NOTES.

New Intermediates and Dyes. Part I. 4-tert.-*Butylphthalic Acid and its Anhydride.*

By R. B. CONTRACTOR and A. T. PETERS.

4-*tert*.-BUTYLPHTHALIC ACID is prepared from 4-*tert*.-butyl-*o*-xylene in 35% yield; this is the first record of an alkylphthalic acid being accessible in reasonable yield, and its reactions are being studied.

The *tert*.-butyl group is resistant to most oxidising agents. Schram (*Monatsh.*, 1888, **9**, 842) stated that *p*-bromo-*tert*.-butylbenzene could be oxidised only with chromic and sulphuric acids, with destruction of the molecule, whilst Verley (*Bull. Soc. chim.*, 1898, **19**, 67) could not completely oxidise di-*tert*.-butylbenzene by any means; Peters (*J.*, 1942, 562) found that the *tert*.-butyl group in *tert*.-butyl- and di-*tert*.-butyl-acenaphthene was resistant to oxidation by a variety of methods. Tsukervanik and Terentieva (*J. Gen. Chem. Russia*, 1937, **7**, 637) recorded that *tert*.-butylnaphthalenes could be orientated by oxidation to the corresponding naphthoic acids by heating with dilute nitric acid in a sealed tube at 150—180° for 15 hours, but Bromby, Peters, and Rowe (*J.*, 1943, 144) failed to effect such oxidation with β-*tert*.-butylnaphthalene, and Gump (*J. Amer. Chem. Soc.*, 1931, **53**, 380) also failed to oxidise di-*tert*.-butylnaphthalene. Bromby *et al.* showed that chromic and acetic acid converted β-*tert*.-butylnaphthalene into 2-*tert*.-butyl-1 : 4-naphthaquinone, and prolonged oxidation of β-*tert*.-butyltetrahydronaphthalene with alkaline permanganate, followed by alkaline peroxide, gave 26·6% of 4-*tert*.-butylphthalic acid.

The authors have now devised a method for preparing 4-*tert*.-butylphthalic acid and its anhydride in 35% yield. 4-*tert*.-Butyl-*o*-xylene (I) was prepared from *o*-xylene, *tert*.-butyl chloride, and zinc chloride; Nightingale and Janes (*J. Amer. Chem. Soc.*, 1944, **66**, 154) found ferric chloride effective. Oxidation of (I) by boiling aqueous potassium permanganate gave 4-*tert*.-butylphthalic acid, readily converted into its anhydride (II).

Condensation of (II) with benzene in the Friedel–Crafts reaction afforded (probably) 2-*benzoyl*-5-tert.-*butylbenzoic acid*, which was readily cyclised by 20% fuming sulphuric acid into β-*tert*.-butylanthraquinone. The latter was identical with that prepared from phthalic anhydride and *tert*.-butylbenzene, followed by ring closure of the resulting 2-(*p*-*tert*.-butylbenzoyl)benzoic acid (cf. Peters and Rowe, *J.*, 1945, 181), and thus the constitutions of (I) and (II) are confirmed.

Experimental.—4-tert.-*Butyl*-o-*xylene*.—*tert*.-Butyl chloride (185 g.; 2 mols.) was added gradually to a well-stirred mixture of *o*-xylene (106 g.; 1 mol.) and anhydrous zinc chloride (68 g.; 0·5 mol.) at 70—80° during 10 hours. Fractional distillation of the liquid gave 4-*tert*.-butyl-*o*-xylene as a colourless oil, b. p. 208—211° (102 g.; 63·6%) (Found: C, 88·9; H, 11·0. Calc. for $C_{12}H_{18}$: C, 88·9; H, 11·1%).

