poured into an optical cell and was inserted in the spectrophotometer. Thus times at which absorption bands passed through their maxima were recorded and the spectra were rescanned until the reaction had gone to 60–90% of completion. Rate constants were obtained as usual. Reverse addition of reactants did not influence reaction rates as was demonstrated in preliminary experiments.

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Mechanism of the Benzidine Rearrangement. VI.[1] Rearrangement of *p*-Hydrazotoluene

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As was reported by Carlin and Wich[3] the reaction of *p*-hydrazotoluene in acidic ethanol produces the *o*-semidine and disproportionation products, *p*-toluidine and *p,p'*-azotoluene. Although more than the expected amount of toluidine is formed the excess is less than previously reported. A transient oxidizing agent of unknown structure is produced. Formation of the unknown oxidant is probably associated with the high yield of toluidine. Disproportionation to amine and azo compound has been shown to be an intermolecular process by inclusion of hydrazobenzene in reaction mixtures in which hydrazotoluene is undergoing rearrangement. In such experiments very little azotoluene is produced although toluidine and the semidine are produced in the expected amounts. It is inferred that an intermediate is reduced to toluidine by reaction with either hydrazo compound.

Carlin and Wich[3] carried out an investigation of the kinetics and products of the reaction of *p*-hydrazotoluene (HzT) in ethanolic hydrogen chloride. They showed that the rate of disappearance of HzT is second order with respect to hydrogen ion and first order with respect to HzT. Three products of the reaction, *p*-toluidine, *p*-azotoluene, and 2-amino,4′,5-dimethyldiphenylamine (an *o*-semidine), were reported by Carlin to account for approximately 40, 20, and 40% (by weight), respectively, of the starting material. This product distribution remained constant throughout each individual reaction and also was found to be invariant in the temperature and acidity ranges studied.

These results are typical for aromatic hydrazo compounds except for one point. Stoichiometric formation of the disproportionation products would require that equal weights (2 to 1 mole ratio) of *p*-toluidine and *p*-azotoluene be observed. However, the results indicated a 2 to 1 weight ratio of these compounds. If these data are correct, there must be a reducing agent (such as solvent) other than HzT which can be readily oxidized by the precursor of *p*-toluidine. Identification of the toluidine precursor might, by implication, lead to a better understanding of the mechanism of the benzidine rearrangement. Accordingly, a thorough investigation of the oxidizing properties of solutions of HzT in acidic ethanol and of the composition of the product mixture obtained from HzT was carried out. In conjunction with these experiments an investigation of the intermolecularity of the disproportionation reaction was conducted. The product studies were performed by employing the technique of isotope dilution. The kinetic measurements and product analyses of Carlin were repeated so that any discrepancy in results could be related to procedural rather than accidenta differences.

Experimental

***p*-Hydrazotoluene.**—Hydrazotoluene (HzT) was synthesized by the method of Carlin and Wich.[3] The crude HzT was separated from filtered zinc and zinc oxides by treatment with hot benzene. Large quantities of benzene had to be used to obtain reported yields.

***p*-Azotoluene.**—*p*-Azotoluene (AzT) was recovered from rearrangements of HzT and purified by recrystallization from ethanol, ethanol–water, and ethanol again. Sublimation at 60–70° and 1 μ sometimes was performed.

***o*-Semidine.**—This compound could be obtained most easily in a relatively pure state by the rearrangement of HzT in the presence of a limited excess of added hydrochloric acid. For example, a solution of 2.5 g. (0.0118 mole) of purified HzT, in 150 ml. of nitrogen-flushed 95% ethanol was initially treated with 0.5 ml. (0.006 mole) of concentrated hydrochloric acid. After 15–20 min. another 0.5 ml. of acid was added. The resulting solution was stirred for another 30 min., cooled with ice–water, and filtered to remove precipitated *p*-azotoluene. Fifty milliliters of water was then added to the filtrate and more *p*-azotoluene was deposited. The yellow-orange solid was separated and the resulting filtrate was neutralized with 2.5 *N* sodium hydroxide. The light orange-brown *o*-semidine which precipitated was separated and weighed 0.5 g. Purification was effected by recrystallization from ethanol–water, sublimation at 70° and 1 μ, and another recrystallization from ethanol–water. The wet product was dried under vacuum, m.p. 110°.

***p*-Toluidine.**—Practical grade *p*-toluidine was purified by four to five recrystallizations from 85–100° ligroin, m.p. 42–43°.

Bindschedler's Green.—Bindschedler's green was prepared by the method described by Dewar.[4]

Würster Blue Perchlorate.—The salt was prepared from N,N,-N′,N′-tetramethyl-*p*-phenylenediamine dihydrochloride by the procedure of Michaelis and Granick.[5]

***p*-Nitrotoluene-1-C^{14}.**—Forty milligrams of toluene-1-C^{14} having an activity of 0.5 mc. was distilled under vacuum into 20 ml. of purified reagent grade toluene contained in a receiver immersed in an acetone solid. This solution was transferred with numer-

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[1] Part V: G. S. Hammond, B. Seidel, and R. E. Pincock *J. Org. Chem.*, **28**, 3275 (1963).

[2] National Institutes of Health Predoctoral Fellow, 1961-1962.

[3] R. B. Carlin and G. S. Wich, *J. Am. Chem. Soc.*, **80**, 4023 (1958).

[4] M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946).

[5] L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).

ous washings to a 250-ml. volumetric flask which was then filled to the mark.

Thirty grams of the toluene was nitrated by the procedure described by Murray and Williams.[6] The components of the product solution were separated by vacuum distillation through a spinning-band column. Recrystallization of the *para* isomer from 95% ethanol gave 6.8 g. of product, m.p. 50–51°; yield, 15%.

p-Hydrazotoluene-4,4C$'^{14}$.—The *p*-nitrotoluene-1-C^{14} was reduced by the procedure of Carlin and Wich.[3] The scale was reduced by a factor of 17. The yield was 68.5%.

Hydrazobenzene.—Hydrazobenzene was prepared by a standard procedure.[7]

Ethanol-O-D.—Ethanol-O-D was prepared by the reaction of sodium ethoxide with deuterium oxide.

