

*Aromatic Substitution meta to a Basic Group. Part II.**
Halogenation of Diphenylmethane Derivatives.

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Halogenation of di-*p*-amino- and di-*p*-methylamino-phenylmethane in concentrated sulphuric acid in presence of silver ions has given products in which the chlorine or bromine atom lies *meta* to the basic group. Syntheses by alternative procedures have confirmed the orientation. During this work the nuclear bromination of di-*p*-nitrophenylmethane was readily achieved by the cationoid procedure whereas more usual methods produced di-*p*-nitrophenylmethyl bromide. A brief study was made of the behaviour of di-*p*-nitrophenylmethyl derivatives in concentrated sulphuric acid: no evidence was obtained for any substantial degree of ionisation. A new instance of thermal dismutation is recorded.

WHEN di-*p*-amino- and di-*p*-methylamino-phenylmethane were halogenated in concentrated sulphuric acid in the presence of silver ions the substituents entered predominantly the position *meta* to the basic groups. Each of the two bases was chlorinated and brominated at about the same rate as the corresponding tertiary amine (Part I) but the crude dihalogeno-compounds, produced in theoretical yield, contained side-products which were difficult to eliminate: purified acetyl derivatives of the 2:2'-dihalogeno-compounds were obtained only after tedious recrystallisation and in reduced yield. The greater degree of purity of the products obtained from bis-*p*-dimethylaminophenylmethane (Part I) is noteworthy, and may be because any tendency towards halogenation *ortho* to the basic group, either under the influence of a halogen atom already substituted in a *meta*-position or as a result of a residual *ortho*-directing effect exerted by the basic group, will be reduced in the dimethylamino-compound by the steric effect of the *N*-methyl groups. In general it would seem that halogenation *meta* to the $-\text{NH}_3^+$ and $-\text{NH}_2\cdot\text{CH}_3^+$ groups, now demonstrated for the first time, is more limited in its practical application than is the corresponding *meta*-halogenation of tertiary amines. This is especially true for amines unsubstituted in the *para*-position since, on analogy with the results of Part I, halogenation of aniline or

• "*p*-Aminodimethylaniline. Part VI" (*J.*, 1953, 1237) is regarded as Part I.

N-methylaniline in sulphuric acid would result in intractable mixtures in which the *m*-halogeno-derivative would inevitably be accompanied by the *para*- and probably the *ortho*-isomer, some dihalogeno-compound, and an equivalent amount of unchanged amine.

The condensation of a *m*-halogeno-aniline with formaldehyde (cf. Wagner, *J. Amer. Chem. Soc.*, 1934, **56**, 1944) provided one alternative route to the di-(4-amino-2-halogenophenyl)methanes: the 2 : 2'-dichloro-compound was obtained in 28% yield by this process. The structures of the two di-(2-halogeno-4-methylaminophenyl)methanes were similarly confirmed by their direct synthesis from *m*-chloro- and *m*-bromo-*N*-methylaniline.

By use of the Sandmeyer procedure the two di-(4-amino-2-halogenophenyl)methanes were obtained from the accessible di-(4-acetamido-2-aminophenyl)methane but the diazonium decompositions gave very low yields of dihalogeno-compound. The di-(4-amino-2-halogenophenyl)methanes were most advantageously prepared by reduction of the appropriate nitro-compound, obtained by cationoid halogenation of di-*p*-nitrophenylmethane in sulphuric acid. The chlorination, like that of di-*p*-aminophenylmethane, initially yielded an impure product requiring tedious recrystallisation; the bromination on the other hand gave an excellent yield of di-(2-bromo-4-nitrophenyl)methane of a high degree of purity. This distinction in the behaviour of the two halogens is compatible with the requirements of the Holleman series for steric impedance of entering groups.

