Acylarylnitrosamines. Part 12.[1] Decomposition of *N*-Nitrosoacetanilide and *p*-Nitro-*N*-nitrosoacetanilide in Bromotrichloromethane. An Answer to the Long-standing Problem of the Mechanism of ' Anomalous ' Dual Halogen Abstractions †

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Whereas phenyl radicals from dibenzoyl peroxide or phenylazotriphenylmethane abstract bromine almost exclusively, rather than chlorine, from bromotrichloromethane, decomposition at 50 °C of *N*-nitrosoacetanilide (NNA), also an established source of phenyl radicals, leads to both bromo- and chloro-benzene thus providing a further example of ' anomalous ' halogen abstraction involving NNA and polyhalogenomethanes. Reaction at 20 °C leads to the precipitation of a mixture of benzenediazonium chloride and acetate, the bromide being absent, and to the formation of bromobenzene and little chlorobenzene. Heating this mixture of diazonium salts at 50 °C in bromotrichloromethane leads to mainly chlorobenzene and some phenyl acetate. Also formed in the reaction of NNA with bromotrichloromethane are significant amounts of carbon dioxide (23 mol per 100 mol NNA), acetic anhydride (14.5), and acetic acid (62). Reaction in the presence of the radical trap, 1,1-diphenylethene (1 mol. equiv.), leads to suppression of chlorobenzene, *i.e.* the reaction is restored to normality. Isolation of 9-phenylphenanthrene is evidence of competing formation of benzyne in this reaction. These results point to the occurrence of abstraction of bromine by phenyl radicals from bromotrichloromethane to give trichloromethyl, which is scavenged by phenyldiazo-oxyl (1) to give trichloromethylbenzenediazoate (2) ; this in turn gives the observed benzenediazonium chloride, and hence chlorobenzene, and phosgene. Reaction of phosgene with NNA leads to more diazonium chloride, carbon dioxide, and acetic anhydride. In support of this, silver benzenediazoate reacts with bromotrichloromethane to give benzenediazonium chloride. The reaction in the presence of 1,1-diphenylethene leads to an increase in yield of bromobenzene thus pointing to decomposition of phenyldiazo-oxyl, in this case, *via* electron transfer with the radical $Ph_2\dot{C}\cdot CH_2\cdot CCl_3$, to give a phenyl radical.

p-Nitro-*N*-nitrosoacetanilide also reacts with bromotrichloromethane *via* dual or ' anomalous ' abstraction of halogen, superimposed on scrambling of aromatic substituents *via* nucleophilic displacement by chloride and acetate of the activated *p*-nitro-group in the *p*-nitrobenzenediazonium ion.

Attention is drawn to the relevance of these results to other anomalous halogen abstraction reactions of NNA in chloroform and in carbon tetrachloride.

REACTIONS of *N*-nitrosoacetanilide (NNA) are a rich source of chemical puzzles.[2] Those involving its modes of radical phenylation of aromatic compounds and conversion into benzyne have now been solved,[1,3] but an explanation of its behaviour on decomposition in polyhalogenomethanes is still awaited after 43 years.[4]

The anomalies can be summarised as follows. (i) Although established sources of phenyl radicals, such as dibenzoyl peroxide [5,6] or phenylazotriphenylmethane,[6,7] react as expected with carbon tetrachloride to give chlorobenzene and hexachloroethane, or 1,1,1-trichloro-triphenylethane, according to the reaction Ph· + CCl₄ ⟶ PhCl + ·CCl₃, decomposition of NNA, also an established source of phenyl radicals, in carbon tetrachloride gives the expected chlorobenzene and, unexpectedly, a precipitate of benzenediazonium chloride,[4] but no hexachlorethane or trichloromethyl-containing product.[4,6] Similarly, the reaction of 4-chloro-*N*-nitrosobenzanilide at 20 °C in carbon tetrachloride gives benzenediazonium chloride (16%), trichloromethyl-containing products again being absent.[8] (ii) Whereas decompositions of dibenzoyl peroxide [5,6] and phenylazotriphenylmethane [6] proceed normally in chloroform to give benzene and products of the trichloromethyl

radical, that of NNA in chloroform gives both chlorobenzene and benzene in similar amounts, trichloromethyl-containing products again being absent.[6] In a related case,[9] pentyl nitrite–aniline reacts with bromotrichloromethane to give both chloro- and bromo-benzene, also unexpectedly, as discussed below.

So far there has been no explanation of these anomalies, which centre on the formation of benzenediazonium chloride, the absence of trichloromethyl-derived products, and the abnormal abstraction of halogen from chloroform and bromotrichloromethane.