A mixture of 14 g. of freshly cut sodium, 55 g. of ethyl phthalate, and 2 l. of absolute ethanol was heated under reflux for several hours. The dried ethanol was then recovered by distillation. To 1300 ml. of the center cut of the distillate was cautiously added 155–160 g. of freshly cut sodium. The mixture was heated at the reflux temperature until all of the sodium had reacted. The excess ethanol was then removed first by distillation at atmospheric pressure and finally by distillation at about 0.01 mm. until no more ethanol was deposited in the Dry Ice traps. The neutralization equivalent of the residual sodium ethoxide was found to be 69.4, calcd. to be 68.1.

To 100 g. of heavy water (>99.5% D_2O) was added 110–120 g. of sodium ethoxide. The liquid was distilled under vacuum from the resulting sludge. The ethanol–water solution that was collected was then distilled through a spinning-band column and about 60 ml. of ethanol was collected at 78°. An infrared spectrum showed little or no O–H absorption and exhibited the expected O–D absorption.

Toluene-α-D$_3$-1-C^{14}.—The preparation has been described elsewhere.[8]

***p,p'*-Ditrideuteriomethylhydrazobenzene-4,4′-C^{14}** was prepared from toluene-α-D$_3$-1-C^{14} by the procedure used for preparation of radioactive HzT from radioactive toluene.

Measurement of Rearrangement Rates.—The kinetic procedure used by Carlin and Wich[3] was repeated carefully with but few modifications. A nitrogen purification train was constructed in which the nitrogen was passed over a copper pile heated to 450–500° and then through Fieser's solution. The gas was then passed through saturating solutions of ethanol and ethanol–hydrogen chloride of the same concentration as that to be employed in the rearrangement. The acid catalyst was prepared by diluting the calculated amount of standardized ethanol–hydrogen chloride to 50 ml. This solution was maintained at the temperature of the constant temperature bath and treated with nitrogen at the same time the other solutions were being flushed. The nitrogen treatment was continued for 1–2 hr., after which time 25 ml. of the catalyst solution was added to a volumetric flask. This flask was placed in the constant temperature bath for a few more minutes and then its contents were added to a solution of approximately 35 mg. of HzT in 250 ml. of 95% ethanol. Before the catalyst was added, the nitrogen was passed through ethanol, the ethanol–HzT solution, the ethanol–hydrogen chloride saturating solution, and finally through the catalyst solution. After the catalyst had been added, the nitrogen was passed from ethanol to ethanol–acid and finally to the HzT solution.

The rate of disappearance of HzT was followed by two methods. One was spectrophotometric method of Carlin and Wich.[3] The data of Carlin were used without any modifications to calculate the concentrations of the various components. The second method involved direct titration[4] of the HzT with aqueous solutions of approximately 150 mg. of Bindschedler's green per liter of water. Ten-milliliter aliquots were withdrawn, partly neutralized with aqueous sodium hydroxide, and titrated.

For all rearrangements for which the t_0 concentrations were obtained before the catalyst was added, the zero time intercepts of the first-order plots were significantly above the points for the initial concentrations. This result was attributed to the presence of the excess local acid concentration that occurred on addition of the catalyst. In support of this idea was the observation that the deviation was lowered by use of a lower acid concentration.

The use of water in the quenching solution seemed to give a shift in the absorption pattern. The calculated *p*-toluidine concentration was proportional to the amount of water and thus seemed to be in error. The use of sodium hydroxide in ethanol as the quenching solution (with no extra water) did not give this trouble and a decent check of the apparent product composition with that reported by Carlin was obtained. Table I gives apparent weight per cent composition of the various products after 5 hr. (5–6 half-lives) of rearrangement of the starting material at 0°.

TABLE I

PER CENT COMPOSITION OF THE PRODUCTS OF THE REARRANGEMENT OF HzT[a]

Run	Azotoluene, %	*p*-Toluidine, %	*o*-Semidine, %
1	22	40	38
2	19	41	41
3	21	40	39
4	20	41	39

[a] There is always some HzT left after 5 hr., but these compositions are calculated only on the basis of the total product and do not include starting material.

The best data were obtained when a fresh blank solution was prepared at the time of sampling the rearrangement solution. Distilled 95% ethanol was used in most of the rearrangements.

Kinetics and the Formation of the Würster Cation.—The oxidation of the Würster base in a residual solution from the rearrangement of HzT was followed by observing the increase in absorption of 6140 Å. Measurements were made with a Beckman Model DU spectrometer, the cell compartment thermostated at 26.3°. The various solutions containing HzT, and the Würster base were brought to this temperature before they were mixed. Prior degassing of the solutions did not affect the rate constants obtained. A typical reaction mixture was prepared by adding 10 ml. of 0.0133 *N* hydrogen chloride in ethanol and 5 ml. of a solution of 51.7 mg. of the Würster base in 10 ml. of ethanol to 4.6 mg. of HzT. Build-up of the cation did not occur until virtually all of the HzT had reacted. In a separate experiment it was shown that the Würster cation oxidized HzT rapidly. Two moles of dye were consumed by one mole of hydrazo compound.

Rearrangement of HzT in the Presence of N,N,N′,N′-Tetramethyl-*p*-phenylenediamine (Würster Base) Dihydrochloride.—Three milliliters of a solution of 93.3 mg. of HzT in 250 ml. of nitrogen-flushed 95% ethanol was added to one compartment of a three-compartment vessel. Five milliliters of a solution of 2.91 ml. of 1.5 *N* hydrochloric acid diluted to 250 ml. with 95% ethanol was added to the second compartment and 14.5 mg. of the Würster base was added to the third. The latter compound was always used as the dihydrochloride. The solutions were degassed five times and the Würster base was then dissolved in the acidic ethanol. The two solutions were then mixed. Within 30 min. the color of the solution had changed from yellow to a clear blue. The initial reaction mixture was 6×10^{-4} *M* in HzT, 7.7×10^{-3} *M* in the Würster base, and 1.1×10^{-2} *N* in added acid.

