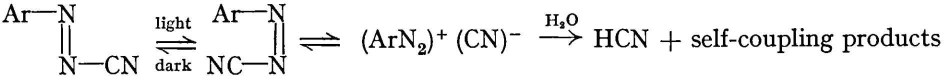
369. *Decomposition Reactions of the Aromatic Diazo-compounds. Part VIII. The Diazocyanides.*

By Oliver Stephenson and William A. Waters.

A study of diazocyanides derived from halogenated aromatic amines has revealed the following facts.

1. *anti*-Diazocyanides, though thermally stable, may be converted photochemically into the isomeric, reactive, *syn*-diazocyanides.
2. *syn*-Diazocyanides exist, in alcoholic solution, in tautomeric equilibrium with diazonium cyanides, for, on treatment with silver nitrate, they rapidly precipitate silver cyanide.
3. Neutral solutions of *syn*-diazocyanides easily give self-coupling products, consequent upon a hydrolysis in which free hydrogen cyanide is liberated.
4. Solutions of *syn*-diazocyanides in non-ionising solvents isomerise to *anti*-diazocyanides even in the absence of light :

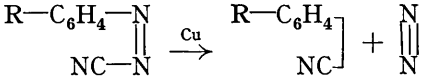


$$\begin{matrix}\text{Ar—N}\\ \|\\ \text{N—CN}\end{matrix} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} \begin{matrix}\text{Ar—N}\\ \|\\ \text{NC—N}\end{matrix} \rightleftharpoons (ArN_2)^+ (CN)^- \xrightarrow{H_2O} \text{HCN} + \text{self-coupling products}$$

5. Copper appears to be the only metal which catalyses the decomposition of the *syn*-diazocyanides.

6. In non-ionising solvents, such as carbon tetrachloride, benzene, and ether, *syn*-diazocyanides yield free radicals upon warming with copper powder, the respective final products being C_6H_4RCl, $C_6H_4R{\cdot}Ph$, and C_6H_5R plus acetaldehyde, together with, in each case, free hydrogen cyanide. Only in carbon tetrachloride solution does the copper appear to be attacked. The main reaction product is always a black tar, which is not a polyazo-compound.

7. It is concluded that Hantzsch's theory that the *syn*-diazo-compounds decompose to give vicinal radicals which promptly unite,



$$\begin{matrix}R—C_6H_4—N\\ \|\\ NC—N\end{matrix} \xrightarrow{Cu} \begin{matrix}R—C_6H_4—\\ NC—\end{matrix} + \begin{matrix}N\\ \|\!|\\ N\end{matrix}$$

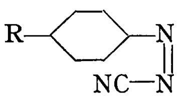
does not accord with experimental fact.

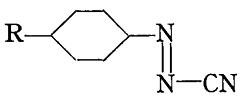
It appears that the radicals formed by the decomposition of the *syn*-diazo-compounds react with neighbouring solvent molecules, and therefore must have an independent free existence.

Diazocyanides can easily be prepared in a state of purity from halogenated aromatic amines, and their reactions in non-aqueous solvents have been examined in order to discover to what extent the theories postulated for the mechanisms of decompositions of diazoacetates, diazohydroxides, and diazonium chlorides can be generalised.

Hantzsch and Schultze (*Ber.*, 1895, **28**, 666), who first studied the diazocyanides, showed that they existed in two isomeric forms of greatly different stability, and pointed out that both isomers were azo-compounds, Ar·N:N·CN, and not diazonium salts, since (*a*) they were coloured, and (*b*) they dissolved readily in non-ionising solvents such as benzene. The labile, reactive, form was given the *syn*-diazo-structure (I), and the stable form the *anti*-diazo-structure (II) in accordance with the generally observed fact that of two geometrical isomers the more stable has the *trans*-structure.

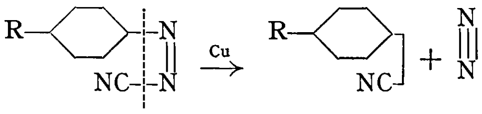
(I.)





(II.)

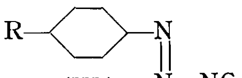
Moreover, these authors discovered that alcoholic solutions of the labile forms of the diazocyanides could be decomposed catalytically by adding copper powder, nitrogen being evolved and an aromatic nitrile formed. This reaction was depicted as a fission of a molecule of nitrogen followed *immediately* by a union of two vicinal radicals :



(A.)

but no significance was attached to the fact that this reaction is in no way quantitative. The scheme (A) was subsequently applied by Hantzsch to all other decompositions of diazo-compounds.

Recent dipole-moment measurements by Le Fèvre and Vine (J., 1938, 431) establish (*a*) that both the *syn*- and the *anti*-diazocyanides are nitriles and not *iso*nitriles, and (*b*) that Hantzsch was correct in assigning the *anti*-diazo-structure (II) to the stable isomers. Orton's suggestion (J., 1903, **83**, 805, footnote) that the *syn*-diazocyanides might be *iso*nitriles of *anti*-structure (III) is disproved by the fact that there is not even approximately a constant difference in dipole moment between all pairs of isomeric diazocyanides independent of the nature and position of the substituents, R.



