which had separated, alcoholic hydrogen chloride solution was added. After standing overnight in the refrigerator, the hydrochloride was filtered off, dissolved in water and the solution filtered with charcoal. The free base was liberated with ammonium hydroxide and extracted with chloroform. The residue from the chloroform solution was purified by recrystallization (see Table I).

In the preparation of VII from III or VI, refluxing with sodium ethoxide was carried out for 96 hours. Even after this time the reaction had gone to an extent of only 75% of completion as indicated by the amount of sodium chloride collected. An excess of alcoholic hydrogen chloride was added to the reaction mixtures, the resulting hydrochloride filtered off, dissolved in water and the base liberated with alkali in the presence of a layer of ether. On standing, VII separated in practically pure form from the ether solution.

Preparation of VIII, XI, XIII and XII (Table I).—The anilino compounds were prepared from the corresponding chloro derivatives by heating with one volume of aniline (two volumes for XII). At about 70° an exothermic reaction occurred in the case of III and V, the temperature rising rapidly to about 150–160°. With II no exothermal reaction occurred until the temperature reached 115°. After the initial reaction the mixtures were heated in the following manner: for VIII, 150° for 15 minutes; XI, 90° for 5 minutes; XIII, 120° for 15 minutes; XII, 180° for 40 minutes. The mixtures were dissolved in five volumes of acetic acid, poured into water and the hydrochlorides of the anilino compounds collected by filtration. These were in turn suspended in water and converted to the free bases by the addition of ammonium hydroxide solution with warming. The hydrochloride of XI was soluble in water and was not isolated.

Preparation of XI by the above method gave a product which was contaminated with considerable amounts of the dianilino compound XII because of the initial temperature rise. When the reaction was run in five volumes of glacial acetic acid at 100° for 10 minutes, only a small amount of the dianilino derivative XII was formed. The latter was separated from the main product by virtue of its insolubility in chloroform.

Preparation of V and IX (Table I).—The hydrochloride IV was treated with six volumes of phosphorus oxychloride. An exothermic reaction occurred immediately and a clear yellow solution resulted within a few minutes. When the free base was used solution had not occurred after ten minutes. However, after the addition of a tenth of a volume (based on the amount of IV) of water, a clear solution was obtained in about two minutes.[10]

Refluxing VIII with three volumes of phosphorus oxychloride for ten minutes gave a clear orange solution. The above two reaction mixtures were worked up as in the preparation of III as previously reported.[2]

(10) Similar observations were reported in the analogous chlorination of 4-chloro-10-hydroxy-1,7-phenanthroline (II).[2] It was postulated that the acid (or water) was necessary to break up the hydrogen bond between the 10-Cl and 1-N atoms by furnishing protons to engage the 1-N in salt formation.

RENSSELAER, NEW YORK

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Mechanism of the Benzidine Rearrangement. III. The Rearrangement of *p,p'*-Dideuterohydrazobenzene

BY GEORGE S. HAMMOND AND WINSTON GRUNDEMEIER

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The rate of rearrangement of *p,p'*-dideuterohydrazobenzene in absolute ethanol containing hydrogen chloride is found to be, at most, 10% slower than that of the undeuterated compound. Furthermore, the ratio of benzidene to diphenyline in the product mixture is identical within experimental error with the deuterated and undeuterated substrates. These results imply that the rate-determining step of the reactions is the formation of the second conjugate acid of hydrazobenzene and that the subsequent product-determining reactions are not implemented by proton removal from the nuclear positions undergoing substitution.

It has been demonstrated recently that the rate of rearrangement of hydrazobenzene to a mixture of benzidine and diphenyline[1] is proportional to the square of the hydrogen ion concentration in the medium[1,2] and is, furthermore, subject to linear general acid catalysis.[3] These data are in accord with the following mechanisms each of which involves the equilibration of hydrazobenzene with its first conjugate acid.

$$C_6H_5NHNHC_6H_5 + H^+ \rightleftharpoons C_6H_5\overset{+}{N}H_2NHC_6H_5 \quad (1)$$

Mechanism A

$$C_6H_5\overset{+}{N}H_2NHC_6H_5 + HA \longrightarrow C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 + A^- \quad (2)$$

$$C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 \xrightarrow[\text{reaction(s)}]{\text{fast}} \text{products} \quad (3)$$

