

Hypovalent Radicals. 6.¹ Electroreduction of Diazodiphenylmethane—Intermediacy of Ph_2CN_2^- and Ph_2C^-

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Abstract: The electrochemical reduction of diazodiphenylmethane (Ph_2CN_2) at a platinum cathode in DMF-0.1 F (*n*-Bu)₄ClO₄ has been shown to afford benzophenone azine (($\text{Ph}_2\text{C}=\text{N}-$)₂) as the principal product, along with lesser amounts of Ph_2CH_2 and several other compounds. Product formation occurs by a chain process in which the carbene anion radical, Ph_2C^- , is produced from electrogenerated Ph_2CN_2^- by rapid loss of nitrogen. Ph_2CH^- , the first-observed intermediate in Ph_2CN_2 electroreduction, is obtained from Ph_2C^- either by protonation followed by reduction or by hydrogen atom abstraction from a component of the solvent-electrolyte system. Propagation of the chain involves coupling of Ph_2CH^- with Ph_2CN_2 to produce $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ followed by proton transfer from this anion to Ph_2C^- to give ($\text{Ph}_2\text{C}=\text{N}-$)₂²⁻ and Ph_2CH^- , respectively. Regeneration of Ph_2CN_2^- occurs by electron transfer from either ($\text{Ph}_2\text{C}=\text{N}-$)₂²⁻ or ($\text{Ph}_2\text{C}=\text{N}-$)₂⁻ to Ph_2CN_2 . Termination of the chain occurs upon protonation of Ph_2CH^- . In the presence of the electroinactive proton donors, diethyl malonate and 2,2,2-trifluoroethanol, azine formation is interdicted and $\text{Ph}_2\text{C}=\text{NNH}_2$ and Ph_2CH_2 are the two major products. Studies of the $\text{Ph}_2\text{CH}_2/\text{Ph}_2\text{C}=\text{NNH}_2$ product ratio as a function of proton donor concentration and temperature have established that protonation (and other reactions) of Ph_2CN_2^- occurs exclusively on terminal nitrogen while Ph_2CH_2 arises via Ph_2C^- . No evidence was obtained for either hydrogen atom abstraction by or protonation of C_α of Ph_2CN_2^- .

Introduction

Studies of preparative methods for carbon-centered reactive intermediates and the determination of their chemistry have largely dealt with carbonium ions, carbanions, free radicals, and carbenes (methylene). The rich chemistry of these four classes of intermediates that developed justified most research efforts. However, when we consider the stepwise loss of R groups (as R⁻, R[•], or R⁺) from a tetravalent carbon substrate to the point of yielding carbon atoms, we find that there are *nine* classes of such carbon-centered fragments. The five additional classes of molecular fragments are carbene anion and cation radicals (R₂C⁻, R₂C⁺), carbynes (RC), and triplet carbyne anion and cation radicals (RC⁻, RC⁺). We have termed these species *hypovalent radicals*—neutral or charged radical species that contain *less* than the number of attached substituents normally associated with the central atom in the uncharged, free radical system.

We recently began studies of these hypovalent radicals in solution and in the gas phase. Carbene anion radicals were selected as the initial target since all bonding and nonbonding MO's would be occupied, thus eliminating (or reducing) the possibilities of skeletal rearrangements. MINDO/3² and GEOMIN-INDO calculations³ of simple carbene anion radicals, H₂C⁻,⁴ F₂C⁻, and (CH₃)₂C⁻, describe their ground-state structures (∠H-C-H = 99.9°, ∠F-C-F = 102.4°, ∠(CH₃)-C-(CH₃) = 125.1°) as essentially those of the corresponding singlet carbenes with an electronic configuration of σ²p¹ at the divalent carbon center. That the electronic structure about the divalent carbon is responsive to other molecular features was shown with cyclopentadienylidene anion radical (c-C₅H₄⁻) where both experiment⁵ and calculations agreed that the ground-state electronic configuration is σ¹π². The structure of c-C₅H₄⁻ was calculated to be similar to that of triplet cyclopentadienylidene.

Since parallel studies in solution and in the gas phase were planned, substrate structures where R₂C⁻ could result from a single one-electron step were deemed necessary.⁶ This consid-

eration, plus previous reports of carbene anion radical formation by electron attachment to diazomethane in the gas phase⁴ and in the polarographic reduction of diazotetracyanocyclopentadiene in acetonitrile,⁷ made diazoalkanes an obvious choice of structure. In addition, Kauffmann and Hage⁸ had reported that reduction of diazodiphenylmethane (Ph_2CN_2) with sodium in ether gave its corresponding diazo anion radical and that the anion radical slowly lost nitrogen at room temperature. It appeared appropriate, therefore, to initiate our investigation with Ph_2CN_2 by using the methods of electrochemistry to probe the processes and the nature of intermediates involved in this reduction.

Results

Cyclic Voltammetry and the Effects of Scan Rate and Temperature. The cyclic voltammograms for the electroreduction of Ph_2CN_2 in DMF-0.1 F (*n*-Bu)₄NClO₄ at a platinum cathode are shown in Figures 1-3. Although the reduction of Ph_2CN_2 is irreversible ($E_{pc} = -0.96$ to -1.4 V) and gives no corresponding anodic peak for the reoxidation of Ph_2CN_2^- at all scan rates up to 100 V/s, one or more anodic processes, depending upon the temperature and the scan rate, arise from the oxidation of decomposition products from Ph_2CN_2^- on the reverse, positive-going sweep. At 0 °C and a scan rate of 50 V/s (Figure 1), the only intermediate discernible is Ph_2CH^- ($E_{pa} = -0.35$ V).⁹ This anodic process is kinetically controlled, the relative magnitude of which decreases with either an increase in temperature or a decrease in scan rate. Concomitantly, as the Ph_2CH^- wave decays, additional anodic peaks appear near -1.32, -0.93, 0.1, and 0.5 V (Figure 2). By comparison to an authentic sample, the two most negative processes result from the stepwise reversible reduction of benzophenone azine (($\text{Ph}_2\text{C}=\text{N}-$)₂) to its dianion ($E_{pc,1} = -0.98$

(1) For paper 5, see: Triebe, F. M.; Hawley, M. D.; McDonald, R. N. *J. Am. Chem. Soc., Chem. Commun.* 1980, 574.

