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Benzidine Rearrangements. XIII. The Role of Reductive Scission. Reactions of N,N'-Dimethylhydrazobenzenes in Acid Solutions[1,2]

Jiin-Duey Cheng[3] and Henry J. Shine*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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N,N'-Dimethyl-p-hydrazoanisole (**6b**) in acetonitrile containing a small amount of hydrochloric acid underwent reductive scission to N-methyl-p-anisidine (**7b**, 70%). Other products formed were 2-amino-4-chloro-4',5-dimethoxy-N-methyldiphenylamine (the monodemethylated chloro-o-semidine, **10**, 5%), 2,7-dimethoxyphenazine (**9b**) and 3-chloro-2,7-dimethoxyphenazine (**11**) as a mixture which could not be separated quantitatively, and traces of 4,4'-dimethoxyazobenzene (**12b**). A radical was detected by ESR and is identified as the cation radical of 2,7-dimethoxy-5,10-dimethyl-5,10-dihydrophenazine (**18b**). Anodic oxidation of **6b**, its o-semidine (**8b**), and N-methyl-p-anisidine each gave rise to the same ESR spectrum, also attributed to **18b**·+. N,N'-Dimethyl-p-hydrazobiphenyl (**6d**) in acetonitrile–hydrochloric acid underwent reduction to N-methyl-p-aminobiphenyl (90%) along with other unidentified products, some of which contained chlorine. Molecular chlorine was not detected during reaction, and succinonitrile could not be found as a reaction product. A radical was detected during reaction under flow conditions only and its spectrum is attributed to **6d**·+ rather than to the analogous dihydrophenazine (**18d**·+). N,N'-Diethyl-p-hydrazoanisole (**16b**) in acetonitrile–hydrochloric acid gave rise to an ESR signal attributed to 2,7-dimethoxy-5,10-diethyl-5,10-dihydrophenazine (**20b**·+). In contrast the spectrum obtained with N,N'-diethyl-p-hydrazobiphenyl (**16d**) is attributed to **16d**·+. Our results suggest that the major reducing agent in reductive scission of **6b** is the first-formed rearrangement product, the o-semidine (**8b**), which is in turn oxidized successively to **18b**, **9b**, and **11**. Analogous reactions are believed to occur with **6d**. Oxidative demethylation of **6b** and **6d** also occurs. The results show, also, that the solvent is not a reducing agent in these reactions. The oxidizing agent is either the cation radical (e.g., **7b**·+) formed by homolytic scission of the diprotonated hydrazo compound or the protonated hydrazo compound itself.

In spite of the large effort that has been made by numerous research groups over the last few decades, the mechanism of the acid-catalyzed benzidine rearrangements remains unsolved. Of the several mechanisms that have been proposed, the polar transition state one from Ingold, Hughes, and Banthorpe remains the most attractive, although it is by no means universally accepted.[4-6] In recent years, indeed, new proposals for the participation of ring-protonated rather than N-protonated intermediates have been made,[7,8] although there is no direct experimental evidence in support of them as has been pointed out by Banthorpe[9] and by Shine.[10] Apart from the problem of explaining the benzidine rearrangements there are the problems also of accounting for two reactions which accompany benzidine rearrangements. One of these reactions is disproportionation. This accompanies all acid-catalyzed benzidine rearrangements, sometimes to a very small degree and sometimes to an extent far larger than rearrangement itself.[4] The mechanism of disproportionation is quite unknown,[4-6,10,11] and so is the way in which disproportionation and rearrangement may be linked together. Nevertheless, a large number of examples of disproportionation are known and the kinetic boundaries of the reaction have been established.[6,11] The second reaction which accompanies acid-catalyzed benzidine rearrangements is reductive scission, and this has been a much more fugitive and perplexing feature of the overall benzidine rearrangement problem. It is this feature with which we are now concerned.

Disproportionation of hydrazoaromatics leads to a 1:2 mole ratio of azoaromatic and scission amine (eq 1). Reduc-

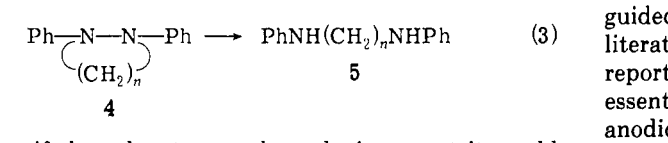
$$\underset{\mathbf{1}}{2\mathrm{ArNHNHAr}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArN{=}{=}NAr}} + \underset{\mathbf{3}}{2\mathrm{ArNH_2}} \qquad (1)$$

tive scission leads to **3** and is detected when the ratio **3:2** obtained from a hydrazoaromatic is more than eq 1 will accommodate. This was first noticed by Carlin and Wich in their very careful analysis of the products of reaction of p-hydrazotoluene with acid,[12] in which it was found that the ratio of the amounts of p-toluidine and p-azotoluene was a little larger than attainable by eq 1. Carlin and Wich concluded that some of their p-hydrazotoluene had undergone reductive scission, and assumed that solvent ethanol was the reducing agent. They did not, however, search for the oxidation product, acetaldehyde, because of the very small amount that would have been formed. Hammond and Clovis[13] confirmed the finding[12] that a small excess of p-toluidine was formed, and were also unsuccessful in accounting for the reaction, although they concluded that a transient oxidizing agent of unknown structure was probably associated with the high yield of p-toluidine. At the same time the reducing agent responsible for the excess of p-toluidine was not designated.

Very little attention has been given to reductive scission since these early reports. It has become noticeable, however, that reductive scission is much more significant in reactions of *N,N'*-dimethylhydrazoaromatics and other hydrazines in which hydrogen is no longer an N substituent. In such compounds, of course, disproportionation into scission amine and azo compound cannot occur. If acid-catalyzed scission of the hydrazo compound did occur, therefore, it is likely that the product would be the scission amine (eq 2). But, again, a reducing agent would have to be involved, too.

$$\mathrm{Ar{-}N(R){-}N(R){-}Ar} \xrightarrow{H^+} \xrightarrow{\text{redn}} 2\mathrm{ArNHR} + ? \qquad (2)$$

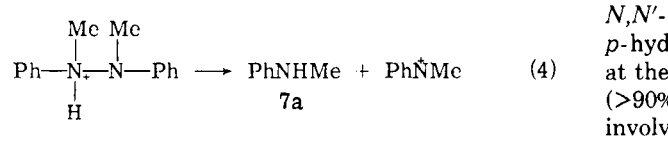
Reductive cleavage of this kind was noted by Wittig[14] with the cyclic hydrazo compound **4a** (n = 3) which, in 2 *N* hydrochloric acid containing a little ether gave 41% and in benzene–dry HCl gave 50% of *N,N'*-diphenylpropane-1,3-diamine (**5a**), eq 3. These results are of considerable interest, since if the solvent were the reducing agent it would have to be either water or the small amount of ether in the one case, or benzene in the other. Similarly, reaction of **4b** (n = 4) with half-concentrated hydrochloric acid (presumably about 6 *N*) gave, besides rearrangement products, 25.5% of the scission product **5b** (n = 4). In this case, the only solvent was water, and presumably, therefore, the only reducing agents available were water or chloride ion. The reducing agent, however, was not identified.[14] It is noteworthy that in each case of treating **4a** and **4b** with acid a blue color was seen.



