hydrazobenzene the products anticipated are the *o*-semidine (IX), the azo compound (VIII), and the amine (IV). Analysis of a synthetic mixture of these compounds, using the extinction coefficients in Table V gave very good agreement between calculated and known concentrations. In the case of 4-*t*-butyl-4′-chlorohydrazobenzene the anticipated products are the azo compound (VI), the *o*-semidine (X), *p*-chloroaniline (III), and *p*-*t*-butylaniline (IV). Analyses of synthetic mixtures of these four compounds did not give reasonable results. Therefore, it was assumed that III and IV would be formed in equal amounts, by disproportionation, and analyses for a "three-component" system were carried out, using extinction coefficients obtained with mixtures of equal concentrations (XI) of III and IV. By this method analyses for VI were about 10% high and for X about 10% low. In calculating the composition of reaction products the results were corrected to compensate for these differences.[22]

Table V

Extinction Coefficients

Compd	$\epsilon \times 10^{-4}$ at 298.5 mμ	287.7 mμ	235.3 mμ
VIII	1.19	0.771	1.42
IV	0.108	0.155	1.03
IX	0.940	0.960	1.99
VI	1.07	0.692	1.37
X	0.795	0.846	1.62
XI[a]	0.128	0.133	0.951

[a] A mixture of equal concentrations of III and IV.

Registry No.—I, 7775-78-2; II, 7775-79-3; IV, 769-92-6; VI, 7775-82-8; VII, 3282-56-2; VIII, 7775-81-7; IX, 7775-84-0; X, 7775-83-9.

The Benzidine Rearrangement. IX.[1,2] *p*-Hydrazobiphenyl. The Mechanisms of Rearrangement and Disproportionation

H. J. Shine and J. P. Stanley

Department of Chemistry, Texas Technological College, Lubbock, Texas 79409

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In aqueous ethanol solutions with acid concentrations in the range 0.0306 to 0.514 *M*, *p*-hydrazobiphenyl disproportionates (75% at 0°, 88% at 25°) and rearranges (25% at 0°, 12% at 25°). The relative extents of disproportionation and rearrangement were not significantly affected by changing the initial substrate concentration and the acidity. However, disproportionation was greater at 25° than at 0°. The rearrangement product is believed to be the *o*-semidine. The destruction of the *p*-hydrazobiphenyl is first order in substrate and second order in acid over this range of acidities. Over the range of 0.00612 to 0.0214 *M* acid the order in acid is 1.8. At low acidities (0.00612 *M*) reduction of the hydrazo compound becomes significant, amounting to 12% at 0°, and 16% at 25°. 4,4′-Dichlorohydrazobenzene appears to be oxidized by *p*-hydrazobiphenyl in acid solution at 0° under which conditions 4,4′-dichlorohydrazobenzene itself is stable. The mechanisms of rearrangement and disproportionation are discussed. It is concluded that the intermediateless, polar-transition-state theory needs to be questioned further, that the steric aspects of the π-complex theory are not supported by experiment, and that intermediates are involved in rearrangement and disproportionation whose natures still need to be elucidated.

Two examples are described in the preceding paper[1] of hydrazoaromatics in which rearrangement and disproportionation follow the same kinetic law. Carlin and Wich[3] have described in careful detail another example, that of *p*-hydrazotoluene. In the present paper we deal with the case of *p*-hydrazobiphenyl and apply our results to a discussion of the concurrent rearrangement and disproportionation reactions. We chose to study the behavior of *p*-hydrazobiphenyl with the belief, based on reports in earlier literature, that this compound did not rearrange in acid solutions, but disproportionated quantitatively to *p*-azobiphenyl and 4-aminobiphenyl. Friebel and Rassow[4] had given the only detailed report on *p*-hydrazobiphenyl, stating that when it was heated with concentrated hydrochloric acid (and when *p*-azobiphenyl was heated in alcohol with stannous chloride and hydrochloric acid) only disproportionation occurred. Another report,[5] confirming the observation of Friebel and Rassow, appeared later. Therein *p*-hydrazobiphenyl was shown only to disproportionate when heated with hydrochloric and sulfuric acids of various strengths. It should be pointed out, for the purpose of record, that the earliest report on the behavior of *p*-hydrazobiphenyl, describing its inertness to hot acids,[6] is invalid because it is evident from the melting point quoted that the compound used was *p*-azobiphenyl.

It has been our belief that a satisfactory mechanism for the benzidine rearrangement cannot be given unless it can also show how some hydrazoaromatics rearrange and disproportionate concurrently under the same kinetic law. In spite of the large amount of work that has been done on the benzidine rearrangement, agreement on a suitable mechanism has not been reached.[7] As for the disproportionation reaction, it has been dealt with mainly only in a speculative way in descriptions of some cases where it accompanies rearrangement.[3,8,9] Therefore, with the feeling that the simplest way of reaching some understanding of how the disproportionation and rearrangement reactions can be fitted together would be to study the former reaction independently, we chose *p*-hydrazobiphenyl for a kinetic and esr investigation. The use of this compound had a particular attraction, because its reported inability to rearrange has been used by Dewar[10] in support of the π-complex theory of the benzidine rearrangement.

