

Similar results were found with several variations of this procedure and also when tetrahydrofuran was the solvent. Bromide 14 was recovered from attempts to treat it with ethereal *n*-butyllithium at -40 , 0° , or 25° (59, 59, and 64.5% recovery, respectively); with *t*-butyllithium in ether at -80 or 0° (57 and 67% recovery); with lithium ribbon under reflux in any one of ether, tetrahydrofuran, or cyclohexane solvents (73, 68, and 66% recovery); with lithium shot in the presence of sodium in hot cyclohexane (68% recovery); with magnesium turnings and tetrahydrofuran under reflux in either toluene (79% recovery) or xylene (78% recovery). No other organic products could be isolated from these attempts upon carbonation and work-up. An attempt to prepare the Grignard reagent from 13 exactly as described for the preparation of 15 led to recovered 13 (74%).

Attempted Displacements on 14. The following reactions on 14 were attempted under reflux for 26 hr without success: potassium cyanide with a trace of potassium iodide in absolute ethanol

(66% recovery of 14); the same process in dimethylformamide (56.5% recovery); cuprous cyanide in the presence of copper bronze in dimethyl sulfoxide (53% recovery).

Registry No.—1, 4486-29-7; 3, 7605-04-1; 4, 7605-05-2; 9, 7605-06-3; 10, 7605-07-4; 11, 7605-08-5; 12, 7605-09-6; 13, 7605-10-9; 14, 7605-11-0; 15, 7605-12-1; 2, 4453-90-1; 6, 7605-14-3.

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The Benzidine Rearrangement. VIII.^{1,2} The Rearrangement and Disproportionation of 4,4'-Di-*t*-butylhydrazobenzene and 4-*t*-Butyl-4'-chlorohydrazobenzene

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The products and rates of disappearance of 4,4'-di-*t*-butylhydrazobenzene (I) at 0° and 4-*t*-butyl-4'-chlorohydrazobenzene (II) at 25° in acidic 95% ethanol have been determined. Rearrangement to an *o*-semidine, accompanied by 40–50% disproportionation, occurred in each case. Neither the rates of disappearance of I and II nor the relative amounts of rearrangement and disproportionation were affected by changing the initial concentration of the hydrazo compound. The disappearance of I is second order in acid; that of II has an order 1.9 in acid. The concentration of the acid did not seriously affect the ratio of the amounts of rearrangement and disproportionation, with the exception of an increase in the extent of rearrangement of II at the highest acid concentration used. It is concluded (1) that steric hindrance by *para* substituents is not a factor in determining the order in acid, and (2) that the role of an intermediate in the rearrangement of hydrazoaromatics cannot be ignored. The latter conclusion is discussed in the following paper (part IX).

Since Carlin and Odioso³ showed that the rearrangement of *o*-hydrazotoluene was kinetically 1.6 order in acid, information has been slowly gathered to explain this fractional acid dependence. Other cases have come to light. Dewar and McNicoll⁴ have reported 1.58 for 4-chloro-4'-methylhydrazobenzene and 1.51 for 4-*t*-butyl-4'-chlorohydrazobenzene. In a series of papers, Banthorpe, Hughes, and Ingold⁵ have shown first-, second-, and varied-order acid dependences among the hydrazonaphthalenes. They have also placed on a firm footing the kinetic dichotomy of the benzidine rearrangement, first proposed by Blackadder and Hinshelwood,⁶ and confirmed by White and Preisman.⁷ Thus, they have shown that where fractional acid dependence prevails, the rearrangement will go toward first-order acid dependence as acidity is lowered and toward second-order as it is raised.

In spite of the settling of the kinetic features of the benzidine rearrangements it is still necessary to know why the order in acid may vary from one compound to

another. Dewar⁸ has proposed that steric effects owing to bulky *p*-substituents would be one of the factors leading to mixed orders in acid. The basis for this proposal is the π -complex theory of the benzidine rearrangement. In this theory a series of π complexes is proposed, each complex corresponding with a product type, *e.g.*, benzidine, semidine, diphenylene, that may arise from a hydrazobenzene. It is predicted that bulky *para* substituents would cause rotation of the π -complexed halves of the protonated hydrazo molecule to a sterically favorable configuration. The theory, which describes the interconversions of the several π complexes, also requires that such a steric effect would result in a lowering of the acid order. Dewar and McNicoll concluded that their results with 4-chloro-4'-methylhydrazobenzene and 4-*t*-butyl-4'-chlorohydrazobenzene were in accord with predictions. While recognizing that the 4-*t*-butyl-4'-chloro isomer might have special steric properties, we were unable to accept that a steric effect was responsible for the difference between the 4-chloro-4'-methyl isomer (order 1.58) and the similarly sized *p*-hydrazotoluene, for which Carlin and Wich⁹ reported an acid dependence of 2, a dependence which has been confirmed.¹⁰ There-