This paper describes experiments leading to a solution of this long-standing puzzle, based on a study of the decomposition of NNA in bromotrichloromethane. This halogenocarbon reacts normally with phenyl radicals derived from dibenzoyl peroxide and phenylazotriphenylmethane [10] to give mainly bromobenzene, only traces of chlorobenzene, and equivalent amounts of trichloromethyl-coupled products, in accord with the reaction Ph· + BrCCl₃ ⟶ PhBr + ·CCl₃. These results and those of the decomposition of NNA in bromotrichloromethane (30 mol. equiv.) at 20 and 50 °C are in the Table.

Reaction at 50 °C leads to anomalous abstraction of chlorine as well as bromine, thus recalling corresponding reactions in chloroform, together with phenyl acetate.

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[1] Part 11, J. Brennan, J. I. G. Cadogan, and J. T. Sharp, *J. Chem. Res.* (S), 1977, 107; (M), 1977, 1156.

[2] J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186.

[3] J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1976, 583.

[4] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1934, 1797.

[5] J. Boeseken and H. Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869; H. Gelissen, *Chem. Zentr.*, 1925, **1**, 47.

[6] D. H. Hey and J. Peters, *J. Chem. Soc.*, 1960, 79.

[7] H. Wieland and K. Heymann, *Annalen*, 1934, **514**, 145.

[8] J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *J.C.S. Perkin I*, 1972, 1296.

[9] J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc.* (C), 1966, 1249.

[10] J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 1965, 3939.

Hexachloroethane was absent (as shown by g.l.c.). At 20 °C partial decomposition occurred to give mainly bromobenzene, with only a trace of chlorobenzene (*i.e.* the reaction showed almost normal behaviour of phenyl radicals in bromotrichloromethane). At the same time, however, a suspension of benzenediazonium chloride (28.5 mol per 100 mol) mixed with benzenediazonium acetate (7 mol per 100 mol) was formed. The diazonium bromide was absent (<0.2%). Separation of this precipitate followed by its decomposition in fresh bromotrichloromethane at 50 °C gave mainly chlorobenzene (Table).

which we return below. We did not isolate any product corresponding to the reaction of trichloromethyl radicals with the alkene, g.l.c.–mass spectrometry showed the presence of a compound (6%) whose mass spectrum was as expected for 1,1,1-trichloro-3,3-diphenylpropane. Also formed was 9-phenylphenanthrene (10%), the [2 + 4] cycloaddition product (Scheme 1) of 1,1-diphenylethene with benzyne, which is always present in reactions of NNA in the presence of this alkene.[1,3] Such cycloadditions of benzyne have been reported previously.[11]

At this stage it is possible to postulate a mechanism

Decompositions of sources of phenyl radicals in bromotrichloromethane

Expt. no.	Source	Temp. (°C)	Products *				
			$PhN_2^+X^-$	PhBr	PhCl	PhOAc	C_2Cl_6
1	$(PhCO_2)_2$	80		145	2		57
2	PhN_2CPh_3	50		99	1		
3	NNA	50		26	12	15	0
4	NNA	20	28.5,† 7 ‡	23	2	5	0
5	$PhN_2^+X^-$ from expt. 4	50		3	16	6	0
6	$NNA + Ph_2C{:}CH_2$	50		39	2	15	0

* Mol per 100 mol of source. † X = Cl. ‡ X = OAc.

The ultimate ratio of PhCl to PhBr was close to that produced in the one-step reaction carried out entirely at 50 °C. The reaction of NNA in bromotrichloromethane therefore appeared to consist of two consecutive steps involving formation and reaction of phenyl radicals and formation of benzenediazonium chloride followed by heterolytic dediazoniation of the diazonium chloride, the formation of phenyl acetate being due to similar heterolytic decomposition of benzenediazonium acetate. Since the latter is merely a rearrangement product of NNA, the presence of phenyl acetate, a by-product, becomes mechanistically insignificant. The marked difference in the ratio of bromine to chlorine abstraction shown by NNA and phenylazotriphenylmethane in bromotrichloromethane clearly lay in the intermediacy of benzenediazonium chloride in reactions of the acylarylnitrosamine. At this stage, therefore, a reasonable postulate was that NNA decomposed normally to give phenyl radicals which abstracted bromine to give bromobenzene and trichloromethyl radicals; these were then converted, by some as yet unknown mechanism, into benzenediazonium chloride, thermolysis of which gave the unexpected chlorobenzene, rapidly at 50 but slowly at 20 °C. If this were so, we argued that addition of a radical trap, such as 1,1-diphenylethene,[3] should intercept at least some trichloromethyl radicals and lead to a decrease in the amount of benzenediazonium chloride, and hence that of chlorobenzene. The results (Table) are in full accord with this. Comparing experiments 3 and 6 it can be seen that the addition of 1,1-diphenylethene (1 mol. equiv.) markedly decreased the yield of chlorobenzene. It is of interest that the addition of 1,1-diphenylethene converted the reaction of NNA into a ' normal ' abstraction by phenyl radicals and, in so doing, led to an *increase* in the yield of bromobenzene, a point to

