

/ELECTROCHEMICAL REDUCTIONS OF DIPHENYLDIAZOMETHANE  
AND AZOBENZENE: THE EFFECT OF ELECTROINACTIVE  
PROTON DONORS

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by

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AND DECOMPOSITION OF  $\text{Ph}_2\text{CN}_2^-$  AND  $\text{Ph}_2\text{CN}_2^{2-}$

Introduction

The interpretation of results from the electrochemical reduction of diphenyldiazomethane ( $\text{Ph}_2\text{C}=\text{N}_2$ ) has been both difficult and controversial.<sup>1-6</sup> Initially,  $\text{Ph}_2\text{C}=\text{N}_2^-$  was reported to be short-lived on the cyclic voltammetric time scale and decomposed by loss of  $\text{N}_2$  to give the corresponding carbene anion radical ( $\text{Ph}_2\text{C}^-$ ) as an unobserved intermediate.<sup>1-3</sup> Bethell and Parker refuted this interpretation, arguing that the anodic peak which we had attributed to the oxidation of  $\text{Ph}_2\text{CH}^-$  was due instead to the oxidation of  $\text{Ph}_2\text{C}=\text{N}_2^-$  and that the separation of up to 1 V between the cathodic and anodic peaks for the  $\text{Ph}_2\text{C}=\text{N}_2/\text{Ph}_2\text{C}=\text{N}_2^-$  redox couple was due to slow heterogeneous electron transfer.<sup>4,5</sup> Subsequent triple-potential-step chronoamperometric results from our laboratory have confirmed Bethell and Parker's interpretation.<sup>6</sup>

The pathways by which the reduction products of  $\text{Ph}_2\text{C}=\text{N}_2$  react under certain solution conditions remain uncertain. For example, whereas Bethell and Parker claimed that  $\text{Ph}_2\text{C}=\text{N}_2^-$  reacted by hydrogen-atom abstraction in the presence of  $(\text{EtO}_2\text{C})_2\text{CH}_2$ ,<sup>5</sup> we found instead that  $\text{Ph}_2\text{C}=\text{N}_2^-$  was protonated rapidly by  $(\text{EtO}_2\text{C})_2\text{CH}_2$  ( $\text{pK}_a^{\text{DMSO}} = 16.4$ )<sup>7</sup> and  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\text{pK}_a \sim 23$ )<sup>8</sup> to give  $\text{Ph}_2\text{CH}_2$  as the principal product.<sup>1</sup> In the absence of an added proton donor, there was consensus that electroreduction of  $\text{Ph}_2\text{C}=\text{N}_2$  initiated a chain reaction which afforded  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  in as much as 81% yield. Although  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  had been detected as an intermediate in the cyclic voltammetric reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  under these conditions, it has not been ascertained



whether  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  lay in the principal product-forming channel or if it was formed by the inadvertent protonation of electrogenerated  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$  by an adventitious proton donor (e.g., water).

The goal of this study was to elucidate the principal reaction pathways for  $\text{Ph}_2\text{C}=\text{N}_2^-$  and  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  and to identify the intermediates which lie in the product-forming channels. Our studies have been conducted under a variety of solution conditions. In order to minimize the deleterious effect which the chain reaction would have on kinetics studies of the reaction of  $\text{Ph}_2\text{C}=\text{N}_2^-$ , weak electroinactive proton donors have been added which protonate some or all of the electrogenerated anions, anion radicals, and dianions (e.g.,  $\text{Ph}_2\text{CH}^-$ ,  $\text{Ph}_2\text{C}=\text{NNH}^-$ ,  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ ,  $\text{Ph}_2\text{C}^-$ ,  $\text{Ph}_2\text{C}=\text{N}_2^-$ , and  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$ ).

### Results and Discussion

Reduction of  $\text{Ph}_2\text{C}=\text{N}_2^-$  to  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$ . In order to study the reduction of  $\text{Ph}_2\text{C}=\text{N}_2^-$  to  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$ , reaction conditions were selected which would facilitate the reduction of  $\text{Ph}_2\text{C}=\text{N}_2^-$  and minimize its decomposition by other pathways.  $(\text{CH}_3)_4\text{N}^+$  was selected as the cation of the supporting electrolyte because of its low proton availability, its favorable cathodic potential limit, and its greater propensity than other tetraalkylammonium ions to ion-pair with  $\text{Ph}_2\text{C}=\text{N}_2^-$ . Ion-pairing facilitates the reduction of  $\text{Ph}_2\text{C}=\text{N}_2^-$ , thereby shifting the cathodic peak for  $\text{Ph}_2\text{C}=\text{N}_2^-$  reduction to more positive potentials and away from the cathodic limit for the solvent and electrolyte. In order to minimize the reaction of electrogenerated  $\text{Ph}_2\text{C}=\text{N}_2^-$  by pathways other than reduction, most cyclic voltammetric and chronoamperometric studies were conducted in the temperature range  $-51^\circ\text{C} \leq T \leq 0^\circ\text{C}$ .

As shown in Figure 1, the cyclic voltammogram of  $\text{Ph}_2\text{C}=\text{N}_2$  at  $-51^\circ\text{C}$  in N,N-dimethylformamide (DMF) and  $0.1\text{ M } (\text{CH}_3)_4\text{BF}_4$  consists of a cathodic peak

for the chemically reversible reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^-$  near  $-1.06$  V and an anodic peak for the reoxidation of  $\text{Ph}_2\text{C}=\text{N}_2^-$  near  $-0.3$  V on the reverse, positive-going sweep. The relatively large separation between the cathodic and anodic peaks for the  $\text{Ph}_2\text{C}=\text{N}_2/\text{Ph}_2\text{C}=\text{N}_2^-$  redox couple has been shown previously to be due to slow heterogeneous electron transfer.<sup>5,6</sup> A similar phenomenon has been observed in the  $(\text{EtO}_2\text{C})_2\text{C}=\text{N}_2/(\text{EtO}_2\text{C})_2\text{C}=\text{N}_2^-$  and fluorenone hydrazone/fluorenone hydrazone anion radical redox couples<sup>6</sup> and is attributed to the substantial decrease in the C-N-N bond angle that presumably occurs upon one-electron reduction to the anion radical (e.g., the O-N-O bond angles in  $\text{NO}_2^+$ ,  $\text{NO}_2$  and  $\text{NO}_2^-$  are  $180^\circ$ ,  $132^\circ$ , and  $115^\circ$ , respectively).<sup>9</sup>

When the cathodic switching potential is made sufficiently negative so as to include the cathodic peak for the reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  at  $-1.9$  V (Figure 2), no anodic peak is seen for the reoxidation of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  for  $v \leq 100$  V/s on the reverse, positive-going sweep. This result places an upper limit of approximately 2 ms on the lifetime of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$ . Although the solution reaction involving  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  is too fast to study by our methods, anodic peaks due to the oxidation of species that arise from the decomposition of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  are seen near 0.28,  $-0.85$  and  $-1.25$  V. The assignment of the anodic peak at 0.28 V to the irreversible oxidation of  $\text{Ph}_2\text{CH}\bar{\text{N}}=\text{CPh}_2$  is based on the facts that (1) authentic  $\text{Ph}_2\text{CH}\bar{\text{N}}=\text{CPh}_2$ , which was prepared by the electrolytic reduction of  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  to  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$  in the presence of a slight excess of water,<sup>10</sup> displays identical cyclic voltammetric behavior; and (2)  $\text{Ph}_2\text{CH}^-$  and  $\text{Ph}_2\text{C}=\text{NNH}^-$ , which are the other most plausible products of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  decomposition, are oxidized instead at  $-0.36$  V<sup>11</sup> and 0.12 V,<sup>6,10</sup> respectively. The assignment of the anodic peaks at  $-1.19$  and  $-0.83$  V to the stepwise oxidation of  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$  is based on the comparison of this cyclic

Figure 1. Cyclic voltammogram for the reduction of 3.55 mM  $\text{Ph}_2\text{C}=\text{N}_2$  at a planar glassy carbon electrode in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-51^\circ\text{C}$ . The scan was initiated in the negative-going direction from 0 V at a rate of 0.5 V/s.

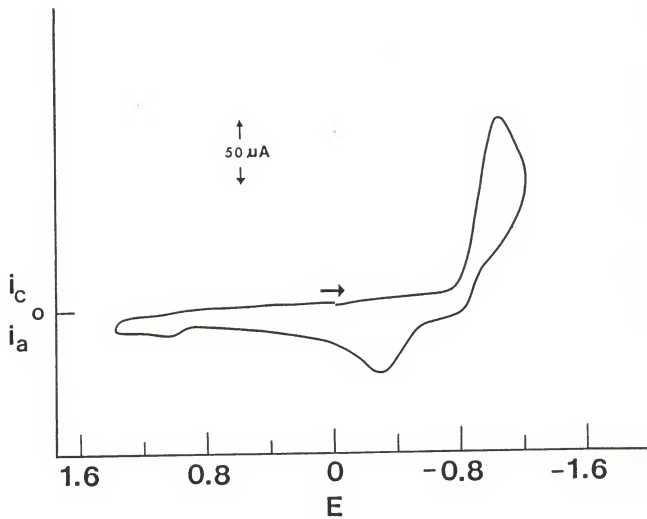
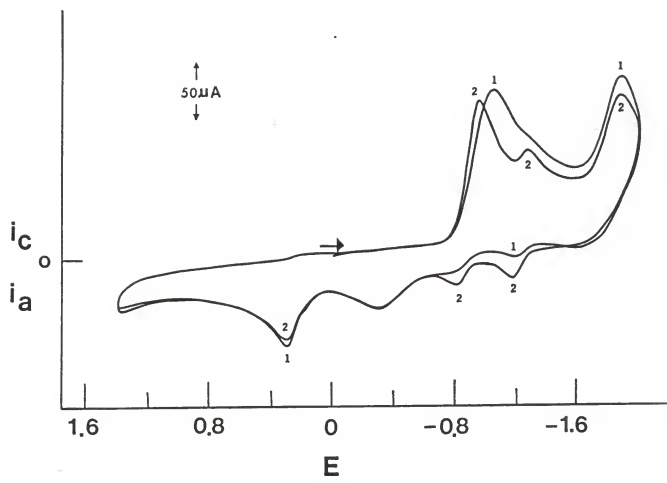
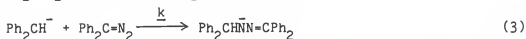
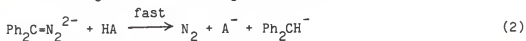
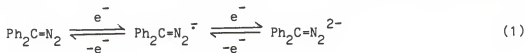


Figure 2. Cyclic voltammogram for the reduction of 3.55 mM  $\text{Ph}_2\text{C}=\text{N}_2$  at a planar glassy carbon electrode in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-51^\circ\text{C}$ . The scan was initiated in the negative-going direction from 0 V at a rate of 0.5 V/s. Numbers 1 and 2 represent the first and second cycles, respectively.



voltammetric behavior with that of authentic material under these reaction conditions.<sup>10</sup>

A sequence of reactions which is consistent with the cyclic voltammetric behavior is described by eq 1-3. The reaction scheme assumes that  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  reacts rapidly at the central carbon site by abstraction of a proton from an unidentified component of the solvent-electrolyte system (e.g.,  $(\text{CH}_3)_4\text{N}^+$ )<sup>12</sup> to give  $\text{N}_2$  and  $\text{Ph}_2\text{CH}^-$  (eq 2). Coupling of  $\text{Ph}_2\text{CH}^-$  with unreacted  $\text{Ph}_2\text{C}=\text{N}_2$  (eq 3)



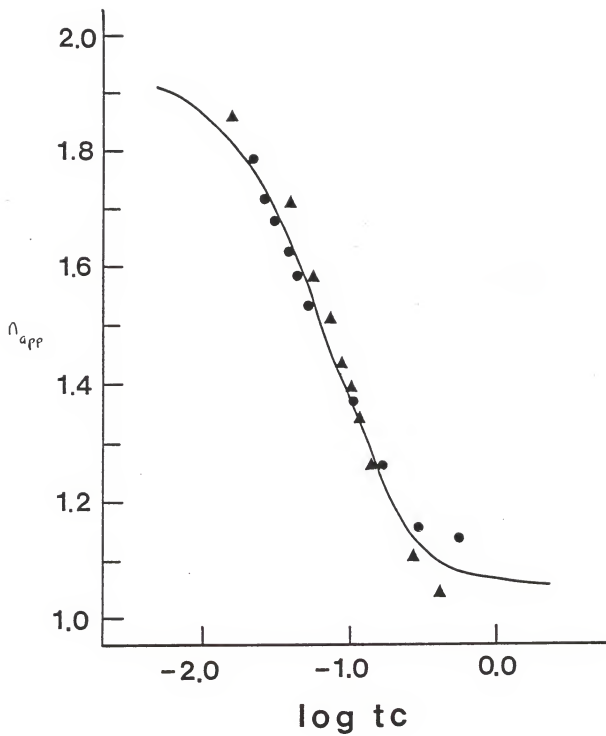
where HA is a component of the solvent-electrolyte system

is proposed to be the rate-determining step in the formation of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ .

