acid, p-$CH_3C_6H_4\overset{+}{N}H$. We doubt that in a hydroxylic solvent either of the latter species would survive long enough to react selectively with the hydrazo compounds.[12]

(12) Experiments designed to show whether or not arylhydroxylamines will oxidize hydrazoarenes have been carried out but are not definitive at the present time because extensive disproportionation and self-condensation of the hydroxylamines occurs under the reaction conditions.

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Mechanism of the Benzidine Rearrangement. VII.[1] Rearrangement of *m*-Hydrazoaniline[2]

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The rate of rearrangement of *m*-hydrazoaniline to 2,2′-diaminobenzidine is inverse first order with respect to hydrogen ion concentration, indicating that one proton is involved in the rate-determining step of the reaction. The compound has been prepared with excess N^{15} in the hydrazo linkage; rearrangement of this compound gives products in which varying amounts of randomization of the isotopic label have occurred. The extent of randomization increases as the acidity of the medium is increased. The results indicate the cleavage of some first conjugate acid produces an intermediate which may either collapse to products or add a second proton to give a totally symmetric system. The first intermediate is probably the unsymmetrical π-complex suggested by Dewar[4] and the second has the properties expected of a complex between a pair of cation radicals. A completely concerted mechanism for this benzidine rearrangement is disallowed by the data.

The benzidine rearrangement and related transformations have long intrigued the imaginations of organic chemists.[5] Three general types of mechanism have been suggested. *Concerted processes*, in which bond making and bond breaking are synchronous, have been suggested in various forms. For example, Hammick and Mason[6] suggested that the various products, benzidines, semidine, and diphenylines, are all formed by independent, concerted transformations. Brownstein, Bunton, and Hughes[7] have suggested a "cart wheel" mechanism which is really a series of concerted rearrangements. Dewar[4,8] has long supported the view that the key step in the various reactions involves formation of a π-complex between the fragments, $\overset{+}{N}H$ and $ArNH_2$, formed by heterolytic fission of the N–N bond of the hydrazo linkage. When it was demonstrated that the rate of rearrangement of hydrazobenzene depends upon the square of the acid concentration,[9] Dewar modified his original suggestion by introduction of an additional stage in the over-all process. The Dewar mechanism can be formulated as follows.

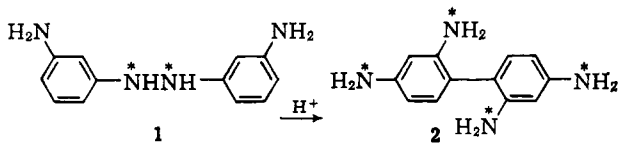
$$ArNHNHAr + H^+ \rightleftharpoons Ar\overset{+}{N}H_2NHAr$$

$$Ar\overset{+}{N}H_2NHAr \rightleftharpoons ArNH_2 \cdot ArNH^+$$

$$ArNH_2 \cdot Ar\overset{+}{N}H + H^+ \longrightarrow \longrightarrow \text{products}$$

In 1903 Tichwinsky[10] suggested that the rearrangement involves dissociation of the hydrazo compound to give free radicals followed by various coupling reactions of the radicals. Repeated demonstration of the intramolecular character of the rearrangements has led to rejection of the radical mechanism on the basis of the belief that, if free radicals are produced, cross coupling should occur in at least some systems. The radical mechanism can be resurrected only if it is presumed that coupling can occur only with geminate radical pairs produced by decomposition of a molecule of hydrazoarene (or its conjugate acids). Dewar[4] has rejected this version of the mechanism on the grounds that cage effects should be negligible when the geminate radical pair are both positively charged. Obviously two requirements must be met if the radical-pair mechanism is to be defended. First, Dewar's criticism of the mechanism must be faced and, second, some reasonable mechanism must be devised to account for the failure of radicals which do escape from cage to recombine. At least partial experimental insight into the first problem is provided by the observation that geminate recombination is an important factor in the decomposition of doubly charged azoamidinium ions.[11] A possible explanation for the failure to see recombination of any but geminate radical pairs may be found in the disproportionation reactions which frequently accompany the various rearrangements. Although no definitive description of this process can now be given, possibilities are discussed in detail elsewhere.

We felt that the character of intermediate stages in the rearrangement might be better defined by a study of the fate of the nitrogen label in *m*-hydrazoaniline-$N^{15}HN^{15}H$ (**1**, HzA). The compound undergoes acid-catalyzed rearrangement to 2,2′-diaminobenzidine, **2**.



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Degradative studies suitable for determination of the distribution of the label between the *ortho* and *para* positions of 2 have been developed.

Experimental

Potassium Nitrate-N^{15}.—Potassium Nitrate-N^{15} was prepared by the neutralization of 6.15 ml. of 5.41 *F* nitric acid-N^{15} (Isomet Corporation) of 99.7% isotopic purity. The end point was determined with a pH meter. A solution of 3.38 g. of potassium nitrate in 25 ml. of water was added to the neutralized solution which was then evaporated to dryness to give 6.71 g. of potassium nitrate. The nitrogen-15 content was approximately 50%.

Methyl *m*-Nitrobenzoate-N^{15}.—A solution to 6.71 g. (0.066 mole) of potassium nitrate-N^{15} in 30 ml. of concentrated sulfuric acid was added dropwise over a 1-hr. period to 9.00 g. (0.066 mole) of methyl benzoate. The resulting mixture was stirred for an additional 90 min. and then poured onto 50 g. of ice. The precipitated solid was separated by filtration and stirred for several hours at 0° in 9 ml. of methanol. The *meta* isomer, which was separated by filtration, weighed 8.57 g. (72% yield), m.p. 79°.

***m*-Nitrobenzoic Acid-N^{15}.**—The 8.57 g. of methyl *m*-nitrobenzoate-N^{15} was added to 3.8 g. of sodium hydroxide in 20 ml. of water which was then heated until solution was completed. The solution was heated for an additional 5 min., after which time it was cooled to room temperature and poured into 20 ml. of cold concentrated hydrochloric acid. The resulting white precipitate was separated and dried to give 7.57 g. (yield, 96%).

