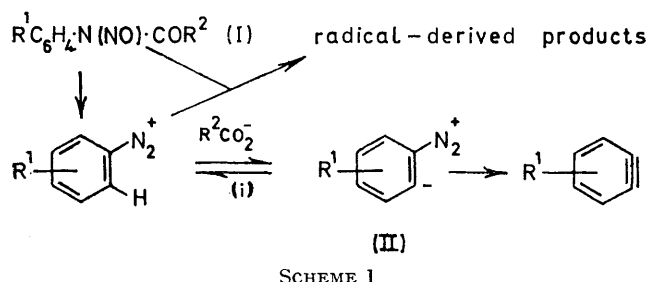


Acylarylnitrosamines. Part V.¹ Decompositions of *N*-Nitrosobenzanilides in Carbon Tetrachloride and Benzene: the Formation of Carboxylic Acids, Anhydrides, and Arynes †

By J. I. G. Cadogan,* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ
D. M. Smith and (Miss) J. B. Thomson, University of St. Andrews, St. Andrews, Scotland

Decomposition of a series of *N*-nitrosobenzanilides [$R^1C_6H_4 \cdot N(NO) \cdot CO \cdot C_6H_4R^2$; $R^2 = Cl$; $R^1 = H$, 2-Br, 3-Br, 4-Br, 3-Me, 4-Me, 3-NO₂, or 4-NO₂. $R^2 = Br$; $R^1 = 4-NO_2$ or 4-Me. $R^1 = H$; $R^2 = NO_2$ or Me] in carbon tetrachloride in the presence or absence of tetraphenylcyclopentadienone has been investigated. In the latter cases the reaction gives the corresponding benzoic acid (p - $R^2C_6H_4 \cdot CO_2H$) (29–79%), benzoic anhydride [$(p$ - $R^2C_6H_4 \cdot CO)_2O$] (12–38%), and aryl chloride ($R^1C_6H_4Cl$) (15–40%) as major products, thus indicating that removal of aromatic protons has occurred, and that attack by carboxylate anion on the nitroso-amide or the isomeric diazocarboxylate has taken place. Reactions carried out in the presence of tetraphenylcyclopentadienone lead to the trapping of arynes, with suppression, in some cases, of formation of the anhydride. The presence of water leads to the suppression of the formation of arynes. Similar results are obtained from corresponding decompositions in benzene with the exception that anhydrides are not formed. 2',4,6'-Trichloro- and 2',4,6'-tribromo-4-chloro-*N*-nitrosobenzanilides, with their *ortho*-positions blocked by halogen atoms, do not give *p*-chlorobenzoic acid on decomposition in benzene and in carbon tetrachloride but rather react primarily by nucleophilic displacement of *ortho*-halogen atoms by *p*-chlorobenzoate anion.

IN Part IV¹ it was shown that decomposition of *N*-nitrosoacetanilide and its derivatives (I) in benzene and various other solvents led not only to the long known² arylated products but also to arynes. Apart from the special case of *o*-*t*-butyl-*N*-nitrosoacetanilide,³ the mechanism proposed involved removal by carboxylate ion of the proton *ortho* to the diazo-function to give the aryne *via* its precursor (II) (Scheme 1).



SCHEME 1

If Scheme 1 does apply it follows (a) that the use of a carboxylate counter ion leading to an insoluble carboxylic acid (e.g. *p*-chlorobenzoic acid) might lead to a higher yield of aryne by altering the equilibrium (i); (b) that the use of such a counter ion in carbon tetrachloride should also lead to the carboxylic acid, thus proving that the acidic hydrogen atom in the acid is derived from the parent diazonium cation, and (c) that the use of a 2,6-disubstituted *N*-nitrosobenzanilide should not lead to the formation of carboxylic acid since neither position *ortho* to the diazonium function carries a hydrogen atom.

We now describe experiments, designed to test these predictions, in which 4-bromo-, 4-chloro-, 4-methyl-, and 4-nitro-*N*-nitrosobenzanilides (III; $R^2 = Br, Cl, Me$, or NO_2 ; $R^1 = H$, 2-, 3-, or 4-Br, 3- or 4-Me, 3- or 4-NO₂, 2,6-Cl₂, or 2,4,6-Br₃) decomposed in carbon tetrachloride

or benzene in the presence and in the absence of tetraphenylcyclopentadienone as an aryne trap. The reactions were carried out first at room temperature until evolution of nitrogen ceased and then at 80° to ensure complete decomposition of any intermediate diazonium salts formed.

EXPERIMENTAL

G.l.c. was carried out as described earlier.³

Preparation of Materials.—*N*-Nitrosobenzanilides. The method was based on that of Miles and Suschitzky⁴ and is exemplified by the case of 4-chloro-*N*-nitrosobenzanilide. A mixture of 4-chlorobenzanilide (10 g), acetic acid (100 ml), acetic anhydride (100 ml), and pyridine (30 ml) was stirred and cooled to 0°. Nitrosyl chloride (20 g) in acetic anhydride (100 ml) was added dropwise during 30 min, stirring was continued for a further 15 min, and the mixture was poured into ice-water. The product was collected, washed with cold water, and dried between filter papers and over phosphoric oxide (0.05 mmHg); yield 7.7 g (60%), m.p. 75° (violent decomposition). It was essential that the material was absolutely dry (see text). In view of the fact that *p*-chlorobenzoic acid and its anhydride were subsequently shown to be products of decomposition of the acylarylnitrosamine care was taken to see that the latter was free of *p*-chlorobenzoic acid. It was shown that the standard procedure gave a product which contained a maximum of 7% *p*-chlorobenzoic acid (by comparison of i.r. spectra with those of standard mixtures). An alternative method of work-up whereby the reaction mixture was poured into excess of ice-cold aqueous sodium hydrogen carbonate (30% w/v) gave a satisfactory product, free of acid, but in lower yield.

Recrystallisation of the nitroso-compounds was not attempted because of the risk of explosion or decomposition. The dry compounds were treated with great care. Complete nitrosation was shown in each case by the absence of absorption in the $>N-H$ region of the i.r. spectrum

² J. I. G. Cadogan, *Chem. Soc. Spec. Publ. No. 24*, 1970, p. 71; *Accounts Chem. Res.*, 1971, **4**, 186.

³ J. I. G. Cadogan, J. Cook, M. J. P. Harger, P. G. Hibbert, and J. T. Sharp, *J. Chem. Soc. (B)*, 1971, 595.

⁴ P. Miles and H. Suschitzky, *Tetrahedron*, 1962, **18**, 1369.

† Preliminary communication, D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, 1967, 727.

¹ Part IV, D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *J. Chem. Soc. (B)*, 1971, 1996.

(3200—3420 cm^{-1}) and also by a shift in the carbonyl frequency from that of the parent benzanilide (1640—1700 cm^{-1}) to the range 1670—1720 cm^{-1} . The yields were always less than 100%, owing to the solubility of the product in the aqueous solution. Data for the nitroso-benzanilides prepared are given in Table 1.