The ease with which di-*p*-nitrophenylmethane undergoes electrophilic bromination in concentrated sulphuric acid stands in sharp contrast to the difficulty of producing this type of reaction in solvents of relatively low ionising power. Under these conditions homolytic bromination in the α -paraffinic position is favoured, as in other benzyl derivatives, owing to the possibility of resonance stabilisation of the di-*p*-nitrophenylmethyl radical initially produced. Thus, in boiling carbon tetrachloride, no product of nuclear bromination was isolated after 7 days' treatment with bromine in the dark in presence of iodine; unchanged di-*p*-nitrophenylmethane (22%) was recovered and the main product (41%) was di-*p*-nitrophenylmethyl bromide, previously obtained by Orazi and Giunti (*Anal. Asoc. Quim. Argentina*, 1951, **39**, 89) by bromination with 1 : 3-dibromo-5 : 5-dimethylhydantoin under irradiation. Under strong illumination bromination in carbon tetrachloride proceeded rapidly to give initially the methyl bromide and, with a second molecule of bromine, dibromodi-*p*-nitrophenylmethane. A similar reaction took place in boiling acetic acid, but the end-product was then 4 : 4'-dinitrobenzophenone (84%) produced by hydrolysis of the dibromide. These observations serve to emphasise the value of Derbyshire and Waters's procedure (*J.*, 1950, 573) in the achievement of nuclear halogenation of compounds preferentially attacked by atomic halogen under ordinary conditions; the ready electrophilic halogenation in sulphuric acid evidently depends on a more powerful evocation by the Br^+ cation, as compared with the formally neutral Br_2 molecule, of a polarisability effect in the ring (cf. de la Mare, *J.*, 1949, 2872).

In di-*p*-nitrophenylmethyl bromide the ionising tendency common to diphenylmethyl derivatives (cf. Burton and Praill, *Quart. Reviews*, 1952, **6**, 302; Gillespie and Leisten, *ibid.*, 1954, **8**, 50) must be near a minimum, since the *p*-nitro-groups strongly oppose the stabilisation of a carbonium ion; this does not of course preclude reaction by an ionic mechanism under favourable conditions. Whereas both diphenylmethyl bromide and its di-*p*-bromo-derivative (Goldthwaite, *Amer. Chem. J.*, 1903, **30**, 450) dissolve in concentrated sulphuric acid, showing the intense orange-red colour characteristic of a stable carbonium ion, the di-*p*-nitro-compound formed a pale yellow solution from which it could be recovered on dilution with water. Addition of silver sulphate to the sulphuric acid solution, however, caused immediate precipitation of silver bromide and, after removal of this, the filtrate remained clear on addition to ice: it evidently contained the un-ionised hydrogen sulphate, for acid hydrolysis gave di-*p*-nitrophenylmethanol or, in concentrated solution, a mixture of this with bisdi-*p*-nitrophenylmethyl ether. 4 : 4'-Dinitrobenzophenone was produced on alkaline hydrolysis owing to ready oxidation of the alcohol. Curtin and Leskowitz (*J. Amer. Chem. Soc.*, 1951, **73**, 2632) have obtained this alcohol by reduction of 4 : 4'-dinitrobenzophenone, and converted it into the ether by the use of toluene-*p*-sulphonic acid: in the present work it was noticed that crystals of the alcohol which had separated from a dilute solution in sulphuric acid occluded sufficient of the acid

to catalyse elimination of water at the melting point with rapid resolidification as the ether, whereas after one recrystallisation from aqueous acetic acid there was no apparent change on melting. The mechanism of this acid-catalysed self-etherification is presumably represented by the equations of Burton and Cheeseman (*J.*, 1953, 832, 986) which require the transitory existence of a carbonium ion. Di-*p*-nitrophenylmethanol differs, however, from such compounds as di-*p*-methoxyphenylmethanol (Balfe, Kenyon, and Thain, *J.*, 1952, 790) and dimesitylmethanol (Fuson and Jackson, *J. Amer. Chem. Soc.*, 1950, 72, 351) in reacting in general as a normal secondary alcohol. Its solution in concentrated sulphuric acid was pale yellow, in contrast to the intense colours shown by analogous solutions containing the diphenylmethylium ion (Welch and Smith, *J. Amer. Chem. Soc.*, 1950, 72, 4748) or its di-*p*-chloro-derivative (Newman and Deno, *ibid.*, 1951, 73, 3646), and evidently contained the un-ionised hydrogen sulphate since the alcohol was regenerated when the colourless solution obtained on addition to ice was heated. Acetic acid had no appreciable action on the alcohol and hot acetic anhydride reacted rather slowly to give the acetate, also readily obtained from the bromide by the action of silver acetate in acetic acid. Both the ether and the acetate gave pale yellow solutions in concentrated sulphuric acid which remained clear when poured on ice: the alcohol was regenerated when the resultant aqueous solution was heated. Dibromodi-*p*-nitrophenylmethane similarly dissolved in sulphuric acid to give a pale yellow solution, but this slowly evolved hydrogen bromide, and gave 4 : 4'-dinitrobenzophenone when added to ice.