A control was run with no HzT. The solution was initially light blue and did not visibly darken. Two grams of HzT (1.7×10^{-2} *M*) was rearranged in 275 ml. of nitrogen-flushed ethanol that was 0.11 *f* in hydrochloric acid and 7.7×10^{-3} *f* in the Würster base. After 1 min. the yellow solution began to darken and after another minute the color was dark blue.

Stability of the Oxidizing Agent.—A solution of 5.0 mg. of HzT in 10 ml. of 0.0134 *N* hydrogen chloride in ethanol was prepared. After 26 min. this solution was neutralized with a solution of sodium ethoxide. Seventy-five minutes later 5 ml. of a solution, prepared from 49.8 mg. of the Würster base and 2 drops of concentrated hydrochloric acid in ethanol, was added. Color began to develop after an induction period of approximately 2 min. and a maximum absorbency (A_∞) of 1.20 was observed. The value of the extinction coefficient for Würster's blue perchlorate was determined to be 1.13×10^4. The concentration of HzT based on the final volume of solution was 1.57×10^{-3} mole/l. while final concentration of Würster blue was 1.1×10^{-4} mole/l.

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[6] A. Murray, III, and D. L. Williams, "Organic Syntheses with Isotopes," Interscience Publishers, Inc., New York, N. Y., 1958, p. 783.

[7] R. Adams and J. R. Johnson, "Laboratory Experiments in Organic Chemistry," The Macmillan Co., New York, N. Y., 1949, p. 359.

[8] J. S. Clovis and G. S. Hammond, *J. Org. Chem.*, **27**, 2284 (1962).

A solution of 5.3 mg. of HzT in 10 ml. of 0.0134 N hydrogen chloride in ethanol was prepared. After 90 min., 5 ml. of a solution of 50.8 mg. of the Würster base in 10 ml. of ethanol was added. A maximum absorbance of 0.600 was obtained. The concentration of HzT was 1.67×10^{-3} mole/l. while the final concentration of Würster blue was 5.3×10^{-5} mole/l.

Ten milliliters of 0.0133 f acidic ethanol was added to 14.8 mg. of HzT. After 35 min., 10 ml. of a solution prepared by dissolving 104.3 mg. of the Würster base (as the dihydrochloride) in 15 ml. of 0.0296 f sodium hydroxide in ethanol was added. After a total of 95 min., 20 ml. of 0.0133 f acidic ethanol was added. Increase in absorption at 6140 Å. did not occur until approximately 0.5 hr. had passed. A maximum of 0.052 was obtained. The original concentration of HzT was 1.74×10^{-4} mole/l.

Recovery of the Reaction Products in Isotope Dilution Analyses.—Approximately 35 mg. of HzT was rearranged at 0° in 275 ml. of 95% ethanol which was 0.015 f in hydrogen chloride. After 5 hr., AzT, p-toluidine, and o-semidine were added in 40-, 80-, and 80-mg. amounts, respectively. The ethanol was removed by distillation under vacuum and the residue was treated in 10 ml. of water. The resulting mixture was filtered and the orange AzT was dissolved in ether which was then dried with calcium chloride. The filtrate was neutralized with sodium hydroxide to precipitate o-semidine which was separated by filtration. This second filtrate was then extracted with ether and the extract was dried with sodium hydroxide.

The AzT was purified by chromatography over alumina with pentane and ether as eluents, sublimation at 60°, and finally recrystallization from 95% ethanol.

o-Semidine was purified by one or two careful fractional recrystallizations from ethanol-water and sublimation at 60–70° (1 μ). The resulting solid was white and melted in the range 108–110°.

p-Toluidine was recovered in two forms. One method involved removal of the ether to give crude p-toluidine, which was purified by sublimation at 30–40°, m.p. 42–43°. The second method involved the addition of 0.5 ml. of acetic anhydride to the dried ether solution. The solution was then heated to produce the anilide and to evaporate the ether. In one reaction the Würster base was added along with the three nonlabeled products. In this case the Würster base was separated from the anilide by bubbling hydrogen chloride through the ether solution. The filtered ether solution was concentrated to 1–2 ml. and water was added to dissolve the acetic acid and acetic anhydride, and to precipitate p-acetotoluide. The latter compound was easily purified by one or two recrystallizations from benzene.

Several rearrangements were carried out in the presence of a large excess of hydrazobenzene. After AzT, p-toluidine and o-semidine were added, the resulting solution was concentrated to 50–75 ml. at which point benzidine was precipitated by the addition of concentrated sulfuric acid. The filtrate from this mixture was concentrated to dryness and the residue was treated with 20–30 ml. of water. The resulting mixture was heated on the steam bath for several minutes and then filtered to remove azobenzene and azotoluene. These compounds were dissolved in ether and the solution was then dried with calcium chloride, concentrated and chromatographed over alumina with ether as the eluent. The ether was removed and the residue was sublimed at 40° (1 μ) to remove azobenzene and then at 60° to obtain AzT which was then recrystallized from ethanol. The filtrate from which azobenzene and azotoluene had been separated was neutralized with aqueous sodium hydroxide to precipitate o-semidine and some diphenyline. The solid material thus obtained was sublimed, fractionally recrystallized from ethanol–water, and finally sublimed a second time. The resulting solid melted in the range 108–110°. The filtrate that was obtained after o-semidine had been removed was completely neutralized and then extracted with ether. The ether solution was dried with sodium hydroxide and treated with 1 ml. of acetic anhydride. The solution was then concentrated to several milliliters and treated with water to precipitate the amides. The resulting solid was sublimed at less than 1 μ and about 110°. The p-acetotoluide which had sublimed was further purified by one or two recrystallizations from benzene.

Liquid Scintillation Counting.—The solvent system used in this work was comprised of a solution of 3.5 g. of 2,5-diphenyloxazole (PPO) and 0.1 g. of p-bis[2-(5-phenyloxazolyl)]benzene (POPOP) in 1 l. of toluene. The compounds studied in these experiments acted as fluors and quenchers. Therefore, data had to be obtained which would show the effect of the concentration of the various compounds on the scintillation rate. Toluene of a predetermined specific activity was used as a standard in calibration experiments. The samples to be counted were prepared by dissolving weighed amounts of the various compounds in 20 ml. of the toluene scintillation solution. They were then counted at 0° with a Tri-carb liquid scintillation counter (Packard Instrument Company). Reproducible data were determined on different days and a plot was made of the specific activity of the radioactive toluene $vs.$ milligrams of the substance added.