***m*-Nitroaniline-N^{15}-O_2.**—The 7.57 g. (0.054 m.) of *m*-nitrobenzoic acid-N^{15} was dissolved in a mixture of 30 ml. of chloroform, 15 ml. of concentrated sulfuric acid, and 11 ml. of 30% oleum. A total of 3.90 g. (0.064 mole) of sodium azide was added to the stirred mixture which was then refluxed for 3 hr., cooled to room temperature, and poured onto 100 g. of ice. The resulting solution was neutralized with a concentrated solution of sodium hydroxide and the precipitate was separated by filtration. The dried *m*-nitroaniline-$N^{15}O_2$ weighed 5.40 g. (86.5% yield), m.p. 111.5–111.8°. The filtrate was extracted with ether which was then dried with magnesium sulfate. Removal of the ether left a residue which was sublimed to give 0.34 g. of a yellow-orange solid, m.p. 80–112°. This solid was dissolved in dilute hydrochloric acid and reprecipitated by the addition of aqueous sodium hydroxide to give 0.24 g. of *m*-nitroaniline-$N^{15}O_2$, m.p. 110–111°.

***m*-Phenylenediamine-N^{15}.**—*m*-Phenylenediamine was prepared by the method of Pietra.[12] A solution of 0.161 g. of *m*-nitroaniline-$N^{15}O_2$ in 3 ml. of absolute ethanol and 0.2 ml. of hydrazine hydrate was heated to 40–50°. To this was added in small portions a total of 5 mg. of 5% palladium on carbon. The mixture was then heated at 80° until gas evolution ceased and the solution appeared colorless. Filtration, removal of the solvent under vacuum, and sublimation of the residue gave 83 mg. (68% yield) of the desired product, 75 mg. of which had m.p. 62.8–63.1°, lit. 62.8°.

***m*-Hydrazinoaniline-$N^{15}HN^{15}H$.**—*m*-Hydrazinoaniline-$N^{15}HN^{15}H$ (HzA) was prepared by the electrolytic reduction of *m*-nitroaniline-$N^{15}O_2$.[13] A porous porcelain cylinder was placed in a 1-l. beaker. The cathode, which was a cylinder of platinum gauze, was placed inside the cylinder while a lead plate which served as the anode was placed between the wall of the beaker and the porcelain cup. The anode was connected directly to the current source while the cathode was connected to the source through an ammeter and a 40-ohm variable resistor. A solution of 2.0 g. of *m*-nitroaniline-$N^{15}O_2$ and 2.5 g. of sodium acetate in 20 ml. of water and 140 ml. of 95% ethanol was placed inside the porcelain cylinder while a concentrated sodium carbonate solution was placed in the anode compartment. Four amperes of current were applied for 60 min. Ethanol was added occasionally to maintain the volume of the boiling solution. The reaction mixture was then cooled by an external application of ice–water and and 2.5 amp. were applied for another 70 min. The resulting mixture was filtered to give 0.76 g. of *m*-hydazoaniline-$N^{15}HN^{15}H$, m.p. 151–158°. The filtrate was treated with an equal volume of water and concentrated to give 0.34 g. of crude *m*-azoaniline (AzA). A clean electrode surface and the stipulated amount of sodium acetate were necessary for complete reduction. In one reduction of labeled material only AzA was formed. The reduction to HzA was completed by bubbling hydrogen through a solution of 60–70 mg. of AzA in 5–10 ml. of ethanol to which platinum dioxide had been added. When the mixture became colorless, it was filtered. The resulting solution was then rearranged under the desired conditions.

2,2′-Diaminobenzidine Tetrahydrochloride.—A 0.4–0.5 g. sample of HzA in 5–10 ml. of glacial acetic acid was heated and then treated with hydrogen chloride. The resulting mixture was treated with ethanol and more hydrogen chloride to complete the reaction and the precipitation of the hydrochloride salt of 2,2′-diaminobenzidine. Approximately 90% yields were generally obtained. The salt could be purified by recrystallization from an ethanol–water–hydrochloric acid solution. The neutralization equivalent of the salt was found to be 90.7 as compared with a theoretical value of 90.0 for the tetrahydrochloride of diaminobenzidine. The ultraviolet spectrum of the neutralized salt was the same as that of the product obtained from the rearrangement of HzA in ethanol.

2,7-Diaminocarbazole Dihydrochloride.—2,7-Diaminocarbazole was prepared by the method of Taüber.[14] A solution of 0.100 g. of the hydrochloride of diaminobenzidine was heated in 2–4 ml. of 6 *M* hydrochloric acid for 10 hr. at 180–190°. The product solution was heated to dryness and the resulting solid was dissolved in a few milliliters of water and purified by adding zinc dust and concentrated hydrochloric acid in small portions. The light yellow solution that was obtained on filtration was treated with a few more milliliters of concentrated hydrochloric acid to precipitate the dihydrochloride of the diaminocarbazole. This salt could be further purified by recrystallization from ethanol–ether. Greater than 90% of the theoretical chloride content was recovered as silver chloride from 23.5 mg. of the acid salt of the carbazole. As high as 97% of the theoretical nitrogen content could be obtained by a Kjeldahl conversion of ammonia. The ultraviolet spectrum of the carbazole showed maxima at 3300 and 2425 Å., a shoulder at 2600, and a minimum at 2850 Å. The spectra of the carbazole obtained from the numerous conversions of diaminobenzidine were used as an indication of the purity of the carbazole. The diaminocarbazole could be converted in low yields to N-nitrosocarbazole by diazotization with nitrous acid and subsequent reduction with hypophosphorous acid.

Azobenzene-N^{15}.—*m*-Azoaniline-N^{15}=N^{15} was deaminated to azobenzene-N^{15} by diazotization with nitrous acid and subsequent reduction of the diazonium salt with hypophosphorous acid. A typical deamination involved dissolution of 50 mg. of AzA in several milliliters of water which contained 0.09 ml. of concentrated hydrochloric acid. The solution was cooled in ice–water and 32 mg. of sodium nitrite in a milliliter of cold water was added to the AzA solution by means of a dropper placed below the surface of the AzA solution. After about 10 min., 23 ml. of 50% hypophosphorous acid was added. The resulting solution was kept at near zero temperatures for 3–6 hr. The final mixture was extracted with ether which was then dried over calcium chloride. The ether was removed and the residue was sublimed at 35–40° and at a pressure of less than 1 μ. The best yields were about 25%. Direct addition of solid sodium nitrite resulted in much lower yields.

