45. *Butylnaphthalenes and their Derivatives. Part I.* β-tert.-*Butylnaphthalene.*

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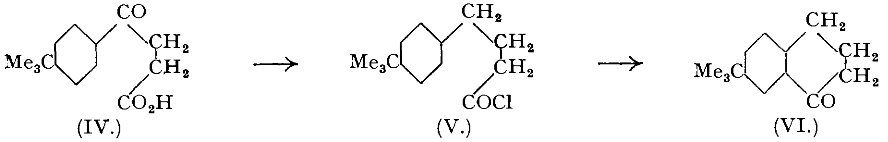
β-tert.-Butylnaphthalene (I), prepared by condensing *tert.*-butyl chloride or *iso*butyl bromide with naphthalene in presence of anhydrous zinc chloride, or by dehydrogenating *β-tert.*-butyltetrahydronaphthalene, has been oriented by oxidation and by synthesis, and literature concerning it clarified. 2-tert.-*Butyl*-1 : 4-*naphthaquinone* and 4-tert.-*butylphthalic acid* and *anhydride* are characterised.

Although α- and β-*tert.*-butylnaphthalenes have been described in the literature, they have not been definitely characterised. Wegscheider (*Monatsh.*, 1884, **5**, 236) and Baur (*Ber.*, 1894, **27**, 1623) prepared a *tert.*-butylnaphthalene, b. p. 280° (picrate, m. p. 96°), from *iso*butyl halide, naphthalene, and aluminium chloride. Gump (*J. Amer. Chem. Soc.*, 1931, **53**, 380) stated that this compound was probably identical with the α-*tert.*-butylnaphthalene, b. p. 278—287°, obtained by Späth (*Monatsh.*, 1913, **34**, 1965) from α-naphthylmagnesium bromide and *tert.*-butyl bromide. By condensing *tert.*-butyl chloride with naphthalene in presence of aluminium chloride, Gump failed to obtain *tert.*-butylnaphthalene and isolated only two di-*tert.*-butylnaphthalenes, m. p. 82—83° and 145—146°, which Wegscheider (*loc. cit.*) had suggested were probably αβ- and αα-dinaphthyls. Fieser and Price (*J. Amer. Chem. Soc.*, 1936, **58**, 1841), however, prepared *tert.*-butylnaphthalene, b. p. 127—131°/9 mm. (picrate, m. p. 99·5—100·5°), by this reaction, and assumed it to be the β-isomeride. Tsukervanik and Terentieva (*J. Gen. Chem. U.S.S.R.*, 1937, **7**, 637) described α-, b. p. 287—289° (picrate, m. p. 92—93°), and β-*tert.*-butylnaphthalene, b. p. 274—276° (picrate, m. p. 84—85°), which they prepared by condensing *tert.*-butyl alcohol with naphthalene, using aluminium chloride, and claimed to have oriented by oxidation to the corresponding naphthoic acids with dilute nitric acid.

We have found anhydrous zinc chloride preferable to aluminium chloride in condensing *tert.*-butyl chloride with naphthalene, as the reaction proceeds readily at 70—100°, without charring, to give an easily purified product, consisting mainly of β-*tert.*-butylnaphthalene (I), b. p. 125°/4 mm. (picrate, m. p. 100—101·5°), together with the two di-*tert.*-butylnaphthalenes described by Gump (*loc. cit.*). *iso*Butyl bromide condenses less readily to give (I). A *tert.*-butyltetrahydronaphthalene has been prepared from the *tert.*-butyl halide and tetrahydronaphthalene in presence of the aluminium halide (Boedtker and Rambech, *Bull. Soc. chim.*, 1924, **35**, 633; Barbot, *ibid.*, 1930, **47**, 1314), but we found that *tert.*-butyl chloride and tetrahydronaphthalene are best condensed in presence of zinc chloride, and dehydrogenation of the product gives (I).

