123. *New Intermediates and Dyes. Part II.* Preparation and Properties of* 4-tert.-*Butylphthalic Anhydride. Orientation of its Condensation Products with Benzenoid Hydrocarbons.*

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The properties of 4-*tert.*-butylphthalic anhydride are examined and many new derivatives are prepared. The carbonyl group *para* to the *tert.*-butyl group is the more reactive in Friedel–Crafts condensations with benzenoid hydrocarbons. The orientation of the derived *tert.*-butylbenzoylbenzoic acids was shown by decarboxylation to the respective *tert.*-butylbenzophenones, which were compared with synthetic specimens.

4-*tert.*-Butyl-*o*-xylene was prepared in 73% yield by interaction of a slight excess of *tert.*-butyl chloride and *o*-xylene in presence of anhydrous ferric chloride at room temperature, whereby loss of *tert.*-butyl chloride (at 70—80°) was eliminated and no di-*tert.*-butyl-*o*-xylene was formed (cf. Nightingale and Janes, *J. Amer. Chem. Soc.*, 1944, **66**, 154; Contractor and Peters, *J.*, 1949, 1314). 4-*tert.*-Butyl-*o*-xylene was unchanged by chromic acid in boiling acetic acid, but was oxidised with potassium permanganate in boiling aqueous pyridine to give 50% of 4-*tert.*-butylphthalic acid and 9% of 4-*tert.*-butyl-2-methylbenzoic acid, which are converted by boiling acetic anhydride into the respective anhydrides. The resistance of the *tert.*-butyl group to oxidation, thus illustrated, has already been discussed (Contractor and Peters, *loc. cit.*).

The constitution of 4-*tert.*-butylphthalic anhydride (I) was confirmed by its conversion into trimellitic acid by dilute nitric acid at 200—210°.

No derivative of this anhydride (I) has been described in the literature, and we have now examined its reactions and compared the effect of the *tert.*-butyl group with that of other alkyl groups in reactions of alkylphthalic anhydrides.

With aqueous ammonia in boiling alcohol, the anhydride gave diammonium 4-*tert.*-butylphthalate, whilst with solely aqueous ammonia at 330° 4-*tert.*-butylphthalimide was formed; the *N*-methylphthalimide was prepared similarly. The anhydride was further characterised as the phthalanil and phthalanildianisidide, and as the pyridinium *tert.*-butylphthalanil of sulphanilic acid and metanilic acid, respectively. It can thus be used as a reagent for the identification of amines, and also of aromatic sulphonic acids (at least, of the two mentioned) (cf. Cross and Chen, *J. Soc. Dyers and Col.*, 1943, **59**, 144). The anhydride was also converted into the liquid dimethyl and diethyl, and the solid di-(*p*-nitrobenzyl) 4-*tert.*-butylphthalate.

Condensation of a 4-alkylphthalic anhydride with an alkylbenzene could theoretically produce six isomeric dialkylbenzoylbenzoic acids; the fact that *meta*-condensation has not been observed reduces this number probably to four; and it has been shown that reaction occurs mainly at the *p*-position of the alkylbenzene. Thus, Peters and Rowe (*J.*, 1945, 181) condensed phthalic anhydride with *tert.*-butylbenzene to give *o*-*p*′-*tert.*-butylbenzoylbenzoic acid, and Fieser and Price (*J. Amer. Chem. Soc.*, 1936, **58**, 1840) obtained β-*p*-*tert.*-butylbenzoylpropionic acid from succinic anhydride.

The 4-*tert.*-butyl anhydride was condensed with benzene, toluene, and *tert.*-butyl-

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* Part I, *J.*, 1949, 1314.

benzene severally in the Friedel–Crafts reaction, using aluminium chloride. Benzene afforded mainly 2-benzoyl-5-*tert.*-butylbenzoic acid; Hayashi (*J.*, 1927, 2516; 1930, 1513) obtained mixed acids in a similar reaction using 4-methylphthalic anhydride. In the case of toluene, the carboxylic acids derived from the *tert.*-butyl anhydride were fractionally crystallised, yielding mainly 5-*tert.*-butyl-2-*p*-toluoylbenzoic acid; on dissolution in cold concentrated sulphuric acid, the latter isomerised to a mixture of *tert.*-butyltoluoylbenzoic acids, a similar phenomenon being observed by Hayashi (*loc. cit.*) in the case of the chlorohydroxymethylbenzoylbenzoic acids derived from *p*-chlorophenol and 3- or 4-methylphthalic acid. *tert.*-Butylbenzene afforded almost exclusively 5-*tert.*-butyl-2-*p*-*tert.*-butylbenzoylbenzoic acid, which was readily purified and was unchanged after treatment with sulphuric acid at room temperature for 24 hours.

