Stable Carbocations. CXXIX.[1] Mechanism of the Benzidine and Wallach Rearrangements Based on Direct Observation of Dicationic Reaction Intermediates and Related Model Compounds

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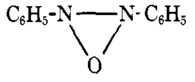
Abstract: Protonation of azo- and azoxybenzenes, pyridine *N*-oxides, hydrazobenzene, phenylhydrazine, and arylamines was studied in SbF_5–FSO_3H–SO_2 solution at low temperature. Diprotonated azo- and azoxybenzene, phenylhydrazine, and 2,4,6-trimethylaniline were obtained and studied by nmr (^1H and ^{13}C) spectroscopy. Two reaction intermediates, diprotonated azoxybenzene and the derived dehydrated dication, were observed for the first time in the Wallach rearrangement. In the benzidine rearrangement the intermediate di-C-protonated benzidine was also observed. Based on these experimental data, a new mechanism is proposed and discussed for the benzidine rearrangement.

The mechanisms of the Wallach[2] and benzidine[3] rearrangements have been intensively investigated but are still not clearly understood. A number of mechanisms for the Wallach rearrangement have been proposed. Shemyakin, Maimind, and Vaichunaite[4] suggested that the rearrangement proceeds through asymmetrical intermediate i or its protonated form ii. They have shown using ^{15}N-labeled azoxybenzene that the rearrangement of the azoxybenzene gave 4-hydroxyazobenzenes, $p\text{-}HOC_6H_4N{=}^{15}NC_6H_5$ and $p\text{-}HOC_6H_4{}^{15}N{=}NC_6H_5$, under various conditions where the two benzene rings were attacked with equal ease. Later, Gore[5] proposed two other possible mechanisms of the Wallach rearrangement. The first one involves mono-O-protonation of azoxybenzene **1** to give **2** and then nucleophilic attack by either water or the HSO_4^- group is restricted to the far ring. The other suggested mechanism involves the symmetrical dication **4**. The essential distinction between the two paths is one of timing; in the former case, removal of the -OH groups is preceded by, while in the later case it precedes the nucleophilic attack. Gore also suggested that the former mechanism, involving the mono-O-protonated azoxybenzene **2**, be favored when the acidity of the medium is low. On the other hand, Oae, Fukumoto, and Yamagami[6] proposed a mechanism of the Wallach rearrangement involving both the protonated acylic *N*-oxide, ii, of Shemyakin and mono-O-protonated azoxybenzene **2** of Gore. Recently, kinetic studies favored the formation of the symmetrical dicationic intermediate **4**, formed by two alternative routes.[7] Buncel and Lawton[7a] also suggested the possibility that the dication **4** might become stabilized in anhydrous acids where water as nucleophile is not available. Thus, it seemed worthwhile to study the Wallach rearrangement in superacids, thus extremely low nucleophilic media, and if possible to directly observe the mono- and/or diprotonated azoxybenzene as well as the symmetrical dication **4**.



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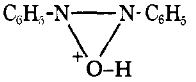

ii

There are three theories relating to the mechanism of the benzidine rearrangement. These are the polar transition state theory, proposed by Banthorpe and Ingold;[8] the π-complex theory proposed by Dewar;[9] and the caged-radical theory.[10] Evidence for the caged-radical and π-complex mechanisms has been reviewed and refuted by Banthorpe.[11] The postulated protonated intermediates were never directly observed. We now wish to report our results on the protonation of hydrazobenzene and phenylhydrazine as well as arylamines and our conclusions drawn relating to the mechanism of the benzidine rearrangement.

Results and Discussion

Wallach Rearrangement. Monoprotonation of azoxybenzene **1** is obtained in FSO_3H–SO_2 solution at −78°. The pmr spectrum of monoprotonated azoxybenzene **2** is shown in Figure 1 (B trace). The aromatic

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[1] Part CXXVIII: G. A. Olah, K. Dunne, Y. K. Mo, and P. Szilagyi, *J. Amer. Chem. Soc.*, **94**, 4200 (1972).

[2] For a review see P. A. Smith, "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, pp 313–315; E. Buncel, "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1968, pp 61–117.

[3] (a) C. K. Ingold, *Chem. Soc., Spec. Publ.*, No. **16**, 118 (1962); (b) H. J. Shine in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1969, pp 191–247.

[4] M. M. Shemyakin, V. I. Maimind, and B. K. Vaichunaite, *Chem. Ind. (London)*, 775 (1958); *Zh. Obshch. Khim.*, **28**, 1708 (1958); M. M. Shemyakin, V. I. Maimind, and T. E. Agadzhanyan, *Chem. Ind. (London)*, 1223 (1961).

[5] P. H. Gore, *ibid.*, 191 (1959).

[6] S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Jap.*, 36, 601 (1963).

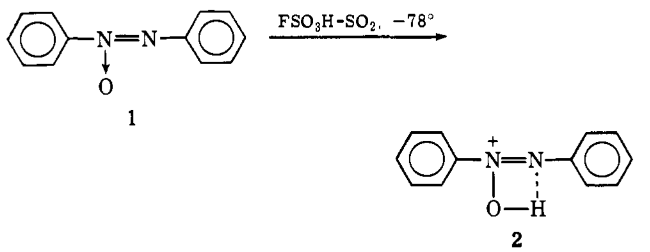
[7] (a) E. Buncel and B. T. Lawton, *Chem. Ind. (London)*, 1835 (1963); (b) E. Buncel and B. T. Lawton, *Can. J. Chem.*, 43, 862 (1965); (c) E. Buncel and W. M. J. Strachan, *ibid.*, 47, 911 (1969); (d) E. Buncel, W. M. J. Strachan, R. J. Gillespie, and R. Kapoor, *Chem. Commun.*, 765 (1969); (e) E. Buncel and W. M. J. Strachan, *Can. J. Chem.*, **48**, 377 (1970).

[8] D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2864 (1964).

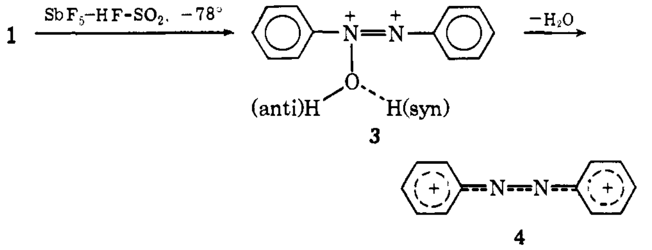
[9] M. J. S. Dewar, *ibid.*, 777 (1946).

[10] Reference 3b, p 223.

[11] D. V. Banthorpe, *Chem. Rev.*, 70, 295 (1970), and ref 8.



protons are deshielded from those of azoxybenzene (Figure 1, A trace). The hydroxyl (OH) proton displays a singlet at δ 14.05. The OH absorption is temperature dependent. It becomes broadened and finally merges into the base line at higher temperature. These results show that monoprotonated azoxybenzene **2** undergoes rapid proton exchange with the acid system. Furthermore, the highly deshielded OH absorption indicates the possibility of hydrogen bonding with the neighboring nitrogen atom lone pair.



Diprotonated azoxybenzene **3** was obtained when **1** was treated with SbF$_5$–HF–SO$_2$ solution at −78°. The pmr spectrum of the solution shows the formation of **3** accompanied by 10% of the dication **4** (Figure 1, C trace). Attempts to prepare diprotonated azoxybenzene without contamination by the dication **4** were not successful even when **1** was protonated carefully at the lowest possible temperature. Presumably, a small amount of dehydration (to form dication **4**) might be caused by the local overheating of the system since protonation is an exothermic reaction. The formation of dication **4** can be recognized by the presence of proton absorptions at δ 9.10 in the pmr spectra (Figure 1, C and D traces). It is interesting to note that the OH proton appears as two singlets at δ 12.72 and 12.80, which collapsed to a broadened singlet at higher temperature. These results indicate the formation of isomeric (syn and anti) diprotonated azoxybenzenes **3**. Similar behavior has been observed in other protonated heteroaliphatic compounds.[12] The NH proton of **3** shows a broadened singlet absorption at δ 12.1 (Figure 1, C trace). However, the proton shift of NH varies with the nature of the medium. For example, when the solution was warmed from −78 to −50° for 1 min and then cooled to −78°, the NH proton shift was shielded to δ 10.9. Meanwhile, the concentration of dication **4** and the hydronium ion (H_3O^+) was also increased (Figure 1, D trace). Finally, when the solution was warmed to −50° for about 5 min, the pmr spectrum showed complete transformation of **3** to the dication **4** (Figure 1, E trace). The hydronium ion absorption was very much increased. The pmr spectrum of **4** shows a characteristic pattern of a phenyl group attached to a charged center. Indeed, the pmr spectrum is almost identical with that of the aromatic protons of the benzoyl cation.[13] The chemical shifts of the ortho and para protons (center at δ 9.1) are deshielded from that of meta protons (center at δ 8.4). The solution of dication **4** was quenched in water to give 4-hydroxyazobenzene.

