

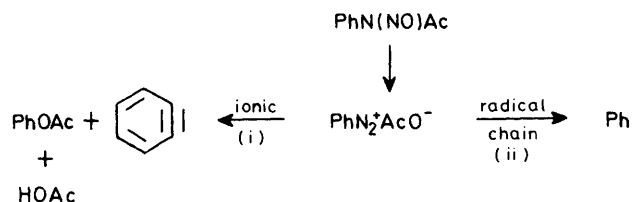
## Acylarylnitrosamines. Part 13.<sup>1</sup> Promotion of Ionic Reactions of *o*- and *p*-Chloro-, *o*- and *p*-Acetoxy-, and *o*-Acetylthio-*N*-nitrosoacetanilides. Formation of Hydroxybenzenediazonium Salts, the Carbene 2-Oxocyclohexa-3,5-dienylidene, and 1,2,3-Benzothiadiazole †

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

New ionic reactions are reported of several arenediazonium salts (derived from corresponding acylarylnitrosamines), involving suppression of the normal radical chain decomposition by addition of 1,1-diphenylethene. Thus *p*-chloro-*N*-nitrosoacetanilide (*p*-Cl-NNA) gave *p*-hydroxybenzenediazonium chloride (27%) and acetic anhydride (62%), and *o*-Cl-NNA gave *o*-chlorobenzenediazonium chloride (62%) and acetic anhydride (62%). That these reactions proceed *via* unprecedented nucleophilic substitution of aromatic chloride by acetate ion, followed by ionic deacetylation of the resultant *o*- or *p*-acetoxybenzenediazonium ions to give acetic anhydride and 2- or 4-diazocyclohexadienone, follows from the results of corresponding 1,1-diphenylethene-promoted reactions of *o*- and *p*-AcO-NNA. Decomposition of the former in boiling xylene gave 2-cyclopentadienyldiene-1,3-benzodioxole (22%), formed by reaction of 2-diazocyclohexadienone with the product of its decomposition, the carbene 2-oxocyclohexa-3,5-dienylidene.

Decomposition of *o*-AcS-NNA in benzene gives 1,2,3-benzothiadiazole (70%).

IN Parts 9<sup>2</sup> and 11<sup>3</sup> we showed that the presence of even a small amount (0.1 mol. equiv.) of 1,1-diphenylethene, acting as a radical trap, in reactions of *N*-nitrosoacetanilide (NNA), and hence of benzenediazonium acetate, in aromatic solvents was sufficient to promote ionic decomposition of NNA [Scheme 1, reaction (i)] relative to the



SCHEME 1

competing radical chain phenylation [reaction (ii)], even in furan, in which the chain reaction is rapid in the

benzenediazonium acetates, which occur on suppression of the familiar competing radical processes by 1,1-diphenylethene.

*Decompositions of p-Chloro- and p-Acetoxy-N-nitrosoacetanilides (Table).*—Decomposition of *p*-Cl-NNA at 50 °C in benzene under standard radical conditions gave the expected 4-chlorobiphenyl in high yield (68%), a precipitate (4%) of 4-hydroxybenzenediazonium chloride, and acetic anhydride (3%). Reactions in the presence of the ionic promoter 1,1-diphenylethene (1 mol. equiv.), profoundly affected the reaction. The yield of radical-derived 4-chlorobiphenyl dropped from 68 to 6% and 4-hydroxybenzenediazonium chloride (27%) was precipitated so cleanly that the reaction has merit as a simple practical preparation. Also formed in almost equivalent amount was acetic anhydride [31 mol per 100 mol (62%)]. The results point to reaction