For orientation the *tert.*-butylbenzoylbenzoic acids were decarboxylated by copper bronze; the catalyst is probably a trace of the copper salt of the carboxylic acid; cessation of evolution of carbon dioxide is accompanied by precipitation of a trace of fine black powder (cf. Newmann and Lord, *J. Amer. Chem. Soc.*, 1944, **66**, 733, who used a trace of the copper salt as catalyst in the decarboxylation of carboxylic acids). The resulting alkylbenzophenones were characterised by comparison with synthetic specimens, except in the case of benzene, the mixed acids from which did not give a pure benzophenone. The preparation of relevant intermediates is now described.

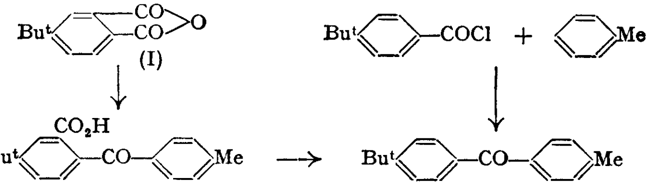
p-*tert.*-Butyltoluene could not be oxidsed by Bialobrzeski's chromic–acetic acid method (*Ber.*, 1897, **30**, 1773). Oxidation by permanganate in aqueous pyridine (see Experimental) gave a 35% yield of *p*-*tert.*-butylbenzoic acid.

Reaction of *tert.*-butyl chloride with excess of toluene in presence of aluminium chloride (cf. Baur, *Ber.*, 1891, **24**, 2833), to give mainly *m*-*tert.*-butyltoluene, was very sensitive to temperature conditions; in one experiment, where we used excess of aluminium chloride at 25°, a dimethylanthracene was obtained, probably identical with that described by Anschütz (*Annalen*, 1886, **235**, 152; cf. Anschütz and Immendorff, *Ber.*, 1884, **17**, 2816; Zincke and Wackendoerff, *Ber.*, 1877, **10**, 1481; Lavaux, *Ann. Chim.*, 1910, **20**, 468). Buu-Hoï and Cagniant (*Bull. Soc. chim.*, 1942, **9**, 887) also report that this reaction gives mainly the *m*-isomer, and state that the results of Shoesmith and McGechen (*J.*, 1930, 2231) are probably due to the fact that both *m*- and *p*-*tert.*-butyltoluene are converted by concentrated sulphuric acid into mixed isomers. Serijan *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 873) agree and add that considerable fractionation is necessary (100 plates) to effect separation of the pure *m*-isomer. We found that our impure *m*-*tert.*-butyltoluene, although resistant to chromic acid, was oxidised by permanganate in aqueous pyridine to give good yields of *tert.*-butylbenzoic acid, separable into a little of the *p*-isomer and a product, m. p. 98°, mainly the *m*-isomer, which could not be further purified. Kelbe and Pfeiffer (*Ber.*, 1886, **19**, 1723) used dilute nitric acid as oxidant, but record no details; the m. p. of *m*-*tert.*-butylbenzoic acid is given as 127°.

The liquid 4-*tert.*-butylbenzophenone was prepared (*a*) by condensing *p*-*tert.*-butylbenzoyl chloride with benzene in presence of aluminium chloride, (*b*) from benzoyl chloride and *tert.*-butylbenzene, and (*c*) by decarboxylation of 2-*p*-*tert.*-butylbenzoylbenzoic acid (Peters and Rowe, *J.*, 1945, 181); in each case, the ketone gave mixed oximes, from which a pure oxime, m. p. 150—152°, was readily obtained.

4-*tert.*-Butyl-4'-methylbenzophenone was synthesised from *p*-*tert.*-butylbenzoyl chloride, toluene, and aluminium chloride; the derived pure oxime, m. p. 177·5—178·5°, was converted by rearrangement (method: Beckmann and Barton, *J. Org. Chem.*, 1939, **3**, 300) into 4'-*tert.*-butyl-*p*-toluanilide, identical with a specimen prepared from *p*-*tert.*-butylaniline and *p*-toluoyl chloride. That 5-*tert.*-butyl-2-*p*-toluoylbenzoic acid was the main condensation product of 4-*tert.*-butylphthalic anhydride and toluene was shown by decarboxylation to 4-*tert.*-butyl-4'-methylbenzophenone, the derived oxime being identical with a synthetic sample. Cyclisation of the acid by 20% fuming sulphuric acid was accompanied by isomerisation and gave 2-*tert.*-butyl-7- and -6-methylanthraquinone.