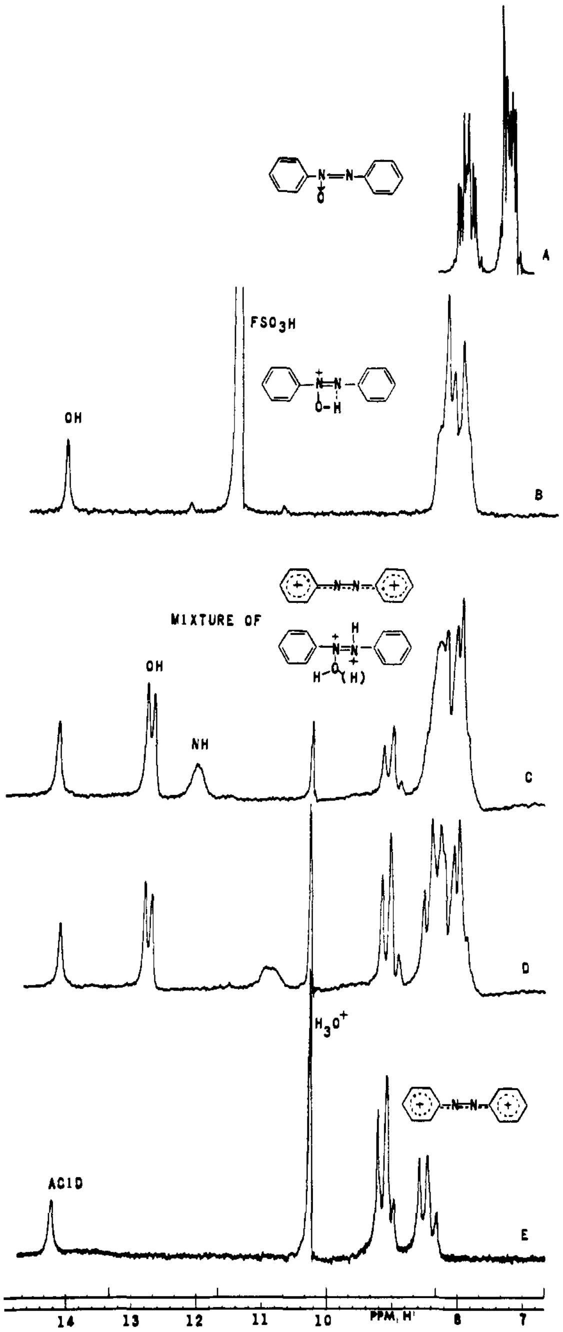


Figure 1. Pmr spectra of (A) azoxybenzene in SO$_2$; (B) azoxybenzene in FSO$_3$H–SO$_2$, monoprotonated azoxybenzene; (C and D) a mixture of diprotonated azoxybenzene and its dication **4**; and (E) the dication **4**.

In addition, we also studied the protonation of 4,4′-dichloroazoxybenzene **5** in strong acids. The pmr spectra of **5** and its monoprotonated 4,4′-dichloroazoxybenzene **6** (in FSO$_3$H–SO$_2$ solution at −78°) are shown in Figure 2 (A and B traces, respectively). The OH proton was found as a slightly broadened singlet

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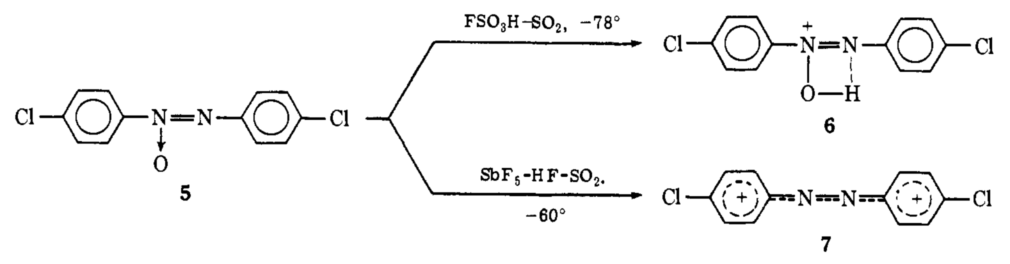
(12) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 70, 561 (1970)

(13) G. A. Olah, J. Lukas, and E. Lukas, *J. Amer. Chem. Soc.*, **91**, 5319 (1969), and previous references given therein.



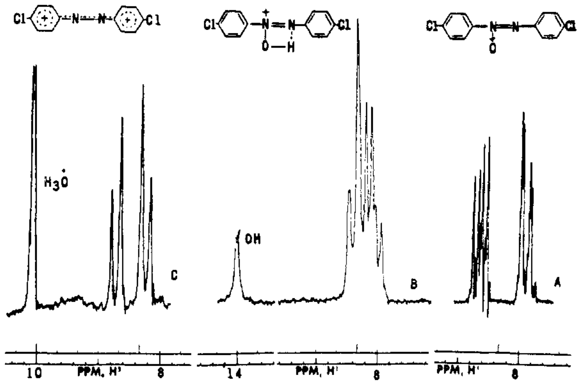


Figure 2. Pmr spectra of (A) 4,4′-dichloroazoxybenzene in SO_2; (B) 4,4′-dichloroazoxybenzene in FSO_3H-SO_2, monoprotonated 4,4′-dichloroazoxybenzene; and (C) the dication prepared from 4,4′-dichloroazoxybenzene and SbF_5-HF in SO_2 solution.

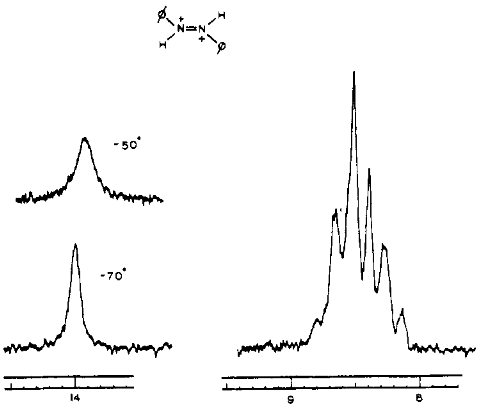
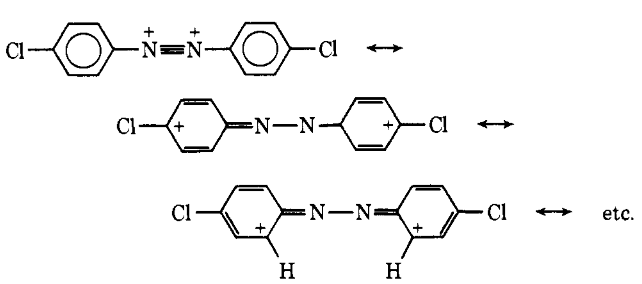


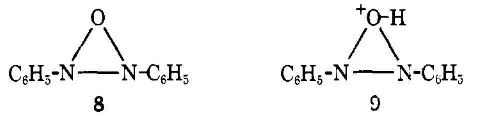
Figure 3. Pmr spectrum of diprotonated azobenzene **12**.

absorption at δ 14.0. The highly deshielded OH proton indicates N–H hydrogen bonding. Isomeric ions (syn and anti) were not observed even at −100°. When **5** was treated with $SbF_5-HF-SO_2$ at −60°, only dication **7** was obtained. The pmr spectrum of dication **7** shows an AB-type quartet indicating the equivalence of the two aromatic rings. The shielded doublet (δ 8.23) is assigned to the protons adjacent to the chlorine atoms and the deshielded doublet to the protons ortho to the nitrogen atoms. These assignments are made in accordance with the important resonance forms of dication **7**