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(1) Part VIII: H. J. Shine and J. T. Chamness, *J. Org. Chem.*, **32**, 901 (1967).

(2) Support from the Robert A. Welch Foundation and the Institute of Science and Engineering, Texas Technological College, is gratefully acknowledged.

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

(4) G. Friebeland B. Rassow, *J. Prakt. Chem.*, **63**, 464 (1901).

(5) F. Bell, J. Kenyon, and P. H. Robinson, *J. Chem. Soc.*, 1239 (1926).

(6) J. Zimmermann, *Ber.*, **13**, 1960 (1880).

(7) M. J. S. Dewar, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

(8) G. S. Hammond and J. S. Clovis, *J. Org. Chem.*, **28**, 3283 (1963).

(9) M. Vecera, L. Synek, and V. Sterba, *Collection Czech. Chem. Commun.*, **25**, 1992 (1960).

(10) M. J. S. Dewar in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 336.

TABLE I

QUANTITATIVE ANALYSIS OF PRODUCTS OF REACTION OF *p*-HYDRAZOBIPHENYL IN ACIDIC AQUEOUS ETHANOL[a,b]

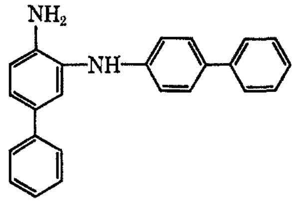
No. of samples	$[H^+]$, *M*	Temp, °C	No. of half-lives	Azo (II), %[c]	Amine (III), %[c]	Semidine (IV), %[c]
2	0.514	0	10	37.0 ± 0.1	38.6 ± 0.1	24.4 ± 0.1
2	0.514	25	10[d]	44.0 ± 0.1	43.4 ± 0.1	12.6 ± 0.1
3	0.0612	0	10	35.9 ± 0.1	36.8 ± 0.1	27.3 ± 0.1
2	0.0612	25	10[d]	42.7 ± 0.1	42.6 ± 0.1	14.7 ± 0.1
4	0.0306	0	8	35.2 ± 1.4	36.1 ± 0.6	28.6 ± 0.8
3	0.00612	0	10	29.1 ± 1.8[e]	41.0 ± 1.6[e]	28.9 ± 1.2
3	0.00612	25	10[d]	32.6 ± 1.8[e]	48.3 ± 2.5[e]	19.8 ± 1.0

[a] See footnote *a* in Table II. [b] The concentration of *p*-hydrazobiphenyl was 2.25×10^{-4} *M* in all cases except in 3 of the 4 runs in 0.0306 *M* acid, where the hydrazo concentration was 1.12×10^{-4} *M*. [c] Mole % of the *p*-hydrazobiphenyl used. [d] The half-life was unknown but was assumed to be 20% of that at 0°. [e] These data show that reduction is an important reaction at the low acidities, amounting to about 12 to 16% of the *p*-hydrazobiphenyl which was used.

The π-complex theory of the rearrangement, as applied to this case, would require first, that protonated *p*-hydrazobiphenyl would form a π complex in which all four phenyl rings were oriented along parallel axes, and next that this π complex would rotate to one which could collapse to an *o*-semidine. Dewar ascribed the failure of *p*-hydrazobiphenyl to rearrange to its inability to form the required first π complex, and the inability to form that π complex to the steric and π-cloud repulsions which would occur between the two *p*-phenyl groups. Our interest in this interpretation of the behavior of *p*-hydrazobiphenyl was in asking, if a π complex cannot form in this case, what *does* form that leads to acid-catalyzed disproportionation?

Results

Products.—A routine spectroscopic examination of the products of reaction of *p*-hydrazobiphenyl with acid, in preparation for the kinetic work, showed that 4-aminobiphenyl was not the only acid-soluble product. Thin layer chromatography and, later, larger scale separations gave a product which we believe is the *o*-semidine (IV). This structure is assigned on the basis of analytical data, the formation of a monoacetyl and a monobenzoyl derivative (rather than diacyl derivatives), and the equivalent weight, determined by titration with perchloric acid.



IV

It is interesting to note that the formation of IV (in an impure state) has been proposed by earlier workers,[5] not from the reaction of *p*-hydrazobiphenyl itself, but from the reaction of 4-hydroxylaminobiphenyl with acid. That reaction was thought to lead to an intermediate, reactive state of *p*-hydrazobiphenyl from which the IV was formed.

The amounts of *p*-azobiphenyl (II), 4-aminobiphenyl (III), and IV formed under various conditions are given in Table I. It is clear that when the temperature is raised the extent of disproportionation increases at the expense of rearrangement. This is possibly the reason for the earlier claims that *p*-hydrazobiphenyl does not rearrange, since in the earlier works the hydrazo compound was heated with acid. Our results with *p*-hydrazobiphenyl follow those of Vecera[9] with hydrazobenzene, whose disproportionation, although quite small (3.3%) at 20°, was increased substantially (to 5.5%) at 50°.

