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Electrochemical Studies of Diazoalkanes: The Formation and Decomposition of $Ph_2C{=}N_2^{\bullet-}$ and $Ph_2C{=}N_2^{2-}$

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$Ph_2C{=}N_2$ undergoes successive one-electron reductions in DMF–0.1 M $(CH_3)_4NBF_4$ at subambient temperatures to give a relatively stable anion radical and an unstable dianion. In the absence of added proton donors, $Ph_2C{=}N_2^{2-}$ undergoes rapid reaction to give an unobserved intermediate, believed to be Ph_2CH^-, that reacts with $Ph_2C{=}N_2$ to give $Ph_2CHN^-N{=}CPh_2^{\bullet}$ ($k = 5 \times 10^4$ M·s^{-1} at −37 °C). $Ph_2C{=}N_2^{\bullet-}$ reacts under these conditions by abstraction of a hydrogen atom from a component of the solvent–electrolyte system ($k = 0.4$ s^{-1} at −23 °C) to give $Ph_2C{=}NNH^-$ as a longer lived intermediate. This species subsequently reacts with $Ph_2C{=}N_2$, giving first $Ph_2CHN^-N{=}CPh_2$ and then the final product, $Ph_2C{=}NN{=}CPh_2$. The transformation of $Ph_2C{=}N_2$ into $Ph_2C{=}NN{=}CPh_2$ occurs by a chain process and is initiated by both $Ph_2C{=}NNH^-$ and $Ph_2CHN^-N{=}CPh_2$. $Ph_2C{=}NNH^-$ and $Ph_2CHN^-N{=}CPh_2$ are proposed to react with $Ph_2C{=}N_2$ by pathways that transfer hydride ion, either directly or indirectly, from the anion to the central carbon of $Ph_2C{=}N_2$. The final steps in the propagation cycle involve the loss of N_2 from $Ph_2CHN_2^-$ and the subsequent coupling of Ph_2CH^- with $Ph_2C{=}N_2$ to regenerate $Ph_2CHN^-N{=}CPh_2$. $Ph_2C{=}N_2^{\bullet-}$ and $Ph_2C{=}N_2^{2-}$ behave as ambient 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, Ph_2CH_2 or $Ph_2C{=}NNH_2$, respectively. The fraction of $Ph_2C{=}NNH_2$ formed increases with decreasing pK_a of the proton donor.

The interpretation of results from the electrochemical reduction of diphenyldiazomethane ($Ph_2C{=}N_2$, **1**) has been both difficult and controversial.[1–6] Initially, we reported that $\mathbf{1}^{\bullet-}$ was short-lived on the cyclic voltammetric time scale and decomposed by loss of N_2 to give the corresponding carbene anion radical ($Ph_2C^{\bullet-}$) as an unobserved intermediate.[1–3] Bethell and Parker refuted this interpretation, arguing that the anodic peak which we had attributed to the oxidation of Ph_2CH^- was due instead to the oxidation of $\mathbf{1}^{\bullet-}$ and that the separation of up to 1 V between the cathodic and anodic peaks for the $\mathbf{1}/\mathbf{1}^{\bullet-}$ redox couple was due to slow heterogeneous electron transfer.[4,5] Subsequent triple-potential-step chronoamperometric results from our laboratory have confirmed Bethell and Parker's interpretation.[6]

The pathways by which the reduction products of **1** react under certain solution conditions remain uncertain. For example, whereas Bethell and Parker claim that $\mathbf{1}^{\bullet-}$ reacts by hydrogen atom abstraction when $(EtO_2C)_2CH_2$ is present,[5] we find instead that $\mathbf{1}^{\bullet-}$ reacts rapidly with $(EtO_2C)_2CH_2$ ($pK_a^{Me_2SO} = 16.4$)[7] and CF_3CH_2OH ($pK_a^{Me_2SO} = 23$)[8] to give Ph_2CH_2 as the principal product.[1] In the absence of an added proton donor, there is consensus that electroreduction of **1** initiates a chain reaction which affords $Ph_2C{=}NN{=}CPh_2$ in as much as 81% yield. Although $Ph_2CHN^-N{=}CPh_2$ has been detected as an intermediate in the cyclic voltammetric reduction of **1** under these conditions, it has not been ascertained whether $Ph_2CHN^-N{=}CPh_2$ lies in the principal product-forming channel or it is formed by the inadvertent protonation of electrogenerated $Ph_2C{=}NN{=}CPh_2^{2-}$ by an adventitious proton donor (e.g., water).

The goal of this study was to elucidate the principal reaction pathways for $\mathbf{1}^{\bullet-}$ and to identify the intermediates that 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 studies of the reaction kinetics of $\mathbf{1}^{\bullet-}$, weak electroinactive proton donors have been added which protonate some or all of the electrogenerated anionic intermediates.