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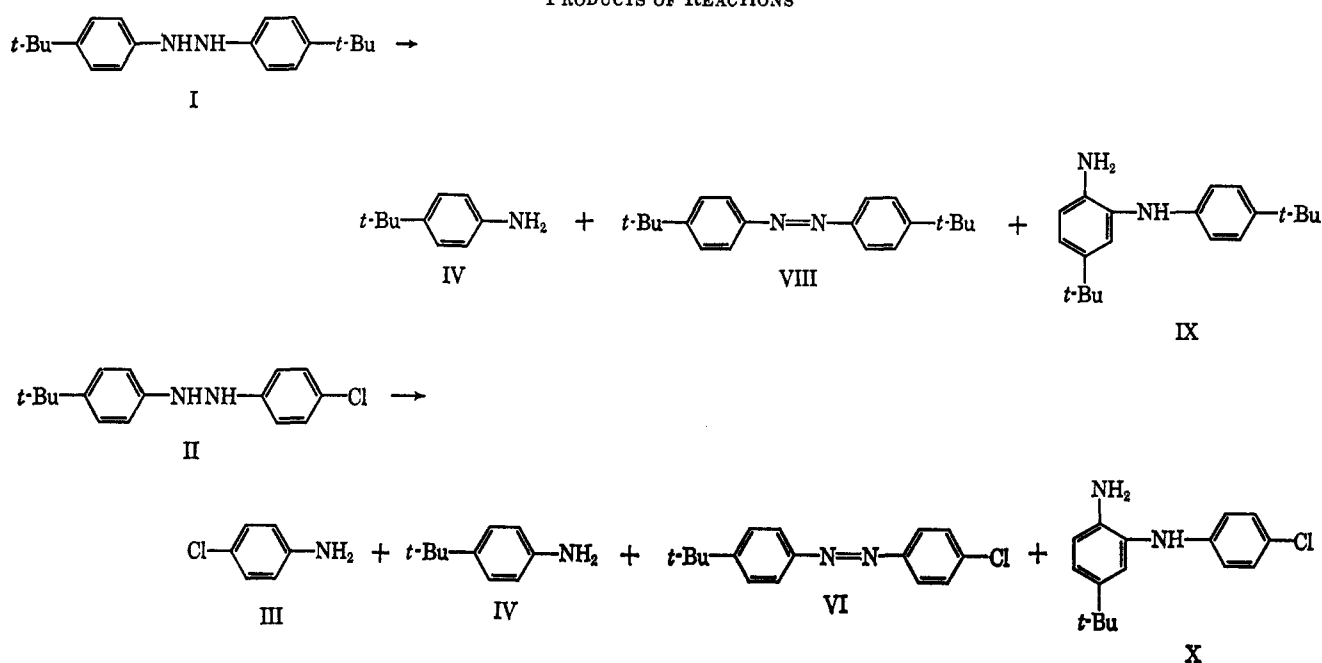
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CHART I
 PRODUCTS OF REACTIONS


fore, we have been investigating the rearrangements of 4,4'-disubstituted hydrazobenzenes. We have reported that the acid-catalyzed reaction of the divinyl compound¹¹ is first order in acid and, briefly, that that of the di-*t*-butyl compound (I) is second order.¹ We now wish to report the details of our rate and product determinations with I and also with 4-*t*-butyl-4'-chlorohydrazobenzene (II).

