MECHANISM OF THE DIAZOAMINOBENZENE CONVERSION

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Received April 29, 1937

1. PRESENT CONTROVERSIAL POSITION

A recent paper by Earl\(^1\) revives the question of the mechanism underlying the conversion of diazoaminobenzene, and its derivatives, to aminoazo compounds. The nature of this mechanism has been debated since the introduction of diazoaminobenzene by Griess\(^2\) in 1862; and the controversial state of the question is evidenced by the more recent literature on the subject\(^3\). While Earl's last paper\(^1\) refers to dynamic isomerism involving mobility of the hydrogen in certain reactions cited\(^4\), it is not clear whether this is intended to support his previous interpretation of the reaction, which postulated the formation of benzenediazoaminazo benzene as an intermediary\(^5\).

2. NEW RESULTS NOT EXPLAINED BY A PREVALENT THEORY\(^6\)

Early in 1933 the author obtained experimental results while working at University College, London, which throw further light on the probable mechanism of this reaction; and the recurring interest in the subject makes their publication seem desirable. The following results were obtained, using an aqueous or alcoholic solution of diazoaminobenzene.

(a) Over 90 mole-per cent. of the diazobenzene constituent in a sample of diazoaminobenzene was recovered from an acidic solution of the latter, in the form of its \(\beta\)-naphthol compound, 2-naphthol-1-azobenzene. This


reaction has been carried out qualitatively by Friswell and Green, and recently by Earl.

(b) Aniline was isolated from the aqueous solution from (a), equivalent to over 90 mole-per cent. of its content (in combined form) in the sample of diazoaminobenzene used. No mention has been found of a previous attempt to isolate aniline from an acidified solution of diazoaminobenzene.

(c) Phenyldiazonium chloride has been directly combined with aniline under homogeneous conditions, the resulting aminoazobenzene separating out of the solution in the form of its hydrochloride, free from diazoaminobenzene or other intermediate product. This result has not previously been accomplished, although Friswell and Green attempted the combination by “varying the conditions in every possible way.”

(d) After a strong hydrochloric acid solution of diazoaminobenzene had been kept at 0-2° for 288 hours, approximately 75 per cent. of the original compound had undergone irreversible chemical change (100 per cent. after 92 days). Only 14 per cent. had been converted to aminoazobenzene. The difference between this figure and the amount of diazoaminobenzene which had undergone change could be accounted for reasonably well by the appearance of phenol and aniline. In a complementary experiment, the rate at which the phenyldiazonium chloride arising from fission of the diazoaminobenzene disappeared was shown to be sensibly linear.

It is considered that a prevalent view of the mechanism of the diazoaminobenzene conversion, originated by Goldschmidt and his collaborators, is inadequate to explain these results. On the other hand, it is felt that the explanation of the mechanism considered in section 5, far from excepting the experimental results upon which Goldschmidt’s theory is based, serves to harmonize these with the present results, and those of other workers.

3. GOLDSCHMIDT’S THEORY OF RESIDUE INTERCHANGE

The intermolecular nature (Cf. “The Benzidine Rearrangement”) of the conversion of diazoaminobenzene to aminoazobenzene seems never to have been in doubt since Kekulé first effected the change, and treated it as a double decomposition. Further evidence of the intermolecular character of the reaction was soon provided by Baeyer and Jaeger,
Meanwhile, however, the actual details of the mechanism were attracting the attention of investigators; and in 1891 Goldschmidt began the series of experiments which has been extended by himself and his collaborators, over a number of years, in support of the theory to which reference has been made.

This theory postulates the formation of an additive compound, \((\text{ArNH})_2\text{NCl}\) (I), and the para-combination of this with a molecule of the basic solvent, forming the compound \((\text{ArNH})_2\text{N} \cdot \text{Ar'NH}_2\) (II), which then breaks down to \(\text{ArNH}_2\) and \(\text{ArN} \cdot \text{Ar'NH}_2\), the aminoazo-compound. The ArNH residue of I may be replaced by other basic residues from the solvent (aniline, toluidine, etc.) before II is formed. In this way the different products from a number of reactions were explained; but it was not certain when residue exchange might be expected, nor why it occurred. This is illustrated by two typical reactions considered in section 5, which were advanced by Goldschmidt and collaborators in 1892 as inconsistencies on the basis of the theory considered in section 4. It will be shown in section 5, when it will be necessary to refer to I and II, that these very examples reveal a weakness in Goldschmidt's theory.