Decompositions in benzene of acylarylnitrosamines [ArN(NO)Ac] \*

| Ar =   | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> |                                     | <i>o</i> -ClC <sub>6</sub> H <sub>4</sub> |                                     | <i>p</i> -AcO·C <sub>6</sub> H <sub>4</sub> |                                     | <i>o</i> -AcO·C <sub>6</sub> H <sub>4</sub> |                                     |
|--|---|-------------------------------------|---|-------------------------------------|---|-------------------------------------|---|-------------------------------------|
|  | Alone                                     | + Ph <sub>2</sub> C:CH <sub>2</sub> | Alone                                     | + Ph <sub>2</sub> C:CH <sub>2</sub> | Alone                                       | + Ph <sub>2</sub> C:CH <sub>2</sub> | Alone                                       | + Ph <sub>2</sub> C:CH <sub>2</sub> |
| ArPh   | 68  | 6                                   | 69  | 3                                   |   |                                     |   |                                     |
| 2-AcO·C <sub>6</sub> H <sub>4</sub> Ph               |   |                                     | 1   | 0.3                                 |   |                                     | 13  | 2                                   |
| 4-AcO·C <sub>6</sub> H <sub>4</sub> Ph               |   | 0.3                                 |   |                                     | 50  | 2.5                                 |   |                                     |
| 2-HO·C <sub>6</sub> H <sub>4</sub> Ph                |   |                                     |   | 0.5                                 |   |                                     | 1.5   | 1.5                                 |
| 4-HO·C <sub>6</sub> H <sub>4</sub> Ph                |   |                                     |   |                                     | 8   | 1                                   |   |                                     |
| 2-HO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> Cl |   |                                     | 1   |                                     |   |                                     |   |                                     |
| 4-HO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> Cl | 4   | 27                                  |   |                                     |   |                                     |   |                                     |
| 2-ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> Cl  |   |                                     |   | 31                                  |   |                                     |   |                                     |
| 4-ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> Cl  |   | 1                                   |   |                                     |   |                                     |   |                                     |
| Ph <sub>2</sub> C:CHAr                               |   | 9                                   |   | 5                                   |   |                                     |   |                                     |
| Ac <sub>2</sub> O                                    | 6   | 31                                  | 2   | 31                                  | 35  | 82                                  | 27  | 96                                  |

\* Yields are in mol per 100 mol of ArN(NO)Ac.

absence of a promoter. Thus, for the first time, it became possible to study ionic reactions of benzenediazonium acetate relatively free from interference by radical chain processes.

In this paper we describe new ionic reactions of *o*- and *p*-chloro-, *o*- and *p*-acetoxy-, and *o*-acetylthio-

† Preliminary communication: J. Brennan, J. I. G. Cadogan, and J. T. Sharp, *J.C.S. Chem. Comm.*, 1976, 850.

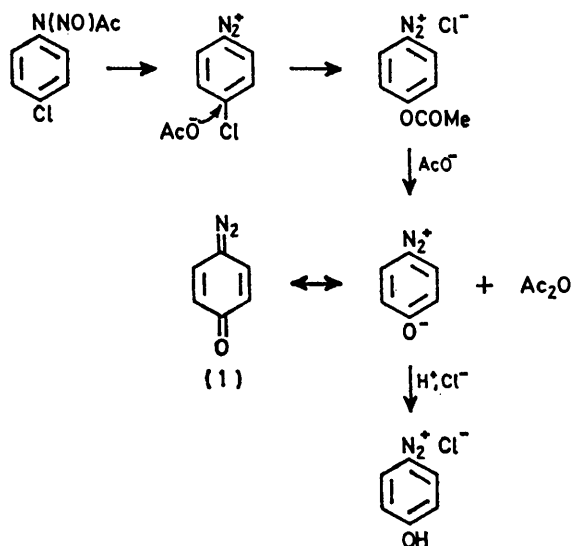
<sup>1</sup> Part 12, J. I. G. Cadogan, J. Cook, R. G. M. Landells, and J. T. Sharp, *J.C.S. Perkin I*, 1977, 1835.

as in Scheme 2, whereby displacement of chloride *para* to the activating diazonium group gives *p*-acetoxybenzenediazonium chloride, which in turn is deacetylated by acetate ion to give 4-diazocyclohexadienone (1) and hence the observed *p*-hydroxybenzenediazonium cation, and acetic anhydride in equivalent amounts. Traces

<sup>2</sup> J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Perkin II*, 1976, 583.

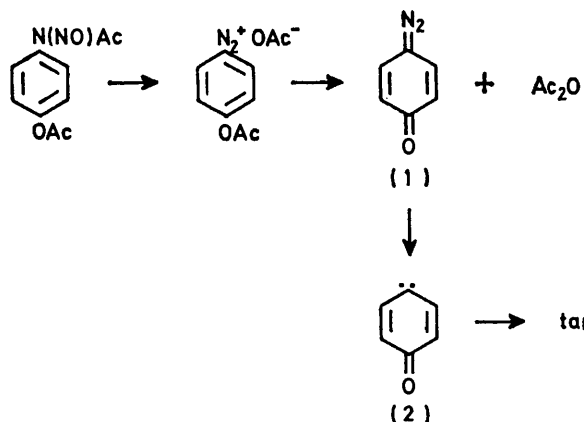
<sup>3</sup> J. Brennan, J. I. G. Cadogan, and J. T. Sharp, *J. Chem. Res.(S)*, 1977, 107; (M), 1977, 1156.