Sodium Hypobromite.—Sodium hypobromite was prepared by the procedure described by Rittenberg.[15] Half of a solution of 50 g. of sodium hydroxide in 75 ml. of water was added to a 200-ml. 3-necked round-bottomed flask immersed in an ice bath. Then 14–15 ml. of bromine was added over a 10-min. period to the rapidly stirred solution. The remainder of the sodium hydroxide solution was then added and the yellow mixture was filtered and stored in the refrigerator. After several days the solution was filtered to remove the sodium bromide which had precipitated.

Kinetics of the Rearrangement of HzA.—The dependence of the rate of rearrangement of HzA on acid concentration was determined by carrying out the rearrangement of 0.1-g. samples of this compound in 280 ml. of 95% ethanolic hydrogen chloride at 40.2–40.5°. The concentration of acid was varied from 0.01 to 0.0442 *F*. The reaction was found to be too slow at 0° to ob-

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serve any rearrangement over the period of 12–24 hr. The disappearance of HzA was followed by titration of residual hydrazoaniline with Bindschedler's green.

One reaction was carried out in a solution which was 0.002 *F* total acid. The observed first-order rate constant was 1.84×10^{-2} min.$^{-1}$, which corresponds to a half-life of 37.6 min. A 67.21-mg. sample of HzA was used, making the concentration 1.12×10^{-3} mole/l. As the concentration of HzA and total acid were very nearly the same, the concentration of free acid and a corrected rate constant could not be accurately calculated.

Procedure for the Determination of the N^{15} Content of the Various Compounds.—The analytical procedure followed was that described by Rittenberg.[15] The procedure involves conversion of the nitrogen of the organic compounds to ammonia by the Kjeldahl method. The ammonia was then trapped in dilute hydrochloric acid. The resulting solution was concentrated to a few milliliters and then mixed with 2 ml. of sodium hypobromite solution in the evacuated collection apparatus. Nitrogen was evolved and then compressed into a 10-ml. glass bulb with a modified Toeppler pump. The mercury column was lowered a few centimeters below the neck of the bulb which was then pulled off by application of a torch. The other end of the bulb was equipped with a 14/35 joint and a break seal. The samples were analyzed with a mass spectrometer (Consolidated Electrodynamics, Model 21-620). The formula used to calculate the per cent of N^{15} was the following.

$$\% N^{15} = \frac{N^{29} + 2N^{30}}{2(N^{28} + N^{29} + N^{30})}$$

The heights of the peaks at 28, 29 and 30 were used directly to measure the abundance of the various isotopes. The N^{28} peak was corrected for air contamination by measuring the peak at mass 32. This peak was multiplied by 4.9 to give the contamination of the N^{28} peak with atmospheric nitrogen. This factor was determined from the ratio of the peak heights at 28 and 32 of a sample of ordinary air.

Conversion of Nitrogenous Compounds to Ammonia.—An apparatus identical to that used by Rittenberg[15] was used for generation and collection of ammonia. All of the compounds that were analyzed, except diaminocarbazole, were dissolved in 3 ml. of concentrated sulfuric acid to which had been added 1 g.

TABLE I

KJELDAHL CONVERSION OF *m*-NITROANILINE TO AMMONIA

No.	Wt. of sample, mg.	Wt. of dextrose, mg.	Digestion time, hr.	N, mg. Caled.	N, mg. Found
1	5.27	70	1	1.08	0.95
2	5.32	70	3	1.08	1.01
3	5.50	97	3	1.11	0.97
4	5.30	65	10	1.07	0.91
5	5.13	50	10	1.04	1.05
6	5.54	50	12	1.19	1.09

TABLE III

KJELDAHL CONVERSION OF AZOBENZENE

No.	Wt. of sample, mg.	Wt. of dextrose, mg.	Wt. of selenium, mg.	Digestion time, hr.	N, mg. Caled.	N, mg. Found
1	6.77	68		10	1.04	0.41
2	6.72	55		3	1.03	.26
3	6.50	70	15	10	1.00	.98
4	6.39	70	16	12	0.982	.97

period the solutions were cooled, treated with 25 ml. of water, and neutralized with 40% sodium hydroxide. The ammonia was driven off by heating the solution with a gentle air stream passing through the mixture and into a flask containing 25 ml. of 0.01 *F* hydrochloric acid. The heating process was carried out for about 45 min. although only about 5 min. was required to turn the originally blue or green mixture to a dirty brown color. The final hydrochloric acid solutions were titrated with 0.01409 *F* sodium hydroxide. The labeled samples were converted under the conditions which gave the best recovery of ammonia. Practice conversions were not carried out on *m*-phenylenediamine. The labeled *m*-phenylenediamine was treated under the same conditions as was *m*-nitroaniline.

Rearrangement of HzA-N^{15}H-N^{15}H.—Weighed amounts (60–70 mg.) of HzA-N^{15}H-N^{15}H were rearranged in ethanolic hydrogen chloride at 40.2–40.5°. The concentration of acid was varied and the rearrangements were carried to 97–99% completion. Reaction times were 5 hr.–14 days, depending on the acid concentrations. The solvent was removed under vacuum and the residue that remained was converted to diaminocarbazole by the procedure described earlier.

Partial Rearrangement of HzA-N^{15}H-N^{15}H and Conversion of the Unrearranged HzA to AzA.—Solutions of HzA-N^{15}H-N^{15}H (0.100 g.) were allowed to react for one half-life. The solutions were partly neutralized and treated with solutions of ethanol containing weighed amounts of Würster's blue perchlorate calculated to be equivalent to unchanged HzA. Solvent was then removed and the residue was treated with about 5 ml. of water. Some of the hydrochloride of AzA did not dissolve and was separated by filtration. That which did dissolve was precipitated by the addition of aqueous sodium hydroxide. The Würster base did not precipitate if the solutions were neutralized carefully. The combined AzA fractions were dissolved in dilute aqueous hydrochloric acid and precipitated by addition of aqueous sodium hydroxide. The dried AzA (35–40 mg.) was deaminated by the procedure described earlier.