4-tert.-*Butylphthalic Acid*.—4-*tert*.-Butyl-*o*-xylene (20 g.) was suspended in water (250 c.c.) in a three-necked flask fitted with a sealed stirrer (quick agitation is necessary), and to the stirred, gently-boiling mixture, an aqueous solution of potassium permanganate (60 g.) was added during 12 hours. Any excess of permanganate was destroyed, sodium hydroxide, (4 g.) was added, and the mixture filtered. Concentration of the filtrate to 100 c.c., followed by acidification wiith hydrochloric acid, gave a sticky solid. The whole was extracted with ether, the ether dried, solvent removed, and the residue boiled with light petroleum (b. p. 60—80°) to give 4-*tert*.-butylphthalic acid, which crystallised from benzene–light petroleum in colourless prisms, m. p. 154° (9·6 g.; 35%) (Found: C, 64·7; H, 6·3. Calc. for $C_{12}H_{14}O_4$: C, 64·9; H, 6·3%).

4-tert.-*Butylphthalic Anhydride*.—The above acid (10 g.) was boiled with acetic anhydride (40 c.c.) for 30 minutes, and the acetic anhydride distilled. The residue crystallised from light petroleum in colourless plates, m. p. 75·5—76·5° (7·8 g.; 84·9%), identical with the anhydride prepared by Bromby *et al.* (*loc. cit.*).

2-*Benzoyl*-5(or 4)-tert.-*butylbenzoic Acid*.—A solution of 4-*tert*.-butylphthalic anhydride (2 g.) in dry benzene (50 c.c.) was treated with anhydrous aluminium chloride (4 g.), and the boiling mixture well stirred for 5 hours. After decomposition by ice-cold hydrochloric acid, and removal of benzene, the residue was extracted with warm aqueous sodium carbonate; acidification of the extract gave 2-*benzyl*-5(or 4)-tert.-*butylbenzoic acid*, which crystallised from chloroform–light petroleum in colourless needles, m. p. 179° (1·7 g.; 61·6%) (Found: C, 76·4; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·4; H, 6·4%).

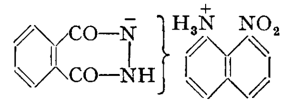
2-tert.-*Butylanthraquinone*.—The foregoing acid (1 g.) was dissolved in fuming sulphuric acid (20%; 6 c.c.) and heated at 100° for 1·5 hours. The mixture was poured on ice, and the precipitate crystallised from methyl alcohol in pale yellow needles, m. p. 104°, not depressed on admixture with 2-*tert*.-butylanthraquinone prepared by the method of Peters and Rowe (*loc. cit.*).—CLOTHWORKERS' RESEARCH LABORATORY, THE UNIVERSITY, LEEDS. [*Received, October* 9*th*, 1948.]

A Convenient Preparation of 8-*Nitro*-1-*naphthylamine.*

By HERBERT H. HODGSON and JOHN RATCLIFFE.

THE best method extant, from the point of view of yield, for the preparation of 8-nitro-1-naphthylamine is that of Hodgson and Crook (*J.*, 1936, 1844; cf. B.P. 439632), which, however, requires the use of ammonia at 130° under pressure for the hydrolysis of the mixture of 4-, 5-, and 8-nitrophthalo-1-naphthylimides obtained when phthalo-α-naphthalide is nitrated, the amines being subsequently separated by preferential solubilities in 10% aqueous sulphuric acid. An alternative hydrolysis of this mixture by boiling ethanolic hydrazine hydrate at atmospheric pressure is now described, which dispenses with an autoclave, and, by working at a lower temperature, minimises the tar formation to which *peri*-derivatives of naphthalene are prone. From the results, it would appear that the 8-nitrophthalo-1-naphthalide is preferentially hydrolysed. Since phthalylhydrazide can be extracted by ammonia from the residues, it follows that only the naphthalene portion of phthalo-α-naphthylimide is nitrated.

This work was carried out in 1944—45, and indicates that in the course of the hydrolysis a labile salt (inset) is probably formed, which partly dissociates into its constituents, 8-nitro-1-naphthylamine and phthalylhydrazide, as the reaction proceeds, as shown by increasing development of a red colour. This salt is subsequently decomposed by cold dilute sulphuric acid (cf. Barber and Wragg, *J.*, 1947, 1332).