(III.)

Both the *syn*- and the *anti*-forms of the diazocyanides are much more stable than are the corresponding diazohydroxides, and one can attribute this to the conjugation of the C≡N and N=N groupings, which makes the whole molecule one concordant resonance system, comparable with that of azobenzene. In accordance with this view, one finds that the dipole moment of the group N=N—C—N (3·3 D.) is appreciably less than that of the nitrile group C≡N (4 D.), just as one would expect if there were some mesomeric electron transference from the CN group to the adjacent C—N link, *i.e.*, $\mathrm{R{-}C_6H_4{-}N{=}N\overset{\frown}{-C{\equiv}}N}$.

The anti-*Diazocyanides*.—The *anti*-diazocyanides are so stable that their simpler members can, like *trans*-azobenzene, be distilled in steam unchanged. The *syn*-diazocyanides, in contrast, are much less stable, and in dry non-ionising solvents change slowly, but completely, into their stable *anti*-forms (Le Fèvre and Vine, *loc. cit.*). Hartley's measurements of absorption spectra (J., 1938, 635) have indicated that the reverse change may be brought about in benzene by exposure to light. This conclusion has been substantiated in two ways for solutions of pure *anti*-diazocyanides in alcohol or acetone.

If silver nitrate is added to a solution of an *anti*-diazocyanide in alcohol, the originally clear solution gradually becomes turbid on exposure to light owing to the precipitation of silver cyanide, and eventually all the *anti*-diazocyanide decomposes, giving a practically colourless solution of a diazonium salt. However, after a time some reduction of the silver salt is also apparent. No such reaction occurs in the dark.

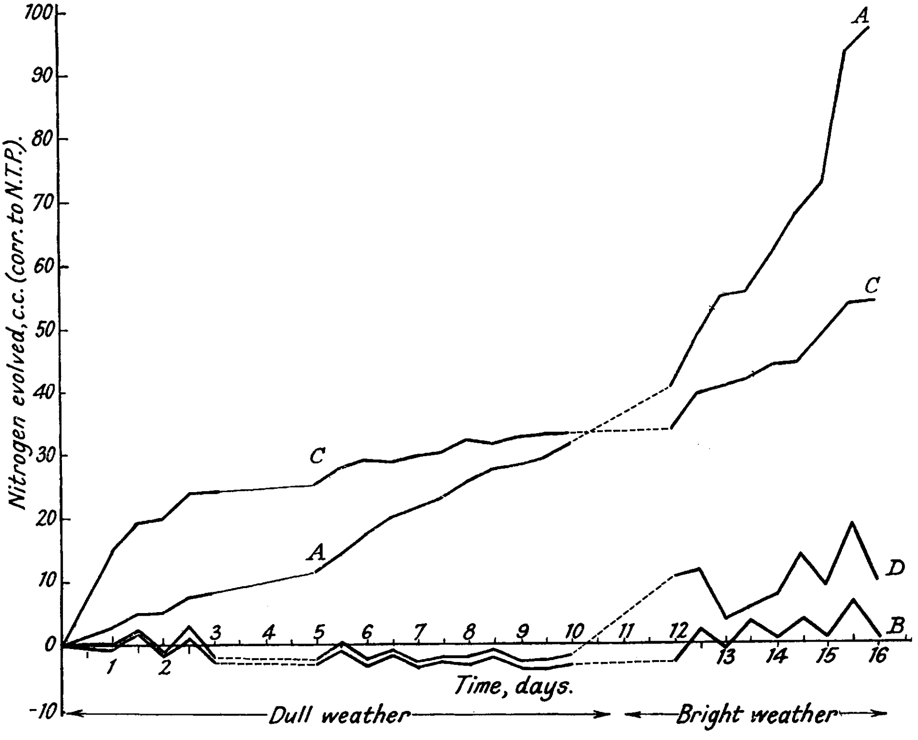
Precipitation of silver cyanide is a reaction typical of solutions of *syn*-diazocyanides in ionising solvents (see below), but as it is also a reaction of the diazonium cyanides, the photochemical change in alcohol or acetone may be either a direct isomerisation of the *anti*- to the *syn*-diazocyanide or its ionisation to the diazonium cyanide. On Hartley's evidence, that the change also occurs in benzene, the former is the more likely course for the reaction.

If one starts from a solution of a pure *anti*-diazocyanide alone, the photochemical change reaches an equilibrium value which, for the substances as yet examined, is overwhelmingly in favour of the *anti*-diazocyanide, since solutions of *anti*-diazocyanides which have been exposed to strong light for a considerable time give only a very faint immediate turbidity upon treatment with silver nitrate solution.

Further, more complicated, changes occur in solutions of *anti*-diazocyanides in alcohol or acetone when they are kept for several days in daylight. Solutions which are exposed to the light in closed vessels darken considerably and gradually evolve nitrogen (see figure), showing that a slow decomposition occurs similar to that occurring when solutions of the corresponding *syn*-diazocyanides are kept ; on the other hand, solutions which are protected from light are but little altered. The eventual decomposition products resulting from the photochemical decomposition of the *anti*-diazocyanides in both ethyl alcohol and acetone are identical with those obtained by the thermal decompositions of the corresponding *syn*-diazocyanides.