Hydronium ion is formed along with the transformation of **5** to dication **7**. Attempts to observe the diprotonated 4,4′-dichloroazoxybenzene are not successful. Presumably, the driving force is the formation of very stable dication **7**. These results can be visualized by chlorine inductively destabilizing diprotonated 4,4′-dichloroazoxybenzene and at the same time being capable of stabilizing the dication *via* lone pair back donation.[14] Similarly, the 4-chlorobenzenium ion is known to be more stable than the parent benzenium ion, $C_6H_7^+$.[15]

We consider our results of significance because they represent the first direct observation of two intermediates (diprotonated azoxybenzene **2** and the dication **3**) in the Wallach rearrangement. Our results clearly rule out the intermediacy of an *N,N*-oxide intermediate **8**



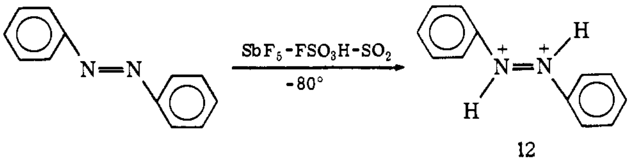
8 **9**

or its protonated form **9** which has been proposed by Shemyakin and associates.[4] The formation of diprotonated azoxybenzene can explain results of ^{15}N-labeled azoxybenzene experiments of Shemyakin and coworkers[4] who observed that azoxybenzene recovered from the reaction remained practically unchanged in isotopic distribution. At the same time, formation of dication **4** explains that the rearrangement of azoxybenzene gave an equal amount of labeled 4-hydroxyazobenzenes **10** and **11**. Other experimental work

$C_6H_5N{=}^{15}NC_6H_4OH$ **10** $C_6H_5{}^{15}N{=}NC_6H_4OH$ **11**

including kinetic studies[7] indicates the involvement of a two-proton process (second protonation is the rate-determining step). This also can be explained by our experimental observation (monoprotonation of **1** and **5** in weaker acid and diprotonation of **1** in stronger superacid).

Diprotonation of azobenzene **12** was achieved in



12

$SbF_5-FSO_3H-SO_2$ ("magic acid") at −80°. The pmr spectrum of **12** (Figure 3) shows a temperature-depen-

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(14) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 3551 (1972).

(15) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **92**, 2654 (1970).

Table I. Pmr Parameters of Protonated and Parent Pyridine *N*-Oxides[a]

Pyridine *N*-oxide (R)	Solvent system	Temp, °C	δ_α	δ_β	δ_γ	δ_R	δ_{OH}
2,4,6-Trimethyl	$CDCl_3$	37				3.01 (s, CH_3, 6 H), 2.77 (s, CH_3, 3 H)	
	SbF_5–FSO_3H–SO_2	−100				2.99 (s, CH_3, 6 H), 2.79 (s, CH_3, 3 H)	8.4 (s, br)
p-CH_3	$CDCl_3$	37	8.13 (d, J = 7.0)	7.15 (d, J = 7.0)		2.37 (s, CH_3, 3 H)	
	SbF_5–FSO_3H–SO_2ClF–SO_2F_2	−100	8.55 (d, J = 7.0)	8.24 (d, J = 7.0)		3.00 (s, CH_3, 3 H)	9.5 (s, br)
p-OCH_3	$CDCl_3$–DMSO-d_6	37	7.32 (d, J = 6.5)	8.59 (d, J = 6.5)		4.04 (s, OCH_3, 3 H)	
	SbF_5–FSO_3H–SO_2ClF	−90	7.66 (d, J = 7.0)	8.54 (d, J = 7.0)		4.37 (s, OCH_3, 3 H)	9.4 (s, br)
m-CH_3	$CDCl_3$	37	8.2 (m)	7.2 (m)	7.2 (m)	2.33 (s, CH_3, 3 H)	
	SbF_5–FSO_3H–SO_2ClF–SO_2F_2	−100	8.9 (m)	8.9 (m)	8.5 (m)	3.00 (s, CH_3, 3 H)	9.7 (br)
H	CCl_4	37	8.10 (m)	7.28 (m)	7.08 (m)		
	SbF_5–FSO_3H–SO_2	−70	8.8 (m)	8.2 (m)	8.6 (m)		9.8 (s, br)
p-CN	DMSO-d_6	37	8.42 (d, J = 7.0)	7.87 (d, J = 7.0)			
	SbF_5–FSO_3H–SO_2	−60	9.40 (d, J = 6.5)	9.08 (d, J = 6.5)			10.9 (s)

[a] Proton chemical shifts are referred to external capillary TMS in parts per million; s = singlet, d = doublet, m = multiplet.

dent singlet absorption at δ 14.0 (2 H). The singlet is assigned to the protons attached to an sp^2 nitrogen atom and their broad temperature-dependent character indicates exchange with the acid solvent and/or quadrupole broadening. The pmr spectrum of dication **12** has a similar feature to that of *trans*-stibene. The aromatic protons of **12** display a multiplet centered at δ 8.5 and are deshielded from those of azobenzene. We also examined the protonation of 4-fluorosulfonatoazobenzene **13**, the Wallach rearrangement product of azobenzene in FSO_3H. The pmr spectrum of **13** in SbF_5–FSO_3H–SO_2, "magic acid" at −80°, shows two different broadened $=^+NH$ absorptions at δ 14.0 and 14.3. The deshielded absorption is assigned to the $=^+NH$ proton attached to $-C_6H_4OSO_2F$.

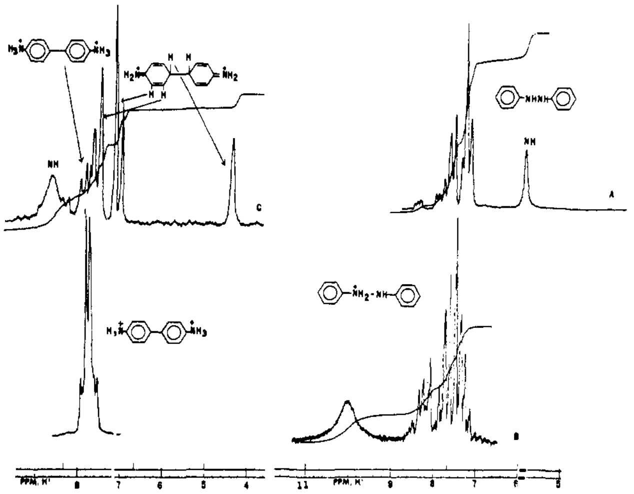
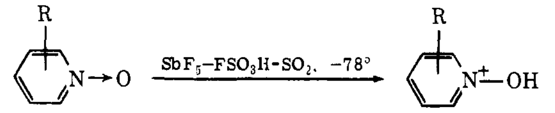


Figure 4. Pmr spectra of hydrazobenzene (A), monoprotonated hydrazobenzene (B), di-C-protonated benzidine (C), and di-N-protonated benzidine (D); the $^+NH_3$ proton absorption is not observable due to rapid exchange with acid.

In the course of our study of the Wallach rearrangement, we were also interested in the *protonation of N-oxides* in superacids. We have already discussed that azoxybenzene is readily mono-O-protonated in FSO_3H–SO_2 solution. It is also known that *N*-oxides are less basic than the corresponding amines. Studies of *N*-oxides, particularly pyridine *N*-oxides **14** and their



14 15

R = 2,4,6-trimethyl, *p*-CH_3, *p*-OCH_3, *m*-CH_3, H, *p*-CN

conjugate acids, have been carried out by Katritzky and Lagowski[16] and Abramovitch and Davis.[17] In "magic acid" solution, the protons on the oxygen of protonated pyridine *N*-oxides **15** can also be observed as temperature-dependent singlets at δ 9.0–11.0. The pmr parameters of pyridine *N*-oxides **14** and protonated pyridine *N*-oxides **15** are summarized in Table I.

