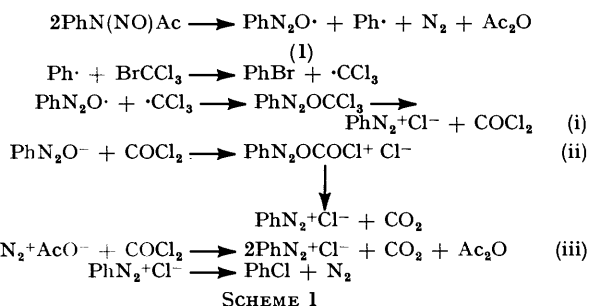


In Situ Formation of Arenediazonium Salts and Aryl Radicals by Aprotic Nitrosation of 1,3-Diaryltriazenes: Dual Halogen Abstraction from Bromotrichloromethane, and Radical Arylation of Aromatic Compounds

By J. I. G. Cadogan,* Robin G. M. Landells, and John T. Sharp, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Nitrosation of 1,3-diaryltriazenes ($\text{XC}_6\text{H}_4\cdot\text{NHN}_2\cdot\text{C}_6\text{H}_4\text{X}$; X = H, 4-Me, 4-MeO, 4-Cl, 4-NO₂, 2-Me, 2-Cl, or 3-Cl) by pentyl nitrite in benzene at 80 °C, and subsequent *in situ* decomposition of the resulting *N*-nitroso-1,3-diaryltriazenes, gives biaryls ($\text{XC}_6\text{H}_4\text{Ph}$) (54–142 mol per 100 mol of triazene). 1-(4-Chlorophenyl)-3-phenyltriazenes gives a mixture of 4-chlorobiphenyl (66 mol per 100 mol) and biphenyl (65 mol per 100 mol). That aryl radicals are involved follows (a) from the formation of 2- (18.5%), 3- (49.5%), and 4- (32%) *t*-butylbiphenyls (total yield 106 mol per 100 mol) on nitrosation of 1,3-diphenyltriazenes in *t*-butylbenzene, and (b) from the relative extents of reaction of this nitrosated triazene with benzene and chlorobenzene (excess of an equimolar mixture; ratio 1 : 1.6, respectively). Reaction of pentyl nitrite with 1,3-diphenyltriazenes in bromotrichloromethane at 15 °C gives a precipitate of benzenediazonium chloride (80 mol per 100 mol). Also formed are bromobenzene (33), chlorobenzene (21), carbon dioxide (10), and pentyl carbanilate (10) mol per 100 mol. At 50 °C the reaction gave chlorobenzene (61) and bromobenzene (49); addition of 1,1-diphenylethene led to an almost complete reversal of these proportions. These results provide another example of anomalous dual halogen abstraction from bromotrichloromethane and support the general mechanism for this type of reaction outlined in the preceding paper.

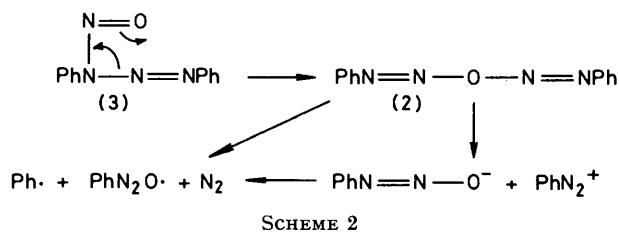
IN the preceding paper,¹ key factors in our explanation of hitherto anomalous dual abstraction of bromine and chlorine from bromotrichloromethane during its reaction with *N*-nitrosoacetanilide (NNA) were the intermediacy of the benzenediazonium, benzenediazoate, and acetate ions, and hence of phenyldiazo-oxyl (1) and phenyl radicals, and phosgene. The essential details of the mechanism are given in Scheme 1. The formation of



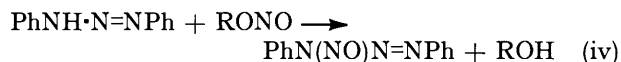
chlorobenzene, the hitherto unexplained product, depends on the formation and ionic dediazonation of benzenediazonium chloride *via* reactions (i)–(iii). We presented evidence for (i) but the operation of (ii) and (iii) was inferred from the formation of carbon dioxide.

The rationale of the experiments described in this paper is as follows: in principle, the desired evidence concerning the importance of reactions (ii) and (iii) and general confirmation of Scheme 1 should be obtainable by study of reactions of the benzenediazonium–benzenediazoate

ion-pair in the absence of acetate ion, since this ion pair, according to Scheme 1, should give all the necessary reactive intermediates. Two possible, known sources are benzenediazoanhydride (2)² and *N*-nitroso-1,3-diphenyltriazenes (3) as shown in Scheme 2. Both are



known^{2,3} to give biaryls on decomposition in aromatic solvents, and in the second case phenyl radicals are present,³ but both are very labile and explosive and accountances on decomposition are low. We sought to overcome these deficiencies by *in situ*, one-flask formation, and subsequent decomposition of *N*-nitroso-1,3-diphenyltriazenes (3) by aprotic nitrosation of 1,3-diphenyltriazenes by pentyl nitrite.