Results and Discussion

The cyclic voltammogram of **1** at −51 °C in *N,N*-dimethylformamide (DMF) and 0.1 M $(CH_3)_4BF_4$ consists of a cathodic peak for the chemically reversible reduction of **1** to $\mathbf{1}^{\bullet-}$ near −1.06 V and an anodic peak for the reoxidation of $\mathbf{1}^{\bullet-}$ near −0.3 V on the reverse, positive-going sweep (Figure 1). The relatively large separation between the cathodic and anodic peaks for the $\mathbf{1}/\mathbf{1}^{\bullet-}$ redox couple has been shown previously to be due to slow heterogeneous electron transfer.[5,6] A similar phenomenon has been observed in the $(EtO_2C)_2C{=}N_2/(EtO_2C)_2C{=}N_2^{\bullet-}$ and fluorenone hydrazone/fluorenone hydrazone anion radical redox couples[6] 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 NO_2^+, NO_2, and NO_2^- are 180°, 132°, and 115°, respectively).[9]

When the cathodic switching potential is made sufficiently negative so as to include the cathodic peak for the reduction of $\mathbf{1}^{\bullet-}$ to $\mathbf{1}^{2-}$ at −1.9 V (Figure 2), no anodic peak is seen for the reoxidation of $\mathbf{1}^{2-}$ on the reverse, positive-going sweep for $v \leq 100$ V/s. Although the solution reaction involving $\mathbf{1}^{2-}$ is too fast to study by our methods, anodic peaks due to the oxidation of species that arise from the decomposition of $\mathbf{1}^{2-}$ 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 $Ph_2CHN^-N{=}CPh_2$ is based on the facts that (1) authentic $Ph_2CHN^-N{=}CPh_2$, which was prepared by the electrolytic reduction of $Ph_2C{=}NN{=}CPh_2$ to $Ph_2C{=}NN{=}CPh_2^{2-}$ in the presence of a

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Table I. Coulometric Data and Product Studies for the Controlled-Potential, Electrolytic Reduction of $Ph_2C{=}N_2$[a]

						product distribution, % yield					
run	$[Ph_2C{=}N_2]$, mM	[acid], mM[b]	$E_{applied}$, V	temp, °C	*n*	$(Ph_2C{=}N)_2$	$Ph_2C{=}NNH_2$	Ph_2CH_2	$Ph_2C{=}O$	$Ph_2CHNH{-}N{=}CPh_2$	Ph_2CN_2
1	3.67	C_6H_5COOH, 37	-1.1	23	2.0		86				13
2	3.48	GP, 32	-1.1	23	2.0		44	50			8
3[c,d]	4.54	DEM, 39	-1.1	23	2.0	0.7	8	85	1	3	2
4[c,d]	3.02	DEM, 32	-1.2	0	2.45	1.3	21	44	3	3	18
5[c,d]	3.49	TFE, 21	-1.0	23	2.0	0.5	2.5	88	0.1	0.4	5
6[d]	4.36	CH_3OH, 87	-1.1	-37	1.5	16	8	45	2	10	27
7[d]	4.25	*t*-BuOH, 21	-1.2	-51	0.55	72	1		2	18	*e*
8	4.94	*p*-$NCC_6H_4NH_2$, 99	-1.1	-51	1.5	15	16	56		*e*	6
9[c,d]	3.70	none	-1.0	23	0.3	81	0.5	8	1.0	1.8	7

[a] All electroreductions were effected at a mercury cathode in DMF–0.1 M $(CH_3)_4NBF_4$ unless otherwise noted. The product distribution was determined by HPLC. [b] GP = guanidinium perchlorate, DEM = diethyl malonate, TFE = CF_3CH_2OH. [c] Reference 1; 0.1 *M* $(n\text{-}Bu)_4NClO_4$ supporting electrolyte. [d] Platinum gauze cathode. [e] Trace.

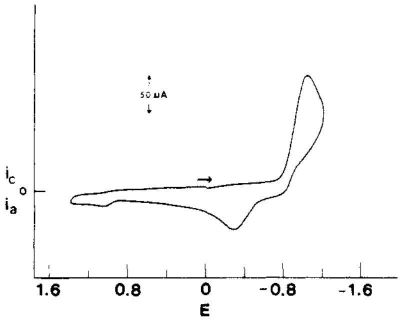

Figure 1. Cyclic voltammogram for the reduction of 3.55 mM 1 at a planar glassy carbon electrode in DMF–0.1 M $(CH_3)_4NBF_4$ at -51 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.5 V/s.

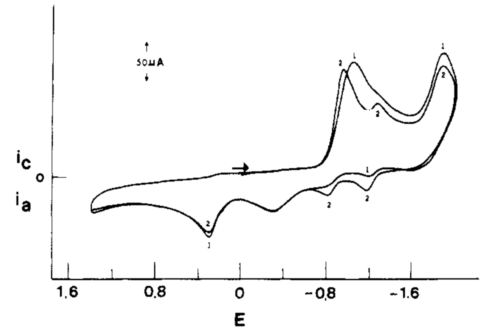

Figure 2. Cyclic voltammogram for the reduction of 3.55 mM 1 at a planar glassy carbon electrode in DMF–0.1 M $(CH_3)_4NBF_4$ at -51 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.5 V/s. Numbers 1 and 2 represent the first and second cycles, respectively.

slight excess of water,[10] displays identical cyclic voltammetric behavior and (2) Ph_2CH^- and $Ph_2C{=}NNH^-$, which are the other most plausible products of 1^{2-} decomposition, are oxidized instead at -0.36[11] and 0.12 V,[10] respectively. The assignment of the anodic peaks at -1.19 and -0.83 V to the stepwise oxidation of $Ph_2C{=}NN{=}CPh_2^{2-}$ to $Ph_2C{=}NN{=}CPh_2$ is based on the comparison of this cyclic voltammetric behavior with that of authentic material under these reaction conditions.[10]