The figure also indicates the effect of adding copper powder as a catalyst. Metallic copper undoubtedly influences the course of the decomposition of the *syn*-diazocyanides, for the final decomposition products are not the same in each case, but, as will be seen, copper has no obvious direct action upon the *anti*-diazocyanides. Curves *B* and *D* were given by solutions immersed in a bath of black dye, through which a little light evidently penetrated on bright days. They seem to indicate that in the dark a small loss of gas occurs, possibly on account of oxidation of the solution.

Photochemical Decomposition of p *Chlorobenzene*-anti-*diazocyanide in Acetone.*

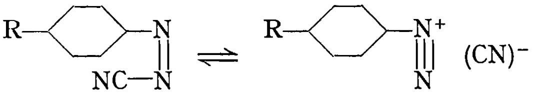


A. 5 *G. in* 50 *c.c. of acetone in daylight.*
B. 5 *G. in* 50 *c.c. of acetone in dark.*
C. 5 *G. in* 50 *c.c. of acetone* + 1 *g. of copper powder in daylight.*
D. 5 *G. in* 50 *c.c. of acetone* + 1 *g. of copper powder in dark.*

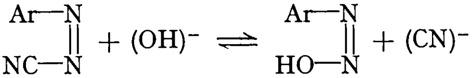
Under non-ionising solvents, such as benzene or carbon tetrachloride, evolution of nitrogen does not occur, for the *anti*-diazocyanides can be recovered quantitatively from their solutions, even after exposure to light, merely by evaporation of the solvent.

The syn-*Diazocyanides and Diazonium Cyanides.*—The reverse change, from the labile *syn*- to the stable *anti*-diazocyanide, does not seem to be a photochemical reaction. With a number of new diazocyanides we have found, in exact accordance with the observations of Le Fèvre and Vine, that the *dry* solids do not isomerise in the dark, but that all solutions rapidly undergo changes. However, the isomerisation of a *syn*- to an *anti*-diazocyanide is quantitative only in non-ionising solvents such as benzene and carbon tetrachloride. Even in ether there is some side reaction, and in alcohol and acetone *syn*-diazocyanides rapidly darken and gradually evolve nitrogen to the extent of 20—40% of the total quantity of the diazo-group present. The residual product from these solvents is a tar, together with free hydrogen cyanide and very little, if any, *anti*-diazocyanide.

This difference in behaviour of a *syn*-diazocyanide in ionising and in non-ionising solvents has been traced to the fact that it is in tautomeric equilibrium with the unstable salt, the diazonium cyanide (IV) (compare Hantzsch, *Ber.*, 1895, **28**, 1746; 1900, **33**, 2161).

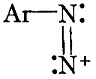

(I.) (IV.) (B.)

When a *freshly prepared* solution of any *syn*-diazocyanide in dilute alcohol is treated with silver nitrate in the same solvent there is a rapid precipitation of silver cyanide, which is complete in about half a minute, and there remains a practically colourless solution of a diazonium nitrate which can be coupled with alkaline β-naphthol (compare Hantzsch and Danziger, *Ber.*, 1897, **30**, 2534; Hantzsch, *Ber.*, 1900, **33**, 2176). Other metallic salts behave in a similar manner, though double cyanides are often formed. The *anti*-diazocyanides do not behave thus, and do not yield conducting solutions (Hantzsch, *loc. cit.*). This conversion of a covalent *syn*-diazocyanide into a diazonium cyanide is a true tautomeric change (B) and not a hydrolysis (C), since it is not inhibited by the presence of considerable quantities of nitric acid.



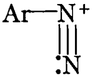
$$\begin{matrix}\mathrm{Ar-N}\\ \quad\| \\ \mathrm{NC-N}\end{matrix} + (\mathrm{OH})^- \rightleftharpoons \begin{matrix}\mathrm{Ar-N}\\ \quad\| \\ \mathrm{HO-N}\end{matrix} + (\mathrm{CN})^- \qquad \text{(C.)}$$

There is no justification for a belief that the diazo-compounds, $\mathrm{Ar{\cdot}N{:}N{\cdot}X}$, and the diazonium salts, $(\mathrm{Ar{\cdot}N{:}N})^+\mathrm{X}^-$, can give rise to two isomeric kations, since the structures (V) and (VI) are electromers, and so would merely be different canonical states of one true resonance structure, which may be represented by (VII). One may therefore use the term " diazonium " for the (kat)ionised form of all aromatic diazo-compounds (VII).



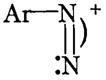
$$\begin{matrix}\mathrm{Ar-N}{:}\\ \| \\ {:}\mathrm{N}^+\end{matrix}$$

(V.)



$$\begin{matrix}\mathrm{Ar-N}^+\\ \||| \\ {:}\mathrm{N}\end{matrix}$$

(VI.)



$$\begin{matrix}\mathrm{Ar-N}^+\\ \| \\ {:}\mathrm{N}\end{matrix}$$

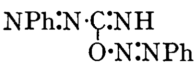
(VII.)