Since tri-*p*-nitrophenylmethanol is converted into the coloured carbonium ion in 80—95% sulphuric acid (Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, 68, 1874; Lowen, Murray, and Williams, *J.*, 1950, 3318, 3322; Newman and Deno, *loc. cit.*) it was of interest to record the behaviour of di-*p*-nitrophenylmethyl derivatives in media of even higher acidity. The pale yellow colour shown by di-*p*-nitrophenylmethyl bromide and the methanol in concentrated sulphuric acid was noticeably intensified in 20% oleum or chlorosulphonic acid but only to a qualitatively similar degree to the enhancement of the pale yellow colour of di-*p*-nitrophenylmethane in the same solvents: the effect may therefore be due to more complete protonation of the nitro-groups (Gillespie, *J.*, 1950, 2547) rather than to stabilisation of the carbonium ion.

These general conclusions are upheld by the observation by Welch and Smith (*J. Amer. Chem. Soc.*, 1953, 75, 1412) that di-*p*-nitrophenylacetic acid gives a stable pale yellow solution in 100% sulphuric acid whereas diphenylacetic acid and its di-*p*-chloro-derivative react to form the carbonium ion with loss of carbon monoxide.

When bisdi-*p*-nitrophenylmethyl ether was heated under reduced pressure it dismutated near its melting-point to a mixture of di-*p*-nitrophenylmethane and 4 : 4'-dinitrobenzophenone. The change did not appear to be catalysed by occluded hydrogen ions (cf. Burton and Cheeseman, *J.*, 1953, 986) as it occurred readily in a sample of bis-ether which had been recrystallised from alcoholic pyridine. Thermal dismutation of diphenylmethyl derivatives has been reported by Nef (*Annalen*, 1897, 298, 234), Goldthwaite (*Amer. Chem. J.*, 1903, 30, 462), and Bacon (*ibid.*, 1905, 33, 90), and may proceed by a free-radical mechanism.

EXPERIMENTAL

Halogenation of Di-p-aminophenylmethane in Sulphuric Acid.—(a) *Bromination.* A solution of the base (1.98 g.) and silver sulphate (3.12 g.) in concentrated sulphuric acid (25 c.c.) was shaken with bromine (3.2 g.). Heat was evolved and after 30 min. the theoretical amount of silver bromide was obtained on filtration. The filtrate was poured into ice-water containing sodium sulphite, and neutralised. On extraction with ether the crude product was obtained as a glass (3.4 g., 96%) which, when treated with acetic anhydride in acetic acid, gave an acetyl derivative (4.2 g.), m. p. ca. 215°. Six recrystallisations from ethanol reduced the yield to 0.55 g., and the material had m. p. 233° and 239° (dimorphic forms) undepressed on admixture with di-(4-acetamido-2-bromophenyl)methane, m. p. 236° and 243° (see below). The crude base, treated in ethanol with hydrochloric acid, very slowly deposited a hydrochloride which gave impure di-(4-amino-2-bromophenyl)methane on basification: the procedure was not, however, an effective method of purification.