A sequence of reactions which is consistent with the cyclic voltammetric behavior is described by eq 1–3. The reaction scheme assumes that 1^{2-} reacts rapidly at the central carbon site by abstraction of a proton from an unidentified component of the solvent–electrolyte system (e.g., $(CH_3)_4N^+$)[12] to give N_2 and Ph_2CH^- (eq 2). Coupling

$$Ph_2C{=}N_2 \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} Ph_2C{=}N_2^{\bullet -} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} Ph_2C{=}N_2^{2-} \quad (1)$$

$$Ph_2C{=}N_2^{2-} + HA \xrightarrow{\text{fast}} N_2 + A^- + Ph_2CH^- \quad (2)$$

$$Ph_2CH^- + Ph_2C{=}N_2 \xrightarrow{k} Ph_2CHN^-N{=}CPh_2 \quad (3)$$

(where HA is a component of the solvent–electrolyte system)

of Ph_2CH^- with unreacted 1 (eq 3) is proposed to be the rate-determining step in the formation of $Ph_2CHN^-N{=}CPh_2$. A single-potential-step chronoamperometric study of the reduction of 1 to 1^{2-} afforded a kinetically controlled *n* value that decreased from an upper limit of 2 for $t \le 3$ ms to 1 at times in excess of approximately 100 ms. A value of 5×10^4 $M{\cdot}s^{-1}$ was obtained for the second-order rate constant for the reaction between 1 and the 1^{2-} decomposition product (eq 3). The description of this experiment, a figure of the variation of the *n* value as a function of *kC* (Figure 3), and the behavior of 1^{2-} as an ambident base when certain weak proton donors are present (Figure 4) are available as supplementary material.

Protonation of $1^{\bullet -}$. The addition of an excess of an electroinactive proton donor such as benzoic acid ($pK_a^{Me_2SO} = 11.0$),[7] guanidinium perchlorate, $(EtO_2C)_2CH_2$ ($pK_a^{Me_2SO} = 16.4$),[7] or CF_3CH_2OH ($pK_a^{Me_2SO} = 23$)' causes the anodic peak for the oxidation of $1^{\bullet -}$ to disappear throughout the temperature ($-51\ °C \le T \le 23\ °C$) and scan rate ($0.1\ V/s \le v \le 100\ V/s$) ranges and the chronoamperometric *n* value for the initial reduction of 1 ($E_{applied} = -1.4$ V) to increase from 1 to 2. Controlled-potential electrolysis of 1 at a large mercury pool cathode at the potential of its first cathodic wave ($E_{applied} = -1.1$ V) nominally requires two electrons per molecule of 1 and affords $Ph_2C{=}NNH_2$ and Ph_2CH_2 as the principal products (entries 1–5, Table I). The $Ph_2C{=}NNH_2/Ph_2CH_2$ product ratio increases significantly with either decreasing pK_a of the acid or decreasing temperature.

We have previously suggested that $1^{\bullet -}$ decomposes relatively rapidly to give N_2 and $Ph_2C^{\bullet -}$ and that Ph_2CH_2 and $Ph_2C{=}NNH_2$ might arise from the protonation of $Ph_2C^{\bullet -}$ and unreacted $1^{\bullet -}$, respectively.[2] However, the demonstrations[4-6] that $1^{\bullet -}$ 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 $1^{\bullet -}$. As in the case of 1^{2-} (vide supra), the central carbon is the more basic site, but when the proton donor is sufficiently strong to protonate the N_β site as well, protonation at the latter site is favored ki-

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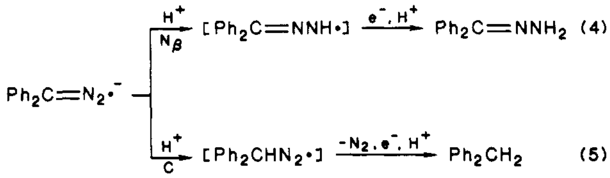
netically. The $Ph_2C{=}NNH_2/Ph_2CH_2$ product ratio reflects the relative overall rates of protonation of $1^{\bullet -}$ at N_β and C to give $Ph_2C{=}NNH^{\bullet}$ and $Ph_2CHN_2^{\bullet}$, respectively (eq 4–5), and the subsequent reductions of these neutral radicals by unreacted $1^{\bullet -}$. Protonation of $1^{\bullet -}$ also shuts down the chain reaction that gives $Ph_2C{=}NN{=}CPh_2$ as the principal product and affords a nominal n value of 2 for the controlled-potential electrolytic reduction of 1 (Table I). Our data do not permit us to determine whether loss of N_2 occurs prior or subsequent to reduction of the proposed intermediate $Ph_2CHN_2\bullet$ (eq 4 and 5).



