

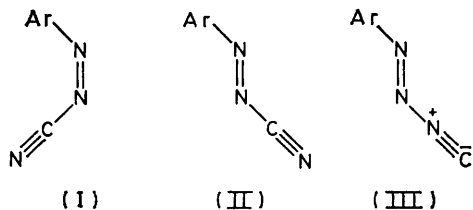
## Structure of Aromatic Diazocyanides; Synthesis of Diazoisocyanides

By **Teresa Ignasiak**, Hydrocarbon Research Centre, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada  
(the late) **Jerzy Suszko and Boleslaw Ignasiak**, Fuel Sciences Division, Alberta Research Council, Edmonton, Alberta, Canada

I.r. spectra of a number of aromatic diazocyanides, prepared under conditions that facilitate isolation and spectral analysis of pure isomeric forms, suggest that extant published data refer to stable isomers only. Substantial differences between the spectra of unstable and stable isomers permitted the quantitative determination of these forms in mixtures and allowed the kinetics of isomerization of unstable to stable forms to be studied.

Although the results from i.r. analysis of aromatic diazocyanides are consistent with the concept of geometric isomerism of these molecules, the long-standing uncertainties concerning the type of isomerism could only be settled finally by synthesis of diazoisocyanides. *p*-Chloro- and *p*-bromo-benzenediazoisocyanides exhibit properties, including vibrational and electronic spectra, entirely different from those of the corresponding diazocyanides. Detailed analysis of the i.r. spectra of a number of *p*-halogeno-benzenediazoisocyanides leads to the conclusion that the diazoisocyanide molecule may be represented as a hybrid of two canonical forms.

SINCE their discovery,<sup>1</sup> diazocyanides have attracted much interest, and particular attention has been focused on their isomerism. Generally, two possibilities have been discussed, *viz.* (a) geometric isomerism, *cis* (I)–*trans* (II) (*syn-anti*) and (b) structural isomerism,



cyanide (II)–isocyanide (III). The concept of geometrical isomerism<sup>1</sup> received strong support from

\* Since our results confirm the concept of geometrical isomerism of diazocyanides, the results will be discussed in terms of *cis-trans* isomers rather than of cyanide–isocyanide or stable–unstable forms.

<sup>1</sup> A. Hantzsch and O. Schultze, *Ber.*, 1895, **28**, 666.

<sup>2</sup> (a) R. J. W. Le Fèvre and J. Northcott, *J. Chem. Soc.*, 1949, 333; (b) R. J. W. Le Fèvre and H. Vine, *ibid.*, 1938, 431, 1878.

measurements of the dipole moments of selected pairs of diazocyanides.<sup>2</sup> However, Hodgson and Marsden<sup>3,4</sup> considered that these measurements do not exclude the possibility of structural isomerism, previously advanced by Orton.<sup>5</sup> Over the range 4 000–900  $\text{cm}^{-1}$  the vibrational (i.r.) spectra of several pairs of diazocyanides measured<sup>6,7</sup> show close similarity in terms of frequency and absorption intensity, and this was taken as convincing evidence of *cis-trans* isomerism. However, Hodgson<sup>4</sup> doubted whether the spectra represent the vibrational characteristics of stable and unstable isomers, and suggested that owing to fast isomerization of the unstable form, the spectra correspond to the stable isomer only. In view of this remaining uncertainty, we attempted to measure the true vibrational characteristics of both the stable and the unstable isomers.\*

<sup>3</sup> H. H. Hodgson and E. Marsden, *J. Chem. Soc.*, 1944, 395.

<sup>4</sup> H. H. Hodgson, *J. Chem. Soc.*, 1948, 1097.

<sup>5</sup> K. J. P. Orton, *J. Chem. Soc.*, 1903, 805.

<sup>6</sup> D. Anderson, R. J. W. Le Fèvre, and J. Savage, *J. Chem. Soc.*, 1947, 445.

<sup>7</sup> N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 1947, 453.

## RESULTS AND DISCUSSION

The spectra of a number of pairs of diazocyanides (Table 1) were measured with a Zeiss UR-10 spectrophotometer. Particular care was taken to ensure that the time between the preparation, including purification, and photometric analysis of the samples did not exceed 90 min. The time between dissolution of the purified isomer and commencement of measurement was 7—8

higher for *cis*-compounds in carbon tetrachloride than in chloroform; for *trans*-compounds this situation is reversed. In *trans*-diazocyanides the type of substituent also leaves the position of the band unaffected, but its intensity increases with the electron-donating properties of the substituent.

(b) *Diazo-group stretching vibrations.* Depending on the substituent, *cis*-isomers show absorption attributable