The orientation of 5-*tert.*-butyl-2-*p*-*tert.*-butylbenzoylbenzoic acid, derived from the anhydride (I), was shown by decarboxylation to 4 : 4'-di-*tert.*-butylbenzophenone, m. p. 133—134° (pure oxime, m. p. 195—196°), identical with specimens synthesised from *p-tert.*-butylbenzoyl chloride, *tert.*-butylbenzene, and aluminium chloride, or from *tert.*-butylbenzene, carbon tetrachloride, and aluminium chloride (cf. Gomberg and Todd, *J. Amer. Chem. Soc.*, 1917, **39**, 2392, who prepared 4 : 4′-dimethylbenzophenone in an analogous manner). Beckmann rearrangement of the oxime afforded 4 : 4′-di-*tert.*-butylbenzanilide, identical with that synthesised from *p-tert.*-butylbenzoyl chloride and *p-tert.*-butylaniline.



Both *m*- and *p*-bromo-*tert.*-butylbenzene were synthesised, but attempted conversion through the corresponding Grignard reagent and *p-tert.*-butylbenzoyl chloride into 3 : 4′- and 4 : 4′-di-*tert.*-butylbenzophenone, respectively, gave oily mixtures.

Cyclisation of 5-*tert.*-butyl-2-*p*-*tert.*-butylbenzoylbenzoic acid afforded 2 : 7-di-*tert.*-butylanthraquinone.

EXPERIMENTAL

M. p.s are corrected. Micro-analyses were carried out by Drs. Weiler and Strauss, of Oxford.

4-tert.-*Butyl*-o-*xylene*.—Anhydrous ferric chloride (1 g.) was added during 30 minutes to a well-stirred mixture of *o*-xylene (106 g., 1 mol.) and *tert.*-butyl chloride (92·5 g., 1 mol.) at room temperature. After the vigorous evolution of hydrogen chloride had subsided, more *tert.*-butyl chloride (20 g.) was added and the mixture stirred for 1 hour and then heated on the water-bath for 15 minutes and filtered (charcoal). 4-*tert.*-Butyl-*o*-xylene, a colourless oil, n^{9} 1·5002, distilled at 211—212° (111 g., 73%) (Found : C, 88·4; H, 11·4. Calc. for $C_{12}H_{18}$: C, 88·9; H, 11·1%).

4-tert.-*Butylphthalic Acid and Anhydride*.—The preparation was much improved as follows : Potassium permanganate (360 g., 2·25 mols.) was added during 1·5 hours to a well-stirred boiling solution of 4-*tert.*-butyl-*o*-xylene (81 g.; 0·5 mol.) in pyridine (500 c.c.) and water (1 l.). The mixture continued to boil without further heating, and, after final refluxing for 30 minutes, excess of permanganate was removed with alcohol, the mixture filtered, and the residue washed well with hot water. Filtrate and washings were distilled to remove pyridine and excess of *tert.*-butyl-*o*-xylene, and concentrated to 300 c.c.; careful addition of hydrochloric acid precipitated a basic potassium salt of 4-*tert.*-butylphthalic acid, which was collected and stirred with hydrochloric acid to yield potassium chloride and impure *tert.*-butylphthalic acid; the latter crystallised from benzene–ligroin (b. p. 60—80°, here and below) in stout, colourless prisms, m. p. 159—161° (59·3 g., 50%) (Found : C, 64·7; H, 6·0. Calc. for $C_{12}H_{14}O_4$: C, 64·9; H, 6·3%). The mixture (100 g.) of potassium chloride and *tert.*-butylphthalic acid was heated with acetic anhydride (200 c.c.), and the orange solution filtered from inorganic salt and distilled, to give 4-*tert.*-butylphthalic anhydride (I), b. p. 311—312°/750 mm., 136°/2 mm., which crystallised from ligroin in colourless plates, m. p. 77° (Found : C, 70·2; H, 5·9. Calc. for $C_{12}H_{12}O_3$: C, 70·6; H, 5·9%). Continuation of the above distillation at 2 mm. gave a pale yellow oil (8·5 g.), b. p. 203—205°/2 mm., which was 4-tert.-*butyl-2-methylbenzoic anhydride* (Found : C, 79·0; H, 8·0. $C_{24}H_{30}O_3$ requires C, 78·7; H, 8·2%). This anhydride was dissolved in boiling dilute sodium hydroxide, and the mixture cooled and acidified; crystallisation of the precipitate from alcohol gave colourless plates, m. p. 142—143°, of 4-*tert.*-butyl-2-methylbenzoic acid, which was readily converted into (I) by further oxidation as above.