Results

Kinetics of the Rearrangement of HzA.—The rearrangement of HzA was carried out in ethanolic hydrogen chloride (95% ethanol) and was followed by titration of unchanged HzA with aqueous solutions of Bindschedler's green. The rate data were fit to first-order plots. The results are given in Table IV.

A reaction was carried out with a total acid concentration of 0.002 *F*. The observed rate constant was 1.84×10^{-2} min.$^{-1}$, which corresponds to a half-life of 37.6 min. The value of "$k_0 \times [H^+]_c$" could not be

TABLE II

KJELDAHL CONVERSION OF DIAMINOCARBAZOLE TO AMMONIA

No.	Wt. of sample, mg.	Wt. of dextrose, mg.	Wt. of selenium, mg.	Wt. of copper sulfate·$5H_2O$, g.	Digestion time, hr.	N, mg. Caled.	N, mg. Found
1	5.00	60	12		1	1.065	0.805
2	4.80	79	15		3	1.022	0.902
3	4.92	91	18		12	1.048	0.972
4	4.95	100	20	0.32	12	1.053	1.010
5[a]	4.38	77	18	.30	14	0.682	0.614
6[a]	4.02	73	15	.28	14	0.625	0.532

[a] No. 5 and 6 were run on the dihydrochloride rather than on the neutral base.

of potassium sulfate and a crystal of copper sulfate pentahydrate. Dextrose and selenium were used in a number of the conversions. The amounts of the various compounds used are listed in the Tables I–III. The mixtures were digested at 350–380° for various time intervals. The samples which contained N^{15} were digested for 12–15 hr. Diaminocarbazole was digested in 5 ml. of concentrated sulfuric acid to which had been added 0.2–0.5 g. of copper sulfate pentahydrate. After the digestion

TABLE IV

RATE DATA OBTAINED FROM THE REARRANGEMENT OF HzA AT 40.2–40.5° IN 95% ETHANOL SOLUTION[a]

Run no.	Total acid × 10^2	$[H^+]_0 \times 10^2$[b]	$k_0 \times 10^4$[c] min.$^{-1}$	$k_0 \times [H^+]_0 \times 10^6$ min.$^{-1}$	$\mu \times 10^2$[d]	Half-life, hr.
1	1.47	1.14	5.50	6.26	1.94[e]	21.0
2	2.94	2.61	2.10	5.50	10.0[e]	55.0
3	2.94	2.61	2.49	6.50	10.0	46.3
4	1.47	1.13	5.50	6.21	10.0	21.0
5	4.42	4.08	1.67	6.83	10.0	69.2
6	2.21	1.88	3.30	6.20	10.0	35.0
7	1.00	0.67	8.71	5.84	10.0	13.3
8	2.94	2.61	2.32	6.05	10.0[e]	49.7
9	1.47	1.14	4.90	5.59	1.94[e]	23.5

[a] There is no HzA's initial concentration. [b] The added hydrogen ion concentration was corrected by assuming that HzA was virtually completely diprotonated in all runs. [c] k_0 is observed first-order rate constant. [d] μ is the ionic strength. [e] Lithium chloride was added in runs 1, 2, and 9; lithium perchlorate was added in the other five runs.

calculated because a lack of knowledge of the equilibrium constants for the protonation of the amino groups of HzA prohibited determination of a corrected hydrogen ion concentration, $[H^+]_c$.

While the data are not highly accurate, the rate of rearrangement clearly exhibits an inverse dependence upon hydrogen ion concentration. The maximum variation of observed rate constants is greater than fivefold while the maximum deviation of the corrected rate constants is only about 20%. The average deviation of the corrected rate constants is approximately 6%. The inability to obtain highly reproducible rate data is a consequence of the kinetic procedure. Exact endpoint determination is difficult as the color of the solution changes from yellow (*m*-azoaniline) to the green (Bindschedler's green). Moreover, the titrant solution is not completely stable over the period of time required for completion of some of the runs.

If variation of the ionic strength has affected the rearrangement, the effect is within the experimental error of the rate data.

Total N^{15} Content of HzA and N^{15} Content of the Hydrazo Linkage.—The analytical procedure that was used involved conversion of the nitrogen of the various samples to ammonia. The ammonia was trapped in dilute hydrochloric acid and was then oxidized to nitrogen with sodium hypobromite. The nitrogen was analyzed with a mass spectrometer.

The total amount of N^{15} that was incorporated into *m*-nitroaniline (and consequently into HzA) was determined. To eliminate any ambiguity that might result from incomplete recovery of the nitrogen of *m*-nitroaniline, the latter compound was converted to *m*-phenylenediamine. As the nitrogen groups of *m*-phenylenediamine are equivalent, incomplete conversion to ammonia could not confuse the results. The values that were obtained are listed in Table V. The attenuation of the mass spectrometer was set at ten for the N^{28} and N^{29} peaks and at three for the N^{30} peak.

TABLE V

N^{15} CONTENT OF *m*-NITROANALINE AND *m*-PHENYLENEDIAMINE

No.	Sample	% N^{15}[a]	Atoms of N^{15} per molecule
1	*m*-Nitroaniline	24.5	0.480
2	*m*-Nitroaniline	24.3	.486
3	*m*-Phenylenediamine	24.8	.496
4	*m*-Phenylenediamine	24.9	.498
5	*m*-Phenylenediamine	24.2	.484
6	*m*-Phenylenediamine	24.5	.490
	Av.	24.5 ± 0.2	0.491 ± 0.006

[a] This refers to the per cent of the total nitrogen of the molecule that is represented by N^{15}.

As the N^{15} contents of *m*-nitroaniline and *m*-phenylenediamine were found to be the same, the Kjeldahl procedure used to decompose *m*-nitroaniline may be assumed to be adequate.