(2) (a) We thank Professor S. D. Worley, Auburn University, for making this computer program available to us and Professor Keith Purcell for his efforts to get it running on our machine. (b) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, 97, 1285, 1294, 1302, 1307.

(3) K. F. Purcell, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind., No. 312.

(4) Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C.; Reinhardt, W. R. *J. Am. Chem. Soc.* 1976, 98, 3732. (b) Davison, R. B.; Hudak, M. L. *Ibid.* 1977, 99, 3918 ($\theta_{\text{HCH}} = 99^\circ$, $r_{\text{CH}} = 1.145$ Å).

(5) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* 1980, 102, 6491.

(6) Sargent, et al., had examined the reduction of alkyl gem-dihalides with sodium naphthalene and concluded that carbene anion radicals were involved as reactive intermediates. However, this conclusion must be considered ambiguous due to the variety of other potential intermediates formed as a result of the required three successive 1 e⁻ reduction steps in R₂CX₂ → R₂C⁻ + 2 X⁻. (a) Sargent, G. D.; Tatum, C. M.; Kastner, S. M. *J. Am. Chem. Soc.* 1972, 94, 7174. (b) Sargent, G. D.; Tatum, C. M.; Scott, R. P. *Ibid.* 1974, 96, 1602.

(7) Webster, O. W. *J. Am. Chem. Soc.* 1966, 88, 4055.

(8) Kauffmann, T.; Hage, S. M. *Angew. Chem., Int. Ed. Engl.* 1963, 2, 156.

(9) The diphenylmethyl anion has been previously prepared (from Ph_2CHCl) and studied: Triebe, F. M.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* 1979, 101, 4637. Although Ph_2C^- might be expected to be oxidized at nearly the same potential as Ph_2CH^- , coupling of Ph_2C^- with Ph_2CN_2 would not give $\text{Ph}_2\text{CHNN}=\text{CPh}_2$. The appearance of an anodic wave for the latter species is kinetically linked to the disappearance of the anodic wave attributed to Ph_2CH^- .

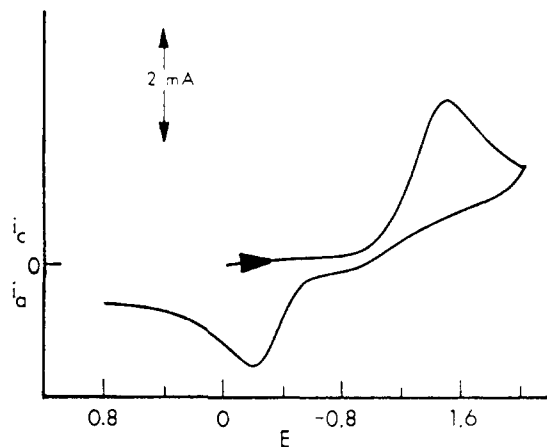


Figure 1. Cyclic voltammogram of 5.30 mM Ph_2CN_2 in DMF-0.1 F $(n\text{-Bu})_4\text{NClO}_4$ at a planar platinum electrode. The scan rate is 50 V/s.

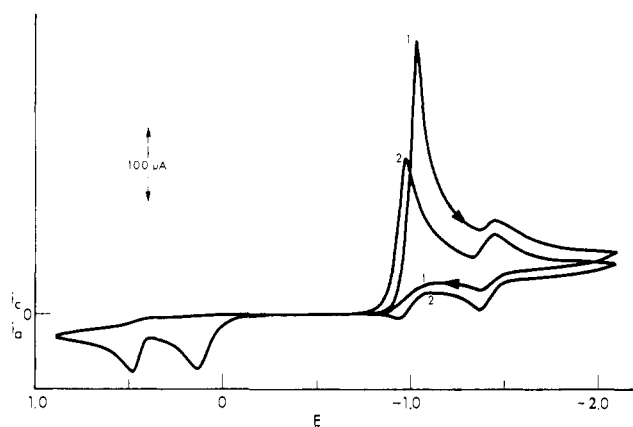


Figure 2. Cyclic voltammogram of 4.05 mM Ph_2CN_2 in DMF-0.1 F $(n\text{-Bu})_4\text{NClO}_4$ at a planar platinum electrode. The scan was initiated at 0 V in the negative direction at a rate of 0.2 V/s. The numbers 1 and 2 denote the first and second cycles, respectively.

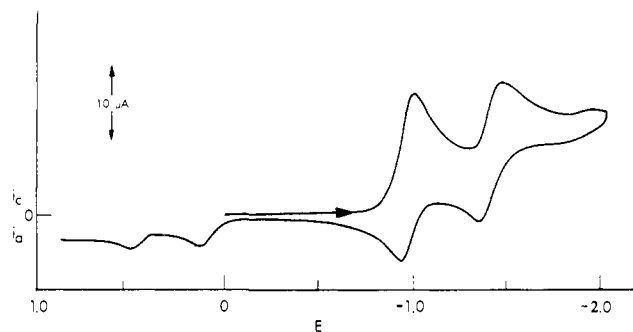
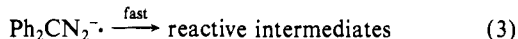
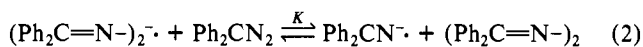
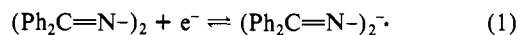


Figure 3. Cyclic voltammogram of an exhaustively electrolyzed solution of 4.53 mM Ph_2CN_2 in DMF-0.1 F $(n\text{-Bu})_4\text{NClO}_4$ at a spherical platinum electrode. The scan rate is 0.2 V/s.