In order to test the feasibility of this model, the reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  was studied by chronoamperometry.<sup>13</sup> In this technique, the potential of the working electrode is stepped from its initial value where  $\text{Ph}_2\text{C}=\text{N}_2$  is electroinactive to a value which is sufficiently negative ( $E = -2.20$  V) such that the concentrations of both  $\text{Ph}_2\text{C}=\text{N}_2$  and  $\text{Ph}_2\text{C}=\text{N}_2^-$  are effectively zero at the electrode surface. The current that is measured as a function of time is proportional to  $\underline{n}$ , where  $\underline{n}$  is the number of electrons required for the reduction of each molecule of  $\text{Ph}_2\text{C}=\text{N}_2$ . As expected for this reaction sequence (eq 1-3), the experimental chronoamperometric  $\underline{n}$  value decreases from an upper limit of 2 at short times to a lower limit of 1 for  $\underline{t}$  in excess of approximately 100 ms (Figure 3). In order to obtain the second-order rate constant  $\underline{k}$  for the coupling of the proposed intermediate  $\text{Ph}_2\text{CH}^-$

Figure 3. Single-potential-step chronoamperometric data for the reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  on a planar glassy carbon electrode in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-37^\circ\text{C}$ . The solid curve was obtained by the digital simulation of a second-order EC process in which  $k = 5 \times 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ . The concentrations of  $\text{Ph}_2\text{C}=\text{N}_2$  are 1.86 mM (circle) and 5.90 mM (triangle).





with unreacted  $\text{Ph}_2\text{C}=\text{N}_2$ , the curve of the experimental  $\underline{n}$  value vs.  $\log \underline{t}$  is fitted to the theoretical working curve that was obtained by digitally simulating<sup>14</sup> the electrochemical and chemical reactions described by eq 1-3. The best fit in terms of both the variation in reaction time  $\underline{t}$  and the concentration of  $\text{Ph}_2\text{C}=\text{N}_2$  was obtained for  $\underline{k} = 5 \times 10^4 \underline{M}^{-1} \cdot \text{s}^{-1}$  at  $-37^\circ \text{C}$ . Although the fit is relatively poor, it is acceptable in view of the numerous experimental difficulties that are unavoidably present. Specific experimental problems include the rapid rate of this reaction, the slow response of the electrochemical cell at  $-37^\circ \text{C}$ , the proximity of the applied potential to background, and competing reactions, including the protonation of  $\text{Ph}_2\text{CH}^-$  by adventitious proton donors such as water. If protonation of  $\text{Ph}_2\text{CH}^-$  were to occur, the coupling reaction between  $\text{Ph}_2\text{CH}^-$  and  $\text{Ph}_2\text{C}=\text{N}_2$  would be precluded, thereby causing the  $\underline{n}$  value to remain at its upper limiting value of 2. This problem should be most acute when the concentration of  $\text{Ph}_2\text{C}=\text{N}_2$  is relatively low.

Reaction of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  as an Ambident Base. A second competing reaction involves protonation on the terminal nitrogen of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$ . In the absence of an added proton donor, protonation of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  appears to occur principally on the central carbon atom to give  $\text{Ph}_2\text{CH}^-$  and  $\text{N}_2$ . However, in the presence of weak proton donors such as  $\text{CH}_3\text{OH}$  ( $\text{pK}_a^{\text{DMSO}} = 29.0$ )<sup>15</sup> and  $\text{H}_2\text{O}$  ( $\text{pK}_a^{\text{DMSO}} = 31.4$ )<sup>15</sup> the magnitude of the cathodic peak assigned to the reduction of  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot -}$  to  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  ( $E_{\text{p,c}} = -1.82 \text{ V}$ ) exceeds that for the one-electron reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  ( $E_{\text{p,c}} = -1.06 \text{ V}$ ) (Figure 4). This result is consistent with protonation of  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  on the nitrogen atom beta to the central carbon atom to give  $\text{Ph}_2\text{C}=\text{NNH}^-$ . This anion is subsequently protonated by either of these proton donors to give  $\text{Ph}_2\text{C}=\text{NNH}_2$ . The increase in the cathodic peak height for

the reduction of  $\text{Ph}_2\text{C}=\text{N}_2^-$  is the result of the concomitant reduction of  $\text{Ph}_2\text{C}=\text{NNH}_2$  ( $E_{\text{p,c}} = -1.72$  V) at the applied potential to give  $\text{Ph}_2\text{CHNH}_2$  and  $\text{NH}_3$  in an overall four-electron process (eq 4).<sup>10</sup>



Protonation of  $\text{Ph}_2\text{C}=\text{N}_2^-$ . The addition of an excess of electroinactive proton donors such as benzoic acid ( $\text{pK}_a^{\text{DMSO}} = 11.0$ ),<sup>7</sup> guanidinium perchlorate, diethyl malonate ( $\text{pK}_a^{\text{DMSO}} = 16.4$ ),<sup>7</sup> and  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\text{pK}_a \sim 23$ ),<sup>8</sup> causes the anodic peak for the oxidation of  $\text{Ph}_2\text{C}=\text{N}_2^-$  to disappear throughout the temperature ( $-51^\circ \text{C} \leq T \leq 23^\circ \text{C}$ ) and scan rate ( $0.1 \text{ V/s} \leq \nu \leq 100 \text{ V/s}$ ) ranges and the chronoamperometric  $n$  value for the initial reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  ( $E_{\text{applied}} = -1.4$  V) to double. Thus, since the reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^-$  in the absence of added acids at  $-51^\circ \text{C}$  is a diffusion-controlled, one-electron process in the time range  $10 \text{ ms} \leq t \leq 200 \text{ ms}$ , the chronoamperometric results in the presence of these proton donors indicate that two electrons are required for the reduction of each molecule of  $\text{Ph}_2\text{C}=\text{N}_2$ .

Controlled-potential electrolysis of  $\text{Ph}_2\text{C}=\text{N}_2$  at a large mercury pool cathode at the potential of its first cathodic wave ( $E_{\text{applied}} = -1.1$  V) nominally requires two electrons per molecule of  $\text{Ph}_2\text{C}=\text{N}_2$  and affords  $\text{Ph}_2\text{C}=\text{NNH}_2$  and  $\text{Ph}_2\text{CH}_2$  as the principal products (Entries 1-5, Table I). It should be noted that the  $\text{Ph}_2\text{C}=\text{NNH}_2/\text{Ph}_2\text{CH}_2$  product ratio decreases significantly with either increasing  $\text{pK}_a$  of the acid or decreasing temperature. We initially suggested that  $\text{Ph}_2\text{C}=\text{NNH}_2$  and  $\text{Ph}_2\text{CH}_2$  arose from the protonation of  $\text{Ph}_2\text{C}=\text{N}_2^-$  and  $\text{Ph}_2\text{C}^-$ , respectively, and that  $\text{Ph}_2\text{C}^-$  was formed as a transient intermediate when  $\text{Ph}_2\text{C}=\text{N}_2^-$  underwent rapid loss ( $t_{1/2} < 10^{-8}$  s) of  $\text{N}_2$ .<sup>1</sup> However, the

Figure 4. Cyclic voltammogram for the reduction of 2.52 mM  $\text{Ph}_2\text{C}=\text{N}_2$  at a planar glassy carbon electrode in the presence of 24.12 mM  $\text{CH}_3\text{OH}$  in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-51^\circ\text{C}$ . The scan was initiated in the negative-going direction from 0 V at a rate of 0.1 V/s.

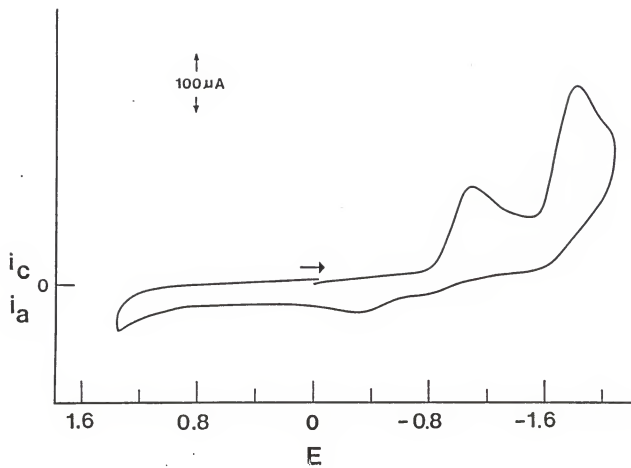


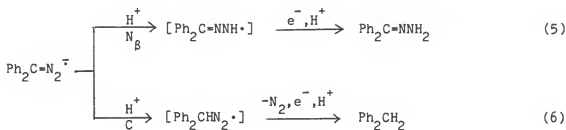
Table I. Coulometric Data and Product Studies for the Controlled-Potential,  
Electrolytic Reduction of  $\text{Ph}_2\text{C}=\text{N}_2$

Table I. Coulometric Data and Product Studies for the Controlled-Potential, Electrolytic Reduction of  $\text{Ph}_2\text{C}=\text{N}_2$ <sup>a</sup>

Run	$[\text{Ph}_2\text{C}=\text{N}_2]$ , mM	$[\text{acid}]$ , mM <sup>b</sup>	$E_{\text{applied}}$ , V	Temp, °C	$\mu$	Product Distribution, % Yield										
						$\text{Ph}_2\text{C}=\text{NH}_2$	$\text{Ph}_2\text{C}=\text{O}$	$\text{Ph}_2\text{CH}=\text{CPh}_2$	$\text{Ph}_2\text{C}=\text{NHPh}_2$	$\text{Ph}_2\text{C}=\text{NPh}_2$	$\text{Ph}_2\text{CH}=\text{NPh}_2$					
1	3.67	$\text{C}_6\text{H}_5\text{COOH}$ , 37	-1.1	23	2.0				86							13
2	3.48	GP, 32	-1.1	23	2.0				44		50					8
3 <sup>c,d</sup>	4.54	DEH, 39	-1.1	23	2.0	0.7			8		85		1		3	2
4 <sup>c,d</sup>	3.02	DEH, 32	-1.2	0	2.45	1.3			21		44		3		3	18
5 <sup>c,d</sup>	3.49	TFE, 21	-1.0	23	2.0	0.5			2.5		88		0.1		0.4	5
6 <sup>d</sup>	4.36	$\text{CH}_3\text{OH}$ , 87	-1.1	-37	1.5	16			8		45		2		10	27
7 <sup>d</sup>	4.25	$\text{t-BuOH}$ , 21	-1.2	-51	0.55	72			1				2		18	trace
8	4.94	$\text{p-NCC}_6\text{H}_4\text{NH}_2$ , 99	-1.1	-51	1.5	15			16		56				trace	6
9 <sup>c,d</sup>	3.70	none	-1.0	23	0.3	81			0.5		8		1.0		1.8	7

<sup>a</sup>All electroreductions were effected at a mercury cathode in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  unless otherwise noted. The product distribution was determined by HPLC. <sup>b</sup>GP = guanidinium perchlorate, DEH = diethyl malonate, TFE =  $\text{CF}_3\text{CH}_2\text{OH}$ . <sup>c</sup>Reference 1; 0.1 M  $(\text{n-Bu})_4\text{NClO}_4$  supporting electrolyte. <sup>d</sup>Platinum gauze cathode.

demonstrations<sup>4-6</sup> that  $\text{Ph}_2\text{C}=\text{N}_2^-$  can be observed on the cyclic voltammetric time scale in the absence of added proton donors refutes this proposal and requires that both products arise from the protonation of  $\text{Ph}_2\text{C}=\text{N}_2^-$ . Evidently,  $\text{Ph}_2\text{C}=\text{N}_2^-$  functions as an ambident base in much the same manner as  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$ ; that is, the central carbon is the more basic site but, when the proton donor is sufficiently strong to protonate the  $\text{N}_\beta$  site as well, protonation at the latter site is favored kinetically. The  $\text{Ph}_2\text{C}=\text{NNH}_2/\text{Ph}_2\text{CH}_2$  product ratio reflects the relative overall rates of protonation of  $\text{Ph}_2\text{C}=\text{N}_2^-$  at  $\text{N}_\beta$  and C to give  $\text{Ph}_2\text{C}=\text{NNH}\cdot$  and  $\text{Ph}_2\text{CHN}_2\cdot$ , respectively (eq 5-6), and the subsequent reductions of these neutral radicals by unreacted  $\text{Ph}_2\text{C}=\text{N}_2^-$ . Protonation of  $\text{Ph}_2\text{C}=\text{N}_2^-$  also shuts down the chain-reaction that gives  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  as the principal product and affords a nominal  $n$  value of 2 for the controlled-potential electrolytic reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  (Table I). Our data do not permit us to determine whether loss of  $\text{N}_2$  occurs prior or subsequent to reduction of the proposed intermediate  $\text{Ph}_2\text{CHN}_2\cdot$ .