TABLE 1

N-Nitrosobenzanilides $\text{XC}_6\text{H}_4\cdot\text{N}(\text{NO})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Y}-p$			
X	Y	Yield (%)	M.p. ($^{\circ}\text{C}$) (decomp.)
H	Cl	60	75
3-Br	Cl	69	57
4-Br	Cl	59	71
4-NO ₂	Br	64	73
3-Me	Cl	58	65
4-Me	Cl	60	68
3-NO ₂	Cl	78	81
4-NO ₂	Cl	84	66
2-Br	Cl	88	68
2,4,6-Br ₃	Cl	80	95 No decomp.
4-Br	Br	75	80
2,6-Cl ₂	Cl	90	67 No decomp.
H	Me	20	62
H	NO ₂	58	79

Substituted phenols and aryl benzoates were prepared by standard methods. New esters prepared are described in Table 2, and new benzanilides in Table 3.

TABLE 2

Substituted aryl benzoates ($\text{RC}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}-p$)			
R	M.p. ($^{\circ}\text{C}$)	C (%) †	H (%) †
3-Br	96—97	49.8 (50.1)	2.3 (2.6)
4-Br	105—106	50.3 (50.1)	3.0 (2.6)
2,3-Cl ₂	120—122	51.7 (51.8)	2.4 (2.3)
2,4,6-Br ₃	96	33.4 (33.3)	1.3 (1.3)
4-Cl-2,6-Br ₂	66	36.9 (36.7)	1.7 (1.4)
2-Cl-4,6-Br ₂	90—93	36.4 (36.7)	1.5 (1.4)
2-Cl-3,5-Br ₂	172	36.5 (36.7)	1.1 (1.4)
2-Cl	59—60	58.4 (58.2)	3.3 (3.0)
2-Br	74—75	50.2 (50.0)	2.8 (2.6)
3-NO ₂	135	56.4 (56.2)	3.1 (2.9)
2,6-Cl ₂	70.5	51.9 (51.8)	2.6 (2.3)

† Required values in parentheses.

TABLE 3

Substituted benzanilides ($\text{RC}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}-p$)			
R	M.p. ($^{\circ}\text{C}$)	C (%) †	H (%) †
2-Br	137—138	50.2 (50.3)	3.2 (2.9)
3-Br	127	50.1 (50.3)	3.0 (2.9)
4-Br	215—216	50.5 (50.3)	3.1 (2.9)
3-Me	127—128	68.5 (68.4)	4.7 (4.9)

† Required values in parentheses.

6-Bromo-1,2,3,4-tetraphenylnaphthalene, m.p. 243—244 $^{\circ}$, was prepared by the standard method from pentyl nitrite and the corresponding bromoanthranilic acid (Found: C, 80.2; H, 4.8. $\text{C}_{34}\text{H}_{23}\text{Br}$ requires C, 79.9; H, 4.5%). Samples of 5- and 6-methyl-1,2,3,4-tetraphenylnaphthalenes were provided by Professor C. W. Rees.

Decomposition of 4-Chloro-N-nitrosobenzanilide in Chlorobenzene.—4-Chloro-N-nitrosobenzanilide (3.08 g) and chlorobenzene (26.5 g) were stirred together at room temperature, the apparatus being protected by a drying tube. There was a vigorous evolution of nitrogen, and the mixture became dark brown in colour. To ensure completion of the reaction, it was boiled under reflux for 8 h. *p*-Chlorobenzoic acid (1.80 g, 98%), m.p. and mixed m.p. 239—241 $^{\circ}$, was removed. G.l.c. analysis of the solution (10% PEGA,

2% NPGS at 140 $^{\circ}$) showed the presence of 2-, 3-, and 4-chlorobiphenyl. The 3- and 4-isomers could not be separated on non-capillary columns but the combined yield of these was found to be 0.42 g (19%) whereas the yield of the 2-isomer was 0.62 g (28%). By use of a capillary column the ratio of isomers (2-:3-:4-) was found to be 60:23:17.

The chlorobenzene was distilled off, and the isomeric mixture of biphenyls (0.94 g) was distilled from the residue (b.p. 65—80 $^{\circ}$ at 0.1 mmHg). The i.r. spectrum of this mixture was identical with that of an authentic mixture. No other products were isolated.

Reactions of Monosubstituted 4-Chloro-N-nitrosobenzanilides in Benzene.—General procedure. The acylaryl-nitrosamine was added to the solvent, and the mixture was stirred at room temperature overnight, the apparatus being protected from atmospheric moisture by a silica-gel guard tube. A feathery precipitate soon appeared in place of the amorphous nitroso-compound. To ensure completion of the reaction, the mixture was then boiled under reflux for 6 h and allowed to cool. A solid was precipitated in all cases. This, after recrystallisation from acetic acid, was shown (m.p., mixed m.p., and i.r. spectrum) to be *p*-chlorobenzoic acid. After removal of the bulk of the solvent by distillation, a further precipitate appeared, which was also *p*-chlorobenzoic acid. The remaining solution was distilled under reduced pressure, yielding, in all cases, the appropriate substituted biphenyl. The involatile residue was chromatographed on alumina. The procedure is exemplified by the following case.

4-Chloro-N-nitrosobenzanilide. The nitroso-compound (3.6 g) decomposed in benzene (175 ml), yielding *p*-chlorobenzoic acid (1.9 g, 88%), m.p. and mixed m.p. 244—245 $^{\circ}$. Distillation of the solution gave (a) a colourless liquid (11.2 g), b.p. 80 $^{\circ}$; (b) a yellow solid (0.89 g), b.p. 130 $^{\circ}$ at 11 mmHg; (c) a yellow solid sublimate (0.06 g), driven over at 160 $^{\circ}$ (bath temp.) and 0.03 mmHg; and (d) a residue (0.46 g). Fraction (a) was shown to be pure benzene by g.l.c. (2% NPGS, 10% SIL at 170 $^{\circ}$). Fraction (b) was recrystallised from light petroleum (b.p. 60—80 $^{\circ}$) giving biphenyl (0.82 g, 38%), m.p. and mixed m.p. 70—71 $^{\circ}$, i.r. spectrum identical with that of authentic biphenyl. G.l.c. (2% NPGS, 10% SIL at 170 $^{\circ}$) of fraction (c) showed only one peak, corresponding to phenyl 4-chlorobenzoate. Benzene was added to this fraction and the insoluble *p*-chlorobenzoic acid (30 mg) was filtered off. Chromatography of the solution, followed by recrystallisation of the product from methanol, gave phenyl 4-chlorobenzoate, m.p. and mixed m.p. 103—104 $^{\circ}$. Chromatography of fraction (d) with light petroleum (b.p. 40—60 $^{\circ}$) gave a white solid. Recrystallisation from methanol gave phenyl 4-chlorobenzoate (10 mg), m.p. 101—103 $^{\circ}$, mixed m.p. 102—103 $^{\circ}$. The total yield of ester produced was 30 mg (1%).

4'-Methyl- and 2', 3', and 4'-bromo-4-chloro-N-nitrosobenzanilides were investigated in a similar fashion. The results are summarised in Table 4.