TABLE I  
Characteristics of aromatic diazocyanides used for i.r. studies

| Diazocyanide  | Isomer           | M.p. (°C) | Lit. m.p. (°C) | Solvent   | Form                 | Analysis (%) |      |      |       |      |       |  |
|---|------------------|-----------|----------------|---|----------------------|--------------|------|------|-------|------|-------|--|
|   |                  |           |                |   |                      | Required     |      |      | Found |      |       |  |
|   |                  |           |                |   |                      | C            | H    | N    | C     | H    | N     |  |
| <i>o</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | <i>cis</i> *     | 60        |                | CCl <sub>4</sub>                                  | Yellow               |              |      |      |       |      |       |  |
|   | <i>trans</i> *   | 68        |                | C <sub>6</sub> H <sub>14</sub>                    | Orange needles       |              |      |      | 47.75 | 2.3  | 31.65 |  |
| <i>m</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | <i>cis</i> *     | 50—52     |                | CCl <sub>4</sub>                                  | Amorphous            |              |      |      | 47.8  | 2.3  | 32.0  |  |
|   | <i>trans</i> *   | 99—100    |                | C <sub>6</sub> H <sub>14</sub>                    | Orange needles       |              |      |      | 47.8  | 2.25 | 31.7  |  |
| <i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | <i>cis</i>       | 46—47†    | 45—47          | C <sub>6</sub> H <sub>12</sub>                    | Yellow needles       |              |      |      |       |      |       |  |
|   | <i>trans</i>     | 85—86     | 86             | C <sub>6</sub> H <sub>14</sub>                    | Red needles          |              |      |      |       |      |       |  |
| <i>o</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | <i>cis</i>       | 48        | 49             | C <sub>6</sub> H <sub>12</sub>                    | Yellow flakes        |              |      |      |       |      |       |  |
|   | <i>trans</i>     | 77        | 78             | C <sub>6</sub> H <sub>14</sub>                    | Red flakes †         |              |      |      |       |      |       |  |
| <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | <i>cis</i> *§    | 38        |                | C <sub>5</sub> H <sub>12</sub>                    | Brown-yellow needles |              |      |      | 50.95 | 2.45 | 25.3  |  |
|   | <i>trans</i> *   | 24        |                | LP¶   | Red needles          |              |      |      | 51.05 | 2.45 | 25.3  |  |
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | <i>cis</i>       | 29        | 29             | C <sub>6</sub> H <sub>12</sub>                    | Orange flakes        |              |      |      |       |      |       |  |
|   | <i>trans</i>     | 105       | 105            | C <sub>6</sub> H <sub>14</sub>                    | Red flakes           |              |      |      |       |      |       |  |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | <i>cis</i>       | 42        | 42—43          | C <sub>6</sub> H <sub>14</sub>                    | Red flakes           |              |      |      |       |      |       |  |
|   | <i>trans</i>     | 133       | 132            | C <sub>6</sub> H <sub>14</sub>                    | Red flakes           |              |      |      |       |      |       |  |
| <i>o</i> -CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | <i>cis</i> *     | (Oil)     |                | C <sub>6</sub> H <sub>12</sub>                    | Red oil              | 59.65        | 4.4  | 26.1 |       |      |       |  |
|   | <i>trans</i> *   | 113       |                | C <sub>6</sub> H <sub>16</sub>                    | Brown needles        |              |      |      | 59.5  | 4.4  | 25.9  |  |
| <i>m</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 | <i>cis</i> *     | (Oil)     |                | LP¶   | Oil **               | 59.65        | 4.4  | 26.1 |       |      |       |  |
|   | <i>trans</i> *   | 31        |                | C <sub>6</sub> H <sub>16</sub>                    | Orange needles       |              |      |      | 59.4  | 4.4  | 26.1  |  |
| <i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 | <i>cis</i> ††    | 50        | 50—51          | C <sub>6</sub> H <sub>12</sub>                    | Orange needles       |              |      |      |       |      |       |  |
|   | <i>trans</i>     | 124       | 121—122        | C <sub>7</sub> H <sub>16</sub>                    | Brown flakes         |              |      |      |       |      |       |  |
| 2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> CN         | <i>cis</i> *     | (Oil)     |                | C <sub>6</sub> H <sub>12</sub>                    | Oil                  | 38.85        | 0.85 | 17.9 |       |      |       |  |
|   | <i>trans</i> *†† | 138—139   |                | C <sub>6</sub> H <sub>14</sub>                    | Red flakes           |              |      |      | 38.7  | 0.9  | 17.75 |  |
| 2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> CN         | <i>cis</i>       | 58—59     | 59—60          | C <sub>6</sub> H <sub>14</sub> -Et <sub>2</sub> O | Yellow flakes        |              |      |      |       |      |       |  |
|   | <i>trans</i> ††  | 149       | 149            | C <sub>6</sub> H <sub>14</sub>                    | Red flakes           |              |      |      |       |      |       |  |
| <i>p</i> -EtOSO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN | <i>trans</i> *§§ | 81        |                | C <sub>6</sub> H <sub>14</sub>                    | Red flakes           | 45.2         | 3.8  | 17.6 | 45.25 | 3.9  | 17.4  |  |

\* Not reported previously. † M.p. 46—47 °C was reached after passing a solution of the *cis*-form in pentane through a silica gel column. ‡ Obtained by freezing out from C<sub>6</sub>H<sub>14</sub>. § *cis*-Form readily decomposes with oil formation; the isomerization into the *trans*-form proceeds with difficulty. ¶ Light petroleum. \*\* Freezing temperature -10 °C. †† Addition of sodium acetate (1 mol l<sup>-1</sup>) to diazotised *p*-anisidine at 0 °C increased the yield of *cis*-form to 89%. ‡‡ *trans*-Form additionally purified by vacuum sublimation. §§ *cis*-Form immediately isomerizes to *trans*-form and could not be isolated.

min. All operations were carried out at the lowest suitable temperature.

The spectra of two chosen pairs of isomeric diazocyanides are reproduced in Figure 1; some of the frequencies characteristic of the remaining investigated pairs of isomeric diazocyanides are presented in Table 2. Analysis of these data leads to the conclusion that there are substantial differences in frequency and intensity of the absorption bands of isomeric diazocyanides. This indicates that the vibrational spectra of aromatic diazocyanides in the extant literature are those of the *trans*-isomers only.

(1) *Spectral Characteristics of Aromatic Diazocyanides.*

—(a) *Nitrile group stretching vibrations.* In *cis*-isomers of the diazocyanides, a very weak band in the range 2 175—2 150 cm<sup>-1</sup> shifts, on transformation into the *trans*-isomer, into the range 2 195—2 190 cm<sup>-1</sup> and also changes its intensity. The type of solvent does not affect the position of this band, but its intensity is

to diazo-group stretching in the region 1 480—1 420 cm<sup>-1</sup>, and *trans*-isomers between 1 460 and 1 390 cm<sup>-1</sup>. Substituents with electron-accepting properties give rise to absorption at higher frequencies, and those with electron-donating properties to absorption at lower frequencies. Band intensities for the *trans*-forms are always substantially greater than for the *cis*-isomers.

Apart from absorption assigned to the diazo-group stretching vibration, a band also occurs at 1 430—1 400 cm<sup>-1</sup>. This may be assigned to a ring vibration of disubstituted benzene derivatives.<sup>8</sup>

(c) *C-N Single bond stretching vibrations.* Bands associated with these vibrations occur in the region 1 300—900 cm<sup>-1</sup>,<sup>9,10</sup> and in diazocyanides separate absorptions would be expected for C<sub>Ar</sub>-N and C<sub>CN</sub>-N, respectively. A weak absorption at 1 190 cm<sup>-1</sup> was

<sup>8</sup> A. R. Katritzky, *Quart. Rev.*, 1959, **13**, 353.

<sup>9</sup> H. W. Thompson, *J. Chem. Soc.*, 1948, 328.

<sup>10</sup> N. V. Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

ascribed to  $C_{Ar}-N$  in *cis*-compounds; but in the spectra of *trans*-isomers this appears at  $1\ 330-1\ 300\text{ cm}^{-1}$ . The intensity of  $C_{Ar}-N$  absorption is much higher in *trans*-than in *cis*-compounds.