for the reaction (Scheme 2). First, we invoke the accepted genesis of a phenyl radical from NNA [2,12,13] [reaction (i)], which abstracts bromine from bromotrichloromethane to give bromobenzene and a trichloromethyl radical; this in turn is scavenged [reaction (ii)] by the persistent phenyldiazo-oxyl radical (1) also formed in (i). This accounts for the absence of hexachloroethane.
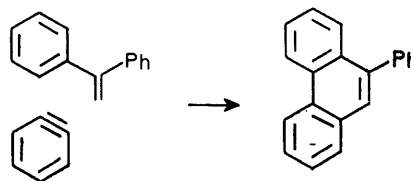
Scheme 1

Decomposition of the resulting trichloromethyl benzenediazoate (2) then gives the observed benzenediazonium chloride and phosgene [reaction (iii)]. Reaction (iv) of another equivalent of benzenediazonium acetate with phosgene gives a second equivalent of the diazonium chloride and the chlorocarbonyl anhydride (3), which in turn gives a third equivalent of the diazonium chloride together with acetic anhydride and carbon dioxide on reaction (v) with a further equivalent of the diazonium acetate. At room temperature the insoluble diazonium chloride appears as a precipitate, but at higher temperatures thermolysis to chlorobenzene occurs [reaction (vi)], thus accounting for the appearance of both chloro- and bromo-benzene.

We now return to the observation that the presence of 1,1-diphenylethene not only reduces the yield of chlorobenzene, but increases the yield of bromobenzene. This cannot be explained solely on the basis of steps (i)—(iii).

[11] R. W. Hoffmann, ' Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967.

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

[13] C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, 1964, 3623.

The increased yield of bromobenzene requires that phenyldiazo-oxyl (1) in the presence of the radical trap (1,1-diphenylethene) is diverted into more phenyl radicals, which then abstract bromine to give bromobenzene. This is most satisfactorily explained by evidence in the following paper.[15] Scheme 2 requires that phosgene be formed and react completely with benzenediazonium acetate to give carbon dioxide and acetic anhydride as well as the diazonium chloride. In accord with this, replicates of experiment 4 (Table) gave,
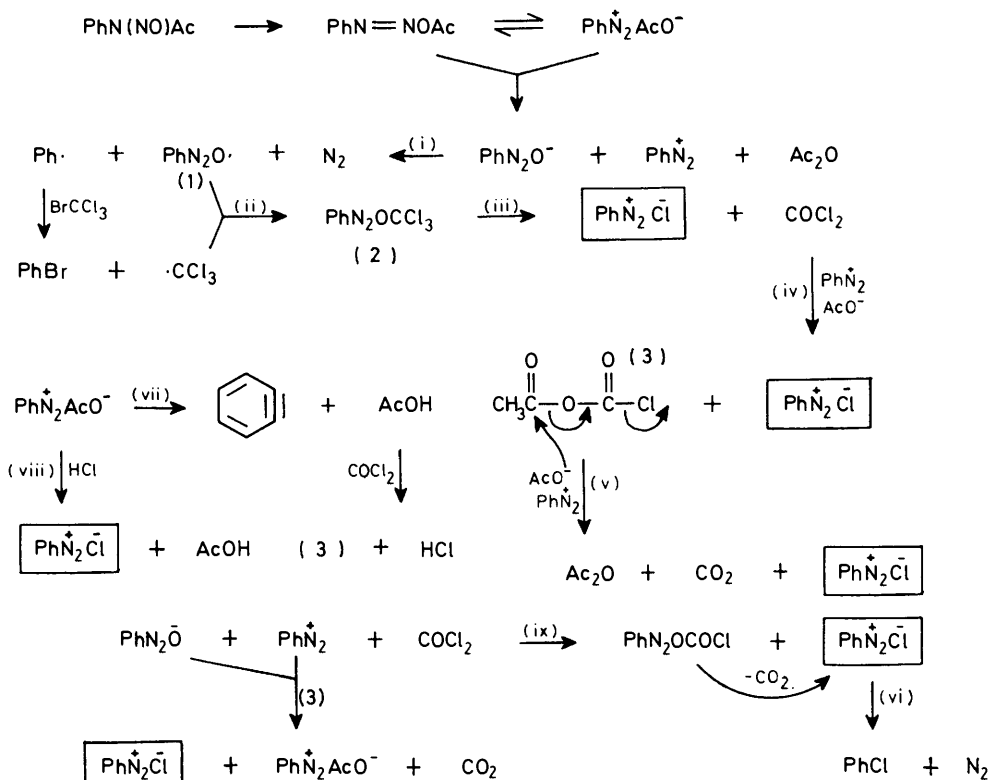
SCHEME 2