of 4-acetoxybiphenyl, formed by homolysis of the former, and *p*-chlorobenzenediazonium chloride were also detected. Also formed was 2-(*p*-chlorophenyl)-1,1-diphenylethane (9%), indicative of the promoting effect of 1,1-diphenylethane, as discussed in Part II.<sup>3</sup> This



SCHEME 2

product is involved in part in the genesis of the proton required to convert 4-diazocyclohexadienone into the *p*-hydroxybenzenediazonium ion. The remaining protons correspond to the biaryls formed and to the small amount of 2-chlorobenzynes known to be produced in the reaction of *o*-Cl-NNA.<sup>4</sup>



SCHEME 3

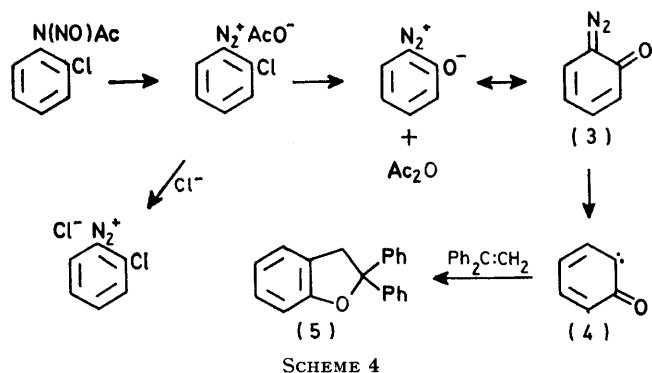
The proposed mechanism, and particularly the intermediacy of the *p*-acetoxybenzenediazonium ion, is supported by the results of decompositions of *p*-AcO-NNA in benzene at 50 °C (Scheme 3). In the absence of 1,1-diphenylethane the radical route was dominant, as expected, to give 4-acetoxybiphenyl (50%). Also

<sup>4</sup> B. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.

<sup>5</sup> J. K. Stille, P. Cassidy, and L. Plummer, *J. Amer. Chem. Soc.*, 1963, **85**, 1318.

formed, however, were products indicative of the competing ionic route, namely 4-hydroxybiphenyl (8%), *via* radical reaction of ionic-derived *p*-hydrobenzenediazonium acetate, and acetic anhydride (35%). As expected, the ionic route was strongly promoted by the presence of 1,1-diphenylethane, leading to a greatly lowered yield of 4-acetoxybiphenyl (2.5) and 4-hydroxybiphenyl (1), and to an increased yield (82%) of acetic anhydride. These show the reality of the proposed deacetylation of the resulting *p*-acetoxybenzenediazonium ion by acetate ion (Schemes 2 and 3). A necessary co-product, however, is 4-diazocyclohexadienone (1). That this was not detected is not surprising because both the diazo-ketone (1)<sup>5</sup> and its 2,6-dibromo-derivative<sup>6</sup> are known to polymerise in organic solvents at 50–70 °C, as we have confirmed, probably by way of the carbene 4-oxocyclohexa-3,5-dienylidene (2).<sup>7</sup> In contrast, the corresponding *o*-diazo-ketone (3) gives a carbene (4) which is detectable by its chemical reactions. In view of this, we turned our attention to ionic decompositions of 2-Cl- and 2-AcO-NNA acetanilides in the expectation of gaining further support for the mechanisms outlined in Schemes 2 and 3.

*Decompositions of o-Chloro- and o-Acetoxy-N-nitrosoacetanilides (Table).*—Decomposition of *o*-Cl-NNA in benzene in the presence of 1,1-diphenylethane led to a



SCHEME 4

reduction of the yields of radical-derived 2-chlorobiphenyl from 69 to 3%, while deacetylation, as measured by the yield of acetic anhydride, increased from 4 to 62%. In this case *o*-chlorobenzenediazonium chloride is the least soluble diazonium salt, which precipitated out. These results are in accord with Scheme 4, whereby deacetylation of the first formed *o*-acetoxybenzenediazonium chloride gives acetic anhydride, 2-diazocyclohexadienone (3), and chloride ion, subsequently precipitated as *o*-chlorobenzenediazonium chloride. A trace of *o*-hydroxybenzenediazonium chloride was also formed in the unpromoted reaction. Again, the detection of 2-(*o*-chlorophenyl)-1,1-diphenylethane points to the mechanism of action of the promoter.<sup>3</sup>

In support of Scheme 4, *o*-AcO-NNA, in the promoted ionic reaction in benzene, gave a very high yield of acetic