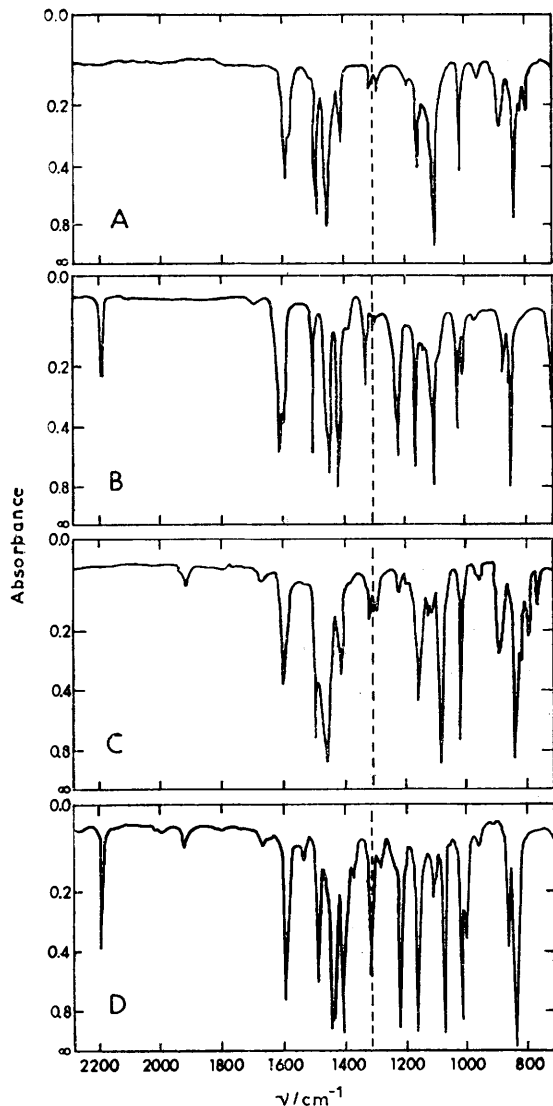
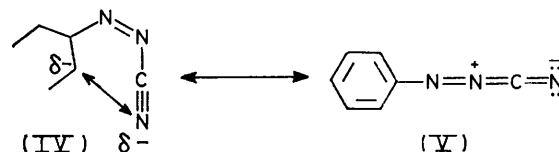


FIGURE 1 I.r. spectra of *cis*- and *trans*-*p*-chlorobenzenediazocyanide (A and B) and *cis*- and *trans*-*p*-bromobenzenediazocyanide (C and D) in carbon tetrachloride ( $2\ 300-1\ 300\text{ cm}^{-1}$ ) and in carbon disulphide ( $1\ 300-700\text{ cm}^{-1}$ )

In summarizing the spectral data, it should be emphasized that the transformation of *cis*- into *trans*-isomer is accompanied by intensification of a number of bands associated with ring skeletal vibrations at *ca.*  $1\ 400\text{ cm}^{-1}$ , C-H in-plane vibrations at  $1\ 250-1\ 000\text{ cm}^{-1}$ , and C-H out-of-plane vibrations at  $900-700\text{ cm}^{-1}$ .<sup>10-12</sup> The shift towards lower wavenumbers of the diazo-band and the greater intensity of absorption by *trans*-forms are due to stronger conjugation when a planar arrangement of atoms in the molecule exists, and supports the concept of *cis-trans* geometrical isomerism.

<sup>11</sup> L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1960.

The surprising shift of the nitrile group stretching vibrations in *cis*-forms of diazocyanides towards lower wavenumbers may be connected with hindered rotation about  $C_{Ar}-N$ , an effect caused by interference of N in the nitrile group and H in an *ortho*-position (IV). Since the distance between H and N is then only  $1.5\text{ \AA}$  (Dreiding model), the induction effect brings about a linear rearrangement of the form (IV). The *cis*-isomer seems to



have the character of a resonance hybrid of *cis*-diazocyanide (IV) and linear cumulene (V); and since delocalization of electrons in the linear cumulene (V) should be facilitated, participation of (V) in hybrid would explain the shift of nitrile group stretching vibrations in *cis*-diazocyanides towards lower frequencies.

The properties of the mesomeric structure would be expected to be affected by the properties of the substituents, with electron-donating groups increasing the participation of (V) in the hybrid; this is reflected in spectrum of *cis-p*-methoxybenzenediazocyanide by the *trans*-band (due to very fast isomerization) and the very strong bathochromic shift of the *cis*-band (Table 2).

Transformation of the linear cumulene into the stable *trans*-isomer (II) seems to cause no difficulties.

(2) *Quantitative Determination of cis- and trans-Isomers in Diazocyanides by I.r. Spectrophotometry.*—Erroneous conclusions from earlier work appear to have been due to lack of a satisfactory method for quantitative determination of both isomeric diazocyanides in their mixtures, but differences in the vibrational spectra of diazocyanides suggested that such a method could be based on i.r. spectrophotometry.

Quantitative measurements were made by using the nitrile stretching vibration band in the range  $2\ 195-2\ 190\text{ cm}^{-1}$ . This band is absent in the spectra of pure *cis*-forms of *p*-chloro- and *p*-bromo-benzenediazocyanide, but appears, and becomes progressively more intense, as isomerization proceeds. The determinations were carried out with carbon tetrachloride or chloroform as solvent.

In order to determine whether solutions of *p*-chloro- and *p*-bromo-benzenediazocyanide obey the Lambert-Beer law, transmission measurements were made on standard solutions of pure *trans*-cyanide, with various solute concentrations. A plot of absorbance *vs.* concentration showed that the compounds did obey the Lambert-Beer law over the concentration range tested and the method can therefore be used for determining concentrations of *trans*-compounds formed by isomerization.

With concentrations of *trans*-isomers of *p*-chloro- and *p*-bromo-benzenediazocyanide in chloroform and carbon

<sup>12</sup> N. B. Colthup, L. H. Dely, and S. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' New York, 1964.