Scheme 3 whereby the intermediate radical (4) formed on addition of trichloromethyl to 1,1-diphenylethene
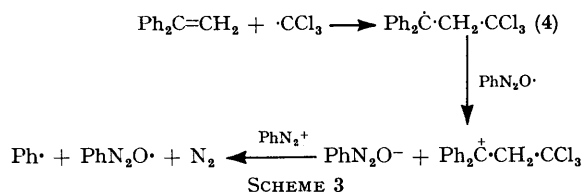
SCHEME 3

undergoes electron transfer with phenyldiazo-oxyl to give the benzenediazoate ion and hence phenyl radicals by reaction with benzenediazonium ion as in step (i), Scheme 1.

Benzenediazonium chloride, and hence chlorobenzene, may also be formed by three further routes: (a) via the formation of benzyne and acetic acid [3] [reaction (vii)], followed by reaction of the latter with phosgene to give hydrogen chloride and hence, by reaction with NNA,[14] the observed diazonium chloride [reaction (viii)]; (b) via the chlorocarbonyl anhydride (3) formed in reaction (vii); and (c) via reaction (ix), for which we present

in addition to benzenediazonium chloride, carbon dioxide (23 mol per 100 mol NNA), acetic acid (62), and acetic anhydride (15). Methyl bromide was shown to be absent (by g.l.c.), thus discounting the possibility that carbon dioxide arose via decarboxylation of acetoxyl radicals ($CH_3 \cdot CO_2 \cdot \longrightarrow \cdot CH_3 + CO_2$). In this connection, Hey and Peters[6] also reported the formation of carbon dioxide (6%) in the reaction of NNA with carbon tetrachloride.

Although we detected traces of free phosgene, by phosgene test paper, this amount was negligible, none being collected in aniline traps on continuous aspiration of the reaction mixture. This is not surprising because it is known that phosgene reacts very rapidly with both carboxylic acids and carboxylates to give carboxylic anhydrides.[16] The earlier work involved reactions in an autoclave, but we have shown that phosgene reacts readily, even under heterogeneous conditions, with potassium acetate suspended in toluene at room temperature and atmospheric pressure to give acetic anhydride (42 mol per 100 mol phosgene), carbon dioxide (59), and chloride ion (51). Thus the absence of free phosgene in the decomposition of NNA in bromotrichloromethane

[14] D. F. de Tar, J. Amer. Chem. Soc., 1951, 73, 1446.
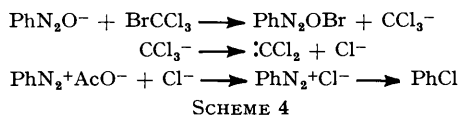[15] J. I. G. Cadogan, R. G. M. Landells, R. M. Paton, and J. T. Sharp, following paper.

[16] R. Hofmann and G. Schoetensack, G.P. 29669/1884; G. M. Dyson, Chem. Rev., 1927, 4, 155.
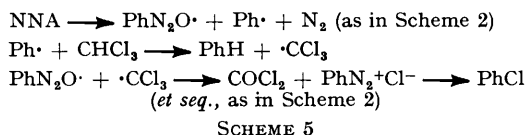
can be explained by its subsequent reaction with benzenediazonium acetate, or acetic acid, to give the diazonium chloride, acetic anhydride, and carbon dioxide as outlined in Scheme 2. There now remains only the key question of the scavenging of the persistent phenyldiazo-oxyl radical (1) by trichloromethyl to give the postulated trichloromethyl benzenediazoate (2), and its subsequent decomposition to benzenediazonium chloride and phosgene. We sought direct evidence of this by synthesis of trichloromethyl benzenediazoate (2) from silver benzenediazoate and bromotrichloromethane ($PhN=NOAg + BrCCl_3 \longrightarrow PhN=NOCCl_3 + AgBr$). The reaction was very slow (only 2% after 4 days at 20 °C) as a result of heterogeneity, but nevertheless it proceeded as expected, leading directly to benzenediazonium chloride.

Finally, it is necessary to refer briefly to alternative reaction pathways which, at first sight, might appear equally satisfactory. Thus, it could be argued that benzenediazonium chloride, and hence chlorobenzene, arises via the ionic route shown in Scheme 4. We discount this, not only because it does not explain the

$$PhN_2O^- + BrCCl_3 \longrightarrow PhN_2OBr + CCl_3^-$$
$$CCl_3^- \longrightarrow {:}CCl_2 + Cl^-$$
$$PhN_2^+AcO^- + Cl^- \longrightarrow PhN_2^+Cl^- \longrightarrow PhCl$$

SCHEME 4

presence of carbon dioxide, but also because no dichlorocarbene was trapped by the efficient traps 1,1-diphenylethene and α-methylstyrene, consumption of the latter by competing radical chain addition being prevented by the addition of 4-hydroxy-2,2,6,6-tetramethylpiperidin-N-oxyl as a radical scavenger. Similarly, we can discount one-electron transfer reactions between the benzenediazoate anions and trichloromethyl radicals ($PhN_2O^- + {\cdot}CCl_3 \longrightarrow PhN_2O{\cdot} + CCl_3^- \longrightarrow {:}CCl_2 + Cl^-$).