(b) *Chlorination.* A solution of the base (1.98 g.) and silver sulphate (3.12 g.) in concentrated

sulphuric acid (40 c.c.) was shaken with excess of dry chlorine in a stoppered 1 l. flask fitted with a tap. After 4 hr. pressure ceased to fall. The excess of chlorine was removed and the acid solution poured into ice-water containing sodium sulphite. After removal of silver chloride the filtrate was neutralised and the crude product (2.6 g., 100%) extracted with ether. Acetylation of the oil and three crystallisations from aqueous ethanol or from acetic acid gave a product (2.2 g., 62%), m. p. 220° and 224—225° (dimorphic forms) not depressed by di-(4-acetamido-2-chlorophenyl)methane, m. p. 226—227° (see below).

Halogenation of Di-p-methylaminophenylmethane in Sulphuric Acid.—(a) *Bromination.* The base (2.26 g.; m. p. 55—56°), prepared according to von Braun (*Ber.*, 1908, **41**, 2148; cf. Wagner, *loc. cit.*), was brominated under the foregoing conditions. After 30 min. the theoretical amount of silver bromide was recovered. The oily product (94%) gave a crude acetyl derivative (2.7 g., 58%), m. p. 126—128° (from aqueous ethanol). Further crystallisation gave *di*-(2-bromo-4-*N*-methylacetamidophenyl)methane in needles or flakes, m. p. 131.5—132.5°, very soluble in ethanol and acetic acid (Found: Br, 34.2. $C_{19}H_{20}O_2N_2Br_2$ requires Br, 34.1%). *Di*-(2-bromo-4-methylaminophenyl)methane, produced on treatment of the acetyl derivative with warm concentrated hydrochloric acid for 12 hr., initially formed a glass, but crystals, m. p. 76—77.5°, were obtained from petroleum (b. p. 90—120°) (Found: N, 7.3; Br, 41.5. $C_{15}H_{16}N_2Br_2$ requires N, 7.3; Br, 41.6%).

(b) *Chlorination.* The base (2.26 g.) was chlorinated within 4 hr. under the foregoing conditions, recovery of silver chloride being quantitative. The oily product (2.86 g., 97%) was converted into its acetyl derivative which gave crystals (2.08 g., 55%), m. p. 114—116°, from aqueous ethanol. Recrystallisation gave *di*-(2-chloro-4-*N*-methylacetamidophenyl)methane in flakes, m. p. 120—121° (Found: C, 60.0; H, 5.3; N, 7.4; Cl, 18.8. $C_{19}H_{20}O_2N_2Cl_2$ requires C, 60.2; H, 5.3; N, 7.4; Cl, 18.7%).

Condensations with Formaldehyde.—(a) *m-Chloroaniline.* A solution of the base (5.9 g.) in ethanol (100 c.c.), concentrated hydrochloric acid (6.6 c.c.), and aqueous formaldehyde (1.74 g.) was refluxed for 65 hr. The mixture was basified, steam-distilled, and then extracted with ether. The resulting oil was distilled twice at *ca.* 240°/0.5 mm., much resin remaining in the flask. The distillate (2.5 g.), when dissolved in ethanol and treated with concentrated hydrochloric acid (2 c.c.), gave a hydrochloride from which *di*-(4-amino-2-chlorophenyl)methane (1.73 g., 28%), m. p. 100—102°, was obtained on basification: there was no depression in m. p. on admixture with the material, m. p. 102.5—103.5°, described below.

(b) *m-Chloro-N-methylaniline.* The toluene-*p*-sulphonyl derivative (19.8 g.) of *m*-chloroaniline, dissolved in warm 10% sodium hydroxide (65 c.c.) and ethanol, was methylated with methyl sulphate (19.5 c.c.), the addition being repeated twice with half-quantities of reagent. The slightly alkaline mixture was cooled with agitation and the solid (20.5 g.), m. p. 77—79°, filtered off and hydrolysed by refluxing it with 75% sulphuric acid (75 c.c.) for 2½ hr. Unchanged material was removed with ether, and the *m*-chloro-*N*-methylaniline extracted from the basified solution and distilled at 234°/760 mm. (von Braun and Kruber, *Ber.*, 1913, **46**, 3474, gave b. p. 235°): the yield was 87%. The base (6.8 g.) was condensed with formaldehyde by the foregoing method during 17 hr., and the resulting oil (5.7 g.) distilled three times at 240—250°/0.3 mm. to separate *di*-(2-chloro-4-methylaminophenyl)methane (3.8 g., 54%) from accompanying resin. The product formed prisms, m. p. 73—74.5°, from light petroleum (b. p. 60—80°) (Found: C, 61.2; H, 5.6; Cl, 24.1. $C_{15}H_{16}N_2Cl_2$ requires C, 61.05; H, 5.5; Cl, 24.0%). Its dihydrochloride, *decomp. ca.* 185°, was very soluble in ethanol from which it was precipitated by ether. On acetylation the base gave *di*-(2-chloro-4-*N*-methylacetamidophenyl)methane, m. p. 120—121°, not depressed by the material previously described.