Benzidine Rearrangement. Hydrazobenzene hydrochloride **17** can be prepared by the action of dry HCl on hydrazobenzene **16** in ether.[18] The pmr spectra of **16** and **17** are shown in Figure 4 (A and B traces, respectively). The aromatic proton absorptions of **16** and **17** are similar but are slightly deshielded in the latter. The $^+NH_2NH$ protons of **17** show a broadened peak at δ 10.0 indicating a rapid proton exchange of –NH– and $-^+NH_2-$. When HCl was treated with **16** in $SO_2(SO_2ClF)$ solution at −78°, a slightly yellow precipitate was formed. The precipitated salt was isolated by evaporating off the SO_2 at room temperature. The pmr spectrum of this precipitated salt (in dimethyl sulfoxide) shows the formation of benzidine dihydrochloride, $^+H_3NC_6H_4C_6H_4NH_3^+$, **18**. However, when **16** was treated with the FSO_3H–SO_2 (SO_2ClF) or HF–SO_2 at −78°, an intermediate **19** was observed in addition to a small amount of diprotonated benzidine **18**. The pmr spectrum (Figure 4, C trace) of the solution shows (in addition to diprotonated benzidine **18** present in about 10% concentration which shows an AB type quartet at δ 8.8) a slightly broadened absorption at δ 4.38, two doublets (or AB type quartet) at δ 7.00 (J = 10 Hz) and 7.60 (J = 10 Hz), and broadened absorption (characteristic of NH) at δ 8.6. These data are consistent with the formation of the intermediate dication

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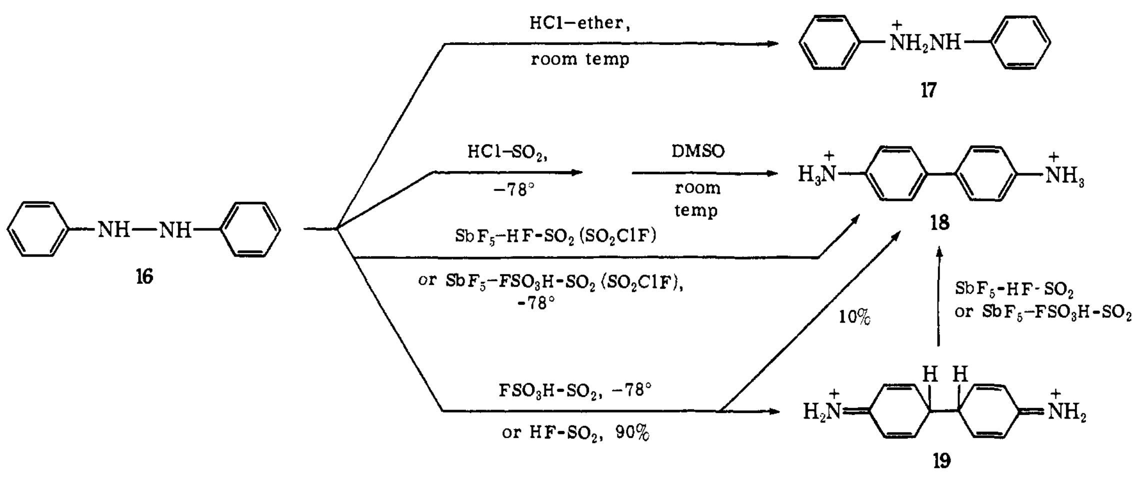
(16) A. R. Katritzky and J. M. Lagowski, *J. Chem. Soc.*, 43 (1961).

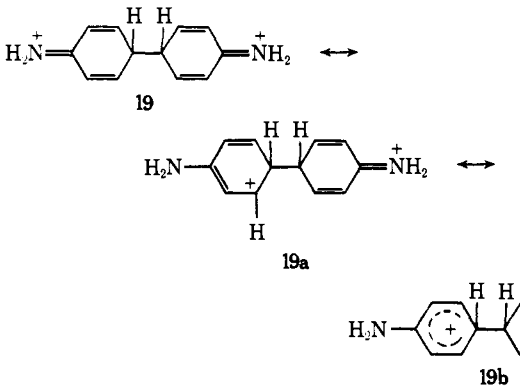
(17) R. A. Abramovitch and J. B. Davis, *J. Chem. Soc. B*, 1137 (1961).

(18) (a) H. Wieland, *Ber. Deut. Chem. Ges.*, **45**, 484 (1912); (b) V. O. Lukashevich, *Tetrahedron*, 23, 1317 (1967).

Scheme I



19. Furthermore, the C_2H protons, which show a deshielded doublet at δ 7.60, are coupled to the methine protons (δ 4.38). Irradiation of the methine absorption caused substantial sharpening of the doublet signal at δ 7.60. The coupling constants in benzenium ions between methylene protons (on sp^3 carbon) and ortho protons are usually small (1–2 Hz).[19] Ion 19 can be considered as di-C-protonated benzidine. The C_2H protons are more deshielded than the C_3H protons due to the resonance contribution forms **19a** and **19b**.

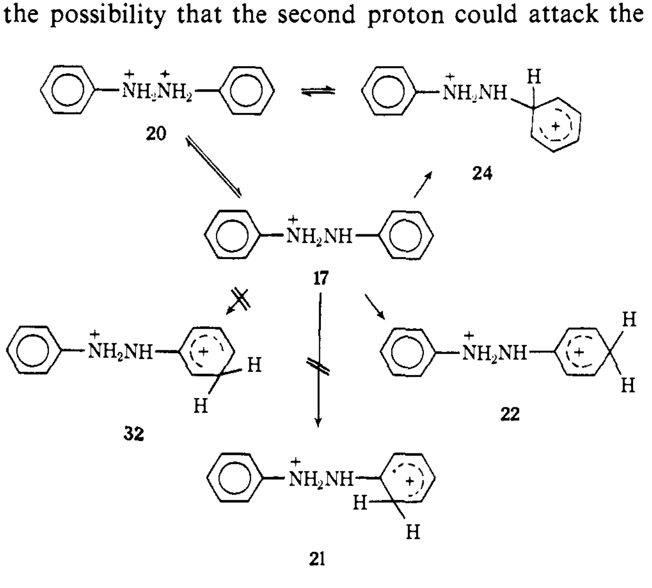


The chemical shifts (δ 4.38) of the methine protons of ion 19 are similar to that of C-protonated phenol (δ 4.50).[19] The NH absorption is temperature dependent indicating a rapid proton exchange with the acid system. Dication 19 can be transformed to di-N-protonated benzidine 18 when SbF_5–HF–SO_2 or SbF_5–FSO_3H–SO_2 was added to its solution at −78°. Alternatively, di-N-protonated benzidine 18 was formed exclusively when hydrazobenzene 16 was treated with SbF_5–FSO_3H–SO_2 (SO_2ClF) or SbF_5–HF–SO_2 (SO_2ClF) at −78°. The pmr spectrum of 18 is shown in Figure 4 (D trace). No intermediate was observed, even at the lowest temperature, in the reaction which presumably proceeds extremely rapidly in these media. The chemical reactions of hydrazobenzene 16 with different strong acid media are shown in Scheme I.

As mentioned, the transformation of 16 or 19 to dication 18 is very rapid in strong superacids. In FSO_3H–SO_2 it is found that complete transformation of 19 to 18 was achieved when the solution was formed at room temperature for about 5 min. The rate of transformation can thus be followed by pmr study. The intensity of the quartet absorption of diprotonated benzidine 18 increases while those of the methine singlet, the two doublets, and the NH absorption of 19 decrease.

Mechanisms. The monoprotonation of hydrazobenzene is known to take place at the nitrogen atom. The pmr spectrum (Figure 4, B trace) of hydrazobenzene hydrochloride 17 shows a three-proton absorption for the NH– and $^+NH_2$ groups. It is rather surprising that hydrazobenzene does not form a dihydrochloride, $C_6H_5NHNHC_6H_5 \cdot 2HCl$. On the other hand, dimethylhydrazine is known to form a stable dihydrochloride salt $CH_3NHNHCH_3 \cdot 2HCl$. The failure to form $C_6H_5NHNHC_6H_5 \cdot 2HCl$ in ether may be due to the monohydrochloride $C_6H_5NHNHC_6H_5 \cdot HCl$ precipitating immediately upon monoprotonation. However, when hydrazobenzene in SO_2 solution was saturated with HCl, benzidine dihydrochloride 18 was formed. This result shows that hydrazobenzene must be diprotonated in SO_2 solution before rearrangement (presumably due to better solubility of $C_6H_5NHNHC_6H_5 \cdot HCl$ in SO_2). The site of the diprotonation is the key relating to the mechanism of the benzidine rearrangement.