TABLE 2  
 Spectral characteristics of investigated aromatic diazocyanides \*

| Diazocyanides   | <i>cis</i>                    |                           |                          |                           |   |                             |                             |                             |
|---|-------------------------------|---------------------------|--------------------------|---------------------------|---|-----------------------------|-----------------------------|-----------------------------|
|   | $\nu(\text{C}\equiv\text{N})$ |                           | $\nu(\text{N}=\text{N})$ |                           | $\nu(\text{C}_{\text{Ar}}-\text{N})$ and $\nu(\text{C}_{\text{CN}}-\text{N})$ |                             |                             |                             |
|   | $\text{cm}^{-1}$              | $\epsilon_{\text{CCl}_4}$ | $\text{cm}^{-1}$         | $\epsilon_{\text{CCl}_4}$ | $\text{cm}^{-1} (\epsilon)$   | $\text{cm}^{-1} (\epsilon)$ | $\text{cm}^{-1} (\epsilon)$ | $\text{cm}^{-1} (\epsilon)$ |
| <i>o</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | 2 170                         | 12.5                      | 1 460                    | 17.9                      | 1 320 (49)  |                             | 1 185 (21)                  | 1 160 (23)                  |
| <i>m</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | 2 165                         | 5.0                       | 1 480                    | 59.4                      | 1 325 (33)  | 1 295 (8.5)                 | 1 180 (33)                  |                             |
| <i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | 2 165                         | 5.0                       | 1 475                    | 44.0                      | 1 330 (69.5)  | 1 300 (39)                  | 1 190 (18)                  | 1 160 (20)                  |
| <i>o</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | 2 170                         | 3.2                       | 1 445                    | 48.9                      | 1 300 (8.5)   | 1 280 (19.1)                | 1 190 (27)                  | 1 145 (40)                  |
| <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | 2 160                         | 4.6                       | 1 475                    | 134.0                     | 1 315 (11.5)  | 1 285 (11.5)                | 1 180 (65)                  | 1 165 (109)                 |
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   |                               |                           | 1 460                    | 176.6                     | 1 320 (23.3)  | 1 290 (26.5)                | 1 190 (15)                  | 1 160 (96)                  |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   |                               |                           | 1 450                    | 170.8                     | 1 315 (22.5)  | 1 290 (25.7)                | 1 190 (12)                  | 1 160 (73.5)                |
| <i>o</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 |                               |                           | 1 450                    | 139.4                     | 1 300 (211)   |                             | 1 190 (47)                  | 1 170 (155)                 |
| <i>m</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 |                               |                           | 1 450                    | 117.0                     | 1 300 (97)  |                             | 1 200 (22.5)                | 1 140 (94)                  |
| <i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 | 2 150                         | 17.9                      | 1 425                    | 361.8                     |   |                             | 1 190 (37)                  | 1 165 (max.)                |
|   | 2 190                         | 14.6                      |                          |                           |   |                             |                             |                             |
| 2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> CN         | 2 175                         | 20.4                      | 1 435                    | 95.5                      |   |                             | 1 205 (32.6)                | 1 160 (51)                  |
|   |                               |                           |                          |                           |   |                             |                             | 1 110 (32)                  |
| 2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> CN         | 2 170                         | 34.4                      | 1 420                    | 96.2                      |   |                             | 1 210 (29)                  | 1 130 (57)                  |
|   |                               |                           |                          |                           |   |                             |                             | 1 110 (26)                  |
| <i>p</i> -EtOSO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN |                               |                           |                          |                           |   |                             |                             |                             |
| <i>trans</i>  |                               |                           |                          |                           |   |                             |                             |                             |
| Diazocyanides   | $\nu(\text{C}\equiv\text{N})$ |                           | $\nu(\text{N}=\text{N})$ |                           | $\nu(\text{C}_{\text{Ar}}-\text{N})$ and $\nu(\text{C}_{\text{CN}}-\text{N})$ |                             |                             |                             |
|   | $\text{cm}^{-1}$              | $\epsilon_{\text{CCl}_4}$ | $\text{cm}^{-1}$         | $\epsilon_{\text{CCl}_4}$ | $\text{cm}^{-1} (\epsilon)$   | $\text{cm}^{-1} (\epsilon)$ | $\text{cm}^{-1} (\epsilon)$ | $\text{cm}^{-1} (\epsilon)$ |
| <i>o</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | 2 195                         | 7.5 †                     | 1 440                    | 101.4                     | 1 320 (25)  | 1 280 (57.6)                | 1 215 (72)                  | 1 165 (24)                  |
| <i>m</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | 2 195                         | 12.5 †                    | 1 435                    | 109.7                     | 1 330 (63)  | 1 290 (20)                  | 1 205 (139)                 | 1 170 (52)                  |
| <i>p</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN    | 2 195                         | 11.5                      | 1 450                    | 68.2                      | 1 330 (205)   | 1 305 (27.4)                | 1 210 (134)                 | 1 165 (76)                  |
| <i>o</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | 2 190                         | 32.8                      | 1 420                    | 217.7                     | 1 310 (39)  | 1 270 (109)                 | 1 220 (139)                 | 1 135(50)                   |
|   |                               |                           |                          |                           |   |                             |                             | 1 145 (43)                  |
| <i>m</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | 2 190                         | 29.9                      | 1 455                    | 99.8                      | 1 315 (39)  | 1 285 (27)                  | 1 210 (162)                 | 1 165 (105)                 |
|   |                               |                           |                          |                           |   |                             | 1 200 (233)                 |                             |
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | 2 195                         | 64.8                      | 1 440                    | 204.8                     | 1 325 (73.5)  |                             | 1 225 (199)                 | 1 165 (240)                 |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                   | 2 190                         | 67.7                      | 1 440                    | 246.7                     | 1 320 (85.5)  |                             | 1 220 (162)                 | 1 165 (211)                 |
| <i>o</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 | 2 190                         | 101.4                     | 1 410                    | 361.8                     | 1 300 (max.)  |                             | 1 210 (218)                 | 1 170 (max.)                |
| <i>m</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 | 2 190                         | 67.2                      | 1 425                    | 167.0                     | 1 300 (100)   |                             | 1 190 (117)                 | 1 150 (177)                 |
| <i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN                 | 2 190                         | 141.4 †                   | 1 400                    | 362.0                     | 1 310 (106)   |                             | 1 200 (51)                  | 1 165 (max.)                |
|   |                               |                           |                          |                           |   |                             | 1 190 (60)                  | 1 160 (111)                 |
| 2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> CN         | 2 195                         |                           | 1 390                    | 96.0                      |   | 1 290 (22)                  | 1 215 (77.6)                | 1 160 (111)                 |
|   |                               |                           |                          |                           |   |                             |                             | 1 090 (60)                  |
| 2,4,6-Br <sub>3</sub> C <sub>6</sub> H <sub>2</sub> N <sub>2</sub> CN         | 2 195                         | 6.5                       | 1 390                    | 104.0                     |   | 1 280 (37)                  | 1 215 (69.4)                | 1 115 (70)                  |
| <i>p</i> -EtOSO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN | 2 190                         | 25.9                      | 1 450                    | 137.9                     | 1 320 (117.5)   | 1 300 (26)                  | 1 210 (185)                 | 1 170 (95.8)                |

\*  $\epsilon_{\text{CCl}_4}$  = molar extinction coefficient in CCl<sub>4</sub>;  $\epsilon$  = molar extinction coefficient in CS<sub>2</sub>. † Saturated solution.

tetrachloride solutions easily measurable, kinetic studies of isomerization of *cis*- to *trans*-forms could also be undertaken. Transmission measurements were made on solutions of individual *cis*-*p*-chloro- and -*p*-bromobenzenediazocyanides at intervals, and from the results (assumed) first-order reaction rates were calculated. Rate constants were determined at 25 and 45 °C, and the activation energy *E* of isomerization was calculated by means of the Arrhenius equation (Table 3).