The weights of the samples of products from reactions of active HzT were chosen so as to correspond to the most reproducible or to the most nearly level portions of the calibration graphs. In six runs a 2-ml. aliquot was withdrawn after a reaction time of 5 hr. and just prior to the addition of the inactive diluents. This aliquot was checked by ultraviolet analysis to give the apparent product concentrations as determined by the method of Carlin and Wich.[3]

Rearrangement of HzT in Ethanol-O-D.—To a solution of 1 g. of HzT and 2 g. of sodium perchlorate in 50 ml. of nitrogen-flushed 95% ethanol-O-D was added 1 g. of the Würster base. This gave an approximate initial acid concentration of 0.084 f. After 20 min., 25 ml. of water was added and the resulting mixture was chilled and filtered free from the precipitated AzT, which weighed 0.30 g. The filtrate was treated with 2 ml. of concentrated ammonium hydroxide and 75 ml. of water to give another 0.23 g. of a light yellow precipitate. The light yellow filtrate was extracted with ether which was then dried with magnesium sulfate. The ether was removed and the resulting oil was dissolved in methanol–ether and passed over an alumina column. The column was eluted first with ether which removed the Würster base and then with methanol which removed p-toluidine. A few milligrams of pure p-toluidine were obtained by sublimation of the residue left after removal of the methanol. Infrared spectra were taken of all three fractions. No C-D absorption was observed.

Attempted Oxidation of the Würster Base with p-Tolylhydroxylamine.—To a solution of 0.125 g. of the Würster base dihydrochloride in 25 ml. of 95% ethanol was added 0.55-mg. of p-tolylhydroxylamine (prepared by the procedure used for the preparation of phenylhydroxylamine). The concentration of the Würster base was 2.11×10^{-2} M, of hydrogen ion approximately $2.11 \times 10^{-2} f$, and of p-tolylhydroxylamine 1.79×10^{-4} M. After 25 min. at 27° the absorption had increased only 0.05 units. Approximately 2 min. were required for a similar increase in absorption in the oxidation of the Würster base (2.11×10^{-2} M) by a solution prepared by the reaction of HzT (6.92×10^{-4} M) in the presence of $2.96 \times 10^{-2} f$ acid.

The Product(s) of Unknown Structure.—To a solution of 2.5 g. of purified HzT in 150 ml. of nitrogen-flushed 95% ethanol was added slowly 0.5 ml. of concentrated hydrochloric acid. After 15 min. another 0.5 ml. of acid was added. The initial concentration of HzT was 0.079 M and the total added acid concentration was 0.08 f. Solid p-azotoluene precipitated from the solution which was chilled in ice–water and then filtered. The clear orange filtrate was concentrated to dryness by removing the solvent under vacuum at room temperature. The residue was treated with 10–15 ml. of water and the mixture was then heated for a few seconds on a steam bath. The mixture was then filtered to remove the insoluble compounds. The filtrate was neutralized to precipitate a third, light colored solid fraction which was separated by filtration. The final filtrate was extracted with ether and the extract was then dried with either sodium hydroxide or potassium hydroxide. Removal of ether left a solid residue whose color depended upon the care taken in the performance of the individual steps of the procedure. In a series of eight experiments the four solid fractions accounted for an average of 26, 12, 20, and 31%, respectively, of the starting material.

The first solid fraction was readily identified as p-azotoluene by its melting point (140–145°) and infrared spectrum. If the material was slowly sublimed, a milligram or so of a brown residue remained. The residue generally contained some p-azotoluene and could account for but a trace of the total products.

The second solid fraction was seen by infrared analysis to be a mixture of p-azotoluene and the o-semidine. No absorption other than that which could be attributed to these two compounds was detected.

The infrared spectrum of the third fraction was essentially identical to that of pure o-semidine. Very weak absorption

TABLE II

YIELDS OF THE PRODUCTS FROM THE REARRANGEMENT OF HzT AS DETERMINED BY ULTRAVIOLET AND ISOTOPE DILUTION ANALYSIS

	Azotoluene, %			*p*-Toluidine, %[a]			*o*-Semidine, %		
Run	Isotope dilution	Isotope dilution cor.[b]	Ultraviolet	Isotope dilution	Isotope dilution cor.[b]	Ultraviolet	Isotope dilution	Isotope dilution cor.[b]	Ultraviolet
1	22.1	18.9	20.8	28.5	29.4	40.0	32.7	33.7	39.2
2	23.2	21.0		26.8	27.6		38.8	40.3	
3	23.2	20.8	18.8	27.6	28.5	41.0	41.4	42.7	40.2
4	23.2	20.9	20.5	27.4	28.3	39.4	38.3	39.5	40.2
5	21.2	18.7	21.1	28.8	29.7	40.4	35.7	36.8	38.5
6	22.7	20.3	20.4	28.1	29.0	39.7	38.2	39.3	39.9
Av.	22.6 ± 0.6	20.1 ± 0.9	20.3 ± 0.6	27.9 ± 0.6	28.8 ± 0.6	40.1 ± 0.5	37.5 ± 2.2	38.7 ± 2.4	39.6 ± 0.6

[a] Counted as *p*-toluidine. [b] These columns represent a corrected concentration for each constituent if it is assumed that the starting material contained 3% *p*-azotoluene. This assumption was derived from the ultraviolet data obtained from the t_0 aliquots.

appeared at about 1685 cm.$^{-1}$. This band was not present in spectrum of the pure *o*-semidine.

The infrared spectrum of the final fraction was very similar to that of *p*-toluidine. Absorptions not characteristic of *p*-toluidine were a small shoulder in the C–H stretching region and a weak band at about 1690 cm.$^{-1}$. The *p*-toluidine was slowly removed by sublimation at room temperature. The residue was in the form of an oil. In the numerus experiments that were performed the color of this oil varied from red to yellow. When the original reaction mixture had a dark color, or the work-up procedure had not been carefully followed, the oil was of a reddish color.