When the acid concentration was increased over the range 0.0306 to 0.514 *M* there was a slight increase in the extent of disproportionation of *p*-hydrazobiphenyl and a small decrease in the extent of its rearrangement. These data suggest that the order in acid for disproportionation is greater than that for rearrangement, that is, that some incursion of one-proton-catalyzed rearrangement was being experienced as the acidity was lowered. We do not really know if this suggestion is correct. Certainly, at still lower acidities, the plot of log *k vs.* log $[H^+]$ deviates slightly toward a slope lower than 2 (Figure 1). Over the range of acidities of 0.0306 to 0.514 *M*, however, we do not detect a change in acid order. Therefore, we are obliged to leave unanswered the questions on the significance of the small changes in products over this range of acidities. At the lowest acidity in which products were determined there is definitely a change in product ratios and types. Reductive scission becomes an important reaction, apparently at the expense of disproportionation. The extent of rearrangement is either unaffected (at 0°) or increases (at 25°) in going to this acid concentration (0.00612 *M*).

Cross Oxidation.—4,4′-Dichlorohydrazobenzene was stable in cold acid solution for at least 30 min. In the presence of *p*-hydrazobiphenyl, however, the 4,4′-dichlorohydrazobenzene was destroyed. For example, in a solution that was 2.5×10^{-3} *M* in 4,4′-dichlorohydrazobenzene, 2.6×10^{-4} *M* in *p*-hydrazobiphenyl, and 0.128 *M* in acid, 5.3% of the 4,4′-dichlorohydrazobenzene was destroyed. That is, 53% of the *p*-hydrazobiphenyl reacted with an external agent, the other hydrazo compound. The stability of 4,4′-dichlorohydrazobenzene in the absence of *p*-hydrazobiphenyl, and our failure to detect *p*-chloroaniline spectroscopically (see the Experimental Section) indicate that the 4,4′-dichlorohydrazobenzene was oxidized by protonated *p*-hydrazobiphenyl or some derivative thereof.

Kinetics.—The reactions of *p*-hydrazobiphenyl in acid solutions are fast. Therefore, the rates of disappearance of the hydrazo compound were measured only at 0°. A spectrophotometric adaptation of the Bindschedler's green method was used. The log absorbance of the Bindschedler's green which was equivalent to unused hydrazo compound was plotted against time and gave good, straight lines. The pseudo-first-order rate constants at constant initial *p*-hydrazobiphenyl concentration are given in Table II. The pseudo-first-order rate constants for constant acid concentration and varied initial *p*-hydrazobiphenyl concentrations are given in Table III. A plot of log *k* *vs.* the log of the acid concentration is given in Figure 1. The data leave no doubt that above the acid concentration of 0.0306 *M* the disappearance of *p*-hydrazobiphenyl is first order in hydrazo compound and second order in acid. The slope of a plot over the range 0.0214 to 0.514 *M* acid was calculated by the method of least squares to be 2.01 ± 0.01. Below 0.0306 *M* the order in acid falls slightly. The slope of a plot over the range 0.00612 to 0.0214 *M* acid was similarly calculated to be 1.81 ± 0.03.

Table II

Pseudo-First-Order Rate Constants for the Disappearance of *p*-Hydrazobiphenyl in Aqueous Ethanol at 0°[a]

$[H^+]$, *M*	10^2k, min^{-1}	$[H^+]$, *M*	10^2k, min^{-1}
0.514	598	0.0214	0.932
0.514	560	0.0214	0.970
0.256	144	0.0122	0.361
0.256	140	0.0122	0.316
0.128	35.6	0.00916	0.178
0.128	34.6	0.00916	0.177
0.0612	7.61	0.00612	0.0969
0.0612	7.58	0.00612	0.0953
0.0306	1.83	0.00612	0.0972
0.0306	1.93		

[a] The concentration of water in the solvent was inadvertently increased slightly from 7.9% by volume at the highest acidity to 9.2% at the lowest; the ionic strength of each solution was maintained constant at 0.514 by the addition (where necessary) of LiCl; $[p\text{-hydrazobiphenyl}]_0 = 2.25 \times 10^{-4}$ *M*.

Table III

Pseudo-First-Order Rate Constants for the Disappearance of *p*-Hydrazobiphenyl in Acidic Aqueous Ethanol at 0°[a]

[Hyd] × 10^4, *M*	10^2k, min^{-1}
2.97	34.3
2.90	34.7
2.78	34.6
2.25	35.3
1.15	33.9
1.14	34.9
0.741	35.3
0.735	33.7

[a] The solvent contained 9% water by volume; the ionic strength was 0.514; $[p\text{-hydrazobiphenyl}]_0 = (0.735\text{–}2.97) \times 10^{-4}$ *M*; $[H^+] = 1.28 \times 10^{-1}$ *M*.

Discussion

Two points stand out immediately. The first is that rearrangement of *p*-hydrazobiphenyl does occur. The second is that although we have not found a system in which disproportionation occurs exclusively, it does occur here to about 75% extent at 0°, and 88% at 25°. There is no reason to believe that the rate law will be different at 25° than at 0°, so that we have in *p*-hydrazobiphenyl a compound which almost entirely disproportionates, and whose kinetics of disproportionation can be set out over a particular range of acidities as being first order in substrate and second order in acid.