It is important to note here, that while Goldschmidt postulates the addition of one molecule of hydrochloric acid to diazoaminobenzene in the initial formation of I, the author has observed that the white crystalline precipitate thrown out of an ethereal solution of diazoaminobenzene by anhydrous hydrochloric acid contains two moles of hydrochloric acid per mole of diazoaminobenzene. This observation finds a consistent explanation in the theory discussed directly.

4. FRISWELL AND GREEN'S THEORY OF PRIMARY FISSION

In 1885 Friswell and Green had put forward an extremely simple theory of the mechanism of this conversion; but this was soon engulfed by the flood of careful experimental work from Goldschmidt's laboratories in support of the above theory. Friswell and Green's explanation was not recognized again until Meyer re-advanced the idea of fission in 1921: and afterwards, Rosenhauer and Unger drew long-overdue attention to the work of Friswell and Green. Earl's 1929 and 1930 papers again revert to the idea of a nuclear condensation, which fails to meet the demands of the majority of the mechanistic aspects of the reaction which have been observed.

Friswell and Green contended that the first stage in this conversion in the presence of hydrochloric acid was a primary fission of diazoamino-
benzene to benzene (i.e., phenyl) diazonium chloride and aniline. This was held to be a rapid and reversible reaction, while aminoazobenzene was said to be formed from the products of the fission by a slow and irreversible reaction. It is this theory, with some additions, which the author regards as giving the most likely, and certainly the most comprehensive, explanation of this conversion and the chemical phenomena which have been observed to accompany it.

5. ELECTRONIC INTERPRETATION OF MECHANISM

(A) General view of system.—Accepting Friswell and Green's postulation of a primary fission (which is in agreement with Goldschmidt's cryoscopic results?), the simplest case of this reaction—namely, when taking place in alcohol or water containing appreciable quantities of hydrochloric acid—may be formulated thus:

\[(i) \quad \text{PhN} : \text{N} \cdot \text{NPH} + \text{HCl} \]

\[\text{pH} < 7 \quad \text{pH} > 7 \]

\[\text{very fast} \quad \text{fast} \]

\[(ii) \quad \ast \text{PHNH}_2 + \text{PHN} : \text{N} \cdot \text{Cl} \]

\[\text{pH} < 7 \quad \text{pH} > 7 \]

\[\text{very slow} \quad \text{less slow} \]

\[(\text{probably fast, pH} > 7) \quad \text{(benzenediazoaminoazobenzene; v. Earl\textsuperscript{1})} \quad \text{PhN} : \text{N} \cdot \text{NPH} : \text{N} \cdot \text{NPh} \]

\[(iii) \quad \text{NH}_2 \text{Ph} ' : \text{N} : \text{NPh} \]

This system will be seen to provide an excellent example of the conflicting advantages that sometimes arise in an interdependent series of reactions. The reaction \((ii)\) to \((iii)\) is aided by the same conditions of basicity as favour the much more rapid reaction \((ii)\) to \((i)\). The pH > 7 necessary for the production of the parents of aminoazobenzene, actually militates against the formation of this compound from them, for the reason discussed in B.

The experiments reported in section 6 were carried out in aqueous medium in order to establish the points given in section 2; but aniline (or toluidine) is normally used as reaction medium, under which conditions the effect of the solvent cannot be ignored. While reaction \((ii)\) to \((i)\) will be greatly favoured by the presence of the base, the formation of aminoazobenzene by the irreversible reaction \((ii)\) to \((iii)\) will eventually reflect the mass law action of the solvent molecules. The effect becomes appreciable when diazoaminobenzene is heated for some hours in aniline containing aniline hydrochloride. The reaction is also favorably affected,

* The aniline will probably be largely in the form of its hydrochloride; and this, and also the phenyldiazonium chloride, partially dissociated.
in general, by the greater stability of phenyldiazonium chloride in aniline, than in an aqueous medium.

It may be noted that benzenediazoaminoazobenzene, which Earl\(^8\) postulated as an intermediary, is formed as a natural consequence of the presence of phenyldiazonium chloride arising from fission, the latter reacting with aminoazobenzene. This view is supported by experimental work on the reaction of phenyldiazonium chloride and aminoazobenzene\(^14\). The author has observed the presence of benzenediazoaminoazobenzene in crude diazoaminobenzene prepared from aniline sulfate and nitrous acid.