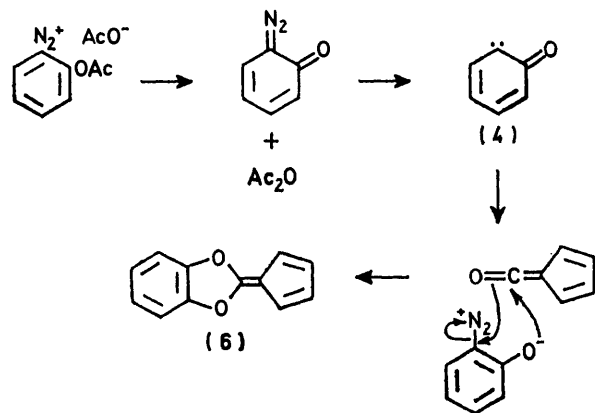
<sup>6</sup> M. J. S. Dewar and A. N. James, *J. Chem. Soc.*, 1958, 917.

<sup>7</sup> G. F. Koser and W. H. Pirkle, *J. Org. Chem.*, 1967, **32**, 1992.

anhydride (96%) and only 2% of the radical-derived 2-acetoxybiphenyl, compared with 27 and 13%, respectively, from the decomposition of *o*-AcO-NNA in benzene in the absence of 1,1-diphenylethene. A clue to the possible intermediacy of the carbene (4) was provided by the detection by g.l.c.-mass spectrometry of 2% of material which has the mass spectrum expected of 2,2-diphenyl-2,3-dihydrobenzofuran (5) (Scheme 4).

Direct evidence for the intermediacy of 2-diazocyclohexadienone (3) and of its decomposition product (4) was obtained on decomposition of *o*-AcO-NNA in boiling *p*-xylene, and in cumene, in the presence or absence of 1,1-diphenylethene. These reactions gave 2-cyclopentadienyldiene-1,3-benzodioxole (6) in up to 22% yield, identical with that produced by thermolysis of 2-diazocyclohexadienone in boiling *p*-xylene.<sup>8</sup> We interpret this reaction as shown in Scheme 5, the key step being the well known Wolff ring contraction of the intermediate carbene (4) to give the keten, which is then attacked by unchanged diazo-ketone (3).

In the foregoing ionic reactions of *o*- and *p*-Cl-NNA, the first step is nucleophilic displacement of chloride ion by acetate (Schemes 2 and 4). This appears to be unprecedented and it is of interest that Miles and Suschitzky<sup>9</sup> reported that it did not occur on decomposition of *o*- and *p*-Cl-NNA in benzene, in contrast to those of the corresponding fluoro-derivatives. We have shown that displacement does occur to a very small extent (1–3%) under radical-forming conditions, and that this



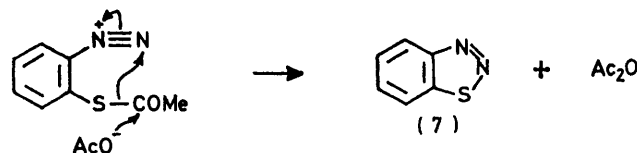
SCHEME 5

hitherto unfavoured ionic reaction becomes predominant on suppression of the radical process.

Extensions of this concept of promotion of ionic reactions by suppression of competing radical chains to the discovery of new reactions of arenediazonium salts will be reported in later papers.

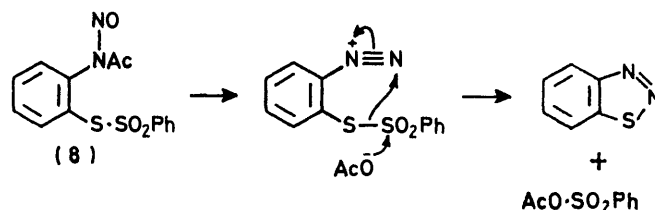
**Conversion of *o*-Acetylthio-*N*-nitrosoacetanilide into 1,2,3-Benzothiadiazole.**—The intermediacy of 2-diazocyclohexadienone (3) during the decomposition of *o*-AcO-NNA suggested that *o*-AcS-NNA should be a good

source of the corresponding diazo-thioketone, which exists as 1,2,3-benzothiadiazole (7). This proved to be correct and the product (7) was obtained in 70% yield from *o*-AcS-NNA (Scheme 6). This is related to the



SCHEME 6

observation<sup>10</sup> that the thiosulphonate derivative (8) (Scheme 7) also gives 1,2,3-benzothiadiazole (42%) on treatment with aqueous sodium hydrogen carbonate at 50 °C. We suggest that a similar mechanism is involved.



