# **320.** *The Reactivity of the Methylene Group in Some Nitrodiphenylmethanes.*

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THE influence of the nitro-group upon the reactivity of a neighbouring methylene group is well known (see, *e.g.*, Bamberger and Schmidt, *Ber.*, 1900, **33**, 2050; Parkes and Williams, J., 1934, 67) and the similar influence of a 2 : 4-dinitrophenyl residue was observed by Meyer (*Ber.*, 1889, **22**, 320).

In order to discover the extent to which the number and positions of the nitro-groups present influence the reactivity of the methylene group the behaviour of the following nitrated derivatives of diphenylmethane with solutions of diazonium salts and with *p*-nitrosodimethylaniline (compare Sachs and Kempf, *Ber.*, 1902, **35**, 1226) has been examined: diphenylmethane itself, 4 : 4′-, 2 : 4′-, 2 : 2′- and 3 : 3′-dinitrodiphenylmethanes, 2 : 4 : 2′ : 4′-tetranitro- and 2 : 4 : 6 : 2′ : 4′-pentanitro-diphenylmethanes. Experiments performed under a variety of conditions showed that in no case can nitrated phenyl residues alone enhance the reactivity of the methylene group to the extent required to bring about coupling with diazonium salts.

Diphenylmethane and 3 : 3′-dinitrodiphenylmethane do not react with *p*-nitrosodimethylaniline, but 4 : 4′-dinitro- and 2 : 4 : 2′ : 4′-tetranitro-diphenylmethane condense smoothly in presence of anhydrous sodium carbonate, yielding purplish-red products. 2 : 4′-Dinitrodiphenylmethane yields, though much less readily (8 hours' boiling), a product of similar appearance. This, however, is apparently a molecular compound, for it is so unstable that in solution in absence of alkali it breaks up into its original constituents. The product from 4 : 4′-dinitrodiphenylmethane is hydrolysed smoothly to 4 : 4′-dinitrobenzophenone by boiling dilute mineral acids, but the product from 2 : 4 : 2′ : 4′-tetranitrodiphenylmethane is unaffected by prolonged boiling with a sulphuric acid (50%)–acetic acid mixture and even forms an unstable hydrochloride. 2 : 2′-Dinitrodiphenylmethane reacts with *p*-nitrosodimethylaniline, but the product could not be obtained pure; it resisted hydrolysis, however, like that from the 2 : 4 : 2′ : 4′-tetranitro-derivative.

The number and positions of the nitro-groups present thus have a marked influence upon the methylene group in nitrated diphenylmethanes, and in the main this influence is of the kind which would be anticipated, but the wide difference in the stability of the products is surprising. The resistance of 2 : 4 : 2′ : 4′-*tetranitrobenzophenone*-p-*dimethylaminoanil* to hydrolysis may be due to steric effects, but the difference in the behaviour of the 4 : 4′- and the 2 : 4′-compound is unexpected, and not simply explicable.

## EXPERIMENTAL.

The nitrodiphenylmethanes were obtained by nitration of diphenylmethane, the 4 : 4′- and the 2 : 4′-isomer by the method of Staedel (*Annalen*, 1894, **283**, 156) and the 2 : 2′-compound according to Schnitzspahn (*J. pr. Chem.*, 1902, **65**, 322). The preparation of 2 : 4 : 2′ : 4′-tetranitrodiphenylmethane by the methods of Doer (*Ber.*, 1872, **5**, 795), Staedel (*Annalen*, 1883, **218**, 319), and Schöpff (*Ber.*, 1894, **27**, 2318) was not altogether satisfactory. The following procedure gave a quantitative yield. A mixture of 45 g. of nitric acid (*d* 1·53) and 150 g. of concentrated sulphuric acid was added very slowly with shaking to 100 g. of diphenylmethane, the temperature being kept below 50°. At the stage corresponding to the formation of dinitrodiphenylmethane yellow crystals separated, and when this occurred the mixture was warmed to 70° on a water-bath, and the remainder of the acid together with a further mixture of 50 c.c. of nitric acid (*d* 1·53) and 100 c.c. of fuming sulphuric acid (20% $SO_3$) added with vigorous shaking. The now clear liquid was kept at 90° for 1 hour, cooled, and poured on ice. The tetranitrodiphenylmethane which separated (190 g.) was washed with sodium bicarbonate solution and recrystallised from glacial acetic acid.