V and $E_{p,c,2} = -1.38$ V). Since $(\text{Ph}_2\text{C}=\text{N})_2$ is the only electroactive species evident in an exhaustively electrolyzed solution of Ph_2CN_2 (Figure 3), the two remaining anodic peaks at 0.1 and 0.5 V must then lie in product-forming channels. Identification of the irreversible wave at 0.1 V as arising from the oxidation of $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ is based upon the facts that (a) deprotonation of this species by electrogenerated bases would afford $(\text{Ph}_2\text{C}=\text{N})_2^{2-}$, (b) this species is the expected product of coupling of Ph_2CH^- with unreacted starting material, thereby establishing the kinetic link between the disappearance of the oxidation wave for Ph_2CH^- and the appearance of the wave under discussion, and (c) an authentic sample of this species, prepared by the addition of $(\text{CH}_3)_4\text{NOH}$ to benzophenone benzydrylhydrazine ($\text{Ph}_2\text{CHNHN}=\text{CPh}_2$), gives a single oxidation wave at this potential. The last, small irreversible wave at 0.5 V remains unidentified; all attempts to link this wave to any one of the several

products, their reduction products, or their conjugate bases were unsuccessful. However, the fact that the magnitude of this peak increases rapidly when the applied potential is made more negative than the cathodic background limit suggests that the process is solvent-electrolyte derived.

Effect of the Electrocatalytic Action of Benzophenone Azine Anion Radical and Other Electrogenerated Reducing Agents. Inspection of Figures 1 and 2 will show that the peak potential for the reduction of Ph_2CN_2 shifts positively more than 0.4 V as the scan rate decreases from 50 V/s (Figure 1) to 0.2 V/s (Figure 2). Although the rapid follow-up chemical reaction involving Ph_2CN_2^- , uncompensated IR loss between the reference and working electrodes, and slow heterogeneous electron transfer to Ph_2CN_2 contribute to this shift, the major cause is due to the electrocatalytic action of electrogenerated $(\text{Ph}_2\text{C}=\text{N})_2^{2-}$. At pen-and-ink recording speeds (Figure 2), the rate of reduction of Ph_2CN_2 by electrogenerated $(\text{Ph}_2\text{C}=\text{N})_2^{2-}$ is so rapid that the peaks for Ph_2CN_2 and $(\text{Ph}_2\text{C}=\text{N})_2$ overlap ($E_{p,c,1} = -0.96$ V). Electrocatalytic action has been observed in other similar systems^{9,10} and results when (a) a species, viz., $(\text{Ph}_2\text{C}=\text{N})_2$, is reduced to a stable, lower oxidation state at a potential more positive than that of the substrate, viz., Ph_2CN_2 , (b) electron transfer occurs from the electrolytically generated reducing agent to the more difficultly reduced substrate, and (c) the reduced substrate undergoes rapid, irreversible decomposition, e.g., loss of nitrogen from the anion radical of Ph_2CN_2^- . Since the chemical reducing agent is continually regenerated at the electrode surface, the concentration of $(\text{Ph}_2\text{C}=\text{N})_2$ can be small and still exert an important effect upon the apparent electrode behavior (eq 1-3).



Reduction of Ph_2CN_2 is also observed with the electrogenerated anion radical and dianion of terephthalonitrile and fluorenone azine, respectively. As expected, however, as the equilibrium constant for electron transfer from electrogenerated reducing agent to Ph_2CN_2 is made smaller, the rate of electrocatalytic reduction of Ph_2CN_2 decreases rapidly.¹¹ Thus, although the cyclic voltammetric cathodic peak height for the one-electron reduction of either terephthalonitrile ($E_{p,c} = -0.84$ V) or fluorenone azine anion radical ($E_{p,c,2} = -0.68$ V) is enhanced by the addition of the more difficultly reduced Ph_2CN_2 , the rate of homogeneous electron transfer from either terephthalonitrile anion radical or fluorenone azine dianion to Ph_2CN_2 is insufficiently rapid on the cyclic voltammetric time scale so as to eliminate a separate, distinct reduction wave for Ph_2CN_2 at more negative potential. The peak height for the one-electron reduction of fluorenone azine ($E_{p,c,1} = -0.28$ V) was not enhanced by the addition of Ph_2CN_2 , indicating that electron transfer between fluorenone azine anion radical and Ph_2CN_2 does not occur on the time scale of this experiment.

Coulometry. The controlled-potential electrolytic reduction of Ph_2CN_2 at a large platinum gauze in the absence of added proton donor affords $(\text{Ph}_2\text{C}=\text{N})_2$ and diphenylmethane (Ph_2CH_2) as the two major products (runs 1-3, Table I); only the azine is electroactive. In addition, small but readily detectable amounts of benzophenone hydrazone ($\text{Ph}_2\text{C}=\text{NNH}_2$), $\text{Ph}_2\text{CHNHN}=\text{CPh}_2$, and benzophenone are observed by high-performance LC.¹² The product distribution is not affected significantly by the variation of the electrode potential (runs 1-3) as it is altered from a value near the base of the first azine wave ($E = -0.90$ V), to

(10) (a) Simonet, J.; Michel, M.-A.; Lund, H. *Acta Chem. Scand., Ser. B* **1975**, *29*, 489. (b) Lund, H.; Simonet, J. *J. Electroanal. Chem.* **1975**, *65*, 205. (c) Britton, W. E.; Fry, A. J. *Anal. Chem.* **1975**, *47*, 95.

(11) Amatore, C.; Chaussard, J.; Pinson, J.; Saveant, J.-M.; Thiebault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.

(12) In our initial studies of this system,¹³ neither $\text{Ph}_2\text{CHNHN}=\text{CPh}_2$ nor $\text{Ph}_2\text{C}=\text{NNH}_2$ was detected by GLC. In addition, benzophenone was incorrectly identified earlier as benzydrylamine.

(13) McDonald, R. N.; January, J. R.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 1268.