$$\mathrm{Ph{-}N{-}N{-}Ph} \longrightarrow \mathrm{PhNH(CH_2)_nNHPh} \qquad (3)$$

$\mathrm{(CH_2)_n}$ — **4** — **5**

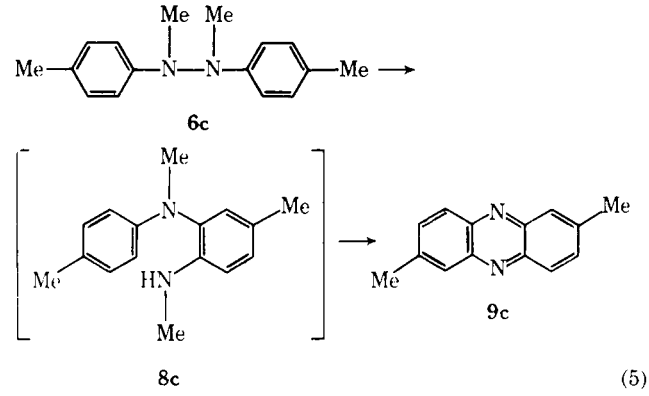
Among simpler N,N'-disubstituted hydrazo compounds, *N,N'*-dimethylhydrazobenzene (**6a**) in an aqueous methanol solution of 0.01 *M* hydrochloric acid gave, in White's laboratory, 11% of *N*-methylaniline.[15] An explanation of the reductive scission was not offered. Reductive scission of **6a** was also encountered by Banthorpe with aqueous dioxane containing perchloric acid.[16] Here the formation of *N*-methylaniline (**7a**) was attributed not to reduction, but to protolytic dismutation, eq 4, of which reaction the second product, the *N*-methylanilino cation, was presumed to hydrolyze to *N*-methylphenylhydroxylamine. The last compound was thought to be the origin of the small amount of tar formed in the reaction of **6a.**



$$\mathrm{Ph{-}N(Me){-}N(H){-}Ph} \longrightarrow \mathrm{PhNHMe} + \mathrm{PhN^{\cdot}Me} \qquad (4)$$

7a

In our own laboratory, two thought-provoking cases were encountered. *N,N'*-Dimethyl-*p*-hydrazoanisole (**6b**) in dioxane–methanol containing hydrochloric acid at 0° gave 46% of rearrangement (to the *o*-semidine) and 42% of scission to *N*-methyl-*p*-anisidine (**7b**).[17] Tarry products were not obtained. Reaction of *N,N'*-dimethyl-*p*-hydrazotoluene (**6c**) in methanolic hydrogen chloride gave a number of products, some of which were not identified, but among which was 2,7-dimethylphenazine (**9c**) in 5% yield. Here, then, we encountered with **9c** a case of oxidative demethylation and oxidative cyclization following, we presumed, rearrangement of **6c** to the *o*-semidine (**8c**), eq 5. We did not find, or look assiduously for, either the rearrangement product **8c** or the scission product, *N*-methyl-*p*-toluidine (**7c**). However, the *o*-benzidine type rearrangement product, 5,5'-dimethyl-2,2'-bis(methylamino)biphenyl (**17c**), was obtained in 8.8% yield.



6c — **8c** — **9c** (5)

In planning to explore further the reactions of *N,N'*-dimethylhydrazoaromatics, and in particular to search for the involvement of solvent in reductive scission, we were guided by some interesting reports in the electrochemical literature. Certain aliphatic amines and amides have been reported to undergo anodic oxidation yet to be recovered essentially without loss. Thus, triethylamine when oxidized anodically in DMSO was recovered as the triethylammonium ion,[18] and a number of amides when oxidized anodically in acetonitrile were recovered in 90–98% yield.[19] Mann interpreted these reactions as involving anodic oxidation of the amine or amide and chemical reduction of the ensuing cation radical by the solvent, e.g., as in eq 6. In the reactions of the amides, S· is the cyanomethyl radical, ·CH_2CN, and most pleasing, O'Donnell and Mann were able to recover the dimer, succinonitrile, in six amide oxidations in yields of 83–94%. Russell had proposed an identical sequence of reactions for the anodic oxidation of triethylamine in acetonitrile, but did not isolate the succinonitrile.[20]

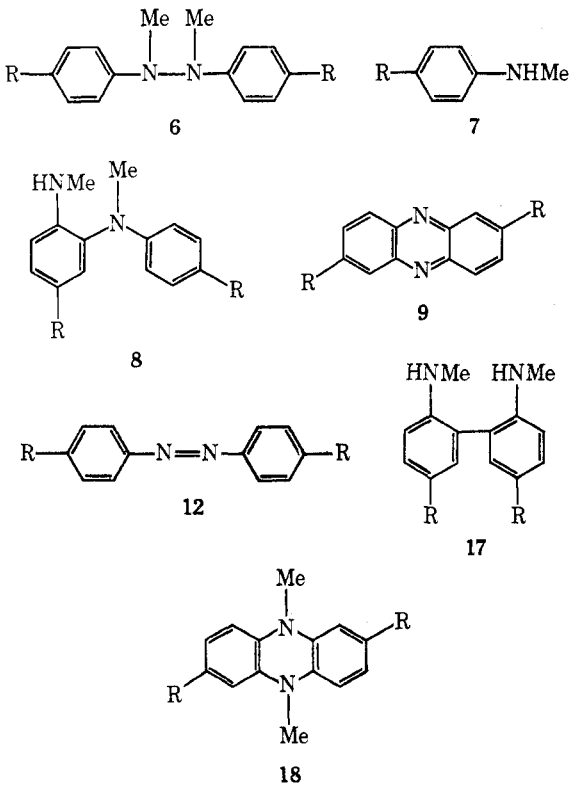
$$(\mathrm{RCONR'_2})^{\cdot+} + \mathrm{SH} \longrightarrow (\mathrm{RCONHR'_2})^{+} + \mathrm{S}\cdot \qquad (6)$$

It was our feeling, therefore, that if reductive scission of hydrazoaromatics could be carried out in acetonitrile solution, and if the solvent were the reducing agent, we should be able to find the oxidation product, succinonitrile, with ease. We have investigated, therefore, the behavior of *N,N'*-dimethyl-*p*-hydrazoanisole (**6b**) and *N,N'*-dimethyl-*p*-hydrazobiphenyl (**6d**) in this solvent. We are able to say at the outset that reductive scission occurred in high yield (>90% with **6d**), but that the solvent does not appear to be involved. Instead, reductive scission is accompanied by an extraordinary series of amino compound oxidation reactions and the formation of cation radicals. We have isolated hitherto unsuspected products of reaction and have applied ESR spectroscopy in our attempts to unravel the courses of reaction.