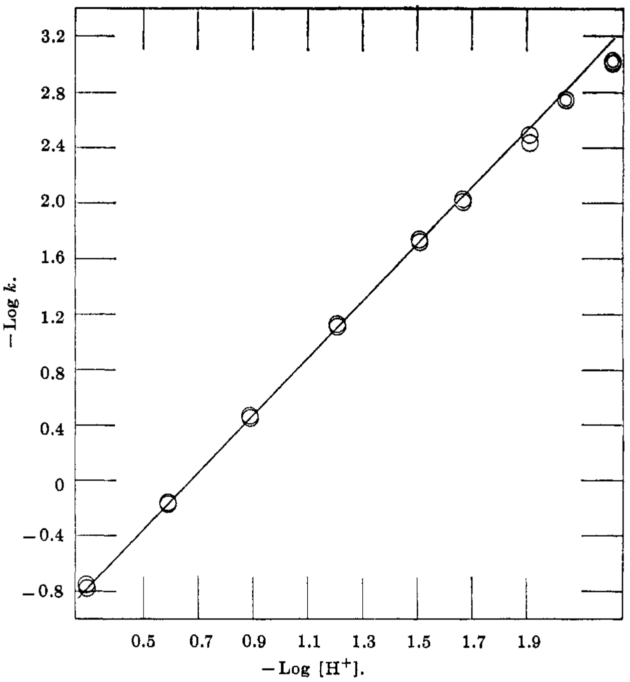
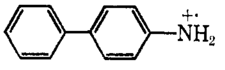


Figure 1.—A plot of −log *k* *vs.* −log $[H^+]$ for the rates of disappearance of *p*-hydrazobiphenyl at various acid concentrations, at constant ionic strength of 0.514 in aqueous ethanol at 0°.

The finding of a rearrangement product destroys the part of the argument for π-complex formation in the benzidine rearrangement which Dewar has based on the behavior of *p*-hydrazobiphenyl. In his discussion of the caged-radical mechanism of the benzidine rearrangement, Dewar refers to *p*-hydrazobiphenyl and points out[11] that the *p*-phenyl substituent could not possibly hinder the dimerization of the ion radical (V) to an *o*-semidine. The implication is that since rearrangement did not occur (as believed hitherto) a pair of caged ion radicals could be ruled out as an intermediate in the benzidine rearrangement. Now that we have shown that rearrangement does occur, Dewar's own arguments could be used in favor of ion-radical intermediates and against π-complex intermediates.



V

The most recently proposed theory of the benzidine rearrangement is the polar-transition-state theory.[12] This theory accounts for all of the presently known facts about most benzidine rearrangements, but it has two important restrictions. The first is that the *p*-semidine rearrangement must be excluded[12] from the family of intramolecular benzidine rearrangements. The reason for this is that in the polar-transition-state theory, N-N bond breaking and C–C (or C–N) bond making are concerted. The geometrical contortion of the transition state for a molecule undergoing the *p*-semidine rearrangement by this process is simply unacceptable. The evidence in the literature for acid-catalyzed *p*-semidine rearrangements is not firm. For

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(11) Reference 10, p 329.

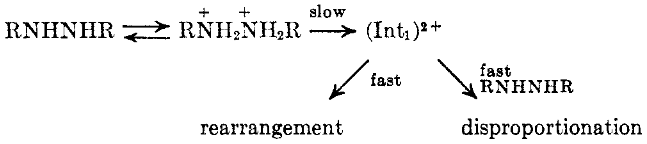
(12) Summarized by D. V. Banthorpe, E. D. Hughes, C. K. Ingold, R. Bramley, and J. A. Thomas, *J. Chem. Soc.*, 2864 (1964).

this reason and the aforementioned transition-state difficulty, the *p*-semidine is excluded from the family of rearrangements and is considered, possibly, to involve the participation of heavy metal ions.[12] However, these are not strong arguments against including the *p*-semidine rearrangement. *No evidence has ever been presented to show that the p-semidine rearrangement cannot occur under the customary metal-free acid conditions.*[13] Its exclusion is necessary for the polar-transition-state theory, but the validity of the exclusion remains to be tested by experiment.

The second restriction to the polar-transition-state theory is that it cannot be adapted to the disproportionation reaction unless that reaction is treated as a separate but concurrent one. The polar-transition-state theory does not provide for the rate-determining formation of an intermediate prior to the product-forming steps. In this theory the monoprotonated and diprotonated substrates go directly through one or more transition states to intermediates, in each of which the product skeleton is already reached. The only requirement thereafter is that prototropic shifts occur. Therefore, protonated molecules which are undergoing scission on their way to rearrangement cannot be intercepted and diverted to the disproportionation reaction.

Some simple schemes can be written to accommodate concurrent rearrangement and disproportionation. These are given below, and are written for the two-proton case since we know of no evidence for disproportionation under first-order acid catalysis. The first (Scheme I) provides for a common intermediate, and, therefore, does not fit the polar-transition-state theory. The polar-transition-state theory could be modified to fit this scheme if that transition state was regarded as the intermediate-forming one.