Effect of Weak Proton Donors Which Do Not Protonate  $\text{Ph}_2\text{C}=\text{N}_2^-$ . All proton donors which we have examined that have  $\text{pK}_a$ 's equal to or less than that of  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\text{pK}_a = 23$ )<sup>8</sup> protonate  $\text{Ph}_2\text{C}=\text{N}_2^-$  at the central carbon and/or  $\text{N}_\beta$  site and afford no discernible cyclic voltammetric anodic peaks for the oxidation of  $\text{Ph}_2\text{C}=\text{NNH}\cdot$ ,  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ , and  $\text{Ph}_2\text{C}=\text{N}_2^-$  on the reverse, positive-going sweep. As the  $\text{pK}_a$  of the added proton donor is raised to approximately 25 and above,



anodic peaks for the oxidation of  $\text{Ph}_2\text{C}=\text{N}_2^{\bar{}}$  and frequently one or more of the other anions can be observed on the cyclic voltammetric time scale. Thus, if the formation of  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  involves coupling of an anionic intermediate with  $\text{Ph}_2\text{C}=\text{N}_2$ , as we have proposed,<sup>1</sup> then this result suggests that it might be possible to shut down the chain reaction by the addition of an appropriate proton donor. This should then allow studies to be performed on the kinetics of  $\text{Ph}_2\text{C}=\text{N}_2^{\bar{}}$  reaction.

In order to determine which anion radicals, anions, and dianions would be protonated by a specific proton donor, numerous cyclic voltammetric experiments involving electrogenerated bases were performed.<sup>16</sup> As judged by the presence or absence of anodic peaks for the several electroactive anions at  $-51^\circ\text{C}$ , the order of decreasing acidity in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  is  $\text{CH}_3\text{OH} > \text{p-NCC}_6\text{H}_4\text{NH}_2 > \text{Ph}_2\text{CHNHN}=\text{CPh}_2 > \text{H}_2\text{O} > \text{Ph}_2\text{C}=\text{NNH}_2 > \text{t-BuOH} > \text{Ph}_2\text{CHNN}=\text{CPh}_2 > \text{Ph}_2\text{CH}_2$ .  $\text{CH}_3\text{OH}$  ( $\text{pK}_a^{\text{DMSO}} = 29.0$ )<sup>15</sup> was eliminated as a potential acid because it reacted with  $\text{Ph}_2\text{C}=\text{N}_2^{\bar{}}$ , presumably by proton transfer, on the time scale of the electrochemical experiments. In addition,  $\text{H}_2\text{O}$  ( $\text{pK}_a^{\text{DMSO}} = \text{CH}_3\text{OH} > \text{p-NCC}_6\text{H}_4\text{NH}_2 > \text{Ph}_2\text{CHNHN}=\text{CPh}_2 > \text{H}_2\text{O} > \text{Ph}_2\text{C}=\text{NNH}_2 > \text{t-BuOH} > \text{Ph}_2\text{CHNN}=\text{CPh}_2 > \text{Ph}_2\text{CH}_2$ . 31.4)<sup>15</sup> and  $\text{t-BuOH}$  ( $\text{pK}_a^{\text{DMSO}} = 32$ )<sup>15</sup> were eliminated because they did not protonate  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  and/or  $\text{Ph}_2\text{C}=\text{NNH}_2$ . Of the four potential acids which were examined, only  $\text{p-NCC}_6\text{H}_4\text{NH}_2$  ( $\text{pK}_a^{\text{DMSO}} = 25.3$ )<sup>17</sup> protonated all anionic intermediates except  $\text{Ph}_2\text{C}=\text{N}_2^{\bar{}}$ .

Single- and double-potential-step chronoamperometric<sup>13</sup> studies of the rate of  $\text{Ph}_2\text{C}=\text{N}_2^{\bar{}}$  reaction were performed in the presence of an excess of  $\text{p-NCC}_6\text{H}_4\text{NH}_2$ . At an applied potential ( $E_{\text{applied}} = -1.4\text{ V}$ ) that was sufficiently negative to reduce  $\text{Ph}_2\text{C}=\text{N}_2$  only to  $\text{Ph}_2\text{C}=\text{N}_2^{\bar{}}$ , a diffusion-controlled chronoamperometric  $it^{1/2}/c$  value corresponding to  $n = 1$  was obtained at  $-23^\circ\text{C}$  in the time ranges 10 ms to 2 s and 10 ms to 200 ms in the

presence and absence of  $p\text{-NCC}_6\text{H}_4\text{NH}_2$ , respectively. A diffusion-controlled  $\underline{n}$  value of 1 would only be expected if  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  were to undergo reaction by hydrogen-atom abstraction. If  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  were instead to abstract a proton, the resulting neutral radical should be reduced by unreacted  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  in bulk solution. This should lead to an  $\underline{n}$  value that varies from 1 for small values of  $\underline{kt}$  to 2 for large values of  $\underline{kt}$ . Similarly, if  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  were to undergo unimolecular loss of  $\text{N}_2$  to give  $\text{Ph}_2\text{C}^{\cdot-}$ ,  $\text{Ph}_2\text{C}^{\cdot-}$  should be rapidly protonated by all of the added proton donors to give  $\text{Ph}_2\text{CH}^{\cdot}$ .<sup>18</sup> Previous studies have shown that  $\text{Ph}_2\text{CH}^{\cdot}$  is reduced to  $\text{Ph}_2\text{CH}^-$  ( $E_{p,a} = -0.36 \text{ V}$ )<sup>11</sup> in a one-electron step at the potential at which  $\text{Ph}_2\text{C}=\text{N}_2$  is reduced. Consequently, rate-determining loss of  $\text{N}_2$  from  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  should also give rise to an  $\underline{n}$  value that varies from a lower limit of 1 for small values of  $\underline{kt}$  to an upper limit of 2 for relatively large values of  $\underline{kt}$ . Because no such increase in the  $\underline{n}$  value is observed for the reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  during the time period in which  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  reacts, we conclude that neither rate-determining abstraction of a proton from a component of the solvent-electrolyte system by  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  nor unimolecular loss of  $\text{N}_2$  from  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  to give  $\text{Ph}_2\text{C}^{\cdot-}$  is a major reaction pathway.

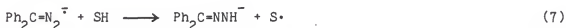
The kinetics of  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  reaction in the presence of an excess of  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  were studied by double-potential-step chronoamperometry.<sup>13</sup> In this experiment the potential is first stepped to a value ( $E_c = -1.4 \text{ V}$ ) that is sufficiently negative so as to reduce  $\text{Ph}_2\text{C}=\text{N}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  at a diffusion-controlled rate. After reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  has been effected for an arbitrary value of time  $\tau$  ( $0.1 \text{ s} \leq \tau \leq 2 \text{ s}$ ), the potential is then stepped positively for the same length of time. The applied potential for the second step ( $E_a = -0.1 \text{ V}$ ) is sufficiently positive to oxidize any unreacted  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  at the electrode surface but insufficiently positive to oxidize either  $\text{Ph}_2\text{C}=\text{NNH}^-$  or  $\text{Ph}_2\text{CHNN}^-\text{CPh}_2$ . The anodic current  $i_{a,t>\tau}$  is measured at several

different values of  $(t-\tau)/\tau$ , where  $t$  is the total elapsed time of the experiment, and then divided by cathodic current  $i_{c,t=\tau}$  that was obtained at  $t = \tau$ . The  $i_{a,t>\tau}/i_{c,t=\tau}$  current ratios are then plotted as a function of  $\tau$  and fitted to dimensionless working curves in which values of  $i_{a,t>\tau}/i_{c,t=\tau}$  are plotted as a function of  $k\tau$  for values of  $(t-\tau)/\tau = 0.2, 0.3$  and  $0.5$ . The working curve for each value of  $(t-\tau)/\tau$  is obtained by the digital simulation<sup>14</sup> of an electrode process in which a first-order chemical reaction follows a heterogeneous electron-transfer reaction. As the results in Figure 5 demonstrate, a reasonable fit is obtained for  $k = 0.4 \text{ s}^{-1}$  at  $-23^\circ \text{C}$  for several different concentrations of both  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  and  $\text{Ph}_2\text{C}=\text{N}_2$ . The fact that the same value of the rate constant is obtained for all concentrations of  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  and  $\text{Ph}_2\text{C}=\text{N}_2$  indicates that (1)  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  is not involved in the rate-determining step, and (2)  $\text{Ph}_2\text{C}=\text{N}_2^-$  reacts by a first-order or a pseudo-first-order pathway. That  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  functions as a proton donor to anionic intermediates that are formed subsequent to the reaction of  $\text{Ph}_2\text{C}=\text{N}_2^-$  is indicated by the appearance of an anodic peak for the irreversible oxidation of  $p\text{-NCC}_6\text{H}_4\text{NH}^-$  near  $0.75 \text{ V}$  on the reverse, positive-going sweep (Figure 6). The small, anodic peak near  $0.2 \text{ V}$  is due to the irreversible oxidation of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ . The peak is kinetically controlled and arises because the transfer of a proton from  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  to  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  is reversible on the time scale of the cyclic voltammetric experiment. At temperatures below approximately  $0^\circ \text{C}$ , the rate of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  regeneration is sufficiently slow that no discernible peak can be seen for the oxidation of the  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  at scan rates in excess of  $0.2 \text{ V/s}$ .

One product arising from the reaction of  $\text{Ph}_2\text{C}=\text{N}_2^-$  can be ascertained from the cyclic voltammogram that is obtained for the reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  in the absence of any added proton donor. When the adventitious water content is

low, as judged by the reversibility of the  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{\cdot-}/\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$  redox couple, and the cathodic switching limit is sufficiently positive such that  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  is not reduced to  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$ , an anodic peak is seen near 0.12 V on the reverse, positive-going sweep (Figure 7). The magnitude of this peak grows with decreasing scan rate and increasing temperature at the expense of the anodic peak for unreacted  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$ . By comparison to authentic material, this anodic peak is attributed to the oxidation of  $\text{Ph}_2\text{C}=\text{NNH}^{\cdot-}$ .

The formation of  $\text{Ph}_2\text{C}=\text{NNH}^{\cdot-}$  indicates that  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  reacts at the nitrogen atom beta to the central carbon atom by hydrogen-atom abstraction from a component of the solvent-electrolyte system to give a solvent-derived radical  $\text{S}\cdot$  (eq 7). Because the chronoamperometric  $\underline{n}$  value for the reduction of



$\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  remains constant at  $\underline{n} = 1$  rather than increasing from 1 to 2 with increasing  $\underline{t}$ ,  $\text{S}\cdot$  cannot be reduced either at the electrode surface or by unreacted  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  in bulk solution. The failure to reduce solvent-derived radicals that are believed to be formed from  $\text{DMF}-0.1 \text{ M R}_4\text{NX}$  in bulk solution has been noted previously.<sup>19</sup> Although the identification of the solvent-derived radical is unknown, it seems likely that it may be  $\text{HC}(\text{O})\text{N}(\text{CH}_3)\text{CH}_2\cdot$ . This suggestion is based on (1) the finding by Swartz and coworkers that  $(\text{CH}_3)_4\text{N}^+$ , the cation of our supporting electrolyte, does not function as a hydrogen-atom donor for aryl radicals,<sup>20</sup> (2) the report by Bethell and Parker<sup>5</sup> of a kinetic isotope effect of  $k^{\text{HC}(\text{O})\text{N}(\text{CH}_3)_2} / k^{\text{DC}(\text{O})\text{N}(\text{CD}_3)_2} = 4$  for  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  reaction, and (3) estimates of the carbon-hydrogen bond energies in DMF of  $\text{D}^\circ((\text{CH}_3)_2\text{NC}(\text{O})-\text{H}) = 95 \text{ kcal/mol}^{21}$  and  $\text{D}^\circ(\text{HC}(\text{O})\text{N}(\text{CH}_3)\text{CH}_2-\text{H}) = 85 \text{ kcal/mol}^{21}$

If  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  reacts principally by hydrogen-atom abstraction to give

Figure 5. Double-potential-step chronoamperometric data for the reduction  $\text{Ph}_2\text{C}=\text{N}_2$  in the presence of excess *p*-cyanoaniline in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-23^\circ\text{C}$ . The working electrode surface was planar glassy carbon. The solid curves were obtained for values of  $(t-\tau)/\tau = 0.2, 0.3$  and  $0.5$  by the digital simulation of a first-order EC process in which  $k = 0.4 \text{ s}^{-1}$ . Concentrations of  $\text{Ph}_2\text{C}=\text{N}_2$  and *p*-cyanoaniline, respectively, are: 2.13 mM and 21.9 mM (open symbols); 2.13 mM and 42.3 mM (half-filled symbols); and 5.90 mM and 59.5 mM (filled symbols).