Arylation of Aromatic Compounds by Pentyl Nitrite–1,3-Diaryltriazenes.—Dou and Metzger⁴ have briefly referred to the possibility of radical arylation *via* this reaction, and Fisera and his co-workers⁵ have recently produced

⁴ H. J. M. Dou and J. Metzger, *Bull. Soc. chim. France*, 1974, 560.

⁵ L. Fisera, J. Kovac, E. Komanova, and J. Lesko, *Tetrahedron*, 1974, 30, 4123.

¹ J. I. G. Cadogan, J. Cook, R. G. M. Landells, and J. T. Sharp, preceding paper.

² E. Bamberger, *Ber.*, 1896, 29, 446.

³ E. Muller and H. Haiss, *Chem. Ber.*, 1962, 95, 1255.

2-arylfurans (30—40%) by this route. Their conclusion that radicals were involved, though reasonable, was not established. Before considering our primary objective of investigating the reaction of pentyl nitrite and 1,3-diphenyltriazine with bromotrichloromethane it was therefore necessary to establish the radical nature of the reaction. We chose the classical diagnostic reactions of benzene derivatives based on measurement of isomer ratios and relative rate ratios.⁶ The results are summarised in Table 1. Typically, pentyl nitrite (1.5 mol.

TABLE 1

Reactions of 1,3-diaryltriazines ($\text{RC}_6\text{H}_4\cdot\text{NHNH}_2\cdot\text{C}_6\text{H}_4\cdot\text{X}$) with pentyl nitrite in aromatic solvents

Triazine		Solvent	Biaryl	
R	X		Subst.	Yield * (mol per 100 mol of triazine)
H	H	PhH	H	114
4-Me	4-Me †	PhH	4-Me	142
4-MeO	4-MeO †	PhH	4-MeO	76
4-Cl	4-Cl	PhH	4-Cl	80
4-NO ₂	4-NO ₂	PhH	4-NO ₂	84
2-Me	2-Me	PhH	2-Me	62
2-Cl	2-Cl	PhH	2-Cl	54
3-Cl	3-Cl	PhH	3-Cl	84
H	4-Cl	PhH	H	65
			4-Cl	66
H	H	PhBu [‡]	Bu [‡]	106
H	H	PhCl + PhH	Cl	68
			H	42

* All biaryls were known and had the reported m.p.s and/or b.p.s. † Control reactions gave biaryl (10 mol per 100 mol). Yields are corrected for this. ‡ Isomeric mixture: 2- (18.5%), 3- (49.5%), 4- (32%).

equiv.) in a small amount of benzene was added over 5 min to a solution of the triazine in a large excess of benzene at the b.p., under nitrogen, to give good yields of biaryls. It is clear from the conversion, in benzene, of the unsymmetrical 1-(4-chlorophenyl)-3-phenyltriazine into an equimolar mixture of biphenyl and 4-chlorobiphenyl, that both aryl rings take part in the reaction. That the reaction is a radical process follows from two observations: (i) the ratios of isomeric t-butylbiphenyls formed in the reaction of 1,3-diphenyltriazine in t-butylbenzene are within experimental error the same as those obtained from dibenzoyl peroxide in the same solvent;⁷ and (ii) the rate ratio (1.6 : 1) from competitive phenylation of an equimolar mixture of chlorobenzene and benzene is within experimental error the same as that (1.5 : 1) obtained using dibenzoyl peroxide as a source of phenyl radicals.⁶ Other observations relevant to the mechanism of the reaction are the high recovery of nitrogen (190 mol per 100 mol of triazine), that the pentyl moiety reappears at the end of the reaction as pentan-1-ol (75 mol per 100 mol), and that thermolysis of 1,3-diphenyltriazine alone does not occur to a significant extent in boiling benzene.

These results, taken with those of Fisera and his co-

⁶ D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1952, 2094.