No naphthoic acid was obtained by attempted oxidation of (I), by potassium permanganate in water, aqueous acetic acid or acetone, by alkaline potassium ferricyanide, or by dilute nitric acid under reflux or at 160—200° in a sealed tube. Compound (I) was oriented by oxidation with chromic acid to a *p*-quinone shown to be 2-tert.-*butyl*-1 : 4-*naphthaquinone* (II) by oxidation with permanganate to phthalic acid. Chromatographic analysis (alumina; ligroin) carried out on accumulated residues from crystallisations of the crude quinone gave pure (II) and no 2-*tert.*-butyl-5 : 8-naphthaquinone. In an attempt to orient the *hydrazones* (III) prepared from (II), *tert.*-butyl chloride, α-naphthol, and anhydrous zinc chloride were brought into reaction in ligroin, but gave an inseparable mixture of *tert.*-butyl-α-naphthols, from which no compound identical with (III) could be isolated after coupling with the appropriate diazo-compound.

The structure of (I) was confirmed by synthesis. *tert.*-Butylbenzene was prepared in 44% and 60% yield by condensing *tert.*-butyl alcohol with benzene in presence of ferric chloride and aluminium chloride, respectively: Potts and Dodson (*J. Amer. Chem. Soc.*, 1939, **61**, 2553), without giving experimental details, claimed yields of 82% and 50%, respectively, in these reactions. *tert.*-Butylbenzene and succinic anhydride (Friedel–Crafts) yielded β-(*p-tert.*-butylbenzoyl)propionic acid (IV), reduced (Clemmensen) to γ-(*p-tert.*-butylphenyl)butyric acid (cf. Fieser and Price, *loc. cit.*). Cyclisation of the corresponding chloride (V) gave 1-*keto*-7-tert.-*butyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VI), reduced (Clemmensen) to 7-*tert.*-butyl-1 : 2 : 3 : 4-tetrahydronaphthalene, which was dehydrogenated by sulphur to β-*tert.*-butylnaphthalene, identical in all respects with (I) obtained from naphthalene or tetrahydronaphthalene.



(IV.) (V.) (VI.)

The experiments of Tsukervanik and Terentieva (*loc. cit.*) were repeated and a low yield of (I) was obtained, but no α-*tert.*-butylnaphthalene or di-*tert.*-butylnaphthalene, m. p. 132° (picrate, m. p. 99°), as described by these authors. In general, our experiments have substantiated the work of Fieser and Price (*loc. cit.*) on β-*tert.*-butylnaphthalene and have shown the views of other workers on the butylation of naphthalene to be partially or wholly incorrect.

4-tert.-*Butylphthalic acid* and *anhydride* were prepared by oxidising β-*tert.*-butyltetrahydronaphthalene with alkaline permanganate, and treating the resulting phthalonic acids with alkaline peroxide.

EXPERIMENTAL.

β-tert.-*Butylnaphthalene.*—(*a*) *Condensation of* tert.-*butyl chloride with naphthalene.* Naphthalene (256 g.; 2 mols.), *tert.*-butyl chloride (92·5 g.; 1 mol.), and powdered anhydrous zinc chloride (68 g.; 0·5 mol.) were agitated and heated in an oil-bath until gentle refluxing with steady evolution of hydrogen chloride began at 70—75°. After the temperature had been raised to 95—105° during 6 hours, the cooled, decanted reaction mixture was filtered, and the filtrate fractionated to give β-*tert.*-butylnaphthalene (I), b. p. 125°/4 mm., 137—139°/17 mm., 274—277°/756 mm. (yield of pure compound, 61 g.; 33·1%) (Found: C, 91·0; H, 8·95. Calc. for $C_{14}H_{16}$: C, 91·3; H, 8·7%). Naphthalene from lower fractions and di-*tert.*-butylnaphthalenes from the higher-boiling fractions are best removed by cooling and filtration. The picrate crystallised from dry alcohol in yellow needles, m. p. 100—101·5° (Found: C, 57·6; H, 4·6; N, 10·4. Calc. for $C_{14}H_{16},C_6H_3O_7N_3$: C, 58·1; H, 4·6; N, 10·2%).