Three different reductions (A, B, C) of labeled *m*-nitroaniline to HzA were carried out. In one of these (synthesis B) no HzA was formed and only *m*-azoaniline could be recovered from the synthetic mixture. The latter material was reduced to HzA by hydrogenation over platinum. Some of the HzA obtained from synthesis A was allowed to react for one half-life. The unchanged HzA was oxidized to *m*-azoaniline which was recovered and purified. *m*-Azoaniline was also isolated from the products formed in synthesis A. A third sample of the HzA obtained from synthesis C was oxidized to *m*-azoaniline. All of the *m*-azoaniline samples were deaminated to azobenzene and the N^{15} content of the latter compound was determined. The results that were obtained are listed in Table VI.

TABLE VI

N^{15} CONTENT OF AZOBENZENE OBTAINED FROM DEAMINATION OF VARIOUS SAMPLES OF *m*-AZOANILINE

Sample no.	% N^{15}	Atoms of N^{15} per molecule	Source[a]
7	48.3	0.966	A
8	49.6	.992	A
9	48.8	.976	A
10	47.9	.958	A
	Av. 48.7 ± 0.5	0.973 ± 0.009	
11	44.9	0.898	A_1[b]
12	45.8	.916	A_1
13	45.5	.910	A_1
	Av. 45.4 ± 0.3	0.908 ± 0.007	
14	47.1	0.942	B
15	47.2	.944	B
16	47.4	.948	B
17	48.6	.972	B
	Av. 47.6 ± 0.5	0.951 ± 0.01	
18	46.5	0.930	C
19	46.8	.936	C
20	47.2	.944	C
	Av. 46.8 ± 0.2	0.937 ± 0.05	

[a] Except as noted, the samples were prepared by oxidation of *m*-hydrazoaniline, from the indicated preparations, followed by deamination of the samples of *m*-azoaniline. [b] "A_1" refers to the *m*-azoaniline recovered from the solution of products from synthesis A.

TABLE VII

N^{15} CONTENT OF 2,7-DIAMINOCARBAZOLE SAMPLES

Reaction no.	Sample no.	Source of hydrazoaniline[a]	[HzA] × 10^3	[H^+] total	% N^{15}	Atoms of N^{15} per molecule
1	21	A	1.12	0.00200	26.7	0.801
1	22	A	1.12	.00200	26.9	.807
1	23	A	1.12	.00200	27.3	.819
1	24	A	1.12	.00200	26.8	.804
1	25	A	1.12	.00200	26.4	.792
					Av. 26.8 ± 0.2	0.805 ± 0.007
2	26	C	1.14	0.00200	27.0	0.810
2	27	C	1.14	.00200	27.1	.813
2	28	C	1.14	.00200	27.2	.816
2	29	C	1.14	.00200	26.2	.786
					Av. 26.9 ± 0.2	0.806 ± 0.010
3	30	A	1.17	0.0100	26.6	0.798
3	31	C	1.17	.0100	26.5	.795
					Av. 26.55 ± 0.005	0.797 ± 0.001
4	32	A	1.10	0.0100	26.2	0.786
4	33	A	1.10	.0100	26.6	.798
4	34	A	1.10	.0100	26.7	.801
					Av. 26.5 ± 0.2	0.795 ± 0.006
5	35	C	1.12	0.0200	26.1	0.783
5	36	C	1.12	.0200	26.2	.786
5	37	C	1.12	.0200	26.7	.801
5	38	C	1.12	.0200	26.0	.780
5	39	C	1.12	.0200	25.3	.759
					Av. 26.1 ± 0.3	0.782 ± 0.010
6	40	C	1.13	0.0200	26.1	0.783
6	41	C	1.13	.0200	26.1	.783
					Av. 26.1 ± 0.00	0.783 ± 0.000
7	42	A	1.17	0.0400	25.5	0.765
7	43	A	1.17	.0400	25.9	.777
7	44	A	1.17	.0400	25.5	.765
7	45	A	1.17	.0400	25.8	.774
7	46	A	1.17	.0400	25.5	.765
					Av. 25.6 ± 0.2	0.769 ± 0.005
8	47	B[b]	1.09	0.0400	25.3	0.759
8	48	B	1.09	.0400	25.3	.759
					Av. 25.3 ± 0.0	0.759 ± 0.000

[a] Refers to various reductions of *m*-nitroanaline, see Table VI. [b] *m*-Azoaniline was reduced to HzA with hydrogen and platinum dioxide.

The N^{15} of the hydrazo linkage of the sample of HzA (from synthesis A) that was rearranged to 50% completion is given by the N^{15} content of samples 7–10. The value of 97.3 atom per molecule is essentially the amount of N^{15} that should be present (*ca.* 98.0%) in the hydrazo linkage had no shuffling occurred during electrolytic reduction of *m*-nitroaniline-$N^{15}O_2$. This result shows that no equilibration of the nitrogen groups of HzA had occurred prior to its rearrangement.

As the N^{15} content of the azo linkage of the various samples of azobenzene is in most cases lower than the total possible content, some shuffling of the label must have occurred during the electrolytic reductions. The difference between the N^{15} contents of the samples obtained from sources A and A_1 indicates that HzA is formed by some path other than, or in addition to, direct reduction of *m*-azoaniline. The mass spectrometer was attenuated at ten for all three nitrogen peaks in the analyses of samples from azobenzene. As the N^{30} peak was attenuated at three in the analyses of samples from *m*-nitroaniline, a small error could be involved in comparison of the N^{15} contents of azobenzene samples with that of *m*-nitroaniline.

N^{15} Content of 2,7-Diaminocarbazole.—HzA-N^{15}-$HN^{15}H$ was rearranged at four different acid concentrations. The solvent was removed after 5–6 half-lives of reaction and the residue was converted to 2,7-diaminocarbazole. The N^{15} content of the carbazole was determined. The mass spectrometer was attenuated at ten, ten, and three for the N^{28}, N^{29}, and N^{30} peaks, respectively. The O^{32} peak was measured in all spectra with the attenuator set at three. The results that were obtained are listed in Table VII.