We suggest, therefore, that Scheme 2 adequately accounts for the reaction of NNA with bromotrichloromethane, and that similar schemes, e.g. Scheme 5, will

NNA $\longrightarrow PhN_2O{\cdot} + Ph{\cdot} + N_2$ (as in Scheme 2)
$Ph{\cdot} + CHCl_3 \longrightarrow PhH + {\cdot}CCl_3$
$PhN_2O{\cdot} + {\cdot}CCl_3 \longrightarrow COCl_2 + PhN_2^+Cl^- \longrightarrow PhCl$
(et seq., as in Scheme 2)

SCHEME 5

account for ' anomalous ' reactions of NNA with chloroform and carbon tetrachloride. Related investigations involving reactions with dichloromethane, dibromomethane, and bromoform, and aqueous (Gomberg) reactions of chloroform, will be described in later papers.

Decomposition of p-Nitro-N-nitrosoacetanilide in Bromotrichloromethane at 50 °C.—This reaction provided another example of dual halogen abstraction and also showed that extensive substituent scrambling in the

aromatic nucleus occurred, thus giving further support to the mechanism outlined in Scheme 2.

The results are summarised in Scheme 6. Formation of both p-bromonitrobenzene (31 mol per 100 mol NNA) and p-chloronitrobenzene (8) is in contrast to the formation of only p-bromonitrobenzene (69 mol per 100 mol) in the corresponding reaction of p-nitrophenyl radicals, from p-nitrophenylazotriphenylmethane. This can be explained as in Scheme 2, p-bromonitrobenzene arising via the radical abstraction route, and the p-chloroanalogue via ionic dediazoniation of p-nitrobenzenediazonium chloride. p-Nitrophenyl acetate (3) arises via ionic dediazoniation of p-nitrobenzenediazonium acetate.

So far, therefore, the reaction parallels that of NNA itself. The differences lie in the scrambling of the aromatic substituents via nucleophilic displacements of the p-nitro-group, which is activated by the strongly electron-withdrawing diazonium function. Thus p-nitrobenzenediazonium chloride can also isomerise into p-chlorobenzenediazonium nitrite, the cation of which, in the presence of acetate and chloride ions in bromotrichloromethane, can be converted into p-bromochlorobenzene, via the radical route, and p-dichlorobenzene via ionic dediazoniation. p-Bromo- and p-chloro-phenyl acetates are similarly formed. There are precedents for such nucleophilic displacements by acetate and by chloride ions in aromatic diazonium salts.[8,17]

EXPERIMENTAL

Solvents.—Rigorously dried solvents were essential.[18] Bromotrichloromethane (100 ml) was stirred with four portions (16 ml) of 98% sulphuric acid for at least 2 h each. The last two portions remained colourless. The bromotrichloromethane was washed with water (40 ml), 0.1M-sodium hydroxide (40 ml), and water (3 × 40 ml), dried overnight over Drierite, then dried over molecular sieve type 4A (1/16 in pellets of sodium aluminosilicate) for at least 30 min, then distilled through a 30 cm column packed with glass helices. The middle 80% of the distillate, b.p. 104—105°, was stored in the dark over molecular sieve. G.l.c. showed the absence of carbon tetrachloride.

Reagents.—The mode of decomposition of N-nitrosoacetanilide is markedly influenced by water.[18] Suitably dry material was prepared as described earlier.[3] p-Nitro-N-nitrosoacetanilide was similarly prepared and had m.p. 68° (lit.,[19] 68—70°).

Silver Benzenediazoate.—Potassium benzenediazoate[20] (3.2 g, 0.02 mol), obtained as pale yellow crystals [m.p. 130° (decomp.); lit.,[20] 130° (decomp.)], in water (100 ml), was added to silver nitrate (3.4 g, 0.02 mol) in water (20 ml). The grey precipitate was washed with water until the filtrate had pH 7, washed with alcohol then with ether, and dried (P_2O_5) at 0.1 mmHg overnight. The product (3.5 g, 76%) detonated at 140° (lit.,[21] 118°).