Trimellitic Acid.—4-*tert.*-Butylphthalic anhydride (1 g.), nitric acid (*d* 1·42) (4 c.c.), and water (2 c.c.) were heated at 200—210° for 8 hours, to give colourless prisms (from acetic acid), m. p. 228—230°, of trimellitic acid (Found : C, 50·9; H, 2·7. Calc. for $C_9H_6O_6$: C, 51·4; H, 2·9%). Sublimation at 180°/0·8 mm. afforded trimellitic anhydride, m. p. 160°. If nitric acid–water (1 : 2) was used, the anhydride (I) was mainly recovered.

Derivatives of 4-tert.-*Butylphthalic Anhydride* (I).—When the anhydride (2 g.) was refluxed with alcohol (5 c.c.) and aqueous ammonia (*d* 0·88; 5 c.c.) for 2 hours, colourless prisms of *diammonium* 4-tert.-*butylphthalate* (2 g.), m. p. 164° (decomp.), separated (Found : N, 10·4. $C_{12}H_{20}O_4N_2$ requires N, 10·9%). Heating the anhydride (1 g.) and aqueous ammonia (*d* 0·88; 5 c.c.) at 330° and then cooling, gave a clear liquid which solidified and crystallised from alcohol in colourless prisms, m. p. 133—134°, of 4-tert.-*butylphthalimide* (0·9 g., 90%) (Found : C, 70·7; H, 6·2; N, 6·7. $C_{12}H_{13}O_2N$ requires C, 70·9; H, 6·4; N, 6·9%). It was also formed by heating the above diammonium salt above its m. p.

A solution of the anhydride (1 g.) in 33% aqueous methylamine (10 c.c.) was refluxed for 1 hour and evaporated to a clear liquid, b. p. 314°; on cooling, the solidified product was recrystallised from alcohol in colourless prismatic needles, m. p. 94—94·5°, of 4-tert.-*butyl*-N-*methylphthalimide* (0·8 g., 74%) (Found : C, 72·2; H, 6·9; N, 6·3. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·9; N, 6·45%).

Aniline (2 g.) and the anhydride (2 g.) were heated at 180° for 10 minutes, the mixture was extracted with dilute hydrochloric acid, and the 4-tert.-*butylphthalanil* (2·4 g., 90%) crystallised from alcohol in colourless needles, m. p. 185° (Found : C, 77·8; H, 6·1; N, 5·1. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1; N, 5·0%).

Sulphanilic acid (2 g.), pyridine (4 c.c.), and the anhydride (I) (2·8 g.) (method : Cross and Chen, *loc. cit.*) were warmed to a clear brown solution, which suddenly became solid. *Pyridinium* 4-tert.-*butylphthalanil-4'-sulphonate* (5·1 g., 85%) crystallised from alcohol in colourless prisms, m. p. 228—229° (Found : C, 62·7; H, 5·1; N, 6·5; S, 7·4. $C_{23}H_{22}O_5N_2S$ requires C, 63·0; H, 5·0; N, 6·4; S, 7·3%). The more soluble *3'-sulphonate* analogue (4·3 g., 72%) crystallised from aqueous alcohol in colourless prisms, m. p. 213—214° (Found : C, 62·6; H, 5·3; N, 6·2; S, 7·1%).

Di-(4-tert.-*butylphthalanil*)*dianisidide*, prepared by heating dianisidine (1·2 g.) with the anhydride (I) (2 g.) until the whole was solid at 300°, separated from aqueous acetic acid as a brown amorphous solid, m. p. above 330° (Found : N, 4·3. $C_{38}H_{36}O_6N_2$ requires N, 4·5%), unsuitable for identification of dianisidine. Dry hydrogen chloride was introduced into a cooled solution of the anhydride (2·5 g.) in methyl alcohol (20 c.c.) until it was saturated at room temperature. Next morning, alcohol and hydrogen chloride were removed and the oily residue was shaken with aqueous ammonia. *Dimethyl* 4-tert.-*butylphthalate* (2·1 g., 67%) distilled at 169—171°/9·3 mm. as a colourless oil (Found : C, 66·9; H, 7·3. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). The diethyl ester (66% yield) distilled at 183°/8 mm.