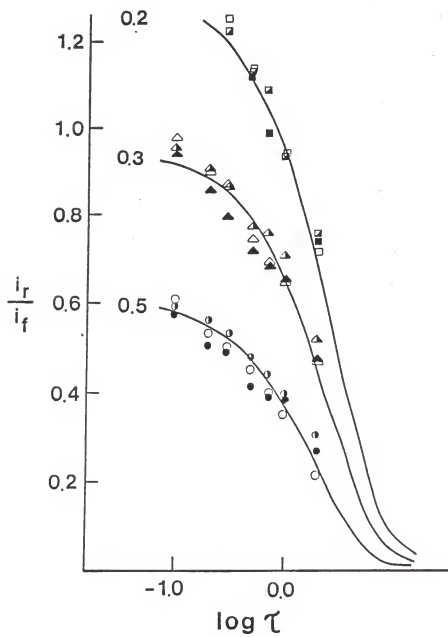


Figure 6. Cyclic voltammogram for the reduction of 8.54 mM  $\text{Ph}_2\text{C}=\text{N}_2$  at a planar glassy carbon electrode in the presence of 42.21 mM p-cyanoaniline in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at 0 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s.

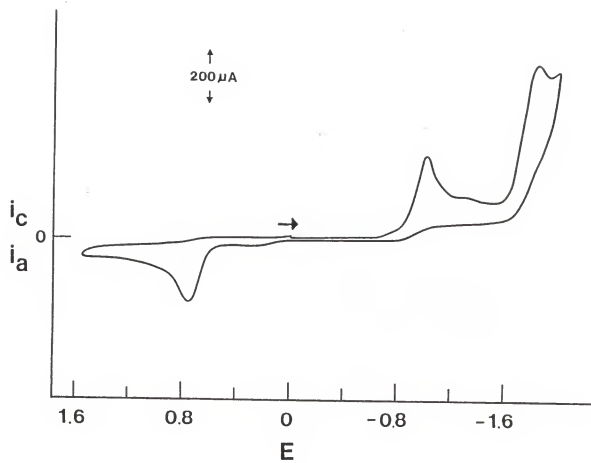
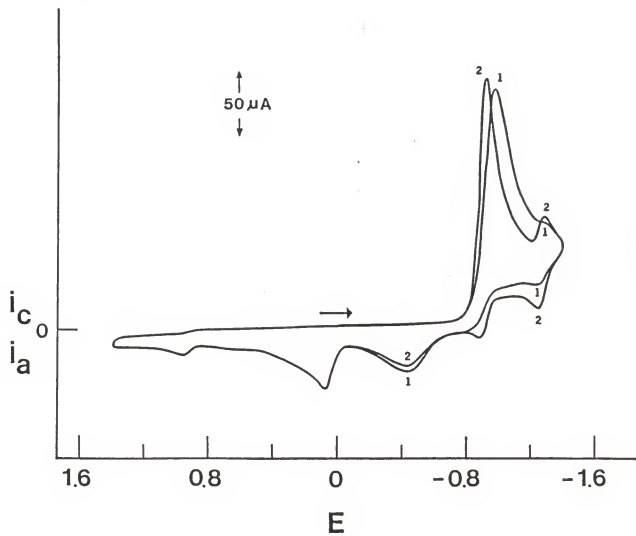
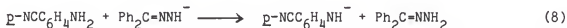




Figure 7. Cyclic voltammogram for the reduction of 5.68 mM  $\text{Ph}_2\text{C}=\text{N}_2$  at a planar glassy carbon electrode in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-51^\circ\text{C}$ . The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s. Numbers 1 and 2 represent the first and second cycles, respectively.

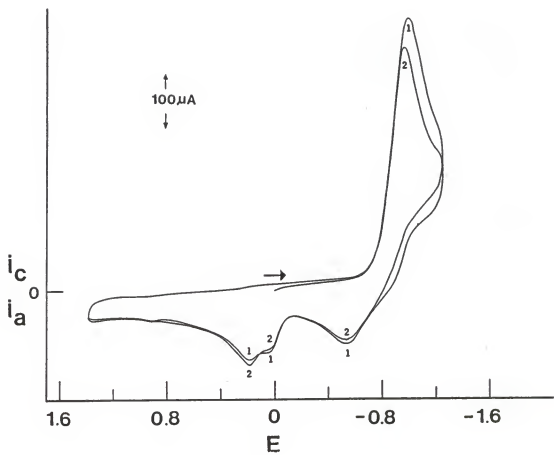


$\text{Ph}_2\text{C}=\text{NNH}^-$ , trapping of  $\text{Ph}_2\text{C}=\text{NNH}^-$  with an added an electroinactive proton donor which will protonate  $\text{Ph}_2\text{C}=\text{NNH}^-$  but not  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  is conceivable. Of the several proton donors which we examined, only  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  satisfied this criterion. Although the addition of  $p\text{-NCC}_6\text{H}_4\text{NH}_2$  is found to increase the yield of  $\text{Ph}_2\text{C}=\text{NNH}_2$  (entry 8, Table I) relative to that obtained in the presence of weak acids which protonate  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  (entry 5, Table I), substantial yields of  $\text{Ph}_2\text{CH}_2$  and  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  are also obtained. The formation of these other products suggests that the rate of  $\text{Ph}_2\text{C}=\text{NNH}^-$  reaction is slowed, but not shut down, by the addition of  $p\text{-NCC}_6\text{H}_4\text{NH}_2$ . This is understandable if the equilibrium constant for proton transfer (eq 8) is not too large.

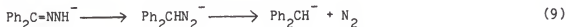


Test for the Possible Occurrence of the Wolff-Kishner Reaction. In addition to the kinetic relationship between the  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  and  $\text{Ph}_2\text{C}=\text{NNH}^-$  anodic peaks, the anodic peak for the oxidation of  $\text{Ph}_2\text{C}=\text{NNH}^-$  is also coupled kinetically to the anodic peak for the oxidation of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  ( $E_{p,a} = 0.28$  V). This is evidenced in the cyclic voltammograms (Figure 8) by the increase in the anodic peak height for the oxidation of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  and a decrease in the anodic peak height for the oxidation of  $\text{Ph}_2\text{C}=\text{NNH}^-$  from the first to the second cycle. Because the cathodic switching potential in Figure 8 ( $E_{\lambda,c} = -1.22$  V) is positive with respect to the reduction of  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^-$  ( $E_{p,c} = -1.30$  V) to  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$ ,  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  that is formed in the cyclic voltammetric reduction of  $\text{Ph}_2\text{C}=\text{N}_2$  probably does not arise from the inadvertent protonation of electrogenerated  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$  by adventitious proton donors. This result suggests  $\text{Ph}_2\text{C}=\text{NNH}^-$  that reacts in some

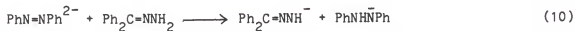
Figure 8. Cyclic voltammogram for the reduction of 5.11 mM  $\text{Ph}_2\text{C}=\text{N}_2$  at a planar glassy carbon electrode in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at 0 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 1.0 V/s. Numbers 1 and 2 represent the first and second cycles, respectively.



unidentified manner to give, first,  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  and, then,  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$ . Since the formation of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  has been suggested above to occur by coupling of  $\text{Ph}_2\text{CH}^-$  with  $\text{Ph}_2\text{C}=\text{N}_2$ , the possibility that  $\text{Ph}_2\text{C}=\text{NNH}^-$  undergoes the Wolff-Kishner reaction (eq 9) to give  $\text{Ph}_2\text{CH}^-$  and  $\text{N}_2$  was examined under these reaction conditions.

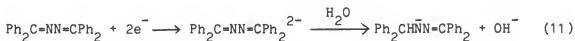


$\text{Ph}_2\text{C}=\text{NNH}^-$  was prepared in situ from  $\text{Ph}_2\text{C}=\text{NNH}_2$  by the electrogeneration of an approximately equimolar amount of the strong base  $\text{PhN}=\text{NPh}^{2-}$  (eq 10).



Experimentally,  $\text{PhN}=\text{NPh}$  was first reduced to  $\text{PhN}=\text{NPh}^-$  at an applied potential that was slightly negative with respect to its first cathodic peak. (Although  $\text{PhN}=\text{NPh}^-$  is also used frequently as an electrogenerated base,  $\text{PhN}=\text{NPh}^-$  is insufficiently basic to effect deprotonation of  $\text{Ph}_2\text{C}=\text{NNH}_2$ .<sup>16</sup>) The applied potential was then made sufficiently negative to reduce  $\text{PhN}=\text{NPh}^-$  to  $\text{PhN}=\text{NPh}^{2-}$ , but insufficiently negative to cause the concomitant reduction of  $\text{Ph}_2\text{C}=\text{NNH}_2$ . After the controlled-potential electrolytic preparation of  $\text{Ph}_2\text{C}=\text{NNH}^-$  was complete (ca. 15 minutes) and the formation of  $\text{Ph}_2\text{C}=\text{NNH}^-$  had been verified by cyclic voltammetry, the solution was acidified with an excess of  $(\text{EtO}_2\text{C})_2\text{CH}_2$  and analyzed by HPLC. Because  $\text{Ph}_2\text{C}=\text{NNH}_2$  was recovered in 96% yield and  $\text{Ph}_2\text{CH}_2$  was not detected as a reaction product, we conclude that the conversion of  $\text{Ph}_2\text{C}=\text{NNH}^-$  into  $\text{Ph}_2\text{CH}^-$  does not occur to any significant extent under our reaction conditions and the time scale of our experiments.

Initiation of the Chain Reaction with  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ .  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  was prepared by the controlled-potential electrolysis ( $E_{\text{applied}} = -1.4 \text{ V}$ ) of  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  in the presence of an excess of  $\text{H}_2\text{O}$  (eq 11). After two

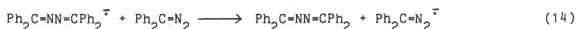
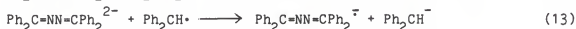
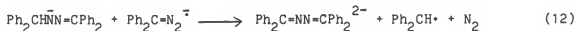


electrons per molecule of  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  had been added, the electrolysis was terminated and equimolar amount of  $\text{Ph}_2\text{C}=\text{N}_2$  was added to the solution of electrogenerated  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ . Reaction occurred rapidly, as evidenced by the immediate evolution of a gas which is presumed to have been  $\text{N}_2$ . Cyclic voltammetric analysis of the reaction mixture showed that  $\text{Ph}_2\text{C}=\text{N}_2$  had been transformed quantitatively into  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$ .