Table I. Coulometric Data and Product Studies for the Controlled-Potential, Electrolytic Reductions of Diphenyldiazomethane^a

run	Ph ₂ CN ₂ , mM	acid, ^b concn in mM	E _{applied} , V	n	% yield of products						
					Ph ₂ C=N-N=CPh ₂	Ph ₂ -CH ₂	Ph ₂ C=O	Ph ₂ C=NNH ₂	Ph ₂ C=NNHCHPh ₂	Ph ₂ -CN ₂	[Ph ₂ CH ₂]/[Ph ₂ C=NNH ₂]
1	3.70	0	-0.90	0.45	72	13	3.5	0.2	c	4	
2	3.70	0	-0.98	0.30	81	8	1.0	0.5	1.8	7	
3	4.53	0	-1.20	0.40	78	5	0.8	0.6	2.2	5	
4 ^d	7.68	0	-0.79	0.25	80	12	1.6	0.1	c	4	
5	3.49	TFE, 21	-1.00	2.00	0.5	88	0.1	2.5	0.4	5	35
6	4.54	DEM, 39	-1.10	2.00	0.7	85	1.0	7.6	3.0	2.4	11
7	5.12	DEM, 32	-1.00	2.50	0.2	80	0.2	4.0	6	1.9	20
8 ^e	3.02	DEM, 32	-1.20	2.45	1.3	44	2.6	21	2.7	18	2.1
9 ^e	1.40	DEM, 143	-1.20	2.00	0.3	34	c	37	2.5	24	0.92
10	4.44	HFIP, 35	-1.00	4 ^f	trace	79	0.3	7.4	0.4	13	11
11	2.85	GP, 29	-1.00	4 ^f	c	11	2.5	21	c	59	0.52

^a Electroreductions at a platinum cathode in DMF-0.1 F (*n*-Bu)₄NClO₄ at room temperature (20-23 °C) unless otherwise noted. ^b TFE = trifluoroethanol; DEM = diethyl malonate; HFIP = hexafluoro-2-propanol; GP = guanidinium perchlorate. ^c Not detected. ^d Reduction of Ph₂CN₂ is mediated by the anion radical of terephthalonitrile (0.37 M); Ph₂CN₂ is electroinactive at the applied potential. ^e Reduction at 0 °C. ^f Reduction of the acid occurred at the applied potential.

the peak of the first azine wave ($E = -0.98$ V), and, finally, to a point between the first and second waves of the azine ($E = -1.20$ V). This result is consistent with our previous observation that reduction of Ph₂CN₂ occurs electrocatalytically with electron transfer mediated by (Ph₂C=N-)₂⁻ (eq 1-2).

The species which initiates electron transfer to Ph₂CN₂ is unimportant, as evidence by the results of run 4 in Table I. In this experiment, the reducing agent, terephthalonitrile anion radical, was generated in situ by the one-electron reduction of terephthalonitrile at a potential which was insufficiently negative ($E = -0.79$ V) to cause reduction of either (Ph₂C=N-)₂ or Ph₂CN₂. Although the *n* value is slightly smaller in this experiment than in runs 1-3, no appreciable change in the product distribution results.

Although the electroactivity of the principal product as the applied potential causes some uncertainty as to when electrolysis should be terminated, and consequently, the proper value of *n* for this experiment, all observed *n* values in runs 1-4 are significantly less than one. This result suggests that (Ph₂C=N-)₂, a species which formally requires no current for its formation from Ph₂CN₂, is produced by one or more chain processes.

Chronoamperometry. In this experiment the current is recorded as a function of time ($1 \text{ ms} \leq t \leq 10 \text{ s}$) after the electrode potential has been stepped abruptly from a value where no reaction occurs to a value sufficiently negative such that the concentration of Ph₂CN₂ is zero at the electrode surface. Since the number of electrons in the electroreduction is proportional to the current, each experimental current-time curve can then be used to construct a corresponding curve of the apparent *n* value, *n*_{app}, vs. time, *t*.

Data from these experiments in the absence of an added proton donor show that concurrent reduction of Ph₂CN₂ and the electrogenerated (Ph₂C=N-)₂ is a diffusion-controlled, overall one-electron process at room temperature for $t \geq 10 \text{ ms}$ ($E_{\text{applied}} \leq -1.50 \text{ V} < E_{\text{p,c,2(azine)}} = -1.38 \text{ V}$). If the reduction is carried out at 0 °C, the process is kinetically controlled with *n* decreasing from an apparent value of 1.4 at 3 ms to 1.0 for $t > 50 \text{ ms}$.

Reaction of Ph₂C=NNH⁻ with Ph₂CN₂. The addition of Ph₂CN₂ to a solution of Ph₂C=NNH⁻ in DMF-0.1 F (*n*-Bu)₄NClO₄ resulted in the immediate evolution of nitrogen and the formation of the distinctive color of the (Ph₂C=N-)₂⁻. Although subsequent analysis of the acidified product mixture showed that all of the Ph₂CN₂ was consumed, only 24% Ph₂C=NNH⁻ had reacted. In addition, the number of μmol of Ph₂CH₂ formed is almost equal to the number of μmol of Ph₂C=NNH⁻ consumed. Since formation of Ph₂CH₂ occurs only upon termination of the chain process (vide infra), we conclude that Ph₂C=NNH⁻ serves only to initiate the chain reaction.

Effects of Added Proton Donors

Cyclic Voltammetry. The addition of electroinactive proton donors causes all anodic peaks resulting from the reduction of Ph₂CN₂ in the absence of such proton donors to disappear.

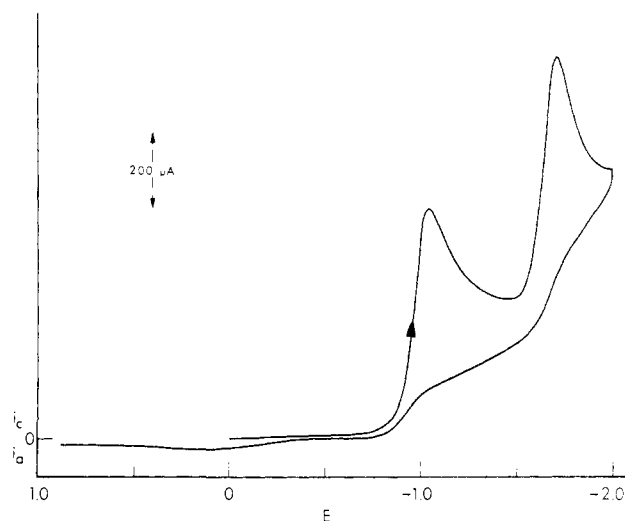


Figure 4. Cyclic voltammogram of 5.30 mM Ph₂CN₂ in DMF-0.1 F (*n*-Bu)₄NClO₄ at 0 °C in the presence of 5.3×10^{-2} F in diethyl malonate. The scan rate at the planar platinum electrode is 0.5 V/s.