(c) *m-Bromo-N-methylaniline.* The toluene-*p*-sulphonyl derivative (16.7 g.) of *m*-bromoaniline, methylated by the foregoing procedure, gave 17.0 g. of product, m. p. *ca.* 85°. Hydrolysis yielded *m*-bromo-*N*-methylaniline as an oil, b. p. *ca.* 253°/760 mm., which darkened rather rapidly in air (Found: Br, 42.7. C_8H_8NBr requires Br, 42.9%): the *picrate* crystallised in yellow needles, m. p. 140—141°, from ethanol (Found: C, 38.0; H, 2.7; Br, 19.0. $C_{13}H_{11}O_7N_4Br$ requires C, 37.6; H, 2.7; Br, 19.25%). The base was condensed with formaldehyde during 17 hr. Purification of the partly resinous product presented considerable difficulty as further resinification appeared to occur on distillation at 0.4 mm. Fractional extraction and crystallisation from light petroleum (b. p. 60—80° and 40—60°) eventually gave a specimen of *di*-(2-bromo-4-methylaminophenyl)methane, m. p. 76—77°, which yielded a *di-N*-acetyl derivative, m. p. 131.5—132.5°. There was no depression on admixture with the compounds described previously.

Sandmeyer Reactions with Di-(4-acetamido-2-aminophenyl)methane.—(a) The base (5.4 g.)

(cf. Ehrlich and Bauer, *Ber.*, 1915, **48**, 505), diazotised in suspension in 24% hydrobromic acid (40 c.c.) with sodium nitrite, was poured into a hot solution of cuprous bromide (excess) in 48% hydrobromic acid. After the vigorous reaction had subsided the solution was cooled, filtered from a solid tar, and made strongly ammoniacal. The resulting precipitate separated from aqueous ethanol (charcoal) as a crystalline powder (0.07 g.), m. p. ca. 107° and 129° (dimorphic), and on acetylation gave di-(4-acetamido-2-bromophenyl)methane, m. p. 235° and 241° (dimorphic) not depressed by either of the specimens described elsewhere.

(b) The base (5.4 g.) was diazotised in hydrochloric acid, and the solution added to cuprous chloride in hot concentrated hydrochloric acid. A small amount of amine, m. p. 96—98°, was isolated which on acetylation gave di-(4-acetamido-2-chlorophenyl)methane, m. p. 218° and 222—223° not depressed by either of the specimens described elsewhere.

Halogenation of Di-p-nitrophenylmethane in Sulphuric Acid.—(a) *Bromination.* A solution of the dinitro-compound (5.16 g.) and silver sulphate (6.3 g.) in concentrated sulphuric acid (18 c.c.) and water (2 c.c.) was shaken with bromine (6.5 g.) for 3 hr. The solution was poured into ice-water and the collected precipitate extracted with methanol to give *di-(2-bromo-4-nitrophenyl)methane* (7.8 g., 94%; m. p. ca. 151°). Crystallisation from acetic acid and from ethanol gave pale yellow prisms, m. p. 153—154° (Found: C, 37.4; H, 2.1; Br, 38.55. $C_{13}H_8O_4N_2Br_2$ requires C, 37.5; H, 1.9; Br, 38.4%).