Discussion

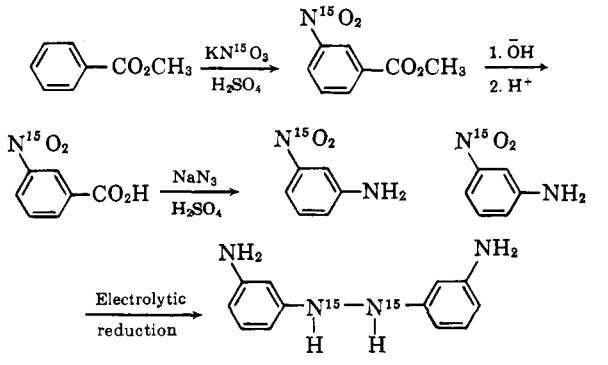
The kinetic data that are given in Table IV show that, in the acidity range studied, the rate of rearrangement of HzA is inversely proportional to the hydrogen ion concentration. Since HzA is undoubtedly nearly stoichiometrically converted to its second conjugate acid under the conditions of the reactions, this result means that the transition state of the reaction involves a monoconjugated acid of HzA.[16] Mixed order dependence upon hydrogen ion concentration has been observed in the case of *o*-hydrazotoluene[17] and other derivatives of hydrazobenzene[4]; so the fact that HzA, a hydrazobenzene derivative, apparently rearranges

(16) Since even the first basicity constant of hydrazobenzene is very small, as shown by attempts to carry out fast potentiometric titrations of the substance, we find it hard to believe that any appreciable fraction of hydrazoaniline is converted to a third conjugate acid.

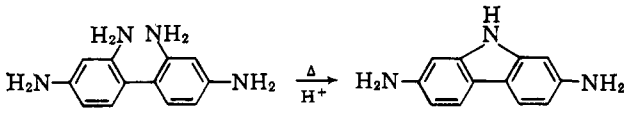
(17) R. B. Carlin and R. C. Odioso, *J. Am. Chem. Soc.*, **76**, 2345 (1954).

to a benzidine by way of a one-proton mechanism is not really surprising although we had not anticipated the behavior.

The synthesis of **1** with N^{15} in the hydrazo linkage was straightforward.

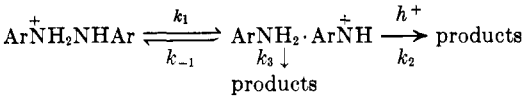


Then N^{15} content of the hydrazo linkage and consequently of the amino groups was readily ascertained. Determination of the N^{15} content of each of the amino groups of the rearrangement product (2,2′-diaminobenzidine) was also quite straightforward. 2,2′-Diaminobenzidine was converted to 2,7-diaminocarbazole by displacement of one-half of the *ortho* amino groups of the benzidine.



If kinetic isotope effects on ring closure are ignored, the difference between the N^{15} content of the carbazole and of the benzidine corresponds to one-half the N^{15} content of the *ortho* amino groups. Consequently, the N^{15} content of the *para* amino groups also is determined.

When this study was originally conceived we had hoped to test Dewar's suggestion[4] that a first step, heterolytic cleavage of the N–N bond, is reversible in rearrangements which show second-order dependence on acid concentration. Unchanged HzA was recovered from reaction mixtures which had been carried to 50% re-



action and was found to have undergone no shuffling of N^{15} between amino and hydrazo groups. Such rearrangement would have been expected if formation of the π-complex were reversible and if the complex were capable of undergoing rotation. However, since the kinetics indicate a one-proton process, the results do not negate the Dewar mechanism in the more usual cases. If the ratio k_3/k_2 is unusually large in this case, it is also reasonable to believe that k_3/k_1 is unusually large, *i.e.*, a step which is irreversible with hydrazobenzene becomes irreversible with HzA.

Rearrangement of unlabeled HzA gives only a single product from any combination of *ortho* and *para* coupling processes involving the less hindered nuclear positions.[18] Limited distinction among these processes can be obtained from the study of labeled **1**. If HzA rearranged with 100% *para* coupling (the benzidine rearrangement), all of the N^{15} of the hydrazo linkage would be retained in the diaminocarbazole which is formed from the rearrangement product. If 100% *ortho* coupling occurs (the 2,2′-diaminobiphenyl rearrangement), the diaminocarbazole would contain only 50% of the N^{15} of the hydrazo linkage. Rearrangement with 50% *ortho* and 50% *para* coupling (the diphenyline rearrangement) would lead to retention of 25% hydrazonitrogen in the carbazole. The exact values that would be observed for these limiting cases can be predicted from the data in Tables V and VI. A maximum of 0.98 and a minimum of 0.49 atoms of N^{15} per molecule of diaminocarbazole is predicted. The results that are given in Table VII are clearly intermediate between the values that are calculated for the two extreme cases.

The most striking feature of the data of Table VII *is the decrease in the N^{15} content of 2,7-diaminocarbazole that accompanies an increase in acid concentrations of the reaction mixtures.* The number of atoms of N^{15} per molecule of 2,7-diaminocarbazole can be used to calculate the amount of *ortho* coupling that has occurred in the formation of 2,2′-diaminobenzidine. Sample calculations are included in the Appendix. The results are summarized in Table VIII.

TABLE VIII

PER CENT *ortho* COUPLING AS A FUNCTION OF ACID CONCENTRATION

Run no.	Sample no.	$[H^+]_c$[a]	Source of HzA	Per cent *ortho* coupling[b]	Relative $[H^+]_c$
1	21–25	$\ll 0.002$	A	35.7	≤ 1
2	26–29	$\ll 0.002$	C	33.9	≤ 1
3	30–31	7.66×10^{-3}	A, C	37.6	24
4	32–34	7.80×10^{-3}	A	37.6	24
5	35–39	1.78×10^{-2}	C	39.2	56
6	40–41	1.77×10^{-2}	C	39.2	56
7	42–46	3.77×10^{-2}	A	43.2	119
8	47–48	3.77×10^{-2}	B	44.8	119

[a] The free acid concentration was corrected by assuming that HzA was completely diprotonated in all runs except the two at the lowest acidity. [b] Calculated using the average values of the per cent of N^{15} retained in 2,7-diaminocarbazole (see col. 4 of Table VII).

The amount of *ortho* coupling in the formation of 2,2′-diaminobenzidine increases as the acidity of the reaction mixtures is increased. Since the change is observed within the range of acidities in which the rates appear to be proportional to the concentrations of BH^+, it is clear that the rate-determining and product-determining steps must be different, implying that at least one metastable intermediate must be involved. The following equations incorporate the necessary features.