Concomitantly, the magnitude of the Ph₂CN₂ reduction wave increases and an irreversible peak due to the reduction of Ph₂C=NNH₂ arises near -1.73 V. The magnitudes of both peaks are dependent upon several variables, including the strength and concentration of the proton donor, the temperature, and the scan rate. Thus, whereas added trifluoroethanol (TFE) gives a hydrazone wave which is barely discernible at room temperature, this peak is nearly equal in magnitude to the Ph₂CN₂ wave when electroreduction is effected in the presence of diethyl malonate (DEM) at 0 °C (Figure 4). Since the ratio of the Ph₂C=NNH₂ to Ph₂CN₂ peak heights generally increases with decreasing temperature and increasing concentration of the proton donor, capture of the short-lived Ph₂CN₂⁻ by protonation is indicated. Quantitative determination of the amount of Ph₂C=NNH₂ which is formed by this pathway is not possible, however, because both the Ph₂CN₂ and the Ph₂C=NNH₂ waves are kinetically controlled in our scan rate range of $0.2 \text{ V/s} < v < 100 \text{ V/s}$.

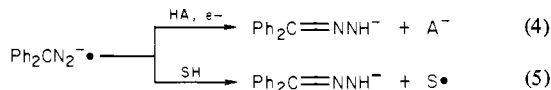
Coulometry. The addition of either DEM or TFE as an electroinactive proton donor interdicts azine formation and causes the yields of Ph₂CN₂ and Ph₂C=NNH₂ to be significantly increased (runs 5-9). As in the cyclic voltammetric studies, the amount of Ph₂C=NNH₂ which is formed is a function of both the temperature and the identity and concentration of the proton donor. When the concentration of DEM is held constant, as in runs 7 and 8, the Ph₂CH₂/Ph₂C=NNH₂ product ratio decreases from 20 to 2.1 as the temperature is reduced from 20 to 0 °C. The influence of proton donor concentration is demonstrated by the results of runs 8 and 9; as the concentration of DEM is increased from 32 to 143 mM at 0 °C, the Ph₂CH₂/Ph₂C=NNH₂ ratio decreases from 2.1 to 0.92.

The attainment of accurate n values for electrolysis conducted at a platinum cathode at relatively negative potentials is inherently difficult, especially when the electrolyses are conducted in the presence of a substantial quantity of proton donor. Nevertheless, the facts that (a) the nominal n value is 2 in runs 5–9, (b) an irreversible anodic wave arises at +1.13 V for the oxidation of $(\text{EtOOC})_2\text{CH}^-$ when electrolyses are effected in the presence of DEM, and (c) both $\text{Ph}_2\text{C}=\text{NNH}_2$ and Ph_2CH_2 are formally two-electron reduction products of Ph_2CN_2 are consistent with the capture of all anion and anion radical intermediates with these two proton donors.

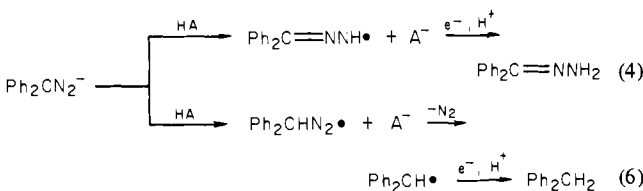
Stronger proton donors such as hexafluoro-2-propanol (HFIP) and guanidinium perchlorate (GP)¹⁴ also cause $\text{Ph}_2\text{C}=\text{NNH}_2$ and Ph_2CH_2 to be formed (runs 10 and 11). However, because these stronger proton donors are also electroactive at the applied potential,¹⁵ the determination of n values in the presence of these acids is precluded. The effect which concurrent reduction of proton donor and Ph_2CN_2 has upon the product distribution cannot be determined unequivocally. Electroreduction of the acid only (either benzoic acid or GP) in the presence of Ph_2CN_2 had no effect on the Ph_2CN_2 concentration.

Discussion

Ph_2CN_2^- as a Discrete Intermediate. The absence of a cyclic voltammetric anodic wave for the oxidation of Ph_2CN_2^- at all scan rates up to 100 V/s establishes a maximum lifetime of 10^{-3} s for this species. Although the actual lifetime of Ph_2CN_2^- may be considerably shorter than this value, dissociative electron transfer to Ph_2CN_2 is predicted by the small, but discernible, amounts of $\text{Ph}_2\text{C}=\text{NNH}_2$ found by high-performance LC analysis of runs 1–4. Formation of $\text{Ph}_2\text{C}=\text{NNH}_2$ may be rationalized by initial protonation on or hydrogen atom abstraction by N_β of Ph_2CN_2^- (eq 4 and 5). Subsequent protonation of $\text{Ph}_2\text{C}=\text{NNH}^-$ by either an added proton donor or $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ (vide infra) would then afford $\text{Ph}_2\text{C}=\text{NNH}_2$. Control experiments have demonstrated that this hydrazone is not formed at the applied potential from either $(\text{Ph}_2\text{C}=\text{N})_2$ or $\text{Ph}_2\text{CHNHN}=\text{CPh}_2$.



Tests for Concomitant Reaction at C_α and N_β in Ph_2CN_2^- . The detection of $\text{Ph}_2\text{C}=\text{NNH}_2$ as a minor product of Ph_2CN_2 reduction in aprotic media prompted us to investigate the effect of proton donors on this electrode process.¹⁶ The reduction of Ph_2CN_2 in the presence of either DEM or TFE as an electroinactive proton donor caused the azine forming reaction channels to be shutdown and Ph_2CH_2 and $\text{Ph}_2\text{C}=\text{NNH}_2$ to be formed as



(14) Breslow, R.; Drury, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 4702.

(15) The observed order of reduction in this solvent–electrolyte system was benzoic acid, $E_{\text{p.c.}} = -0.38$ V, HFIP, $E_{\text{p.c.}} = -0.62$ V, and GP, $E_{\text{p.c.}} = -0.85$ V. However, we emphasize that the locations of the cathodic peak potentials were difficult to reproduce. The peak potentials frequently were shifted by the addition of an electroactive component such as Ph_2CN_2 , by an increase in the cyclic voltammetric scan rate, and by an increase in the concentration of the proton donor.