Reactions of Monosubstituted 4-Chloro- and 4-Bromo-N-nitrosobenzanilides in Carbon Tetrachloride.—General procedure. The N-nitrosobenzanilide in a 200 molar excess of the solvent was stirred overnight at room temperature, the apparatus being protected from atmospheric moisture by a silica-gel guard tube. After this time nitrogen evolution had ceased. To ensure completion of the reaction, the mixture was then boiled under reflux for 6 h, during which

it became very dark in colour. The solution was allowed to cool, and the precipitate was removed. In all cases this proved to be *p*-chlorobenzoic acid (mixed m.p. and i.r. comparison) and was recrystallised from acetic acid. The bulk of the solvent was removed by distillation and on

TABLE 4

Products (%) of reactions of 4-chloro-*N*-nitrosobenzanilides in benzene *

	R in $\text{RC}_6\text{H}_4\cdot\text{N}(\text{NO})\cdot\text{COAr}$ (Ar = <i>p</i> -ClC ₆ H ₄)				
	H	4-Me	4-Br	3-Br	2-Br
ArCO ₂ H	88	90	80	92	77
RC ₆ H ₄ Ph	38	37	50	62	68
RC ₆ H ₄ ·O·COAr	1	0	0	0	0
ArCO·NH·C ₆ H ₄ R	0	2	2	0	0
Ar (% acc. for)	89	92	82	92	77
RC ₆ H ₄ (% acc. for)	39	39	52	62	68

* All products were isolated, and identified by direct comparison (mixed m.p.; n.m.r. and i.r. spectra) with authentic materials.

cooling the solution a precipitate of *p*-chlorobenzoic anhydride was formed. After recrystallisation from dry benzene, this compound was identified by mixed m.p. and i.r. comparison. All remaining volatile products were removed successively by distillation (a) at atmospheric pressure, (b) at 10–15 mmHg, and (c) at 0.02–0.05 mmHg.

To investigate the possibility of phosgene being one of the products, an aqueous aniline trap was connected to the reaction vessel and a stream of nitrogen was passed through the mixture to carry any gaseous products into the trap. This had been shown previously to be an effective method for trapping phosgene, but in this case no diphenylurea was found in the trap although the yields of other products were identical with those obtained in the previous reactions.

4'-Methyl-, 4'-nitro-, and 4'-, 3'-, and 2'-bromo-4-chloro-*N*-nitrosobenzanilides and 4,4'-dibromo- and 4-bromo-4'-nitro-*N*-nitrosobenzanilides were investigated in a similar fashion. The results are summarised in Table 5.

Reactions of ortho,ortho-Disubstituted 4-Chloro-N-nitrosobenzanilides.—2',4,6'-Trichloro-*N*-nitrosobenzanilide in carbon tetrachloride. The nitrosamide (9.5 g) decomposed in carbon tetrachloride (400 ml) in the usual way; when cool the solution deposited an unidentified brown amorphous solid (0.95 g). A further 1.42 g was obtained after removal of the bulk of the solvent. Distillation gave (a) a yellow liquid (2.27 g), b.p. 103–105° at 10 mmHg, (b) an orange sublimate (0.36 g) driven over at 160° (bath temp.) and 0.15 mmHg, and (c) a residue (3.45 g). Fraction (a) had a pungent odour and the i.r. spectrum indicated (by comparison with that of an authentic sample) that it was mainly *p*-chlorobenzoyl chloride. A portion (0.33 g) was esterified by boiling under reflux with ethanol (3 ml) for 5 h. Analysis of the resulting solution by g.l.c. (10%

TABLE 5

Products (%) of reactions of substituted *N*-nitrosobenzanilides in carbon tetrachloride ^a

Product	R in $\text{RC}_6\text{H}_4\cdot\text{N}(\text{NO})\cdot\text{COAr}$							
	Ar = <i>p</i> -ClC ₆ H ₄						Ar = <i>p</i> -BrC ₆ H ₄	
	H	4-Br ^b	4-NO ₂ ^c	4-Me	3-Br ^d	2-Br ^e	4-NO ₂ ^f	4-Br ^g
ArCO ₂ H	45	49	68	79	57	29	65	46
(ArCO) ₂ O	30	38	18	12	26	34	26	34
RC ₆ H ₄ ·Cl	26	26	32	20	32	15	40	33
RC ₆ H ₄ Br		5			2	11	1	7
RC ₆ H ₄ ·O·COAr	18	0.1		0.5	0.2			0.5
Ar (% acc. for)	93	94	97	92	83	65	98	87
RC ₆ H ₄ (% acc. for)	44	63	34	21	35	38	50	49

^a All products were isolated, and identified by direct comparison (mixed m.p., n.m.r., and i.r. spectra) with authentic specimens. Also were formed: ^b *p*-Cl₂C₆H₄ (25), *p*-ClC₆H₄·O·COAr (6), ArCOCl (1); ^c *p*-Cl₂C₆H₄ (2), *p*-ClC₆H₄·O·COAr (11); ^d PhCl (0.1), PhBr (0.1), *m*-Cl₂C₆H₄ (1); ^e *o*-Cl₂C₆H₄ (12), *o*-ClC₆H₄·O·COAr (1), ArCOCl (0.5); ^f *p*-ClBrC₆H₄ (0.2), *p*-Cl₂C₆H₄ (2), *p*-ClC₆H₄·O·COAr (7); ^g *p*-Cl₂C₆H₄ (15), *p*-ClC₆H₄·O·COAr (3), ArCOCl (0.3).

The involatile residue was chromatographed on alumina. Control experiments showed that neither *p*-chlorobenzoyl chloride nor the anhydride was hydrolysed to the acid under the reaction conditions.

The volatile products were identified and estimated by a combination of mixed m.p., i.r., n.m.r., and g.l.c. procedures as indicated in the following typical example.

4-Chloro-N-nitrosobenzanilide. The nitroso-amide (6.4 g) decomposed in carbon tetrachloride (300 ml). *p*-Chlorobenzoic acid (1.71 g, 45%), m.p. 239–240°, mixed m.p. 240–241°, and *p*-chlorobenzoic anhydride (1.05 g, 15%), m.p. 190°, mixed m.p. 190–191°, were produced. Distillation of the solution gave (a) chlorobenzene (1.1 g), b.p. 131–133°, identified by i.r. spectrum, (b) phenyl 4-chlorobenzoate (1.2 g), m.p. and mixed m.p. 103–104°, identified by i.r. spectrum [after recrystallisation from ethanol; g.l.c. of the original distillate (b) confirmed the presence of this ester only], and an intractable residue (1.1 g).

A similar reaction carried out under nitrogen gave identical results.

PEGA, 10% SIL at 180°) showed the presence of 1,2,3-trichlorobenzene (0.038 g) and ethyl 4-chlorobenzoate (0.38 g). The i.r. spectra of the product after esterification and the authentic ester were identical. A second portion (0.5 g) gave 4-chlorobenzanilide (m.p. and mixed m.p. 193–194°) on treatment with aniline.

Fraction (b), on fractional recrystallisation from ethanol, gave (i) *p*-chlorobenzoic anhydride (0.03 g, 1%), m.p. and mixed m.p. 191–192°, *p*-chlorobenzoic acid (0.09 g, 2%), m.p. 239–240°, mixed m.p. 239–241°, and 2,3-dichlorophenyl 4-chlorobenzoate (0.23 g, 2.5%), m.p. and mixed m.p. 118–119°. G.l.c. analysis (2% NPGS, 10% SIL at 200°) showed the presence of only one compound in the ester fraction.