Di-p-*nitrobenzyl* 4-tert.-*butylphthalate* (method : Reid and Lyman, *J. Amer. Chem. Soc.*, 1917, **39**, 124, 701) separated from 95% alcohol in colourless needles, m. p. 122—113° (Found : C, 63·3; H, 4·7; N, 5·2. $C_{26}H_{24}O_8N_2$ requires C, 63·4; H, 4·9; N, 5·7%).

p-tert.-*Butyltoluene.*—Dry toluene (92 g., 1 mol.), *tert.*-butyl chloride (92·5 g., 1 mol.), and anhydrous ferric chloride (1 g.) gave *p-tert.*-butyltoluene, b. p. 191° (124 g., 88%) (Found : C, 89·2; H, 10·6. Calc. for $C_{11}H_{16}$: C, 89·2; H, 10·8%).

p-tert.-*Butylbenzoic Acid.*—Potassium permanganate (110 g.) was added during 1 hour to a boiling mixture of *p-tert.*-butyltoluene (50 g.) in pyridine (300 c.c.) and water (600 c.c.); if more pyridine is used to obtain complete solution, reaction is violent, whereas complete omission of pyridine led to a poor yield. After a further hour's stirring and removal of manganese dioxide, acidification gave *p-tert.*-butylbenzoic acid (21 g., 35%), which crystallised from ligroin in colourless prismatic needles, m. p. 162—164° (Found : C, 73·7; H, 7·8. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%). The acid (25 g.) was converted by thionyl chloride (25 c.c.) into the chloride (20·5 g., 75%), b. p. 266—273° (Found : C, 67·2; H, 6·7; Cl, 18·1. Calc. for $C_{11}H_{13}OCl$: C, 67·2; H, 6·6; Cl, 18·1%), and thence into the amide, colourless plates (from alcohol), m. p. 173° (Kelbe and Pfeiffer, *Ber.*, 1886, **19**, 1725, give m. p. 171°) (Found : C, 74·4; H, 8·4; N, 7·4. Calc. for $C_{11}H_{15}ON$: C, 74·6; H, 8·5; N, 7·9%).

m-tert.-*Butyltoluene.*—Anhydrous aluminium chloride (10 g.), toluene (125 c.c., 1·2 mols.), and *tert.*-butyl chloride (25 c.c., 0·23 mol.) at 0—5° (temperature important) for 3 hours gave impure *m-tert.*-butyltoluene (13 c.c.), b. p. 186—195° (Found : C, 88·7; H, 10·8. Calc. for $C_{11}H_{16}$: C, 89·2; H, 10·8%). When 20 g. of aluminium chloride were used at 25°, pale yellow plates (from benzene) (2·2 g.), m. p. 225°, with a strong blue fluorescence, were obtained [Found : C, 93·1; H, 6·6%; *M* (in camphor), 200, 202. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%; *M*, 206]. This was almost certainly the dimethylanthracene, m. p. 225°, recorded by Lavaux (*loc. cit.*).

m-tert.-*Butylbenzoic Acid.*—*m-tert.*-Butyltoluene was unchanged by sodium dichromate in boiling acetic acid, or boiling nitric acid of varying strengths, but in pyridine (225 c.c.) and water (150 c.c.), the hydrocarbon (15 g., 0·1 mol.) was oxidised by potassium permanganate (45 g., 0·3 mol.) (at the b. p. for 1 hour) to give a little *p-tert.*-butylbenzoic acid and the more soluble *m*-isomer (11·3 g., 64%), which on crystallisation from ligroin gave colourless prisms, m. p. 98°, unchanged by further recrystallisation from ligroin or acetic acid (Found : C, 73·7; H, 7·8. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%). It probably retains a little of the *p*-isomeride. The derived acid chloride, b. p. 256—260°, afforded an amide, which crystallised from aqueous alcohol in colourless, prismatic needles, m. p. 107°, unchanged in m. p. on repeated crystallisation (Found : C, 74·1 ; H, 8·6 ; N, 7·8. Calc. for $C_{11}H_{15}ON$: C, 74·6 ; H, 8·5 ; N, 7·9%).

p-tert.-*Butylaniline.*—To *tert.*-butylbenzene (78 g.) (method of preparation : Bromby *et al., loc. cit.*), nitric acid (*d* 1·5 ; 78 g.) was added at 20—25° during 3 hours, and the product distilled with steam ; unchanged *tert.*-butylbenzene distilled first, followed by the less-volatile *p*-nitro-*tert.*-butylbenzene (63 g., 69%), b. p. 264—268° ; this was reduced by Shoesmith and Mackie's method (*J.*, 1928, 2334) to *p-tert.*-butylaniline (41·3 g., 60%), b. p. 248—250°, isolated through the *hydrochloride*, m. p. 270—274° (sealed tube) (Found : C, 64·8 ; H, 8·7 ; N, 7·5 ; Cl, 18·7. $C_{10}H_{16}NCl$ requires C, 64·7 ; H, 8·6 ; N, 7·4 ; Cl, 19·1%). The acetyl derivative crystallised from aqueous alcohol in plates, m. p. 173°.