(18) A referee has pointed out that 2,2,2′,2′-tetraaminobiphenyl and 2,2,2′,4′-tetraaminobiphenyl also conceivably could be formed. Such a possibility exists since no attempts were made to establish an exact material balance although the absorption spectra of reaction mixtures indicate that only diaminobenzidene is formed. The principal product is not purified easily and is quite sensitive to air oxidation. If by-products are produced in *variable* yields, extension of the argument presented would require the same kind of interpretation as offered for the observed variations.

$$HzA + H^+ \overset{K_1}{\rightleftharpoons} HzAH^+$$

$$HzAH^+ + H^+ \overset{K_2}{\rightleftharpoons} HzAH_2^{+2}$$

$$HzAH^+ \xrightarrow{k_3} X \xrightarrow{k_4} \text{benzidine } (\sim 35\% \textit{ ortho} \text{ coupling})$$

$$k_5[H^+] \downarrow$$

$$Y \longrightarrow \text{benzidine } (50\% \textit{ ortho} \text{ coupling})$$

Although the free hydrogen ion concentration in runs 1 and 2 was very much smaller[19] than that used in run 3, the decrease in the amount of *ortho* coupling is rather small. Consequently, we believe that the lower limit is about 35% *ortho* coupling.

It would, of course, be interesting to estimate the upper limit to the extent of *ortho* coupling. The data are too limited to permit an accurate estimate of the value and it is not feasible to carry out experiments at very high acidities because the reaction rates become very slow. If a value for the upper limit is assumed, one can calculate the values expected at the two highest acidities from the data at low acidity and the assumption that the lower limit is 35%. Samples of such calculations are shown in Table IX. The assumption that the upper limit is 50%, *i.e.*, complete randomization of the N^{15} label, fits better than alternative, higher values. Since small errors in the measurement of N^{15}/N^{14} ratios would have a marked effect on the calculations, the results can be considered no more than suggestive.

TABLE IX

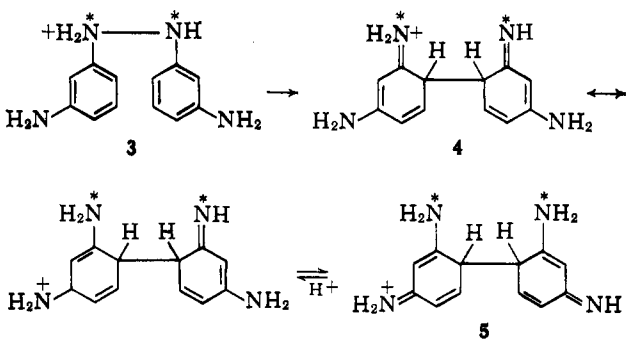
COMPARISON OF PREDICTED AND OBSERVED AMOUNTS OF *ortho* COUPLING[a]

Assumed maximum *ortho* coupling	[H][b] × 10^2	*ortho* Coupling, % Predicted	*ortho* Coupling, % Observed
0.50	1.78	40.2	39.2
0.50	3.77	43.0	44.0 ± 0.8
0.75	1.78	40.9	39.2
0.75	3.77	45.8	44.0 ± 0.8
1.00	1.78	41.1	39.2
1.00	3.77	47.1	44.0 ± 0.8

[a] Minimum possible *ortho* coupling taken as 35.8%. [b] Values taken from Table VIII.

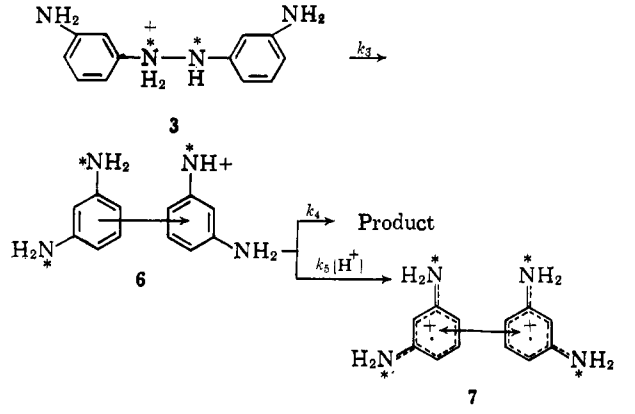
Mechanism

These observations are incompatible with the "cartwheel" mechanism of Brownstein, Bunton, and Hughes,[7] which would be written as follows.



As proton exchange among the various nitrogen atoms of the intermediates **4** and **5** should be more rapid than carbon–carbon bond breakage, all of the possible isomers of **4** would be equivalent. Accordingly, a minimum value of 50% *ortho* coupling would occur in the formation of 2,2′-diaminobenzidine. This prediction is incompatible with the observed minimum of 35%.

The following modification of the Dewar mechanism offers an explanation for the results.



Intermediate **6** is composed of one symmetrical and one unsymmetrical fragment, if free rotation occurs. If 20% of the *ortho* carbon atoms and 80% of the *para* carbon atoms of the unsymmetrical ring attack equally the *ortho* and *para* carbon atoms of the symmetrical ring, the observed requirement of a minimum of 35% *ortho* coupling would be satisfied. Addition of a proton to **5** would result in the formation of intermediate **6** which is composed of two completely symmetrical cation radicals. Formation of benzidine from **6** would thus occur with equal amounts of *ortho* and *para* coupling. Formation of a second, symmetrical intermediate is not *demanded* by the data but gives a reasonable explanation for the increased randomization caused by a second proton.