Benzenediazonium chloride [m.p. 101° (detonation), $v_{max.}$ 2 300 cm^{-1} ($-N_2^+$)] was prepared by Vogel's method.[22]

[17] J. Brennan, J. I. G. Cadogan, and J. T. Sharp, J.C.S. Chem. Comm., 1976, 850; J.C.S. Perkin I, 1977, 0000.
[18] B. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, J.C.S. Perkin I, 1972, 2563.
[19] M. Gomberg and A. Campbell, J. Amer. Chem. Soc., 1898, 20, 780.
[20] C. Schraube and C. Schmidt, Ber., 1894, 27, 514.
[21] A. Wohl, Ber., 1892, 25, 3631.
[22] A. I. Vogel, ' Practical Organic Chemistry,' Longman, Green and Co., London, 3rd edn., 1956.

Benzenediazonium bromide [22] had m.p. (detonation) 112° (lit., 109°), $v_{max.}$ 2 290 cm⁻¹ (–N_2^+). 1,1-Dichloro-2,2-diphenylcyclopropane (m.p. 111—113°; lit.,[23] 113—114°) was prepared by the reaction of 1,1-diphenylethene and bromotrichloromethane in ether with butyl-lithium, by Miller's method.[24]

Gas Chromatography.—A Pye 104 chromatograph, with flame ionisation detector, was used together with 2 m × 2.2 mm (inside diameter) packed columns. Quantitative measurements were made after calibration of the instrument with known mixtures of authentic samples and internal standards. The carrier gas was nitrogen. Reaction mixtures were also analysed in conjunction with a VG Micromass 12 single-focusing mass spectrometer, with helium as carrier gas, to confirm the identities of volatile products.

Reactions of N-*Nitrosoacetanilide with Bromotrichloromethane.*—All reactions were carried out with stirring under dry, oxygen-free nitrogen.

(i) *At* 20 °C. N-Nitrosoacetanilide (0.42 g, 2.6 mmol) was allowed to decompose in bromotrichloromethane (12.8 g, 65 mmol). After a few minutes a precipitate began to form and after 17 h it was filtered off, washed with a little bromotrichloromethane, and dried. G.l.c. of the filtered dark red mixture (4-t-butyltoluene as internal standard) gave the yields of chlorobenzene (2.7 mol per 100 mol), bromobenzene (21.6), and phenyl acetate (3.4). A replicate experiment afforded chlorobenzene (1.5 mol per 100 mol), bromobenzene (23.5), and phenyl acetate (6.8).

The precipitated solid (0.13 g) contained the diazonium moiety [$v_{max.}$ 2 280 cm⁻¹ (ArN$_2^+$)], giving 1-phenylazo-2-naphthol, m.p. and mixed m.p. 131°, in good yield. The dry diazonium salt was dissolved in water and gave a white precipitate of silver chloride with silver nitrate solution and nitric acid. The precipitate 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 by Mohr's method and by Volhard's method showed that 79% of the precipitated diazonium salt consisted of benzenediazonium chloride. The i.r. spectrum of the precipitated material showed the presence of acetate ion (1 700 cm⁻¹). This, together with the observed formation of phenyl acetate on thermolysis (see below) suggests that the remainder of the precipitate was benzenediazonium acetate.

(ii) *Decomposition of the mixture of diazonium salts obtained in* (i), *in bromotrichloromethane at* 50 °C. The entire yield of diazonium salt obtained from a replicate of the above experiment was allowed to decompose at 50 °C in bromotrichloromethane. Analysis showed the presence of chlorobenzene (16 mol per 100 mol NNA), bromobenzene (3), and phenyl acetate (6).

(iii) *At* 50 °C. The experiment was conducted as in (i) at 50 °C for 69 h. The precipitated solid soon decomposed. Analysis showed the presence of chlorobenzene (12 mol per 100 mol), bromobenzene (26), and phenyl acetate (15).

(iv) *At* 50 °C *in the presence of* 1,1-*diphenylethene.* N-Nitrosoacetanilide (0.36 g, 2.2 mmol) was allowed to decompose in bromotrichloromethane (12.5 g, 63 mmol) in the presence of 1,1-diphenylethene (0.40 g, 2.2 mmol) at 50 °C