m-*Bromo*-tert.-*butylbenzene* (cf. Marvel *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 914, who record no details).—Bromine (24 g., 0·3 mol.) was added slowly to *p-tert.*-butylacetanilide (19 g., 0·1 mol.), acetic acid (75 c.c.), and iron filings (0·1 g.) at 35°. After 5 hours' stirring, the mixture was added to ice-water, and the 2-bromo-4-*tert.*-butylacetanilide crystallised from alcohol in colourless plates, m. p. 156—158° (25 g., 92%) (Found : N, 5·4. Calc. for $C_{12}H_{16}ONBr$: N, 5·2%) (cf. Gelzer, *Ber.*, 1888, **21**, 2941) ; 11·6 g. were hydrolysed by boiling with hydrochloric acid (20 c.c.) and 95% alcohol (30 c.c.) for 3 hours ; concentration gave 2-*bromo*-4-tert.-*butylaniline hydrochloride* (10 g., 88·5%) in colourless plates, m. p. 193—194° (Found : N, 5·4. $C_{10}H_{15}NClBr$ requires N, 5·3%), and thence the free amine, a colourless oil, b. p. 98—99°/0·7 mm. (Found : N, 6·2 ; Br, 34·3. Calc. for $C_{10}H_{14}NBr$: N, 6·1 ; Br, 35·1%). The hydrochloride (27 g.) in acetic acid (150 c.c.), water (100 c.c.), and concentrated hydrochloric acid (35 c.c.) at 0°, were treated with sodium nitrite (7·6 g.) in water (50 c.c.), and then added to hypophosphorous acid (180 c.c.). After 3 days, the separated oily *m*-bromo-*tert.*-butylbenzene was extracted and distilled, as a colourless oil, b. p. 222—223°/758 mm. (14 g., 66%), which did not solidify at −15°.

p-*Bromo*-tert.-*butylbenzene.*—The following method is much better than that given by Marvel *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 2773), who employed sunlight and no halogen carrier. Bromine (80 g., 1 mol.) was added slowly to *tert.*-butylbenzene (67 g., 0·5 mol.) and iron filings (1 g.) at room temperature ; next morning, addition to water gave an oil, which was washed successively with aqueous sodium hydrogen sulphite, sodium carbonate, and water. *p*-Bromo-*tert.*-butylbenzene distilled as a colourless oil, b. p. 228—229°, f. p. 10—11° (77·3 g., 73%).

p-tert.-*Butylbenzophenone.*—(*a*) (cf. Bergmann *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 2748) *p-tert.*-Butylbenzoyl chloride (4·9 g.) in dry benzene (25 c.c.) was treated with aluminium chloride (10 g.) at 20°. After the mixture had been kept overnight and then decomposed, *p-tert.*-butylbenzophenone (3·9 g., 66%), b. p. 151—160°, was obtained which gave an oxime (2·2 g., 87%), mixed isomers, m. p. 125—141°, and thence by crystallisation from alcohol, a pure *oxime*, colourless prismatic needles, m. p. 150—152° (Found : N, 5·2. $C_{17}H_{19}ON$ requires N, 5·5%). The general method used in preparing oximes described in this paper was to add hydroxylamine hydrochloride (1·4 g., 0·02 mol.) in water (3 c.c.) to the ketone (0·01 mol.) in alcohol (15 c.c.), followed by potassium hydroxide (2·25 g., 0·04 mol.) in water (2·5 c.c.), the mixture being refluxed for 5 hours and then added to water (60 c.c.).

(*b*) Benzoyl chloride (4·2 g.) and *tert.*-butylbenzene (25 c.c.) in presence of aluminium chloride (10 g.) similarly gave *p-tert.*-butylbenzophenone (4·5 g., 76%) and thence the impure, m. p. 125—140°, and pure oxime, m. p. 150—152°, identical with that prepared by method (*a*).

(*c*) *o-p'-tert.*-Butylbenzoylbenzoic acid (5 g.) was decarboxylated by heating it with a little copper bronze at 250° until evolution of carbon dioxide ceased. After the mixture had cooled, alcohol was added and the whole filtered from a trace of black powder ; the alcohol was removed and the residue distilled, to yield *p-tert.*-butylbenzophenone (3·1 g., 73%), b. p. 130—140°/0·5 mm., and thence the pure oxime, m. p. and mixed m. p. with those prepared by methods (*a*) and (*b*), 150—152°.

