

**815.** *A Study of Diazo-Compounds by Use of Nitrogen Isotopes. The Reduction of Mixed Diazonium Salts of Anthranilic Acid and Aniline.*

By P. F. HOLT and (Mrs.) B. I. HOPSON-HILL.

Benzenediazonium chloride is reduced by the cuprammonium ion to yield mainly azobenzene. *o*-Carboxybenzenediazonium chloride yields mainly diphenic acid. When the mixed solutions are reduced the nitrogen of azobenzene-2-carboxylic acid, which is also formed, is derived not from the benzenediazonium but from the carboxybenzenediazonium radical.

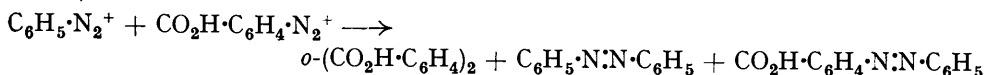
REDUCTION of a diazonium salt may yield, besides nitrogen, one or more of the following products: a diaryl, an azo-compound, an aryl halide, or a phenol. The products formed depend on the nature of the amine and of the reducing agent, and on the conditions.

Vorlander and Meyer (*Annalen*, 1901, **320**, 122) found that the action of ammoniacal cuprous oxide on the diazo-compounds from *m*-xylydine and cumidine gave symmetrical azo-compounds in good yields. Similarly Hodgson, Leigh, and Turner (*J.*, 1942, 744) obtained symmetrical azo-compounds in high yields by the action of freshly precipitated cuprous oxide on acid solutions of naphthalenediazonium sulphates. However, Vorlander and Meyer demonstrated that, when the diazo-compound has chlorine or carboxyl substituents, diaryls are the main product in ammoniacal solution.

The reduction of many different diazotized amines with various reducing agents has been studied extensively by Atkinson, Morgan, Warren, and Manning (*J. Amer. Chem. Soc.*, 1945, **67**, 1513). In particular they examined the products formed when diazotized amines

are reduced with the cuprammonium ion and when mixtures of diazotized amines are reduced, thus synthesizing an unsymmetrical diaryl.

When diazotized *o*- or *p*-nitroaniline is mixed with diazotized anthranilic acid and then reduced with the cuprammonium ion, the products are identical with those obtained by reducing the diazonium salts separately. Reducing a mixture of the diazonium salts of anthranilic acid and aniline, however, gives, not only the expected symmetrical compounds diphenic acid (produced when diazotized anthranilic acid is reduced alone) and azobenzene (produced when diazotized aniline is reduced alone), but also the unsymmetrical azobenzene-2-carboxylic acid (Atkinson, Reynolds, and Murphy, *J. Amer. Chem. Soc.*, 1950, **72**, 1397):



Since the product from diazotized aniline, reduced alone, contains nitrogen and that from diazotized anthranilic acid, reduced alone, does not, it appears likely that the nitrogen atoms present in the azo-group of the azobenzene-2-carboxylic acid are derived from the benzenediazonium ions and that the nitrogen from the diazotized anthranilic acid is eliminated. This part of the reaction mechanism has been studied by isotopically labelling one of the diazonium salts with  $^{15}\text{N}$ . Evaluation of the isotope distribution in the reaction products has shown that the nitrogen of the azobenzene-2-carboxylic acid is derived from the diazotized anthranilic acid.

#### EXPERIMENTAL

**$^{15}\text{N}$ -Labelled Potassium Nitrite.**—Isotopically labelled potassium nitrate (2.8 g.; atom-%  $^{15}\text{N}$  32.4) was fused with potassium hydroxide (0.95 g.) in a crucible. Sodium sulphite (4.5 g.) was added in small portions. A solution of the melt in water was nearly neutralised with hydrochloric acid, and its nitrite content determined colorimetrically (Rider and Mellon, *Ind. Eng. Chem., Anal.*, 1946, **18**, 96). The yield was usually 50–60%. Vaughan, McCane, and Sloane (*J. Amer. Chem. Soc.*, 1951, **73**, 2298) reported yields of 64% by reduction with lead.

**Reduction of Diazonium Salts.**—Anthranilic acid (0.99 g.), suspended in concentrated hydrochloric acid (1.8 ml.) and water (3 ml.), was diazotized with a solution of potassium nitrite (atom-%  $^{15}\text{N}$  32.4). Aniline (2.03 g.) in water (10 ml.) and hydrochloric acid (7 ml.) was diazotized with unlabelled potassium nitrite (2.5 g. in 20 ml. water). Both diazonium solutions were kept below 5°. Copper sulphate (71.5 g. of  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ) was dissolved in water (30 ml.) and concentrated ammonia (12.6 ml.) and cooled to 10°. A solution of hydroxylamine hydrochloride (2.19 g. in 5 ml. of 6*N*-sodium hydroxide and 7.2 ml. of water) was also cooled to 10° and then added with stirring to the copper sulphate solution.