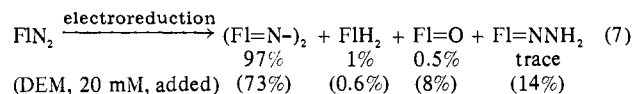
(16) (a) Professor Fred Bordwell, private communication to R.N.M., lists the $\text{p}K_a$'s of DEM and TFE as 16.4 and >20, respectively, in Me_2SO at 25 °C. (b) TFE has been shown in gas phase reactions with cyclopentadienylidene anion radical to function only as a proton donor.³ The similarity here in product distributions for reduction conducted in the presence of TFE and DEM, the inherently greater acidity of DEM,¹⁷ and the electrochemical detection of $(\text{EtOOC})_2\text{CH}^-$ in the electrolyzed mixtures of Ph_2CN_2 and DEM suggest, but do not require, that DEM function as a proton donor rather than as a hydrogen atom donor.

(17) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979, Vol. 2.

(18) Wright, R. E.; Vogler, A. *J. Organomet. Chem.* **1978**, *160*, 1976.

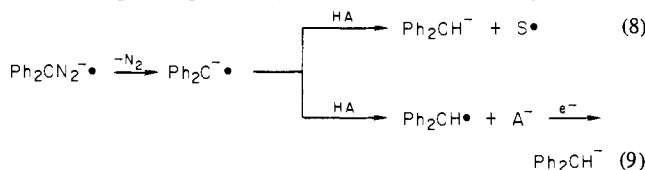
the principal products. The inability of these acids to prevent hydrocarbon formation can possibly be rationalized if Ph_2CN_2^- functions as an ambident base and is protonated on both N_β (eq 4) and C_α (eq 6).

To test this possibility, the electroreduction of 9-diazofluorene (FIN_2) was examined in $\text{DMF}-0.1 \text{ F} (n\text{-Bu})_4\text{NClO}_4$ in both the absence and presence (yields in parentheses) of DEM (eq 7).¹



This system is particularly well suited for the test of ambident behavior of diazoalkane anion radicals since (a) the fluorenylidene ring should stabilize the negative charge of the anion radical and (b) its planar structure should permit ready access of C_9 to proton donors and other potential reactants. The data show that while DEM is capable of capturing FIN_2^- by protonation at N_β , no increase in the yield of FIH_2 results from reaction with the proton donor. The failure to observe protonation at C_9 in the presence of DEM not only means that FIN_2^- does not react as an ambident base, but it strongly suggests that more sterically hindered diazoalkane anion radicals, e.g., Ph_2CN_2^- , also do not react with DEM at the central carbon. If Ph_2CN_2^- were to react as an ambident base, we would expect the $\text{Ph}_2\text{CH}_2/\text{Ph}_2\text{C}=\text{NNH}_2$ product to be independent of the proton donor concentration and nearly independent of the temperature. However, the data show that a significant decrease in the $\text{Ph}_2\text{CH}_2/\text{Ph}_2\text{C}=\text{NNH}_2$ ratio occurs when either the concentration of the proton donor is increased or the temperature is lowered from 22 to 0 °C (runs 6–9). Therefore, we conclude that Ph_2CN_2^- reacts principally, if not exclusively, at N_β . Since proton-transfer processes generally involve lower activation barriers than most other reactions, i.e., hydrogen atom abstractions, this conclusion bears on the general reactivity of Ph_2CN_2^- . Specifically, our results require that an alternate pathway to that described in eq 6 must exist for the formation of Ph_2CH_2 .

The Intermediacy of Ph_2C^- in Ph_2CH_2 Formation. We believe that the most plausible route for formation of Ph_2CH_2 in the absence and presence of proton donors involves the carbene anion radical, Ph_2C^- (eq 8 and 9). If the solvent–electrolyte derived



radical, S^\bullet , is reduced, both reactions (eq 8 and 9) formally involve two electrons and two protons. Although our data do not allow us to distinguish between these pathways, we favor hydrogen atom abstraction by (eq 8) and protonation of Ph_2C^- (eq 9) in the absence and presence of added or generated proton donors, respectively. The formation of carbene anion radicals from diazoalkanes has ample precedent in the gas phase (generated by dissociative electron attachment to both diazomethane^{4a} and diazocyclopentadiene⁵) and in solution (electroreduction of diazotetracyanocyclopentadiene⁷).

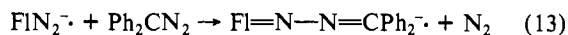
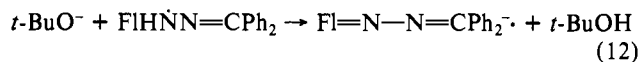
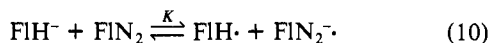
The rate of nitrogen loss from Ph_2CN_2^- to give Ph_2C^- was shown above to occur rapidly on the cyclic voltammetric time scale, even at scan rates as large as 100 V/s. Although these cyclic voltammetric data require only that the first-order rate constant for decomposition exceed 10^3 s^{-1} , the results from proton donor studies indicate that this rate constant is several orders of magnitude larger. The failure to capture all Ph_2CN_2^- as $\text{Ph}_2\text{C}=\text{NNH}_2$ when the electrolyses are conducted in the presence of a large amount of proton donor requires that the rates of protonation and loss of nitrogen be comparable. If the protonation reaction is diffusion controlled, then the rate constant for the loss of nitrogen from Ph_2CN_2^- must be 10^8 s^{-1} or larger. We conclude, therefore, that formation of Ph_2C^- from Ph_2CN_2^- most probably occurs in the electrical double layer.

As a possible test of this hypothesis, the reduction of Ph_2CN_2 was effected in the presence of guanidinium perchlorate (GP).¹⁴

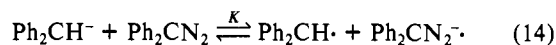
Since this positively charged proton donor should be incorporated preferentially into the electrical double layer, protonation of Ph_2CN_2^- should be facilitated relative to decomposition. Although the smallest value for the $\text{Ph}_2\text{CH}_2/\text{Ph}_2\text{C}=\text{NNH}_2$ product ratio is obtained when GP is present (run 11), we hasten to add that GP is also electroactive as the applied potential. The concomitant reduction of Ph_2CN_2 and GP will obviously cause an increase in the experimental n value and a corresponding decrease in GP concentration immediately adjacent to the electrode surface. Whether or not the product distribution is also affected cannot be tested directly. We note, however, that electroreduction of either benzoic acid or GP at a potential insufficiently negative to reduce Ph_2CN_2 causes no change in the concentration of Ph_2CN_2 .