2',4',6'-Tribromo-4-chloro-N-nitrosobenzanilide in carbon tetrachloride. After reaction of the nitroso-amide (9.95 g) in carbon tetrachloride (280 ml) in the usual way, removal of the bulk of solvent gave a precipitate, shown (i.r. spectrum) to be neither *p*-chlorobenzoic acid nor the anhydride; it was probably a mixture of an ester and the

starting benzanilide. T.l.c. on alumina showed the presence of two components. Chromatography on alumina gave (a) an ester (i.r. spectrum) (1.65 g), m.p. 186° (discussed later) and (b) 2',4',6'-tribromo-4-chlorobenzanilide (1.4 g) (i.r. spectrum; m.p. and mixed m.p. 210—212°). Distillation of the remaining solution gave (c) *p*-chlorobenzoyl chloride (0.3 g), b.p. 110° at 11 mmHg, identified by i.r. spectrum and conversion into ethyl 4-chlorobenzoate, identical with an authentic specimen (i.r.; g.l.c.), (d) a yellow sublimate (0.44 g) driven over at 150° (bath temp.) and 0.05 mmHg, and (e) a residue (4.8 g).

Addition of benzene to fraction (d) precipitated *p*-chlorobenzoic acid (0.15 g); chromatography of the benzene solution gave a mixture (0.25 g), m.p. 90—93°, of 1,2,3,5-tetrabromobenzene (0.19 g, 2%) and 1,3,5-tribromo-2-chlorobenzene (0.05 g, 1%) [by i.r. and g.l.c. analysis (2% NPGS, 10% SIL at 120°)]. Fraction (e) on chromatography on alumina gave (f) a compound identical with fraction (a) (0.6 g, m.p. 188°, mixed m.p. 186—188°) and (g) 2',4',6'-tribromo-4-chlorobenzanilide (1.0 g) (i.r. spectrum; mixed m.p. 211—212°).

The combined fractions (a) and (f) were shown to be a mixture of 2-chloro-3,5-dibromophenyl 4-chlorobenzoate (0.31 g, 4%) and 2,3,5-tribromophenyl 4-chlorobenzoate (1.93 g, 21%) (Found: C, 34.3; H, 1.6%) as follows. Hydrolysis of a portion (0.5 g) gave *p*-chlorobenzoic acid (0.07 g) and a phenol (0.20 g) whose n.m.r. spectrum showed absorption at τ 4.3 (OH) and doublets centred at 2.59 (1H) and 2.81 (1H) (*J* 2.1 Hz) consistent with a 2,3,5-trisubstituted phenol. This spectrum was very similar to those of 2,3,5-tribromophenol and 2-chloro-3,5-dibromophenol. The i.r. spectrum was very similar to that of 2,3,5-tribromophenol. G.l.c. (2% NPGS at 170°) showed that the phenolic portion contained two components, 2-chloro-3,5-dibromophenol and 2,3,5-tribromophenol, in the ratio 1 : 6.2. A mixture of authentic samples of these two esters was prepared and the i.r. spectrum was identical with that of fractions (a) and (f). This was further support for the identity of the two compounds, which could not be separated.

2',4',6'-Trichloro-N-nitrosobenzanilide in benzene. The nitroso-amide (8.9 g) was stirred overnight in benzene (345 ml) at room temperature, the apparatus being protected from atmospheric moisture by a drying tube. To ensure completion of the reaction, the mixture was boiled under reflux for 6 h, and allowed to cool. No precipitate was formed. The bulk of the solvent was removed by distillation, leaving a solid (0.45 g) which (i.r. spectrum) seemed to be a mixture of *p*-chlorobenzoic acid and its anhydride. By fractional crystallisation from benzene these two compounds were isolated: *p*-chlorobenzoic acid (0.19 g), m.p. and mixed m.p. 241—243°, and *p*-chlorobenzoic anhydride (0.23 g), m.p. and mixed m.p. 191—192°. Distillation of the solution gave the following fractions: (a) a yellow liquid (1.2 g), b.p. 90° at 10 mmHg, (b) a mixture of a solid and a liquid (0.65 g), b.p. 105° at 0.05 mmHg, and (c) a residue (6 g). The sharp smell and the i.r. spectrum indicated that fraction (a) was mainly *p*-chlorobenzoyl chloride, confirmed by conversion of a portion (0.5 g) into 4-chlorobenzanilide, m.p. 194°, mixed m.p. 193—194°, identified by i.r. spectrum. A second portion (0.6 g) was esterified by boiling under reflux with ethanol (5 ml) for 4 h. G.l.c. (10% PEGA, 10% SIL at 180°) of the resulting solution showed the products to be 1,2,3-trichlorobenzene (0.075 g) and ethyl 4-chlorobenzoate

(0.48 g). The original solution must therefore have contained 1,2,3-trichlorobenzene (0.15 g, 3%) and *p*-chlorobenzoyl chloride (0.92 g, 19%). The solvent was removed from a portion of the esterified solution; the i.r. spectrum of the product was identical with that of ethyl 4-chlorobenzoate.

T.l.c. of fraction (b) in benzene showed the presence of four components. *p*-Chlorobenzoic acid was removed by dissolving the other components in benzene. Chromatography on alumina (benzene elution) gave only one solid (0.25 g), m.p. 64—65°, the i.r. spectrum of which indicated that it contained an hydroxy-group. This compound was later identified as 2-chloro-6-hydroxybiphenyl (see later).

Chromatography of fraction (c) gave (d) a yellow oil (1.87 g) and 2',4,6'-trichlorobenzanilide (0.9 g, 11%), m.p. and mixed m.p. 193—195°, identified by its i.r. spectrum. T.l.c. of fraction (d), which slowly solidified, showed one component, identified as 2-chloro-6-(*p*-chlorobenzoyloxy)-biphenyl, m.p. 79—80° (from methanol) (Found: C, 66.5; H, 3.4; Cl, 20.6. C₁₈H₁₂Cl₂O₂ requires C, 66.5; H, 3.5; Cl, 20.7%), by hydrolysis of a portion (0.48 g) to *p*-chlorobenzoic acid, m.p. and mixed m.p. 240—242°, and 2-chloro-6-hydroxybiphenyl (0.19 g), m.p. 66—67° (Found: C, 70.2; H, 4.3. C₁₂H₉ClO requires C, 70.4; H, 4.4%), τ 5.2 (s, OH), 3.12 (1H, dd, *J* 3 and 8.5 Hz), 2.92 (1H, dd, *J* 9 and 8.5 Hz), 2.68 (1H, dd, *J* 3.5 and 9 Hz), and 2.53br (5H, s). The phenol from fraction (b) was identical with this product.

Reactions of Substituted N-Nitrosobenzanilides in Carbon Tetrachloride in the Presence of Arynophiles.—(i) *With furan.* 4-Chloro-*N*-nitrosobenzanilide (7.62 g, 0.029 mol) and furan (1.98 g, 0.029 mol) were stirred in dry carbon tetrachloride (400 ml) overnight while protected from atmospheric moisture, and then boiled under reflux for 6 h. 2-Phenylfuran and 1,4-*endo*-epoxy-1,4-dihydronaphthalene were absent (by g.l.c.). Standard work-up gave *p*-chlorobenzoic acid (0.65 mol. equiv.), m.p. and mixed m.p. 239—241°, *p*-chlorobenzoic anhydride (0.09 mol. equiv.), m.p. and mixed m.p. 190—191°, chlorobenzene (0.28 mol. equiv.), and phenyl 4-chlorobenzoate (0.04 mol. equiv.).