In the benzidine rearrangement diprotonation is considered to be rate determining. There are five possible positions (-NH- and C_1–C_4 of the NHC_6H_5 ring) that the second proton could attack in monoprotonated hydrazobenzene 17. We do not consider the possibility that the second proton could attack the



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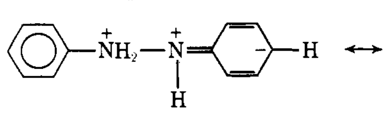
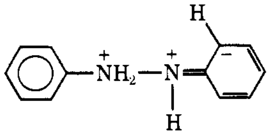
(19) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 5341 (1972).

$C_6H_5NH_2^+$ ring because of charge–charge repulsion. If diprotonation takes place on the NH nitrogen atom of **17**, the dication $C_6H_5{}^+NH_2NH_2{}^+C_6H_5$ **20** will form. However, di-N-protonated hydrazobenzene **20** has no driving force to form a carbon–carbon bond at the 4 and 4′ positions (charge delocalization into the aromatic ring is limited in ion **20**[20]). Although ion **20** may be formed, it is unlikely that it is involved as an intermediate in the rearrangement process. Ion **20** obviously can be deprotonated to **17** in an equilibrium. The other basic site is the aromatic ring (NHC_6H_5). Due to the possible resonance contribution forms of **17**



17a

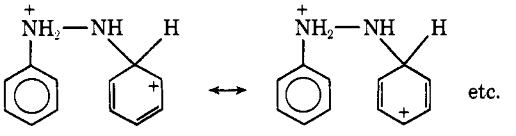


17b

C-protonation of **17** at C_2 and C_4 positions will give the benzenium ions **21** and **22**, respectively. Ion **22** again cannot be an intermediate in the benzidine rearrangement even though it forms (see subsequent discussion). Ions **23** (proton attack at C_3 position) and **21** are ruled out because the benzidine obtained from the reaction of hydrazobenzene with D_2SO_4 showed no hydrogen–deuterium incorporation into the aromatic rings (deuterium incorporation is only into the NH_2 groups). Similarly, no hydrogen–deuterium incorporation into C_2 and C_3 is found even when hydrazobenzene was treated with SbF_5–DF–SO_2ClF solution. Furthermore, it is known that the carbon-3 (meta carbon of the benzenium ring) of **21** carries essentially no charge. Thus, alkylative coupling between carbons 4 and 4′ is unlikely.

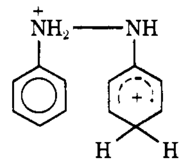
Finally, the diprotonation of **17** can take place at the C_1 position and give ion **24**. Alternatively, ion **24** can be formed by protonation of the unprotonated nitrogen atom 20 followed by fast intramolecular hydrogen transfer.

Carbon-4 (para carbon of the benzenium ring) of ion **24** has more charge than any other carbons.[21] This highly charged carbon atom can be regarded as a trivalent carbenium carbon since **24a** is the major resonance-contributing form. Furthermore, the charge–charge repulsion of ion **24a** is smaller than in any other resonance-contributing forms. Consequently, we propose that ion **24** is the most likely diprotonated intermediate in the benzidine rearrangement even though its formation is only indirectly substantiated and could not so far, even at very low temperatures, be directly observed.

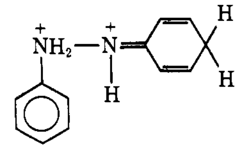


24b **24a**

As discussed, monoprotonation of hydrazobenzene is at a nitrogen atom (**17**). The proton, however, can exchange from one nitrogen atom to the other, at a rate much faster than that of the diprotonation. As a result of monoprotonation, the basicity of the unprotonated nitrogen atom is decreased by the adjacent positive charge and exchange process. Diprotonation results in the formation of an arenium ion, either by direct protonation of the aromatic ring (C_1) or by protonation of the unprotonated nitrogen atom followed by fast intramolecular proton transfer. The absence of carbon-2 and carbon-3 hydrogen–deuterium incorporation in the benzidine (recovered from the D_2SO_4–hydrazobenzene reaction) indicates that the 1,2-hydrogen shift of ion **24** to ion **21** and then to ion **23** is not feasible. We have discussed that the diprotonation of **17** may have occurred at the C_4 position, since the para-substituted arenium ion **22** can be stabilized by conjugation with the amino nitrogen atom. However, conjugation can only occur when the arenium ion and the sp^2 nitrogen atom are coplanar, *i.e.*, **22a**. This would increase the distance between the aromatic and arenium ion rings and inhibit the rearrangement.



22



22a

Based on the above argument, we conclude that the benzidine rearrangement involves the arenium ion **24**. The rearrangement step can be considered as an intramolecular aromatic alkylation reaction.[22] The pmr and cmr spectra of benzenium ions[21] indicate that the sites of the highest positive charge are the C_2 and C_4 carbons. It is therefore these carbons, C_2 and C_4, which show primary electrophilic reactivity in the intramolecular alkylation related to the benzidine rearrangement. Electrostatic interaction between the aromatic and arenium ion rings (an outer π complex in Mullikens terminology[23]) holds the rings in a suitable conformation as the N–N bond length increases (the activation energy of N–N bond cleavage is greatly reduced by monoprotonation[24]), and the C–N–N bond angle decreases. In the transition state the aromatic and arenium rings are almost parallel oriented and bond formation *via* intramolecular electrophilic aromatic substitution between the two can readily occur at the ortho and para carbons. Thus, dication **19** is formed by the intramolecular electrophilic aromatic substitution of the benzenium-type ion **24a** (see Scheme II). We consider the direct observation of the di-C-protonated benzidine **19** of substantial importance. This is the first time ever that an intermediate was observed in the benzidine rearrangement. The transformation of **19** to **18** is an aromatization process similar to that of cyclohexadienone to phenol. The rate of transforma-

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(20) Unpublished results.

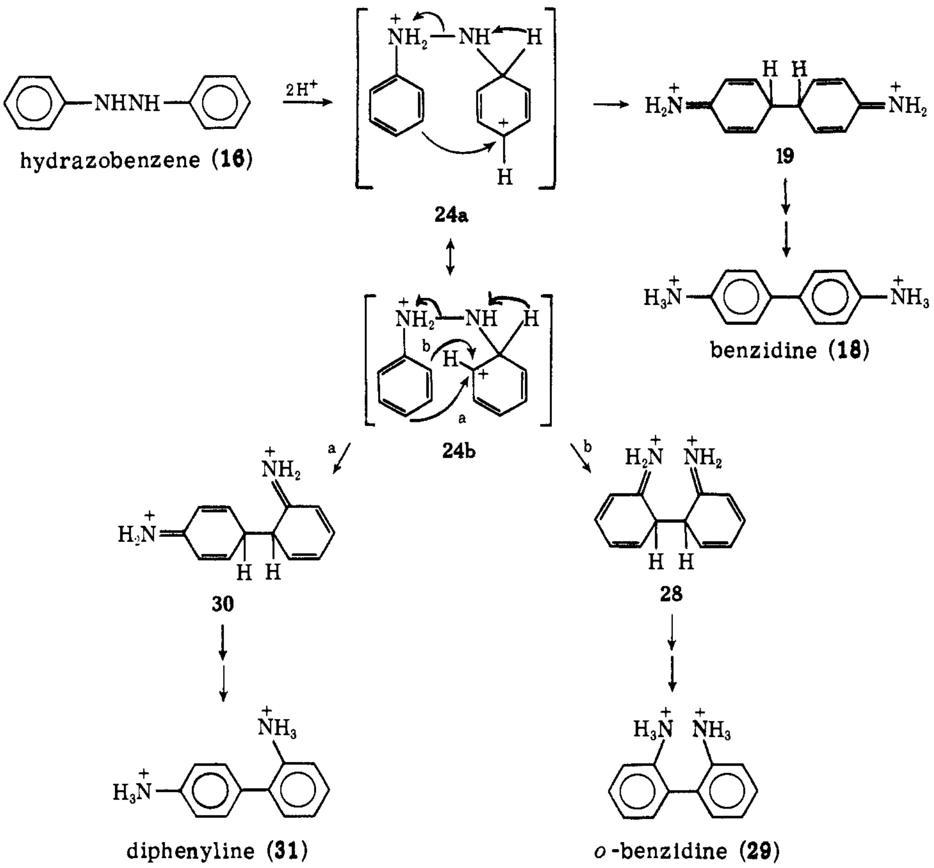
(21) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972).