Identification of Ph_2CH^- as the Principal Intermediate in Azine Formation. The cyclic voltammetric studies of Ph_2CN_2 at 0 °C demonstrated that Ph_2CH^- is the only oxidizable intermediate at scan rates in excess of 10 V/s. In addition, as the scan rate was decreased, the following sequence of kinetically linked intermediates was observed: $\text{Ph}_2\text{CH}^- \rightarrow \text{Ph}_2\text{C}=\text{NNCHPh}_2 \rightarrow (\text{Ph}_2\text{C}=\text{N}-)_2^{2-}$. These observations specifically require Ph_2CH^- , and exclude Ph_2CN_2^- , $\text{Ph}_2\text{C}=\text{NNH}^\bullet$, $\text{Ph}_2\text{C}=\text{NNH}^-$, $\text{Ph}_2\text{C}^\bullet$, and $\text{Ph}_2\text{CH}^\bullet$, as the principal species to react first with Ph_2CN_2 in the formation of the azine.

Coupling of Ph_2CH^- with Ph_2CN_2 . The reaction of carbanions with diazoalkanes to produce azines has been studied briefly by several groups.¹⁹ Although FIH^- does not react with Ph_2CN_2 alone, the addition of $\text{FI}=\text{N}^{15}\text{N}=\text{N}$ to a solution of FIH^- and Ph_2CN_2 was observed by Bethell and co-workers^{19a} to give a mixed azine, $\text{FI}=\text{N}-\text{N}=\text{CPh}_2$, in which partial incorporation of ¹⁵N (40%) occurred. These researchers suggested that azine formation must involve electron transfer from FIH^- to FIN_2 , followed by the addition of the free radical to unreacted diazoalkane (eq 10–13).

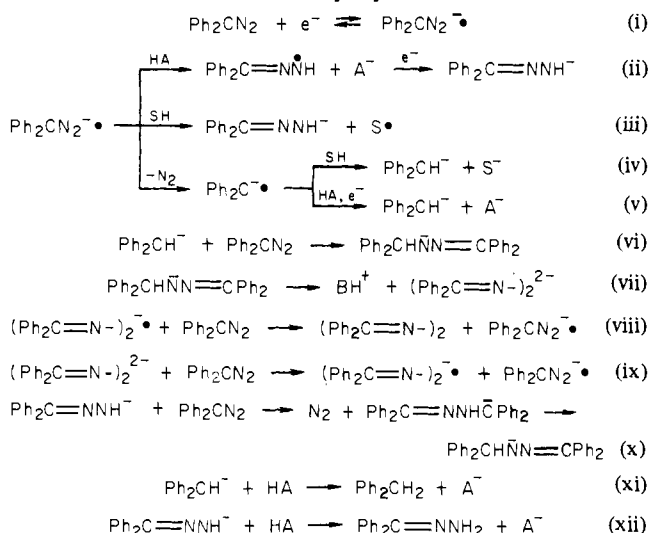


Our data indicate that electron transfer from Ph_2CH^- to Ph_2CN_2 is neither thermodynamically nor kinetically feasible. Although the effect of rapid, irreversible decomposition of Ph_2CN_2^- and uncompensated IR loss between the reference and working electrodes prevent the determination of the standard reduction potential of Ph_2CN_2 , rapid scan cyclic voltammetric studies (see Figure 1) show that E° for this process must be more negative than -1.2 V. Since the irreversible oxidation of Ph_2CH^- occurs at a potential more positive than -0.4 V (again, see Figure 1), an upper limit of 10^{-13} can be readily calculated for the value of the equilibrium constant for eq 14. If electron transfer in the



reverse direction, i.e., from diazoalkane anion radical to the alkyl radical, is then assumed to be diffusion controlled and approximately equal to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, an upper limit of $10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ is then estimated for the rate constant for electron transfer in the forward direction. This value is 6 orders of magnitude smaller than the rate constant of $10^3 \text{ M}^{-1} \text{ s}^{-1}$ which we estimate from cyclic voltammetric data for reaction of Ph_2CH^- with Ph_2CN_2 at room temperature.

Although the complexity of this electrode process prevents a more accurate determination of the value of the rate constant for the reaction of Ph_2CH^- and Ph_2CN_2 , our conclusion regarding the absence of initial electron transfer is supported by the results

Scheme I. Electroreduction of Ph_2CN_2^a 

^a B = $\text{Ph}_2\text{C}^\bullet$, Ph_2CN_2^- , $\text{Ph}_2\text{C}=\text{NNH}^\bullet$, and $\text{Ph}_2\text{CHNN}=\text{CPh}_2$. HA = $\text{Ph}_2\text{CHNN}=\text{CPh}_2$, $\text{Ph}_2\text{C}=\text{NNH}_2$, $(n\text{-Bu})_4\text{N}^+$, and added proton donor. e^- = electron from the electrode, $(\text{Ph}_2\text{C}=\text{N}-)_2^{2-}$, and/or $(\text{Ph}_2\text{C}=\text{N}-)_2^\bullet$. SH = solvent-supporting electrolyte acting as a hydrogen atom donor.

of the electrocatalytic studies. As we noted in the Results, the reduction of Ph_2CN_2 can be effected by electrogenerated reducing agents such as $(\text{Ph}_2\text{C}=\text{N}-)_2^-$ ($E_{\text{pa}} = -0.90$ V) and fluorenone azine dianion ($E_{\text{pa}} = -0.60$ V). Although the former species causes rapid reduction of Ph_2CN_2 , reduction of Ph_2CN_2 by electrogenerated fluorenone azine dianion occurs relatively slowly at a cyclic voltammetric scan rate of 0.2 V/s. Since the equilibrium constant, and, presumably, the rate constant, for electron transfer from Ph_2CH^- ($E_{\text{pa}} \geq -0.35$ V) to Ph_2CN_2 will be still smaller (eq 14), reaction as described by eq 14 does not appear feasible.