Reactions in the Propagation Cycle of the Chain Reaction. The sequence of intermediates that is detected by cyclic voltammetry (Figure 7) for the electron-transfer initiated chain reaction which transforms  $\text{Ph}_2\text{C}=\text{N}_2$  into  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  in the absence of added proton donors appears to be  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-} \longrightarrow \text{Ph}_2\text{C}=\text{NNH}^- \longrightarrow \text{Ph}_2\text{CHNN}=\text{CPh}_2$ . A plausible reaction sequence must also be consistent with the following observations: (1) both  $\text{Ph}_2\text{C}=\text{NNH}^-$  and  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  initiate the chain reaction and convert  $\text{Ph}_2\text{C}=\text{N}_2$  into  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  quantitatively;<sup>1</sup> (2) only small amounts of products containing N-H and C-H bonds (specifically,  $\text{Ph}_2\text{C}=\text{NNH}_2$ ,  $\text{Ph}_2\text{CH}_2$  and  $\text{Ph}_2\text{CHNHN}=\text{CPh}_2$ ; see entry 9, Table I) are formed; (3) the kinetics are consistent with  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  reacting in the absence of added proton donors by rate-determining hydrogen-atom abstraction from DMF to give  $\text{Ph}_2\text{C}=\text{NNH}^-$ ; (4)  $\text{Ph}_2\text{C}=\text{NNH}^-$  is not transformed into  $\text{Ph}_2\text{CH}^-$  and  $\text{N}_2$  under these reaction conditions; and (5) the  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{\cdot-}/\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^{2-}$

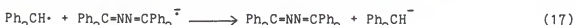
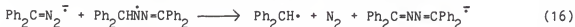
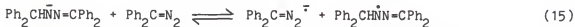
redox couple is obtained even when the anodic switching potential is 0.0 V and neither  $\text{Ph}_2\text{C}=\text{NNH}^-$  nor  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  is oxidized.

A propagation cycle (eq 12-14 plus eq 3) that includes a step in which a proton is transferred from  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$ <sup>1</sup> has been suggested previously. However, in view of the observations reported herein that



$\text{Ph}_2\text{CHNN}=\text{CPh}_2$  initiates a chain reaction with  $\text{Ph}_2\text{C}=\text{N}_2$  and that  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  is a poor proton donor towards  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  (see order of acidities above), protonation of  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$  by  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  now appears to be both unnecessary and unlikely.

At least two pathways can be proposed by which  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  initiates the chain reaction and hydrogen is transferred from a reduction product of benzophenone azine to either  $\text{Ph}_2\text{C}=\text{N}_2$  or its reduction product,  $\text{Ph}_2\text{C}=\text{N}_2^{\cdot-}$ . The pathway which we favor involves a series of electron- and proton-transfer reactions (eq 15-17). Although the first electron-transfer reaction



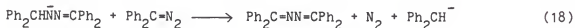
is endergonic ( $E_{p,a}(\text{Ph}_2\text{CHNN}=\text{CPh}_2) = 0.13$  V;  $E_{p,c}(\text{Ph}_2\text{C}=\text{N}_2) = -0.9$  V at 23 °C), the reaction is driven to completion because both products are consumed in a follow-up proton-transfer reaction (eq 16). The  $pK_a$  of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  is



unknown; however, because  $(\text{EtO}_2\text{C})_2\text{CH}_2$  ( $\text{pK}_a^{\text{DMSO}} = 16.4$ )<sup>7</sup> does not protonate  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2^-$ ,<sup>10</sup> its upper limit must be less than 16. Since both  $(\text{EtO}_2\text{C})_2\text{CH}_2$  and  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\text{pK}_a \sim 23$ )<sup>8</sup> protonate  $\text{Ph}_2\text{C}=\text{N}_2^-$  rapidly (vide supra), it is reasonable to conclude that proton transfer from  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  to  $\text{Ph}_2\text{C}=\text{N}_2^-$  should occur rapidly. The second electron-transfer reaction (eq 17) is exergonic ( $E_{p,c}(\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2) = -0.91 \text{ V}$ ; <sup>10</sup> $E_{p,a}(\text{Ph}_2\text{CH}^-) = -0.36 \text{ V}$ )<sup>11</sup> and affords  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  as a final product and  $\text{Ph}_2\text{CH}^-$  as a short-lived, unobserved intermediate.

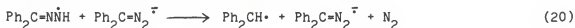
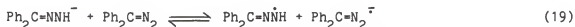
The final step in all propagation cycles which we<sup>1</sup> or others<sup>22</sup> have proposed involves the coupling of  $\text{Ph}_2\text{CH}^-$  with unreacted  $\text{Ph}_2\text{C}=\text{N}_2$  to give  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  (eq 3). This proposal is consistent with: (1) our kinetics studies involving the reaction of a  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  decomposition product, which is believed to be  $\text{Ph}_2\text{CH}^-$ , with  $\text{Ph}_2\text{C}=\text{N}_2$  (eq 2-3); (2) kinetics studies which show that  $\text{Ph}_2\text{C}=\text{N}_2^-$  reacts by a first-order or pseudo-first-order reaction pathway; and (3) the fact that  $\text{Ph}_2\text{C}=\text{NNH}^-$  initiates the chain reaction in the transformation of  $\text{Ph}_2\text{C}=\text{N}_2$  into  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$ , but is not the chain-carrying species.<sup>1</sup> Although we have attempted to obtain direct evidence of the reaction of  $\text{Ph}_2\text{C}=\text{N}_2$  with  $\text{Ph}_2\text{CH}^-$  that has been prepared from another precursor, our efforts have been unsuccessful. The problems which we have encountered include: (1) the more-difficult reduction of the  $\text{Ph}_2\text{CH}^-$  precursor (e.g.,  $\text{Ph}_2\text{CHCl}$ ) than  $\text{Ph}_2\text{C}=\text{N}_2$ ; and (2) the more-rapid reaction of  $\text{Ph}_2\text{CH}^-$  with its precursor (e.g.,  $\text{Ph}_2\text{CHBr}$ ) than with  $\text{Ph}_2\text{C}=\text{N}_2$ .

An alternative scheme that cannot be distinguished experimentally from the first scheme (eq 15-17) by our techniques involves hydride transfer (eq 18). This reaction was first proposed by Bethell and McDowall<sup>22</sup> to be the



initial step in the propagation cycle of the chain reaction that converts  $\text{PhC(O)C(N}_2\text{)Ph}$  into the corresponding azine. It is written here as it would occur in the  $\text{Ph}_2\text{C=N}_2$  case. The propagation cycle is concluded by the rapid coupling of  $\text{Ph}_2\text{CH}^-$  with  $\text{Ph}_2\text{C=N}_2$  to regenerate  $\text{Ph}_2\text{CHNN=CPh}_2$  (eq 3).

Conversion of  $\text{Ph}_2\text{C=NNH}^-$  into  $\text{Ph}_2\text{CHNN=CPh}_2$ . The results above have demonstrated that  $\text{Ph}_2\text{C=NNH}^-$  is not converted into  $\text{Ph}_2\text{CH}^-$  and  $\text{N}_2$  in the absence of  $\text{Ph}_2\text{C=N}_2$  and that the disappearance of  $\text{Ph}_2\text{C=NNH}^-$  in the presence of  $\text{Ph}_2\text{C=N}_2$  is linked kinetically to the appearance of  $\text{Ph}_2\text{CHNN=CPh}_2$ . If the propagation step of the chain reaction involves electron transfer from  $\text{Ph}_2\text{CHNN=CPh}_2$  to  $\text{Ph}_2\text{C=N}_2$  (eq 15), then it is reasonable to attribute the formation of  $\text{Ph}_2\text{CHNN=CPh}_2$  from  $\text{Ph}_2\text{C=NNH}^-$  and  $\text{Ph}_2\text{C=N}_2$  to the succession of electron- and proton-transfer reactions described by eq 19, 20, and 17. The final step



in the formation of  $\text{Ph}_2\text{CHNN=CPh}_2$  would then involve coupling of  $\text{Ph}_2\text{CH}^-$  with  $\text{Ph}_2\text{C=N}_2$  (eq 3).

Although this reaction sequence is analogous to that proposed for the reaction of  $\text{Ph}_2\text{CHNN=CPh}_2$  with  $\text{Ph}_2\text{C=N}_2$ , the initial electron transfer reaction between  $\text{Ph}_2\text{C=NNH}^-$  and  $\text{Ph}_2\text{C=N}_2$  is more favorable because of the more ready oxidation of  $\text{Ph}_2\text{C=NNH}^-$  ( $E_{p,a} = 0.1$  V) than  $\text{Ph}_2\text{CHNN=CPh}_2$  ( $E_{p,a} = 0.2$  V at  $T = -51^\circ\text{C}$ ). However, because reaction 19 is still thermodynamically unfavorable, the subsequent proton transfer reaction (eq 20) must proceed rapidly and irreversibly. This is plausible if the carbon site is more basic than the nitrogen site in  $\text{Ph}_2\text{C=N}_2^-$  and/or the loss of  $\text{N}_2$  from  $\text{Ph}_2\text{CHN}_2^\cdot$  is also rapid

and irreversible. Each of these requirements is consistent with the results that have been obtained when  $\text{Ph}_2\text{C}=\text{N}_2$  is reduced in the presence of proton donors that protonate  $\text{Ph}_2\text{C}=\text{N}_2^-$ .

An alternative reaction pathway can also be written which involves hydride transfer from  $\text{Ph}_2\text{C}=\text{NNH}^-$  to  $\text{Ph}_2\text{C}=\text{N}_2$  (eq 21). Reaction by this pathway



would be expected to occur if reaction of  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  with  $\text{Ph}_2\text{C}=\text{N}_2$  were to occur by hydride transfer (eq 18).

Comparison of Reaction Pathways of Diazoalkane Anion Radicals. One of the general objectives of our work with diazoalkane anion radicals and dianions is to accumulate sufficient data such that their reactions can be predicted under a variety of solution conditions. With the possible exception of diazofluorene,<sup>23,24</sup> each of the several diazoalkanes has afforded an anion radical that is sufficiently stable so as to give an anodic peak for its reoxidation.<sup>5,19,22,25</sup> When proton donors are present which have  $\text{pK}_a$ 's that are approximately 6 or more units less than the  $\text{pK}_a$  of the corresponding hydrocarbon, the diazoalkane anion radical has behaved as an ambident base and has been rapidly protonated at the carbon and nitrogen sites to give the corresponding hydrocarbon and hydrazone, respectively.<sup>19</sup> In each case that we have examined, the fraction of the hydrazone product increases with decreasing  $\text{pK}_a$  of the proton donor. Carbene anion radical formation has been observed in several cases where the  $\text{pK}_a$  of the corresponding hydrocarbon has been 20 or less (e.g.,  $(\text{EtO}_2\text{C})_2\text{C}=\text{N}_2$ ,<sup>19</sup>  $\text{PhC}(\text{O})\text{C}(\text{N}_2)\text{Ph}$ ,<sup>22</sup> and diazodimedone<sup>25</sup>). However, this criterion may not be sufficient if the diazoalkane affords the azine as the principal product and the azine is readily reduced to a stable dianion.

For example, diazofluorene anion radical ( $\text{pK}_a^{\text{DMSO}}$  (fluorene) = 22.6)<sup>26</sup> undergoes either dimerization or coupling with unreacted fluorene to give a tetrazine dianion that is slowly converted to fluorenone azine and  $\text{N}_2$  upon oxidation.<sup>23,24</sup> In the three systems in which the intermediacy of the carbene anion radical has been claimed, the carbene anion radical has been an unobserved, short-lived intermediate that reacts with the solvent by hydrogen-atom abstraction or with added Brønsted acids by proton abstraction. The ability to control the reactions of the carbene anion radicals for synthetic purposes in the condensed phase has yet to be demonstrated.

Finally, in the one case ( $\text{Ph}_2\text{C}=\text{N}_2$ ) where the  $\text{pK}_a$  of the corresponding hydrocarbon has been greater than 30, the diazoalkane anion radical has undergone rate-determining hydrogen-atom abstraction in the absence of added proton donors. Since certain diazoalkane anion radicals can also be reduced to their corresponding dianions, a total of six pathways have been reported for the reaction of diazoalkane anion radicals in the condensed phase. Although prediction of the reaction pathway that is most likely to be observed will require knowledge of the electronic configurations of the intermediates and bond energies, information of this kind is largely unavailable. In the absence of such information, it is tempting to use easily measured  $\text{pK}_a$ 's of the corresponding hydrocarbons as a guide to reactivity. Whether or not this quantity has any predictive utility will require additional study.