It was found that rate constants depend on the solvent used: in a polar solvent (chloroform), *k* is substantially larger (at 25 °C 0.043 and at 45 °C  $0.39 \times 10^{-3} \text{ s}^{-1}$ ) than in a non-polar solvent (carbon tetrachloride) ( $k^{25} 0.013$ ;  $k^{45} 0.13 \times 10^{-3} \text{ s}^{-1}$ ). Le Fèvre and Northcott,<sup>13</sup> who calculated *k* values from dielectric constants, report that isomerization of *p*-chlorobenzenediazocyanide proceeds with the same rate in chloroform ( $k^{25} 0.020$ ;  $k^{45} 0.203 \times 10^{-3} \text{ s}^{-1}$ ) as in carbon tetrachloride ( $k^{25} 0.020$ ;  $k^{45} 0.214 \times 10^{-3} \text{ s}^{-1}$ ). It is likely that these discrepancies arise from experimental errors, especially since Le Fèvre *et al.*<sup>13</sup> emphasize the occurrence of certain 'initial disturbances' at the beginning of each of their kinetic measurements.

<sup>13</sup> R. J. W. Le Fèvre and J. Northcott, *J. Chem. Soc.*, 1949, 944.

<sup>14</sup> M. A. Saboor, *Indian J. Phys.*, 1943, 17, 223.

The values for *E* (64–70 kJ mol<sup>-1</sup>) (Table 3) agree with published data.<sup>13,14</sup>

TABLE 3

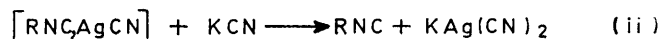
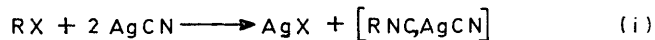
Results of kinetic studies

| Solvent           | Temp. (°C)        | $k \times 10^{-3} / k_{\text{av}} \times 10^{-3} / \text{s}^{-1}$ |  | <i>E</i> /kJ mol <sup>-1</sup> |       |
|-------------------|-------------------|---|--|--------------------------------|-------|
|                   |                   | $k \times 10^{-3} / \text{s}^{-1}$                                | $k_{\text{av}} \times 10^{-3} / \text{s}^{-1}$ |                                |       |
| CCl <sub>4</sub>  | 25                | 0.013   | 0.013  | 91                             |       |
|                   | 45                | 0.13  | 0.13   |                                |       |
|                   | CHCl <sub>3</sub> | 25  | 0.044  |                                | 0.043 |
|                   |                   | 45  | 0.40   |                                | 0.39  |
| CHCl <sub>3</sub> | 25                | 0.043   | 86   |                                |       |
|                   | 45                | 0.38  |  |                                |       |
|                   | CCl <sub>4</sub>  | 25  |  | 0.012                          | 0.012 |
|                   |                   | 45  |  | 0.14                           | 0.13  |
|                   | CHCl <sub>3</sub> | 25  |  | 0.13                           | 86    |
|                   |                   | 45  |  | 0.045                          |       |
| 45                |                   | 0.45  | 0.40   |                                |       |
|                   |                   | 0.35  |  |                                |       |

(3) *Synthesis, Properties, and Spectral Analysis of p-Chloro- and p-Bromo-benzenediazoisocyanide.*—Although the results from i.r. analysis of diazocyanides investigated are consistent with geometrical isomerism, nevertheless, to clarify ultimately the type of isomerism of these compounds, aromatic diazoisocyanides had to be

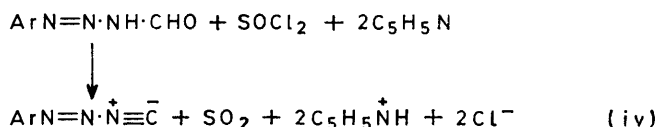
synthesized and their properties compared with those of the corresponding diazocyanides.

During initial attempts to synthesize the diazoisocyanides, we used a reaction sometimes employed for preparation of aliphatic isocyanides,<sup>15</sup> *i.e.* treatment of diazonium salts with silver cyanide in dry ethanol [reactions (i) and (ii)]. The i.r. spectra of the resultant complexes [ $\nu_{\text{max}}$  2 095 and 2 140 (isocyanide stretching), 2 170 (AgCN cyanide), and 2 290  $\text{cm}^{-1}$  (diazonium stretching)] showed that the silver cyanide acts as a



complexing agent for the diazoisocyanide produced as well as for the diazonium chloride. However, regardless of precautions to prevent decomposition of the diazoisocyanides during treatment of the [RNC,AgCN] complex with potassium cyanide, the yield of diazoisocyanides obtained in this manner is small (7–9%). The main products were in all cases symmetrical diazo-amino-compounds.

obtained from decomposition of complex silver salts as well as by dehydration of 3-formyl-1-*p*-halogenophenyltriazenes proved the identity of products from both sources.



Aromatic diazoisocyanides clearly differ, even in appearance, from the corresponding diazocyanides; the characteristics of diazoisocyanides synthesized in this study are presented in Table 4.

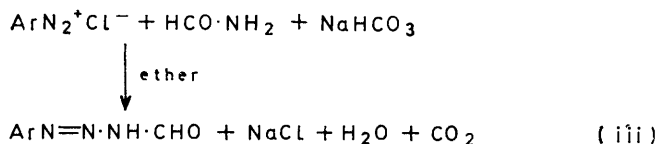
*p*-Halogenobenzenediazoisocyanides proved relatively unreactive. Attempts to reduce the isocyanide group with metallic sodium in *n*-pentyl alcohol or to hydrate it to give a 3-formyltriazene with aqueous oxalic or acetic acid failed, even though common isonitriles will, under similar conditions, readily undergo reduction or hydration. The diazoisocyanides are, however, light-sensitive, and decompose almost instantly under a quartz lamp to yield unidentified solids.