Experimental.—Phthalo-α-naphthalide, prepared from α-naphthylamine (300 g.), was nitrated according to the procedure of Hodgson and Crook (*loc. cit.*), and the mixture (374 g.) of 4-, 5-, and 8-nitro-phthalo-1-naphthylimides so obtained was suspended in ethanol (1 l.) containing hydrazine hydrate (150 c.c.) and boiled under the reflux for *ca.* 1 hour; the minimum reflux period necessary for prevention of tar formation, and consequent loss of 8-nitro-1-naphthylamine, was gauged from the intensity of the deep red colour which develops. The cold mixture was then acidified with aqueous sulphuric acid (50% by volume), the solid filtered off and extracted several times with cold 2N-sulphuric acid (*ca.* 5 l. in all), the extracts combined with the previous filtrate, and the whole basified with aqueous ammonia at 0°; crude 8-nitro-1-naphthylamine (*ca.* 80 g., m. p. 90—93°) was then precipitated; this was purified (70 g., m. p. 93—96°) by extraction with 10% aqueous sulphuric acid, and the extract basified by aqueous ammonia at 0°, the filtered solid being finally crystallised from ligroin; m. p. 96—97° (Hodgson and Crook, *loc. cit.*, and Meldola and Streatfeild, *J.*, 1893, **63**, 1055, give m. p. 96—97°). Phthalylhydrazide was extracted from the final residues by aqueous ammonia, and precipitated from the extract by acidification (m. p. 339°), and recrystallised from ethanol; m. p. 342—345° (lit., 342—346).

The authors thank Imperial Chemical Industries Ltd. (Dyestuffs Division), for gifts of chemicals.—TECHNICAL COLLEGE, HUDDERSFIELD. TECHNICAL COLLEGE OF SOUTH-EAST ESSEX, DAGENHAM.
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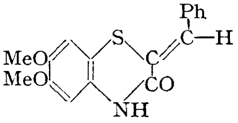
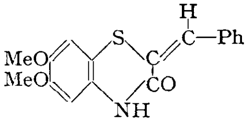
The Benzylidene Derivative of 3-*Keto*-6 : 7-*dimethoxy*-2 : 3-*dihydrobenz*-1 : 4-*thiazine*. By ALEXANDER MACKIE.

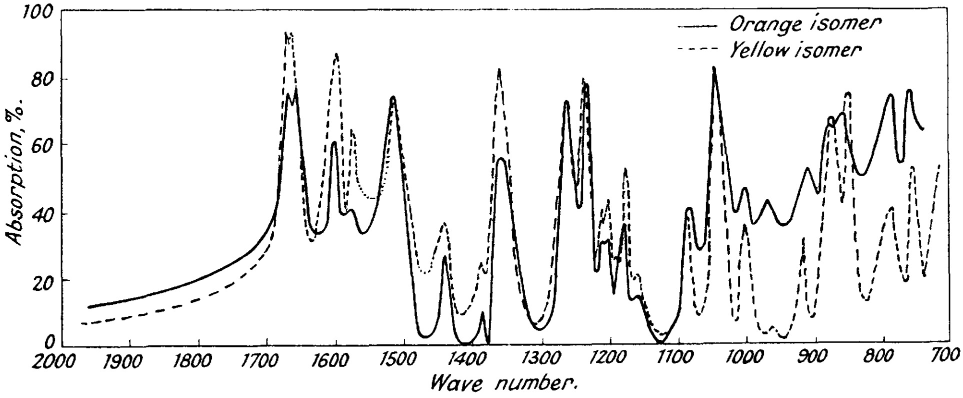
3-KETO-6 : 7-DIMETHOXY-2 : 3-DIHYDROBENZ-1 : 4-THIAZINE (Baldick and Lions, *J. Proc. Roy. Soc. New South Wales*, 1937—38, **71**, 113) has been condensed with benzaldehyde and yields two isomeric *benzylidene* derivatives which appear to be *cis*- and *trans*-isomerides, (I) and (II), respectively. Their infra-red absorption spectra were therefore determined. Inspection of the diagram shows that the absorption bands are identical throughout, but there are marked differences in the intensity of the bands in the two spectra. This substantiates the above suggestion: in all probability the yellow isomer is the *cis*-form, owing to its higher m. p. and greater absorption in the infra-red. Much greater differences in the spectra would be expected if it were a case of keto–enol tautomerism, and both compounds appear to contain a ketonic group. It should be stated, however, that the apparatus used did not allow examination of that end of the spectrum where any hydroxyl groups would appear.