Results

The rate constants for the disappearance of I and II are given in Tables I and II. The reaction of I is rapid

TABLE I
 KINETIC DATA FOR THE DISAPPEARANCE
 OF 4,4'-DI-*t*-BUTYLHYDRAZOBENZENE (I)
 IN ACIDIC 95% ETHYL ALCOHOL AT 0°

Run ^a	[H ⁺], ^b M	k ^c × 10 ³ , min ⁻¹
94 ^d	0.05	18.9
95 ^d	0.05	19.2
118	0.04	11.5
120	0.04	10.7
110 ^e	0.03	6.79
116	0.03	6.72
112 ^e	0.02	2.47
117	0.02	2.52
123	0.02	2.61
119 ^e	0.01	0.867
121	0.01	0.728

^a All runs were 2.5 × 10⁻³ M in I except run 123 (5 × 10⁻⁴ M).
^b LiCl was added where necessary to keep a total ionic strength of 0.05. ^c Calculated by the method of least mean squares. ^d Sample and acid were contained in a Y tube. ^e Product analyses on samples from these runs are given in Table III.

at room temperature so that the rate measurements were made at 0°. In contrast, it was possible to work with II at 25°. The rates of disappearance gave good, first-order plots for all acid concentrations. Changing

the concentrations of I and II fivefold did not affect their rates of disappearance. The dependence on acid was 1.99 (*r* = 0.996) for I and 1.88 (*r* = 0.997) for II.

TABLE II
 KINETIC DATA FOR THE DISAPPEARANCE
 OF 4-*t*-BUTYL-4'-CHLOROHYDRAZOBENZENE (II)
 IN ACIDIC 95% ETHYL ALCOHOL AT 25°

Run ^a	[H ⁺], ^b M	k ^c × 10 ³ , min ⁻¹
152	0.10	13.3
153 ^d	0.10	13.0
141 ^d	0.08	6.26
143 ^d	0.08	5.72
147 ^d	0.06	3.95
156	0.06	4.63
158 ^d	0.06	4.13
159 ^d	0.06	4.00
146 ^d	0.04	1.93
148	0.04	2.07
151	0.02	0.576
154	0.02	0.542
160	0.01	0.135
161	0.01	0.153

^a All runs were 2.5 × 10⁻³ M in II, except runs 141 (2.43 × 10⁻³ M), 158 (5 × 10⁻³ M), and 159 (5 × 10⁻⁴ M). ^b LiCl was added to keep the total ionic strength 0.10. ^c Calculated by the method of least mean squares. ^d Product analyses on samples from these runs are given in Table IV.

The products of reaction (see Chart I) were obtained under the conditions of the rate measurements and were determined by ultraviolet spectroscopy. The results are given in Tables III and IV. It can be seen that disproportionation is extensive in both compounds. The relative amounts of rearrangement and disproportionation of I do not change with acid concentration. With II, however, the amount of rearrangement is higher at the highest acid concentration. It should be noted that in Table III, runs 112 and 134, and Table IV, runs 145, 147, 158, and 159, where only the concentrations of the hydrazo compound were changed, the product ratios are essentially the same.

TABLE III
PRODUCTS^a OF REACTION FROM 4,4'-DI-*t*-BUTYLHYDRAZOBENZENE (I) IN ACIDIC ETHYL ALCOHOL AT 0°

Run	[H ⁺], ^b <i>M</i>	Azo (VIII), 10 ⁵ × <i>M</i>	Amine (IV), 10 ⁵ × <i>M</i>	Semidine (IX), 10 ⁵ × <i>M</i>	Total, ^c 10 ⁵ × <i>M</i>	Rearrn, % ^d	Dispropn, % ^d	Oxidn, % ^d
97	0.05	1.35	2.31	2.27	4.78	47.6	48.4	4.0
114	0.04	1.46	2.59	2.42	5.18	46.8	50.1	3.1
110	0.03	1.40	2.37	2.31	4.90	47.2	48.4	4.4
112	0.02	1.35	2.33	2.25	4.77	47.3	48.9	3.8
134	0.02	1.56	2.54	2.28	5.11	45.7	50.9	5.8
119	0.01	1.38	2.21	2.12	4.61	46.1	48.0	5.9

^a Determined by ultraviolet analysis using the extinction coefficients in Table V. ^b Anhydrous LiCl was added to keep the total ionic strength 0.05. ^c All solutions were originally $2.5 \times 10^{-3} M$ in I, except run 134 which was $5 \times 10^{-4} M$. Analysis was carried out after dilution to give a solution that contained 1 equiv of $5 \times 10^{-5} M$ of I. The total represents the sum of the products in terms of I, and gives an indication of the error in the analytical data. ^d Of the product, based on the total in column 6. Disproportionation is based on the total amount of amine. Oxidation is based on the amount of azo compound in excess of half the amount of amine.