Condensation of 4-tert.-*Butylphthalic Anhydride* (I) *with Toluene ;* 4- *and* 5-tert.-*Butyl*-2-p-*toluoylbenzoic Acid.*—The anhydride (I) (10 g., 0·05 mol.), aluminium chloride (13·3 g., 0·1 mol.), and excess of dry toluene (50 c.c.) were stirred on the steam-bath for 3 hours ; after decomposition, toluene was removed with steam, and the residue extracted with boiling 5% aqueous sodium carbonate ; acidification of the alkaline extract gave a colourless precipitate, m. p. 100—120° (13·4 g., 90%), of mixed carboxylic acids. Crystallisation from benzene–ligroin and then from acetic acid afforded 5-tert.-*butyl*-2-p-*toluoylbenzoic acid* (*A*), colourless prisms (1·5 g.), m. p. 204—205° (Found : C, 77·3 ; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·0 ; H, 6·8%). The mother-liquors yielded an impure isomer (*B*) (1 g.), m. p. 165—175°, depressed in m. p. on admixture with (*A*). On leaving either (*A*) or (*B*) in concentrated sulphuric acid at room temperature for 24 hours, isomerisation occurred to give a similar mixture of acids, m. p.

130—140°. The carboxylic acid (*A*) (1 g.) was heated with 20% fuming sulphuric acid (5 c.c.) at 95° for 3 hours and the resulting deep red solution poured on ice. The solid was extracted with dilute aqueous ammonia, and the residue crystallised from methyl alcohol in lemon-yellow prisms, m. p. 83—95°, not purified further by crystallisation or chromatographic means (Found : C, 81·7; H, 6·3. Calc. for $C_{19}H_{18}O_2$: C, 82·0; H, 6·5%). This was probably a mixture of 2-*tert.*-butyl-7- and -6-methylanthraquinone.

4-tert.-*Butyl-4'-methylbenzophenone.*—Aluminium chloride (20 g., 0·15 mol.) was added to *p-tert.*-butylbenzoyl chloride (9·8 g., 0·05 mol.), dry toluene (9·2 g., 0·1 mol.), and carbon disulphide (15 c.c.) at room temperature, and the whole refluxed for 3 hours. By the usual procedure, 4-tert.-*butyl-4'-methylbenzophenone* distilled as a very pale blue oil (7·4 g., 59%), b. p. 148—150°/0·4 mm. (Found : C, 85·7; H, 7·9. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%). The *p*-nitrophenylhydrazone could not be prepared, but the derived *oxime*, m. p. 153—163°, was crystallised several times to yield a pure isomer, colourless prismatic needles (from aqueous alcohol), m. p. 177·5—178·5° (Found : C, 80·8; H, 8·0; N, 5·4. $C_{18}H_{21}ON$ requires C, 80·9; H, 7·9; N, 5·2%). Rearrangement (method : Beckmann and Barton, *J. Org. Chem.*, 1939, **3**, 300) of the pure oxime (0·5 g.) with phosphorus pentachloride (1 g.) in benzene (15 c.c.) gave 4'-*tert.*-butyl-*p*-toluanilide (0·4 g.), which crystallised from benzene–ligroin in colourless prisms, m. p. and mixed m. p. 150—151° (see below).

4-tert.-*Butylbenzo*-p-*toluidide.*—*p-tert.*-Butylbenzoyl chloride (from 1·7 g. of acid) was treated with a solution of *p*-toluidine (1·1 g.) in benzene (10 c.c.); reaction was vigorous and after 30 minutes' refluxing, filtration, and concentration, the *toluidide* was obtained as colourless prisms (benzene–ligroin), m. p. 129—130° (1·6 g.) (Found: N, 4·8. $C_{18}H_{21}ON$ requires N, 5·2%).

4'-tert.-*Butyl*-p-*toluanilide.*—*p*-Toluic acid (2·7 g.) was converted into the chloride with thionyl chloride; refluxing with *p-tert.*-butylaniline (3 g.) in benzene (20 c.c.) for 2 hours gave colourless silky needles, m. p. 150—151°, of the *toluanilide* (1·8 g.) (Found : N, 5·2. $C_{18}H_{21}ON$ requires N, 5·2%), identical with that obtained by the above rearrangement.

Decarboxylation of 5-tert.-*Butyl*-2-p-*toluoylbenzoic Acid.*—The acid (1 g.) was heated with a little copper bronze at 250° until reaction ceased; alcohol was added and the mixture filtered; to the filtrate, hydroxylamine hydrochloride (0·4 g.) and potassium hydroxide (0·75 g.) were added and 4-*tert.*-butyl-4'-methylbenzophenone oxime, m. p. and mixed m. p. with the above specimen, 177·5—178·5°, was obtained.

m-tert.-Butylbenzoyl chloride, toluene, and aluminium chloride afforded a pale blue oil, b. p. 172—174°/2·2 mm., which gave a trace of 4-*tert.*-butyl-4'-methylbenzophenone oxime, but no further solid product.