TABLE 4  
Characteristics of aromatic diazoisocyanides

| Diazoisocyanide   | M.p.<br>(°C) | Form                | $d_{20}^{20}$ | $M^*$ | Analysis (%) |     |       |       |      |       |
|---|--------------|---------------------|---------------|-------|--------------|-----|-------|-------|------|-------|
|   |              |                     |               |       | Required     |     |       | Found |      |       |
|   |              |                     |               |       | C            | H   | N     | C     | H    | N     |
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> NC | 21           | Colourless flakes † | 1.26          | 169   | 50.75        | 2.4 | 25.35 | 50.5  | 2.45 | 25.15 |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> NC | 28           | Colourless flakes ‡ | 1.47          | 205   | 40.0         | 1.9 | 20.0  | 39.8  | 2.0  | 20.1  |

\* By ebullioscopy in methanol. † Intense smell; above 21 °C light yellow oil, insoluble in water. ‡ Intense but pleasant smell; above 28 °C light yellow oil, insoluble in water.

Since aliphatic and aromatic isocyanides can be synthesized by dehydration of *N*-formyl derivatives with phosphoryl or toluene-*p*-sulphonyl chloride,<sup>16,17</sup> we then concentrated attention on 1-aryl-3-formyltriazenes as possible intermediates in the synthesis of diazoisocyanides. 1-Aryl-3-formyltriazenes were synthesized in good yield by treating an ethereal suspension of the solid diazonium salt and formamide with sodium hydrogen carbonate [reaction (iii)]. The products were remarkably stable, showing no changes in m.p. or i.r.

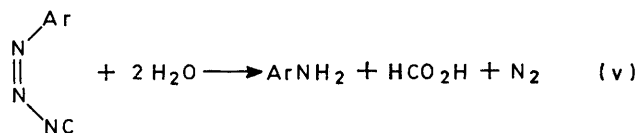


spectra even after several months *in vacuo*. Dehydration of 3-formyl-1-*p*-halogenophenyltriazenes was achieved only with thionyl chloride in pyridine [reaction (iv)]. The pure diazoisocyanides were obtained in satisfactory yield by distilling the crude products under vacuum or passing them down a silica gel column (pentane as eluant).

Physical constants and i.r. spectra of diazoisocyanides

<sup>15</sup> Houben-Weyl, 'Methoden der Organische Chemie, VIII,' p. 352.

As already noted, the individual purified compounds always exhibit properties independent of the mode of synthesis or of the origin of the compound (*p*-chloro- or *p*-bromo-benzenediazoisocyanide); this suggests that they do not occur in isomeric forms. However the i.r. spectra of the crude products show bands characteristic of primary amino-groups (N–H stretching vibrations at 3 500 and 3 400  $\text{cm}^{-1}$  and N–H deformation vibrations at 1 630  $\text{cm}^{-1}$ ). This, and the fact that dehydration of 3-formyltriazenes proceeds almost instantaneously (with evolution of gas), indicates that anilines are secondary products, possibly formed by decomposition of the *cis*-diazoisocyanides. Inspection of a Dreiding model leads to the inference that the integrity of the *cis*-diazoisocyanide molecule cannot be maintained, but that



it decomposes yielding formic acid and nitrogen [reaction (v)]. The supposed presence of water in a system containing efficient drying agents raises some objections,

<sup>16</sup> I. Ugi and R. Meyr, *Chem. Ber.*, 1960, **93**, 239.

<sup>17</sup> W. R. Hertler and E. J. Corey, *J. Org. Chem.*, 1958, **23**, 122.

and the suggested reaction path (v) ought to be viewed with caution. However, this path would explain the formation of symmetrical diazonium compounds during preparation of diazoisocyanides *via* the silver cyanide-diazonium salt complexes.

In the light of these observations it seems that the relatively stable diazoisocyanides studied in this investigation are best represented by a *trans*-model (III).

The i.r. spectra of *p*-halogenobenzenediazoisocyanides (Figure 2) exhibit remarkable differences from those of

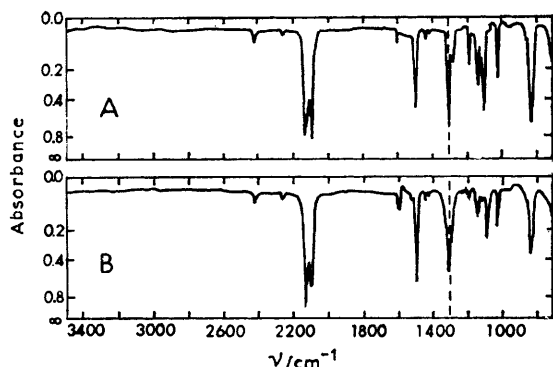


FIGURE 2 I.R. spectra of *p*-chloro- (A) and *p*-bromo-benzenediazoisocyanide (B) in carbon tetrachloride (3 500—1 300  $\text{cm}^{-1}$ ) and in carbon disulphide (1 300—700  $\text{cm}^{-1}$ )

corresponding *cis-trans*-diazocyanides (Figure 1) or *p*-halogenophenyl isocyanides. The most important differences occur in the region assigned to stretching vibrations of cyanide and isocyanide groups. In spectra of *p*-halogenophenyl isocyanides, the isocyanide stretching vibrations appear at 2 135 (for *p*-chloro-) and 2 130  $\text{cm}^{-1}$  (for *p*-bromo-), whereas in the spectra of diazoisocyanides, characteristic doublets are observed at 2 135—2 130 and 2 100—2 095  $\text{cm}^{-1}$  respectively. A similar doublet occurs in the spectra of compounds (*e.g.* carbodiimides or azides) which contain a bond system typical of cumulenes,<sup>12</sup> but the reason for it remains unknown.

We emphasize that the doublet in the spectra of *p*-halogenobenzenediazoisocyanides is the strongest absorption and that its location does not depend on the method by which the spectra are recorded (*i.e.* potassium bromide pellets or polar or non-polar solvents). This is remarkable in view of the findings<sup>18</sup> that in aromatic isocyanides polar solvents will stabilize the charge separation of the triple bond ( $\overset{+}{\text{N}}\equiv\bar{\text{C}}$ ) and so increase the bond force constant with a resultant shift towards higher wavenumbers.

More detailed measurements also showed that in aromatic isocyanides the molar absorption coefficient of the isocyno-group is *ca.* ten times larger than that assigned to cyano-group stretching vibrations in *trans*-diazocyanides. Gillis and Occolowitz<sup>19</sup> explain this by assuming greater separation of charges in the isocyno- ( $\overset{+}{\text{N}}\equiv\bar{\text{C}}$ ) than in the cyano-group ( $\bar{\text{C}}\equiv\text{N}$ ). In turn, the

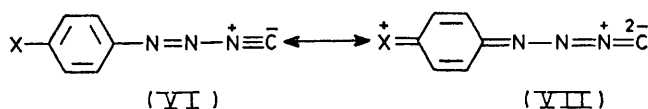
isocyno-group absorption in *p*-halogenobenzenediazoisocyanide is twice as strong as in the corresponding isocyanides.