Mechanism B

$$C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 + H^+ \rightleftharpoons C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 \quad (4)$$

$$C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 + A^- \longrightarrow \text{products} \quad (5)$$

Mechanism C

$$C_6H_5\overset{+}{N}H_2NHC_6H_5 + HA \longrightarrow \text{products} \quad (6)$$

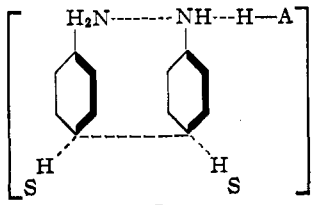
On intuitive grounds mechanism A was preferred over either of the other two despite the fact that it would involve an unprecedented rate-determining transfer of a proton from oxygen to nitrogen. This prejudice was shown to be in accord with the observation that the solid compound, hydrazobenzene dihydroiodide, underwent rearrangement at a rate about four times the rate of its reversion to hydrazobenzene when it was dissolved in an alcohol–water solvent.[3]

In mechanism B the general acid catalysis would be due to the participation of the anion of the weak acid in removing a proton from one of the positions to which rearrangement is occurring. If this were the mechanism, it would follow that the rate should show a kinetic isotope effect if a *para* hydrogen were replaced by deuterium. The same might be true of the completely concerted mechanism C although this would not necessarily be the case. It would be quite conceivable that in a transition state such as I (where S represents solvent molecules), bond breaking at the *para* position might not have made enough progress to show an isotope effect.

(1) R. B. Carlin, R. G. Nelb and R. C. Odioso, THIS JOURNAL, **73**, 1002 (1951).

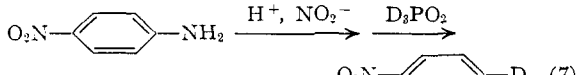
(2) G. S. Hammond and H. Shine, *ibid.*, **72**, 220 (1950).

(3) M. D. Cohen and G. S. Hammond, *ibid.*, **75**, 880 (1953).



I

In order to differentiate further among the possible mechanisms, p,p'-dideuterohydrazobenzene was prepared and its rearrangement was studied. The preparative method is indicated by equations 7 and 8.



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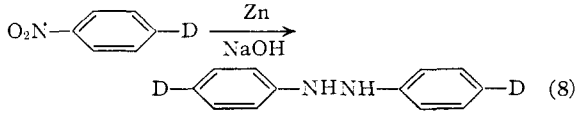


(8)

The deuteration of hypophosphorous acid was accomplished by exchanging crystalline H_3PO_2 with D_2O, concentrating the product by distillation and equilibrating a second time with D_2O. The product of the second exchange was examined by infrared analysis. The spectrum showed a broad band with a maximum at 1720 cm.$^{-1}$ which was absent in the spectrum of the normal acid. This is attributed to the P–D stretching frequency. Comparison of the intensity of the band with that at 2380 cm.$^{-1}$ indicates that approximately 60% exchange had occurred. Since it was found that the nitrobenzene contained 10 atom per cent. deuterium, 50% of the theoretical, it is indicated that the deamination reaction involves a kinetic isotope effect. This is consistent, although it is by no means definitive, with the suggestion that the deamination involves the removal of deuterium from phosphorous by an aryl radical.[4]

The rates of rearrangement of the deuterated and undeuterated compounds may be compared by the data presented in Table I. These data would indicate that the rearrangement of the deutero compound is slightly slower than is the case with the undeuterated material. The difference is, however, not much larger than the expected deviation from run to run and is certainly too small to be consistent with mechanism B. In a reaction such as 5 in which the substrate discriminates among various bases in solution it would be anticipated that the proton transfer would have made extensive progress in the transition state. Such a reaction should show nearly the maximum isotope effect.[5] We therefore feel safe in associating the base indicated by the observation of general acid catalysis with a proton which is transferred to nitrogen in the slow step of the reaction.

TABLE I

THE RATE OF REARRANGEMENT OF HYDRAZOBENZENE IN ETHANOL AT 0°

Run	Molarity of HCl	$k \times 10^2$, min.$^{-1}$[a]
5	0.0994	4.51
6	.0987	4.53
7	.0975	4.46
8	.0985	4.15
9	.0987	4.55
10	.0990	5.07
12[b]	.0956	4.12
13[b]	.0931	4.09

[a] Pseudo first-order rate constant. [b] Runs with deutero compound.