Effect of Weak Proton Donors That Do Not Protonate $1^{\bullet -}$. All proton donors that we have examined that have pK_a's equal to or less than that of CF_3CH_2OH (p$K_a^{Me_2SO}$ = 23)[8] react rapidly with $1^{\bullet -}$ and afford no discernible cyclic voltammetric anodic peak for the oxidation of $Ph_2C{=}NNH^-$, $Ph_2CHN^-N{=}CPh_2$, or $1^{\bullet -}$ on the reverse, positive-going sweep. As the pK_a of the added proton donor is raised to approximately 25 and above, anodic peaks for the oxidation of $1^{\bullet -}$ and frequently one or more of the other anions can be observed on the cyclic voltammetric time scale. If the formation of $Ph_2C{=}NN{=}CPh_2$ involves coupling of an anionic intermediate with 1, as we have proposed,[1] then these results suggest 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 $1^{\bullet -}$ 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.[13] As judged by the presence of anodic peaks for the several electroactive anions at −51 °C, the order of decreasing acidity in DMF–0.1 M $(CH_3)_4NBF_4$ is CH_3OH > p-$NCC_6H_4NH_2$ > $Ph_2CHNHN{=}CPh_2$ > H_2O > $Ph_2C{=}NNH_2$ > t-BuOH > $Ph_2CHN^-N{=}CPh_2$ > Ph_2CH_2. CH_3OH (p$K_a^{Me_2SO}$ = 29.0)[14] was eliminated because it reacted with $1^{\bullet -}$, possibly by proton transfer, on the time scale of the electrochemical experiments. In addition, H_2O (p$K_a^{Me_2SO}$ = 31.4)[14] and t-BuOH (p$K_a^{Me_2SO}$ = 32)[14] were eliminated because they did not protonate $Ph_2CHN^-N{=}CPh_2$ and/or $Ph_2C{=}NNH^-$. Of the four potential acids that were examined, only p-$NCC_6H_4NH_2$ (p$K_a^{Me_2SO}$ = 25.3)[15] protonated all anionic intermediates except $Ph_2C{=}N_2^{\bullet -}$.

Single- and double-potential-step chronoamperometric[16] studies of the rate of $1^{\bullet -}$ reaction were performed in the presence of an excess of p-$NCC_6H_4NH_2$. At an applied potential ($E_{applied}$ = −1.4 V) that was sufficiently negative to reduce 1 only to $1^{\bullet -}$, a diffusion-controlled chronoamperometric $it^{1/2}/c$ value corresponding to $n = 1$ was obtained at −23 °C in the time ranges 10 ms to 2 s and 10–200 ms in the presence and absence of p-$NCC_6H_4NH_2$, respectively. A diffusion-controlled n value of 1 would only be expected if $1^{\bullet -}$ were to undergo reaction by hydrogen atom abstraction. If $1^{\bullet -}$ were instead to abstract a proton, then the resulting neutral radical should be reduced by unreacted $1^{\bullet -}$ in bulk solution. This should lead to an n value that varies from 1 for small values of kt to 2 for large values of kt. Similarly, if $1^{\bullet -}$ were to undergo unimolecular loss of N_2 to give $Ph_2C^{\bullet -}$, $Ph_2C^{\bullet -}$ should be rapidly protonated by the added proton donor to give $Ph_2CH^{\bullet}$.[17,18] Previous studies have shown that $Ph_2CH^{\bullet}$ is reduced to Ph_2CH^- ($E_{p,a}$ = −0.36 V)[11] in a one-electron step at the potential at which 1 is reduced. Consequently, rate-determining loss of N_2 from $1^{\bullet -}$ should also give rise to an n value that varies from a lower limit of 1 for small values of kt to an upper limit of 2 for relatively large values of kt. Because no such increase in the n value is observed for the reduction of 1 during the time period in which $1^{\bullet -}$ reacts, we conclude that neither rate-determining abstraction of a proton from a component of the solvent–electrolysis system by $1^{\bullet -}$ nor unimolecular loss of N_2 from $1^{\bullet -}$ to give $Ph_2C^{\bullet -}$ can be a major reaction pathway.

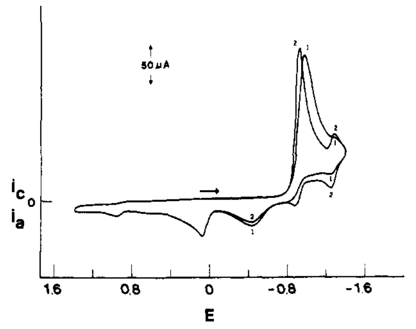


Figure 7. Cyclic voltammogram for the reduction of 5.68 mM 1 at a planar glassy carbon electrode in DMF–0.1 M $(CH_3)_4NBF_4$ at −51 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 0.2 V/s. Numbers 1 and 2 represent the first and second cycles, respectively.

The kinetics of $1^{\bullet -}$ reaction in the presence of an excess of p-$NCC_6H_4NH_2$ were studied by double-potential-step chronoamperometry.[16] A value of k = 0.4 s^{-1} at −23 °C was obtained for the reaction of $1^{\bullet -}$ for several different concentrations of both p-$NCC_6H_4NH_2$ and 1. This indicates that (1) p-$NCC_6H_4NH_2$ is not involved in the rate-determining step and (2) $1^{\bullet -}$ reacts by a first-order or a pseudo-first-order pathway. A complete description of the double-potential-step chronoamperometric experiment, the results of the kinetics studies (Figure 5), and a discussion of the cyclic voltammetric behavior of 1 in the presence of p-$NCC_6H_4NH_2$ (Figure 6) may be found in the supplementary material.

One product arising from the reaction of $1^{\bullet -}$ can be ascertained from the cyclic voltammogram that is obtained for the reduction of 1 in the absence of any added proton donor. When the adventitious water content is low, as judged by the reversibility of the $Ph_2C{=}NN{=}CPh_2^{\bullet -}/Ph_2C{=}NN{=}CPh_2^{2-}$ redox couple, and the cathodic switching limit is sufficiently positive such that $1^{\bullet -}$ is not reduced to 1^{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 $1^{\bullet -}$. By comparison to authentic material, this anodic peak is attributed to the oxidation of $Ph_2C{=}NNH^-$.