SCHEME I



$$\begin{tikzcd} \mathrm{RNHNHR} \arrow[r, shift left] & \mathrm{R\overset{+}{N}H_2\overset{+}{N}H_2R} \arrow[l, shift left] \arrow[r, "\text{slow}"] & (\mathrm{Int_1})^{2+} \arrow[dl, "\text{fast}"] \arrow[dr, "\text{fast}", "\mathrm{RNHNHR}"'] & \\ & \text{rearrangement} & & \text{disproportionation} \end{tikzcd}$$

In Scheme I the intermediate undergoes two, fast, competitive reactions. The disproportionation reaction is bimolecular in substrate, so that at a given acid concentration we should expect the ratio of disproportionation to rearrangement to increase with increasing initial concentration of substrate. We have not been able to detect such a change in ratio, either in this case or in those of 4,4′-di-*t*-butylhydrazobenzene and 4-*t*-butyl-4′-chlorohydrazobenzene (part VIII[1]). No change was detected by Carlin and Wich with *p*-hydrazotoluene.[3] Vecera[9] reported that an increase in the extent of disproportionation of hydrazobenzene occurred when the initial concentration of the hydrazobenzene was increased fourfold. The yield of benzidine fell from 70.3 to 69.4% and the extent of disproportionation rose from 5.0 to 5.7%. It seems doubtful that these small changes should be considered seriously. The net result is that the product-ratio evidence seems not to be in accord with Scheme I. In spite of this, we are not certain that Scheme I should be rejected, because those tests which have been made with product analyses are not completely satisfactory. Large variations in initial substrate concentrations have not been made, and the analytical data do not have a high enough accuracy to permit the Scheme I to be rejected with confidence.

If further work shows without doubt that the ratio of disproportionation to rearrangement is independent of the initial hydrazo concentration, Scheme I can be modified to suit this situation. The modification would be to have the intermediate $(\mathrm{Int_1})^{2+}$ break up into fragments which rapidly abstract hydrogen atoms from the hydrazo compound. In this way, the competitive reactions undergone by $(\mathrm{Int_1})^{2+}$ would be rearrangement and dissociation and the relative extents of these would be independent of the free hydrazo concentration.

Proposals that the disproportionation reaction involves fragments from a dissociated intermediate have been made occasionally.[8,9] The most reasonably described fragments are cation radicals. The search for cation radicals in rearrangement systems has been fruitless.[12] Possibly, reactions in which only rearrangement occurs may not be best suited for this sort of search, but we have been quite unsuccessful also in searching for radicals by esr spectroscopy with *p*-hydrazobiphenyl and 4,4′-dichlorohydrazobenzene, in which disproportionation is marked. This, of course, is not certain evidence against the existence of cation radicals in these reactions. Their concentrations may have been too small or their lives too short for detection. An esr signal has been detected recently by Wittig[14a] with the use of N,N′-trimethylenehydrazobenzene. This compound does not rearrange but, instead, is reduced to 1,3-dianilinopropane (in 41% yield). The analogous N,N′-pentamethylenehydrazobenzene does rearrange to pentamethylenediphenyline (in 93% yield). Although an esr signal was not reported for N,N′-pentamethylenehydrazobenzene, the reaction of this compound in the presence of nitric oxide was similar to the reaction of N,N′-trimethylenehydrazobenzene in the presence of nitric oxide. These are the first demonstrations of the presence of radicals in acid-catalyzed hydrazoaromatic reactions. Even so, it now appears that the radicals are associated with side reactions rather than with rearrangements.[14b]

Our results with *p*-hydrazobiphenyl and Vecera's results[9] with hydrazobenzene show that disproportionation is favored at higher temperatures. This may be taken as indicating the involvement of radicals in disproportionation—radicals which are formed more easily at the higher temperature by the temperature-sensitive dissociation of the intermediate $(\mathrm{Int_1})^{2+}$. We can do no more than mention this as a possibility. We cannot explain, for example, the absence of an anticipated, related reaction of the radicals with the solvent.

It is possible to write a second scheme of reactions which embodies the polar-transition-state theory and also allows for a constant ratio of disproportionation to rearrangement. In this (Scheme II) the diprotonated

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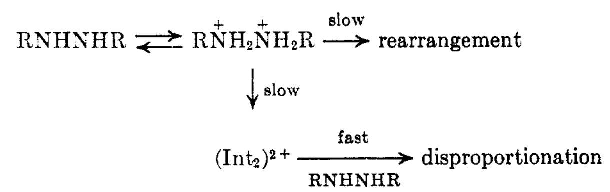
(13) The attempts by D. L. Hammick and D. C. Munro [*J. Chem. Soc.*, 2049 (1950)] to do this with 4-ethoxyhydrazobenzene are experimentally unsatisfactory.