The diazo-solutions were then mixed and added during 15 minutes to the cuprammonium solution. The crude azobenzene precipitated was filtered off and purified by steam-distillation. It was extracted from the distillate with ether and crystallized (m. p. 67–68°). The ammoniacal distillate was acidified slowly with hydrochloric acid at 90°. At this temperature the azobenzene-2-carboxylic acid collects as a tar but the diphenic acid remains as a supersaturated solution. The azobenzene-2-carboxylic acid, filtered and purified by reprecipitation from a dilute bicarbonate solution, was obtained as an orange solid, m. p. 90–91° (lit., 95° and 92°).

The experiment was repeated,  $^{15}\text{N}$ -nitrite being used to diazotize the aniline (0.6 g.), and  $^{14}\text{N}$ -nitrite to diazotize the anthranilic acid (0.3 g.).

**Measurement of Isotope Ratios.**—Nitrogen samples for examination in the mass spectrometer were prepared from the azobenzene and the azobenzene-2-carboxylic acid by the usual procedure (Rittenberg, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1948, p. 31) except that glucose rather than selenium was used in the Kjeldahl digestion. Test estimations carried out after benzene→azo-2-naphthol had been subjected to the Rittenberg procedure indicate that the prolonged digestion, which is necessary to ensure the complete removal of volatile substances such as methylamine which interfere with the spectrometric assay, results in the loss of a substantial part of the nitrogen sample when selenium is used (see Table).

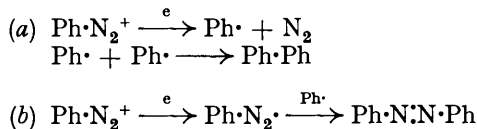
Catalyst	Wt. of benzeneazo-2-naphthol (mg.)	Yield of ammonia (% of calc. value)
Selenium .....	28.4, 33.3	6.9, 6.8
Glucose .....	28.0, 26.0	70.5, 72.0

*Results.*—The distribution between the azobenzene and the azobenzene-2-carboxylic acid of the isotopically labelled nitrogen is shown in the annexed Table. The values indicate that the nitrogen of the carboxylic acid is derived from diazotized anthranilic acid.

	<sup>15</sup> N content of azobenzene (atom-% <sup>15</sup> N)	<sup>15</sup> N content of azobenzene-2- carboxylic acid (atom-% <sup>15</sup> N)
Anthranilic acid + K <sup>15</sup> NO <sub>2</sub> .....	0.496	15.4
Aniline + K <sup>15</sup> NO <sub>2</sub> .....	16.4	0.55
<sup>15</sup> N content of K <sup>15</sup> NO <sub>2</sub> 32.4 atom-%.		

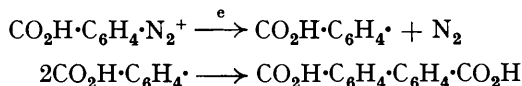
### DISCUSSION

The formation of symmetrical azo-compounds and symmetrical diaryls by the action of certain reducing agents on aromatic diazo-compounds has been suggested as proceeding with free radicals as intermediates. The mechanism for the action of cuprous hydroxide on acid diazonium sulphate has been described as follows (Hodgson, Leigh, and Turner, *loc. cit.*). The diazonium group accepts an electron from the reducing agent and this either (a) causes the elimination of molecular nitrogen, leaving an aryl radical which can combine with another to form a diaryl, or (b) causes rearrangement of electrons of the diazonium group, to form a diazo-radical, which can then combine with an aryl radical to form an azo-compound :

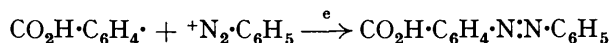


The formation of an azo-compound requires a diazo-radical; and whether this exists for an appreciable time or whether it at once loses nitrogen to give the aryl radical is determined by the degree of positivity of the carbon atom to which the diazonium group is attached. Saunders and Waters (*J.*, 1946, 1154) also assume that, in the action of ammoniacal cuprous oxide on aromatic diazo-compounds, free aryl radicals are intermediates, but that in this case they are formed from undissociated diazo-hydroxide.

In the case of anthranilic acid the mechanism is similar to that for diazotized aniline, the electron from the reducing agent causing the elimination of molecular nitrogen and the formation of a carboxyphenyl radical, two of which unite to form diphenic acid :



Since there is no evidence of the formation of the symmetrical azobenzene-2 : 2'-dicarboxylic acid, it is concluded that the carboxybenzenediazonium radical has only a transient existence. This suggests that unsymmetrical azobenzene-2-carboxylic acid resulting from the reduction of a mixture of the diazo-compounds, is formed by the union of a carboxyphenyl radical from the diazotized anthranilic acid and a diazo-cation from the diazotized aniline, the nitrogen of the product being derived from the diazotized aniline :



Atkinson assumed this since, although he suggested no mechanism for the reaction, he stated that "it is apparent that the tendency to form an azo-compound, which diazotized aniline exhibits, predominates over the tendency to form a biaryl which diazotized anthranilic acid exhibits."