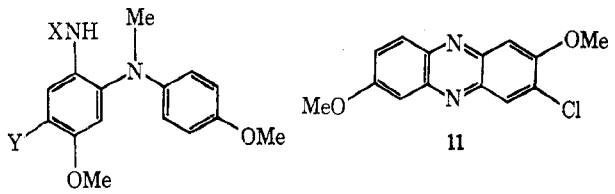
Results. Products of Reaction

Compounds **6–20,** to which reference is frequently made, are listed in the chart of compounds.

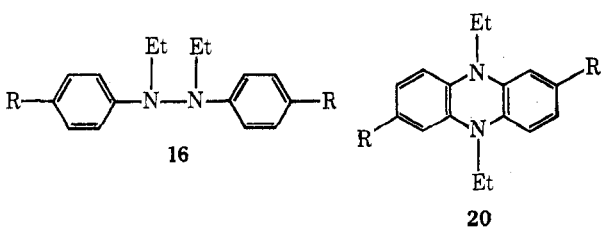
Reactions of *N,N'*-Dimethyl-*p*-hydrazoanisole (6b). Reaction of **6b** with hydrochloric acid in acetonitrile solution was carried out in an ice bath under nitrogen gas. The products were separated by column chromatography and are listed in Scheme I. **7b** was identified by melting point and mixture melting point. The monodemethylated chloro-*o*-semidine (**10**) was identified by the NMR, elemental analysis, and mass spectrum parent peak of its *p*-nitrobenzoyl derivative (**14**), mp 181.5–182.5°. The two phenazines, **9b** and **11,** were obtained as a mixture. Each component



a, R = H; b, R = OMe; c, R = Me; d, R = Ph



10, X = H; Y = Cl
13, X = Y = H
14, X = $O_2NC_6H_4CO$-; Y = Cl
15, X = $O_2NC_6H_4CO$-; Y = H

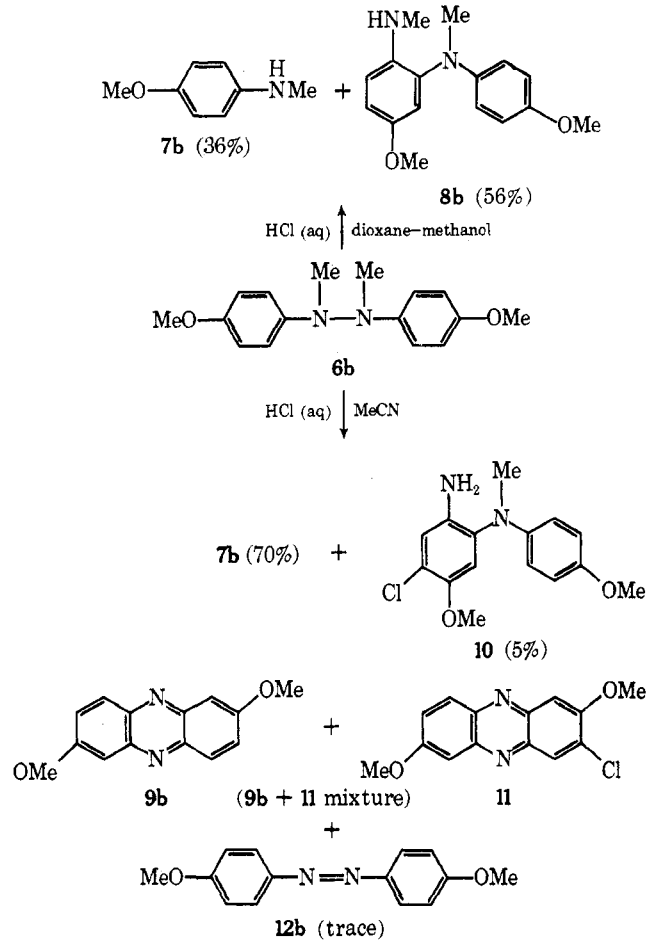


b, R = OMe; d, R = Ph

was separated in low yield and identified by mass spectrum. Thus, **9b** was isolated in 0.3% yield, mp 239.5–241.5°, *m/e* 240.05, and **11** in 0.7% yield, mp 234–237°, *m/e* 274.05. These two compounds were formed in larger yields than those stated, but analysis of the mixture of **9b** and **11** was not successful. *p*-Azoanisole (**12b**) was obtained only in a very small amount and was identified by mp 156–161° and *m/e* 242.1. One other product was isolated, a red solid, mp 189–190°, *m/e* 409.12, but has not been identified.

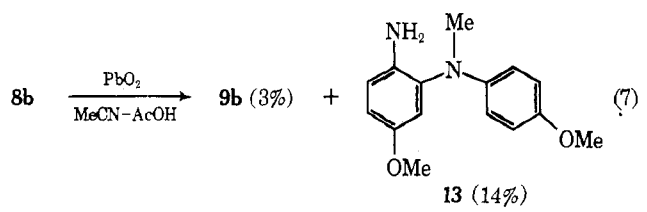
These results differed from those obtained earlier using hydrochloric acid in dioxane–methanol in that a large amount of the *o*-semidine (**8b**) was obtained earlier.[17] Therefore, the reaction in dioxane–methanol was repeated and a result similar to the earlier one was obtained. That is, **7b** and **8b** were obtained in 36 and 56% yields, respectively, as compared with 42 and 46% formerly. In the present

Scheme I



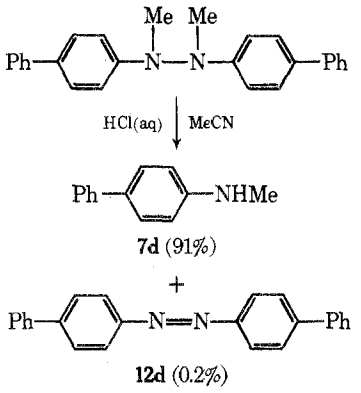
work, however, a small amount (14 wt %) of a purple solid was also obtained which gave a single, broad ESR signal with $g = 2.0036$. This material was not identified.

Oxidation of 8b with PbO_2. Because compounds **9b, 10, 11,** and **12b** most probably arose from oxidations of first-formed **8b,** the direct oxidation of **8b** with PbO_2 in acetic acid–acetonitrile was carried out. After 1.5 hr 27% of **8b** was recovered. Two products, **9b** (3%) and the monodemethylated *o*-semidine (**13,** 14%), were isolated (eq 7). The



latter had been synthesized earlier,[17] and it was identified here as a product by its NMR spectrum and *p*-nitrobenzoyl derivative (**15**), mp 134.5–135°. A third product, mp 155–157°, *m/e* 510.2, was isolated in 13 wt % yield but has not been identified.