### Experimental

Instrumentation. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential losses between the reference and working electrodes.<sup>27</sup> Control of the potentiostat and acquisition and

processing of the rapid-scan cyclic voltammetric and chronoamperometric data were performed with a laboratory digital computer (ADAC Model 2000, LSI 11/2). The three-electrode potentiostat which was used for the controlled-potential electrolysis has been described previously.<sup>28</sup>

Cell, Electrodes, and General Procedures. All electrochemical experiments were performed on an all-glass vacuum line. Approximately 30 mL of the solvent was transferred by trap-to-trap distillation into an uncompartimentalized (for cyclic voltammetry and chronoamperometry) or a compartimentalized (for coulometry) electrochemical cell that had been loaded previously with the supporting electrolyte. A positive pressure of helium was maintained when the reference electrode and compounds were transferred into the cell. Traces of oxygen, if present, were removed by several freeze-pump-thaw cycles. Helium was used to bring the cell up to atmospheric pressure.

Planar platinum and vitreous carbon working electrodes were used for most cyclic voltammetric and chronoamperometric experiments. The auxiliary electrode was a piece of platinum foil (ca.  $1 \text{ cm}^2$ ) that was parallel to and approximately one cm away from the working electrode. All potentials listed were measured with respect to a cadmium chloride/cadmium amalgam reference electrode; the solvent in this electrode was DMF and was saturated with respect to both sodium chloride and cadmium chloride (Type A-III).<sup>29</sup> The potential of this electrode is  $-0.75 \text{ V vs. SCE}$ . Dual reference electrodes were used in all cyclic voltammetric and chronoamperometric experiments.<sup>30</sup> The second reference electrode was a platinum wire which is in series with a  $0.1 \mu\text{F}$  capacitor and was placed in parallel with the cadmium chloride/cadmium amalgam reference electrode. A glass frit separated the cadmium

chloride/cadmium amalgam reference electrode from the working and auxiliary electrode compartment.

Coulometry. The progress of large-scale electrolyses were monitored periodically by cyclic voltammetry. At the conclusion of an electrolysis, the mixture was protonated in a dry helium atmosphere with  $(\text{EtO}_2\text{C})_2\text{CH}_2$  and analyzed by HPLC within 48 hours. In order to determine if the acid which was used for protonation of the anionic electrolysis products might catalyze the decomposition of unreacted  $\text{Ph}_2\text{C}=\text{N}_2$ , a ten-fold excess of benzoic acid, acetic acid,  $(\text{EtO}_2\text{C})_2\text{CH}_2$ ,  $\text{CF}_3\text{CH}_2\text{OH}$  or  $(\text{CF}_3)_2\text{CHOH}$  was added to a solution of  $\text{Ph}_2\text{C}=\text{N}_2$  in DMF.<sup>31</sup> With the exceptions of benzoic acid and acetic acid, none of the proton donors caused any discernible change in the absorption spectrum of  $\text{Ph}_2\text{C}=\text{N}_2$  after reaction for 48 hours at room temperature.

Chromatography. The products of the electrolyzed solutions were separated by HPLC using a 4.60-mm diameter, 25-cm length stainless-steel column packed with Alltech C8, 10- $\mu\text{m}$  mean particle size. The eluting solvent was a mixture of methanol and water; the solvent ratio, which varied from 60/40 to 90/10 methanol/water, was optimized for each product composition. The flow rate of the eluting solvent was 1.1 mL/min. Two HPLC systems were used. The first system consisted of a Water Associates Model 6000A pump and a Schoeffel Instrument Corp. Model SF 770 UV-VIS variable wavelength detector. The second system consisted of a Beckman Model 332 Gradient Liquid Chromatograph with two Model 110A pumps and a Model 153 UV detector. The wavelength used in the analysis of all products was 254 nm.

Chemicals. One-liter aliquots of DMF (Burdick and Jackson) were purified by passage through a column of alumina (500g, 80-200 mesh, Brockman activity 1, activated at 600 °C overnight) and was collected over a mixture of Davison 4-A molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Either  $(\text{CH}_3)_4\text{NBF}_4$  or  $(\text{CH}_3)_4\text{NPF}_6$  was used as the supporting electrolyte; these materials were stored in a vacuum oven over phosphorus pentoxide.  $\text{Ph}_2\text{C}=\text{N}_2$ <sup>32</sup> and  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$ <sup>33</sup> were synthesized according to reported procedures. Several recrystallizations were performed until sharp melting points were obtained. All other compounds were commercially available. The purities of all compounds were checked by melting point, HPLC, and/or cyclic voltammetry.

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II. ELECTROGENERATED BASES: THE ROLE OF WEAK ELECTROINACTIVE  
PROTON DONORS AND THE EFFECT OF ELECTROCATALYSIS ON  
THE REDOX BEHAVIOR OF AZOBENZENE

Introduction

The electrochemical reduction of azobenzene ( $\text{PhN=NPh}$ ) in aprotic media is reported to occur in two successive one-electron steps.<sup>1-6</sup> Although  $\text{PhN=NPh}^-$  is quite stable in the absence of added proton donors and can be reoxidized quantitatively on the cyclic voltammetric time-scale, the lifetime of the corresponding dianion is sufficiently short in most solvent-electrolyte systems so as to preclude a cyclic voltammetric anodic peak for its reoxidation. Rapid reaction of the dianion involves its protonation by acidic impurities such as water and is generally believed to afford hydrazobenzene ( $\text{PhNHNHPh}$ ) or its conjugate base as the principal product.<sup>4</sup>

Because of the basicity of  $\text{PhNN}^-\text{Ph}$  and the ease with which it can be prepared in known amount, electrogenerated  $\text{PhNN}^-\text{Ph}$  has been used widely as a strong base in electroorganic synthesis<sup>7-10</sup> and diagnostic electrochemical studies.<sup>11-12</sup> Our current interest in  $\text{PhNN}^-\text{Ph}$  as an electrogenerated base was created by our need to prepare certain carbanions and nitranions in *N,N*-dimethylformamide (DMF) in order to measure their oxidation potentials and to determine their reactivities with selected substrates. Although evidence indicated that electrogenerated  $\text{PhNN}^-\text{Ph}$  reacted rapidly with the added proton donor, a cyclic voltammetric anodic wave for the oxidation of the conjugate base of the proton donor frequently could not be found on the reverse, positive-going sweep. The studies that are described here examine the chemical and electrochemical reactions that cause this behavior.

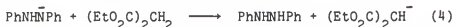
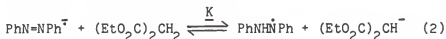
## Results and Discussion

The basicity of the electrogenerated bases in the azobenzene series increases in the order  $\text{PhN=NPh}^- < \text{PhNH}\bar{\text{N}}\text{Ph} < \text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$ . In order to illustrate the effects of varying acid strength on the redox behavior of  $\text{PhN=NPh}$ , proton donors that are electroinactive in the potential range of interest have been selected which cause protonation of (a) all electrogenerated anions and anion radicals, (b)  $\text{PhNH}\bar{\text{N}}\text{Ph}$  and  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$ , but not  $\text{PhN=NPh}^-$ , (c)  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$  only, with proton transfer irreversible on the cyclic voltammetric time-scale, or (d)  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$  only, but with proton transfer reversible. The order of presentation is in ascending value of the  $\text{pK}_a$  of the electroinactive proton donor.

Protonation of all electrogenerated anion radicals and anions. The cyclic voltammetric reduction of azobenzene in  $\text{DMF-0.1 M (CH}_3)_4\text{NPF}_6$  is seen in Figure 9a to occur in two successive one-electron steps to give, first, the anion radical at  $\text{E}_{p,c,1} = -0.64 \text{ V}$  and, then, the dianion at  $\text{E}_{p,c,2} = -1.39 \text{ V}$ . Both processes are chemically reversible at either platinum or glassy carbon working electrodes as long as care is taken to exclude large amounts of water, other acidic impurities, and supporting electrolytes which function of proton donors (e.g.,  $(n\text{-Bu})_4\text{N}^+$ ). When a relatively strong, electroinactive proton donor is added, such as  $(\text{EtO}_2\text{C})_2\text{CH}_2$  ( $\text{pK}_a^{\text{DMSO}} = 16.4$ )<sup>13</sup>, the expected behavior that is associated with protonation of the electrogenerated  $\text{PhN=NPh}^-$  occurs: the cathodic peak for the initial reduction of  $\text{PhN=NPh}$  shifts slightly in the anodic direction and doubles in magnitude, while the peaks that are associated with both the reduction ( $\text{E}_{p,c} = -1.39 \text{ V}$ ) and the oxidation ( $\text{E}_{p,a} = -0.58 \text{ V}$ ) of  $\text{PhN=NPh}^-$  disappear (Figure 9b). Concomitantly, two new anodic peaks appear on the reverse,

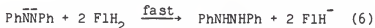
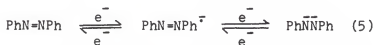
positive-going scan for the irreversible oxidation of  $(\text{EtO}_2\text{C})_2\text{CH}^-$  ( $E_{p,a} = 1.09$  V) and  $\text{PhNHNHPh}$  ( $E_{p,a} = 1.28$  V).<sup>14</sup> This behavior, which is well understood, is consistent with the reactions that are described by eq 1-4.

Scheme I



Protonation of  $\text{PhNNPh}$  and  $\text{PhNHNPh}$  but not  $\text{PhN=NPh}^-$ . Fluorene ( $pK_a^{\text{DMSO}} = 22.6$ )<sup>15</sup> does not protonate  $\text{PhN=NPh}^-$  at a significant rate, as evidenced by the presence of cathodic ( $E_{p,c,2} = -1.21$  V)<sup>16,17</sup> and anodic ( $E_{p,a,1} = -0.58$  V) peaks for the reduction and oxidation, respectively, of  $\text{PhN=NPh}^-$  (Figure 10). Protonation of both  $\text{PhNNPh}$  and  $\text{PhNHNPh}$  is indicated by the disappearance of the anodic peak for the reoxidation of  $\text{PhNNPh}$  near  $-1.2$  V and the appearances of two new anodic peaks for the irreversible oxidations of 9-fluorenyl anion<sup>18</sup> at  $E_{p,a} = 0.12$  V and of  $\text{PhNHNHPh}$  at  $E_{p,a} = 1.28$  V. A scheme that is consistent with this behavior is described by eq 5-6.

Scheme II



where  $\text{FlH}_2$  = fluorene

Irreversible protonation of  $\text{PhNNPh}$ . As demonstrated above, a necessary condition for the appearances of anodic peaks for the oxidations of  $\text{PhNHNHPh}$  and the conjugate base of the proton donor is protonation of either  $\text{PhN=NPh}^-$

Figure 9. (a) Cyclic voltammogram for the reduction of 5.5 mM PhN=NPh at a planar platinum electrode in DMF - 0.1 M  $(\text{CH}_3)_4\text{NPF}_6$  at 22 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s. (b) Same as (a) except 11 mM diethyl malonate is present.

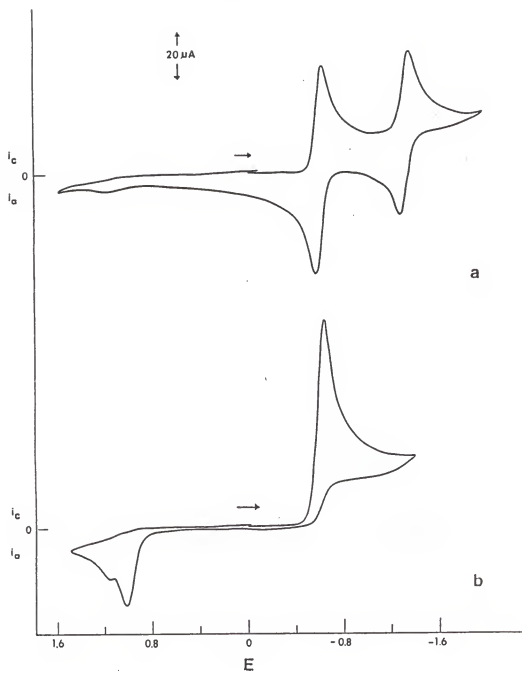
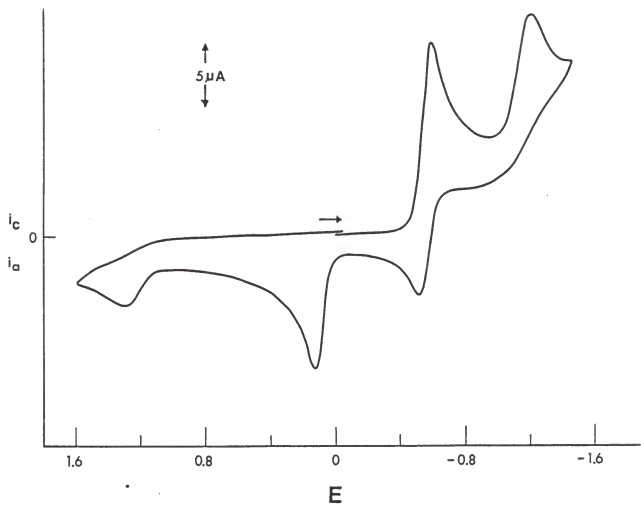


Figure 10. Cyclic voltammogram for the reduction of 5.2 mM PhN=NPh at a planar platinum electrode in the presence of 11.3 mM fluorene in DMF - 0.1 M  $(\text{CH}_3)_4\text{NPF}_6$  at 22 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s.