The formation of $Ph_2C{=}NNH^-$ indicates that $1^{\bullet -}$ reacts at the nitrogen atom β to the central carbon atom by

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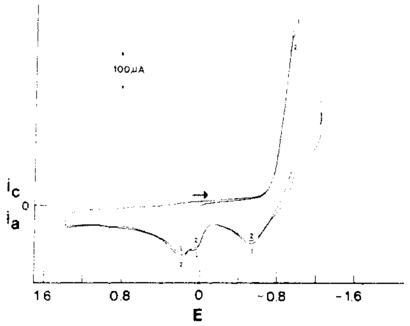

Figure 8. Cyclic voltammogram for the reduction of 5.11 mM 1 at a planar glassy carbon electrode in DMF–0.1 *M* $(CH_3)_4NBF_4$ at 0 °C. The scan was initiated in the negative-going direction from 0 V at a rate of 1.0 V/s. Numbers 1 and 2 represent the first and second cycles, respectively.

hydrogen atom abstraction from a component of the solvent–electrolyte system to give a solvent-derived radical, $S^{\bullet}$. Because the chronoamperometric *n* value for the reduction of $1^{\bullet-}$ remains constant at $n = 1$ rather than increasing from 1 to 2 with increasing *t*, $S^{\bullet}$ cannot be reduced either at the electrode surface or by unreacted $1^{\bullet-}$ in bulk solution. The failure to reduce solvent-derived radicals that are believed to be formed from DMF–0.1 M R_4NX in bulk solution has been noted previously.[18] Although the identity of $S^{\bullet}$ is not known, it is most likely $HC(O)N(CH_3)CH_2^{\bullet}$. This suggestion is based on (1) the finding by Swartz and coworkers that $(CH_3)_4N^+$, the cation of our supporting electrolyte, does not function as a hydrogen atom donor for aryl radicals,[19] (2) the report by Bethell and Parker[5] of a kinetic isotope effect of $k^{HC(O)N(CH_3)_2}/k^{DC(O)N(CD_3)_2} = 4$ for $1^{\bullet-}$ reaction, and (3) estimates of the carbon–hydrogen bond energies in DMF of $D°((CH_3)_2NC(O){-}H) = 95$ kcal/mol and $D°(HC(O)N(CH_3)CH_2{-}H) = 85$ kcal/mol.[20]

If $1^{\bullet-}$ reacts principally by hydrogen atom abstraction to give $Ph_2C{=}NNH^-$, trapping of $Ph_2C{=}NNH^-$ with an electroinactive proton donor that will protonate $Ph_2C{=}NNH^-$ but not $1^{\bullet-}$ is conceivable. Of the several proton donors that we examined (vide supra), only $p\text{-}NCC_6H_4NH_2$ satisfies this criterion. Although the addition of $p\text{-}NCC_6H_4NH_2$ is found to increase the yield of $Ph_2C{=}NNH_2$ (entry 8, Table I) relative to that obtained in the presence of weak acids which protonate $1^{\bullet-}$ (entry 5, Table I), substantial yields of Ph_2CH_2 and $Ph_2C{=}NN{=}CPh_2$ are also obtained. The formation of these other products suggests that the rate of $Ph_2C{=}NNH^-$ reaction with 1 is slowed, but not shut down, by the addition of $p\text{-}NCC_6H_4NH_2$. This is understandable if the equilibrium constant for proton transfer between $p\text{-}NCC_6H_4NH_2$ and Ph_2NNH^- is not too large.

Test for the Possible Occurrence of the Wolff–Kishner Reaction. In addition to the kinetic relationship between $1^{\bullet-}$ and $Ph_2C{=}NNH^-$, the anodic peak for the oxidation of $Ph_2C{=}NNH^-$ is also coupled kinetically to the anodic peak for the oxidation of $Ph_2CHN^-N{=}CPh_2$ ($E_{p,a} = 0.28$ V). This is evidenced in the cyclic voltammograms (Figure 8) by the increase in the anodic peak height for the oxidation of $Ph_2CHN^-N{=}CPh_2$ and a decrease in the anodic peak height for the oxidation of $Ph_2C{=}NNH^-$ 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 $Ph_2C{=}CPh_2^{\bullet-}$ ($E_{p,c} = -1.30$ V) to $Ph_2C{=}NN{=}CPh_2^{2-}$, $Ph_2CHN^-N{=}CPh_2$ that is formed in the cyclic voltammetric reduction of 1 should not arise from the inadvertent protonation of electrogenerated $Ph_2C{=}NN{=}CPh_2^{2-}$ by adventitious proton donors. This result suggests that $Ph_2C{=}NNH^-$ reacts in some unidentified manner to give, first, $Ph_2CHN^-N{=}CPh_2$ and, then, $Ph_2C{=}NN{=}CPh_2$. Since the formation of $Ph_2CHN^-N{=}CPh_2$ has been suggested above to occur by coupling of Ph_2CH^- with 1, the possibility that $Ph_2C{=}NNH^-$ undergoes the Wolff–Kishner reaction to give Ph_2CH^- and N_2 was examined under these reaction conditions. $Ph_2C{=}NNH^-$ was prepared in situ from $Ph_2C{=}NNH_2$ by the stepwise reduction of azobenzene to its dianion. The latter species is a strong base which rapidly deprotonates $Ph_2C{=}NNH_2$ to give $PhNHN^-Ph$ and $Ph_2C{=}NNH^-$.[13] After the controlled-potential electrolytic reduction of $PhN{=}NPh$ was complete (ca. 15 min) and the formation of $Ph_2C{=}NNH^-$ had been verified by cyclic voltammetry, the solution was acidified with an excess of $(EtO_2C)_2CH_2$ and analyzed by HPLC. Because $Ph_2C{=}NNH_2$ was recovered in 96% yield and Ph_2CH_2 was not detected as a reaction product, the conversion of $Ph_2C{=}NNH^-$ into Ph_2CH^- cannot occur to any significant extent under our reaction conditions and on the time scale of our experiments.