TABLE IV
PRODUCTS^a OF REACTION FROM 4-*t*-BUTYL-4'-CHLOROHYDRAZOBENZENE (II) IN ACIDIC 95% ETHYL ALCOHOL AT 25°

Run	[H ⁺], ^b <i>M</i>	Azo (VI), 10 ⁵ × <i>M</i>	Amine (XI), ^c 10 ⁵ × <i>M</i>	Semidine (X), 10 ⁵ × <i>M</i>	Total, ^d 10 ⁵ × <i>M</i>	Rearrn, % ^e	Dispropn, % ^e	Oxidn, % ^e
153	0.10	1.44	1.72	2.71	5.01	54.1	34.3	11.6
154	0.10	1.63	2.04	3.35	6.00	55.8	34.0	10.2
140	0.09	1.58	2.14	2.62	5.27	49.7	40.6	9.7
141	0.08	1.40	2.02	2.52	4.93	51.1	41.0	7.9
143	0.08	1.46	2.07	2.68	5.17	51.8	40.0	8.3
142	0.07	1.48	2.25	2.74	5.34	51.3	42.1	6.7
145	0.06	1.54	2.35	2.50	5.21	47.9	45.1	7.1
147	0.06	1.59	2.15	2.56	5.22	49.0	41.2	9.9
158	0.06	1.56	2.27	2.50	5.19	48.1	43.7	8.3
159	0.06	1.54	2.19	2.57	5.21	49.3	42.0	8.4
146	0.04	1.42	2.32	2.68	5.26	51.0	44.1	4.9
155	0.04	1.67	2.17	2.40	5.15	46.6	42.1	11.6

^a See footnote a in Table III. ^b Anhydrous LiCl was added where necessary to keep the total ionic strength 0.10. ^c Both III and IV. ^d All solutions were originally $2.5 \times 10^{-3} M$ in II, except runs 154 ($2.84 \times 10^{-3} M$), 141 ($2.43 \times 10^{-3} M$), 158 ($5 \times 10^{-3} M$), and 159 ($5 \times 10^{-4} M$). Analysis was carried out after dilution to give a solution that contained 1 equiv of $5 \times 10^{-5} M$ of II, except in runs 154 ($5.68 \times 10^{-5} M$) and 141 ($4.86 \times 10^{-5} M$). Thus, the total here represents the sum of the products in terms of II and gives an indication of the error in the analytical data. ^e See footnote d in Table III.

Discussion

It is evident immediately that our acid dependence for I does not fit Dewar's theory. The fivefold range of acid concentrations which was used with I is not large, but it overlaps the range of acidities for which II has an acid dependence of 1.9. With II we appear to be in the range of mixed orders. If the bulkiness of the substituent is a factor which controls the order in acid, we would have expected it to be more evident in I than II. Our result with II differs from that of Dewar and McNicoll (1.51).⁴ They used 75% alcohol as solvent and did not state the range of acid concentrations or any rate data; so proper comparison cannot be made. It is still debatable as to whether π complexes are intermediates in the benzidine rearrangement. But, the kinetic and steric-effect features of the π -complex theory⁸ of the rearrangement seem to be no longer supportable.

The fractional acid dependences in the reactions of II and 4-chloro-4'-methylhydrazobenzene indicate a contribution from first-order, acid-catalyzed reactions. The reason for these contributions may be like that proposed by Banthorpe, Hughes, and Ingold,¹² for other first-order acid catalyses, namely the combination in the monoprotonated molecule of the low basicity of the chlorophenyl-substituted nitrogen atom and the scission-promoting electron donation of the *p*-alkyl group.