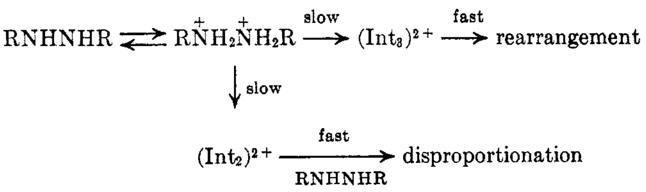
(14) (a) G. Wittig, P. Börzel, F. Neumann, and G. Klar, *Ann.*, **691**, 109 (1966); (b) private communication from Professor Wittig.

Scheme II



$$\begin{tikzcd}
\mathrm{RNHNHR} \arrow[r, shift left] & \mathrm{R\overset{+}{N}H_2\overset{+}{N}H_2R} \arrow[l, shift left] \arrow[r, "\text{slow}"] \arrow[d, "\text{slow}"] & \text{rearrangement} \\
& (\mathrm{Int_2})^{2+} \arrow[r, "\text{fast}", "\mathrm{RNHNHR}"'] & \text{disproportionation}
\end{tikzcd}$$

Scheme III



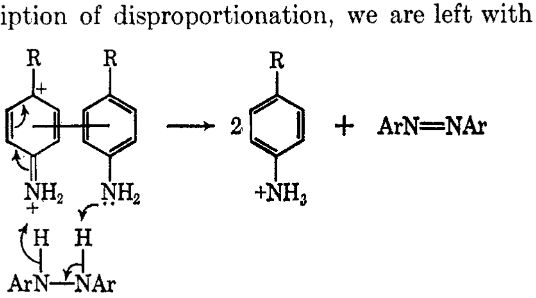
$$\begin{tikzcd}
\mathrm{RNHNHR} \arrow[r, shift left] & \mathrm{R\overset{+}{N}H_2\overset{+}{N}H_2R} \arrow[l, shift left] \arrow[r, "\text{slow}"] \arrow[d, "\text{slow}"] & (\mathrm{Int_3})^{2+} \arrow[r, "\text{fast}"] & \text{rearrangement} \\
& (\mathrm{Int_2})^{2+} \arrow[r, "\text{fast}", "\mathrm{RNHNHR}"'] & \text{disproportionation}
\end{tikzcd}$$

substrate is shown to rearrange along one path without forming an intermediate and to go toward disproportionation along a second path with forming an intermediate. The ratio of disproportionation to rearrangement would not be affected by the concentration of the free substrate, provided that this was always larger than that of the protonated substrate (which is a reasonable expectation over most of the reaction period).

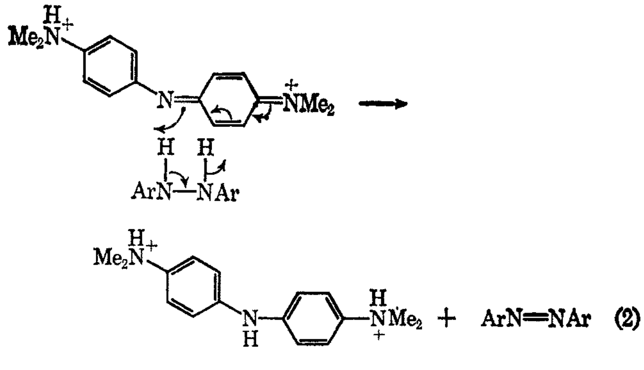
The Scheme II would not be able to accommodate the *p*-semidine rearrangement. Whether this should be accommodated or not remains to be seen, but if it should we could do so by modifying Scheme II with the inclusion of an intermediate, labeled as $(\mathrm{Int}_3)^{2+}$, in the rearrangement branch (Scheme III).

The schemes in which intermediates $(\mathrm{Int}_1)^{2+}$ and $(\mathrm{Int}_3)^{2+}$ feature in the rearrangement paths are not much different from Dewar's most recent proposal for the benzidine rearrangement.[7] In this, π complexes (designated as π_0, π_1, and π_2 for the thermal, one-proton, and two-proton rearrangements) are considered to be the best description of the intermediates. It is acknowledged that caged-radical pairs would also serve, although these are thought not to be consistent with essentially complete intramolecularity of rearrangements.[7] If the intermediates in rearrangement are to be designated as π complexes, they can no longer have the restrictions placed on them in Dewar's earlier theories for the rearrangement.[10]

Disproportionation can be represented with a π-complex reaction, particularly within the framework of the Scheme III. We can draw an analogy between this reaction (eq 1) and the very rapid oxidation of hydrazo compounds by Bindschedler's green (eq 2). If this kind of reaction (*i.e.*, eq 1) is not a suitable description of disproportionation, we are left with the alternatives that the intermediate, *e.g.*, $(\mathrm{Int}_2)^{2+}$, is a π complex or a pair of caged-cation radicals from either of which free cation radicals are formed.