for 69 h. No precipitate formed. G.l.c. of the dark brown mixture (4-t-butyltoluene as internal standard) showed the presence of chlorobenzene (2 mol per 100 mol), bromobenzene (39), and phenyl acetate (15). G.l.c. at 190—230 °C showed the presence of six compounds (four in less than 2% yield, the other two in 6 and 10% yield), which were not present in the products of the parallel reaction with no added 1,1-diphenylethene. G.l.c. also showed that 1,1-dichloro-2,2-diphenylcyclopropane and hexachloroethane were absent. G.l.c.–mass spectrometric analysis showed the two main compounds to have mass spectra consistent with the following structural assignments: 1,1,1-trichloro-3,3-diphenylpropane [m/e 302/300/298 (intensities 1 : 3 : 3) and 167 (strong fragment peak)] and 9-phenylphenanthrene [m/e 254 (parent peak)]. The reaction mixture from a parallel reaction carried out at 60 °C for 17.5 h was chromatographed on alumina (elution with light petroleum–ether). 9-Phenylphenanthrene (10 mol per 100 mol) was collected and after recrystallisation from light petroleum it had m.p. and mixed m.p. 105—106°. The i.r. and n.m.r. spectra were also identical with those of authentic sample.[25] In a control reaction, 1,1-diphenylethene (0.42 g, 2.3 mmol) in bromotrichloromethane (12.3 g, 62 mmol) was stirred at 50 °C for 5 days under dry nitrogen. G.l.c. showed none of the six compounds found previously to be present.

In a related experiment involving added 4-hydroxy-2,2,6,6-tetramethylpiperidin-N-oxyl (1 mol. equiv.) and α-methylstyrene (6 mol equiv.), no 1,1-dichloro-2-methyl-2-phenylcyclopropane was formed, as shown by g.l.c. (0.01% would have been detected).

Spectroscopic Determination of Carbon Dioxide from the Decomposition of N-*Nitrosoacetanilide in Bromotrichloromethane at Room Temperature.*—Nitrogen, which had been passed through calcium hydroxide solution, was bubbled through bromotrichloromethane (6 g, 30 mmol) in a Zeisel reaction flask [26] for 25 min at 15 ml min⁻¹. The flow rate, stabilised by needle valves and passage through a large reservoir fitted with capillary outlet, was adjusted by a Rotameter, type 704, calibrated over the range 4—25 ml min⁻¹. The Zeisel flask was connected by delivery tube to a trap immersed in liquid nitrogen. N-Nitrosoacetanilide (0.08 g, 0.5 mmol) was added to the deoxygenated bromotrichloromethane and the mixture was left for 16 h with the trap immersed in liquid nitrogen but no carrier gas flowing. Nitrogen was then passed at 10 ml min⁻¹ for 2 h through the mixture into the trap, the exit of which was attached to a calcium hydroxide bubbler. The volatile and gaseous products were carried by the flow gas into the trap. The trapped products were later volatilised into an i.r. gas-cell. The quantitative yield of carbon dioxide was determined by comparing the height of the carbon dioxide absorption at 2 350 cm⁻¹ in the i.r. spectrum of the sample with a calibration curve. This curve was constructed by trapping (in liquid nitrogen) mg quantities of carbon dioxide given by known weights of sodium carbonate (reagent grade) when treated with acid, and volatilising the carbon dioxide into the i.r. gas cell. After the known weight of carbon dioxide was transferred to the gas cell, dry air was admitted so that the cell contents were at atmospheric pressure. This minimised pressure broadening effects, and the trace of carbon dioxide so introduced was compensated by the

[23] D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, 1965, **87**, 4147.
[24] W. T. Miller, jun., and C. S. Y. Kim, *J. Amer. Chem. Soc.*, 1959, **81**, 5008.

[25] F. B. Mallory and C. S. Wood, *Org. Synth.*, 1965, **45**, 91.
[26] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70; D. M. W. Anderson, S. Garbutt, and S. S. H. Zaidi, *Analyt. Chim. Acta*, 1963, **29**, 39.

double beam operation of the spectrometer. The above procedure gave the yields of carbon dioxide from three parallel reactions as 23, 19.4, and 26 mol per 100 mol of nitrosamide. A control reaction gave a trace ($<1\%$) of carbon dioxide which was subtracted from each product yield. I.r. analysis of the very strong absorption by methyl bromide at 1 306 cm^{-1} [27] showed that methyl bromide was not a product of the reaction (0.4% would have been detected).

Estimation of Acetic Acid and Acetic Anhydride produced in the Decomposition of N-Nitrosoacetanilide in Bromotrichloromethane.—N-Nitrosoacetanilide (0.476 g, 2.9 mmol) was dissolved in bromotrichloromethane (40 g, 0.2 mol). After a few moments a yellow solid was seen to precipitate. The mixture was stirred at room temperature under dry nitrogen for 18.5 h and then heated at 60 °C for 7 h; the solid decomposed. Aniline (0.3 g, 3.3 mmol) was added to half the mixture and the solution stirred under nitrogen for 2 h. Sodium hydroxide (0.124 2M; 25 ml) was added to the solution and the aqueous layer separated. Back titration against standard 0.1M-hydrochloric acid (phenolphthalein) gave a value of 0.150 6 g for the total acid present in the solution after treating the anhydride with aniline. Sodium hydroxide (0.124 2M; 25 ml) was added to the other half of the reaction mixture. Back titration of the aqueous layer against standard 0.1M-hydrochloric acid gave the total quantity of acetic acid from acetic acid and acetic anhydride in the reaction mixture as 0.176 4 g. The difference between the two values (0.025 8 g) is equivalent to half the acetic acid produced by hydrolysis of the acetic anhydride. This corresponds to a yield of 0.043 9 g of acetic anhydride (15 mol per 100 mol nitrosamide), which would give the amount of acetic acid present originally as 0.124 8 g (72 mol per 100 mol nitrosamide). Results from a parallel experiment were (acetic anhydride) 14.5 and (acetic acid) 74 mol per 100 mol of nitrosamide. A control experiment showed that sodium hydroxide (0.124 2M) hydrolysed phenyl acetate to acetic acid and phenol, which could be subsequently converted into its sodium salt.

