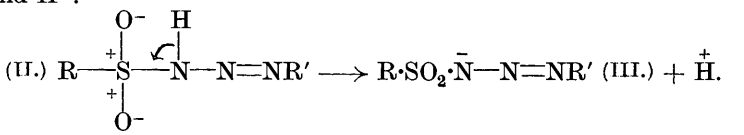
CCLXIV.—*The Action of Diazo-salts on Aromatic Sulphonamides. Part II. The Mechanism of the Reaction and the Constitution of the Diazosulphonamides.*

By ARTHUR KEY and PAVITRA KUMAR DUTT.

THE object of this investigation was to elucidate the mechanism of the reaction

$$R{\cdot}SO_2{\cdot}NH_2 + R'{\cdot}N_2X \longrightarrow R{\cdot}SO_2{\cdot}NH{\cdot}N{:}NR' \longrightarrow R{\cdot}SO_2H + R'N_3 \quad (I.)$$

(Dutt, Whitehead, and Wormall, J., 1921, **119**, 2088; Dutt, J., 1924, **125**, 1463), which takes place with extreme facility in the presence of alkali even at very low temperatures. Several examples of the formation of sulphinic acids under comparable conditions from other sulphonamide derivatives have also been recorded by Forster and Kunz (J., 1914, **105**, 1720) and by Holmes and Ingold (J., 1926, 1305). These reactions are apparently similar in their mechanism, being probably due to the action of hydroxyl ions on the hydrogen which is incipiently ionised because of the strong electron attraction exercised by some neighbouring centre (Holmes and Ingold, *loc. cit.*). For example, in the case of the diazo-sulphonamide (II) such electron attraction actuated by the neighbouring positive charges should induce it to ionise into the complex ion (III) and H^+.



After the removal of the proton as water the complex ion (III) should then undergo further change due to the proximity of the positively charged sulphur; the latter would appropriate the two electrons between the sulphur and the nitrogen, resulting in its fission into the sulphinate ion $R{\cdot}SO_2'$ and $R'N_3$. According to this scheme the residue $R'—\dot{N}=\dot{N}—\dot{N}:$ should by subsequent movement of electrons be capable of existing in one of the two forms $R'—N=\overset{+}{N}=\overset{-}{N}$ and $R'—\overset{-}{N}—\overset{+}{N}\equiv N$. The distinction of any of these forms from the third possible formula for azoimide, $R'N<\overset{N}{\underset{N}{\|}}$, may perhaps be elucidated by parachor determination.

The reaction (I) may, on the other hand, be a case of true migration of the hydrogen atom from the nitrogen to the oxygen, followed by fission into the two final products. This hypothesis was tested by heating the pure dry sulphonamide (R = *p*-tolyl and R' = Ph) both by itself and in solution in a non-ionising solvent, such as pyridine, at a temperature above its decomposition point (87—88°). In the former case a minute quantity of the azoimide was obtained, probably owing to the action of the alkali of the glass or a trace of moisture or both, but none of it was formed in the latter experiment.

It is therefore evident that the ionic interpretation offers a plausible explanation of the reaction.

The reaction of the diazo-sulphonamide with an acid hydrolytic agent, forming only $R{\cdot}SO_2{\cdot}NH_2$ and R'OH but no $R'NH_2$, is consistent with formula (II), because, of the two possible tautomeric forms, (II) and $R{\cdot}SO_2{\cdot}N{:}N{\cdot}NHR'$, the proximity of the positive charge on the sulphur should favour the stability of the ion (III) owing to its tendency to neutralise the negative charge on the nearest nitrogen atom. The two lone pairs of electrons on this nitrogen would then appropriate two hydrogen ions, completing the system $R{\cdot}SO_2{\cdot}NH_2$ and leaving a positive ion, $R'—N\equiv N$, which is responsible for the formation of the phenol. In this instance, therefore, the electronic condition is such that the substance ceases to be tautomeric.

The action of acid hydrolytic agents fails to distinguish, as Forster and Garland have pointed out (J., 1909, **95**, 2056), between the tautomeric forms of an aromatic diazoamine, although phenyl-α-naphthyltriazene (Dimroth, Elbe, and Gruhl, *Ber.*, 1907, **40**, 2390) may have the constitution $NHPh{\cdot}N{:}N{\cdot}C_{10}H_7$, because it yields only aniline and no α-naphthylamine when hydrolysed by means of hydrochloric acid in a freezing mixture.