In accord with our previous observations, absorption near 1 440  $\text{cm}^{-1}$  was ascribed to the diazo-group stretching vibration.

In the spectra of *p*-halogenobenzenediazoisocyanides, there is also a doublet at 1 305—1 280  $\text{cm}^{-1}$ . Its weaker wing at 1 280  $\text{cm}^{-1}$  seems to result from vibrations of the phenyl-nitrogen bond; the strong peak at 1 305  $\text{cm}^{-1}$  is ascribed to N-N<sub>NC</sub> stretching vibrations.

To summarize, the i.r. spectra of benzenediazoisocyanides are characterized by (1) the presence of a remarkably strong doublet at 2 135—2 095  $\text{cm}^{-1}$ , with absorptions at 2 135  $\text{cm}^{-1}$  assigned to  $\nu(\overset{+}{\text{N}}\equiv\bar{\text{C}})$  and at 2 095  $\text{cm}^{-1}$  to a bond system typical of a cumulene ( $-\overset{+}{\text{N}}=\bar{\text{N}}-\text{C}$ ); (2) the weak diazo-group ( $-\text{N}=\text{N}-$ ) absorption at 1 440  $\text{cm}^{-1}$  probably resulting from participation of the cumulene system in a mesomeric structure ( $-\text{N}=\text{N}-\overset{+}{\text{N}}\equiv\bar{\text{C}} \leftrightarrow -\text{N}=\text{N}=\overset{+}{\text{N}}=\bar{\text{C}}$ ); and (3) the high wavenumber absorption assigned to N-N<sub>NC</sub> stretching vibration and associated with the increase of bond strength due to participation of the cumulene system in the above mesomeric structure.

These correlations allow the conclusion that the molecule of *p*-halogenobenzenediazoisocyanide is a hybrid of two canonical forms [(VI)  $\leftrightarrow$  (VII)]. Although the existence of (VII), characterized by a rarely encountered



separation of charges, may seem questionable, the electronic spectra of *p*-halogenobenzenediazoisocyanides do not rule out the participation of this structure in a resonance hybrid.

TABLE 5  
U.v. absorption bands

|   | $\lambda_{\text{max.}}/\text{nm}$ ( $\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$ ) |
|---|---|
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> NC | 196 (30 276), 253 (19 796), 286 (2 906),<br>296 (2 000)                           |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> NC | 199 (46 964), 255 (24 084), 287 (4 236),<br>297 (3 064)                           |
| <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN | 191 (8 222), 193.5 (8 996), 233.5 (6 108),<br>241 (4 990), 355.5 (10 995)         |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> CN | 194 (10 314), 195 (10 174), 236.5 (5 886),<br>242 (5 548), 337 (12 766)           |
| <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> NC                | 199.5 (5 144), 236 (2 845), 244.5 (2 838)   |

The essential difference amongst the u.v. spectra of diazoisocyanides, corresponding *trans*-diazocyanides, and *p*-bromophenyl isocyanide (Table 5) is an absence of strong absorption at 335 nm in the spectra of diazoisocyanides. This absorption is due to  $\pi-\pi^*$  type transitions attributable to a delocalized  $\pi$ -electron system in the molecule and, in *trans*-diazocyanides, characteristic of a chromophoric cyanide group which participates in the resonance of the entire molecule through the diazo-group.

<sup>18</sup> W. D. Horrocks and R. H. Mann, *Spectrochim. Acta*, 1963, **9**, 1375.

<sup>19</sup> R. G. Gillis and I. L. Occolowitz, *Spectrochim. Acta*, 1963, **19**, 873.

This absorption is strong, but in diazoisocyanides the corresponding absorption at 297 nm is weak which indicates that the  $\pi$ - $\pi^*$  transition probability is significantly reduced and that the rigid, semi-polar bonded isocyanide group ( $-\dot{N}=\bar{C}$ ) is non-chromophoric and hindering formation of polar resonance forms.

On the other hand, absorption at 196—199 and 253—255 nm in the spectra of diazoisocyanides is bathochromically shifted relative to corresponding absorption in diazocyanides (191—194, 193—195, and 233.5—236.5 nm). This indicates that the remainder of the diazoisocyanide molecule, comprising the substituent, aromatic ring, and diazo-group, is much more conjugated than in diazocyanides. This is likely in view of the fact that the positively charged nitrogen atom in the isocyanide molecule is an electron-attracting centre and a halogen in the *para*-position will facilitate electron delocalization in the same direction.

#### EXPERIMENTAL

*Preparation of Aromatic Diazocyanides.*—Aromatic amines used were purified either by crystallization or, in the case of liquid amines, by distillation.

Diazotization in aqueous solutions was conducted with sodium nitrite; in non-aqueous solution *n*-pentyl nitrite was employed.

With the exception of 2,4,6-trichlorobenzene- and *p*-ethoxysulphonylbenzene-diazocyanides, diazocyanides were synthesized by Le Fèvre and Vine's procedure,<sup>20</sup> modified as follows. To a stirred solution of amine (0.1 mol) in concentrated hydrochloric acid (*d* 1.19; 45 mol) and water (45 ml) sodium nitrite (0.1 mol) in water (20 ml) was slowly added at 0 °C. Following filtration, the solution was cooled with solid carbon dioxide in acetone to -10 °C. In order to decrease the freezing point, ethanol (50 ml) was added, and potassium cyanide (0.2 mol) in water (25 ml) was then slowly added with vigorous stirring. After the reaction was complete (a drop of potassium cyanide solution and the reaction mixture placed on filter paper did not yield a coloured product), ice-water (100 ml) was added. This speeded up filtration and prevented decomposition of the *cis*-isomer on the filter paper. The wet precipitate of *cis*-diazocyanide was then dissolved in the minimum volume of a non-polar solvent, usually *n*-pentane, carbon tetrachloride, or *n*-hexane, and cooled to 10 °C. The solution was dried with sodium or magnesium sulphate, filtered, and cooled with solid carbon dioxide. The resultant *cis*-diazocyanides were either purified by freezing out from the solvents (Table 1) or directly isomerized into the respective *trans*-forms. The latter was accomplished by warming the hexane, carbon tetrachloride, or chloroform solution of the unstable *cis*-form at 50—60 °C for *ca.* 5 h. Evaporation on a water-bath left the crude *trans*-compound, which was crystallized (Table 1). In order to obtain pure compounds, the freezing out (of *cis*-forms) or crystallization (of *trans*-forms) from boiling solution was repeated several times. The *cis*-diazocyanides were dried in the dark over potassium hydroxide.