\(B\) The prototropic system; an analogy with the mobility and fission of keto-enol systems.—The prototropic system\(^15\) \(\text{N} = \text{N} = \text{NH}\) may become operative by the direct attraction of an alkaline catalyst for the ionising proton\(^16\); or indirectly by addition or electrostriction of an acidic catalyst\(†\), in such a way as to increase the positive field of the atom from which the proton separates, by increasing the attraction of its shared electrons to another center in the system\(\uparrow\). In the case of the diazoaminobenzene conversion, which is effected under acidic conditions, the mobility of the system must be due to the latter electromeric effect. Another familiar example of the same effect is found in Meyer’s work on the equilibrium system of ethyl malonate\(^18\), in which it is shown that the enol content of the freshly-acidified system changes from about 3 per cent. enol to nil in one minute.

It appears likely that fission of the diazoaminobenzene follows as a consequence of the electron mobility of the system; and here, again, one finds an analogy in the aceto-acetic ester type of system. Hydrolysis of these esters by dilute alkalis—when the ester molecule is known to contain a mobile ionic system\(^16\)—leads to the familiar “ketonic hydrolysis”. Dilute acids give the same result, and it may be assumed that it is fission of the enolic form \(\text{i.e., Me·C(OH)=CH·COOEt}\) which occurs, giving rise in the first place to the enolic form of the ketone \(\text{i.e., Me·C(OH)=CH}_{2}\)\(^19\). The slower reaction with acids, during which only the electromeric effect would influence the keto-enol equilibrium, lends support to this view; and

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† Since this paper was written, an interesting paper bearing on this point has appeared: vide Hunter, *J. Chem. Soc.*, **1937**, 320.


the fact that a much higher temperature (boiling) is required to effect fission of the mobile carbon system, as compared with the ease of fission of the mobile nitrogen system, is quite understandable.

The PhNH$_3^+$ ion has been advanced as the active catalyst in the diazoaminobenzene conversion; but even if it were allowed that this ion could play a part in the early stages of the reaction, its presence to any appreciable extent would certainly retard para-recombination in the later stage. The deactivating effect of a positive pole attached to the benzene nucleus on the latter, and especially on the ortho, and para, positions is well known. The present importance of the activity of the para position is well illustrated by the rapid combination of PhN·N·Cl with (Me)$_2$NPh, or PhO$^-$.

It is, therefore, reasonable to suppose that even in a distinctly acidic solution of diazoaminobenzene, the second stage involving $p$-combination of PhN·N·Cl with ArNH$_2$, takes place with the free base in the equilibrium mixture, ArNH$_2$·HCl=ArNH$_2$ + HCl.

(C) Secondary effect of solvent medium.—The conversion of diazoaminobenzene in aqueous, alcoholic, or aniline solution, can give rise to only the one simple aminoazocompound, aminoazobenzene, even if proton transference should occur. Such is not the case, however, with benzenediazoaminotoluene, a consideration of which will serve to illustrate the various examples around which the controversy of this mechanism has centered. In this case one has, in addition to the influence of the acidic catalyst on the prototropic system, a permanent inductive effect within the molecule.

Equation (iv) represents the two forms of diazo compound.

(iv) $\text{Me} \rightarrow \begin{array}{c}
\text{Me} \\
\text{H}^+
\end{array} \begin{array}{c}
\text{NH} \\
\text{Ph}
\end{array} \rightarrow \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \begin{array}{c}
\text{Me} \\
\text{H}^+
\end{array}
$

Ignoring secondary factors, a preponderance of IV might be expected in the equilibrium mixture. Fission of IV and para-recombination would give rise, when carried out in toluidine solution, to $\text{Me} \cdot \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \cdot \text{NH}_2 \cdot (\text{Me})$, as Goldschmidt observed; and IV would arise from a solution of diazoaminobenzene in toluidine containing acid, by the reactions indicated in (A) and (iv) above. In seeking a congruous explanation of the many results that have been reported, however, the influence of the solvent cannot be ignored; and this is illustrated by examining two typical results which Goldschmidt thought to be inconsistent with a theory of fission.