(b) *Chlorination.* A solution of the dinitro-compound (2.58 g.) and silver sulphate (3.12 g.) in concentrated sulphuric acid (50 c.c.) was shaken with an excess of chlorine. After 5 hr. pressure ceased to fall and recovery of silver chloride was quantitative. The crude product, m. p. 112—113°, obtained on dilution of the filtered solution was recrystallised seven times from acetic acid, giving *di-(2-chloro-4-nitrophenyl)methane* (50—60%) in pale yellow prisms, m. p. 124—125° (Found: N, 8.6; Cl, 21.7. $C_{13}H_8O_4N_2Cl_2$ requires N, 9.0; Cl, 21.7%).

Reduction of Di-(2-halogeno-4-nitrophenyl)methanes.—(a) The dibromo-compound (4.85 g.) was reduced with iron and acetic acid (70 c.c.), and the product treated with acetic anhydride to give *di-(4-acetamido-2-bromophenyl)methane* (4.48 g.) which after crystallisation from ethanol had m. p. 236° and 243° (dimorphic) (Found: C, 46.3; H, 3.9; Br, 36.5. $C_{17}H_{16}O_2N_2Br_2$ requires C, 46.4; H, 3.7; Br, 36.3%). Hydrolysis with 50% sulphuric acid followed by crystallisation from petroleum (b. p. 90—120°) and from aqueous ethanol gave *di-(4-amino-2-bromophenyl)methane*, m. p. 109—110° and 129—130° (dimorphic forms) (Found: C, 43.85; H, 3.9; Br, 44.65. $C_{13}H_{12}N_2Br_2$ requires C, 43.85; H, 3.4; Br, 44.9%).

(b) Powdered dichloro-compound (1.42 g.) was washed with ethanol into a hot solution of stannous chloride (9 g.) in concentrated hydrochloric acid (30 c.c.). *Di-(4-amino-2-chlorophenyl)methane* (1.2 g.) was obtained on basifying the clear solution: it separated from aqueous ethanol as a crystalline powder, m. p. 102.5—103.5° (Found: C, 58.5; H, 4.4; Cl, 26.6. $C_{13}H_{12}N_2Cl_2$ requires C, 58.4; H, 4.5; Cl, 26.55%). *Di-(4-acetamido-2-chlorophenyl)methane* crystallised from aqueous ethanol in fine needles, m. p. 226—227° (Found: N, 8.0; Cl, 20.1. $C_{17}H_{16}O_2N_2Cl_2$ requires N, 8.0; Cl, 20.2%). The low m. p. form encountered in previously described specimens of slightly lesser purity could not be detected in the highly purified compound (cf. *J.*, 1950, 407).

Bromination of Di-p-nitrophenylmethane in Organic Solvents.—(a) The dinitro-compound (3.55 g.) was gently refluxed with bromine (4.8 g., 2.2 mols.) in carbon tetrachloride (100 c.c.) containing iodine (0.05 g.) for 7 days with almost complete exclusion of light. The solvent, which still contained bromine, was evaporated and the residue warmed with methanol. The crystals (3.5 g.; m. p. ca. 100°) obtained on cooling gave unchanged dinitro-compound (0.77 g., 22%) when recrystallised from acetic acid. Dilution of combined mother-liquor and crystallisation of the precipitate from acetic acid or methanol gave *di-p-nitrophenylmethyl bromide* (1.9 g., 41%) in pale yellow prisms, m. p. 97—98° (Found: C, 46.5; H, 3.0; Br, 23.2. Calc. for $C_{13}H_8O_4N_2Br$: C, 46.3; H, 2.7; Br, 23.7%). Orazi and Giunti (*loc. cit.*) recorded m. p. 98—98.5°.

(b) The reaction mixture described in (a), but without addition of iodine, was refluxed under illumination (incandescent lamp, 200 w) until the bromine had largely reacted (<2 hr.). Crystallisation of the product from acetic acid gave *dibromodi-p-nitrophenylmethane* (3.1 g., 54%) in pale yellow prisms, m. p. 168—169° (Found: C, 37.6; H, 1.8; Br, 38.5. $C_{13}H_8O_4N_2Br_2$ requires C, 37.5; H, 1.9; Br, 38.4%). When refluxed in acetic acid for 15 hr. this compound was converted into 4:4'-dinitrobenzophenone. The same product resulted when the pale yellow solution formed by the dibromide in concentrated sulphuric acid was poured on ice.