The preparation of 2,4,6-trichlorobenzenediazocyanide was based on Hantzsch's procedure.<sup>20</sup>

*p*-Ethoxysulphonylbenzenediazocyanide.—Because of the difficulties encountered during direct esterification of

sulphanilic acid, synthesis of this compound included: (a) preparation of *p*-nitrobenzenesulphonic acid; (b) preparation of *p*-nitrobenzenesulphonyl chloride; (c) reaction of *p*-nitrobenzenesulphonyl chloride with ethanol; (d) reduction of ethyl *p*-nitrobenzenesulphonate. The details are described elsewhere.<sup>21</sup>

*Preparation of Triazines and Diazoisocyanides.*—1-*p*-Chlorophenyl-3-formyltriazenes. To a suspension of *p*-chlorobenzenediazonium chloride (4.02 g) in diethyl ether (50 ml), freshly distilled formamide (2.5 g; b.p. 111 °C at 20 mmHg) was added with vigorous stirring. The mixture was then brought to boiling and aqueous 7% sodium hydrogen carbonate (35 ml) was slowly added (5 ml every 15 min). The product passed into the ether layer which, over *ca.* 85 min, was changed three times. After the reaction was complete, the extracts were combined, dried (MgSO<sub>4</sub>), and evaporated to leave a crystalline product (3 g). This was shaken for several minutes in previously cooled 1 : 1 ether-hexane (20 ml). Oily compounds passed into solution, and the residue was transferred to the ether, to which a small quantity of activated charcoal had been added, and shaken for a few minutes. After filtration and evaporation the triazine obtained was recrystallized from boiling hexane or 70% ethanol; m.p. 130—131 °C (decomp.); yield 74% (Found: C, 45.55; H, 3.3; N, 22.7. C<sub>7</sub>H<sub>6</sub>ClN<sub>3</sub>O requires C, 45.75; H, 3.25; N, 22.85%).

1-*p*-Bromophenyl-3-formyltriazenes. This triazine was obtained in a manner similar to that for the chloro-derivative; yield 75% (Found: C, 37.0; H, 2.6; N, 18.25. C<sub>7</sub>H<sub>6</sub>NrN<sub>3</sub>O requires C, 36.85; H, 2.65; N, 18.4%).

*p*-Chlorobenzenediazocyanide from the triazine.—To 1-*p*-chlorophenyl-3-formyltriazenes (340 mg, 1.8 mmol) dissolved in anhydrous pyridine (4 ml), freshly distilled thionyl chloride (0.22 ml, 3 mmol) was added dropwise over 10 min at -5 °C. The mixture was protected against moisture with a Drierite-filled absorption tube. After 1 h stirring in an ice-bath, the excess of pyridine was removed under reduced pressure, and the residue was shaken with pentane. The pentane extract, containing diazoisocyanide, was further purified by short-path distillation at 60 °C and 0.8 mmHg or by separation on silica gel; yield 50%; for characteristics see Table 4.

*p*-Bromobenzenediazocyanide from the triazine. To a cooled solution (0 °C) of 1-*p*-bromophenyl-3-formyl triazine (0.114 g 0.5 mmol) in anhydrous pyridine (2 ml), thionyl chloride (0.07 ml, 0.9 mmol) was added dropwise. Thereafter, the procedure for the bromo-compound was as for dehydration of the chloro-analogue; yield 40%; for characteristics see Table 4.

*Spectra.*—I.r. spectra of diazo- and diazoisocyanides were obtained with a Zeiss UR-10 spectrophotometer. Solutions (0.09—0.02 mol) were examined in sodium chloride (700—1 800 cm<sup>-1</sup>) and lithium fluoride (1 800—3 600 cm<sup>-1</sup>) cells of 0.6 mm thickness; compensating cells containing pure solvents were placed in the reference beam.

U.v. spectra of compounds listed in Table 5 were obtained, over the range 187—360 nm, with a Unicam SP 700 instrument (*n*-hexane as solvent). Standard quartz cells (1 cm thickness) were used. Below 200 nm the spectra were recorded in a nitrogen atmosphere.

*Quantitative Determination of Benzenediazocyanides.*—The *cis*-forms of *p*-chloro- and *p*-bromo-diazocyanides were

<sup>20</sup> A. Hantzsch, *Ber.*, 1838, **31**, 340.

<sup>21</sup> T. Ignasiak, Ph.D. Thesis, A. Mickiewicz University, Poland, 1967.

purified by freezing out from n-pentane, with lack of absorption at  $2190\text{ cm}^{-1}$  used as a criterion of purity (m.p. *p*-Cl,  $29\text{ }^{\circ}\text{C}$ ; *p*-Br,  $42\text{ }^{\circ}\text{C}$ ). The *trans*-forms, obtained by isomerization of the respective *cis*-forms, were purified by crystallization from n-hexane (m.p. *p*-Cl,  $105\text{ }^{\circ}\text{C}$ ; *p*-Br,  $133\text{ }^{\circ}\text{C}$ ).

For kinetic measurements,  $0.1\text{M}$  solutions of the *cis*-forms in chloroform and in carbon tetrachloride were placed in thermostatted baths at  $25$  and  $45\text{ }^{\circ}\text{C}$  ( $\pm 0.1\text{ }^{\circ}\text{C}$ ). At definite intervals, the spectra of the samples were scanned over the range  $2150\text{--}2200\text{ cm}^{-1}$  (Zeiss UR-10) spectrophotometer, slit width 4; scanning rate  $32\text{ cm}^{-1}\text{ min}^{-1}$ ; recording time

$50\text{ s}$ ; recording scale  $32\text{ mm per }100\text{ cm}^{-1}$ ; gain 5,5; band width 2; time constant 2; diaphragm correction 3, time delay 'on'). Solutions were examined in sodium chloride cells of  $0.6\text{ mm}$  thickness, a compensating cell containing the pure solvent being placed in the reference beam.

We thank Dr. N. Berkowitz for assistance in preparation of the manuscript, and Drs. R. M. Eloffson and O. Strausz for critical reading of the paper. Suggestions made during experimental work by Professor M. Wiewiorowski are greatly appreciated.

[5/027 Received, 7th January, 1975]

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