(22) (a) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971). (b) We would like to give credit to Mr. M. E. Lupes who in a letter in 1970, when our own studies were nearing completion, communicated to us some of his mechanistic ideas related to the intramolecular benzenium ion alkylation concept; see also ref 53.

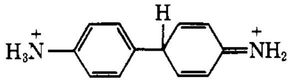
(23) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(24) V. Sterba and M. Vecera, *Collect. Czech. Chem. Commun.*, 31, 3486 (1966).

Scheme II



tion of **19** to **18** is extremely rapid in stronger acids. It also increases with temperature. The transformation may be considered as a concerted process. As the proton (present in large excess) starts to partially interact with the nitrogen lone pair, the C–H (methine) bond becomes weakened. This is a concerted protonation–deprotonation process. Aromatization of the benzenium ring must be fast since the intermediate **25** is not observable. On the other hand, we do not consider the transformation of **19** to **18** to involve any trications such as **26** and **27** because of obvious charge–charge repulsion.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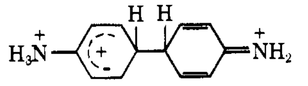
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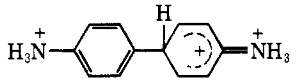
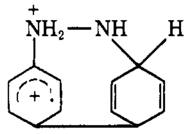

27

It is known that besides benzidine (the major product) formation in the benzidine rearrangement, other products such as *o*-benzidine **29**, diphenyline **31**, and *p*-semidine are also formed. The product distribution is dependent largely on the substituents and solvent.[22] The mechanisms for the formation of di-N-protonated benzidine **18**, *o*-benzidine **29**, and diphenyline **31** are shown in Scheme II.

We have discussed the mechanism for the rearrangement of **19** to **18**. Similar mechanisms should be applied to the rearrangement of **28** and **30** to the *o*-benzidine **29** and diphenyline **31**, respectively. Preferential bond formation between the para and para′ carbons gives rise to benzidine, the major product. Bonding between the para and ortho′ carbons or ortho and para′ carbons forms diphenyline (**31**). Similarly, ortho,ortho′ bonding forms *o*-benzidine (**29**). Formation of semidines, usually in minor amounts, unless the ortho,para carbons are substituted, indicates that the N–N bond is considerably weakened in the transition state and that the rearrangement not go through an intermediate such as **32** but is a hydrogen shift of **33** followed by a concerted process, **34**. Substitution on the ortho and para carbons results in the corresponding *o*- and *p*-semidines, respectively (also see subsequent discussion).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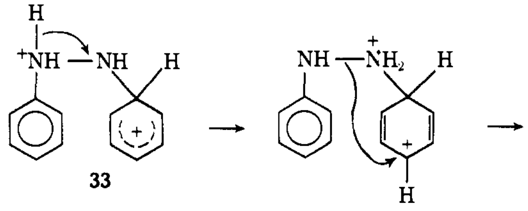
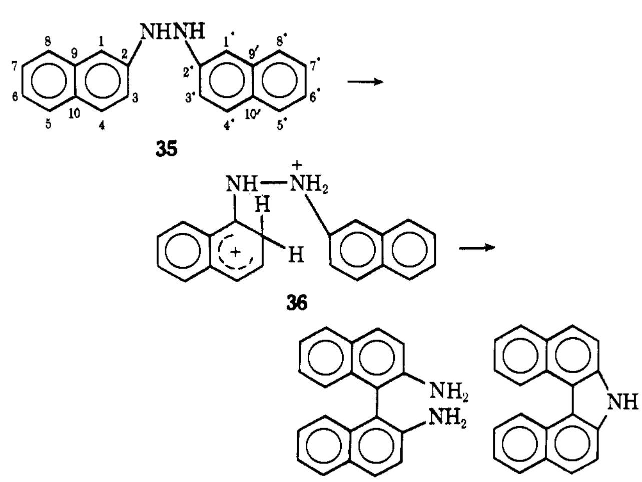


p-semidine

Although a benzidine derivative is the major product in most cases of the rearrangement, there are exceptions. The proposed mechanism can explain these exceptions,



35

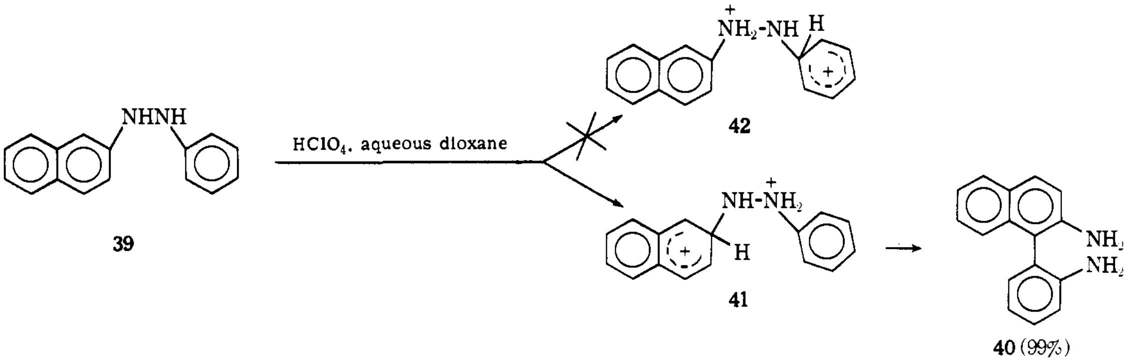
36

37 (92%)

38 (6%)

remembering that the least stable arenium ion is the most reactive species and that bonding is between the most positive and electronegative carbons (normally ortho and para), respectively.

o-**Benzidine.**[25] 2,2′-Hydrazonaphthalene **35** is diprotonated at nitrogen and C_2 to form the arenium ion **36** without disrupting the aromaticity of the second ring. The carbons with greatest positive charge density are the C_1 carbon and the C_3 carbon. Preferential substitution of β-naphthalene derivatives is, however, at the C_1 carbon. Similarly, substitution of the second naphthalene ring should take place at carbon-1′, -3′, or -10′ due to the ortho,para-directing amino group and resonance effects with carbon-1′ preferred. Bond formation at carbons C_1 and $C_1{}'$ forms the product, 2,2′-diamino-1,1′-dinaphthyl (**37**), with no significant semidine formation. A small amount of dibenzocarbazole **38** (6%) was found in this reaction. On the other hand, *N*-2-naphthyl-*N*′-phenylhydrazine (**39**) rearranged to the *o*-benzidine product **40** almost quantitatively.[25c] This result clearly indicates that the intermediate arenium ion **41** is more stable than ion **42** because a better charge delocalization can be achieved in arenium ion **41**. Recently, we have shown that the naphthalenium ion is more stable than the benzenium ion, $C_6H_7{}^+$.[15,26]

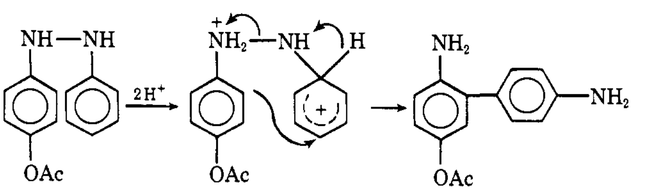


39

42

41

40 (99%)