Acidified solutions of *syn*-diazocyanides are remarkably stable and give quantitative precipitates of silver cyanide even after being kept for a considerable time, but neutral solutions of *syn*-diazocyanides in aqueous alcohol darken appreciably on keeping for a few minutes and then do not give a quantitative precipitation of silver cyanide upon treatment with alcoholic silver nitrate. The filtrates from acidified solutions couple instantly, but the coloured filtrates from the neutral solutions which have been allowed to stand do not couple appreciably.

The amount of potential cyanide ion in a neutral solution decreases in about 30 minutes to a steady value, which is not less than 50% of the amount of the active cyanide group initially present (see Table I), and the percentage of silver cyanide finally obtainable is not altered either by keeping the mixture of diazocyanide and silver nitrate for some hours before filtering or by acidifying the mixture after the reaction in neutral solution has proceeded for some hours.

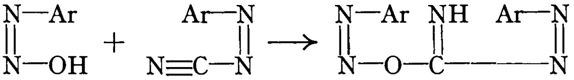
Since the occurrence of tautomeric change (equation B) would not alter the total amount of silver cyanide which should be formed, it follows that neutral alcoholic solutions of *syn*-diazocyanides decompose on keeping to give products containing altered, or non-ionisable, cyanide groups. One possible product is, of course, the *anti*-diazocyanide, but this is evidently *not* the major reaction product, since if the fall in the quantity of ionisable cyanide were solely due to the formation of *anti*-diazocyanide, the solution should eventually give no precipitate with silver nitrate. Moreover, alcoholic solutions of *syn*-diazocyanides which have been kept do not yield *anti*-diazocyanide in any quantity if evaporated or if extracted with benzene. Free hydrogen cyanide distils with the alcohol and the residue is a dark tar.

Now, Heller and Meyer (*Ber.*, 1919, **52**, 2287) reported that attempts to prepare a *syn*-diazocyanide in a slightly alkaline solution afforded instead a red alkali-metal salt of a compound of type (VIII), solutions of which, on keeping, give off nitrogen and leave tarry products smelling of *iso*-cyanide. They considered (VIII) to be derived from the diazonium cyanide, for it could easily be obtained by a partial hydrolysis (C), followed by a coupling reaction :



$NPh{:}N{\cdot}C({:}NH){\cdot}O{\cdot}N{:}NPh$

(VIII.)



(D.)

or, in brief, $2Ar{\cdot}N_2{\cdot}CN + H_2O = Ar{\cdot}N_2{\cdot}O{\cdot}C(NH){\cdot}N_2{\cdot}Ar + HCN$; whence, 2 mols. of *syn*-diazocyanide should yield 1 mol. of free hydrogen cyanide.

The great facility with which the cyano-group of the *syn*-diazocyanides will condense with compounds of the types ROH and R″NH has also been demonstrated by Hantzsch and Schultze (*Ber.*, 1895, **28**, 2078), who found that, in the presence of a trace of alkali, alcoholic solutions of *syn*-diazocyanides reacted as follows :

$$Ar{\cdot}N_2{\cdot}CN + ROH \longrightarrow Ar{\cdot}N_2{\cdot}C({:}NH){\cdot}OR$$

One may conclude, therefore, that the moderately rapid decomposition which occurs in neutral solutions of *syn*-diazocyanides in alcohol is due to hydrolysis and self-coupling, and one can therefore understand why Hantzsch and his colleagues found that the *syn*-diazocyanides had to be prepared by adding potassium cyanide solution to a cold acid solution of a diazonium salt, and not by adding a diazonium salt solution to an excess of an alkaline solution of potassium cyanide.

Since the neutral solutions of the *syn*-diazocyanides in ionising solvents can soon change in this way, their ultimate thermal decomposition reactions, in which nitrogen is evolved, are not necessarily decomposition reactions of the *syn*-diazocyanides themselves.

In water, dilute acid, alcohol, or acetone, the ultimate decomposition of a *syn*-diazocyanide produced some nitrogen, hydrogen cyanide, a little *iso*cyanide, and much tar, and is a complex decomposition in which the solvent can play an integral part. From solutions of *syn*-diazocyanides in ethyl alcohol about 40% of the diazo-groups present may be evolved as nitrogen, acetaldehyde is an invariable reaction product, and, in part, the diazocyanide group is replaced by hydrogen. If copper powder is added, the initial rate of evolution of nitrogen is accelerated and the total percentage of nitrogen evolved is somewhat greater, though only a little of the aromatic nitrile is formed.

Solutions of *syn*-diazocyanides in acetone evolve about 20% of their diazo-groups in the form of nitrogen, but give scarcely any simple products, other than hydrogen cyanide. Again, the decomposition in acetone is catalysed by copper powder. In this case over 50% of the diazo-groups may be eliminated as nitrogen, free hydrogen cyanide is not formed, but some aromatic nitrile is formed instead. The decomposition of the *syn*-diazocyanides in alcohol or acetone is not catalysed by metals other than copper (compare the diazonium chlorides; J., 1937, 2007; this vol., p. 864).