Reaction of *N,N'*-Dimethyl-*p*-hydrazobiphenyl (6d). Reaction of **6d** with hydrochloric acid in acetonitrile at 0° was accompanied by a fleeting blue color. After 4 hr the reaction gave *N*-methyl-4-aminobiphenyl (**7d,** 91%) and *p*-azobiphenyl (**12d,** 0.2%), eq 8. **7d** was identified by NMR and its benzenesulfonyl derivative, mp 151–152°, while **12d** was identified by mp 248–250° and *m/e* 334. Three other compounds were obtained, but we have been unable to identify them. One was an oil in 7.6 wt % yield, while the



(8)

other two were solids, mp 134–137°, *m/e* 202 (6.4 wt %), and mp 149–180°, *m/e* 670 (9 wt %). The two solids gave positive Beilstein halogen tests.

Succinonitrile was not found as a product of reaction. Search was made for this product both among the organic products and in the water solution of the beginning work-up procedure. Search was made for succinonitrile directly as a solid and indirectly by infrared (–C≡N band) spectroscopy. No evidence for succinonitrile was found.

Results. ESR Spectra

An ESR spectrum (Figure 1A) was obtained when solutions of **6b** in acetonitrile and hydrochloric acid in acetonitrile were mixed in a gravity flow system just before entering the ESR cell.[21] The color of the solution leaving the cell was pale brown. A similar ESR signal could be detected if the solutions were mixed and the mixture was placed in the cell. The ESR spectrum obtained by flow reaction was at first thought to be of **6b**·$^+$. Guided by the results of anodic oxidation and cyclic voltammetry of **6b**, in which **6b** appeared to be oxidized rapidly to 2,7-dimethoxy-5,10-dimethyl-5,10-dihydrophenazine (**18b**),[22] **18b** was synthesized and oxidized anodically in the ESR cavity and gave an ESR spectrum (Figure 1B) identical with that in Figure 1A. The same spectrum was also obtained by oxidizing the *o*-semidine **8b** with a solution of **6d** in benzene and acidic acetonitrile under static conditions. Better resolution of ESR spectra was obtained by anodic oxidations of **6b** and **8b**. The better resolved spectrum was also obtained by the anodic oxidation of *N*-methyl-*p*-anisidine (**7b**). All of these spectra suggest that the responsible radical is the cation radical **18b**·$^+$, and that it is formed rapidly in oxidations of **6b**, **7b**, and **8b**. This suggestion is supported by cyclic voltammetry results.[22] An identical ESR spectrum was obtained also by the oxidation of **8b** with PbO_2 in acetic acid. Further evidence that the *N,N'*-methyl groups were involved in ESR coupling was obtained from the reaction of **6b**-d_6 in acetone containing hydrochloric acid.

Reaction of **6d** in acetonitrile containing hydrochloric acid gave a fleeting blue color and an ESR spectrum (a_N = 8.98 G) recordable only under flow conditions. In contrast, anodic oxidations of **6d**, **7d**, and **8d** gave ESR spectra with a_N = 6.50 G. Cyclic voltammetry[22] showed that **6d** undergoes anodic cyclization to 2,7-diphenyl-5,10-dimethyl-5,10-dihydrophenazine (**18d**). Consequently, it is probable that the ESR spectrum from anodic oxidation of **6d** is due to **18d**·$^+$, whereas that from **6d** in acidic acetonitrile is due to **6d**·$^+$.

Similarly, **16b** in acidic acetonitrile gave the 2,7-dimethoxy-5,10-diethyl-5,10-dihydrophenazine cation radical (**20b**·$^+$), whereas **16d** gave **16d**·$^+$.

Coupling constants obtained with the aid of simulated spectra are given in Table I. These coupling constants can

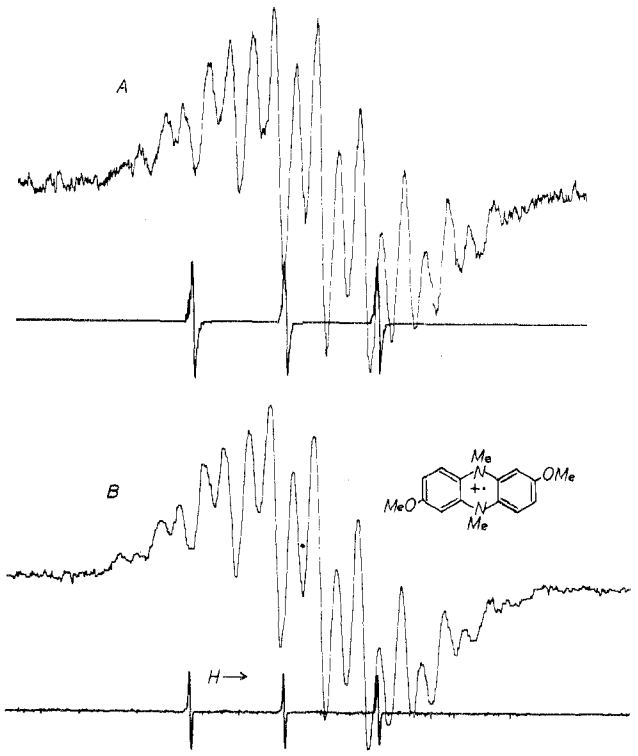


Figure 1. A. ESR spectrum obtained by flow mixing in the ESR cavity 500 ml of an 0.0147 *M* solution of **6b** in MeCN with a solution of 2 ml of concentrated hydrochloric acid in 500 ml of MeCN. The spectrum is attributed to **18b**·$^+$. The standard spectrum is of Fremy's salt, 13-G splitting. B. ESR spectrum of **18b**·$^+$ obtained by anodic oxidation of 2,7-dimethoxy-5,10-dimethyl-5,10-dihydrophenazine (**18b**) in MeCN containing tetra-*n*-butylammonium perchlorate.

be regarded only as approximate. The spectra from which they were measured are not fully resolved, and were either simulated or fitted by stick diagrams with the assumption that the nitrogen and attached alkyl-group coupling constants were equivalent. The simulations were very reasonable agreements, and so were the stick diagrams, but in the absence of fully resolved spectra the coupling constants in Table I can be taken only as guides to the spectra we recorded, yet they do provide some support for our assignments as explained in the Discussion. (See paragraph at end of paper regarding supplementary material.)

Discussion

ESR Spectra. The ESR spectrum (Figure 1A) obtained with solutions of **6b** in acetonitrile–hydrochloric acid appears to be that of the cation radical of 2,7-dimethoxy-5,10-dimethyl-5,10-dihydrophenazine, that is, of **18b**·$^+$. The same spectrum is obtained by anodic oxidation of **18b** itself (Figure 1B). These spectra consist of 19 not-well-resolved lines, to which the central 19 of 23 lines of a stick diagram could be fitted if it were assumed that coupling by only two of the six ring protons in **18b**·$^+$ was detectable, and that couplings by the nitrogen atoms and N substituents were equal. A better resolved spectrum was obtained by the anodic oxidation of **6b**, and of its *o*-semidine (**8b**), and also by the anodic oxidation of *N*-methyl-*p*-anisidine (**7b**), but again no more than 19 lines were obtained.