The products from I and II are those of rearrangement and disproportionation. In the case of I the relative amounts of rearrangement and disproportionation do not depend on the initial concentration of I or of acid. This means that rearrangement and disproportionation follow the same kinetic law over the range of concentrations used. Thus, the same situation prevails here as in the case of *p*-hydrazotoluene.⁹ A disproportionation reaction which is first order in substrate is not easily interpreted, but any mechanism which is to describe the rearrangement of the substrate properly must also be able to accommodate a disproportionation reaction with this kinetic characteristic. Since the protonations of hydrazoaromatics are not rate determining,⁵ the division into two paths (to rearrangement and disproportionation) must occur after protonation has occurred. Two sequences for the division may be considered. They will be described here and discussed in the succeeding paper (part IX) which deals with *p*-hydrazobiphenyl. The two sequences will be considered in terms of the diprotonated hydrazoaromatic molecule, since, as far as we know, no evidence exists for concomitant rearrangement and disproportionation under clean, first-order acid catalysis. The first sequence to be considered is that in which the diprotonated hydrazoaromatic molecule forms an intermediate in a rate-determining step, and this intermediate undergoes competitive, fast rearrangement and disproportionation reactions. The second sequence is that in which the diprotonated hydrazoaromatic

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molecule may take two rate-determining paths: one of them directly to rearrangement products (this would correspond with the polar-transition-state theory⁵ of rearrangement), and the other to an intermediate which next engages in the rapid disproportionation reaction with unprotonated hydrazoaromatic molecules. If the first sequence operated in rearrangement and disproportionation we might expect that the relative extents of these reactions with a given substrate would vary if the initial concentration of unprotonated substrate was changed. In our experience, with cases of wholly second-order acid kinetics and in Carlin's with *p*-hydrazotoluene,⁹ the ratio of rearrangement to disproportionation was not affected by changing either the substrate concentration or acid concentration. This point is discussed further in part IX. The data in Table IV show that the extent of rearrangement of 4-*t*-butyl-4'-chlorohydrazobenzene is somewhat larger at the highest acid concentration than at the lower concentrations. We are reluctant to use these data to diagnose which sequence of paths a hydrazoaromatic takes in undergoing rearrangement and disproportionation. The data in Table IV result from the spectroscopic analysis of a four-component system and do not have the accuracy that is desirable for making comparisons among experiments with different acid and substrate concentrations.

The rate and product data which we have for these two 4,4'-disubstituted hydrazobenzenes (I and II) are useful in helping to dispose of steric effects as a cause of low acid orders and in indicating that discussions of a mechanism of rearrangement of hydrazoaromatics should properly include the mechanism of disproportionation.

Experimental Section

***p*-Nitro-*t*-butylbenzene (VII).**—A mixture of 178 g of concentrated nitric acid and 383 g of concentrated sulfuric acid was added over a period of 3 hr to 262 g of *t*-butylbenzene (Phillips pure grade), while stirring at 25–30°. After additional stirring for 3 hr at this temperature and for 1 hr at 40°, the mixture was poured onto ice. The organic layer was washed with 10% sodium bicarbonate solution, dried, and fractionally distilled through a 3-ft, vacuum-jacketed column packed with glass helices. The product [bp 133° (10 mm), n_D^{25} 1.5308, 175 g] was collected in seven fractions. Thirteen earlier fractions were discarded [lit.¹³ bp 135° (10 mm), n_D^{20} 1.5337].

4,4'-Di-*t*-butylazobenzene (VIII) was made by adding 10 g of zinc dust in small portions to a boiling solution of 5 g of VII in 50 ml of 95% ethyl alcohol and 10 ml of 20% sodium hydroxide. After filtration of the solution, air was bubbled through it until a test sample did not decolorize aqueous Bindschedler's green. Evaporation and recrystallization from aqueous acetone gave 2.0 g (50%), mp 185–186° (lit.¹⁴ mp 183°).

***p*-Chloroaniline (III)** was obtained commercially and was recrystallized from aqueous methanol, mp 69–70.5°.

***p*-*t*-Butylaniline (IV)** was made by boiling 20 g of the nitro compound with tin and 50% hydrochloric acid. The solution was boiled until a sample remained clear on dilution with water. After making alkaline and extracting with ether, 13 g (70%) of a brown oil was obtained. A small amount of this was vacuum distilled for recording ultraviolet data. The remainder was used as described below.

***p*-Chloronitrosobenzene (V)** was made by the method of Lutz and Lytton.¹⁵ The crude product [mp 78–81° (lit.¹⁵ mp 89.5°)] was used without further purification as follows.