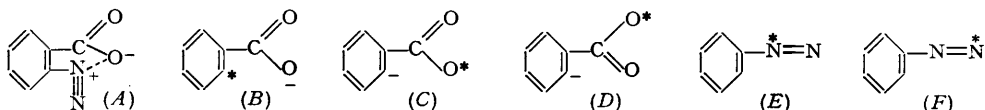
In fact the experimental results prove that this cannot be so, and that this mechanism for the reaction is inadequate. The following may be more probable.

It appears that, in the reduction of a mixture of the diazonium compounds, the cation from the diazotized anthranilic acid is capable of combining with a phenyl radical, whereas no azo-compound is produced when diazotized anthranilic acid is reduced by itself. The diazonium salt from anthranilic acid is known to exist as an internal salt (A) (Taylor and

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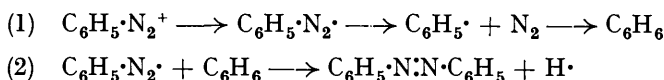
Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, p. 404).

Addition of an electron to the group  $\text{CO}\cdot\bar{\text{O}} \dots \overset{+}{\text{N}}_2$  results in disappearance of the electrovalency, elimination of nitrogen, and formation of a carboxyphenyl radical. The latter is mesomeric, having canonical forms such as (B—D). As in the case of the benzyl radical,

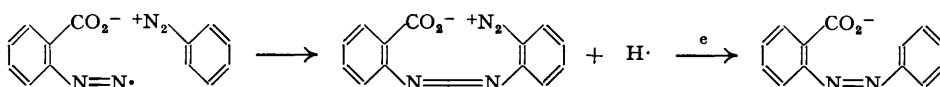


this resonance denotes an appreciable degree of stability and presumably the radical has a long enough life to react with a similar radical to form diphenic acid.

The addition of an electron to a benzenediazonium ion produces a benzenediazonium radical for which also mesomeric forms are possible. Two canonical forms may be written as (E—F), and others may be derived from the several forms of the benzenediazonium ion enumerated by Dewar ("The Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 182). When nitrogen is evolved from a benzenediazonium radical a phenyl radical is formed which cannot exhibit mesomerism of the type shown by the carboxyphenyl and the benzenediazonium radical. The phenyl radical is, then, highly reactive but, since diphenyl is not a main reaction product, it does not, apparently, dimerize. It could, either by reaction with water [which is considered improbable (Merz and Waters, *J.*, 1949, 2427)] or by reduction with the cuprammonium salt, form benzene. The benzene is then liable to attack by benzenediazonium radicals with formation of azobenzene. The relevant stages are represented as follows:



Benzenediazonium hydroxide is a stronger base than the amphoteric carboxybenzenediazonium hydroxide and is in excess. In a mixed solution the two would be expected to associate (giving  $\text{N}\equiv\overset{+}{\text{N}}\cdot\text{C}_6\text{H}_4\cdot\overset{\ominus}{\text{C}}(\text{O})\text{O}^- \text{N}_2^+\cdot\text{C}_6\text{H}_5$ ), thus freeing the diazo-group of the carboxybenzenediazonium ions. In this case the reduction of the ion produces a radical which would react intramolecularly with the cation of this ionic complex in a manner similar to that in which a free diazonium radical reacted with benzene in the earlier example:



Loss of nitrogen from the diazonium group of this molecule produces azobenzenecarboxylic acid containing nitrogen atoms previously part of the diazotized anthranilic acid.

On the assumption that a hydrocarbon or equivalent compound, formed by the addition of hydrogen to a free radical, reacts with another free radical, the reaction becomes an extension of the Gomberg reaction (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, 46, 2339; Gomberg and Pernert, *ibid.*, 1926, 48, 1372), for the preparation of unsymmetrical diaryls, which has been proved to proceed with free radicals as intermediates (Waters, "The Chemistry of Free Radicals," Oxford Univ. Press, 1948, p. 153).

In this suggested mechanism a hydrocarbon is initially formed. Traces of hydrocarbon have been isolated in certain reactions (Waters, *J.*, 1937, 2014) and the mechanism advanced by Saunders and Waters (*J.*, 1946, 1154) for the production of these by-products is identical with the initial stages of the mechanism suggested here to explain the main reaction of diazo-salts in alkaline solutions.

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