Non-polar Decompositions of syn-*Diazocyanides.*—Solutions of *syn*-diazocyanides in the non-ionising solvents carbon tetrachloride, benzene, *cyclo*hexane, and ether do not lose nitrogen on warming, but give the stable *anti*-diazocyanides. However, a decomposition can be initiated in these solvents also by adding copper powder, and 30—50% of the diazo-groups present may be eliminated as nitrogen, leaving complex tarry residues from which simple reaction products, other than some *anti*-diazocyanide, can be isolated only in small yields. This copper-catalysed reaction has been studied by using the purified *syn*-diazocyanides obtained from *o*- and *p*-chloroanilines, *p*-bromoaniline, 4- and 5-chloro-*o*-toluidine, and the simpler reaction products have been isolated by steam-distillation and characterised.

When carbon tetrachloride was used, the aryl chloride $C_6H_4R{\cdot}Cl$ was formed from the cyanide $C_6H_4R{\cdot}N_2{\cdot}CN$ in 10—20% yield. Hydrogen cyanide was also formed, and aqueous extracts of the reaction products regularly contained both cupric and chloride ions. No appreciable quantities of the nitrile could be isolated, so one must conclude that the

Gattermann reaction is suppressed. In the presence of other metals no similar decomposition of the *syn*-diazocyanide occurs.

When benzene was used as solvent, a small quantity (up to 2%) of the unsymmetrical diaryl $C_6H_4R{\cdot}Ph$ was isolated. Hydrogen cyanide was again a product, but neither with benzene nor with the other solvents enumerated below was there any evidence of chemical attack on the copper. From a decomposition carried out in *cyclo*hexane some aromatic nitrile was isolated. Decompositions carried out in ethereal solution also yielded up to 3% of the aromatic nitrile, mixed, however, with a larger quantity (up to 10%) of the hydrogen-substituted product, C_6H_5R. Acetaldehyde was also formed in all decompositions carried out in ethereal solution.

Since the reactions

$$\begin{array}{llll} \text{(i)} & Ph{\cdot} + CCl_4 & \longrightarrow Ph{\cdot}Cl & + {\cdot}CCl_3 \\ \text{(ii)} & Ph{\cdot} + C_6H_6 & \longrightarrow Ph{\cdot}C_6H_5 & + {\cdot}H \\ \text{(iii)} & Ph{\cdot} + H{\cdot}Alkyl & \longrightarrow Ph{\cdot}H & + {\cdot}Alkyl \end{array}$$

are typical of the neutral phenyl radical (J., 1937, 2007), one can ascribe to the copper-catalysed decompositions of the *syn*-diazocyanides in these non-ionising solvents a non-ionic mechanism, and suppose that the *syn*-diazocyanide decomposes in the presence of metallic copper into nitrogen and two free neutral radicals, which do not unite together instantly, as Hantzsch supposed, but react in a complex manner with vicinal solvent molecules, as described in earlier papers of this series. The free cyanide radical would be expected to react as follows,

$$\text{(iv)}\quad {\cdot}CN + HX\ (= \text{aromatic substance}) \longrightarrow HCN + {\cdot}X$$

and thus it is a significant fact in support of the non-ionic theory of the decomposition of covalent aromatic diazo-compounds that aromatic nitrile formation (the Gattermann reaction), which may occur by either reaction (v) or (vi), is by no means one of the principal

$$\begin{array}{llll} \text{(v)} & R{\cdot}C_6H_4{\cdot} + {\cdot}CN & \longrightarrow R{\cdot}C_6H_4{\cdot}CN & \\ \text{(vi)} & R{\cdot}C_6H_4{\cdot} + HCN & \longrightarrow R{\cdot}C_6H_4{\cdot}CN & + {\cdot}H \end{array}$$

resultant chemical changes. The chemical attack on the copper, which has been observed only in carbon tetrachloride solution, may be a reaction of the ${\cdot}CCl_3$ radical.

It is noteworthy that the tars which are produced in these decompositions constitute the major portion of the resultant aromatic products. They can be regarded as the end-products of complicated chain-reaction processes. An alternative suggestion—*viz.*, that the tars are polyazo-compounds produced by chain-coupling reactions—can be ruled out, since the tars have been found to contain only about 10% of nitrogen, which corresponds to about one nitrogen atom per aryl group, and not to two nitrogen atoms, which the structure $Ar{\cdot}N_2{\cdot}[C_6H_3X{\cdot}N_2]_n{\cdot}Ar$ would require. Further, after vigorous reduction with stannous chloride or zinc in hydrochloric acid, the tars do not yield detectable quantities of diamines, though they do yield small quantities of the corresponding monoamines. In part, the nitrogen content of the tars is due to the presence in them of nitrile groups, for ammonia is evolved when they are boiled with sodium hydroxide. The tars themselves are insoluble in the solvents used for bringing about the decompositions, but dissolve to some extent in concentrated sulphuric acid to give brownish solutions. The other experimental evidence obtained from the decomposition reactions carried out in benzene, in conjunction with the experimental evidence of Part VII (preceding paper), in which it has been shown that aryl groups can add on to the CN group, would indicate that these tars may be partly polyphenyl, *i.e.*, $R{\cdot}C_6H_4{\cdot}[C_6H_3X]_n{\cdot}Ar$ [where X may be CN or N=N—CN (*anti*)], and partly polyamine, *i.e.*, $R{\cdot}C_6H_4{\cdot}\underset{\wedge}{C}{\cdot}\underset{|}{N}{\cdot}Ar$— or $Ar{\cdot}\underset{|}{N}{\cdot}[C_6H_3X]{\cdot}\underset{|}{N}$—.