⁷ J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 3352.

workers,⁵ provide good evidence for the formation of the nitrosotriazine (3) according to reaction (iv) and its decomposition according to Scheme 2, subsequent arylation following the established path.⁸

Reactions of 1,3-Diphenyltriazene with Pentyl Nitrite in Bromotrichloromethane.—The results of these experiments are given in Table 2. Reaction at 50 °C gave high yields of both chlorobenzene and bromobenzene, thus paralleling the 'anomalous' behaviour of *N*-nitrosoacetanilide in bromotrichloromethane. Further, the same reaction at 15 °C afforded benzenediazonium chloride in high yield (80 mol per 100 mol of triazine) together with bromobenzene, chlorobenzene, and carbon dioxide, again according to the pattern, but demonstrat-

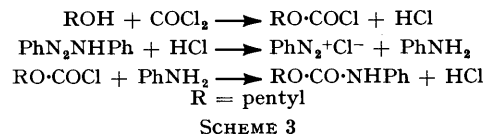
TABLE 2

Products * of reactions of 1,3-diphenyltriazene with pentyl nitrite in bromotrichloromethane

	15 °C	50 °C	60 °C + DPE †
PhCl	21	61	43
PhBr	33	49	68
PhN ₂ Cl	80	0	
PhNHCO ₂ C ₅ H ₁₁	9		
CO ₂	10		
Accountance (%)	72	55	55

* Yields in mol per 100 mol of triazine. † DPE = Ph₂C-CH₂.

ing that acetate ions are not essential precursors of benzenediazonium chloride, and providing indirect evidence for reaction (ii). The low temperature experiment also provided the first direct evidence for the participation of phosgene in dual halogen abstractions, by the isolation of pentyl carbanilate (10 mol per 100 mol). This is assumed to arise as outlined in Scheme 3 by reaction of pentan-1-ol with phosgene to give pentyl chloroformate and hydrogen chloride, which in turn heterolyses 1,3-diphenyltriazene to give benzenediazonium chloride and aniline,⁹ and thence pentyl carbanilate.



The isolated carbon dioxide and pentyl carbanilate, of which only the latter can we claim to be quantitatively collected, account for 57% of the precipitated benzenediazonium chloride on the basis of Schemes 1 and 3.

The reaction of pentyl nitrite with 1,3-diphenyltriazene in bromotrichloromethane in the presence of 1,1-diphenylethene completes the parallelism with the corresponding reaction of NNA.¹ The yield of chlorobenzene is reduced by the scavenging of trichloromethyl radicals, thus allowing the production of phenyl radicals, and hence bromobenzene, to become favoured.

⁸ J. I. G. Cadogan, R. M. Paton, and C. Thomson, *J. Chem. Soc. (B)*, 1971, 583.

⁹ A. I. Vogel, 'Practical Organic Chemistry,' Longman, Green and Co., 3rd edn., London, 1956.

EXPERIMENTAL

G.l.c.-mass spectrometric analyses were performed as described earlier¹.

Reagents.—1,3-Diaryltriazenes (Table 1)⁹ were all known compounds having m.p.s. as reported and correct elemental analyses. Pentyl nitrite had b.p. 104° (lit.,⁹ 104°). Pentyl carbanilate had m.p. 45–46° (lit.,¹⁰ 46°).

Reactions of 1,3-Diaryltriazenes with Pentyl Nitrite.—(i) *In benzene.* Pentyl nitrite (1.25 g, 10.7 mmol) in benzene (10 ml) was added dropwise over 5 min to a solution of 1,3-diphenyltriene (1.4 g, 7.1 mol) in boiling benzene (100 ml) the reaction being carried out in an atmosphere of dry nitrogen. The yellow colour due to the dissolved triene rapidly changed to deep red. Boiling under reflux was continued for a further 6 h. T.l.c. showed that the triene had been completely consumed. The mixture was chromatographed on alumina (elution with light petroleum-ether). Biphenyl (1.24 g, 114 mol per 100 mol) was collected as the only major product, m.p. and mixed m.p. 70° (i.r. spectrum). Nitrogen (190 mol per 100 mol) was collected. A parallel experiment in benzene at 50 °C gave biphenyl (124 mol per 100 mol). Yields were obtained by g.l.c. analysis (bibenzyl as internal standard). Control experiments with 1,3-diphenyltriene in benzene at 80 °C and at room temperature gave no biphenyl.

In the above way, a series of 1,3-diaryltriazenes was nitrosated with pentyl nitrite and subsequently decomposed in boiling benzene. Dry column chromatography of the residue on alumina (elution with light petroleum), afforded the biaryl. 4-Nitrophenyl was eluted with ether. 1,3-Bis-(4-nitrophenyl)triene was not very soluble in benzene; thus the reaction mixture was heterogeneous. The molar ratio of nitrite to 1,3-diaryltriene required to nitrosate the derivative was 3:1 and for 1,3-bis-(2-chlorophenyl)triene was 2.6:1. The results are summarised in Table 1.