(a) \( \text{Me} \cdot \text{N=N} \cdot \text{NH} \cdot \text{Me} \), in aniline, gave \( \text{Me} \cdot \text{N=N} \cdot \text{NH} \cdot \text{Ph} \), and \( \text{Me} \cdot \text{N=N} \cdot \text{NH}_2 \), but not \( \text{Ph} \cdot \text{N=N} \cdot \text{NH} \cdot \text{Ph} \). The first two compounds follow directly from the reactions of section (A), and for the reason discussed in the previous paragraph, the latter would not be expected. (b) \( \text{Ph} \cdot \text{N=N} \cdot \text{NH} \cdot \text{Me} \), in aniline, gave \( \text{Ph} \cdot \text{N=N} \cdot \text{NH}_2 \), but not \( \text{Me} \cdot \text{N=N} \cdot \text{NH}_2 \). The first compound is again explained by the reactions of section (A), but the absence of the latter compound casually appears to be at variance with the reaction which might have been expected from equation (iv); i.e. \( \text{Me} \cdot \text{N=N} \cdot \text{NH}_2 \) might have been expected by the formation of IV from the starting compound, followed by fission, and para-recombination. In reaction (b) the solvent is aniline; and should the equilibrium mixture have tended to establish itself in the direction of IV, the fission of IV in aniline—itself an equilibrium—would have been suppressed by the effect of the preponderating aniline (solvent) molecules. Fission of the starting material will therefore take place preferentially, giving a reaction mixture very much richer in phenyldiazonium, than in tolyldiazonium, chloride; and one must consequently expect to find essentially phenyldiazo, and not tolyldiazo compounds in the product of conversion.

Examination of a number of similar apparent contradictions of the fission theory, in the literature, has shown that these lend themselves to a satisfactory explanation on the basis discussed in sections (A) and (B), provided that account is taken of all factors affecting the system during conversion.

It is interesting to apply Goldschmidt’s results (a) and (b) to his own theory (section 3). In (b) the Me \( \cdot \text{N=N} \cdot \text{NH} \) residue was preferentially ejected from his postulatory compound II, when only one such residue could have been present in the compound. On the other hand, his postulatory compound I, which would arise in the initial stages of (a), must be assumed to contain two Me \( \cdot \text{N=N} \cdot \text{NH} \) residues; and yet neither of these was displaced by the aniline molecules present in large excess, in that stage where residue exchange is most to be expected. The author feels that such elucidating experimental results as those just considered require no more complex interpretation than that of a simple fission and para-recombination; and the side-reactions which make this
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6. EXPERIMENTAL PROCEDURE AND RESULTS

(a) Preparation of diazoaminobenzene, and preliminary tests.—The diazoaminobenzene used in these experiments was prepared by standard methods, and after several recrystallizations from ethanol containing a trace of ammonium sulfide, it melted sharply at 98°. When this compound was shaken with an 18% aqueous solution of hydrochloric acid at 0°, and the solution was kept for 3 days below 2°, a purple solid was obtained; if the solution were allowed to warm the solid which resulted was sticky. On treating the purple solid with dilute ammonia, and crystallizing the product from petroleum ether, the latter was shown to be aminoazobenzene; m.p., 125°; m.p. of mixture with authentic aminoazobenzene (127°), 126°.

Analysis, found: C, 73.2; H, 5.6; N, 21.6. Aminoazobenzene requires: C, 73.1; H, 5.6; N, 21.3.

This result was repeatable with different concentrations of aqueous acid, the yield of product—always small—being greater with weaker acidity, within limits.

When anhydrous hydrogen chloride was passed into an ethereal solution of pure diazoaminobenzene, avoiding excess hydrogen chloride, a white crystalline precipitate was obtained. The same result was obtained with an alcoholic solution, by shaking out with ether, after passing hydrogen chloride.

Analysis of the “crude” solid gave the following results. Found: C, 52.6; H, 4.6; Cl, 26.3. Required by equimolecular proportions of phenyldiazonium chloride and aniline-hydrochloride: C, 53.2; H, 4.8; Cl, 26.3.

When crude diazoaminobenzene was used for this experiment, the solid precipitated was partially colored (reddish). On filtering this by suction, and washing the solid with a large quantity of cold water, a clean yellow solid remained; m.p., without recrystallization, 119-120°, sharp. The melting point of benzenediazoaminobenzene is 119.5°; and it has been shown in section 5(A) how this compound would arise in the preparation of diazoaminobenzene.