SCHEME 7

#### EXPERIMENTAL

G.l.c. analyses were performed as described in previous Parts.<sup>1</sup> Reaction mixtures were also examined with a V. G. Micromass 12 single focusing gas chromatograph-mass spectrometer, and this technique was used to confirm the presence of compounds in mixtures; in such cases the spectrum was generally compared with that of an authentic sample. In cases where assignment was made totally on the basis of the observed mass spectrum, comparison was made with a positional isomer or parent compound.

**High-speed Liquid Chromatography.**—The injection head used was of a design developed by Knox.<sup>11</sup> The pump was a Jobling eluant delivery unit with pressure damper, normally delivering 300 lb in<sup>-2</sup>. The detector was a Cecil C. E. 212 u.v. spectrophotometer fixed at 254 nm with an 8 μl flow cell. Columns were 5 mm i.d. × 250 mm, of polished stainless steel and slurry packed.

Hexane was passed through an alumina column to remove u.v.-active contaminants and water was added to the ethyl acetate (reagent grade) to give 0.6% water in solution. Fuller details of the practice of this technique are given elsewhere.<sup>12</sup>

**Materials.**—Acylarylnitrosamines were prepared as described earlier.<sup>2</sup> The *o*-chloro-, *p*-chloro-, and *p*-acetoxy-derivatives were known compounds and had correct characteristics. *o*-Acetoxy-*N*-nitrosoacetanilide had m.p. 54° (decomp.) (Found: C, 53.8; H, 4.6; N, 12.2. C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub> requires C, 54.1; H, 4.5; N, 12.6%). 2-Acetylthio-*N*-nitrosoacetanilide, an oil, was synthesised in the usual way and extracted from the aqueous medium after hydrolysis; details of the isolation procedures are given in the description of the reactions of this compound. *o*- and

<sup>10</sup> C. G. Overberger, M. P. Mazzeo, and J. J. Godfrey, *J. Org. Chem.*, 1959, **24**, 1407.

<sup>11</sup> J. H. Knox, *Chem. and Ind.*, 1975, 29.

<sup>12</sup> J. I. G. Cadogan, J. N. Done, G. Lunn, and P. K. K. Lim, *J.C.S. Perkin I*, 1976, 1749.

<sup>8</sup> R. Clinging, F. M. Dean, and G. H. Mitchell, *Tetrahedron*, 1974, **30**, 4065.

<sup>9</sup> P. Miles and H. Suschitzky, *Tetrahedron*, 1962, **18**, 1369.

*p*-Hydroxybenzenediazonium chlorides were prepared by Vogel's method<sup>13</sup> and characterised as their coupling products with 2-naphthol. 4-Diazocyclohexa-2,5-dienone had m.p. 88° (decomp.) [lit.,<sup>14</sup> 91—93° (decomp.)]. 2-(4-Chlorophenyl)-1,1-diphenylethene had m.p. 76—77° (lit.,<sup>15</sup> 76—77°).

*Decompositions of N-Nitrosoacetylarylamines.*—These were carried out in benzene with or without added 1,1-diphenylethene. In each case the work-up differed according to products, but essentially all relied on g.l.c., g.l.c.–mass spectrometry, and column chromatography. Details are given of two experiments. In the remainder reference is made only to key points.

(i) *o*-Cl-NNA in benzene. *o*-Cl-NNA (0.4 g, 2 mmol) was added to stirred benzene (5.5 ml) at 50 °C under nitrogen and the solution was heated at this temperature for 2.5 h, after which no gas evolution was observed. Filtration of the cooled solution yielded a solid residue (0.0027 g), which gave a positive test for ionic chloride with aqueous silver nitrate; the i.r. spectrum was that of 2-hydroxybenzenediazonium chloride. Addition to alkaline 2-naphthol gave a red product which had the same  $R_F$  value in t.l.c. (silica; elution with ether) as 1-(2-hydroxyphenylazo)-2-naphthol, and mass spectrometry showed this red material to have  $M^+264$ . The original solid was identified as 2-hydroxybenzenediazonium chloride (0.0027 g, 1 mol per 100 mol of 2-chloro-*N*-nitrosoacetanilide).

The reaction mixture was examined by g.l.c. (2% CAR; 170 °C) and biphenyl and phenanthrene were added as standards. 2-Chlorobiphenyl (69 mol per 100 mol 2-Cl-NNA) and 2-acetoxybiphenyl (0.7 mol per 100 mol 2-Cl-NNA) were identified by g.l.c. retention times; the former assignment was confirmed by g.l.c.–mass spectrometry, and the latter, which did not give a sufficiently intense signal for g.l.c.–mass spectrometry, was supported by a peak of the same g.l.c. retention time as 2-acetoxybiphenyl being observed on a different phase (3% NPGS; 210 °C).