(4) N. Kornblum, G. D. Cooper and J. E. Taylor, THIS JOURNAL, **72**, 3013 (1950).

There existed the possibility that mechanisms A and C could be distinguished unambiguously by another device. In mechanism A the products of the reaction are determined in discrete steps which follow the rate-determining step. Since at some stage proton removal must be involved these *might* show an isotope effect. If this were the case the ratio of benzidene to diphenyline in the product mixture should be influenced by the introduction of deuterium in the *para* position of one of the rings. We used Carlin's method to determine the benzidene:diphenyline ratio and obtained the results reported in Table II. The agreement with the results of the earlier workers is excellent and there is no significant change in the product distribution when the deutero compound is employed as the substrate.

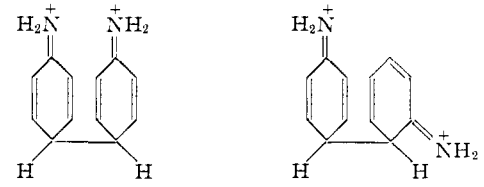
TABLE II

ANALYSIS OF REACTION MIXTURES

Run	Benzidine, %	Diphenyline, %
1	69.7	30.4
2[a]	68.3	31.9
2[a]	70.1	29.8

[a] Runs with deutero compound.

This indicates that the products must be determined in transition states which may be represented partially by structures II and III.



(9)

II, benzidine formation III, diphenyline formation

The above structures are drawn in such a way as to emphasize the similarity between the rearrangements and electrophilic aromatic substitution. This similarity is dramatized by the fact that aromatic nitration and bromination have been shown to be insensitive to the substitution of tritium for protium at the seat of the displacement.[6]

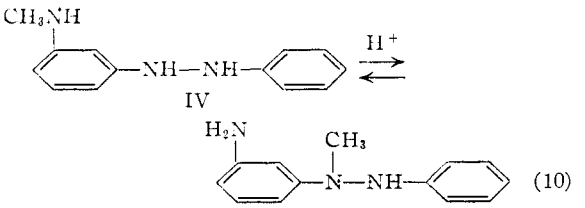
Despite the fact that the transition states for the benzidine and diphenyline rearrangements can now be described with unusual precision, we cannot as yet distinguish unambiguously between stepwise and completely concerted mechanisms. We can only specify that if the reaction does proceed in steps there must be only minor variations in the energy of the rearranging system subsequent to arrival at the transition state in which the second proton is attached to nitrogen.

(5) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(6) L. Melander, *Arkiv. Kemi*, **2**, 211 (1950); *Nature*, **163**, 599 (1949).

Despite the failure of what might have been a specific test for the stepwise mechanism we are still inclined to favor it. First of all the fact that the second conjugate acid may be isolated under proper conditions indicates that its existence as a discrete intermediate under rearrangement conditions is energetically reasonable. A second reason is the insensitivity of the benzidine:diphenyline ratio to external reaction conditions.

It is difficult to see how similar changes can lead to the formation of II and III if the formation of these transition states is synchronous with the breaking of the nitrogen–nitrogen bond. If a rotation of the two halves of the molecule with respect to each other is to precede the formation of the new bonds, one is forced to a description of the process which is very similar to that suggested by Dewar.[7] As has been pointed out previously,[2] the binding force required to maintain contact between the two fragments during the rotation is not obvious if this rotation is to occur with the doubly charged intermediate. It is our understanding that Prof. Dewar has suggested that the first conjugate acid is equilibrated with a singly charged π-complex and that the rate-determining step is the attachment of the second proton to the π-complex. In view of the limitations which we have placed upon the mechanism, Dewar's suggestion must be given serious consideration. The mechanism is fortunately subject to a specific test since it would predict that the rearrangement of suitably substituted aminohydrazobenzenes such as IV should occur more rapidly than rearrangements of the benzidine type in acid solution.