The infrared spectrum of the oil was taken. A strong carbonyl group was present in the 1680–1685-cm.$^{-1}$ region. Four strong C–H stretching bands from 2840–3020 cm.$^{-1}$ were present. Three of these bands were identical to those present in *p*-toluidine. The fourth band (2963 cm.$^{-1}$) was not present in spectra of *p*-toluidine or the *o*-semidine. The n.m.r. spectrum of the oil in carbon tetrachloride showed the presence of aromatic and vinyl protons, N–H protons, methyl and possibly methylene protons. At least four aliphatic C–H bearing groups were present. One or two of these were split although no pattern could be established. One of the signals was only 9 c.p.s. downfield from the reference band of tetramethylsilane (external standard). The chemical shifts of one or two of the signals presumed to be methyl because of the appearance of signals at relatively high field were quite similar to the shifts of the signals due to methyl groups in the spectra of *p*-toluidine and the *o*-semidine.

Hydrogenations of the oil (*ca.* 30 mg. in 10 ml. of ethanol) were carried out at 150–200° and 1500–2000 p.s.i. in the presence of Raney nickel. Infrared spectra of the residues obtained from various hydrogenations were rather ambiguous. Some showed the presence of an O–H group at about 3620 cm.$^{-1}$ and absence of a carbonyl band, while one spectrum showed no O–H absorption and a double carbonyl absorption that occurred at about 1725–1750 cm.$^{-1}$. Strong C–H bands were observed at 2855 and 2933 cm.$^{-1}$. (The starting material had bands at 2863 and 2926 cm.$^{-1}$.) A broad band in the N–H stretching region (3200–3500 cm.$^{-1}$) also was observed.

Two molecular weight measurements were made in acetone solution with a specially constructed osmometer giving values of 267 and 257.[9] The samples were prepared by removal of *p*-toluidine by vacuum sublimation and dissolution of the resulting residue in acetone. The weight of the oil was taken as the difference between the weight of the flask before acetone was added and the weight of the flask after it had been rinsed with acetone and dried.

A control experiment was carried out in which 0.800 g. of *p*-azotoluene, 0.802 g. of the *o*-semidine, and 0.901 g. of *p*-toluidine (all three solids were previously purified) were added to 150 ml. of nitrogen-treated 95% ethanol. One milliliter of concentrated hydrochloric acid was added to the resulting solution which was then worked up by the procedure used to isolate the unknown oil. The residue that was left after the *p*-toluidine had been removed from the fourth fraction showed none of the characteristics, of the unknown oil. The four fractions accounted for 24, 32, 9, and 30%, respectively, of starting material. The second fraction was large and the third small because addition of water to the residue that remained after solvent had been removed was not accompanied by application of sufficient heat to dissolve much of the *o*-semidine.

Results

Kinetics of the Rearrangement of HzT.—The spectrophotometric procedure that Carlin and Wich[3] used to determine the rate of rearrangement of HzT was repeated. The absorption data that they determined for starting material and the three products were used without modification. The disappearance of HzT also was followed by titration with aqueous solutions of Bindschedler's green. The results by both methods agreed internally and with the data previously reported.

Products.—The apparent yields of products indicated by ultraviolet analysis were also in good agreement with the values obtained by Carlin and Wich.[3] Determination of yields by isotopic dilution analysis gave very similar results for *p*-azotoluene and the semidine but gave consistently lower values for the yield of *p*-toluidine. The yields of *p*-toluidine, *o*-semidine, and *p*-azotoluene indicated by the two methods are given in Table II.

Comparison of the two sets of results shows that ultraviolet analysis gives a value for *p*-toluidine that is 10% too large (33 relative %).

Attempts to Alter Yields of Products.—Radioactive HzT was rearranged in the presence of added hydrazobenzene, *p*-toluidine, and *o*-semidine. In one experiment the Würster base was added after 5 hr. of reaction. The yields of the products that were determined are given in Table III.

The results of runs 7–17 show that the addition of *p*-toluidine, the *o*-semidine, and the Würster base had no significant effect upon the yields of the products of the reaction of HzT. The addition of hydrazobenzene clearly reduced the yield of *p*-azotoluene. Since less *p*-azotoluene was formed, a larger yield of the other products would be expected. From the amount of *p*-azotoluene formed in these experiments and from the results given in Table II, the amounts of *p*-toluidine and *o*-semidine which should be formed can be calculated. The experimental results are in rather good agreement with the predicted values of 44–52% for the *o*-semidine and 34.5–37.5% for *p*-toluidine.

Rearrangement of *p,p'*-Ditrideuteriomethylhydrazobenzene-4,4'-C^{14}.—Some of the radioactive toluene that was used as a precursor of HzT was converted to toluene-α-D_3-1-C^{14}. An infrared spectrum showed that only trace amounts of hydrogen were present in the methyl group. No methyl hydrogen signal could

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[9] J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

Table III

Effect of the Addition of Various Compounds on the Yields of the Products Obtained from the Rearrangement of HzT as Determined by Isotope Dilution Analysis

Run	AzT, %	p-Toluidine,[a] %	o-Semidine, %	Conditions
7	22.3	26.5		After 5 hr., 0.784 g. of the Würster base was added
8		25.9		Nothing added
9	27.4	25.2[b] 25.9[a]	40.4	32.71 mg. of *o*-semidine at start of rearrangement
10	29.1	26.4	35.0	80.63 mg. of *o*-semidine
11	28.0	26.3	36.1	80.00 mg. of *o*-semidine
12	28.6	26.7	35.5	80.71 mg. of *o*-semidine
13	26.8[c]	26.9	36.6	Nothing added
14	7.7[d]	35.4 (38.3)[e]	44.5 (48.3)	0.10096 g. of hydrazobenzene initially added
15	4.4	36.3 (38.0)	42.9 (44.9)	0.30165 g. of hydrazobenzene initially added
16	3.6	36.4 (37.7)	43.7 (45.3)	0.5000 g. of hydrazobenzene initially added
17	22.8	29.1	37.3	80.94 mg. of *p*-toluidine added at start

[a] Counted as *p*-acetotoluide. [b] Counted as *p*-toluidine. [c] Runs 9–12 were performed with HzT which had aged 5 weeks since runs 7 and 8 had been performed. Run 13 was carried out to determine whether or not the *p*-azotoluene content of the starting material had increased. The value of 26.8% obtained for *p*-azotoluene shows that this increase had occurred. [d] Purified HzT which contained no more than 3% *p*-azotoluene was used for runs 14–17. [e] The numbers in parentheses give the per cent composition of the total products, other than *p*-azotoluene, represented by the compounds in question.

be detected by n.m.r. HzT, which was prepared from this deuterated toluene, was rearranged. Yields of products were determined and are listed in Table IV.