Addition of aniline (0.19 g, 2 mmol) to the solution and heating at 50 °C for 0.5 h gave rise to a component identified by g.l.c. retention time (2% CAR; 170 °C) and g.l.c.–mass spectrometry as acetanilide (2 mol per 100 mol 2-Cl-NNA).

(ii) *o*-Cl-NNA in benzene in the presence of 1,1-diphenylethene. *o*-Cl-NNA (0.4 g, 2 mmol) was added to a stirred solution of 1,1-diphenylethene (0.36 g, 2 mmol) in benzene (5.5 ml) at 50 °C under nitrogen and maintained at this temperature for 2 h, after which no gas evolution was observed. The precipitate which had formed was filtered off and dried to give a buff coloured, non-crystalline solid (0.11 g); the solution was heated for a further 1 h at 50 °C but no further precipitation was observed. Aqueous silver nitrate was added to an aqueous solution of a small portion of the precipitate; the white precipitate which formed dissolved upon addition of concentrated aqueous ammonia but not upon addition of concentrated nitric acid or glacial acetic acid; this indicated the presence of ionic chlorine.

The i.r. spectrum of the solid showed a diazonium absorption (2 270  $\text{cm}^{-1}$ ) and when the solid (0.08 g) was added to alkaline 2-naphthol a red precipitate was obtained. This was purified by wet column chromatography (silica; elution with benzene) and the product was identified as 1-(2-chlorophenylazo)-2-naphthol (0.118 g), m.p. and mixed m.p.

166—168° (lit.,<sup>16</sup> 168—169°), i.r. spectrum identical with that of the authentic compound;  $M^+282/284$ .

The original precipitate was therefore *o*-chlorobenzenediazonium chloride; a sample was precipitated from acetonitrile with ether (Found: C, 40.7; H, 2.3; N, 15.85. Calc. for  $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2$ : C, 41.2; H, 2.3; N, 16.0%). The yield of the solid precipitate was therefore 31 mol per 100 mol of 2-Cl-NNA, and the yield of coupling product with 2-naphthol was 91 mol per 100 mol of 2-chlorobenzenediazonium chloride.

Biphenyl (0.03 g), phenanthrene (0.0471 g), and 4-terphenyl (0.05 g) were added as standards to the original filtered reaction mixture. 2-Chlorobiphenyl (3 mol per 100 mol 2-Cl-NNA) was identified by g.l.c. retention time and by g.l.c.–mass spectrometry (10% PEGA); and 2-(2-chlorophenyl)-1,1-diphenylethene (5.5 mol per 100 mol 2-Cl-NNA) was identified by g.l.c.–mass spectrometry only (10% SE30; 220 °C;  $m/e$  292, 290, 254, 240, 239, and 230), using the mass spectrum of the 4-chlorophenyl isomer for comparison and the calibration of this isomer against 4-terphenyl for calculating the yield.

G.l.c. (2% CAR; 190 °C) indicated the presence of 2-acetoxybiphenyl (0.3 mol per 100 mol 2-Cl-NNA) and 2-hydroxybiphenyl (0.5 mol per 100 mol 2-Cl-NNA); these assignments could not be confirmed by g.l.c.–mass spectrometry because of the low concentrations.

This experiment was repeated and after filtering off the precipitate aniline (0.19 g, 2 mmol) was added to the filtrate and heating was continued for a further 0.5 h at 50 °C. Phenanthrene standard (0.0321 g) was added and g.l.c. and g.l.c.–mass spectrometry (2% CAR; 175 °C) showed the presence of acetanilide (31 mol per 100 mol 2-Cl-NNA), which had not been present before the addition of the aniline.

(iii) *p*-Cl-NNA in benzene. *p*-Cl-NNA (0.44 g, 2.2 mmol) was added to stirred benzene under nitrogen at 50 °C and the mixture was maintained at this temperature for 3 h. Filtration gave 4-hydroxybenzenediazonium chloride (0.014 g, 3.7 mol per 100 mol 4-Cl-NNA); this gave a white precipitate with aqueous silver nitrate solution which would dissolve in concentrated aqueous ammonia but not in concentrated nitric acid or glacial acetic acid, indicating the presence of ionic chlorine. The filtrate had an i.r. spectrum identical with that of authentic 4-hydroxybenzenediazonium chloride, and when 0.01 g was coupled with aqueous alkaline 2-naphthol a red solid was obtained which was chromatographed (silica wet column; elution with ether) to give 1-(4-hydroxyphenylazo)-2-naphthol (0.008 g), m.p. and mixed m.p. 192—194° (lit.,<sup>17</sup> 194°). Standard methods (see above) showed the presence of acetic anhydride (6 mol per 100 mol) and 4-chlorobiphenyl (68 mol per 100 mol 4-Cl-NNA).