The final conclusion is, therefore, that the non-ionic decompositions discovered with the diazoacetates (Waters, J., 1937, 113; Grieve and Hey, J., 1934, 1797), and presumed to occur with the diazohydroxides and diazonium chlorides (J., 1937, 2014, 2007), proceed in an exactly similar manner with these *syn*-diazocyanides in the complete absence of water or of any ionising solvent. This still further substantiates the theory of free-radical fission of the aromatic diazo-compounds, and makes it quite evident that this decomposition is characteristic of the covalent diazo-compounds and not of the diazonium kation.

Moreover, it is also evident that the two radicals which result from the scission of the azo-group as nitrogen gas do not unite at once, even with the *syn*-diazo-compounds, but react in a complex manner with vicinal solvent molecules. Hantzsch's mechanism for the decomposition of the aromatic diazo-compounds (A; p. 1797) has therefore no foundation in experimental fact. In contrast, one can point out that the Gattermann reaction, $C_6H_4R{\cdot}N_2{\cdot}CN \xrightarrow{Cu} C_6H_4R{\cdot}CN + N_2$, is favoured only when ionisation is possible, and the view that this reaction may be a reaction of a diazonium salt (this vol., p. 864) thus receives some further slight support.

EXPERIMENTAL.

syn-Diazocyanides were prepared from (*a*) *p*-chloroaniline, (*b*)*o*-chloroaniline, (*c*) *p*-bromoaniline, (*d*) 4-chloro-*o*-toluidine, and (*e*) 5-chloro-*o*-toluidine by the procedure of Le Fèvre and Vine (*loc. cit.*). Damp reaction products were rapidly purified by dissolving them in ice-cold ether–light petroleum, shaking the solution for 10 mins. with sodium sulphate, filtering, and then blowing off the ether with a current of dry air.

The following diazocyanides have not been described previously: o-*Chlorobenzene*-syn-*diazocyanide*, m. p. 49°, orange (Found: Cl, 21·1. $C_7H_4N_3Cl$ requires Cl, 21·45%); o-*chlorobenzene*-anti-*diazocyanide*, m. p. 78°, bright red (Found: Cl, 21·4%); 4-*chloro*-o-*toluene*-syn-*diazocyanide*, m. p. 49°, orange-yellow (Found: Cl, 19·6. $C_8H_6N_3Cl$ requires Cl, 19·7%); 4-*chloro*-o-*toluene*-anti-*diazocyanide*, m. p. 68°, red (Found: Cl, 19·6%); 5-*chloro*-o-*toluene*-syn-*diazocyanide*, m. p. 60°, orange (Found: Cl, 19·7%); 5-*chloro*-o-*toluene*-anti-*diazocyanide*, m. p. 75°, red (Found: Cl, 19·7%).

Dry specimens of the *syn*-diazocyanides could be kept for some days in the dark, but damp specimens gave off hydrogen cyanide on keeping, and formed tarry products, smelling of *iso*cyanide and containing only a little *anti*-diazocyanide.

Freshly prepared alcoholic solutions of the *syn*-diazocyanides of the above five bases reacted immediately with alcoholic silver nitrate, precipitating silver cyanide and leaving practically colourless diazonium nitrate solutions which would couple with alkaline β-naphthol. After a short time the alcoholic solutions turned reddish-brown and then would not couple. Acidified solutions, however, did not change colour on keeping. The data in Table I were obtained by treating solutions of 5-chloro-*o*-toluene-*syn*-diazocyanide with silver nitrate after various times, and collecting and weighing the silver cyanide formed.

TABLE I.

Sample 1.		Sample 2.			
Dissolved in neutral EtOH (0·0189M).		Dissolved in neutral EtOH (0·0147M).		Dissolved in EtOH made N/2 with HNO_3 (0·0148M).	
Time, mins.	% of CN reacting.	Time, mins.	% of CN reacting.	Time, mins.	% of CN reacting.
1·25	68·2	3·7	78·3	3·0	93·9
4·5	64·3	10	70·0	5·5	93·4
8·0	58·1	24	65·3	8·0	93·3
11·5	55·4	41	63·5	20·0	93·5
22·0	50·1	60	65·2	90	92·6
40	47·3	145	64·6	228	93·8
82	48·4	285	59·9γ	260	93·8α
187	47·3γ	3 days	58·7γ	3 days	75·5β

In the above calculations the diazocyanide was assumed to be 100% pure, but evidently the purity of Sample 2 was 93·5% and that of Sample 1 still less. The reactions with Sample 2 were carried out in a darkened room, except for α which had been exposed to sunlight for ½ hour, and for β which had been exposed to light for 2 days. The estimations γ were carried out by adding acidified silver nitrate. With other *syn*-diazocyanides figures ranging from 98% to 77% of the theoretical CN content were obtained by dissolving dry specimens in alcohol and adding silver nitrate as soon as all the solid had dissolved.