Fractional crystallisation from alcohol of the solid residues (yield, approximately 12%) from the fractions, b. p. 280—330°, yielded the di-*tert.*-butylnaphthalenes described by Gump, and by Fieser and Price (*loc. cit.*), *viz.*, large colourless plates, m. p. 146—147° (Found: C, 90·0; H, 9·8. Calc. for $C_{18}H_{24}$: C, 90·0; H, 10·0%) (does not form a picrate), and colourless needles, m. p. 85—90° (repeated crystallisation raises m. p. to 90—95°), best purified by conversion into its picrate, golden-yellow needles, m. p. 157—158°, and regeneration by warm dilute alkali.

(*b*) *Condensation of* iso*butyl bromide with naphthalene.* Naphthalene (85 g.), *iso*butyl bromide (44 g.), and powdered anhydrous zinc chloride (30 g.) were refluxed on the water-bath for 24 hours. Distillation of the dark reaction mixture gave β-*tert.*-butylnaphthalene, b. p. 275—278° (yield, 14 g.; 23·7%), identical with (I). No di-*tert.*-butylnaphthalene was obtained.

(*c*) *Dehydrogenation of* β-tert.-*butyltetrahydronaphthalene.* Tetrahydronaphthalene (396 g.; 3 mols.), *tert.*-butyl chloride (92·5 g.; 1 mol.), and powdered anhydrous zinc chloride (28 g.; 0·2 mol.) reacted, under conditions similar to those described in (*a*), to give β-*tert.*-butyltetrahydronaphthalene, b. p. 138—140°/18 mm., 262—264°/752 mm. (yield, 57 g.; 30·3%) (Found: C, 89·5; H, 10·6. Calc. for $C_{14}H_{20}$: C, 89·4; H, 10·6%), which does not form a picrate. It (56 g.) was heated with sulphur (19·5 g.) in an oil-bath at 215—230° for 4 hours and gave β-*tert.*-butylnaphthalene, b. p. 274—278° (yield, 32 g.; 58·4%), identical with (I).

2-tert.-*Butyl*-1 : 4-*naphthaquinone* (II).—Chromic acid (10 g.) in 50% aqueous acetic acid (25 c.c.) was added rapidly to a solution of (I) (5 g.) in acetic acid (35 c.c.), and the mixture stirred at 65—70° for 2 hours. The diluted reaction mixture was distilled with steam. 2-tert.-*Butyl*-1 : 4-*naphthaquinone* (II) (yield, 1·8 g.; 31%) crystallised from alcohol or ligroin in yellow plates, m. p. 76—77° (Found: C, 79·05; H, 6·5. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). When (II) (1 g.) was refluxed in water (20 c.c.), and potassium permanganate (2 g.) in water (50 c.c.) added, phthalic acid (0·12 g.) was obtained. The derived *phenylhydrazone* (III*a*) crystallised from alcohol in red needles with a green reflex, m. p. 190—191° (Found: C, 78·3; H, 6·7; N, 9·3. $C_{20}H_{20}ON_2$ requires C, 78·95; H, 6·6; N, 9·2%), and the p-*nitrophenylhydrazone* (III*b*) from acetic acid in minute, orange prisms, m. p. 264—265° (decomp.) (Found: C, 68·6; H, 5·4; N, 12·3. $C_{20}H_{19}O_3N_3$ requires C, 68·8; H, 5·4; N, 12·0%).