Condensation of 4-tert.-*Butylphthalic Anhydride* (I) *with* tert.-*Butylbenzene;* 5-tert.-*Butyl*-2-p-tert.-*butylbenzoylbenzoic Acid.*—The anhydride (I) (10 g., 0·05 mol.), excess of *tert.*-butylbenzene (50 c.c.), and aluminium chloride (13·3 g., 0·1 mol.) on the boiling water-bath gave, by the usual procedure, the *carboxylic acid* (10·1 g., 60%), which crystallised from aqueous acetic acid and then benzene–ligroin in colourless prisms, m. p. 234—235° (Found : C, 77·6; H, 7·6. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%). There was no isomerisation when the acid was kept in concentrated sulphuric acid for 24 hours at room temperature. No isomer could be detected in the mother-liquors from the above crystallisations, but some 4-*tert.*-butylphthalic acid, m. p. and mixed m. p. 152°, was isolated.

2 : 7-*Di*-tert.-*butylanthraquinone.*—Cyclisation of 5-*tert.*-butyl-2-*p-tert.*-butylbenzoylbenzoic acid (1 g.) by 20% fuming sulphuric acid (5 c.c.) at 95° for 4 hours gave, after addition to water and extraction of the precipitate with aqueous ammonia, 2 : 7-*di*-tert.-*butylanthraquinone* (0·6 g.), which crystallised from methyl alcohol in pale yellow prisms, m. p. 119—121° (Found : C, 82·3; H, 7·6. $C_{22}H_{24}O_2$ requires C, 82·5; H, 7·5%). An attempt by Elbs and Wittick's method (*Ber.*, 1885, **18**, 348) to prepare a dimethylanthracene from toluene and chloroform gave only a resin.

4 : 4'-*Di*-tert.-*butylbenzophenone.*—(*a*) p-*tert.*-Butylbenzoyl chloride (7·5 g.) was added slowly to dry *tert.*-butylbenzene (13 g.) and aluminium chloride (10 g.) at 5°; after the mixture had been kept overnight at room temperature and then heated on the water-bath for 1 hour and decomposed, benzene was added and the solvent layer afforded 4 : 4'-di-*tert.*-butylbenzophenone in colourless rosettes, m. p. 133—134° (Found : C, 85·2; H, 8·8. Calc. for $C_{21}H_{26}O$: C, 85·7; H, 8·8%). Cristol *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 913) record m. p. 134—135·5° for the ketone, which was prepared from 4 : 4-di-*p-tert.*-butylstyrene. Repetition of the experiment with *m-tert.*-butylbenzoyl chloride gave impure 3 : 4'-di-*tert.*-butylbenzophenone as a pale yellow oil, b. p. 190°/1·8 mm., which did not give a solid oxime.

4 : 4′-*Di*-tert.-*butylbenzophenone oxime* was readily formed, and crystallised from alcohol in colourless prismatic needles, m. p. 195—196° (Found: C, 81·2; H, 8·3; N, 4·23. $C_{21}H_{27}ON$ requires C, 81·6; H, 8·7; N, 4·5%), which by Beckmann rearrangement gave 4 : 4′-di-*tert.*-butylbenzanilide, m. p. 156—157°.

(*b*) Carbon tetrachloride (46·2 g., 0·3 mol.) and aluminium chloride (13·3 g., 0·1 mol.) were stirred at 5° during addition of *tert.*-butylbenzene (26·8 g., 0·2 mol.) in 2 hours, kept overnight, and then treated with water. Distillation with steam removed excess of *tert.*-butylbenzene and decomposed the dichlorodiphenylmethane derivative; extraction of the residue with benzene gave 4 : 4′-di-*tert.*-butylbenzophenone, b. p. 180—190°/0·7 mm., which crystallised from alcohol in colourless prisms, m. p. 133—134°.

(*c*) 5-*tert.*-Butyl-2-*p*-*tert.*-butylbenzoylbenzoic acid (1·3 g.) was heated with a trace of copper bronze at 250°, and the usual procedure afforded 4 : 4′-di-*tert.*-butylbenzophenone, m. p. and mixed m. p. with the specimens prepared by methods (*a*) and (*b*), 133—134° (oxime, m. p. and mixed m. p. 195—196°).

4 : 4′-*Di*-tert.-*butylbenzanilide.*—*p*-*tert.*-Butylbenzoyl chloride (from 1·8 g. of acid) and *p*-*tert.*-butylaniline (1·5 g.) in dry benzene (4 c.c.) were refluxed for 1 hour, benzene (50 c.c.) was added, and the mixture was filtered. The filtrate gave colourless needles, m. p. 156—157°, of the *benzanilide* (Found: C, 81·7; H, 8·6; N, 4·4. $C_{21}H_{27}ON$ requires C, 81·6; H, 8·7; N, 4·5%), not depressed on admixture with the product obtained from the above Beckmann rearrangement.

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