Further, the diazo-sulphonamide is readily methylated in the cold, forming only one monomethyl derivative which, from the evidence

of its reduction products ($R{\cdot}SO_2{\cdot}NH_2$, NH_3, $R'{\cdot}NHMe$, $R'NMe{\cdot}NH_2$, and $R'MeN{\cdot}N{:}N{\cdot}NMeR'$), must be regarded as having the constitution $R{\cdot}SO_2{\cdot}N{:}N{\cdot}NMeR'$ (V). The electronic hypothesis in our opinion offers an explanation of this behaviour. Obviously the methyl derivative cannot have been formed by direct substitution because of the greater stability of the form (II), which should have given the isomeride, $R{\cdot}SO_2{\cdot}NMe{\cdot}N{:}NR'$, and consequently its formation must have been preceded by salt formation with CH_3X at one of the nitrogen atoms. The velocity of methylation is much greater than that of the reaction (I); in other words, it is the substance (II), and not the ion (III), that takes part in this reaction. Now the electron pull due to the positive charges should influence all the nitrogen atoms in the chain, but the farthest one should have its lone pair of electrons comparatively free to take part in any salt formation. This should lead to the formation of the complex (IV), which would subsequently eliminate HX and form (V).

$$\text{(IV.)}\ [R{\cdot}SO_2{-}NH{-}N{=}\overset{\overset{CH_3}{|}}{\underset{}{N}}{-}R']\bar{X} \longrightarrow R{\cdot}SO_2{-}\overset{-}{N}{-}N{=}\overset{\overset{CH_3}{|}}{\underset{}{N}}{-}R' \longrightarrow R{\cdot}SO_2{-}N{=}N{-}N(CH_3){\cdot}R' \quad \text{(V.)}$$

The isomeric methyl derivative, $R{\cdot}SO_2{\cdot}NMe{\cdot}N{:}NR'$, prepared from $R{\cdot}SO_2{\cdot}NHMe$ and $R'{\cdot}N_2Cl$, on reduction yields products ($R'NH_2$ and $R'NH{\cdot}NH_2$) which indicate that it is distinct from the substance (V).

In contrast with the formation of the monomethyl derivative of the diazo-sulphonamide, attention may be directed to the examples containing the system $\cdot CO{\cdot}\underset{|}{C}H{\cdot}N{:}N{\cdot}R$ described by Auwers (*Annalen*, 1911, **378**, 242), which on direct methylation yield two monomethyl derivatives, one an *O*-methyl and the other an *N*-methyl (next to the group R) derivative. In our opinion this difference is due to the fact that the diazo-sulphonamides do not possess the unsaturated centres that are necessary for enolisation previous to *O*-methylation.

EXPERIMENTAL.

*Action of Heat on Benzenesulphon-*p*-tolyldiazoamide* (II; R = Ph, R' = C_7H_7).—The diazo-sulphonamide (10 g., purified as previously described and dried in a vacuum desiccator over phosphoric oxide during several weeks) was heated in a vacuum. At about 80°, slow decomposition took place, producing much tar, and a few drops of an oily liquid distilled which smelt strongly of phenylazoimide (identified in the usual way). It is not advisable to use more of the diazo-sulphonamide for each experiment or heat it to a much higher temperature, as it is liable to explode.

The diazo-sulphonamide dissolves readily in cold pyridine and is precipitated unchanged on addition of water. The pure material (5 g.) was dissolved in 50 c.c. of pyridine and heated on the steam-bath for 12—15 hours; the solution was then cooled and poured into sufficient ice-cold dilute sulphuric acid (about 2%) to give an acid solution. Some resinous product separated, but no phenylazoimide.

Action of Glacial Acetic Acid on the Diazo-sulphonamide.—The crude substance (10 g., prepared in very dilute alkaline solution and precipitated by acetic acid) was treated with about 50 c.c. of glacial acetic acid, slowly warmed a few degreesabove the ordinary temperature, and occasionally stirred. It dissolved readily, the colour of the solution, at first light red, gradually darkened, and slow decomposition took place with evolution of gas. From the mixture, diluted with a large volume of water and made alkaline, ether extracted a trace of tar but no aniline. The aqueous solution was acidified and distilled in steam, and phenol identified in the distillate. The residue on cooling gave crystals of *p*-toluenesulphonamide (identified by mixed melting point).