(b) Quantitative isolation of the diazobenzene constituent of diazoaminobenzene.—To 1.3 g. of diazoaminobenzene, 60 cc. of concentrated hydrochloric acid added with periodical vigorous shaking, and maintaining the temperature below 0°. An hour later 100 cc. of water at 0° was added, and the solution was filtered. The filtrate was stirred slowly into a solution of 1 g. of β-naphthol in excess caustic soda. The mixture was made slightly acidic, and filtered at 0°, the filtrate being preserved for subsequent examination. The solid was washed with cold water, cold dilute caustic, then cold dilute hydrochloric acid and water; yield of β-naphthol derivative, 1.5 g., or 91% of that theoretically possible. It melted without recrystallization at 128°, and mixed with pure 2-naphthol-1-azobenzene (130.5°) at 129°. This reaction is examined more fully under (e).

(c) Quantitative isolation of aniline from acid solution of diazoaminobenzene.—The acid filtrate and first aqueous washings from the precipitate of β-naphthol derivative in (b) were made alkaline, cooled, and well extracted with ether. This extract was filtered of scum, dehydrated for four days, and refiltered. Anhydrous hydrogen chloride precipitated from the ether a white crystalline solid, which melted at 106°.

11 Gries, Ann., 137, 58 (1866); Stae del and Bauer, Ber., 19, 1952 (1886).
Mixed with pure aniline hydrochloride (198°), it melted at 197°. Yield of aniline hydrochloride, 0.82 g., or 96% of that theoretically possible. The oil obtained by neutralization gave positive reactions for aniline by standard qualitative tests.

(d) Direct formation of aminoazobenzene from phenyldiazonium chloride and aniline.—One mole (15 g.) of freshly-distilled aniline was stirred into 2 moles (11.8 g.) of hydrogen chloride in 450 cc. of water. To this solution at −2°, 0.5 mole (5.57 g.) of dissolved sodium nitrate was added slowly with stirring, keeping the temperature below 0°. The resulting solution, which was definitely acid to litmus, showed no sign of cloudiness; after 10 minutes at 0° it had turned red, but remained perfectly clear. This solution was stored in the dark in a glass-stoppered flask at 0-2°. After 17 hours the solution was a deep clear red; and the first sign of a solid—in the form of fine, dark-purple, metallic-looking needles—was observed 21 hours after the commencement of the experiment. When the flask was held in reflected light the small glinting crystals could be seen suspended in the red solution. After 48 hours, the bottom of the flask was covered with fine, sharply-defined, crystals, and the supernatant liquid was clear save for innumerable tiny particles suspended in it; i.e. it was not opaque. Thus this solution behaved in all respects like a slowly crystallizing solution of a pure compound. The experiment was allowed to stand for 7 days at 0-2°, during which time the crop of crystals grew slowly, but fairly steadily, and the color of the body of the solution deepened to a bluish-red. The solution was then suction-filtered through a cold funnel into a flask surrounded by ice. The clear filtrate was immediately replaced in cold storage. The crystals were washed with 75 cc. of water at 2°; yield, 0.2 g. On treatment with dilute ammonia, these yielded a light-brown solid which melted at 126° sharply, after crystallization from petroleum ether; m.p. of mixture with pure aminoazobenzene (126°), 126°.

A further 0.22 g. of clean, lustrous, purple crystals was obtained after 8 more days. This filtrate again yielded a third small lot of crystals after standing for another 23 days in the cold; but these showed a definite stickiness on filtering, and possessed an odor of phenol. The body of the liquid was intensely colored by this time, and was slightly opaque.

(e) Behavior of acid solution of diazoaminobenzene on prolonged standing at low temperature.—Five separate 0.5-g. samples of finely-powdered diazoaminobenzene were stirred slowly into separate 25-cc. lots of concentrated hydrochloric acid cooled to 0°, in small glass-stoppered flasks. The flasks were then shaken vigorously, which resulted in almost complete solution of the solid; at this stage the flasks were stored in the dark at 0-2°. Subsequently 25 cc. of water at 0° was added to each flask. Addition to number 1 flask was made after an hour, and just before examining its contents; and to flasks 2, 5, addition was made after 20 hours. At different times the contents of individual flasks were examined for phenyldiazonium chloride content by filtering the solution and adding the filtrate gradually to a cold solution of β-naphthol in excess caustic soda. The resulting 2-naphthol-1-azobenzene was shown to be reasonably pure, in each case, by a melting-point determination upon a mixture with a pure specimen of this compound.