(10)

Experimental

Deuterohypophosphorus Acid.—The method used was a modification of that of Alexander and Burge.[8] Thirty per cent. commercial hypophosphorous acid was concentrated by evaporation below 100° to a purity of 99% as indicated by density measurements. Forty-four ml. of the concentrated acid was added to 50 g. of 99.8% deuterium oxide and the solution was allowed to stand at room temperature for 30 hours. The resulting solution was then concentrated again and the exchange procedure was repeated with the residue. A sample from the resulting solution was concentrated and the residue was submitted for infrared analysis. The spectrum, which was determined in a capillary cell, showed a new intense maximum at 1720 cm.$^{-1}$ which was somewhat stronger than the P–H peak at 2380 cm.$^{-1}$. The relative intensities of the two bonds were read from a common base line and the results indicated that at least 60% exchange had been accomplished.

***p*-Deuteronitrobenzene.**—The method of Alexander and Burge was followed in detail. A solution was prepared from 50 g. of deuterium oxide, 40 ml. of concentrated hydrochloric acid and 13.8 g. of *p*-nitroaniline. This solution was cooled to −5° and a solution of 7.2 g. of sodium nitrite in 17.5 ml. of water was added to it over a period of an hour. The solution was filtered and cooled again to −5°. The deuterohypophosphorous acid described above was precooled and added to the diazonium salt solution at a rate such that the temperature was maintained below 0°. The resulting solution was allowed to stand in a refrigerator for 40 hours. The solution was then extracted with ether and the extract was washed with aqueous sodium hydroxide, dried, and concentrated on a water-bath. Distillation of the residue gave 5.04 g. of nitrobenzene (42%).

***p,p'*-Dideuterohydrazobenzene.**—A sample of 4.4 g. of the deuterated nitrobenzene was reduced by the method of Fischer.[9] The product was recrystallized from hot ethanol, m.p. 128–129°, yield 2.84 g. (86%).

Deuterium Analysis.—The nitrobenzene was burned in air in a combustion tube packed with cupric oxide and lead dioxide. The water was collected in a Dry Ice trap. Two drops of the water were added to calcium metal and the gas evolved was admitted to the ion chamber of a mass spectrometer. Two consecutive determinations gave values of 0.088 and 0.10 for the D:H ratio in the gas. In the first determination unreacted water was observed and the first result would furthermore be influenced by the "memory" of the instrument. The second result is believed to be accurate to 2%.

Kinetic Runs.—The method of Cohen and Hammond[3] was used with slight modification. A solution prepared from concentrated hydrochloric acid and absolute ethanol was placed in the bottom of the flask and a weighed sample of hydrazobenzene was placed in the reservoir. The flask was then flushed with nitrogen, closed off, and immersed in the ice–water-bath for one hour. The contents then were rapidly mixed. Sampling and analysis for unreacted hydrazobenzenes were carried out as previously described.

All runs gave a reasonable fit to the first-order rate law except that extrapolated zero time concentrations were all smaller than the calculated values. It is believed that this is due to the occurrence of some rearrangement during the equilibration period. That this was not observed in the earlier work is probably associated with the fact that the vapor pressure of hydrogen chloride over the ethanol solution is higher than over a solution in 70:30 ethanol–water. This would permit some transfer of hydrogen chloride to the reservoir during the equilibration period.

Product Distribution.—The analytical method was that of Carlin, *et al.*[1] The rearrangement was carried out for one hour under conditions identical to those of the kinetic runs and the absorbancy of the product mixture was measured at 245, 270 and 285 mμ. Using the extinction coefficients reported by Carlin the values for benzidine and diphenyline concentrations were found as reported in Table II. As would be expected, the concentration of hydrazobenzene was undetectably small.

Acknowledgments.—We are indebted to Dr. Harry Svec who carried out the isotopic analysis and to the Ames Laboratory for the use of the mass spectrometer for this work. We are similarly indebted to Mr. Richard Hedges and to the Iowa State Institute for Atomic Research for the infrared analysis.

AMES, IOWA

(7) M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946); "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, Chapt. 11.

(8) E. R. Alexander and R. E. Burge, Jr., THIS JOURNAL, **72**, 3100 (1950).

(9) E. Fischer, "Anleitung zur Darstellung organischen Präparate," Williams and Norgate, London, 1909, p. 41.