(I.)





(II.)



3-Keto-6 : 7-dimethoxy-2 : 3-dihydrobenz-1 : 4-thiazine would not condense with anisaldehyde, 2 : 4-dimethoxybenzaldehyde, *p*-hydroxybenzaldehyde, or *p*-dimethylaminobenzaldehyde.

Experimental.—(Temperatures are uncorrected.) 3-*Keto*-6 : 7-*dimethoxy*-2-*benzylidene*-2 : 3-*dihydrobenz*-1 : 4-*thiazine*. Veratrole (Ullmann, *Annalen*, 1903, **327**, 115) was converted into veratrole-4-sulphonyl chloride (Brown and Robinson, *J.*, 1917, **111**, 953), which was reduced (Fries, Koch, and

Stuckenbrock, *Annalen*, 1929, **468**, 172). From the thiol obtained, 3-keto-6 : 7-dimethoxy-2 : 3 dihydrobenz-1 : 4-thiazine was prepared (Baldick and Lions, *loc. cit.*).

Benzylidene derivatives. Benzaldehyde (2·5 c.c.) and 10% aqueous sodium hydroxide (50 c.c.) were successively added to the ketone (5 g.), dissolved in hot alcohol. The hot mixture was shaken for 10 mins., the colour of the reaction mixture gradually changing to dark red. The reaction was completed by heating on the steam-bath for 45 mins. The alcohol was distilled off till crystallisation commenced, and the residue was then cooled. The orange crystals were filtered off, washed free from alkali, and recrystallised from aqueous alcohol. During the recrystallisation, a yellow residue was found, which was only sparingly soluble in aqueous alcohol. This residue was filtered off, and the filtrate on cooling gave orange needles, m. p. 196—198° (2 g.) (Found : C, 65·6; H, 4·4; N, 4·6. $C_{17}H_{15}O_3NS$ requires C, 65·2; H, 4·8; N, 4·5%). The yellow residue crystallised from absolute alcohol as feathery needles, m. p. 222—223° (1 g.) (Found : C, 65·2; H, 4·8; N, 4·5%).

The two components give different colour reactions with concentrated sulphuric acid, the orange a reddish-brown becoming purple, the yellow an olive-green becoming brown. Both compounds are sparingly soluble in ether, soluble in benzene, acetic acid, and readily soluble in chloroform.

The author's thanks are due to Professor Nisbet for his interest and helpful advice in this work, to Miss J. T. Radford of the Chemical Inspectorate, Ministry of Supply, who carried out the spectrographic work, and to Mr. A. M. Macdonald for the microchemical analyses.—HERIOT-WATT COLLEGE, EDINBURGH.
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Reactions of Aromatic Nitro-compounds with Alkaline Sulphides. Part II. The Three Dinitrobenzenes.