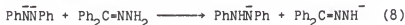
or  $\text{PhNH}\bar{\text{N}}\text{Ph}$ . However, when the  $\text{pK}_a$  of the proton donor is raised sufficiently such that  $\text{Ph}\bar{\text{N}}\text{NPh}$  is the only species protonated, relatively unusual electrochemical behavior results. As seen in Figure 11a, benzophenone hydrazone ( $\text{Ph}_2\text{C}=\text{NNH}_2$ ), a proton donor that creates this behavior, is reduced near  $-1.76$  V when no azobenzene is present. Although  $\text{Ph}_2\text{C}=\text{NNH}_2^-$  is too short-lived to give a corresponding anodic peak for its reoxidation on the reverse, positive-going sweep, an anodic peak is seen near  $0.15$  V for the irreversible oxidation of  $\text{Ph}_2\text{C}=\text{NNH}^-$ .  $\text{Ph}_2\text{C}=\text{NNH}^-$  presumably is formed when anionic products of the  $\text{Ph}_2\text{C}=\text{NNH}_2^-$  decomposition reaction abstract a proton from unreacted  $\text{Ph}_2\text{C}=\text{NNH}_2$ .<sup>19</sup>

When an equimolar amount of the more readily reduced  $\text{PhN}=\text{NPh}$  is added to the solution of  $\text{Ph}_2\text{C}=\text{NNH}_2$ , the cathodic peak for  $\text{Ph}_2\text{C}=\text{NNH}_2$  at  $-1.76$  V disappears while cathodic peaks due to the stepwise reduction of  $\text{PhN}=\text{NPh}$  to its dianion ( $\underline{E}_{p,c,1} = -0.64$  and  $\underline{E}_{p,c,2} = -1.28$  V) arise on the negative-going scan (Figure 11b). After the direction of the potential scan is reversed at  $-2.0$  V, a single anodic peak ( $\underline{E}_{p,a} = -0.58$  V) arises at the same potential as that for the reversible oxidation of  $\text{PhN}=\text{NPh}^-$  to  $\text{PhN}=\text{NPh}$ . Interestingly, while the disappearance of the  $\text{Ph}_2\text{C}=\text{NNH}_2$  cathodic peak at  $-1.76$  V clearly indicates that  $\text{Ph}_2\text{C}=\text{NNH}_2$  has been consumed by electrogenerated  $\text{Ph}\bar{\text{N}}\text{NPh}$ , neither an anodic peak for the oxidation of  $\text{Ph}_2\text{C}=\text{NNH}^-$  near  $0.15$  V nor an anodic peak for either  $\text{PhNH}\bar{\text{N}}\text{Ph}$  or  $\text{PhHNHPh}$  ( $\underline{E}_{p,a} = 1.28$  V) is evident in Figure 11b. The explanation for the absence of anodic peaks for  $\text{Ph}_2\text{C}=\text{NNH}_2$  and  $\text{Ph}_2\text{C}=\text{NNH}^-$  becomes apparent when more rapid scan rates are employed. At  $5$  V/s and  $\underline{T} = -51^\circ\text{C}$ , a second anodic peak is seen ( $\underline{E}_{p,a} = -0.34$  V) on the positive-going sweep at a potential which is slightly more positive than the peak that is due to the oxidation of  $\text{PhN}=\text{NPh}^-$  ( $\underline{E}_{p,a} = -0.54$  V at  $-51^\circ\text{C}$ ) (Figure 11c). The relative magnitude of

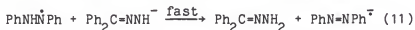
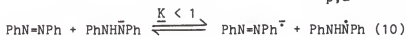
the more positive of these anodic processes increases at the expense of the more negative anodic peak for  $\text{PhN}=\text{NPh}^{\bar{}}$  with increasing scan rate. We assign the more positive anodic peak to the irreversible oxidation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$  and the cause of this relatively unusual electrochemical behavior to the electrocatalytic oxidation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$  by  $\text{PhN}=\text{NPh}$ . A reaction scheme that is consistent with these results is described by eq 7-12.

Scheme III

Negative-going scan:



Positive-going scan

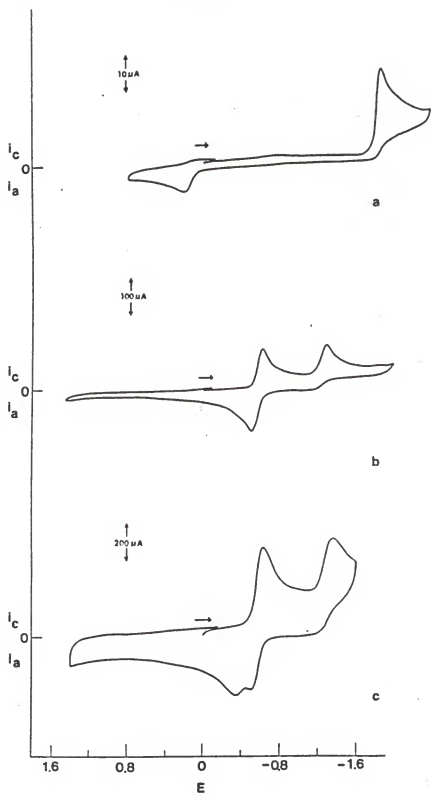


Several aspects of the cyclic voltammograms in Figure 11 require comment. First, the absence of an anodic peak for the reoxidation of  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$  near -1.2 V in the presence of added  $\text{Ph}_2\text{C}=\text{NNH}_2$  demonstrates that the transfer of a proton from  $\text{Ph}_2\text{C}=\text{NNH}_2$  to  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$  (eq 8) is irreversible on the time-scale of this experiment. Second, significant cathodic current is normally expected in the potential range from -0.7 to -1.1 V (Figures 11b and 11c) on the reverse, positive-going sweep because of the continual diffusion of  $\text{PhN}=\text{NPh}$  from bulk solution to the electrode surface. Thus, the absence of any current in this potential span means that all  $\text{PhN}=\text{NPh}$  that diffuses from bulk solution is consumed before it reaches the electrode surface by some nonelectrochemical reaction. The reactions (eq 10-11) that are responsible for the disappearance of  $\text{PhN}=\text{NPh}$  are the same reactions that

cause the anodic peak for  $\text{PhNH}\bar{\text{N}}\text{Ph}$  to disappear at slower scan rates. On the basis of the difference ( $\Delta E = 200$  mV at  $-51^\circ\text{C}$ ) in the anodic peak potentials for the reversible oxidation of  $\text{PhN}=\text{NPh}^{\bar{}}$  and the irreversible oxidation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$ , an upper limit of  $10^{-4.5}$  can be calculated from the expression  $\Delta E = (RT/nF) \ln K$  for the equilibrium constant in eq 10. We emphasize that this is an upper limit for  $K$  because the follow-up reaction (eq 11) involving the removal of a proton from  $\text{PhNH}\bar{\text{N}}\text{Ph}$  by  $\text{Ph}_2\text{C}=\text{NNH}^{\bar{}}$  will facilitate the oxidation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$ , thereby causing the anodic peak for  $\text{PhNH}\bar{\text{N}}\text{Ph}$  to shift to more negative potential.<sup>17</sup> Even though the actual value of the equilibrium constant may be considerably smaller than the upper limit given here, reaction 10 can proceed rapidly because the equilibrium concentration of  $\text{PhNH}\bar{\text{N}}\text{Ph}$  is rendered small by proton-transfer reaction 11. The occurrence of reaction 11 also explains why an anodic peak is not observed for the oxidation of  $\text{Ph}_2\text{C}=\text{NNH}^{\bar{}}$  near 0.15 V on the reverse, positive-going sweep. Whether or not an anodic peak is observed for the oxidation of unreacted  $\text{PhNH}\bar{\text{N}}\text{Ph}$  depends on the cyclic voltammetric scan rate and the overall rate of reactions 9-11. At the relatively rapid scan rate that was employed in Figure 11c, the sequence of chemical reactions that causes all  $\text{PhNH}\bar{\text{N}}\text{Ph}$  to be oxidized by electrogenerated  $\text{PhN}=\text{NPh}$  was "outrun" by the cyclic voltammetric experiment.

The occurrences of reactions 10-11 have practical importance in the synthetic preparation of the conjugate bases of weak proton donors via electrogenerated  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$ . In the presence of the stronger proton donors that were used to effect the reactions described in Schemes I and II, a pathway involving oxidation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$  by unreacted  $\text{PhN}=\text{NPh}$  would be precluded by

Figure 11. (a) Cyclic voltammogram for the reduction of 4 mM  $\text{Ph}_2\text{C}=\text{NNH}_2$  at a spherical platinum electrode in DMF - 0.1 M  $(\text{CH}_3)_4\text{NPF}_6$  at  $-51^\circ\text{C}$ . The scan rate is 1 V/s. (b) Cyclic voltammogram for the reduction of 2.4 mM  $\text{PhN}=\text{NPh}$  at a planar glassy carbon electrode in the presence of 2.5 mM  $\text{Ph}_2\text{C}=\text{NNH}_2$  in DMF - 0.1 M  $(\text{CH}_3)_4\text{NPF}_6$  at  $-51^\circ\text{C}$ . The scan rate is 0.2 V/s. (c) Same as (b) except that the scan rate is 5 V/s.



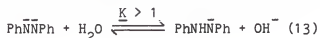
the competing pathway involving the rapid protonation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$ . In Schemes I and II the number of equivalents of conjugate base of the proton donor that are generated during the electroreduction of  $\text{PhN}=\text{NPh}$  equals the number of equivalents of  $\text{PhN}=\text{NPh}$  that are reduced ( $E < -0.6$  V for Scheme I and  $E < -1.2$  V for Scheme II). In contrast, if the proton donor cannot protonate  $\text{PhNH}\bar{\text{N}}\text{Ph}$  and, instead,  $\text{PhNH}\bar{\text{N}}\text{Ph}$  is oxidized by unreacted  $\text{PhN}=\text{NPh}$  (Scheme III), no accumulation of the conjugate base of the proton donor will be possible until all  $\text{PhN}=\text{NPh}$  has been reduced to its anion radical. Thereafter, the rate of accumulation of the conjugate base of the added proton donor will equal the rate of the electrochemical reduction of  $\text{PhN}=\text{NPh}^-$  to  $\text{Ph}\bar{\text{N}}\text{NPh}$ .

Electrocatalysis, as used in this context, involves the indirect electrochemical oxidation of a more difficultly oxidized substrate ( $\text{PhNH}\bar{\text{N}}\text{Ph}$ ) by a more readily prepared electrogenerated oxidant ( $\text{PhN}=\text{NPh}$ ). Although this redox reaction (eq 10) is thermodynamically unfavorable, the reaction proceeds rapidly because one product,  $\text{PhN}=\text{NPh}^-$ , is oxidized (eq 9) at the applied potential while the second product,  $\text{PhNH}\bar{\text{N}}\text{Ph}$ , is rapidly deprotonated by the conjugate base of the added proton donor (eq 11). The feature that distinguishes this example from most other electrocatalytic reactions<sup>20-23</sup> (e.g., the chemical reduction of the more difficultly reduced bromobenzene by electrogenerated benzonitrile anion radical<sup>23</sup>) is that the follow-up deprotonation reaction (eq 11) also generates the reduced form of the reagent that participates in the electrocatalytic reactions. Other examples in which follow-up chemical reactions generate additional reagent for the electrocatalytic cycle include the oxidation of 9-aminofluorenyl anion by electrogenerated fluorenone imine,<sup>11</sup> the oxidation of the conjugate bases of certain hydroquinones by electrogenerated quinones,<sup>24</sup> and the base-induced

decomposition of 1,2-diphenylethanol by electrogenerated benzophenone anion radical.<sup>25</sup>

Reversible protonation of PhNNPh. As in the cases of Ph<sub>2</sub>C=NNH<sub>2</sub> and fluorene, the addition of water ( $pK_a^{DMSO} = 31.4$ )<sup>26</sup> as a weak, electroinactive proton donor has no effect on either the cyclic voltammetric peak height or the peak potential location for the reversible reduction of PhN=NPh to PhN=NPh<sup>-</sup>. However, unlike the proton donors above, water causes a new reversible cyclic voltammetric peak to appear at a potential that is approximately 200 mV more positive than the original peak for the reversible reduction of PhN=NPh<sup>-</sup> to PhNNPh (Figure 12). This new reversible peak grows at the expense of the original peak for the reduction of PhN=NPh<sup>-</sup> to PhNNPh with increasing water concentration. The original peak disappears entirely when the ratio of water to azobenzene exceeds one.

