. p. 177° (Found: C, 69.6; H, 5.2; N, 11.7. C₂₀H₁₉O₃N₃ requires C, 68.8; H, 5.5; N, 12.0%).

(b) 2-Naphthol (40 g.; 1 mol.), light petroleum (150 c.c.), *tert.*-butyl chloride (54 g.; 3 mols.), and anhydrous aluminium chloride (5 g.; 0.2 mol.) at 50—60° for 5 hours also gave (IV) (12 g.), m. p. 119—120° (confirmed by picrate), and its *tert.*-butyl ether (21 g.), m. p. 138°, not depressed on admixture with the products obtained by method (a).

(c) 2-Naphthol (30 g.), phosphoric acid (*d* 1.75; 65 c.c.), and *tert.*-butyl alcohol (20 g.), stirred at 95° for 3 hours and then at 100—110° for 4 hours, afforded (IV) (8 g.) and its *tert.*-butyl ether (12 g.).

1-Amino-2-hydroxy-4(?)-tert.-butyl-naphthalene.—1-*p*-Nitrobenzeneazo-4(?)-tert.-butyl-2-naphthol (15 g.), m. p. 250—253°, was reduced with boiling aqueous-alcoholic sodium hydrosulphite (dithionite) for 4 hours; removal of alcohol and cooling gave the *amino-naphthol*, which crystallised from benzene in pale yellow plates, decomp. 150° (Found : C, 77.6; H, 7.7; N, 7.0. $C_{14}H_{17}ON$ requires C, 78.1; H, 7.9; N, 6.5%).

Oxidation of Di-tert.-butyl-naphthalene, m. p. 145—146°.—Chromium trioxide (44 g.) in acetic acid (80 g.) and water (40 c.c.) was added to a stirred solution of the di-tert.-butyl-naphthalene (22 g.) in acetic acid (200 c.c.); reaction was vigorous, and after boiling under gentle reflux for one hour, the mixture was added to ice; the precipitate (15 g.) was collected and crystallised from alcohol in pale yellow leaflets, m. p. 83—84°, of a steam-volatile di-tert.-butyl-1 : 4-naphthaquinone (Found : C, 79.8; H, 8.1. Calc. for $C_{18}H_{12}O_2$: C, 79.7; H, 8.1%) (cf. Price *et al.*, *loc. cit.*, who record m. p. 83—83.5°), which does not give a quinoxaline derivative with *o*-phenylenediamine in acetic acid (*e.g.*, *o*-quinones), but affords a *phenylhydrazone*, red needles (from alcohol), m. p. 188° (Found : C, 80.2; H, 7.7; N, 8.0. $C_{24}H_{28}ON_2$ requires C, 80.0; H, 8.0; N, 7.7%). With boiling acetic acid (8 c.c.), acetic anhydride (30 c.c.), anhydrous sodium acetate (2 g.), and zinc dust (3 g.), 3 g. of quinone gave 2.5 g. of 1 : 4-diacetoxydi-tert.-butyl-naphthalene, which crystallised from light petroleum in colourless needles, m. p. 133° (Found : C, 74.0; H, 7.7. Calc. for $C_{22}H_{28}O_4$: C, 74.1; H, 7.9%) (Price *et al.* record m. p. 139—140°). Oxidation of the quinone (10 g.) was carried out by suspending it in water (300 c.c.) and adding a solution of potassium permanganate (20 g.) in water (600 c.c.) to the stirred mixture during 3 hours. After boiling for a total of 8 hours, excess of permanganate was destroyed and the mixture made alkaline with sodium hydroxide. It was then filtered and the filtrate (charcoaled) acidified with hydrochloric acid and extracted with ether; the ether extract was dried (Na_2SO_4) and after removal of ether, the oily residue (5 g.) was dissolved in hydrogen peroxide (5 c.c.; 100 vols.) and aqueous sodium hydroxide (25 c.c.; 10%) and left for 12 hours at room temperature. Ether extraction gave an oily residue which was boiled with light petroleum for 10 minutes, this separating the product into an insoluble colourless solid and a filtrate which yielded a sour-smelling oil. The solid was crystallised several times from chloroform-light petroleum to give colourless cubes (0.8 g.), m. p. 184—185°, the analysis agreeing with that required for a di-tert.-butylphthalic acid (Found : C, 69.3; H, 7.6. $C_{18}H_{22}O_4$ requires C, 69.1; H, 7.9%), but which gave an oil on boiling with acetic anhydride.

Oxidation of Di-tert.-butyl-naphthalene, m. p. 85—90°.—The di-tert.-butyl-naphthalene (5 g.), regenerated from its picrate, was boiled with chromic acid (10 g.), acetic acid (80 c.c.), and water (25 c.c.) for one hour, and gave a sticky yellow quinone, which could not be crystallised. It gave a *phenylhydrazone*, orange-red needles (from alcohol), m. p. 178—180° (Found : C, 79.4; H, 7.7; N, 7.6. $C_{24}H_{28}ON_2$ requires C, 80.0; H, 8.0; N, 7.7%), which depressed the m. p. of the isomer described above to 165—170°. The crude quinone was converted by reductive acetylation into colourless needles, m. p. 114—120° rising on repeated crystallisation from light petroleum to 132—133°, which on admixture with the diacetoxy-derivative described above showed no depression in m. p. The crude quinone was further oxidised as above to give colourless needles (from chloroform-light petroleum), m. p. 129—130° (Found : C, 62.8; H, 6.5. Calc. for $C_{13}H_{14}O_5$: C, 62.4; H, 5.6%), possibly of a mono-tert.-butylphthalonic acid.

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