Initiation of the Chain Reaction with $Ph_2CHN^-N{=}CPh_2$. $Ph_2CHN^-N{=}CPh_2$ was prepared by the controlled-potential electrolysis ($E_{applied} = -1.4$ V) of $Ph_2C{=}NN{=}CPh_2$ in the presence of an excess of H_2O (eq 6). After two electrons per molecule of $Ph_2C{=}NN{=}CPh_2$

$$Ph_2C{=}NN{=}CPh_2 + 2e^- \rightarrow Ph_2C{=}NN{=}CPh_2^{2-} \xrightarrow{H_2O} Ph_2CHN^-N{=}CPh_2 + OH^- \quad (6)$$

had been added, the electrolysis was terminated, and an equimolar amount of 1 was added to the solution of electrogenerated $Ph_2CHN^-N{=}CPh_2$. Reaction occurred rapidly, as evidenced by the immediate evolution of a gas which is presumed to have been N_2. Cyclic voltammetric analysis of the reaction mixture showed that 1 had been transformed quantitatively into $Ph_2C{=}NN{=}CPh_2$.

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 1 into $Ph_2C{=}NN{=}CPh_2$ in the absence of added proton donors appears to be $1^{\bullet-} \rightarrow Ph_2C{=}NNH^- \rightarrow Ph_2CHN^-N{=}CPh_2$. A plausible reaction sequence must also be consistent with the following observations: (1) both $Ph_2C{=}NNH^-$ and $Ph_2CHN^-N{=}CPh_2$ initiate the chain reaction and convert 1 into $Ph_2C{=}NN{=}CPh_2$ quantitatively;[1] (2) only small amounts of products containing N–H and C–H bonds (specifically, $Ph_2C{=}NNH_2$, Ph_2CH_2, and $Ph_2CHNHN{=}CPh_2$; see entry 9, Table I) are formed; (3) the kinetics are consistent with $1^{\bullet-}$ reacting in the absence of added proton donors by rate-determining hydrogen atom abstraction from DMF to give $Ph_2C{=}NNH^-$; (4) $Ph_2C{=}NNH^-$ is not transformed into Ph_2CH^- and N_2 under these reaction conditions; and (5) the $Ph_2C{=}NN{=}CPh_2^{\bullet-}/Ph_2C{=}NN{=}CPh_2^{2-}$ redox couple is obtained even when neither $Ph_2C{=}NNH^-$ nor $Ph_2CHN^-N{=}CPh_2$ is oxidized.

At least two pathways can be proposed by which $Ph_2CHN^-N{=}CPh_2$ initiates the chain reaction and hydrogen is transferred from a reduction product of $Ph_2C{=}NN{=}CPh_2$ to either 1 or its reduction product, $1^{\bullet-}$. One pathway involves a series of electron- and proton-transfer reactions (eq 7–9). Although the electron-transfer reaction

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$$\mathrm{Ph_2CHN^{-}N{=}CPh_2 + Ph_2C{=}N_2 \xrightleftharpoons{K \ll 1} Ph_2C{=}N_2^{\bullet -} + Ph_2CH\dot{N}N{=}CPh_2} \quad (7)$$

$$\mathrm{Ph_2C{=}N_2^{\bullet -} + Ph_2CH\dot{N}N{=}CPh_2 \rightarrow Ph_2CH^{\bullet} + N_2 + Ph_2C{=}NN{=}CPh_2^{\bullet -}} \quad (8)$$

$$\mathrm{Ph_2CH^{\bullet} + Ph_2C{=}NN{=}CPh_2^{\bullet -} \rightarrow Ph_2C{=}NN{=}CPh_2 + Ph_2CH^{-}} \quad (9)$$

is endergonic ($E_{p,a}$($Ph_2CHN^-N{=}CPh_2$) = 0.13 V; $E_{p,c}$(1) = −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 8). The pK_a of $Ph_2CH\dot{N}N{=}CPh_2$ is unknown; however, because $(EtO_2C)_2CH_2$ (p$K_a^{Me_2SO}$ = 16.4)[7] does not protonate $Ph_2C{=}NN{=}CPh_2^{\bullet -}$,[10] its upper limit must be less than 16. Since $(EtO_2C)_2CH_2$ and CF_3CH_2OH protonate $1^{\bullet -}$ rapidly (vide supra), it is reasonable to conclude that proton transfer from $Ph_2CH\dot{N}N{=}CPh_2$ to $1^{\bullet -}$ should occur rapidly. The second electron-transfer reaction (eq 9) is exergonic ($E_{p,c}$($Ph_2C{=}NN{=}CPh_2$) = −0.91 V;[10] $E_{p,a}$(Ph_2CH^-) = −0.36 V)[11] and affords $Ph_2C{=}NN{=}CPh_2$ as a final product and Ph_2CH^- as a short-lived, unobserved intermediate.