A similar reaction of 4-chloro-4'-methyl-*N*-nitrosobenzanilide (5.0 g) with a ten-molar excess of furan (12.45 g) in carbon tetrachloride (270 ml) again did not give 2-*p*-tolylfuran or the aryne-furan adduct (by g.l.c.) but *p*-chlorobenzoic acid (0.72 mol. equiv.), the anhydride (0.06 mol. equiv.), and *p*-chlorotoluene (0.05 mol. equiv.) were isolated.

(ii) *With tetraphenylcyclopentadienone.* (a) *General procedure.* The pattern of products obtained from *N*-nitrosobenzanilide and 3'-substituted analogues differed from those obtained from 2'- and 4'-substituted-*N*-nitrosobenzanilides; a slightly different procedure was used in each of these two categories, therefore. For *N*-nitrosobenzanilide and its 3'-substituted analogues, the nitroso-compound together with a one-molar excess of 2,3,4,5-tetraphenylcyclopentadienone, was stirred in carbon tetrachloride overnight at room temperature, the mixture being kept free from moisture. After being boiled under reflux for 6 h to complete the reaction, the mixture was allowed to cool. The appropriate benzoic acid was precipitated, and was identified (i.r. spectrum; m.p., and mixed m.p.) after recrystallisation. The bulk of the solvent was removed by distillation; the resultant dark precipitate in no case showed anhydride carbonyl absorption in the i.r. spectrum. A portion of the solution was retained for analysis by g.l.c.

The remaining solution, which was shown by t.l.c. to contain the appropriate tetraphenylnaphthalene, together with the dark solid precipitate, was adsorbed on to alumina and chromatographed to yield the tetraphenylnaphthalene(s). The precipitated carboxylic acids were separated from any tetraphenylcyclopentadienone by extraction into alkali and subsequent acidification of the alkaline layer.

For reactions of 2'- and 4'-substituted 4-chloro-*N*-nitrosobenzanilides the procedure was similar; differences were as follows. After completion of the reaction, the precipitate obtained on cooling the mixture and that left after removal of the bulk of the solvent showed the same i.r. spectra, that of mixtures of *p*-chlorobenzoic acid, *p*-chlorobenzoic anhydride, and tetraphenylcyclopentadienone. No tetraarylnaphthalenes were detected in these precipitates by t.l.c. To separate the components of this mixture, the

4-chloro-3'-methyl-*N*-nitrosobenzanilide gave a mixture of 5-methyl- and 6-methyl-1,2,3,4-tetraphenylnaphthalenes in the ratio (5 : 6-) of 7 : 4 as shown by analysis (Found: C, 94.1; H, 6.0. Calc. for $C_{25}H_{26}$: C, 94.1; H, 5.9%) and by direct comparison of the n.m.r. spectrum of the mixture with that of a made-up mixture of the authentic components.

4-chloro-3'-nitro-*N*-nitrosobenzanilide gave 5-nitro-1,2,3,4-tetraphenylnaphthalene as yellow needles from acetic acid, slowly darkening on exposure to light, m.p. 254° (Found: C, 85.2; H, 5.2; N, 3.0. $C_{34}H_{23}NO_2$ requires C, 85.5; H, 4.9; N, 2.9%), τ 3.18 (10H, s), 2.90 (5H, s), 2.79 (5H, s), 2.68 (1H, 2 \times d, *J* 8.2 and 7.2 Hz, H-7), 2.30 (1H, 2 \times d, *J* 7.3 and 1.9 Hz, H-6), and 2.18 (1H, 2 \times d, *J* 8.3 and 2.0 Hz, H-8). The presence of three phenyl resonances is due to the presence of the 5-substituent.

TABLE 6

Yields of product (mol. equiv.) obtained in reactions of *N*-nitrosobenzanilides [$XC_6H_4 \cdot N(NO) \cdot CO \cdot C_6H_4 X$ - *p*] with carbon tetrachloride in the presence of tetraphenylcyclopentadienone ^a

Product (Ar = <i>p</i> -YC ₆ H ₄)	X = H Y = Cl	H ^b Cl	2-Br Cl	3-Br Cl	4-Br Cl	3-Me Cl	4-Me Cl	3-NO ₂ Cl	4-NO ₂ Cl	H NO ₂	H Me
ArCO ₂ H	0.49	0.69	0.24	0.82	0.18	0.71	0.63	0.84	0.04	0.44	0.52
(ArCO) ₂ O	0	0.14	0.22	0	0.23	0	0.11	0	0.18	0	0
Adduct ^c	0.32	0.02	0	0.70	0.04	0.33	0.01	0.63	0	0.14	0.29
XC ₆ H ₄ ·NH·COAr	0		0	0	0	0	0	0.05	0.06	0	0
XC ₆ H ₄ Cl	0.04	0	0.09	0.02	0.09	0.05	0.23	0	0.09	0.16	0
XC ₆ H ₄ Br			0.13	0	0.09						
<i>o</i> -ClC ₆ H ₄ Cl			0.11								
<i>p</i> -ClC ₆ H ₄ Cl					0.01		0		0		
PhO·COAr	0									0.10	0.10
ArO·COAr	0		0	0	0	0	0	0	0.09	0	0
Accountance of XC ₆ H ₄ (%)	36	2	33	72	23	38	24	84	24	40	39
Accountance of Ar (%)	49	97	68	82	64	71	85	68	40	54	62

^a All products were identified by comparison (m.p. or b.p.; i.r. and n.m.r. spectra; g.l.c.) with authentic materials with the exception of certain new tetraphenylnaphthalenes, identified (see text) by n.m.r. analysis. ^b In the presence of water (1 mol. equiv.). ^c Tetraphenylnaphthalene(s) (see text for details).

solid was stirred with sodium hydroxide solution. *p*-Chlorobenzoic acid was precipitated on acidification of the alkaline solution, and was identified by m.p., mixed m.p., and i.r. spectrum. The residual solid was then boiled under reflux with sodium hydroxide solution to hydrolyse the anhydride. Acidification of the alkaline solution gave *p*-chlorobenzoic acid, from the amount of which the yield of *p*-chlorobenzoic anhydride was calculated. A portion of the remaining solution, after removal of the above precipitates, was retained for g.l.c. The remainder was chromatographed on alumina. The results of the experiments are summarised in Table 6.

(b) *Identification of the substituted tetraphenylnaphthalenes isolated in the foregoing experiments.* All these materials exhibited the characteristic u.v. absorption envelope.

3'-Bromo-4-chloro-*N*-nitrosobenzanilide gave 5-bromo-1,2,3,4-tetraphenylnaphthalene as plates (from acetic acid), m.p. 235–236° (Found: C, 79.5; H, 4.7. $C_{34}H_{23}Br$ requires C, 79.8; H, 4.5%), τ 3.21 (10H, s), 2.91 (5H, s), 2.81 (5H, s), 2.89 (1H, 2 \times d, *J* 8.7 and 7.0 Hz, H-7), 2.35 (1H, 2 \times d, *J* 8.7 and 1.7 Hz, H-6), and 2.20 (1H, 2 \times d, *J* 7.0 and H, 1.4 Hz, H-8). Comparison with the n.m.r. spectrum of 6-bromo-1,2,3,4-tetraphenylnaphthalene established that the 6-isomer was not present in admixture with the isolated 5-isomer.