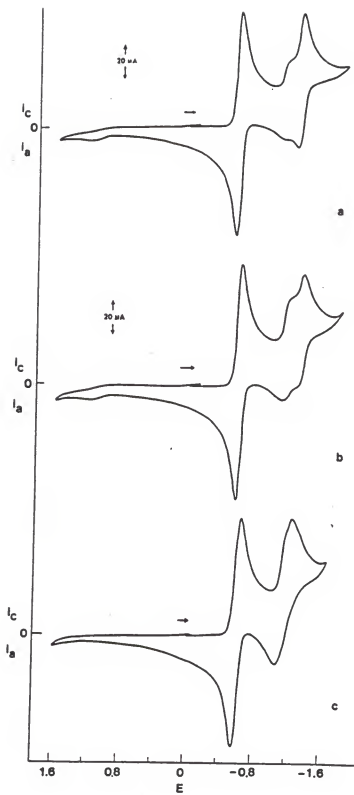
The appearance of a reversible process at a more positive potential when water is added as a proton donor is consistent with a proton transfer from water to PhNNPh (eq 13) that is reversible on the time-scale of this



experiment.<sup>27</sup> From the difference in the peak potential for the reduction of PhN=NPh<sup>-</sup> to PhNNPh in the presence ( $E_{p,c,2} = -1.19$  V) and absence ( $E_{p,c,2} = -1.39$  V) of water, we calculate a value of approximately  $10^{3.4}$  for the equilibrium constant for this reaction at room temperature. This result now allows us to estimate the  $pK_a$  of PhNHNP in DMF. From the relationship  $pK_a(\text{PhNHNP}) = pK_a(\text{H}_2\text{O}) + \log K$  and the  $pK_a$  of 34.7 that has been reported by Sawyer and coworkers<sup>28</sup> for H<sub>2</sub>O in DMF,  $pK_a(\text{PhNHNP})$  is estimated to be 38.1. Although presumably more accurate static measurements of  $pK_a^{DMF}(\text{H}_2\text{O})$



Figure 12. Cyclic voltammograms for the reduction of 9.0 mM PhN=NPh at a planar platinum electrode in DMF - 0.1 M  $(\text{CH}_3)_4\text{NPF}_6$  at 23 °C. The scan rate is 0.2 V/s. The mole ratio of water to PhN=NPh is: (a) 30 %, (b) 59%, and (c) 100 %.



may cause  $pK_a^{DMF}(H_2O)$  and, hence,  $pK_a^{DMF}(PhNH\bar{N}Ph)$  to be revised downward by as much as 3 or 4  $pK_a$  units, the results still clearly indicate that  $Ph\bar{N}NPh$  is an extremely strong base with considerable synthetic utility.

PhNHNHPh as an added proton donor. If PhNHNHPh were to protonate  $Ph\bar{N}NPh$  reversibly, as in the case of  $H_2O$ , the displacement in the reversible reduction potential for the  $PhN=NPh^{\bar{r}}/Ph\bar{N}NPh$  redox couple upon addition of PhNHNHPh would permit calculation of  $pK_a^{DMF}(PhNHNHPh)$  relative to  $pK_a^{DMF}(PhNH\bar{N}Ph)$ . Unfortunately, the effect of PhNHNHPh is similar to that for  $Ph_2C=NNH_2$  (vide ante); that is, while the peak for the reduction of  $PhN=NPh^{\bar{r}}$  is shifted in the positive direction by the addition of PhNHNHPh, there is no corresponding peak for the reoxidation of  $Ph\bar{N}NPh$ . Although this result means that proton transfer is irreversible on the time-scale of this experiment, the rate constant for proton transfer from PhNHNHPh to  $Ph\bar{N}NPh$  can be calculated from the magnitude of the shift of the cathodic peak potential.<sup>17</sup> In the present case, the shift of 180 mV at a scan rate of 0.2 V/s affords a value of approximately  $10^5 s^{-1}$  for the pseudo-first-order rate constant, from which a value of  $4 \times 10^6 M^{-1} s^{-1}$  is calculated for the second-order rate constant.

Comparison of the acidities of PhNHNHPh and PhNH $\dot{N}$ Ph. Although the methods that were employed here can not be used to measure  $pK_a^{DMF}(PhNHNHPh)$ , its value is not expected to be too different from that for  $PhNH_2$  ( $pK_a^{DMSO} = 30.7$ ).<sup>29</sup> In the case of PhNH $\dot{N}$ Ph, the fact that fluorene ( $pK_a^{DMSO} = 22.6$ )<sup>15</sup> is unable to protonate  $PhN=NPh^{\bar{r}}$  at a significant rate under the conditions of our cyclic voltammetric experiments suggests that  $pK_a^{DMF}(PhNH\bar{N}Ph) \ll pK_a^{DMF}(\text{fluorene})$ . The actual measurement of  $pK_a^{DMF}(PhNHNHPh)$  is precluded in

the condensed phase because of the ready reduction of  $\text{PhNH}\dot{\text{N}}\text{Ph}$  by  $\text{PhN}=\text{NPh}^-$  when the reduction product,  $\text{PhNH}\dot{\text{N}}\text{Ph}$ , is subsequently protonated.

Even though the  $\text{pK}_a$ 's of  $\text{PhNH}\dot{\text{N}}\text{HPh}$  and  $\text{PhNH}\dot{\text{N}}\text{Ph}$  are not attainable from our results, our data require  $\text{PhNH}\dot{\text{N}}\text{Ph}$  to be a significantly stronger proton donor than  $\text{PhNH}\dot{\text{N}}\text{HPh}$ . The lower basicity of  $\text{PhN}=\text{NPh}^-$  than  $\text{PhNH}\dot{\text{N}}\text{Ph}$  is consistent with the greater delocalization of charge in the anion radical. The fact that  $\text{PhN}=\text{NPh}^-$  and many other relatively stable anion radicals serve effectively as electrogenerated bases is due either to the rapid reduction of the conjugate acid by unreacted anion radical, which renders proton transfer to the anion radical irreversible, or to the disproportionation of the anion radical to give the more strongly basic dianion.

### Experimental

Instrumentation, Cell, Electrodes and General Procedures are the same as previously described in the experimental section of chapter I.

Chemicals. On liter aliquots of DMF (Burdick and Jackson) were purified by passage through a column of alumina (500 g, 80-200 mesh, Brockman activity 1, activated at 600 °C overnight) and was collected over a mixture of Davison 4-A molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Benzophenone hydrazone, synthesized according to a reported procedure, had m. p. 97-98 °C (lit. m. p. 97-98 °C).<sup>30</sup> All other compounds were commercially available. Purities and identities of all compounds were verified electrochemically, chromatographically (GC and/or HPLC), and spectroscopically.

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ELECTROCHEMICAL REDUCTIONS OF DIPHENYLDIAZOMETHANE  
AND AZOBENZENE: THE EFFECT OF ELECTROINACTIVE  
PROTON DONORS

by

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ABSTRACT

$\text{Ph}_2\text{C}=\text{N}_2$  undergoes successive one-electron reductions in DMF-0.1 M  $(\text{CH}_3)_4\text{NBF}_4$  at  $-51^\circ\text{C}$  to give a relatively stable anion radical and an unstable dianion. In the absence of added proton donors  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  undergoes rapid reaction to give an unobserved intermediate, believed to be  $\text{Ph}_2\text{CH}^-$ , that reacts with  $\text{Ph}_2\text{C}=\text{N}_2$  to give  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  ( $k = 5 \times 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$  at  $-37^\circ\text{C}$ ).  $\text{Ph}_2\text{C}=\text{N}_2^-$  reacts under these conditions by abstraction of a hydrogen atom from DMF ( $k = 0.4 \text{ s}^{-1}$  at  $-23^\circ\text{C}$ ) to give  $\text{Ph}_2\text{C}=\text{NNH}^-$  as a relatively long-lived intermediate. In the presence of  $\text{Ph}_2\text{C}=\text{N}_2$ ,  $\text{Ph}_2\text{C}=\text{NNH}^-$  is transformed first into  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  and then into the final product,  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$ . The transformation of  $\text{Ph}_2\text{C}=\text{N}_2$  into  $\text{Ph}_2\text{C}=\text{NN}=\text{CPh}_2$  occurs by a chain process and is initiated by both  $\text{Ph}_2\text{C}=\text{NNH}^-$  and  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ .  $\text{Ph}_2\text{C}=\text{NNH}^-$  and  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$  are proposed to react with  $\text{Ph}_2\text{C}=\text{N}_2$  by a sequence of electron and proton transfers that, in effect, transfers hydride ion from the anion to the central carbon of  $\text{Ph}_2\text{C}=\text{N}_2$  to give  $\text{Ph}_2\text{CH}^-$  and  $\text{N}_2$ . The final step in the propagation cycle involves coupling of  $\text{Ph}_2\text{CH}^-$  and  $\text{Ph}_2\text{C}=\text{N}_2$  to regenerate  $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ .  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  and  $\text{Ph}_2\text{C}=\text{N}_2^-$  behave as ambident bases in the presence of Brønsted acids which can effect their protonation and afford, depending upon whether the central carbon or the terminal nitrogen is protonated,  $\text{Ph}_2\text{CH}_2$  or  $\text{Ph}_2\text{C}=\text{NNH}_2$ , respectively. The fraction of  $\text{Ph}_2\text{C}=\text{NNH}_2$

formed from both  $\text{Ph}_2\text{C}=\text{N}_2^-$  and  $\text{Ph}_2\text{C}=\text{N}_2^{2-}$  increases with decreasing  $\text{pK}_a$  of the proton donor.

The stepwise electrochemical reduction of  $\text{PhN}=\text{NPh}$  in  $\text{DMF}-0.1 \text{ M } (\text{CH}_3)_4\text{NPF}_6$  can give, depending upon proton availability, three anionic reduction products. The basicities of these electrogenerated bases increase in the order  $\text{PhN}=\text{NPh}^- < \text{PhNH}\bar{\text{N}}\text{Ph} < \text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$ . Water ( $\text{pK}_a^{\text{DMSO}} = 31.6$ ), which is capable only of protonating  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$ , causes the reversible  $\text{PhN}=\text{NPh}^-/\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$  redox couple to shift to more positive potential. From the magnitude of the potential shift and the reported value of  $\text{pK}_a^{\text{DMF}}(\text{H}_2\text{O}) = 34.7$ ,  $\text{pK}_a^{\text{DMF}}(\text{PhNH}\bar{\text{N}}\text{Ph})$  is estimated to be 38.1.  $\text{Ph}_2\text{C}=\text{NNH}_2$  and  $\text{PhNHNHPh}$  both protonate  $\text{Ph}\bar{\text{N}}\bar{\text{N}}\text{Ph}$  irreversibly. The  $\text{PhNH}\bar{\text{N}}\text{Ph}$  that is produced in this reaction is subsequently consumed in an electrocatalytic cycle which involves  $\text{PhN}=\text{NPh}$  as the oxidant, the less-easily oxidized  $\text{PhNH}\bar{\text{N}}\text{Ph}$  as the reductant, and proton transfer from  $\text{PhNH}\bar{\text{N}}\text{Ph}$  to the conjugate base of the added proton donor as the rapid, irreversible follow-up reaction. The anodic peak for the irreversible oxidation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$  is discernible only at scan rates in excess of about 1 V/s at  $-51^\circ \text{C}$ . Protonation of  $\text{PhNH}\bar{\text{N}}\text{Ph}$  by both diethyl malonate ( $\text{pK}_a^{\text{DMSO}} = 16.4$ ) and fluorene ( $\text{pK}_a^{\text{DMSO}} = 22.6$ ) and of  $\text{PhN}=\text{NPh}^-$  by diethyl malonate is irreversible and affords  $\text{PhNHNHPh}$  and the conjugate base of the added proton donor as the principal electroactive products.