(iv) *p*-Cl-NNA in benzene in the presence of 1,1-diphenylethene. *p*-Cl-NNA (0.374 g, 1.88 mmol) was added to a stirred solution of 1,1-diphenylethene (0.34 g, 1.88 mmol) in benzene (6 ml) at 50 °C under nitrogen and the mixture was maintained at this temperature for 3 h. Work up gave 4-hydroxybenzenediazonium chloride (0.079 g, 27 mol per 100 mol 4-Cl-NNA)  $\delta$  [( $\text{CD}_3$ )<sub>2</sub>SO] 7.35 (2 H, d), 8.58 (2 H, d), and 10.7br (1 H, s) (Found: C, 45.2; H, 3.05; N,

<sup>15</sup> W. Tadros, K. Farahat, and J. M. Robson, *J. Chem. Soc.*, 1949, 439.

<sup>16</sup> H. H. Hodgson and R. J. H. Dyson, *J. Chem. Soc.*, 1935, 946.

<sup>17</sup> A. Niementowski, *Chem. Zentr.*, 1902, 2, 938.

<sup>13</sup> A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longman, Green and Co., London, 1959.

<sup>14</sup> L. Kazitsyna, B. S. Kikof, B. V. Rassadin, and O. A. Reutov, *J. Gen. Chem. (U.S.S.R.)*, 1963, 33, 221.

17.5. Calc. for  $C_6H_5ClN_2O$ : C, 46.05; H, 3.2; N, 17.9%. Coupling of the solid with alkaline 2-naphthol and crystallisation from ethanol gave 1-(4-hydroxyphenylazo)-2-naphthol, m.p. 193–194° (lit.,<sup>17</sup> 194°) (Found: C, 72.8; H, 4.6; N, 10.5. Calc. for  $C_{16}H_{12}N_2O_2$ : C, 72.7; H, 4.6; N, 10.5%).

Standard g.l.c.–mass spectrometry gave 4-chlorobiphenyl (6 mol per 100 mol 4-Cl-NNA) and 2-(4-chlorophenyl)-1,1-diphenylethane (9 mol per 100 mol 4-Cl-NNA), and reaction with aniline (0.25 g, 3 mmol) gave acetanilide (31 mol per 100 mol 4-Cl-NNA). The presence of 4-acetoxibiphenyl (0.3 mol per 100 mol 4-Cl-NNA) was indicated on g.l.c. (3% NPGS; 195 °C) by a signal having the same retention time as an authentic sample, but this was too weak to be confirmed by g.l.c.–mass spectrometry.

In a replicate experiment, the solids from the reaction were filtered off, washed with dry benzene (5 ml), and dissolved in ice-cold water (30 ml); this solution was added slowly to a solution of 2-naphthol (0.43 g, 3 mmol) and sodium hydroxide (0.16 g, 4 mmol) in ice-water (20 ml) and the mixture was stirred for 3 h while it came to room temperature. It was acidified with dilute hydrochloric acid and the water-insoluble dark red products were extracted into ether. 3-Nitroaniline standard (0.1140 g) was added to the solution and high-speed liquid chromatography (h.s.l.c.) (Spherisorb S.10W silica; 10% EtOAc in hexane) showed the presence of components of  $R_F$  values identical with those of 1-(4-hydroxyphenylazo)-2-naphthol (15 mol per 100 mol 4-Cl-NNA) and 1-(4-chlorophenylazo)-2-naphthol (1 mol per 100 mol 4-Cl-NNA).

Control experiments in which authentic 4-hydroxybenzenediazonium chloride was treated under the above conditions yielded 1-(4-hydroxyphenylazo)-2-naphthol (50 mol per 100 mol 4-hydroxybenzenediazonium chloride) as measured by h.s.l.c. (as above).

In a separate experiment 2-(4-chlorophenyl)-1,1-diphenylethane was isolated in 8% yield by chromatography of the reaction mixture on alumina; m.p. and mixed m.p. 75–76° (lit.,<sup>15</sup> 76–77°), i.r. spectrum identical with that of an authentic sample (Found: C, 82.6; H, 5.0. Calc. for  $C_{20}H_{15}Cl$ : C, 82.6; H, 5.2%).

(v) *o*-AcO-NNA in benzene. *o*-AcO-NNA under the standard conditions gave the results shown in the Table.