(c) The dinitro-compound (7.1 g.) was gently refluxed with bromine (4.8 g., 1.1 mol.) in carbon tetrachloride (150 c.c.) under illumination (200 w) for 30 minutes. On removal of the solvent and crystallisation of the residue from acetic acid it was possible to recover (preferably with

seeding) crops of unchanged material and of dibromodi-*p*-nitrophenylmethane (on one occasion 1.6 g., 14%) and ultimately of di-*p*-nitrophenylmethyl bromide (35–40%).

(d) When the dinitro-compound (7.1 g.) was refluxed with excess of bromine in acetic acid (140 c.c.) containing iodine (0.1 g.) the only product isolated after 90 hr. was 4 : 4'-dinitrobenzophenone (6.2 g., 84%). After 15 hr., however, di-*p*-nitrophenylmethyl bromide was isolated in ca. 10% yield.

Behaviour of Di-p-nitrophenylmethyl Bromide in Sulphuric Acid.—(a) The powdered dinitro-compound readily formed a pale yellow solution in the concentrated acid and was regenerated essentially unchanged when poured into water.

(b) To a solution of the dinitro-compound (2.84 g.) in concentrated sulphuric acid (20 c.c.) was added silver sulphate (1.6 g.) in the same solvent (10 c.c.); silver bromide was precipitated immediately. The mixture was added to ice and filtered after 1 hr. The filtrate was boiled gently until crystals appeared, filtered, and heated further to ensure maximum recovery of hydrolysis product. The crystals (1.7 g., 74%) melted at 169° (rapid heating) followed by solidification of the melt and further melting at ca. 280° (with slow heating there was no lower m. p.). Crystallisation from aqueous acetic acid gave di-*p*-nitrophenylmethanol in platelets, m. p. 169–170° (no change after raising bath temperature to 280°, cooling and redetermining m. p.) (Found : C, 57.3; H, 3.7; N, 10.0. Calc. for $C_{13}H_{10}O_5N_2$: C, 56.9; H, 3.7; N, 10.2%). Curtin and Leskowitz (*loc. cit.*) found m. p. 168–169° for this alcohol.

When the original sulphuric acid solution was filtered through sintered glass to remove the silver bromide and poured into water instead of on ice, some of the alcohol was precipitated. If the filtrate was then basified with sodium hydroxide a deep orange-red colour developed, evidently due to the anion of the sulphonated alcohol. This solution slowly and continuously deposited 4 : 4'-dinitrobenzophenone with progressive fading of the colour. In the same way the pale bronze-coloured solution of di-*p*-nitrophenylmethanol (0.07 g.) in methanol containing sodium methoxide (from 0.01 g. of sodium) slowly deposited 4 : 4'-dinitrobenzophenone and was fully oxidised within 42 hr.

(c) A solution of the dinitro-compound (1.34 g.) in sulphuric acid was treated as in (b) and the silver bromide recovered (quantitative). The filtrate was diluted with water, with shaking, so that considerable heat was generated. The resultant precipitate (0.98 g.) was removed, dried at 50°, and boiled with acetic acid. Filtration of the cool suspension gave bisdi-*p*-nitrophenylmethyl ether (0.26 g., 25%), which when crystallised from acetic acid (extractor) had m. p. 284–286° (Found : C, 59.05; H, 3.5. Calc. for $C_{26}H_{18}O_9N_4$: C, 58.9; H, 3.4%) (Curtin and Leskowitz, *loc. cit.*, gave m. p. 286–287°). On dilution with water the acetic acid filtrate gave di-*p*-nitrophenylmethanol (0.65 g., 60%), m. p. 169–170°.

The ether (m. p. 284–286° from acetic acid) was also obtained by heating the crude methanol from (b), m. p. 169° and ca. 280°, for several minutes at 180–200°.