4-*t*-Butyl-4'-chloroazobenzene (VI).—This compound was pre-

pared by the general method of Ogata and Takagi.¹⁶ To a solution of 1 g of IV and 1 g of V in a slight excess of 95% ethyl alcohol at 70° was added 2 ml of acetic acid. The solution was heated for 1.5 hr at 70° after which about one-fourth of the alcohol was distilled off. Water was added slowly after cooling and the brown precipitate obtained was crystallized from 95% ethyl alcohol, giving 0.7 g (45%), mp 115.5–116.5°.

Anal. Calcd for C₁₆H₁₇N₂Cl: C, 70.44; H, 6.28; N, 10.27. Found: C, 70.44; H, 6.27; N, 10.48.

4,4'-Disubstituted hydrazobenzenes were made as needed from the azo compounds by reduction with zinc dust and ammonium chloride in aqueous acetone.¹⁷ The melting points, by the capillary tube method at a heating rate of 3°/min, were 127–129° for 4,4'-di-*t*-butylhydrazobenzene (I) and 87–89° for 4-*t*-butyl-4'-chlorohydrazobenzene (II).

2-Amino-4',5-di-*t*-butyldiphenylamine (IX) was prepared from I by the method of Wilberg¹⁸ for the dichloro analog. The product obtained in poor yield had mp 104–105° (lit.¹⁴ mp 101°).

2-Amino-4'-chloro-5-*t*-butyldiphenylamine (X) was obtained similarly from II as a gray solid in very poor yield (about 2%). Recrystallization from aqueous methyl alcohol gave mp 72–73°. The rearrangement of II can, in principle, give two *o*-semidines, that is, X and the one in which the chloro and *t*-butyl groups have exchanged positions. It is assumed that X has the structure cited on the basis of analogous rearrangements in the early literature,¹⁹ and Ingold's rules.⁵

Kinetic Method.—The method devised by Dewar²⁰ with Bindschedler's green and titanous chloride solution was used for following the disappearance of the hydrazo compounds. The solvent used in each case was 95% ethyl alcohol, the same supply being used for all rate work. Solutions of hydrogen chloride in ethyl alcohol were made by dropping concentrated sulfuric acid onto solid sodium chloride and bubbling the generated hydrogen chloride through fresh sulfuric acid and then into the ethyl alcohol.

At low acid concentrations both I and II rearrange readily. The rates of rearrangement of I were measured at 0° while those of II were measured at 25°. For this purpose a solution of the calculated amount of hydrazo compound was made in one 50-ml volumetric flask and a solution of acid and salt (to maintain constant ionic strength) was made in a second. Both flasks were flushed with nitrogen prior to use and were kept at the appropriate temperature for 1 hr before the contents were mixed by pouring rapidly into a standard-taper, nitrogen-flushed flask, also at the appropriate temperature. Aliquots were removed by pipet at time intervals and discharged into aliquots of Bindschedler's green solution. In the case of I the pipet used was surrounded by an ice jacket. In the case of II it was observed that, unless the Bindschedler's green aliquots were titrated without delay, colored end points were obtained.²¹

First-order rate calculations were made from the plots of log [titanous chloride volume] vs. time. The results are given in Tables I and II.²²

Product Analysis.—Analyses were carried out by ultraviolet spectroscopy. Five-milliliter aliquots were used and were taken either from solutions used for rate determinations or from solutions prepared solely for analytical work. In the latter case, the concentrations of reactants and the conditions of reaction were the same as those used in the kinetic work. Thus, the products were formed under the same conditions as those under which the rate of disappearance of the hydrazo compound was measured. The aliquot was removed after enough time of reaction to ensure that little or no hydrazo compound remained. After transferring the aliquot to a volumetric flask, and partially diluting with solvent, a calculated amount of aqueous base, either 0.08 *N* potassium hydroxide or 0.19 *N* sodium hydroxide, was added. Further dilution by solvent gave solutions in the 10⁻⁵ *M* range for ultraviolet use.

Extinction coefficients for the anticipated products in the two systems studied are listed in Table V. In the case of di-*t*-butyl-

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(21) We wish to thank Dr. Charles Dais for help with the fast runs with this compound.

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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 m μ	287.7 m μ	235.3 m μ
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

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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 paper¹ of hydrazoaromatics in which rearrangement and disproportionation follow the same kinetic law. Carlin and Wich³ 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 Rassow⁴ 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 Dewar¹⁰ in support of the π -complex theory of the benzidine rearrangement.

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