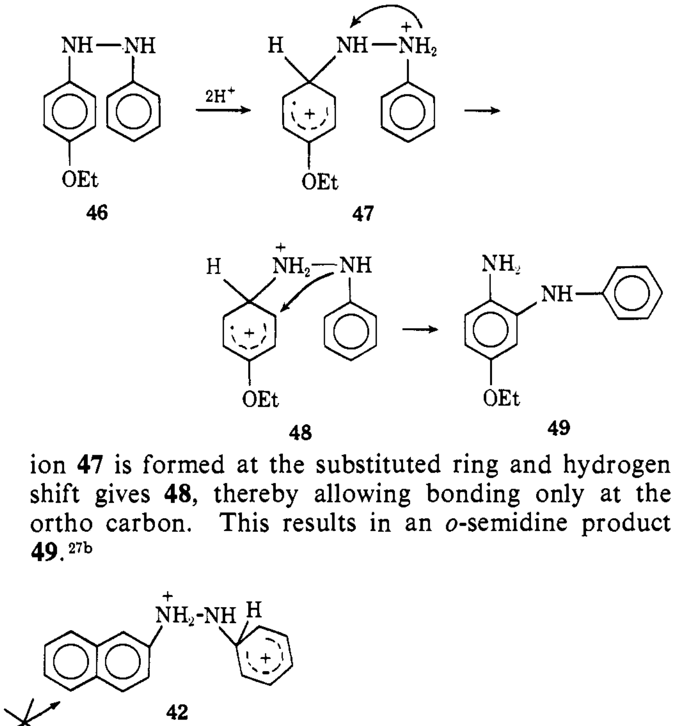
43

44

45

Diphenylines and *o*-Semidines. Acid-catalyzed rearrangement of para-substituted hydrazobenzenes gives a diphenyline **45** if R, the substituent, is an electron-withdrawing group (**43**) and an *o*-semidine **49** if R is an electron donor (**46**).[27] If R is an electron-withdrawing group, the arenium ion **44** will be formed involving the aromatic ring of higher electron density, *i.e.*, the unsubstituted ring. Bond formation occurs at the ortho position for two reasons: the NH group is ortho,-para-directing with the para position substituted, and the electron-withdrawing substituent is meta-directing (that is, to the ortho carbon).

When R is an electron-donor group (**46**), the arenium ion **47** is formed at the substituted ring and hydrogen shift gives **48**, thereby allowing bonding only at the ortho carbon. This results in an *o*-semidine product **49**.[27b]



46

47

48

49

p-**Semidine** formation was thought to be caused by heavy metal ions but has now been recognized[28] as a true product of the benzidine rearrangement. Although normally found only in trace amounts, some para-substituted hydrazobenzenes form *p*-semidines in yields of up to 20%. N-Substitution is preferred as the electron density of the aromatic ring is decreased, for example, by an $-NO_2$ group **50**.[29] It is also possible

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[25] (a) D. V. Banthorpe, *J. Chem. Soc.*, 2407 (1962); (b) D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *ibid.*, 2386 (1962); (c) D. V. Banthorpe, *ibid.*, 2429 (1962).

[26] G. A. Olah, Gh. D. Mateescu, and Y. K. Mo, *J. Amer. Chem. Soc.*, in press.

[27] (a) P. Jacobson, *Justus Liebigs Ann. Chem.*, 428, 76 (1922); (b) *ibid.*, 427, 142 (1922).

[28] (a) M. Vecra, J. Petranek, and J. Gasparic, *Collection Czech. Chem. Commun.*, 22, 603 (1957); (b) D. V. Banthorpe, A. Cooper, and C. K. Ingold, *Nature (London)*, 216, 232 (1967).

[29] D. V. Banthorpe, A. Cooper, and O'Sullivan, *J. Chem. Soc. B*, 2054 (1971).

Table II. Pmr Parameters of Protonated Arylamines ($R{-}C_6H_4{}^+NH_3(R')$)[a]

Protonated arylamine	Solvent system	Temp, °C	Aromatic	Substituent (R or R′)	NH
$C_6H_5NH_3^+$	SbF_5–FSO_3H–SO_2	−80	7.8 (s, br)		7.6 (br, 3 H)
p-$CH_3C_6H_4NH_3^+$	SbF_5–FSO_3H–SO_2ClF	−85	7.7 (s, br)	2.63 (s)	7.5 (br, 3 H)
o-$CF_3C_6H_4NH_3^+$	SbF_5–FSO_3H–SO_2	−70	7.9 (br)		7.9 (br)
p-$CF_3C_6H_4NH_3^+$	SbF_5–FSO_3H–SO_2	−85	7.10 (d, J = 8), 7.32 (d, J = 8)		7.1 (br)
o-$NO_2C_6H_4NH_3^+$	SbF_5–FSO_3H–SO_2	−80	8.1–8.7 (m, 3 H), 9.1 (m, 1 H)		8.5 (s, 3 H)
m-$NO_2C_6H_4NH_3^+$	SbF_5–FSO_3H–SO_2	−60	8.2–8.6 (m)		8.1 (s, 3 H)
p-$NO_2C_6H_4NH_3^+$	SbF_5–FSO_3H–SO_2	−70	8.3 (d, J = 9), 9.1 (d, J = 9)		7.8 (s, br)
$(C_6H_5)_2NH_2^+$	SbF_5–HF–SO_2	−30	7.8 (m, 10 H)		9.4 (s, br)
$(C_6H_5)_3NH^+$	SbF_5–FSO_3H–SO_2	−55	7.7 (m, 5 H), 8.0 (m, 10 H)		12.6 (s, br)
$C_6H_5{}^+NH(CH_3)_2$	SbF_5–FSO_3H–SO_2	−60	7.5 (s, br)	3.88 (d, J = 5.5), N–CH_3	7.5 (q, J = 5.5)
o,o-$(CH_3)_2C_6H_3NH_3^+$	SbF_5–FSO_3H–SO_2	−90	7.3 (m, 3 H)	2.53 (s)	7.4 (s, br, 3 H)

[a] Proton chemical shifts are referred to external capillary TMS in parts per million; s = singlet, d = doublet, q = quartet, m = multiplet, and br = broad.

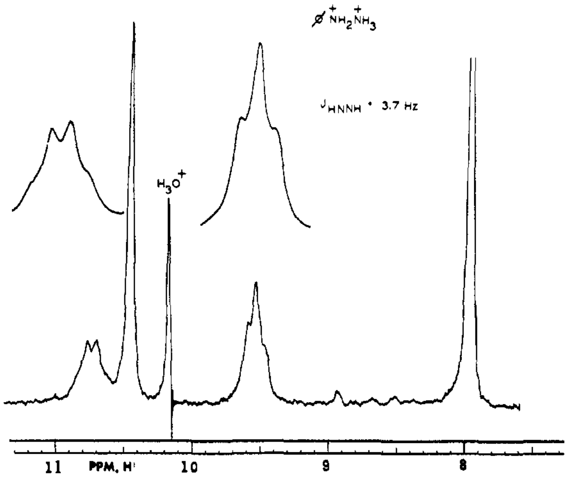
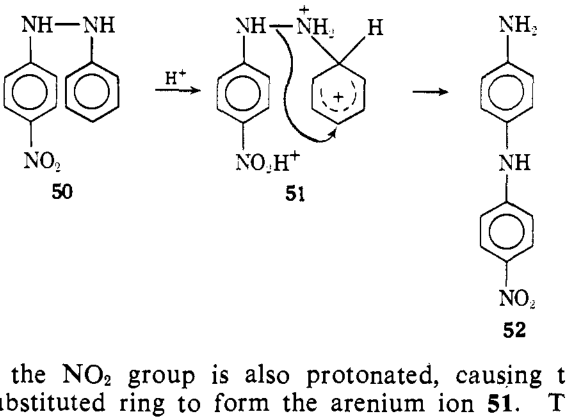


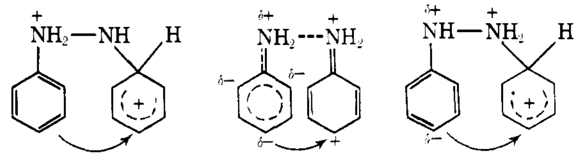
Figure 5. Pmr spectrum of diprotonated phenylhydrazine.