A potential difficulty with this scheme may be the small value of the equilibrium constant for the homogeneous electron-transfer reaction in eq 7. Since the heterogeneous rate constant for reduction of 1 to $1^{\bullet -}$ is slow and the oxidation of $Ph_2CHN^-N{=}CPh_2$ occurs irreversibly (vide supra), the standard potentials for the 1 and the $Ph_2CHN^-N{=}CPh_2$ redox systems are unknown. Accordingly, an exact value of the equilibrium constant cannot be calculated. However, if $\Delta E°$ exceeds approximately 0.6 V (i.e., $K < 10^{-10}$), then reduction of 1 by $Ph_2CHN^-N{=}CPh_2$ (eq 7) probably occurs too slowly to account for the observed results. An alternative reaction which may circumvent this difficulty involves hydride transfer (eq 10).

$$\mathrm{Ph_2CHN^{-}N{=}CPh_2 + Ph_2C{=}N_2 \rightarrow Ph_2C{=}NN{=}CPh_2 + N_2 + Ph_2CH^{-}} \quad (10)$$

This reaction was first proposed by Bethell and McDowall[21] to be the initial step in the propagation cycle of the chain reaction that converts $PhC(O)C(N_2)Ph$ into the corresponding azine. It is written here as it would occur in the case of 1.

The final step in all propagation cycles which we[1] or others[21] have proposed involves the coupling of Ph_2CH^- with unreacted 1 to give $Ph_2CHN^-N{=}CPh_2$ (eq 3). This proposal is consistent with (1) our studies involving the reaction kinetics of a 1^{2-} decomposition product, which is believed to be Ph_2CH^-, with 1 (eq 2–3), (2) kinetics studies which show that $1^{\bullet -}$ reacts by a first-order or pseudo-first-order reaction pathway, and (3) the fact that $Ph_2C{=}NNH^-$ initiates the chain reaction in the transformation of 1 into $Ph_2C{=}NN{=}CPh_2$, but is not the chain-carrying species.[1] Although we have attempted to obtain direct evidence of the reaction of 1 with Ph_2CH^- 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 Ph_2CH^- precursor than 1 (e.g., Ph_2CHCl) and (2) the more rapid reaction of Ph_2CH^- with its precursor than with 1 (e.g., Ph_2CHBr).

Conversion of $Ph_2C{=}NNH^-$ into $Ph_2CHN^-N{=}CPh_2$. Results above have demonstrated that $Ph_2C{=}NNH^-$ is not converted into Ph_2CH^- and N_2 in the absence of 1 and that the disappearance of $Ph_2C{=}NNH^-$ in the presence of 1 is linked kinetically to the appearance of $Ph_2CHN^-N{=}CPh_2$. If the propagation step of the chain reaction involves electron transfer from $Ph_2CHN^-N{=}CPh_2$ to 1 (eq 7), then it is reasonable to attribute the formation of $Ph_2CHN^-N{=}CPh_2$ from $Ph_2C{=}NNH^-$ and 1 to the succession of electron- and proton-transfer reactions described by eq 11–13. The final step in the formation of $Ph_2CHN^-N{=}CPh_2$ would then involve coupling of Ph_2CH^- with 1 (eq 3).

$$\mathrm{Ph_2C{=}NNH^{-} + Ph_2C{=}N_2 \rightleftharpoons Ph_2C{=}N\dot{N}H + Ph_2C{=}N_2^{\bullet -}} \quad (11)$$

$$\mathrm{Ph_2C{=}N\dot{N}H + Ph_2C{=}N_2^{\bullet -} \rightarrow Ph_2CH^{\bullet} + Ph_2C{=}N_2^{\bullet -} + N_2} \quad (12)$$

$$\mathrm{Ph_2CH^{\bullet} + Ph_2C{=}N_2^{\bullet -} \rightarrow Ph_2CH^{-} + Ph_2C{=}N_2} \quad (13)$$

Although this reaction sequence is analogous to that proposed for the reaction of $Ph_2CHN^-N{=}CPh_2$ with 1, the initial electron-transfer reaction between $Ph_2C{=}NNH^-$ and 1 should be more favorable because of the more ready oxidation of $Ph_2C{=}NNH^-$ ($E_{p,a}$ = 0.1 V) than $Ph_2CHN^-N{=}CPh_2$ ($E_{p,a}$ = 0.2 V at T = −51 °C). However, because reaction 11 is still endergonic, the subsequent proton-transfer reaction (eq 12) must proceed rapidly and irreversibly. This is plausible if the carbon site is more basic than the nitrogen site in $1^{\bullet -}$ and/or the loss of N_2 from $Ph_2CHN_2^{\bullet}$ is also rapid and irreversible. Each of these requirements is consistent with the results that have been obtained when 1 is reduced in the absence of proton donors that protonate $1^{\bullet -}$. An alternative reaction pathway can also be written which involves hydride transfer from $Ph_2C{=}NNH^-$ to 1 (eq 14). Reaction would be expected to occur by this pathway if reaction of $Ph_2CHN^-N{=}CPh_2$ with 1 were to occur by hydride transfer (eq 7).

$$\mathrm{Ph_2C{=}NNH^{-} + Ph_2C{=}N_2 \rightarrow Ph_2C{=}N_2 + Ph_2CH^{-} + N_2} \quad (14)$$

Comparison of Reaction Pathways of Diazoalkane Anion Radicals. One of the general objectives of our work with $R_2C{=}N_2^{\bullet -}$ is to accumulate sufficient data so that their reactions can be predicted under a variety of solution conditions. Loss of N_2 from $R_2C{=}N_2^{\bullet -}$ and the formation of $R_2C^{\bullet -}$ has been observed only when one or more carbonyl groups (e.g., $(EtO_2C)_2C{=}N_2$,[18] $PhC(O)C(N_2)Ph$,[21] and diazodimedone[23]) are α to the carbon-bearing nitrogen and facilitate the delocalization of the negative charge away from the departing N_2. On the basis of the limited data available, the rate of N_2 loss from these $R_2C{=}N_2^{\bullet -}$ increases with decreasing pK_a of the corresponding acid, R_2CH_2. In each of the three systems in which intermediacy of $R_2C^{\bullet -}$ is still 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 carbene anion radicals for synthetic

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purposes in the condensed phase has yet to be demonstrated.