Resolved ESR spectra of 5,10-disubstituted 5,10-dihydrophenazine cation radicals are not available in the literature for comparison with our results. Well-resolved spectra of 5-methyl-5,10-dihydrophenazine cation radical (so-called MPH·$^+$) have been reported but not analyzed.[23,24] Well-resolved spectra of the parent 5,10-dihydrophenazine

Table I
ESR Parameters

Reaction	Figure[e]	Radical	g	a_{2N}	a_{R_1}	a_{R_2}	a_{2H}
6b, HCl–MeCN	1A	**18b**·⁺	2.0033	6.24	6.24[a]	6.24[a]	2.69[b]
18b, anodic oxidn	1B	**18b**·⁺					
8b, anodic oxidn	3	**18b**·⁺		6.18	6.18[a]	6.18[a]	2.59[b]
6b-d_6, HCl–MeCN	4A	**18b**-d_6·⁺	2.0035	6.69			
13, PbO_2–AcOH	5A	**19b**·⁺		6.29	6.29[a]	[c]	2.60[b]
6d, HCl–MeCN	6A	**6d**·⁺	2.0034	8.98	8.98[a]	8.98[a]	
6d, anodic oxidn	7A	**18d**·⁺		6.50	6.50[a]	6.50[a]	
8d, anodic oxidn		**18d**·⁺		6.50	6.50[a]	6.50[a]	
16b, HCl–MeCN	8A	**20b**·⁺	2.0034	6.34	3.19[d]	3.19[d]	3.19[b]
16d, HCl–MeCN	9A	**16d**·⁺	2.0038	8.14	8.14[d]	8.14[d]	

[a] *N*-Methyl group. [b] 3,8 hydrogens. [c] N–H proton unresolved. [d] Methylene hydrogens in *N*-ethyl group. [e] See paragraph at end of paper regarding supplementary material.

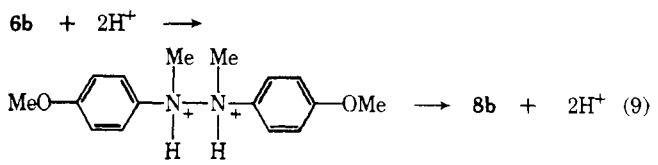
cation radical itself have been reported,[25,26] and complete analysis[27] gives a_N = 6.14 G, a_{NH} = −6.49 G, a_{H_1} = 0.66 G, and a_{H_2} = −1.71 G. That is, the hydrogen atoms in the 2, 3, 7, and 8 positions of the ring have the larger coupling, and the a_N and a_{NH} couplings are very close (earlier analysis had them as equal[26]).

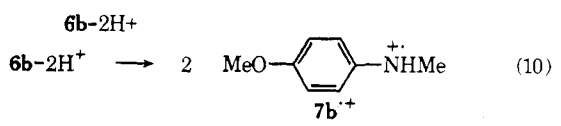
Cauquis, Genies, and Serve[28] have summarized data for cation radicals obtainable from tetraphenylhydrazine (TPH). Among these is TPH·⁺ itself (a_N = 7.9,[28] 7.25 G[29]), and 5,10-diphenyl-5,10-dihydrophenazine cation radical (a_N = 6.4 G).

These data support our analysis for **18b**·⁺, that $a_N = a_{N-Me} \simeq 6$ G, and coupling from only two hydrogens is detected. How valid our coupling constant is for these (2.69 G) can only be settled, however, with better resolved spectra.

Similarly, dihydrophenazine cation radicals appear to be formed by anodic oxidation of **6d** and **8d** (giving **18d**·⁺, a_N = 6.50 G), and by reaction of **16b** in acidic acetonitrile (giving **20b**·⁺, a_N = 6.34 G). In contrast, **6d** in acidic acetonitrile appears to give **6d**·⁺ (a_N = 8.9 G), and **16d** to give **16d**·⁺ (a_N = 8.14 G).

Products and Course of Reaction. Two major structural changes occur in **6b** in acidic solution. These are rearrangement to the *o*-semidine (**8b**) and scission to the amine (**7b**). Once **8b** has been formed it becomes a reducing agent available for participation in reductive scission of **6b**, since there can be little doubt that **8b** is the origin of the phenazines, **9b** and **11**, which we have isolated. Furthermore, there can be little doubt, also, that interposed between **8b** and these phenazines is the formation of 2,7-dimethoxy-5,10-dimethyl-5,10-dihydrophenazine (**18b**), detectable as its cation radical (**18b**·⁺), although not itself isolated.



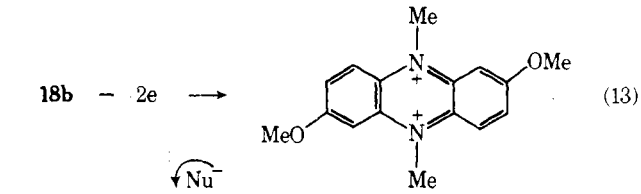


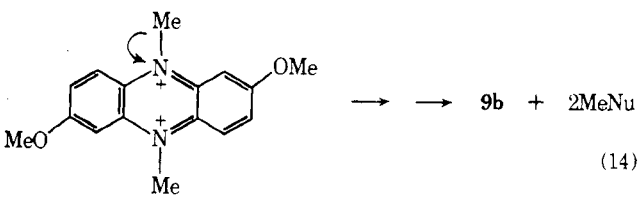
$$2\ 7b^{\cdot+} + 8b \longrightarrow\longrightarrow 18b + 2\ 7b + 2H^+ \quad (11)$$

$$2\ 7b^{\cdot+} + 18b \longrightarrow\longrightarrow 2\ 7b + 9b + \text{products} \quad (12)$$

These major events can be expressed as in eq 9–12, but these equations are most likely an oversimplification. Intramolecular rearrangement of **6b** to **8b** is to be expected. Whether or not diprotonated **6b** also cleaves homolytically to **7b**·⁺ is not certain, although it is an attractive idea. We have not detected the formation of **7b**·⁺ by ESR, and therefore we cannot rule out the possibility that protonated or diprotonated **6b** may be reduced directly.

Reduction of **6b** to **7b** is a two-electron process. After the rearrangement of **6b** to **8b** (which is not a redox process) occurs, two oxidative sequences would lead to **9b**. The first of these (eq 11) is a two-electron process, while the second (the demethylation of **18b**) can also be written most simply as a two-electron process, in which the oxidation steps (the formation of $18b^{2+}$) are followed by nucleophilic removal of the methyl groups (eq 13 and 14). Other than the formation





of **9b**, we have no evidence that the methyl groups are removed in this way. It may be that they are removed also from **8b** before the formation of **18b**, as suggested by the formation of **10**, Scheme I, but the overall electron balance between **8b** and **9b** will be the same. It is also possible that demethylation is itself an oxidation process, that is, that the methyl groups are eventually converted into formaldehyde.

This redox balance presents us with a problem in accounting entirely for the reductive scission of **6b** (and, below, **6d**). If oxidative cyclization and demethylation of **8b** were the only way of supplying electrons to **6b**, we would expect to see much larger amounts of **9b** than we do. That is, there should be 4 mol of **7b** per mol of **9b**, and the amount of **7b** is far in excess of that. At the same time, however, other oxidation products (**11** and **12b**, Scheme I) which were isolated indicate that other, but related, sources of electrons were available for the reduction of **6b**.