(vi) *o*-AcO-NNA in benzene in the presence of 1,1-diphenylethane. Standard conditions gave the results shown in the Table. In addition, g.l.c.–mass spectrometry (2% CAR; 220 °C) showed peaks corresponding to two further substances; the larger had  $M^+$  272 and a fragmentation consistent with 2,3-dihydro-2,2-diphenylbenzofuran; the smaller had  $M^+$  318 and a fragmentation consistent with 2-(2-acetoxyphenyl)-1,1-diphenylethane.

The g.l.c. response of the above compounds relative to the standards indicated low yields. In order to quantify these results two parallel experiments were run in which 2-acetoxy-*N*-nitrosoacetanilide (0.222 g, 1 mmol) was added to boiling solutions of 1,1-diphenylethane (0.27 g, 1.5 mmol) in benzene [(A) 3 ml; (B) 11 ml]. Reaction, as observed by gas evolution, was complete in 5–10 min and after 1 h triphenylethane standard (0.03 g) was added to each solution. Assuming the w/w response of the g.l.c. detector to be *ca.* 1 : 1 for triphenylethane and the  $M^+$  272

compound, then it could be estimated that this compound was present in (A) as 2 mol per 100 mol 2-AcO-NNA and in (B) as 3 mol per 100 mol 2-AcO-NNA. Owing to the apparently low yields no attempt was made to isolate this product.

(vii), (viii) *p*-AcO-NNA in benzene in the presence or absence of 1,1-diphenylethane. Standard conditions gave the results shown in the Table.

(ix) *o*-AcO-NNA in *p*-xylene. *o*-AcO-NNA (0.444 g, 2 mmol) was added in one portion to boiling *p*-xylene (25 ml) under nitrogen; a vigorous reaction set in immediately and after heating under reflux for a further 0.5 h phenanthrene (0.05 g) was added and 2-cyclopentadienylidene-1,3-benzodioxole (22%) was shown to be present by g.l.c. (2% CAR; 190 °C). Chromatography of the products of a larger scale experiment (2.4 g NNA) gave the same product (0.09 g) as yellow needles, m.p. and mixed m.p. 167° (decomp.) (lit.,<sup>8</sup> 168°).

Similar results were obtained in the presence of 1,1-diphenylethane and in boiling cumene.

(x) *o*-AcS-NNA in benzene. Nitrosyl chloride (0.9 g, 16.5 mmol; 30% w/v in acetic anhydride) was added over 15 min to a stirred solution of 2-acetylthioacetanilide (1.71 g, 8 mmol) in acetic acid (12 ml) and acetic anhydride (6 ml) containing potassium acetate (2 g; fused) and phosphoric oxide (0.1 g) while the temperature was maintained below 5 °C. Stirring was continued at this temperature for 1.5 h and then the mixture was poured into a stirred ice-water slurry (400 g). After 0.5 h the resulting tacky oil was extracted into benzene (150 ml); the extract was dried ( $MgSO_4$ ), filtered, and heated under nitrogen at its b.p. under reflux for 1 h, in which time the colour of the solution changed from pale to dark yellow. Naphthalene standard (0.5615 g) was added and 1,2,3-benzothiadiazole (100 mol per 100 mol 2-AcS-NNA) was shown to be present by g.l.c. (2% CAR; 150 °C). Chromatography on alumina gave 1,2,3-benzothiadiazole (0.78 g, 70 mol per 100 mol 2-AcS-NNA), m.p. and mixed m.p. 36–37° (lit.,<sup>18</sup> 36–37°), i.r. spectrum identical with that of an authentic sample.

*Decomposition of 4-Diazocyclohexa-2,5-dienone in Benzene and 1,1-Diphenylethane.*—The diazo-ketone (0.24 g, 2 mmol) was added to a boiling solution of 1,1-diphenylethane (0.36 g, 2 mmol) in benzene (6 ml) and reflux was maintained for 4 h under nitrogen, after which time gas evolution had ceased. Bicumyl standard (0.1 g) was added and 4-hydroxybiphenyl (14 mol per 100 mol diazo-ketone) and benzophenone (4 mol per 100 mol of diazo-ketone) were identified by g.l.c. and g.l.c.–mass spectrometry (3% NPGS; 220 °C). No other material was observed by g.l.c. (3% NPGS; 220 °C or 1% SE30; 220 °C). G.l.c. of the highly coloured mixture (alumina or silica with a variety of solvents) failed to detect further relatively volatile materials.

We are grateful to the S.R.C. for support and to Mr. T. Naisby for technical assistance.

[7/303 Received, 21st February, 1977]

<sup>18</sup> P. Jacobson, *Ber.*, 1888, **21**, 3104.