(ii) *In t-butylbenzene and in equimolar chlorobenzene-benzene.* 1,3-Diphenyltriene (0.72 g, 3.7 mmol) was dissolved in t-butylbenzene (50 ml) and the mixture heated with stirring to 80 °C, under dry nitrogen. Pentyl nitrite (0.62 g, 5.3 mmol) in t-butylbenzene (5 ml) was added dropwise over 3 min and the mixture stirred for a further 6.5 h. T.l.c. showed that the triene had been completely consumed. The ratios of the isomeric t-butylbiphenyls were established by g.l.c. In the above way, 1,3-diphenyltriene was nitrosated and subsequently decomposed in 50:50 benzene-chlorobenzene. Analysis was performed by g.l.c. The results are given in Table 1.

(iii) *In bromotrichloromethane at 15 °C.* Pentyl nitrite (0.18 g, 1.5 mmol) in bromotrichloromethane (1.5 ml) was added dropwise over 10 min to a solution of 1,3-diphenyltriene (0.19 g, 0.96 mmol) in bromotrichloromethane (6 g, 30 mmol) at 15 °C under dry nitrogen with stirring. The mixture turned cloudy and after a few minutes a pale yellow precipitate began to form. After 25 h the precipitate was filtered off, washed with a little bromotrichloromethane, and dried. The precipitate (0.115 g) [ν_{\max} , 2280 cm⁻¹ (-N_2^+)] with alkaline 2-naphthol formed 1-phenylazo-2-naphthol, m.p. and mixed m.p. 132°. The dry diazonium salt was dissolved in water and a sample of this solution gave a positive test with silver nitrate solution in nitric

acid, indicating the presence of a halide, but the precipitated silver halide was soluble in dilute ammonia. A test for bromide using sodium hypochlorite gave a negative result (0.2% would have been detected). Quantitative analysis for chloride using Mohr's method indicated that the precipitate contained 94.4% of benzenediazonium chloride. The yield of benzenediazonium chloride was therefore 80 mol per 100 mol of triene. The i.r. spectrum contained a weaker diazonium absorption (2180 cm⁻¹) indicating the possibility of benzenediazonium nitrate forming the remainder (5.6%) of the precipitate. A parallel experiment gave benzenediazonium chloride (76 mol per 100 mol of triene). G.l.c. (10% APL; 145 °C) of the filtered reaction mixture (4-t-butyltoluene as internal standard) gave the yields of chlorobenzene (21.4) and bromobenzene (33 mol per 100 mol of triene). G.l.c.-mass spectrometric analysis (1% SE30; 180 °C) showed the presence of a compound with *m/e* 207. The mixture from a parallel reaction carried out at room temperature for 27.5 h was chromatographed on alumina (elution with light petroleum-ether). Pentyl carbanilate (8 mol per 100 mol of triene) was collected, and after sublimation had m.p. and mixed m.p. 44–46°. The mass, i.r., and n.m.r. spectra were identical with those of an authentic sample.¹⁰ G.l.c. analysis (1% SE30; 160 °C) of the mixture from a repeat experiment (fluoranthene as internal standard) showed the presence of pentyl carbanilate (9 mol per 100 mol of triene).

Carbon dioxide (10 mol per 100 mol) was also detected as described earlier.¹

(iv) *In bromotrichloromethane at 50 °C.* Pentyl nitrite (0.36 g, 3 mmol) in bromotrichloromethane (1 ml) was added dropwise over 10 min to a stirred solution of 1,3-diphenyltriene (0.406 g, 2 mmol) in bromotrichloromethane (12.1 g, 60 mmol) at 50 °C under dry nitrogen. The mixture began to darken immediately and deposited a pale yellow solid which quickly decomposed. The temperature of the well stirred mixture was maintained at 50 °C for 48 h. G.l.c. analysis (10% APL; 145 °C) (4-t-butyltoluene as internal standard) showed the presence of chlorobenzene (61.2 mol per 100 mol of triene) and bromobenzene (48.8). A parallel experiment gave chlorobenzene (63), bromobenzene (48), and pentan-1-ol (75.4 mol per 100 mol). The presence of these compounds was confirmed by g.l.c.-mass spectrometric analysis.

(v) *In bromotrichloromethane in the presence of 1,1-diphenylethene at 60 °C.* This experiment was performed as for experiment (iv), but with 1,1-diphenylethene (2 mmol) added. G.l.c. analysis (10% APL; 145 °C) (4-t-butyltoluene as internal standard) showed the presence of chlorobenzene (42.8) and bromobenzene (67.6 mol per 100 mol of triene). G.l.c. (1% SE30; 150–190 °C) showed that 1,1-dichloro-2,2-diphenylcyclopropane and 9-phenylphenanthrene were not produced. The results from the reactions of 1,3-diphenyltriene with pentyl nitrite in bromotrichloromethane are collected in Table 2.

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¹⁰ E. Blaise and L. Picard, *Ann. Chim. Phys.*, 1912, **25**, 261.