By HERBERT H. HODGSON and EDWARD R. WARD.

o-DINITROBENZENE reacts with sodium hydrogen sulphide (prepared by the method of Hodgson and Ward, *J.*, 1948, 242) in aqueous methanol to give sodium *o*-nitrothiophenoxide, 2 : 2′-dinitrodiphenyl sulphide by subsequent reaction between this product and *o*-dinitrobenzene, and 2 : 2′-dinitrodiphenyl disulphide, formed probably by oxidation of the above thiophenoxide by the concurrently liberated sodium nitrite (cf. the use of sodium nitrite in the manufacture of sulphur dyes). When about 0·4 g.-mol. of reducing agent is used per g.-mol. of *o*-dinitrobenzene, only the monosulphide is obtained, but with more of the reagent both mono- and di-sulphide are formed, and excess reduces the disulphide to thiophenoxide. The amounts of the products vary according to temperature, time of reaction, alkalinity, quantity of reagent, and rate of its addition; the presence of sodium hydrogen carbonate favours the formation of thiophenoxide rather than of disulphide.

The results of Blanksma and his co-workers with sodium sulphide (*Rec. Trav. chim.*, 1901, **20**, 115) have been confirmed, but with sodium disulphide no sodium *o*-nitrophenyl disulphide could be identified, and with sodium tri-, tetra-, and penta-sulphides, no aryl polysulphide higher than the disulphide could be prepared; these tri- and tetra-sulphides, reported by Blanksma *et al.* (*ibid.*, p. 144), appear to be mixtures of the disulphide with sulphur in varying amounts, and crystalline products resembling them have been made by allowing a mixture of the disulphide and the requisite amount of sulphur to crystallise from acetic acid.

The many previous failures reported in the literature to obtain 100% yield of *m*-nitroaniline by reduction of *m*-dinitrobenzene with alkaline sulphides would appear to be due to concurrent formation of *m*-phenylenediamine, and its subsequent interaction with the sodium thiosulphate always present in alkaline sulphide reductions (cf. Bernthsen's thiosulphate process for methylene-blue). Sodium hydrogen sulphide in hot aqueous methanol is now found to give 90—95% yields of *m*-nitroaniline free from azoxy-compound even under ice-cold conditions, thiophenoxide and consequent accompaniment of sodium nitrite not being observed.

p-Dinitrobenzene reacts with sodium hydrogen sulphide in aqueous methanol to give mainly 4 : 4′-dinitroazobenzene with some 4 : 4′-diaminoazobenzene, *p*-nitroaniline, and probably *p*-phenylenediamine; there was no evidence of replacement of a nitro- by a mercapto-group with liberation of sodium nitrite.

Experimental.—(Analyses are by Drs. Weiler and Strauss, Oxford.) *Reactions with* o-*dinitrobenzene.* Procedure. *o*-Dinitrobenzene (1 g.) in methanol (15 c.c.) is treated dropwise with the reagent, which contains sodium hydrogen sulphide (3·6 g.) in aqueous methanol (100 c.c.) (cf. Hodgson and Ward, *loc. cit.*), and the mixture, after being heated under reflux for the time stated in the table below, is poured into ice-water and filtered, the solid is washed with water, and the washings are added to the filtrate.

*Reactions with sodium hydrogen sulphide.**

NaSH, g.-mol.	Reaction conditions.	Products.
0·9	2 Days at 15°	Mixture (0·7 g.) of mono- and di-sulphide, with thiophenoxide in filtrate
0·4	5 Mins.' refluxing	Pure monosulphide (S, 11·3%) and unchanged *o*-dinitrobenzene
0·6	15 ,,	Mixture (0·7 g.) of mono- and di-sulphide, m. p. 120—160° (S, 13·74%), with thiophenoxide in filtrate
1·0	15 ,,	Mixture (0·3 g.) as above, m. p. 120—160°; thiophenoxide in filtrate
1·0	15 Mins.' refluxing; $NaHCO_3$ (0·25 g.) present	Only thiophenoxide formed
0·9	15 Mins.' refluxing, but nitro-compound added to reagent	Pure disulphide (0·35 g.) with thiophenoxide in filtrate

* Monosulphide refers to 2 : 2′-dinitrodiphenyl sulphide (m. p. 122°; S, 11·6%), and disulphide to 2 : 2′-dinitrodiphenyl disulphide (m. p. 197°; S, 20·8%).