Di-p-nitrophenylmethyl Acetate.—(a) Di-*p*-nitrophenylmethyl bromide (0.33 g.) was added to a suspension of silver acetate (1.8 g.) in acetic acid (15 c.c.), which was refluxed for 5 min., filtered, and diluted with water. The acetate (0.32 g.) formed crystals, m. p. 175–176°, from acetic acid (Found : C, 57.2; H, 3.8; N, 8.9. $C_{15}H_{12}O_8N_2$ requires C, 56.95; H, 3.8; N, 8.9%). The same compound was formed, with some side-product of high m. p., when the bromide was refluxed with potassium acetate in acetic acid.

(b) Di-*p*-nitrophenylmethanol remained unchanged after 65 hr. in acetic acid solution at 20° and after 2 hr. at 100°. It was partly acetylated after 5 min. in boiling acetic anhydride but on addition of a trace of sulphuric acid it reacted completely to give the acetate, m. p. 175–176°.

The acetate was hydrolysed to the alcohol when refluxed in methanol (30 c.c.) in presence of sulphuric acid (1 c.c.). Its alcoholic solution developed a violet colour on addition of potassium hydroxide; the colour gradually faded with deposition of 4 : 4'-dinitrobenzophenone.

Action of Sulphuric Acid on Di-p-nitrophenylmethanol and its Derivatives.—The alcohol dissolved in concentrated sulphuric acid to a pale yellow solution which gave only a slight amorphous precipitate when added to ice : after centrifugation the solution remained clear for 3½ days at 0° in presence of a crystal of the alcohol. A portion of the solution regenerated the alcohol on gentle boiling : another portion, basified with potassium hydroxide, gave a deep orange-red solution which deposited 4 : 4'-dinitrobenzophenone.

When a sulphuric acid solution of the alcohol was quickly diluted with water the precipitate which formed consisted of regenerated alcohol in admixture with a lesser quantity of the ether.

Both the acetate and the ether formed pale yellow solutions in sulphuric acid. The clear solutions obtained on addition to ice regenerated the alcohol when heated.

Action of Oleum and Chlorosulphonic Acid on Di-p-nitrophenylmethyl Derivatives.—Equivalent quantities (0.002 mol.) of di-*p*-nitrophenylmethane, di-*p*-nitrophenylmethyl bromide, and di-*p*-nitrophenylmethanol were dissolved separately in concentrated sulphuric acid (3 c.c.), in oleum (20% w/w free SO₃) (3 c.c.), and in chlorosulphonic acid (3 c.c.). The three solutions in sulphuric acid were pale yellow and almost identical in appearance: the six solutions in oleum and chlorosulphonic acid were bright yellow and almost identical in appearance. After 1 hr., during which time there was no appreciable colour change, the solutions were added to ice. Di-*p*-nitrophenylmethane was in each case recovered unchanged. Di-*p*-nitrophenylmethyl bromide, unchanged by sulphuric acid, had been converted in oleum into the hydrogen sulphate: on boiling the clear solution the alcohol was regenerated. The alcohol had also been sulphonated by oleum. The products from chlorosulphonic acid were not further examined.

Dismutation of Bisdi-p-nitrophenylmethyl Ether.—A specimen of the ether (0.17 g.), which had been crystallised from acetic acid, was heated to 290°/0.2 mm. with a view to sublimation. The sublimate (0.14 g.) was a mixture, m. p. 150—153°, readily separated by the use of Girard reagent *r* into di-*p*-nitrophenylmethane (0.05 g.) and 4:4'-dinitrobenzophenone (0.04 g.). These products on crystallisation from acetic acid had m. p.s 186—187° and 191—192°, respectively, not depressed by authentic specimens (Hunsberger and Amstutz, *J. Amer. Chem. Soc.*, 1949, **71**, 2638, record m. p.s 188.6—189.4° and 189.6—190.6°, whereas the older literature gives m. p.s 183° and 189° respectively).

A specimen of the ether which had been recrystallised twice from alcoholic pyridine behaved similarly when heated to 290°.

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