50 **51** **52**

that the NO_2 group is also protonated, causing the unsubstituted ring to form the arenium ion **51**. The lone pair of NH of **51** can now interact with the carbenium center of the arenium ion. The resulting product is a p-semidine **52**.

The rate of the benzidine rearrangement is found to increase as the solvent becomes more polar, indicating a polar transition state.[3b] In the "polar transition state" theory proposed by Banthorpe, Hughes, and Ingold, there are two kinetic paths for benzidine rearrangement and therefore two types of polar transition to be described. One of them involves a single proton and the other two. Our proposed mechanism has some similarities to the latter case. In the transition state for the two-proton mechanism half of the heterolyzing, diprotonated molecule has the character of an arylamine and the other has the character of a dication **53**.[30]



24 **53** **54**

Protonation of Phenylhydrazine and Arylamines. The pmr spectrum of phenylhydrazine in SbF_5–FSO_3H–SO_2 shows a broad quartet at δ 10.8 (2 H) coupled (as shown by decoupling) to a triplet at δ 9.5 (3 H) (Figure 5). Cooling the solution results in broadening of the quartet (rather than sharpening when exchange with acid is involved) due to an increase in quadrupole interaction. This observation of diprotonated phenylhydrazine is significant since this is the first time, to our knowledge, that vicinal interproton coupling has been observed through two nitrogen atoms. The value of J_{HNNH} = 3.7 Hz is similar to that observed in diprotonated alcohols ($J_{HCOH_2^+}$ = 3.6 Hz).[31]

C- and O-protonation of phenol is well known. Arylamines with acids generally form only anilinium ions (N-protonation). In the study of the benzidine rearrangement, we propose both N- and C-protonation of hydrazobenzene to occur (in the studied acid media). It was therefore interesting to examine (by nmr) some arylamines in SbF_5–FSO_3H–SO_2 (magic acid) solution

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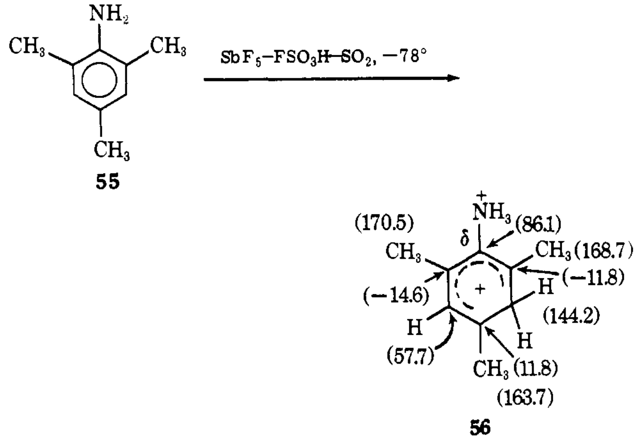
(30) Note Added in Proof. Since submission of our paper Allan, in accordance with Lupes' suggestion,[22b] has proposed an intermediate, **54**, for the benzidine rearrangement (Z. J. Allan, *Tetrahedron Lett.*, 4225 (1971)). The nature of **54** is between the two-electron polar transition state **53** and our proposed intermediate **24**. It is unlikely that $-{}^+NH_2$ is attached to a benzenium ring because of the strong charge–charge repulsion. However, Allan's proposed intermediate **54** is probable in the cases where o- and p-semidines are the final products in the rearrangement (**48** and **51**).

Subsequently, Banthorpe commented on Allan's mechanistic proposal in pointing out that it was not supported by any experimental evidence (D. V. Banthorpe, *ibid.*, 2707 (1972)). He suggested, however, that if a ring-protonated dicationic intermediate would be involved it should not be **54**, but **24**, as proposed in our present work. The first suggestion for such an intermediate should be credited to L. Hammick and S. F. Mason (*J. Chem. Soc.*, 638 (1946)).

(31) G. A. Olah, J. Sommer, and E. Namanworth, *J. Amer. Chem. Soc.*, 89, 3576 (1967)).

to see whether C-protonation of arylamines can also be achieved. Our results show, in most cases, that the only detectable product was the anilinium ion. The pmr parameters of some anilinium ions are tabulated in Table II. However, 2,4,6-trimethylaniline **55** forms



55

56

a stable diprotonated arenium ion. The pmr spectrum (Figure 6) shows the methylene proton absorption at δ 5.24 and the characteristic $-^{+}NH_3$ broad absorption at δ 7.9. The *p*-methyl and one of the *o*-methyl (adjacent to the $-^{+}NH_3$) groups show a coincidental singlet at δ 3.02 indicating the inductive effect of the $-^{+}NH_3$ group. Furthermore, the structure of dication **56** was also confirmed by carbon-13 nmr data (cmr shifts are shown in parentheses on the structure). The methylene carbon shows an sp^3-type cmr shift at δ^{13}C 144.2. The meta carbon to which NH_2^+ is attached shows an unusually shielded carbon shift at 86.1 ppm.

Protonation can occur initially either on the nitrogen atom with the basicity of the ring sufficiently increased by the inductive effect of the methyl groups to facilitate a second protonation to give **56** or first ring protonation could occur forming a benzenium ion sufficiently stable to allow protonation of the amino group. In comparison, we recently found that some diprotonated di- and trihydroxy(methoxy)benzenes have an $-^{+}OH_2$ or $-^{+}O(H)CH_3$ group at the meta position of the benzenium ion.[18]

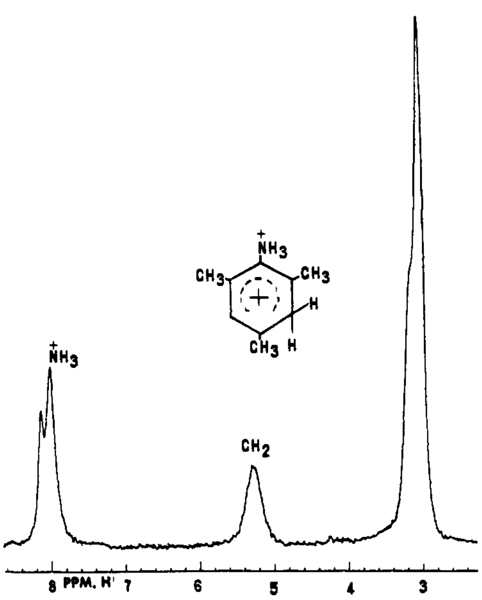


Figure 6. Pmr spectrum of diprotonated 2,4,6-trimethylaniline.

Conclusions

Experimental evidence for the mechanism of the Wallach rearrangement has been obtained, based on the direct observation (in superacid media) of two reaction intermediates: diprotonated azoxybenzene **3** and the derived dehydrated dication **4**. Although these intermediates were observed only in superacid solutions, they give strong indication for the general pathway of the Wallach rearrangement. Studying possible intermediates of the benzidine rearrangement, the direct observation and nmr spectroscopic characterization of di-C-protonated benzidine (**19**) were achieved. Together with extensive study of dicationic model compounds, the absence of hydrogen–deuterium incorporation into the benzidine rings during rearrangements in deuterated acids, and general considerations of benzenium ions in alkylative systems, a new mechanism for the benzidine rearrangement is proposed involving N,C-diprotonated hydrazobenzene **24** as the key intermediate.

Experimental Section

Materials. All starting compounds used were commercially available materials.

Nmr Spectra. The pmr spectra were obtained using Varian Associates Model A56/60 and HA-100 spectrometers equipped with variable-temperature probes and using external TMS as reference. Carbon-13 indor spectra were obtained on a Varian Associates Model HA-100 nmr spectrometer as described previously.[32]

Preparation of Ions. The procedure used for the preparation of ions was identical with that described previously.[33]

Rearrangement in D_2SO_4. Hydrazobenzene in dry ether was treated with D_2SO_4–D_2O (1:1 v/v) for 1 hr. The mixture was then quenched with excess ice-water and neutralized with sodium bicarbonate, and the benzidine was extracted with ether. A similar procedure was used for the rearrangement in DF–SbF$_5$, using SO$_2$ClF as solvent.

Acknowledgment. Support of our work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(32) A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).
(33) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5194 (1967).