With the exception of $Ph_2C{=}N_2^{\bullet -}$, few data are available concerning the reactions of $R_2C{=}N_2^{\bullet -}$ with proton donors. $(EtO_2C)_2C{=}N_2^{\bullet -}$ is not protonated by relatively strong acids such as PhCOOH ($pK_a^{Me_2SO} = 11.0$)[7] and $(CF_3)_2CHOH$.[18] Interestingly, diazodimedone anion radical[22] reacts rapidly with CF_3CH_2OH ($pK_a^{Me_2SO} = 23$)[8] but not with $(EtO_2C)_2CH_2$ ($pK_a^{Me_2SO} = 16.4$).[7] This difference in behavior is under current investigation.

Only two diazoalkanes that do not contain one or more carbonyl groups have been studied extensively. In the case of both 1 and diazofluorene, electroreduction initiates a chain reaction that ultimately affords the corresponding azine as the principal product. However, whereas diazofluorene anion radicals dimerize to give a tetrazine that slowly loses N_2,[23,24] $1^{\bullet -}$ is believed to react initially by hydrogen atom abstraction. As Bethell and Parker[5] have noted, hydrogen atom abstraction is an unusual reaction pathway for anion radicals. Whether or not other diazoalkanes will react by hydrogen atom abstraction or dimerization remains to be determined.

Experimental Section

Instrumentation, Cell, Electrodes, and General Procedures. The electrochemical and data acquisition equipment have been described previously.[13] All electrochemical experiments were performed on an all-glass vacuum line. Planar platinum and vitreous carbon working electrodes were used for most cyclic voltammetric and chronoamperometric experiments. 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).[25] The potential of this electrode is −0.75 V vs. SCE. Dual reference electrodes were used in all cyclic voltammetric and chronoamperometric experiments.[26] The second reference electrode was a platinum wire which is in series with a 0.1-μF capacitor and was placed in parallel with the cadmium chloride/cadmium amalgam reference electrode.

Coulometry. The progress of large-scale electrolyses was monitored periodically by cyclic voltammetry. At the conclusion of an electrolysis, the mixture was protonated in a dry helium atmosphere with $(EtO_2C)_2CH_2$ and then analyzed by HPLC. In order to determine if the acid that was used for protonation of the anionic electrolysis products might catalyze the decomposition of unreacted 1, a tenfold excess of PhCOOH, CH_3COOH, $(EtO_2C)_2CH_2$, CF_3CH_2OH, or $(CF_3)_2CHOH$ was added to a solution of 1 in DMF.[27] With the exceptions of PhCOOH and CH_3COOH, none of the proton donors caused any discernible change in the absorption spectrum of 1 after reaction for 48 at room temperature.

Chemicals. DMF (Burdick and Jackson) was 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-Å 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 $(CH_3)_4NBF_4$ or $(CH_3)_4NPF_6$ was used as the supporting electrolyte; these materials were stored in a vacuum oven over phosphorus pentoxide. $Ph_2C{=}N_2$[28] and $Ph_2C{=}NN{=}CPh_2$[29] were synthesized according to reported procedures. 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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Registry No. 1, 883-40-9; $1^{\bullet -}$, 75558-05-3; p-$NCC_6H_4NH_2$, 873-74-5; $Ph_2C{=}NN{=}CPh_2$, 983-79-9; $Ph_2CHN^{-}N{=}CPh_2$, 81667-74-5.

Supplementary Material Available: Kinetics studies of 1^{2-}, the chronoamperometric study of $1^{\bullet -}$, the plot of $n_{apparent}$ vs. log tc for 1 (Figure 3), cyclic voltammograms for the reduction of 1 (Figure 4 and 6), and the double-potential-step chronoamperometric data for the reduction of 1 (Figure 5) [see text for specific conditions] (7 pages). Ordering information is given on any current masthead page.

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An Investigation of 1,8-Diazafluorenylidene. A Carbene with Unusual Properties

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Irradiation of 9-diazo-1,8-diazafluorene initiates a series of photochemical reactions that lead to isomerization to the diazirine and to loss of nitrogen to form a carbene. The carbene has a triplet ground state but reacts primarily from its upper singlet state. The chemical and physical properties of the diazo compound and the carbene are compared with those for 9-diazofluorene. The differences between these compounds are assigned tentatively to a combination of through-space interaction of the lone pair electrons of the heteroatomic ring atoms with the nonbonding in-plane orbital of the carbene carbon and the electron-withdrawing nature of the pyridine-like nitrogens.

The chemical and physical properties of carbenes vary widely in response to the electronic character of the attached substituent groups.[1] This has long been recognized for simple methylenes and an empirical correlation has been developed that relates the properties of the substituents to the properties of the carbenes.[2] The issue is considerably more complex in the case of diarylcarbenes.

Arnold and co-workers, in a seminal study, attempted to invert the normal ordering of triplet diphenylcarbene

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