Methylation of the Diazo-sulphonamide.—A solution of 51 g. of *p*-toluenesulphonamide in 3 l. of 2% aqueous sodium hydroxide, cooled in ice and salt, was treated with a diazo-solution (made from 28 g. of aniline dissolved in 90 c.c. of concentrated hydrochloric acid and 120 c.c. of water and diazotised with 22 g. of sodium nitrite dissolved in 70 c.c. of water). To the clear alkaline solution of the diazo-sulphonamide, 80 g. of methyl sulphate were added during one hour, and the agitation continued for 3—4 hours longer. The reddish-brown amorphous mass that separated was collected, washed, and dried in a vacuum desiccator; m. p. 115—118° (decomp.), yield about 75 g. It smelt strongly of phenylazoimide.* After crystallising twice from methyl alcohol (animal charcoal), it was obtained in colourless prismatic needles, m. p. 124—125° (decomp.) (Found: S, 10·9; N, 14·7. $C_{14}H_{15}O_2N_3S$ requires S, 11·1; N, 14·5%).

Reduction of the Methyl Derivative (V).—A suspension of 20 g. of the pure methyl derivative in 300 c.c. of methyl alcohol was reduced with 600 g. of sodium amalgam (2½%). The evolution of ammonia was soon noticed, and as the reaction progressed the ether dissolved and finally a small amount of a crystalline substance separated. The whole mixture was then distilled in steam. The residue in the distilling flask, which contained the crystals (A) referred to above, was filtered off and well washed with water. The filtrate, on

* When the diazo-sulphonamide itself is stirred even for much longer periods with alkali of the strength used in this experiment, very little of the azoimide is formed, showing that the methylation proceeds at a much faster rate.

acidification with hydrochloric acid, gave a colourless solid which was identified as *p*-toluenesulphonamide (mixed m. p.) after recrystallisation. The presence of *p*-toluenesulphonmethylamide could not be detected in this product.

The crystalline residue (A) on recrystallisation from spirit (animal charcoal) separated in almost colourless plates, m. p. 141—142° (decomp.), and proved to be identical with diphenyldimethyltetrazene, NPhMe·N:N·NMePh, prepared by oxidising αα-phenylmethylhydrazine in chloroform solution by means of mercuric oxide (Fisher, *Annalen*, 1877, **190**, 167; Tafel, *Ber.*, 1885, **18**, 1744). The melting point observed by us was, however, 4° higher than that recorded in the literature.

The steam-distillate from the original reduction mixture was acidified with hydrochloric acid and evaporated to dryness. From the dark brown residue (B), hot chloroform extracted monomethylaniline, which was isolated and identified in the form of the hydrochloride, m. p. 125—126° (the material obtained from several experiments was sufficient for the preparation of the acetyl derivative). No other basic substance could be detected in the chloroform extract.

The portion of the residue (B) insoluble in chloroform was extracted with absolute alcohol, which left behind crystals of ammonium chloride. The extracts of the residue from several experiments were collected together and the base was liberated by means of alkali, extracted with ether, dried, and distilled in a vacuum. The pale yellow, oily liquid, b. p. 160°/70 mm., gave an acetyl derivative in hexagonal prisms, m. p. 92—93°, and a crystalline hydrochloride, m. p. 221—222° (decomp.), both identical with those obtained from an authentic specimen of *as*-phenylmethylhydrazine. No trace of methylamine hydrochloride could be detected in the residue insoluble in chloroform.

Action of Benzenediazonium Chloride on p-*Toluenesulphonmethylamide.*—A solution of 5 g. of the methyl ether in dilute aqueous sodium hydroxide was treated in the cold with the diazo-solution made from 5 g. of aniline. The reaction was very slow and a brownish-red viscous mass gradually separated. As this did not show any sign of solidifying, it was washed several times by trituration with water. The gummy residue was soluble in most organic solvents but did not crystallise from any of them.

When its alcoholic solution was reduced by means of sodium amalgam as before, the evolution of ammonia was soon noticed. The mixture after reduction was poured into excess of water and extracted with ether. The ethereal extract on evaporation gave a dark oil, soluble in dilute acids, which was apparently a mixture of

aniline and phenylhydrazine, as it gave the carbylamine reaction, and phenylazoimide and phenol on treatment with nitrous acid. No trace of methylaniline could be detected in the residue.

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