Table IV

Yields of Products from the Rearrangement of *p,p'*-Ditrideuteriomethylhydrazobenzene-4,4'-C^{14}

Run	p-Azotoluene, %	p-Toluidine, %	o-Semidine, %
18	19.5	28.7	40.3
19	20.0	29.9	39.9
Av.	19.75 ± 0.25%	29.3 ± 0.6%	40.1 ± 0.2%

The presence of deuterium in the methyl groups of HzT did not affect the product distribution. The pseudo first-order rate constant for the rearrangement of the deuterated HzT was found to be 1.40×10^{-2} min.$^{-1}$ at an acid concentration of 0.0154 *f*. This value is essentially the same as that which would be obtained for HzT itself.

Other Product(s).—A careful investigation of the *p*-azotoluene, *o*-semidine, and *p*-toluidine fractions obtained from the reaction of HzT revealed the presence of an unknown oil. Although the infrared spectrum of the oil showed that *p*-toluidine and the *o*-semidine were not present, many features of the spectrum resembled those in the spectrum of *p*-toluidine; in addition there was a strong band in the region (1680–1685 cm.$^{-1}$) characteristic of conjugated carbonyl groups. N.m.r. spectra of the oil contained signals which indicated the presence of a number of methyl (or methylene) groups. One of these signals was only 9 c.p.s. downfield from the reference band of tetramethylsilane and was significantly more intense than the rest of the signals. No assignment could be made to the various signals that were observed. The molecular weight of the oil was determined to be approximately 260. Attempts to hydrogenate the oil and obtain further structural information proved unsuccessful.

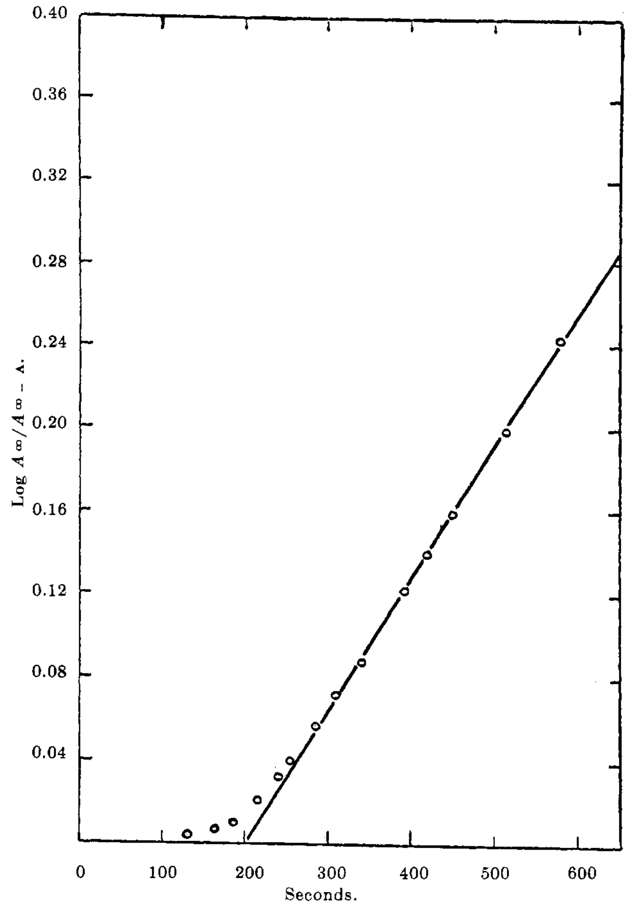
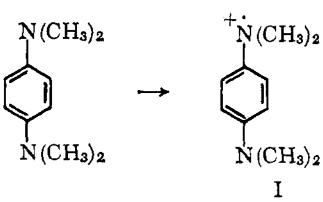


Fig. 1.—Rate of oxidation of the Würster base, absorbance measured at 6140 Å.; original conentrations, HzT, 6.92×10^{-4}; Würster's base, 2.11×10^{-2}; acid, 2.97×10^{-2}.

Oxidizing Properties of Reaction Mixtures.—When HzT was rearranged in the presence of N,N,N',N'-tetramethyl-*p*-phenylenediamine dihydrochloride (the Würster base), a blue solution was produced. This color was attributed to the Würster cation (I). Control experiments showed that the presence of both the Würster base and HzT was required for development of the blue color.



I

The rate of formation of Würster's blue was followed spectrophotometrically. A typical first-order plot of the rate data (Fig. 1) shows that there is an induction period. Since the Würster cation readily oxidizes

TABLE V

RATES OF OXIDATION OF THE WÜRSTER BASE BY THE TRANSIENT IN CONSTANT HYDRAZOTOLUENE CONCENTRATION OF 6.92×10^{-4} *M*

Run	$[Cl^-] \times 10^2$	$\mu \times 10^2$	$[H^+]^a \times 10^2$	$[W.B.]^b \times 10^2$	$k_a \times 10^2$, sec.$^{-1c}$	A_∞^e
1	4.15	4.15	2.92	1.06	9.42	0.805
2	4.17	4.17	2.93	1.06	10.2	0.800
3	5.44	5.44	2.96	2.11	7.03	0.815
4	5.46	5.46	2.97	2.11	7.10	0.815
5	25.5	25.5	2.97	2.11	9.64	1.040
6	5.5	25	2.97	2.11	12.2	1.200
7	45.5	45.5	2.97	2.11	10.9	0.975
8	5.5	44.5	2.97	2.11	17.1	1.360
9	5.22	5.22	1	2.11	4.31	0.81
10	5.22	5.22	0.3	2.11	3.11	0.80
11	7.32	7.32	1.86	3.16	4.75	0.81
12	9.44	9.44	1.77	4.22	4.49	0.83
13[d]	9.44	9.44	1.77	4.22	4.48	0.67