(1)



(2)

The oxidation of 4,4′-dichlorohydrazobenzene by *p*-hydrazobiphenyl in acid solution is similar to the reaction between *p*-hydrazotoluene and hydrazobenzene reported by Hammond and Clovis.[8] These results lead to the following observation about intermediates in these reactions. A diprotonated (presumably) hydrazo compound will oxidize another hydrazo compound which is in excess; yet, evidence for the oxidation of the solvent has never been found. The lack of this evidence is usually cited as an argument against cation-radical intermediates in hydrazoaromatic reactions. The same paradox must apply, however, if the intermediate in these cross-oxidations and in ordinary disproportionation reactions was an undissociated complex. The apparent absence of reaction with the solvent may be due only to the fact that the intermediates (complexes or aminium ions) are not sufficiently strong oxidizing agents to oxidize the alcoholic solvents in which the hydrazoaromatic reactions are usually carried out.

A puzzling feature in our results which has a connection with the above observation on intermediates is that reduction of *p*-hydrazobiphenyl was significant at low acidities (0.00612 *M*). The results suggest that an intermediate arising from the monoprotonated substrate is more easily reduced by solvent than an intermediate from the diprotonated substrate.

Our summary is that a complete description of the reactions of hydrazoaromatics in acid solution still awaits making. The case for the intermediateless, polar-transition-state theory of rearrangement cannot go unquestioned, and the steric aspects of the π-complex theory, as earlier described,[10] are not supported by experiment. In our view, intermediates which can lead to disproportionation and rearrangement by the same kinetic law are involved and their natures still need to be elucidated.

Experimental Section[15]

4-Nitrobiphenyl from the Columbia Organic Chemicals Co., Inc., was used without further purification, mp 114° (lit.[16] mp 114–114.5°).

***p*-Azobiphenyl (II)** was prepared by the reduction of 4-nitrobiphenyl, using the general method of Vogel.[17] The crude product was purified by reduction to the hydrazo compound with zinc and ammonium chloride, and oxidation of the hydrazo compound with sodium hypobromite. The *p*-azobiphenyl was recrystallized from benzene, giving red plates, mp 251° (lit.[18] mp 248°).

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[15] Analyses were by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

[16] I. M. Heilbron, Ed., "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, N. Y., 1946, p 142.

[17] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p 604.

[18] O. H. Wheeler and D. Gonzalez, *Tetrahedron*, **20**, 189 (1964).

4-Aminobiphenyl (III) was prepared by the reduction of 4-nitrobiphenyl with tin and hydrochloric acid. Crystallization from aqueous ethanol gave mp 52° (lit.[19] mp 53°).

***p*-Hydrazobiphenyl** (I) was prepared as needed by the reduction of *p*-azobiphenyl with zinc dust and ammonium chloride in slightly aqueous acetone.[20] The product was used without further purification.

Bindschedler's green was prepared as described earlier.[21]

Product Isolation.—A solution of hydrogen chloride in aqueous ethanol was added to a solution of I in ethanol, and the mixture was allowed to stand overnight. The II which precipitated during this time had mp 251° after filtration. The filtrate was evaporated to dryness at room temperature in a rotary evaporator. The residue was treated with aqueous sodium hydroxide. Thin layer chromatography [on Brinkman Instrument's silica gel GF254 with 4% ethanol in ligroin (bp 60–90°)] showed the presence of II, III, and IV. Preparative-scale isolation of IV was accomplished as follows. The dry, free-base mixture was triturated several times with ligroin. (The ligroin solution precipitated III on concentration.) The portion of the free-base residue which was insoluble in ligroin was recrystallized from ethanol, giving colorless plates (IV): mp 201–203°, λ_{max} (95% ethanol) 336 mμ (ϵ 4.3 × 10^4).

Anal. Calcd for $C_{24}H_{20}N_2$ (336.4): C, 85.68; H, 5.99; N, 8.34. Found: C, 85.98; H, 5.94; N, 8.48.

Reaction with acetic anhydride in benzene gave a monoacetyl derivative, mp 271–272° (95% ethanol).

Anal. Calcd for $C_{26}H_{22}N_2O$ (378.4): C, 82.51; H, 5.86. Found: C, 82.45; H, 5.98.

Reaction with benzoyl chloride in benzene gave a monobenzoyl derivative, mp 265–267° (95% ethanol).

Anal. Calcd for $C_{31}H_{24}N_2O$ (440.5): N, 6.19. Found: N, 6.36.

The equivalent weight of IV, determined by potentiometric titration with perchloric acid in anhydrous acetic acid, was 326.

Quantitative Product Analysis.—Solutions of I and hydrochloric acid in ethanol were mixed and allowed to react for 8–10 half-lives. The concentrations used were the same as those used for rate-constant determinations. The mixture was then neutralized with ammonium hydroxide, diluted to appropriate volumes with ethanol, and analyzed spectrophotometrically. A Cary Model 14 spectrophotometer was used. Extinction coefficients for compounds II, III, and IV were obtained with solutions in 95% ethanol containing a small amount of ammonium hydroxide, and are given in Table IV. The absorbance of 4-aminobiphenyl (III) at wavelengths 336 and 362 mμ was 0 in the range of concentrations used. The extinction coefficients were used in the analysis of five known mixtures of the three components. The results were in very good agreement with the the known concentrations. The results of the analyses of the unknown, experimental product mixtures are given in Table I.