For those rearrangements which are second order in hydrogen ion concentration, the mechanism which has been advocated by Dewar required that attack of proton on the "π-complex" be rate (and product) determining. Banthorpe, Hughes, and Ingold[20] however have shown that at least in several cases (including hydrazobenzene) the second proton is probably transferred prior to the rate-determining step, at least under some conditions. For the Dewar mechanism to be compatible with these results, the protonation of the

(19) The value of $[H^+]_c$ for the run carried out in the presence of a total acid concentration of 2.00×10^{-3} *F* can be estimated from the kinetic data. We assume that the value of k_0 is given by the following expression.

$$k_0 = \frac{k_3}{1 + K_2[H^+]}$$

Ratios of the rate constants for any pair of runs would then be given by the following expression.

$$\frac{k_{01}}{k_{02}} = \frac{1 + K_2[H^+]_2}{1 + K_2[H^+]_1}$$

Ratio of the rate constant for the run at low acid concentration to that for the run carried out with a total acid concentration of 1.00×10^{-2} ($[H^+]_c = 6.70 \times 10^{-3}$) was 21.1. Introduction of these values gives the following expression for the value of the free acid concentration in the run at low acidity.

$$[H^+]_c = 0.000317 - \frac{20.1}{21.1K_2}$$

If a realistic value of 10^4 is assumed for K_2 the value of $[H^+]_c$ in run with dilute acid is calculated to be 2.17×10^{-4}. If K_2 is assumed to be 10^6, the value $[H^+]_c$ is calculated to be 3.17×10^{-4}. The latter value was used to calculate the numbers shown in the last column of Table VIII.

(20) D. V. Banthorpe, E. D. Hughes, and C. I. Ingold, *J. Chem. Soc.* 2386 (1962), and subsequent papers.

"π-complex" would have to lead to the formation of a second intermediate which would undergo transformation in the rate-determining step of the reaction. If the rearrangement of HzA proceeds by the same reaction sequence as the rearrangement of hydrazobenzene, the attack of proton on the "π-complex" would have to result in the formation of a second intermediate. A very likely candidate for the second intermediate would be a pair of cation radicals.

Observation that oxidation of diphenylamine,[21] α-naphthylamine,[22] and N,N-dimethylaniline[23] in acid solution leads to the formation of the corresponding substituted benzidines lends support to the proposed radical intermediate. As further evidence Hammond and Seidel[24] have observed that production of N,N'-diphenylbenzidine by acid-catalyzed rearrangement of tetraphenyltetrazine is accompanied by formation of by-products suggestive of the involvement of free radicals.

The probability that two positively charged cation radicals could form a "π-complex" might at first seem to be quite low; however, Hausser[25] has presented evidence that the Würster cation (the positively charged radical obtained by oxidation of N,N,N',N'-tetramethyl-*p*-phenylenediamine) can exist in such a form. The results of Hammond and Neuman[11] show that geminate recombination of pairs of cation radicals can be rather significant.

(21) H. Wieland, *Ber.*, **46**, 3296 (1913).

(22) Reverdin and de la Harpe, *Chemiker-Ztg.*, **16**, 1687; Beilstein, "Handbuch der Organische Chemie," Vol. 12, Springer, Berlin, 1929, p. 1213.

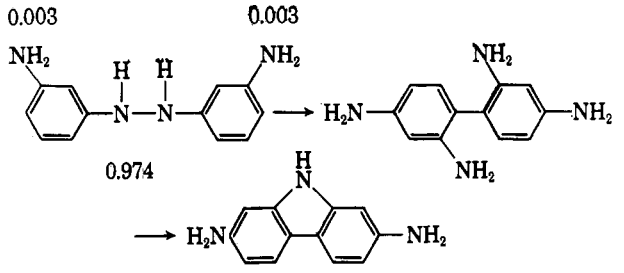
(23) W. Michler and S. Pattinson, *Ber.*, **14**, 2161 (1881).

(24) G. S. Hammond, B. Seidel, and R. E. Pincock, *J. Org. Chem.*, **28**, 3275 (1963).

(25) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

Appendix

Calculation of the amount of *ortho* coupling took into account the N^{15} that appeared in amino groups during reduction of *m*-nitroaniline. Since there are three coupling processes, *para–para*, *ortho–ortho*, and *ortho–para*, there is insufficient data to allow complete analysis of the problem; *e.g.*, a *para* coupling fraction of 0.5 could arise from either *ortho–para* coupling or from equal amounts of the other two processes. The following example, involving HzA from synthesis A, illustrates the method of calculation.



$$z = (0.974 + 0.003)x + \left(\frac{0.974}{2} + 0.006\right)y$$

where x = *para* coupling fraction, y = *ortho* coupling fraction, z = number of nitrogen atoms per molecule of 2,7-diaminocarbazole, and $x + y = 1$.

Acknowledgment.—We are grateful to Professor James N. Pitts and to the University of California at Riverside for the use of the mass spectrometer. The work was partially supported by the National Science Foundation.

Mechanisms of Photochemical Reactions in Solution. XVI.[1] Photosensitized Dimerization of Conjugated Dienes

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Conjugated dienes are dimerized by irradiation in the presence of various photosensitizers. Structural assignments have been made to the dimers of 1,3-butadiene, isoprene, and cyclopentadiene. Preliminary studies of the dimerization of the piperylenes and 2,3-dimethyl-1,3-butadiene have been made. Formally, all of the observed products are consistent with the addition of triplet diene to another molecule to form diallylic biradicals.

Photosensitized irradiation of 1,3-butadiene,[3] cyclopentadiene,[4] and isoprene[5] has been reported in preliminary form. This paper relates some details of these and related reactions with emphasis on assignment of structures of the products. Preliminary discussion of mechanistic considerations have appeared elsewhere.[3-5]

Results

Photosensitized dimerizations of conjugated dienes were carried out by irradiation of solutions or neat liquid dienes containing various carbonyl compounds. Different sensitizers gave products in varying relative amounts in some cases, but there was no instance in which a product formed in the presence of any one sensitizer was absent from the product mixture formed in the presence of another sensitizer. Reactions were run both on a preparative scale and in degassed, sealed tubes. The two procedures gave no detectable differences in product distributions.

1,3-Butadiene.—These products, **1**, **2**, and **3** are produced from the photosensitized dimerization of butadiene.[3] *trans*-1,2-Divinylcyclobutane (**1**) is the major product in most experiments. The *cis* isomer, **2**, is formed in small amounts in all experiments, while the amount of 4-vinylcyclohexene (**3**) varies from 43% to 2%. The composition of the product mixtures depends strongly on the sensitizer employed.[3,5]

(1) Part XV: G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.*, 63 (1963).

(2) (a) National Science Foundation Predoctoral Fellow, 1960–1963; (b) Du Pont Summer Fellow, 1962; Woodrow Wilson Summer Fellow, 1963.

(3) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83** 4674 (1961).

(4) N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962).

(5) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).