The results are summarized in Table I, in which column 2 gives the time elapsed before examining the contents of the flask in question, and column 5 gives the per cent of phenyldiazonium chloride calculated from the β-naphthol derivative, and based on that which could arise theoretically from the diazoaminobenzene originally taken.

These results indicate essentially: (a) the presence of phenyldiazonium chloride in practically theoretical amount in a freshly acidified solution of diazoaminobenzene; and (b) the slow disappearance of the former, due to irreversible p-combinin-
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...tion with the aniline arising from fission, and to its slow decomposition and side reactions. The course of the latter is shown roughly by the following semi-quantitative experiment.

Powdered diazoaminobenzene (14.4 g.) was shaken vigorously with 150 cc. of concentrated hydrochloric acid, and after standing for 12 days in the dark at 0-2°, 400 cc. of water at 0° was added without temperature rise. The content of the flask was filtered cold and the solid collected was washed with ether. The solid was crude aminoazobenzene hydrochloride, as shown by neutralization with ammonia, and recrystallization of the resulting yellow compound from petroleum ether, giving a product m.p., 126°; m.p. of mixture with pure specimen, 126°. The yield of crude product accounted for approximately 14% of the diazoaminobenzene used.

The ether washings were added to an ether extract of the acidic filtrate, which was filtered of scum and dried. Thus, phenol corresponding to about 15% of the diazoaminobenzene was recovered; b.p., 175°; white ppt. with bromine water (m.p., 91°); violet color with ferric chloride; characteristic odor.

The aqueous portion from the ether extract was stirred periodically, and allowed to stand until the traces of ether had evaporated. It was then made alkaline, and a dark mass separated on the surface; when filtered, washed with cold water, and dried,

<table>
<thead>
<tr>
<th>EXPT. NO.</th>
<th>TIME IN HOURS</th>
<th>8-NAPHTHOL DERIVATIVE, G.</th>
<th>M. P. CRUDE</th>
<th>% PHENYLDIAZO-NIUM CHLORIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.61</td>
<td>129°</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>74</td>
<td>0.47</td>
<td>127°</td>
<td>74</td>
</tr>
<tr>
<td>3</td>
<td>215</td>
<td>0.24</td>
<td>128°</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>309</td>
<td>0.15</td>
<td>129°</td>
<td>24</td>
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<tr>
<td>5</td>
<td>2200</td>
<td>0.00</td>
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this solid accounted for 40% by weight of the original diazoaminobenzene. It was an impure mixture of brown crystals, with some green ones, and attempts to effect a separation were unsuccessful. The mixture melted sluggishly in the region of 90°, and decomposed with a puff when heated further, suggesting the presence of an appreciable proportion of reformed diazoaminobenzene.

The alkaline filtrate and washings yielded, on ether extraction, aniline corresponding to nearly 20% of the original diazoaminobenzene; b.p., 175-80°; basic odor; sparingly soluble sulfate; violet hypochlorite reaction.

A small amount of p-hydroxyazobenzene was also detected in this system; m.p., crude, 145°; crystallized from petroleum ether, 152°; m.p. of mixture with a pure specimen of p-hydroxyazobenzene, 151.5°. Per cent. N, found, 13.8; required by p-hydroxyazobenzene, 14.1.

ACKNOWLEDGMENT

The author wishes to acknowledge with appreciation assistance received from Professor C. K. Ingold, F. R. S., in whose laboratories at University College, London, the experimental work was carried out.

SUMMARY

(1) The controversial position of the question of the diazoaminobenzene conversion mechanism has been reviewed.
(2) A prevalent theory of the mechanism of conversion of diazoamino compounds, which postulates unstable intermediary complexes, has been examined briefly. This has been shown to be less satisfactory in explaining certain results than a theory of primary fission and subsequent para-combination.

(3) Other experimental results are reported for which the former theory is inadequate. These include the isolation of phenyldiazonium chloride, and also aniline, in sensibly theoretical amounts from an acidic solution of diazoaminobenzene, and success in effecting the direct combination of phenyldiazonium chloride with aniline (in acidic medium) to give aminoazobenzene.

(4) The important rôle of the solvent medium has been discussed.

(5) Attention has been drawn to the analogy between the prototropic mobility and consequent fission of diazoamino, and keto-enol, systems.
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