2 : 4 : 6 : 2′ : 4′-*Pentanitrodiphenylmethane* was obtained by addition with shaking to 50 g. of powdered 2 : 4 : 2′ : 4′-tetranitrodiphenylmethane of a mixture of 110 g. of fuming nitric acid (*d* 1·5) and 250 c.c. of fuming sulphuric acid (20% $SO_3$). The mixture was kept at 100° for 3 days and poured on ice. The solid which separated was washed with sodium bicarbonate solution and extracted with hot acetic acid, in which the by-product 2 : 4 : 2′ : 4′-tetranitrobenzophenone was only very sparingly soluble. On cooling, the filtered extracts deposited unchanged 2 : 4 : 2′ : 4′-tetranitrodiphenylmethane, which was removed; and on long standing 2 : 4 : 6 : 2′ : 4′-pentanitrodiphenylmethane separated. After repeated crystallisation from acetic acid it formed pale yellow, rhombic plates (10 g.), m. p. 200° (Found: N, 17·8. $C_{13}H_7O_{10}N_5$ requires N, 17·8%).

Hexanitrodiphenylmethane could not be obtained, since no further nitration took place at 100° and at higher temperatures oxidation occurred.

The following modification of Schöpff's method (*loc. cit.*) was found satisfactory for the preparation of 3 : 3′-dinitrodiphenylmethane. A mixture of 120 g. of nitrobenzene, 700 g. of concentrated sulphuric acid, and 50 c.c. of 40% formalin was maintained at 60—70° for three weeks. After dilution with water, the excess of nitrobenzene was removed by steam distillation and the 3 : 3′-dinitrodiphenylmethane remaining was washed with water and crystallised three times from acetic acid (charcoal) (50 g.).

*Condensations with* p-*Nitrosodimethylaniline*.—20 G. of 4 : 4′-dinitrodiphenylmethane (1 mol.), 12 g. of *p*-nitrosodimethylaniline (1 mol.), and 25 g. of anhydrous sodium carbonate were refluxed for 3 hours with 200 c.c. of ethyl alcohol. On cooling to 0°, a reddish solid separated, which was washed with acetic acid, and then with hot water until the washings were colourless. The compound was dissolved in boiling acetone, and hot alcohol added; on cooling, 4 : 4′-*dinitrobenzophenone*-p-*dimethylaminoanil* separated as a reddish-brown amorphous substance, m. p. 155° (Found: N, 14·2. $C_{21}H_{18}O_4N_4$ requires N, 14·4%).

2 : 4 : 2′ : 4′-*Tetranitrobenzophenone*-p-*dimethylaminoanil*, prepared similarly from 25 g. of tetranitrodiphenylmethane, 14 g. of *p*-nitrosodimethylaniline, and 30 g. of anhydrous sodium carbonate, and purified by precipitation from hot benzene solution with hot ligroin, was an almost black, amorphous solid which, when dried on a water-bath, yielded a reddish-black powder, m. p. 143° (decomp.) (Found: N, 17·6. $C_{21}H_{16}O_8N_6$ requires N, 17·5%).

2 : 2′-Dinitro- and 2 : 4 : 6 : 2′ : 4′-pentanitro-diphenylmethane gave purplish-black reaction products which could not be obtained in pure crystalline forms. The colour change seems to indicate, however, that reaction can take place.

*Hydrolysis of the Condensation Products*.—A solution of 5 g. of 4 : 4′-dinitrobenzophenone-*p*-dimethylaminoanil in 30 c.c. of acetic acid was boiled for 5 minutes with 10 c.c. of concentrated hydrochloric acid. The red colour faded and dilution with water gave 4 : 4′-dinitrobenzophenone (2 g.).

A similar solution of 2 : 4 : 2′ : 4′-tetranitrobenzophenone-*p*-dimethylaminoanil underwent no change after many hours' boiling and the original compound was recovered unchanged.

The crude condensation product from 2 : 2′-dinitrodiphenylmethane showed a similar resistance to hydrolysis, for the colour showed no sign of diminution after 2 hours' boiling with concentrated hydrochloric acid diluted with an equal volume of water. No 2 : 2′-dinitrobenzophenone could be isolated and the bulk of the condensation product was recovered unchanged.

Dry hydrogen chloride, passed into a solution of 2 : 4 : 2′ : 4′-tetranitrobenzophenone-*p*-dimethylaminoanil in dry benzene, precipitated a greenish-yellow solid, which was probably a hydrochloride. It rapidly lost hydrogen chloride when removed from the solution, leaving a residue of the original anil.

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