Analysis of a replicate experiment by g.l.c. (2-bromotoluene as internal standard) gave the yield of acetic acid as 62 mol per 100 mol nitrosamide.

Thus, taking the yield of phenyl acetate into account, 105% of the acetate moiety of NNA was accounted for.

Decomposition of Silver and Potassium Benzenediazoates in Bromotrichloromethane at Room Temperature.—Silver benzenediazoate (0.574 g, 2.5 mmol) was added to bromotrichloromethane (12 g, 60 mmol) and the grey heterogeneous solution stirred in the dark at room temperature under nitrogen for 96 h. The solution was filtered, washed with a little bromotrichloromethane, and dried. An i.r. spectrum of the yellow-grey solid was similar to that of authentic silver benzenediazoate, but also showed a weak diazonium absorption at 2 280 cm^{-1}. The solid was washed with water and the aqueous filtrate added to alkaline 2-naphthol. 1-Phenylazo-2-naphthol (1.3 mol per 100 mol diazoate), m.p. and mixed m.p. 133°, was formed. Authentic silver benzenediazoate, which is insoluble in water, gave no azo-dye with alkaline 2-naphthol. A sample of the aqueous filtrate gave a white precipitate with silver nitrate solution in nitric acid, indicating the presence of a halide. The precipitate was soluble in dilute ammonia. The yellow-grey solid from the heterogeneous reaction mixture therefore contained benzenediazonium chloride (2 mol per 100 mol diazoate).

A parallel reaction of potassium benzenediazoate in bromotrichloromethane at room temperature stirred in the dark under nitrogen for 120 h gave no benzenediazonium chloride.

Reaction of Phosgene with Potassium Acetate in Toluene at Room Temperature.—Phosgene (0.099 g, 1 mmol) in solution (12% w/v) in toluene was added to fused potassium acetate (0.5 g, 5 mmol) in toluene (9 ml), and the solution stirred under dry nitrogen for 22.5 h then filtered. Acetic anhydride (42 mol per 100 mol phosgene) was estimated as acetanilide (g.l.c.) after reaction with an excess of aniline. The residue was dissolved in water and chloride was estimated as silver chloride (51 mol per 100 mol COCl$_2$). Silver acetate was absent.

Spectroscopic Determination of Carbon Dioxide from the Reaction of Phosgene with Potassium Acetate in Toluene at Room Temperature.—Phosgene (0.016 g, 0.16 mmol) in solution (12% w/v) in toluene was added to a deoxygenated solution of fused potassium acetate (0.085 g, 0.9 mmol) in toluene (3 ml) in a Zeisel reaction flask, and the sealed flask was left for 24 h with the trap immersed in liquid nitrogen but no carrier gas flowing. At the end of the reaction nitrogen was passed at 15 ml min^{-1} for 15 min through the mixture into the trap. I.r. analysis, as described above, of the vapour trap contents showed the presence of carbon dioxide (59 mol per 100 mol phosgene).

Decomposition of p-Nitro-N-nitrosoacetanilide in Bromotrichloromethane at 50 °C.—The nitrosamide (2.74 g, 13.1 mmol) was allowed to decompose in bromotrichloromethane (48.40 g, 0.24 mol) at 50 °C for 12 h. G.l.c. analysis gave the results summarised in Scheme 6.

Scheme 6 Numerals represent yields (mol per 100 mol NNA). R represents radical route, I represents ionic route, as in Scheme 2

Decomposition of p-Nitrophenylazotriphenylmethane in Bromotrichloromethane at 50 °C.—The azo-compound (0.90 g, 2.3 mmol) in bromotrichloromethane (12.05 g, 0.061 mol) after 24 h at 50 °C gave p-bromonitrobenzene (69 mol per

[27] Ta-You Wu, *J. Chem. Phys.*, 1942, **10**, 116.

100 mol) (by g.l.c.–mass spectrometry). *p*-Chloronitrobenzene was absent (0.1 mol per 100 mol would have been detected).