[a] Calculated using the values 5×10^4 and 7 as the first and second basicity constants of the Würster base. [b] Würster base concentration. [c] Calculated by dividing the observed rate constant by the total concentration of the Würster base. [d] Run 13 was allowed to stand for 10 min. before addition of the Würster base. [e] These values must be estimated as the blue color gradually disappears. The reaction cells were allowed to stand for a period equal to the time required to reach the observed A_∞. One-half of the decrease in absorption was added to the observed A_∞ to obtain the values of A_∞ listed.

HzT, this induction corresponds to the period of time in which unchanged HzT is still present. The induction period depended on the hydrogen ion concentration and was generally less than 25 min. under the conditions employed. The ionic strength and the concentration of hydrogen ion and of the Würster base were varied for the different runs, while the concentration of HzT was kept constant. The results that were obtained are listed below in Table V. These data show that the rate and amount of oxidation are increased by an increase in ionic strength (runs 5–8). The rate of oxidation appears to be dependent on the hydrogen ion concentration (runs 9, 10), while the amount of oxidation of the Würster base is seen to be independent of the concentrations of hydrogen ion and of the Würster base.

The oxidizing agent was found to be rather unstable in acidic ethanol. A solution that was allowed to stand for 90 min. before addition of the Würster base was found to have lost two-thirds of its oxidizing power. The oxidizing agent was more stable in alkaline ethanol than in acidic ethanol. A reaction mixture was neutralized, allowed to stand 90 min., and then reacidified; only one-third of its oxidizing power had disappeared.

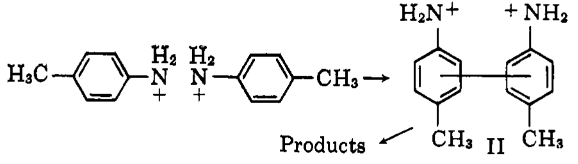
As none of the reported products of the rearrangement of HzT will oxidize the Würster base, an additional compound must be formed. Carlin's spectrophotometric analysis indicated that the sum of the concentrations of the products and of unrearranged starting material was equal to the initial concentration of HzT. However, the amount of Würster cation formed indicated that the oxidizing agent accounts for 5–10% of starting material. This observation provided the motive for measurement of the yields by isotope dilution (*vide supra*).

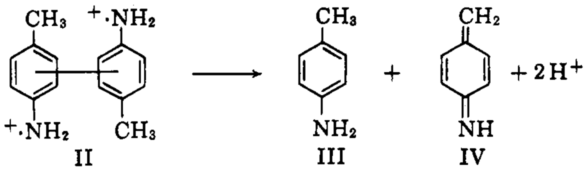
Discussion

The presence of an unknown product was first considered as a consequence of the observation that the solution of products obtained from HzT would readily oxidize the Würster base to Würster's blue. The yield of the oxidant was calculated to be either 5 or 10% depending on what assumptions are made as to the equivalent weight of the oxidizing agent. This result does not in itself require that the spectrophotometric analysis be in error as the reported excess of *p*-toluidine could conceivably be formed from the oxidizing agent.

However, isotope dilution analyses show that an unknown product(s) must account for approximately 10% of the HzT. The yields of *p*-azotoluene and *o*-semidine are in rather good agreement with the values obtained by ultraviolet analysis. *p*-Toluidine, however, accounts for only 30% of starting material rather than 40%. As *p*-azotoluene accounts for 20% of starting material, the correct value for the yield of *p*-toluidine is still 10% higher than would be predicted for a stoichiometric disproportionation reaction. This "excess" of *p*-toluidine may well be related to the 5–10% of oxidizing agent that is formed from HzT.

A mechanism that has been sometimes proposed for the benzidine rearrangement involves the intermediate formation of a pair of cation radicals. Escape of these radicals from their initial solvent cage could lead to oxidation of starting material with the resultant formation of equal amounts (by weight) of *p*-azotoluene and *p*-toluidine. On the other hand, geminate recombination of the radical pair would produce, after tautomeric rearrangement of primary products, the familiar products of benzidine-like rearrangement. A pair of *p*-tolylimminium radicals (II) also conceivably might disproportionate to give *p*-toluidine and *p*-benzoquinoneiminemethide (IV).



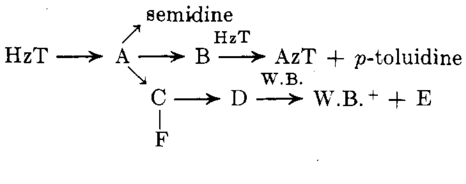


We gave serious consideration to the possibility that the unknown oxidant was IV. This possibility was clearly ruled out by three separate experiments. The reduction product of IV (or a derivative of IV) would be expected to be *p*-toluidine. The possible formation of the latter compound from IV may be excluded since rearrangement of HzT in ethanol-O-D did not lead to the incorporation of deuterium in the methyl group of *p*-toluidine and since inclusion of the Würster base (run 7, Table III) did not alter the yield of *p*-toluidine. These results did not rule out the intramolecular disproportionation reaction; but simply require that, if IV is formed, it cannot be reduced to *p*-toluidine. For the disproportionation reaction to occur, hydrogen must be abstracted from the methyl group of the tolylamino cation radical, a reaction that should show a kinetic isotope effect. Since rearrangement of *p,p'*-ditrideuteriomethylhydrazobenzene gave the same product distribution as is obtained from HzT, we conclude that disproportionation of two caged radicals is not responsible for the excess of *p*-toluidine or for the oxidizing properties of product solutions.