Reactions with sodium mono-, di-, tri-, tetra-, and penta-sulphide.

Reagent (g.; g.-mol.).	Reflux period, mins.	Products.
Na_2S (0·25; 0·5)	15	Immediate intense blue colour followed by slow formation of monosulphide (0·8 g.) (S, 11·7%)
Na_2S_2 (0·36; 0·5)	15	Disulphide (0·8 g.), m. p. 193—194°; recrystallised from glacial acetic acid, m. p. 196—198° (Blanksma, *loc. cit.*, gives m. p. 195°) (Found: S, 21·0%)
Na_2S_2 (0·5; 0·7)	15	Pure disulphide, after addition of iodine (1 g.) in methanol to filtrate
Na_2S_3 (0·43; 0·5)	5	Yellow crystalline precipitate (1 g.), m. p. 178—182°; recrystallised from glacial acetic acid, m. p. 187—188°. Crude product (S, 37·8%)
Na_2S_4 (0·55; 0·5)	5	Yellow crystalline product (2 g.), m. p. 184—185°
Na_2S_5 (0·6; 0·5)	5	Yellow crystalline product (2·2 g.), m. p. 180—183°; recrystallised from glacial acetic acid, m. p. 186—188° (S, 45·51%)

The products from sodium tri-, tetra-, and penta-sulphides after extraction with carbon disulphide had m. p.s 197—198°, 195—197°, and 195—198°, with sulphur contents of 22·0, 21·0, and 21·2%, respectively, and were thus almost pure 2 : 2′-dinitrodiphenyl disulphide (S, 20·8%). When amounts of the pure disulphide (m. p. 195—197°) and sulphur were dissolved in the minimum amount of boiling glacial acetic acid in g.-mol. ratios of 1 : 1 and 1 : 3, the solutions on cooling deposited products of m. p. 184—190° (S, 32·0%) and 170—185° (S, 40·6%), respectively.

Reactions with m-*dinitrobenzene.* *m*-Dinitrobenzene (10 g.) in methanol (75 c.c.) was heated under reflux for 15 minutes with sodium hydrogen sulphide (5·5 g. in 140 c.c. of aqueous methanol; theory for complete reduction to *m*-nitroaniline is 5 g.) and then heated for a further 10 minutes, and the methanol removed by distillation (150 c.c.); the mixture when added to ice-water (500 g.) gave a precipitate of *m*-nitroaniline (8·3 g., >90% yield). When a deficiency of sodium hydrogen sulphide (*ca.* 4 g.) was used, the yield of *m*-nitroaniline (6·5 g.) decreased and it was mixed with unchanged *m*-dinitrobenzene.

Reactions with p-*dinitrobenzene.* *p*-Dinitrobenzene (5 g.) in methanol (75 c.c.) is treated dropwise for 10 minutes under reflux with sodium hydrogen sulphide (1 g.) in methanol (15 c.c.) and water (10 c.c.). The initial red colour preceded a dark red precipitate and, after a further 5 mins.' heating, the mixture is added to ice-water (150 c.c.) and filtered; the residue is steam-distilled to remove unchanged nitro-compound and then is found to be 4 : 4′-dinitroazobenzene (1·35 g.; m. p. 222°). Concentration of the filtrate to 75 c.c. afforded *p*-nitroaniline (0·5 g.; m. p. 142—144°). With more sodium hydrogen sulphide (1·5 g.), there is no unchanged nitro-compound, and 4 : 4′-dinitroazobenzene (2·5 g.) is obtained, whilst both *p*-nitroaniline and 4 : 4′-diaminoazobenzene are in the filtrate.

When 4 : 4′-dinitroazobenzene or *p*-dinitrobenzene was heated under reflux with a solution of sodium thiosulphate (5 g.) in methanol (40 c.c.) and water (10 c.c.), there was no loss of azo-compound, but a 25% loss of *p*-dinitrobenzene occurred with separation of sulphur.

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