Synthesis of β-tert.-*Butyl-tetrahydronaphthalene and -naphthalene.*—*tert.*-Butyl alcohol (74 g.; 1 mol.) was condensed with benzene (390 g.; 5 mols.) by stirring at room temperature with anhydrous ferric chloride (162·5 g.; 1 mol.) or aluminium chloride (133·5 g.; 1 mol.), for 7 or 4 hours, respectively, to give *tert.*-butylbenzene, b. p. 164—168° (yield, 59 g., 44%, or 81 g., 60·5%, respectively) (cf. Potts and Dodson, *loc. cit.*). This was converted into β-(*p*-*tert.*-butylbenzoyl)-propionic acid (IV) (cf. Fieser and Price, *loc. cit.*); the *semicarbazone* crystallised from aqueous acetic acid in colourless prisms, m. p. 204—205° (decomp.) (Found: C, 62·4; H, 7·2. $C_{15}H_{21}O_3N_3$ requires C, 61·8; H, 7·2%). Compound (IV) (35 g.) was refluxed with hydrochloric acid (300 c.c.) and amalgamated zinc (70 g.) for 15 hours, and the mixture cooled and filtered; the solid, together with an ethereal extract of the filtrate, yielded γ-(*p*-*tert.*-butylphenyl)butyric acid, b. p. 218—221°/30 mm., which crystallised from ligroin in colourless, prismatic needles, m. p. 59—60° (yield, 27 g.; 82%). It (45 g.) was heated with thionyl chloride (52 g.) in ligroin (230 c.c.; b. p. 60—80°) on the water-bath for 3·5 hours and yielded γ-(*p*-*tert.*-butylphenyl)butyryl chloride (V), b. p. 152—154°/14 mm. (yield, 41·5 g.; 85%). The corresponding *butyramide* crystallised from alcohol in colourless plates, m. p. 132—134° (Found: C, 77·0; H, 9·45; N, 6·55. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·6; N, 6·4%).

Compound (V) (31 g.) in ligroin (30 c.c.; b. p. 60—80°) was added to aluminium chloride (21 g.) covered with ligroin, and the mixture refluxed for 3 hours. The cooled mixture was decomposed with cold dilute hydrochloric acid and filtered hot; the ligroin layer, combined with an ethereal extract of the residue and aqueous liquor, yielded 1-*keto*-7-tert.-*butyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (VI), which crystallised from alcohol in colourless leaflets, m. p. 101—102·5° (yield, 19 g.; 72·3%) (Found: C, 83·0; H, 8·8. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). The *semicarbazone* crystallised from alcohol in colourless prismatic needles, m. p. 225—226° (Found: C, 69·4; H, 7·9. $C_{15}H_{21}ON_3$ requires C, 69·5; H, 8·1%).

The ketone (VI) (14·6 g.) was refluxed with hydrochloric acid (350 c.c.) and amalgamated zinc (100 g.) for 30 hours. The hydrocarbon was removed by distillation with steam, and unreduced ketone further treated as described. Ethereal extracts of the combined steam distillates gave β-*tert.*-butyltetrahydronaphthalene, b. p. 135—136°/16 mm. (yield, 5·8 g.; 43%). It (5·64 g.) was heated with sulphur (1·92 g.) at 220—230° for 3·5 hours, and the dark oil distilled with steam in presence of sodium carbonate. The resulting β-*tert.*-butylnaphthalene, b. p. 124—125°/5 mm. (yield, 4·1 g.; 74·3%), afforded a picrate, m. p. 100—101·5°, identical with that obtained from (I), and chromic acid oxidation of the hydrocarbon gave (II), m. p. and mixed m. p. 76—77°.

4-tert.-*Butylphthalic Acid and Anhydride.*—β-*tert.*-Butyltetrahydronaphthalene (36 g.) was stirred vigorously under reflux with water (200 c.c.) and sodium carbonate (30 g.) at 95°, and potassium permanganate (210 g.) added gradually during 30 hours. After filtration, an ethereal extract of the acidified filtrate gave a sticky substance (29·3 g.), which was probably a mixture of the two isomeric *tert.*-butylphthalonic acids with some *tert.*-butylphthalic acid. This mixture (18·3 g.) was dissolved in 12% cold aqueous sodium hydroxide (60 c.c.), and hydrogen peroxide (100 vol.; 20 c.c.) added slowly, with shaking. There was some effervescence and, after 3 hours at room temperature, the mixture was acidified with hydrochloric acid and extracted with ether. Removal of the ether gave an oil (15·5 g.) which solidified after several hours at room temperature. Crystallisation from benzene gave 4-tert.-*butylphthalic acid* in colourless plates, m. p. 160—161° (yield, calc. on the β-*tert.*-butyltetrahydronaphthalene, 26·6%) (Found: C, 64·5; H, 6·15. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%). Heating with acetic anhydride gave 4-tert.-*butylphthalic anhydride*, which crystallised from ligroin in colourless plates, m. p. 75·5—76·5° (Found : C, 70·8; H, 5·7. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%). These compounds gave a strongly positive fluorescein test.

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