The 6-nitro-isomer would be expected to show only two phenyl resonances (*cf.* 6-methyl-1,2,3,4-tetraphenylnaphthalene and 6-bromo-1,2,3,4-tetraphenylnaphthalene) and a doublet with *J* 9 Hz for H-8, a double doublet with *J* 9 and 2 Hz for H-7 and a doublet with *J* 2 Hz for H-5.

*Reaction of 4-chloro-*N*-nitrosobenzanilide with Tetraphenylcyclopentadienone in Carbon Tetrachloride in the Presence of Water.*—4-chloro-*N*-nitrosobenzanilide (2.55 g), water (0.2 g, 1 mol. equiv.), and tetraphenylcyclopentadienone (7.8 g) reacted in carbon tetrachloride (136 ml). *p*-Chlorobenzoic acid (1.08 g, 0.69 mol. equiv.), m.p. and mixed m.p. 240–242°, and *p*-chlorobenzoic anhydride (0.35 g, 0.14 mol. equiv.), m.p. and mixed m.p. 189–191°, were isolated as described for the reaction without tetraphenylcyclopentadienone. G.l.c. (2% NPGS, 10% SIL at 85°) showed that no chlorobenzene was present.

Chromatography of the solution gave the following fractions: (a) a yellow solid (0.15 g), eluted with light petroleum (b.p. 40–60°)–benzene (9 : 1), (b) tetraphenylcyclopentadienone, eluted with benzene, and (c) a brown gum, eluted with methanol. Recrystallisation of fraction (a) from acetic acid gave 1,2,3,4-tetraphenylnaphthalene (0.10 g, 0.02 mol. equiv.), m.p. and mixed m.p. 198–200°. I.r., n.m.r., and u.v. spectra were identical with those of the authentic sample.

An identical experiment carried out without water (Table 6) gave the adduct in 32% yield.

Reactions of N-Nitrosobenzanilides in Benzene in the Presence of Tetraphenylcyclopentadienone.—The standard procedure was used, involving, for example, equimolar *N*-nitrosobenzanilide (4 g) and tetraphenylcyclopentadienone in benzene (175 ml). The results are summarised in Table 7.

TABLE 7

Yields of products (mol. equiv.) obtained in reactions of substituted 4-chloro-*N*-nitrosobenzanilides [$\text{XC}_6\text{H}_4\text{-N}(\text{NO})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl-}p$] with benzene in the presence of tetraphenylcyclopentadienone

Product	X = H	2-Br	3-Br
(Ar = <i>p</i> -ClC ₆ H ₄)			
ArCO ₂ H	0.79	0.69	0.87
(ArCO) ₂ O	0	0	0
XC ₆ H ₄ Ph	0.04	0.21	0.01
PhO·COAr	0.06		
Adduct ^a	0.37	0	0.73
Accountance of Ar (%)	85	69	87
Accountance of XC ₆ H ₄ (%)	47	21	74

^aTetraphenylnaphthalene(s).

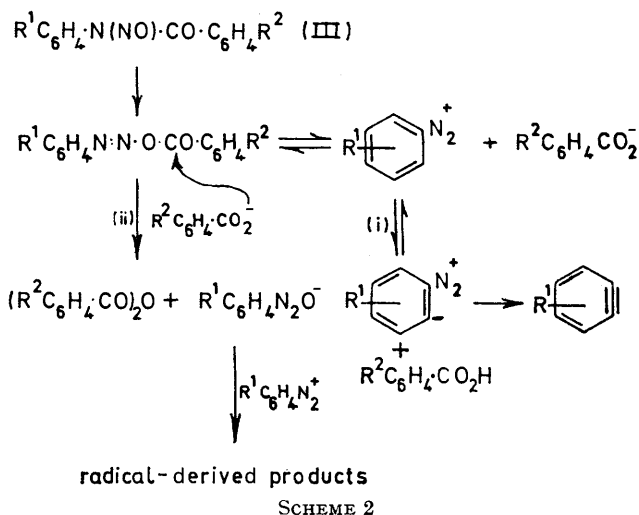
Reaction of 4-Chloro-N-nitrosobenzanilide with Carbon Tetrachloride at Room Temperature (with Dr. J. COOK).—The nitroso-amide (1.83 g, 7.0 mmol) decomposed in carbon tetrachloride (42.54 g, 0.27 mol) at room temperature during 12 h. The precipitate (0.91 g) was filtered off, washed with a little fresh solvent, and dried; ν_{max} (Nujol) 3000br (OH), 2300 (diazonium group), and 1680br cm⁻¹ (C=O). With alkaline β -naphthol, a portion gave phenylazo- β -naphthol, m.p. and mixed m.p. 132°. Halogen analysis (Volhard, Mohr) showed that the precipitate contained benzenediazonium chloride (16%), the remainder being a mixture of diazonium *p*-chlorobenzoate and *p*-chlorobenzoic acid. Analysis of the filtrate by g.l.c. (2% NPGS at 75–180°; 3% QF1 at 75–180°) (*p*-dichlorobenzene as marker) showed the presence of chlorobenzene (17%). Subsequent decomposition of a portion of the precipitated diazonium salt in fresh carbon tetrachloride gave, after g.l.c. analysis as before chlorobenzene (13%) and phenyl 4-chlorobenzoate (0.1 g). *p*-Chlorobenzoic acid (0.25 g) was filtered from the reaction mixture.

A parallel reaction in which the precipitate was filtered off after 30 min showed a lower percentage of benzenediazonium chloride (9.3%) in the precipitate. A broad i.r. absorption at 3000 cm⁻¹ indicated the presence of *p*-chlorobenzoic acid.

DISCUSSION

Decomposition of N-Nitrosobenzanilides (III) in Carbon Tetrachloride.—(i) *Formation of carboxylic acids and arynes.* The results summarised in Tables 5 and 6 reveal, as predicted by Scheme 1, that decomposition in dry carbon tetrachloride of 4-chloro-*N*-nitroso-2'-bromo-, 3'-bromo-, 4'-bromo-, 4'-methyl-, and 4'-nitro-benzanilides (III; R² = Cl; R¹ = 2-Br, 3-Br, 4-Br, 4-Me, or 4-NO₂), 4-chloro-*N*-nitrosobenzanilide (III; R² = Cl; R¹ = H), 4-bromo-*N*-nitroso-4'-bromo- and 4'-nitro-benzanilides (III; R² = Br; R¹ = 4-NO₂ or 4-Br), in all cases gives rise to significant yields (29–79%) of *p*-chloro- or *p*-bromo-benzoic acid as a primary

product, control experiments having shown that the corresponding aryl chlorides or anhydrides are not precursors (Scheme 2). There is no correlation between