The chlorination products **10** and **11** represent oxidation stages, and in so doing add to the overall redox balance another two-electron stage per chlorine atom introduced into the ring. These products do not appear to come from reac-

tion of molecular chlorine, however, since tests for the formation of chlorine (in reactions of **6d**, below) were negative. Instead, it appears that nucleophilic attack of chloride ion on oxidatively formed cations is the source of **10** and **11**.

In addition, the separation and isolation of oxidation products was difficult and by no means quantitative. Some of the oils from which oxidation products were isolated remained uncharacterizable and unidentified.

Our summation of the reactions of **6b** is that reductive scission can be explained with the formation of **18b** and the several other products of oxidation (**9b, 10, 11, 12b**), even though the quantitative results are not as good as we would like.

Reactions of **6d** are more of a problem, but again we feel that reductive scission must have the same origins as those of **6b**. The large yield of *N*-methyl-4-aminobiphenyl (**7d**, 91%) means that oxidations must be very extensive. Products were obtained, two of which contained chlorine, but we have been unable to identify them. The only oxidation product identified, but obtained in very small yield, was the azo compound (**12d**, 0.2%).

In these reductive scissions chloride ion is a potential reducing agent (eq 15). It is an attractive possibility, since

$$2R_2NH^{\cdot+} + 2Cl^- \longrightarrow 2R_2NH + Cl_2 \qquad (15)$$

some cation radicals (e.g., of perylene[30]) oxidize chloride ion to chlorine. However, molecular chlorine was not found in the reactions of **6d** in acetonitrile–hydrochloric acid. Ledwith[31] has shown that the tris(*p*-bromophenyl)amine cation radical reacts with chloride ion, and becomes monochlorinated either directly or *via* disproportionation, much in the way that chloride ion reacts with the phenothiazine cation radical[32] and N-substituted phenothiazine cation radicals.[33] Chlorine is not formed in these reactions, and the products are formed by entry of chloride ion into the cation radical or corresponding dication. The same route(s) appear to be responsible for the chlorination products in the present work. Therefore, the only reducing agents identifiable in the present reactions appear to be **8b** and its descendants.

The deductions we have made about reactions of **6b** and **6d** apply also, we believe, to those of **6a**[17] and of the ethyl analogs **16b** and **16d**. In addition, it may be that **6d** and **16d** are themselves oxidized by scission amine cation radicals (e.g., **7d**$\cdot^+$, eq 16).

$$7d^{\cdot+} + 6d \longrightarrow 7d + 6d^{\cdot+} \qquad (16)$$

It is possible that we have missed small amounts of succinonitrile in our search for solvent involvement. The situation remains, however, that the only reducing agents that we *have* been able to find are the *o*-semidines, their cyclized descendants, and, to a very small extent, the hydrazo compounds themselves (*via* their demethylation).

As far as we know, our results with *N*-alkyl-*N*-arylhydrazoaromatics are the first of their kind. Reactions of tetraarylhydrazines with acids were described long ago by Wieland. In fact, reaction of tetra-*p*-tolylhydrazine led to di-*p*-tolylamine, 2,7-dimethyl-5,10-di-*p*-tolyl-5,10-dihydrophenazine, and also its dichlorination product.[34,35] The reactions of tetraphenylhydrazine with acids are complicated but not unlike those we have discussed, and lead in various circumstances to rearrangement and the formation of polymers,[36–38] to the tetraphenylhydrazine cation radical and the cation radical of the rearrangement product (*N,N,N'*-triphenyl-*p*-phenylenediamine),[29] and to the cation radical of 5,10-diphenyl-5,10-dihydrophenazine.[28,39] Thus, the reactions we have observed are part of the general chemistry of hydrazoaromatics, and are likely to occur as side reactions when hydrazoaromatics rearrange. Benzidine rearrangements have never been found to be intermolecular. There are proposals that cation radicals are involved in the intramolecular rearrangements,[4] but these have little or no experimental support. If scission of protonated tetraarylhydrazoaromatics leads to diarylaminium radicals,[35,36] we might expect that they may recombine as rearrangement products. Cauquis has proposed a similar recombination in the reaction of perchloric acid with triphenylhydrazine.[40] We might expect the same behavior of our *N*-alkyl-*N*-arylaminium radicals if they are formed as in eq 10. These several recombinations would constitute *intermolecular* benzidine rearrangements. Because there is no direct evidence, as yet, that benzidine rearrangements are anything but intramolecular, we would conclude that where it accompanies a benzidine rearrangement as a minor event, reductive scission may involve the protonated hydrazoaromatic directly. On the other hand the reason that reductive scission is so rarely seen along with benzidine rearrangements may well be that reductive scission requires cation radicals, and that it is these that are rarely formed in benzidine rearrangements. Certainly, the possibility that intermolecular rearrangements may occur in tetrasubstituted hydrazoaromatics such as compounds **6** and the tetraaryl analogs is most intriguing.

Experimental Section

N,N'-Dimethyl-*p*-hydrazoanisole (**6b**), *N,N'*-dimethyl-*p*-hydrazobiphenyl (**6d**), the scission amines (**7b, 7d**), the *o*-semidines (**8b, 8d**), the azo compounds (**12b, 12d**), and 6-amino-3,4'-dimethoxy-*N*-methyldiphenylamine (the demethylated *o*-semidine, **13**) have been described earlier.[17]

***N,N'*-Dimethyl-d_6-*p*-hydrazoanisole (6b-d_6).** A solution of 4 g (16.4 mmol) of *p*-hydrazoanisole in 100 ml of dry THF was added to 3.5 ml of commercial 90% *n*-butyllithium in hydrocarbon solvent until the mixture became orange yellow. To this was added 5.6 g (38.7 mmol) of MeI-d_3 in 20 ml of THF. The solution was stirred for 2 hr, diluted with ether, washed with 10% NaOH and water, and worked up after drying over K_2CO_3 to give 4.31 g (95%) of **6b**-d_6, mp 104–106°.

***N,N'*-Diethyl-*p*-hydrazoanisole (16b).** The procedure above was used with 6.54 g (26.2 mmol) of *p*-hydrazoanisole, 5 ml of *n*-BuLi, and EtBr, to give 7.7 g (96%) of **16b** as an oil. This was treated with active carbon in cyclohexane and obtained again as an oil, NMR (CCl_4) δ 1.67 (t, 6 H), 3.36 (q, 4 H), 3.63 (s, 6 H), 6.69 (s, 8 H).

Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 72.0; H, 8.05; N, 9.33. Found: C, 71.8; H, 8.04; N, 9.54.

***N,N'*-Diethyl-*p*-hydrazobiphenyl (16d).** The same procedure was used with 6.9 g (20.5 mmol) of *p*-hydrazobiphenyl, 5 ml of *n*-BuLi solution, and EtBr to give 6.89 g (86%) of **16d**, mp 126–127° (from ethanol–ether), NMR (CCl_4) δ 1.29 (t, 6 H), 3.57 (q, 4 H), 7.75 (d, 4 H), 7.5 (m, 14 H).

Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.7; H, 7.19; N, 7.14. Found: C, 85.8; H, 7.21; N, 7.16.

Reaction of 6b in Acidic Dioxane–Methanol. To a cold solution of 250 mg (0.92 mmol) of **6b** in 10 ml of dioxane and 40 ml of methanol was added 0.1 ml of concentrated HCl in 10 ml of methanol. The brown solution was stirred under nitrogen for 30 min on an ice bath and quenched with ammonia gas. The solvent was removed at room temperature on a rotary evaporator, and the residue was triturated with benzene to leave 90 mg of a purple, paramagnetic solid. Evaporation of the benzene gave 230 mg of brown oil. The oil was assumed to be a mixture of *N*-methyl-*p*-anisidine (**7b**) and the *o*-semidine (**8b**).[17] Quantitative analysis by NMR spectroscopy gave yields of 36% of **7b** and 56% of **8b** from this reaction of **6b**. The purple solid was dissolved in basic, aqueous NaI solution. Extraction with ether gave 36 mg of a brown oil whose NMR spectrum indicated one methyl and two methoxy groups. A *p*-nitrobenzoyl derivative was obtained, and was not that of 2-amino-4',5-dimethoxy-*N*-methyldiphenylamine (**13**). The brown oil remains unidentified.

2,7-Dimethoxy-5,10-dimethyl-5,10-dihydrophenazine (18b). 2,7-Dimethoxyphenazine (**9b**) was made by boiling for 6 hr under nitrogen a mixture of 10 g of *p*-nitroanisole, 10 g of *p*-anisidine,

and 30 g of powdered KOH. Instead of steam distilling,[41] the mixture was poured into water and stirred with 500 ml of benzene. The organic layer was washed with water until the washings were almost colorless, dried, and evaporated to give an oily residue. Trituration with benzene gave 2.1 g of yellow solid which was boiled with 40 ml of acetic anhydride (to convert the phenazine *N*-oxide into the phenazine). The cool solution was poured into water which was then neutralized and extracted with chloroform, which gave a brown oil. Crystallization from benzene gave 920 mg (4.7%) of **9b**, mp 246–247° (lit.[41] mp 246°).

Crude **9b** (711 mg, 2.98 mmol) was methylated in dry dimethoxyethane with potassium and methyl iodide. Work-up gave some unused **9b** and, by chromatography on alumina, 86 mg of *p*-azoanisole and 100 mg (12.5%) of **18b**, mp 142–142.5° (from ether), NMR (acetone-d_6) δ 3.66 (s, 9 H), 6.01 (s, 3 H), and 6.25 (br s, 6 H).

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.1; H, 6.71; N, 10.4. Found: C, 71.0; H, 6.78; N, 10.6.

Reaction of 6b in Acidic MeCN. Cold solutions of 2 g (7.35 mmol) of **6b** in 100 ml of MeCN and of 2 ml of 12 *N* HCl in 50 ml of MeCN were mixed and stirred under N_2 for 1 hr while in an ice bath. The only color observed on mixing was light brown. The mixture was quenched with 30 ml of 10% NaOH and diluted with 200 ml of ether. The ether layer, after washing with 2 × 50 ml of 10% NaOH and with water and drying over K_2CO_3, gave 2.17 g of brown oil.

The alkaline water layer was acidified with 10% HCl, neutralized with $NaHCO_3$, and extracted with ether to give 64 mg of **7b**, identified by TLC and NMR. The aqueous layer appeared not to contain an aminophenol.

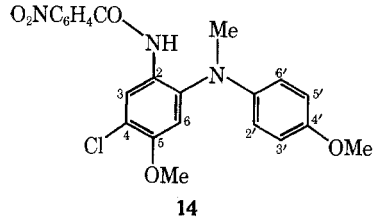
The brown oil was triturated with benzene and deposited 7 mg of a yellow solid, mp 234–237°. This solid gave a positive Beilstein halogen test. The mass spectrum showed peaks at *m/e* 240.05 and 274.05. The former corresponds with **9b** and the latter with **11**. The melting point of this solid indicated that it was mostly **11**, contaminated with **9b**.

The benzene filtrate (from the trituration) was chromatographed on alumina (Woelm activity III, 2.2 × 33 cm). Elution with petroleum ether (300 ml, bp 30–60°) was ineffective. Elution with petroleum ether–ether mixtures gave a sequence of fractions as follows: 2 l. of 95:5, fractions 4–27; 500 ml of 90:10, fractions 28–33; 500 ml of 80:20, fractions 34–39; 1.5 l. of 50:50, fractions 40–57; and 700 ml of ether, fractions 58–66. Fractions 5–7 gave 17 mg of yellow oil from which was crystallized a trace of **12b** from ethanol, mp 156–161° (lit.[17] mp 158°), *m/e* 242.2. Fractions 8–37 gave 1.34 g of **7b**, mp 35–36° (from *n*-hexane), mmp 35–37°. This with the earlier portion is a 70% total yield of **7b**.

Fractions 38–44 gave 160 mg of an oily solid. This was triturated with benzene to give 6 mg of yellow solid which was sublimed at 170° (25 mm) to give 3 mg of **9b**, mp 239.5–241.5°, *m/e* 240.05; this solid was contaminated with traces of **11**. The benzene filtrate was concentrated to give 10 mg of impure **11**. This was sublimed and crystallized from benzene to give impure **11**, mp 234–237°, *m/e* 274.05. The product gave a positive Beilstein halogen test. The benzene concentrate was evaporated and the residue was triturated with *n*-hexane, and the *n*-hexane filtrate gave 106 mg of yellow oil. The oil appeared to be a single compound and is believed to have been 2-amino-4-chloro-4',5-dimethoxy-*N*-methyldiphenylamine (the monodemethylated chloro-*o*-semidine, **10**), in which case its yield was 5%. The *p*-nitrobenzoyl derivative (**14**) of **10** had mp 181.5–182.5 (from ether) and *m/e* 441.1

Anal. Calcd for $C_{22}H_{20}N_3O_5Cl$: C, 59.8; H, 4.53; N, 9.51; Cl, 8.03. Found: C, 59.8; H, 4.68; N, 9.77; Cl, 8.21.

Assignment of the position of the chlorine atom in **10** was made by comparing the NMR spectrum of **14** with that of the *p*-nitrobenzoyl derivative (**15**) of 2-amino-4',5-dimethoxy-*N*-methyldiphenylamine (**13**). The NMR ($CDCl_3$) of **14** follows: δ 3.27 (s, 3 H), 3.73, 3.83 (2 s, 6 H), 6.75 (s, 5 H), 7.58 (d, 2 H), 8.14 (d, 2 H), 8.33, 8.53 (2 s, 2 H). The NMR of **15** (see later) had a 1 H singlet at δ 8.45 (assigned to proton 6) and a 6 H singlet at δ 6.73 assignable to the remaining numbered ring protons. These correspond with the



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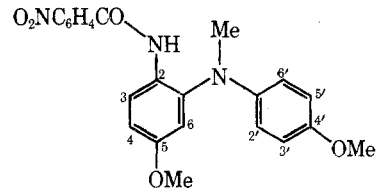

15

5 H singlet (2', 3', 3, 5', 6' protons) at δ 6.75 and the 1 H singlet at δ 8.53 in **14**. The sharpening of the singlet at δ 8.53 in 14 is assigned to proton 6.