TABLE IV

EXTINCTION COEFFICIENTS OF THE COMPOUNDS II, III, AND IV

	$\epsilon \times 10^{-4}$		
λ, mμ	II	III	IV
362	3.28	. . .	1.04
336	2.32	. . .	4.32
278	0.798	1.90	1.41

Kinetic Method.—Because of the low solubility of I in ethanol and aqueous ethanol, and because of the rapid reaction of I in acidic solution, the following kinetic method was devised. Aliquots of a solution of I in ethanol were kept in flasks in a bath at 0°. A stock solution of hydrogen chloride (and lithium chloride, where necessary) in aqueous ethanol was also kept at 0°. An aliquot of the acid solution was injected into an aliquot of the I solution with a syringe which had also been precooled to 0°. After the necessary time interval the reaction was quenched by injecting into the acidic solution an aliquot of a cold, aqueous solution of Bindschedler's green. A precooled syringe was used for this injection. Each syringe was provided with a stop device to deliver the same volume at each usage. The quenched solution was diluted to a known volume with water and extracted with benzene. The visible spectrum of the aqueous layer was recorded. Control experiments were performed with solutions containing no I. The logarithms of the differences between the absorbances of a control and experimental solutions were plotted against time, and good, first-order plots were obtained. The slopes of the plots from all kinetic runs were calculated by the method of least squares using an IBM 1620 computer. The rate constants are given in Tables II and III.

Cross Oxidation.—A solution of 0.1250 g of 4,4'-dichlorohydrazobenzene in 100 ml of 95% ethanol (4.95 × 10^{-3} *M*) was kept in an ice bath. A solution of 0.0173 g of *p*-hydrazobiphenyl in 100 ml of 95% ethanol (5.15 × 10^{-4} *M*) was similarly cooled. Four 10-ml aliquots of the 4,4'-dichlorohydrazobenzene solution were placed in separate flasks and each was acidified so as to be 0.256 *N* in acid. One of the aliquots was quenched immediately with 10 ml of Bindschedler's green solution (0.3007 g/100 ml of water). The other three aliquots were quenched after periods of 10, 15, and 30 min, respectively. Each quenched solution was titrated with titanous chloride solution, and each titer was 7.45 ml as compared to 32.21 ml for the Bindschedler's green alone. Thus the 4,4'-dichlorohydrazobenzene aliquots were equivalent to 24.76 ml of Bindschedler's green.

A similar set of three 4,4'-dichlorohydrazobenzene aliquots was prepared. To each of these after the acidification was added with stirring over a period of 5 min 10 ml of the cooled *p*-hydrazobiphenyl solution. The solutions were allowed to stand for another 5, 10, and 15 min, respectively, and then quenched with Bindschedler's green. The aliquots were titrated with titanous chloride. The titers were close in value and averaged 8.77 ml. The hydrazo content of the solutions, therefore, was equivalent to 23.44 ml of Bindschedler's green, that is, lower than the hydrazo content of the first set of 4,4'-dichlorohydrazobenzene aliquots by an amount equivalent to 1.32 ml of Bindschedler's green.

The half-life of *p*-hydrazobiphenyl in 0.128 *N* acid is approximately 2 min (see Table II). Therefore, in the absence of reaction between the two hydrazo compounds almost all of the *p*-hydrazobiphenyl in the mixture should have reacted in its normal way, and the Bindschedler's green titer would then have been either a little smaller than or equal to 7.45 ml. The results show that some of the 4,4'-dichlorohydrazobenzene was destroyed by the *p*-hydrazobiphenyl. The obvious route to destruction is that one of the protonated hydrazo compounds oxidized the other. The more likely of these reactions is the oxidation of 4,4'-dichlorohydrazobenzene to 4,4'-dichloroazobenzene by protonated *p*-hydrazobiphenyl (or an intermediate derived therefrom). The ultraviolet spectrum of the recovered free bases from the mixture reactions (*i.e.*, after removal of azo compounds) showed the presence of 4-aminobiphenyl but not *p*-chloroaniline. More definite evidence for the absence of *p*-chloroaniline could not be obtained. With this assumption about the oxidation reaction it is seen that 5.3% (1.32/24.76 × 100) of the 4,4'-dichlorohydrazobenzene was oxidized. This means that approximately 53% of the *p*-hydrazobiphenyl was used in the intermolecular oxidation.

Esr Experiments.—Solutions of hydrochloric acid in ethanol and *p*-hydrazobiphenyl in ethanol were allowed to mix under gravity flow in a cell in the cavity of a Varian Associates esr spectrometer. The concentrations of reactants on mixing were similar to those of the kinetic runs. Radicals were not detected in any of these flow experiments.

Registry No.—I, 4088-58-8; II, 5326-53-4; III, 92-67-1; IV, 7731-05-9.

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[19] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1961, p 602.

[20] H. J. Shine and J. C. Trisler, *J. Am. Chem. Soc.*, **82**, 4054 (1960).

[21] H. J. Shine, R. L. Snell, and J. C. Trisler, *Anal. Chem.*, **30**, 383 (1958).