the yield of acid and the basicity of the corresponding anion because the basicity relates to solvated ions in aqueous solution and different considerations apply to benzene solutions. Nevertheless it is clear that the proton of the benzoic acid originates in the aryl-diazonium system. If this proton is *ortho* to the diazonium function the corresponding aryne (or arynes) and/or its precursor should be produced and it is not easy to predict how these would react with the various species present in the reaction mixture. It is significant that whereas a high accountance for the carboxylate portion was obtained in most cases, the corresponding accountance for the diazonium portion was low, the main product being unidentified high molecular weight tars. The use of tetraphenylcyclopentadienone, however, led to isolation in varying yields (Table 6) of the corresponding tetraphenylnaphthalene derivatives, indicating the presence of the corresponding arynes. Thus, 4-chloro-*N*-nitrosobenzanilide (III; R² = Cl; R¹ = H), and its 3'-bromo-, 3'-nitro-, and 3'-methyl-derivatives (III; R² = Cl; R¹ = 3-Br, 3-NO₂, or 3-Me) gave, respectively, 1,2,3,4-tetraphenylnaphthalene (32%), 5-bromo- (70%) and 5-nitro- (63%) 1,2,3,4-tetraphenylnaphthalenes, and a mixture (33%) of 5- and 6-methyl-1,2,3,4-tetraphenylnaphthalenes in the ratio (5 : 6-) of 7 : 4. In none of these cases was the yield of aryne adduct quite as high as the yield of carboxylic acid, suggesting that hydrogen atoms are being removed from other positions in the diazonium portion and/or that the efficiency of trapping the resultant aryne is low. This discrepancy is particularly marked in the cases of 4-chloro-*N*-nitroso-2'- and 4'-bromo-benzanilides (III; R² = Cl; R¹ = 2-Br or 4-Br) (acid 18–24%; aryne trapped 0–4%) and less so in the cases of 4-nitro- and 4-methyl-*N*-nitrosobenzanilides (III; R² = 4-NO₂ or 4-Me; R¹ = H). This effect of substituent on aryne

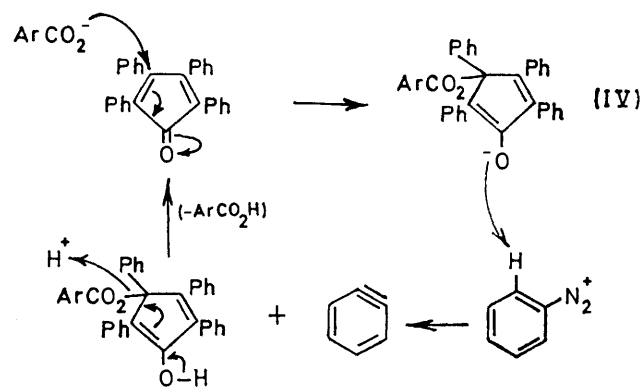
formation from acylarylnitrosamines (and hence diazonium carboxylates) is not yet fully understood and is under investigation. In this connection, however, it is particularly significant that the presence of water (1 mol. equiv., which in our experiments corresponds to *ca.* 0.1% v/v of solution) depresses the yield of aryne adduct (in the case of 4-chloro-*N*-nitrosobenzanilide from 32 to 2%) and increases the yield of *p*-chlorobenzoic acid. For this reason all our experiments were carried out with carefully dried materials and it is unlikely that the discrepancies can be attributed to the presence of water. Since the formation of the carboxylic acid and the aryne is very dependent on the existence of the diazonium carboxylate ion pair (Scheme 2), the observed effect of water is explicable, since it could interfere with the removal of the aromatic proton by solvation of the constituents of the ion pair, *e.g.* by making the acetate ion less 'basic'. The possibility that it could reverse the equilibrium (i) (Scheme 2) also cannot be discounted. This discovery has an important bearing on the successful one-step conversion of aniline into benzyne⁵ *via* an *in situ* diazotisation, the full scope and mechanism of which will be discussed in a later paper.

(ii) *Formation of carboxylic anhydrides* (Tables 5 and 6). In every case studied, reactions in carbon tetrachloride in the absence of tetraphenylcyclopentadienone gave the corresponding benzoic anhydride in significant yield (12–38%). Carboxylic anhydrides have not previously been reported as products of decomposition of acylarylnitrosamines, although Suschitzky⁶ and Rüchardt and Freudenberg⁷ have discussed the possibility of their formation. We consider that the most likely route to the anhydrides involves attack by the carboxylate ion on the carbonyl group of the unchanged nitroso-amide or the isomeric diazocarboxylate [Scheme 2; reaction (ii)], with the concomitant formation of the arenediazoate ion. The diazoate ion can then be consumed by unchanged diazonium cation to give products as previously described.⁷ Thus, in carbon tetrachloride, reaction (ii) of Scheme 2 competes relatively successfully with removal of a proton from the aryldiazonium cation to give arynes. This reaction is not confined to benzanilides: a corresponding reaction of *N*-nitrosoacetanilide itself in carbon tetrachloride gave, among other products, acetic anhydride in 15% yield.

Reactions in benzene, described previously^{1,2,7} and later in this paper, do not give anhydrides, because the alternative reaction of the intermediate arylocyclohexadienyl cation, or arenediazoate (ArN_2OH), with the carboxylate anion, discussed earlier^{1,2,7} is preferred, as might be expected. In carbon tetrachloride these alternatives are not available.

The results of corresponding reactions of *N*-nitrosobenzanilides in carbon tetrachloride carried out in the presence of tetraphenylcyclopentadienone (Table 6) show that in those cases giving rise to high yields of aryne adducts [*e.g.* 3'-bromo-4-chloro-*N*-nitrosobenz-

anilide (III; $\text{R}^2 = \text{Cl}$; $\text{R}^1 = 3\text{-Br}$)] the yield of the anhydride drops from *ca.* 30%, obtained in reactions carried out in the absence of tetraphenylcyclopentadienone, to zero, with the 'lost' carboxylate portion appearing as additional free carboxylic acid. These results show that in cases where aryne production is high, tetraphenylcyclopentadienone diverts the carboxylate anion from its reaction with the aryldiazonium carboxylate [to give anhydride: Scheme 2, reaction (ii)]. This, taken with the previously unexplained observation^{1,2} that tetraphenylcyclopentadienone diverts the decomposition of *N*-nitrosoacetanilide from the 'normal' radical route to the formation of aryne suggests the role of the dienone is two-fold, first to interact with the diazonium ion pair in such a way as to increase the ease of removal of the proton *ortho* to the diazonium group, possibly *via* the more basic intermediate (IV) in Scheme



SCHEME 3

3, which need be present only in small, equilibrium concentration, which ultimately regenerates the dienone and gives the carboxylic acid, and second to act as a trap for the resulting aryne. This very tentative suggestion is being tested.

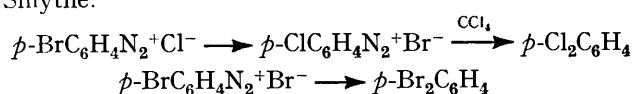
(iii) *Formation of aryl halides and esters.* Aryl chlorides (ArCl) were formed in 15–40% yield in reactions of the nitrosobenzanilides [$\text{ArN}(\text{NO})\text{-COR}$] in carbon tetrachloride in the absence of tetraphenylcyclopentadienone. It is possible that these arose *via* the competing radical path (Scheme 1), $\text{Ar}\cdot + \text{CCl}_4 \longrightarrow \text{ArCl} + \cdot\text{CCl}_3$. In accord with this, and with corresponding observations of the decomposition of *N*-nitrosoacetanilide in benzene, the reaction in carbon tetrachloride in the presence of tetraphenylcyclopentadienone led to a reduction in yield of the aryl halide. On the other hand, no evidence for the formation of trichloromethyl radicals or the expected dimer, hexachloroethane, was discovered. This aspect of the reaction is still under investigation and the mechanism is likely to prove to be more complicated in view of the very early isolated observation, which we have confirmed, that decomposition of *N*-nitrosoacetanilide in carbon tetrachloride

⁶ H. Suschitzky, *Angew. Chem. Internat. Edn.*, 1967, **6**, 596.