Reaction of 6d in Acidic MeCN. A. A cold solution of 1.3 ml of concentrated HCl in 20 ml of MeCN was added to a cold suspension of 1 g (2.74 mmol) of **6d** in 80 ml of MeCN. The mixture turned blue and became brown within 1 min. Stirring in an ice bath under N_2 was continued for 4 hr. The solution was neutralized with 10% KOH, and the organic layer was evaporated at reduced pressure. The residue was taken up in $CHCl_3$ dried over K_2CO_3 to give 1.27 g of a brown oil, whose ir spectrum failed to indicate the presence of –C≡N groups.

The oil was chromatographed on silica gel (Davison 950, 60–200 mesh, 2.2 × 28 cm) with petroleum ether–ether elution. Five hundred milliliters of 98:2 gave 56 mg of orange-red solid from which trituration with ethanol–CCl_4 gave 2 mg (0.2%) of **12d**. One thousand milliliters of 97:3 gave 76 mg of an oil which could not be identified. One and five-tenths liters of 95:5 gave 910 mg (91%) of **7d**, identified by NMR, ir, and benzenesulfonyl derivative, mp 151–152° (lit.[17] mp 152–153°). Five hundred milliliters of 90:10 gave 64 mg of a solid, mp 134–137° (from MeCN), *m/e* 202. Two hundred milliliters of ether gave 90 mg of a solid, mp 149–180° (from MeCN), *m/e* 670. The last two solids gave positive Beilstein halogen tests, but remain unidentified.

B. Reaction was repeated and the mixture was neutralized with 6 ml of concentrated NH_4OH. The solvent was removed as before and the residue was dissolved in CCl_4 in which succinonitrile is poorly soluble. The CCl_4 solution was washed twice with water, in which succinonitrile is soluble. The water solution was evaporated at 40° and after the residue was dried (in $CHCl_3$) its ir spectrum gave no evidence of –C≡N groups.

Oxidation of 8b with PbO_2. A solution of 500 mg (1.84 mmol) of **8b** in 20 ml of MeCN and 0.7 ml of AcOH was stirred with 1 g of PbO_2 in an ice bath under N_2 for 1.5 hr. After the AcOH was neutralized the mixture was worked up to give 400 mg of brown oil, which was chromatographed on alumina (Woelm activity III, 1.7 × 29 cm). A series of 75-ml fractions of petroleum ether–ether eluates was collected. Fractions 7–10 (90:10) gave 135 mg of recovered **8b**, identified by NMR and mp 60–60.5° (from *n*-hexane). Fractions 11–31 (85:15) gave 115 mg of solid. Crystallization from benzene gave 14 mg (3%) of **9b**, mp 248–249.5°, *m/e* 240.09. Evaporation of the benzene filtrate gave 64 mg (14%) of **13**, identified by NMR.[17] The *p*-nitrobenzoyl derivative (**15**) of **13** had mp 134.5–135° (from ethanol) and NMR ($CDCl_3$) δ 3.25 (s, 3 H), 3.73, 3.78 (2 s, 6 H), 6.73 (s, 6 H), 7.54 (d, 2 H), 8.13 (d, 2 H), 8.26 and 8.4 (2 s, 2 H).

Anal. Calcd for $C_{22}H_{21}N_3O_5$: C, 64.9; H, 5.20; N, 10.3. Found: C, 64.9; H, 5.23; N, 10.3.

Fractions 32–38 (ether) gave 65 mg of solid. Crystallization from *n*-hexane–ether gave mp 155–157°, *m/e* 510.2. This compound remains unidentified.

Reaction of 6b with D_2SO_4 in Acetone-d_6. Search for CIDNP. A solution of 109 mg of D_2SO_4 in 0.5 ml of acetone-d_6 was made and added to 0.3 ml of acetone-d_6 containing a weighed sample for investigation, and the NMR spectrum was scanned over a period of time in a Varian A-60 spectrometer. The NMR spectrum was compared with that of an identical solution made without D_2SO_4. Samples of **7b** and **8b** were used as controls. When **6b** and **6b-d_6** were used in D_2SO_4 solution, the only NMR signals observed were those of **7b**. No enhanced absorption or emission lines were observed, and the *o*-semidine (**8b**) signals were not observed either.

ESR Spectra. Three techniques were used. In the flow reactions, the substrate solution and solution of acid in the same solvent were allowed to flow by gravity into a mixing chamber inserted into a Varian Associates flat cell. Before flowing the solutions were purged with N_2. Static chemical oxidations were carried out with the apparatus in Figure 2. Tubes A and B were charged with reactants, degassed by freeze–thaw technique, and mixed for transfer to the esr capillary. Occasionally, a break-seal was placed

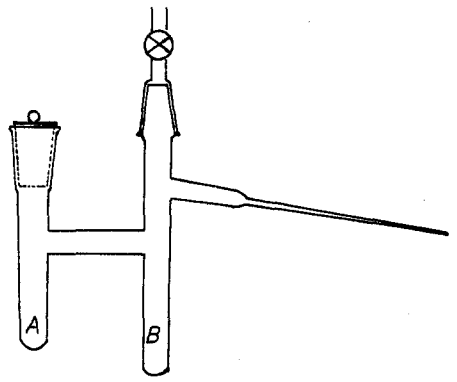

Figure 2. Apparatus for recording ESR spectra in static oxidations. Occasionally tubes A and B were separated by a break-seal and arranged appropriately for degassing.

between A and B. Anodic oxidations were carried out with a Varian Associates flat cell and Pt gauze anode.

A copper wire was inserted into the upper neck of the cell. Reference cells were not used. An applied voltage of about 2.5 V at 30 μA was used, and no attempt was made to seek refined or optimum conditions.

Registry No.—**6b,** 30724-67-5; **6b-d_6,** 53731-00-3; **6d,** 30788-03-5; **7b,** 5961-59-1; **8b,** 30745-00-7; **8d,** 30724-70-0; **9b,** 5051-19-4; **10,** 53731-01-4; **11,** 53731-02-5; **12b,** 501-58-6; **13,** 30788-10-4; **14,** 53731-03-6; **15,** 53731-04-7; **16b,** 53731-05-8; **16d,** 53731-06-9; **18b,** 53731-07-0; MeI-d_3, 865-50-9; EtBr, 74-96-4; *p*-hydrazobiphenyl, 4088-58-8; *p*-hydrazoanisole, 1027-40-3.

Supplementary Material Available. Figures 3–9 listed in Table I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-703.

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