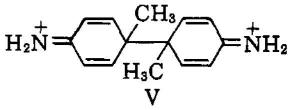
The structure and detailed properties of the unknown oxidizing agents are still undefined. A thorough analysis of the kinetic data of Table V develops a very complex picture which does little to pin down the nature of the unknown, although at least one important conclusion can be reached. Since the amount of Würster cation that is formed by the oxidation of the Würster base can be varied with a change in ionic strength, there must be at least two paths by which the unknown can be destroyed. The observed oxidation reaction is, however, not directly competitive with other paths of destruction of the unknown as variation of the concentration of the Würster base does not alter the amount of Würster's blue that is formed. Consequently, the unknown oxidant cannot be formed directly from HzT, but must come from some other reaction product which has at least two modes of decomposition.

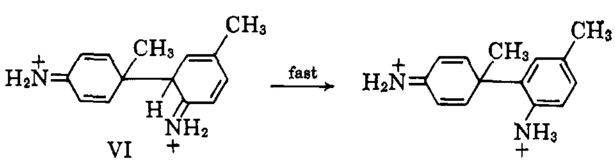
Since addition of excesses *p*-toluidine and the *o*-semidine to solutions in which HzT underwent acid-catalyzed reactions had no significant effect on the product-determining steps of the reaction, the oxidizing agent cannot be involved in any sort of equilibrium with the reported products. Furthermore, the presence of hydrazobenzene did not alter the relative yields of *p*-toluidine, *o*-semidine, and the unknown product of the decomposition of HzT. The absolute yields of these compounds did increase, but only in a manner which would have been predicted from the decreased yield of *p*-azotoluene. These results indicate that the precursor of *p*-toluidine and the oxidant that reacts with the Würster base are not the same species. If they were, addition of a large excess of hydrazobenzene should have led to a disproportionately large increase in the yield of *p*-toluidine.

As is indicated by the following, schematic mechanism, an uncomfortably large number of unknown species must be involved if it is assumed that there is one common rate-limiting step.



It is very possible that C is formed by coupling reactions involving *para* positions to form species such as V and VI. Tautomerization of VI would produce one unit having an ultraviolet spectrum similar to that of *p*-toluidine and other such absorbing units could be formed by rearrangements analogous to the dienone–phenol transformation. Derivatives of the dienimines, *e.g.*, carbinol amines, might dissociate slowly[10] to form species capable of oxidizing the Würster base. Coupling at substituted *para* carbon atoms has been observed previously.[11] Chlorine, bromine, iodine, and carboxyl are among the substituents which have been displaced from *para* carbon atoms of hydrazobenzenes in the course of benzidine rearrangements.


V



VI

The reactions of radioactive HzT that were carried out in the presence of an excess of hydrazobenzene resulted in decreased yield of *p*-azotoluene. This result may be explained in one of two ways. Hydrazobenzene either traps the intermediate oxidizing agent that is normally responsible for *p*-azotoluene formation, or it reduces *p*-azotoluene back to HzT. Since HzT reacts 100 times as rapidly as hydrazobenzene under the conditions of the experiments, most of the latter compound would have still been present when the inactive diluents are added. If reduction of radioactive *p*-azotoluene by hydrazobenzene were responsible for the decreased yield of the former compound, the unlabeled *p*-azotoluene which had been added as a diluent should also have been reduced. This reduction would result in the formation of unlabeled HzT and accordingly more unlabeled *p*-toluidine and *o*-semidine would be present than had been added (as diluents). The consequent dilution of these products with inactive material would have lowered their apparent yields. In actuality the per cent of HzT that rearranged to *p*-toluidine and *o*-semidine (and the unknown) was unaffected by the addition of hydrazobenzene. The conclusion may thus be drawn that *the disproportionation reaction proceeds by way of an intermolecular oxidation of HzT to produce p-azotoluene and, undoubtedly, p-toluidine.*

We believe that the transient responsible for oxidation of the hydrazo compounds is either the tolyliminyl radical, p-$CH_3C_6H_4\dot{N}H$, or its conjugate acid, p-$CH_3C_6H_4\overset{\cdot\,+}{N}H_2$. The only other likely candidates would seem to be tolylnitrene, p-$CH_3C_6H_4N$, or its conjugate

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[10] For example, by reversion to the dienimine.

[11] (a) P. Jacobson, M. Jaenicke, and F. Meyer, *Ber.*, **29**, 2681 (1896); (b) P. Jacobson and A. Loib, *ibid.*, **36**, 4088 (1903); (c) P. Jacobson and A. Steinbreck, *Ann.*, **303**, 384 (1898).

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

Acknowledgment.—Partial support of this study by the National Science Foundation is gratefully acknowledged.

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[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.

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

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Contribution No. 2915 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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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, $Ar\overset{+}{N}H$ 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.

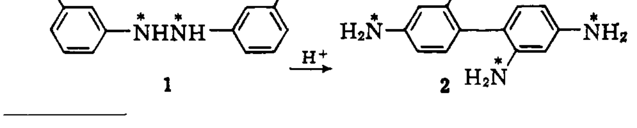
$$ArNHNHAr + H^+ \rightleftharpoons Ar\overset{+}{N}H_2NHAr$$

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

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

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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[1] Part VI: G. S. Hammond and J. S. Clovis, *J. Org. Chem.*, **28**, 3283 (1963).

[2] J. S. Clovis and G. S. Hammond, *Tetrahedron Letters*, 945 (1962).

[3] National Institutes of Health Predoctoral Fellow, 1961-1962.

[4] M. J. S. Dewar, "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths, London, 1959, p. 195 ff.

[5] C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. 11.

[6] D. L. Hammick and S. F. Mason, *J. Chem. Soc.*, 638 (1946).

[7] S. Brownstein, C. A. Bunton, and E. D. Hughes, *Chem. Ind.* (London), 981 (1956).

[8] M. J. S. Dewar, *J. Chem. Soc.*, 777 (1946).

[9] G. S. Hammond and H. J. Shine, *J. Am. Chem. Soc.*, **72**, 220 (1950).

[10] M. Tichwinsky, *J. Russ. Chem. Soc.*, **35**, 667 (1903).

[11] G. S. Hammond and R. C. Neuman, *J. Am. Chem. Soc.*, **85**, 1501 (1963).