⁷ C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, 1964, 3623.

⁵ J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Comm.*, 1971, 1.

gives benzenediazonium chloride at room temperature.⁸ Our experiments with nitrosoaranilides, in the main, were carried out at 80°, under which conditions diazonium chlorides would not survive. In control experiments at room temperature 4-chloro-*N*-nitrosobenzanilide (III; R² = Cl; R¹ = H) in carbon tetrachloride gave a precipitate estimated to contain 16% benzenediazonium chloride, the remainder being a mixture of benzenediazonium *p*-chlorobenzoate and *p*-chlorobenzoic acid. Similar results were obtained from 3'-bromo-4-chloro-*N*-nitrosobenzanilide. Although we do not yet have an explanation for the formation of the diazonium chlorides, their intermediacy in these reactions may be invoked in an explanation of the formation of 'mixed' halides which are also produced in these reactions (Table 4). Thus, 4'-bromo-4-chloro-*N*-nitrosobenzanilide (III; R² = Cl; R¹ = 4-Br) gave *p*-dichlorobenzene (25%) and *p*-dibromobenzene (5%), explicable on the basis of nucleophilic displacement of nuclear halogen as shown long ago by Hantzsch and Smythe.⁹



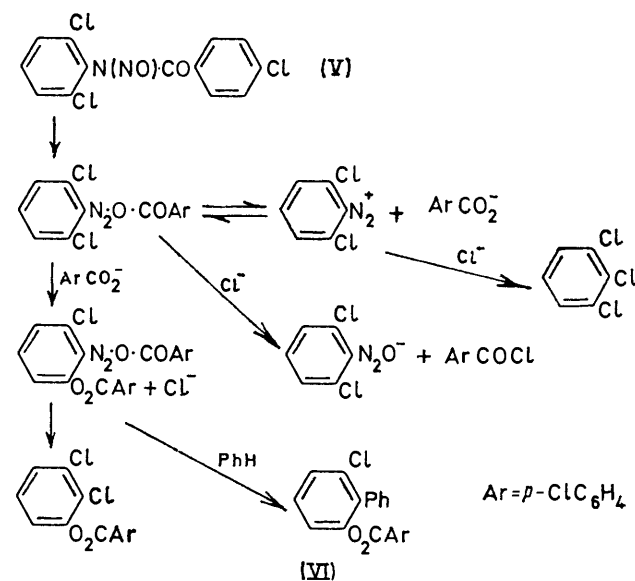
Formation of the observed esters (Table 5) can be rationalised similarly. Thus the formation of aryl benzoates (ArO·COAr') from nitrosobenzanilides [ArN(NO)·COAr'] is explicable on the basis of ArN₂⁺Ar'CO₂⁻ → ArO·COAr', while that of *p*-chlorophenyl *p*-bromobenzoate from 4,4'-dibromo-*N*-nitrosobenzanilide follows from *p*-BrC₆H₄N₂⁺O⁻·CO·C₆H₄Br → *p*-BrC₆H₄N₂⁺Cl⁻ → *p*-ClC₆H₄N₂⁺O₂C·C₆H₄Br → *p*-ClC₆H₄O₂C·C₆H₄Br.

Decomposition of N-Nitrosoaranilides (III) in Benzene.—These decompositions led to the corresponding biaryl and carboxylic acid as the main products. Carboxylic anhydrides were absent. That the biaryl was derived *via* aryl radicals followed from the observation that 4-chloro-*N*-nitrosobenzanilide (III; R² = Cl; R¹ = H) in chlorobenzene gave a mixture of isomeric chlorobiphenyls (47%), the ratio of isomers (2- : 3- : 4- : : 60 : 23 : 17) determined by g.l.c. pointing to the presence of phenyl radicals, in comparison with the ratio (62 ± 3 : 24 ± 3 : 14 ± 3) found in the phenylation of chlorobenzene by authentic sources of phenyl radicals.¹⁰

In the presence of added tetraphenylcyclopentadienone (Table 7) aryne adducts were obtained at the expense of the biaryl in the case of 4-chloro-*N*-nitrosobenzanilide and its 3'-bromo-derivative but not in the case of the 2'-bromo-derivative. These results therefore parallel those obtained for decompositions of substituted *N*-nitrosoacetanilides in aromatic solvents.¹

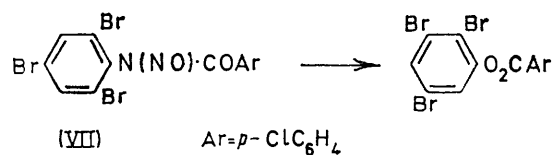
Decompositions of 2,6-Disubstituted N-Nitrosobenzanilides.—In each case studied, allowance for starting material was low. 2',4,6'-Trichloro-*N*-nitrosobenzanilide

(V) on decomposition in benzene or carbon tetrachloride gave only traces of *p*-chlorobenzoic acid, thus indicating that a free *ortho*-position is necessary for abstraction of nuclear hydrogen from the arenediazonium cation. In both solvents the major product was *p*-chlorobenzoyl chloride (45% in carbon tetrachloride). It is considered that this arises by nucleophilic substitution (Scheme 4) similar to that proposed to explain the



SCHEME 4

formation of acyl fluorides from reactions of *p*-fluoro-*N*-nitrosoacetanilide in benzene.^{4,11} That such a nucleophilic substitution is the predominant first step in the reaction follows from the isolation of 2-chloro-6-(*p*-chlorobenzoyloxy)biphenyl (VI), and the corresponding phenol, formed by hydrolysis, in total yield of 24%, rather than 2,6-dichlorobiphenyl (Scheme 4). Also formed in low yield were 1,2,3-trichlorobenzene and 2,3-dichlorophenyl *p*-chlorobenzoate, again *via* the established nucleophilic substitution route. Nucleophilic displacement also predominated in the decomposition of



SCHEME 5

4-chloro-2',4',6'-tribromo-*N*-nitrosobenzanilide (VII) in carbon tetrachloride when the major isolated product was 2,3,5-tribromophenyl *p*-chlorobenzoate (21%) (Scheme 5) together with traces of the 2-chloro-3,5-dibromophenyl analogue, 1,3,5-tribromo-2-chlorobenzene and 1,2,3,5-tetrabromobenzene.

After this work was completed and a preliminary

⁸ W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1934, 1797.

⁹ H. Hantzsch and J. S. Smythe, *Ber.*, 1900, **33**, 505.

¹⁰ D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1952, 2094; 1953, 44.

¹¹ I. K. Barben and H. Suschitzky, *J. Chem. Soc.*, 1960, 2735.

report published,¹² Rüchardt and Tan¹³ described reactions of *N*-nitrosobenzanilides in carbon tetrachloride and reported for the first time the isolation of arenediazonium arenecarboxylates from reactions carried out wholly at room temperature. They did not detect the presence, under their conditions, of the additional diazonium chloride which we now report, nor the presence of carboxylic anhydrides. Rüchardt and Tan also confirmed our observation of the formation of 1,2,3,4-tetra-phenylnaphthalene during the thermolysis (65–70°) of

4-chloro-*N*-nitrosobenzanilide in carbon tetrachloride. It should be noted that in our experiments, the intermediate diazonium carboxylate was allowed to form at room temperature and then decomposed at the b.p. of the solvent.

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