Alcoholic solutions of all the *anti*-diazocyanides gave no immediate precipitates when treated with alcoholic silver nitrate, but on exposure to light silver cyanide was gradually formed and the solution became paler. Eventually, reduction of the white silver cyanide precipitate occurred.

The effect of prolonged exposure to light of solutions of the *anti*-diazocyanides has already been given (p. 1797, and see figure). The following results were obtained in decomposition experiments carried out on a larger scale with freshly prepared samples of *syn*-diazocyanides, the following procedure being used : Solutions were warmed under reflux by immersion in water until reaction set in, the evolved nitrogen was collected by displacement of water and measured, the solvent was distilled off and tested for volatile products, the remainder was distilled in steam, the distillate examined, and the residual tar collected, dried, and analysed for its nitrogen content by the Kjeldahl method, and subsequently for copper by thiosulphate titration. The letters (*a*)—(*e*) relate to experiments upon the *syn*-diazocyanides derived from the bases (*a*)—(*e*) (see p. 1802). For the copper-catalysed reactions, 5 g. of copper powder were used in each case. All aromatic nitriles obtained in the reactions were identified by hydrolysis to the corresponding acids.

Decompositions in Ethyl Alcohol (100%).—These gave in each case free hydrogen cyanide and acetaldehyde : (*b*) (26 g. in 300 c.c.) gave a 20% yield of chlorobenzene and a trace of the *anti*-diazocyanide; (*e*) (28 g. in 450 c.c.) gave a 15% yield of *m*-chlorotoluene, identified both by oxidation to *m*-chlorobenzoic acid, m. p. and mixed m. p. 158°, and by nitration to 3-chloro-2 : 4 : 6-trinitrotoluene, m. p. and mixed m. p. 149°.

In the presence of copper powder, (*b*) (21 g. in 280 c.c.) gave a 20% yield of chlorobenzene and a trace of *o*-chlorobenzonitrile, and (*e*) (12 g. in 200 c.c.) gave a 25% yield of *m*-chlorotoluene and a 1% yield of 5-chloro-*o*-toluonitrile. There was no evidence of any chemical attack on the copper. Mercury, antimony, and zinc did not affect the decomposition. Diazocyanides from (*a*) and (*d*) reacted similarly.

Decompositions in Acetone.—Those carried out without the addition of copper yielded free hydrogen cyanide, tar, and some *anti*-diazocyanide (from *a, c, d, e*). Methyl acetate solutions behaved similarly. In the presence of copper there was no free hydrogen cyanide, but nitriles were formed : *e.g.*, (*b*) (22 g. in 250 c.c.) gave 4% of chlorobenzene and 10% of *o*-chlorobenzonitrile, and (*d*) (20 g. in 200 c.c.) gave 6% of *p*-chlorotoluene, identified by oxidation to *p*-chlorobenzoic acid, m. p. and mixed m. p. 236°, and 9% of 4-chloro-*o*-toluonitrile. There was no evidence of any chemical attack on the copper. Mercury, antimony, zinc, and silver were all without any effect on the decomposition.

Decompositions in Carbon Tetrachloride.—When kept in carbon tetrachloride solution, all *syn*-diazocyanides isomerised to the corresponding *anti*-compounds, which needed no further purification. This method was therefore adopted for the preparation of these substances.

When copper powder was added to the freshly prepared *syn*-diazocyanide solutions (10% by volume), nitrogen, together with hydrogen cyanide, was evolved after gentle warming. The resulting products, after evaporation and steam-distillation, gave aqueous extracts containing cupric chloride, and a cokey mass containing some cuprous chloride. The copper was attacked even when chalk was added to the reaction mixture. No decomposition was brought about by the use of silver, mercury, iron, lead or zinc.

The *syn*-diazocyanide from (*a*) gave 9% of *p*-dichlorobenzene, m. p. and mixed m. p. 53° (Found : Cl, 48·6. Calc. : Cl, 48·3%); that from (*b*) gave 14% of *o*-dichlorobenzene, b. p. 170—185°, identified as its dinitration product, m. p. and mixed m. p. 110°, together with 4% of *o*-chlorobenzonitrile; (*c*) gave 10% of *p*-chlorobromobenzene, m. p. and mixed m. p. 67°; (*d*) gave a little nitrile and 15% of 2 : 4-dichlorotoluene, b. p. 200°, identified by oxidation to 2 : 4-dichlorobenzoic acid, m. p. 163°, and by conversion into the dinitro-derivative, m. p. and mixed m. p. 104—105°; (*e*) gave 20% of 2 : 5-dichlorotoluene, identified by nitration to 3 : 6-dichloro-2 : 4-dinitrotoluene, m. p. and mixed m. p. 101°.

Decompositions in Dry Benzene.—These proceeded very similarly to those in carbon tetrachloride, addition of copper powder bringing about the evolution of nitrogen mixed with hydrogen cyanide. The aqueous residues from steam distillates contained no copper salts, and the tar did not appear to contain any cuprous cyanide. (*a*) (28 g. in 250 c.c.) gave ½ g. (= 1½%) of 4-chlorodiphenyl, m. p. and mixed m. p. 77°; (*b*) (18 g. in 200 c.c.) gave 7% of *o*-chlorobenzonitrile and ½ g. of an oil, b. p. 270—275° (= 3% crude), which on nitration gave yellow crystals, m. p. 155°, not depressed by admixture with the dinitration product of authentic 2-chlorodiphenyl (m. p. 157°) [Mascarelli and Gatti (*Gazzetta*, 1933, **63**, 654) give dinitro-2-chlorodiphenyl, m. p. 158—159° and believe it to be the 3′ : 4′-dinitro-compound]; (*c*) (15 g. in 250 c.c.) gave 5% of *p*-bromobenzonitrile and 0·15 g. (= 1%) of 4-bromodiphenyl, m. p. 89°; (*d*) and (*e*) yielded traces of nitriles, but no other products volatile in steam. The specimen of 2-chlorodiphenyl needed for purposes of comparison was prepared by the method of Part VI from *o*-chlorobenzenediazonium chloride and benzene in acetone.

When silver or zinc was used in place of copper powder there was no reaction. When iron filings were used there was a slight evolution of nitrogen, and a trace of 4-chlorodiphenyl was isolated from (*a*).

Decompositions in Dry Ether.—These were not easy to control for, although there was some evolution of nitrogen when copper was added, even after standing for some days the solutions tended to decompose violently upon evaporation to dryness. They gave residues smelling strongly of *iso*cyanide. The ethereal distillates invariably contained acetaldehyde (identified as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 164°) and also free hydrogen cyanide. From (*b*) (17 g. in 250 c.c.) 6% of chlorobenzene and 3% of *o*-chlorobenzonitrile were obtained; (*c*) (22 g. in 200 c.c.) gave 6% of bromobenzene, identified by nitration, and also 3% of nitrile; (*d*) (28 g. in 250 c.c.) gave 8% of *p*-chlorotoluene, identified by oxidation to *p*-chlorobenzoic acid, and 4% of nitrile; (*e*) (21 g. in 220 c.c.) gave 10% of *m*-chlorotoluene (identified as its trinitro-derivative, m. p. 149°) and 2% of nitrile.

From a decomposition of (*a*) in *cyclo*hexane a little nitrile was obtained.

The tars obtained from decompositions carried out in alcohol or acetone in the absence of copper were dark brown, pitch-like materials which easily softened on warming. Those obtained from all decompositions carried out with the use of copper were hard, black, porous, cokey materials, which could easily be dried and powdered. They did not tend to soften on warming, and dissolved only with difficulty in warm concentrated sulphuric acid. It was not possible to separate the organic matter from the finely divided copper particles. Table II gives, for the actual experiments detailed above, the percentage of the diazo-group evolved as nitrogen, the yield of non-volatile tar, and also its nitrogen content, the last two figures being calculated for organic copper-free material.

TABLE II.

syn-Diazo-compound.	Solvent and catalyst.	% of diazo-group evolved as N_2.	% of tar formed.	% of N in tar.
b	EtOH, no Cu	36	60	—
e	EtOH, no Cu	39	41	—
b	EtOH + Cu	51	55	14·3
e	EtOH + Cu	56	53	13·9
c	Acetone, no Cu	25	73	—
e	Acetone, no Cu	21	*ca.* 95	—
b	Acetone + Cu	46	46	12·7
d	Acetone + Cu	67	58	10·9
a	C_6H_{12} + Cu	—	71	17·5
a	Ether + Cu	—	51	12·7
c	Ether + Cu	—	60	12·4
b	Ether + Cu	40	—	16·9
d	Ether + Cu	67	66	15·3
e	Ether + Cu	—	46	14·0
b	Benzene + Cu	33	63	13·8
b	Benzene + Cu	36	64	13·0
c	Benzene + Cu	33	63	10·5
e	Benzene + Cu	—	76	10·1
b	CCl_4 + Cu	57	72	10·2
b	CCl_4 + Cu	55	71	10·4
d	CCl_4 + Cu	45	80	7·5
e	CCl_4 + Cu	—	45	10·2

A tar containing one nitrogen atom per aryl group should give 9—11% of nitrogen and one containing two such atoms per aryl group should afford 16—20%.

The tars all evolved some ammonia on boiling with sodium hydroxide solution. Reduction of several was carried out by means of both stannous chloride and hydrochloric acid in alcoholic solution and also of zinc and hydrochloric acid in glacial acetic acid solution. The reduction products contained small quantities of the monoamines (*a*)—(*e*) originally used, but no sign of diamines.

The authors thank Mr. K. H. Saunders for his helpful suggestions, and the Dyestuffs Research Committee of Imperial Chemical Industries, Ltd., for gifts of chemicals.

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[*Received, August* 9*th*, 1939.]