Propagation and Chain Termination Steps. The coupling of Ph_2CH^- with Ph_2CN_2 affords first the conjugate base of benzo-phenone benzhydrylhydrazone, $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ (Scheme I, eq vi); loss of a proton from this species to any of several electrogenerated bases, including $\text{Ph}_2\text{C}^\bullet$, then gives the azine dianion (eq vii). Since both $(\text{Ph}_2\text{C}=\text{N}-)_2^{2-}$ and $(\text{Ph}_2\text{C}=\text{N}-)_2^\bullet$ are capable of reducing Ph_2CN_2 and Ph_2CH^- (eq viii and ix), a chain reaction ensues in which Ph_2CH^- is the principal chain-carrying species (see Scheme I).

Termination of the chain occurs upon protonation of Ph_2CH^- (eq xi). Since Ph_2CH_2 is formally a two-electron reduction product of Ph_2CN_2 and the yields of $\text{Ph}_2\text{C}=\text{NNH}_2$ and $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ are negligibly small, the experimental n value should be approximately 2 times the fraction of the Ph_2CH_2 yield. Although the measured n value is usually several times the calculated value, we emphasize that the absolute error in n is generally less than 0.25 electron per molecule of Ph_2CN_2 . Since no attempt was made to correct for the small amount of background or for the reduction of the principal product, $(\text{Ph}_2\text{C}=\text{N}-)_2$, at the applied potential, this accuracy is considered acceptable.

Other Azine-Producing Reaction Channels. The results of gas-phase studies⁵ and studies herein show that both $\text{R}_2\text{C}^\bullet$ and $\text{R}_2\text{C}=\text{NNH}^\bullet$ (eq x) can couple with R_2CN_2 to form the corresponding azine. Although chain reactions can be written for each of these processes, the contributions from these pathways must be small compared to that from Ph_2CH^- . The failure of $\text{Ph}_2\text{C}=\text{NNH}^\bullet$ to propagate the chain reaction is consistent with the inability of proton donors to capture all Ph_2CN_2^- as $\text{Ph}_2\text{C}=\text{NNH}_2$. On the basis of studies involving DEM, TFE, and GP as proton donors, we have concluded that the rates of protonation and decomposition of Ph_2CN_2^- are comparable and that these reactions are so rapid that they most likely occur in the electrical double layer. The fact that the formation of Ph_2CH^- precedes the formation of $\text{Ph}_2\text{CHNN}=\text{CPh}_2$ and azine then requires more rapid reaction of $\text{Ph}_2\text{C}^\bullet$ with proton and hydrogen atom donors than with Ph_2CN_2 .

(19) (a) Bakke, J. M.; Bethell, D.; Galsworthy, P. J.; Handoo, K. L.; Jackson, D. J. *Chem. Soc., Chem. Commun.* 1979, 890. (b) McDonald, R. N.; Lin, K.-W. *J. Am. Chem. Soc.* 1978, 100, 8028. (c) Beringer, F. M.; Farr, J. A.; Sands, S. *Ibid.* 1953, 75, 3984.

Conclusions

Electrochemical studies of Ph_2CN_2 in the presence and absence of proton donors in DMF at room and reduced (0°C) temperatures have shown that (1) although $\text{Ph}_2\text{CN}_2^{\cdot-}$ is very short-lived, its lifetime is sufficient to be partially trapped by proton donors to give $\text{Ph}_2\text{C}=\text{NNH}_2$, (2) protonation of $\text{Ph}_2\text{CN}_2^{\cdot-}$ occurs only on terminal nitrogen, thereby precluding "ambident" behavior of this species in this and other reactions, (3) the carbene anion radical, $\text{Ph}_2\text{C}^{\cdot-}$, is formed by loss of nitrogen from $\text{Ph}_2\text{CN}_2^{\cdot-}$ and is the principal, if not the only, precursor to $\text{Ph}_2\text{CH}^{\cdot-}$, (4) the coupling of $\text{Ph}_2\text{CH}^{\cdot-}$ with unreacted Ph_2CN_2 cannot involve initial electron transfer followed by coupling of $\text{Ph}_2\text{CH}^{\cdot-}$ with Ph_2CN_2 , (5) $\text{Ph}_2\text{CH}^{\cdot-}$ is the principal chain-carrying species in the formation of benzophenone azine, and (6) $\text{Ph}_2\text{C}=\text{NNH}^{\cdot-}$ also initiates azine formation, but the extent of reaction by this chain process is minor compared to that of $\text{Ph}_2\text{CH}^{\cdot-}$.

Experimental Section

Electrochemical Instrumentation, Cells, Electrodes, and Electrolysis Procedures. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.²⁰ Control of the potentiostat and the acquisition and processing of chronoamperometric data were performed with a laboratory computer (LAB 8/e, Digital Equipment Corp.).

All electrochemical experiments were performed on an all-glass vacuum line. The solvent, dimethylformamide, was transferred into the cell on the vacuum line by trap-to-trap distillation. All potentials listed are with respect to a cadmium amalgam which is in contact with an anhydrous dimethylformamide solution that is saturated with both sodium chloride and cadmium chloride (Type A-III).²¹ The potential of this electrode is -0.75 V vs. SCE. The surface on all working electrodes was platinum; the area of the planar button electrode which was used in all chronoamperometric and most cyclic voltammetric experiments was 0.25 cm^2 .

The extent of large-scale electrolyses was monitored periodically by cyclic voltammetry. At the conclusion of the experiment, the electrolysis mixture was either oxidized at a potential which would oxidize all anions and anion radicals that had been produced or protonated in a dry helium atmosphere with an appropriate proton donor (e.g., DEM). The mixtures were then analyzed directly by high-performance liquid chromatography.

Chromatography. The products of the electrolyzed solutions were separated by high-performance LC by using a 6.35-mm diameter, 25-cm length stainless-steel column packed with LiChrosorb RP8, $10\text{-}\mu\text{m}$ mean particle size. The eluting solvent was 80/20 methanol/water; the flow

rate was 1 mL/min . The detector was a Schoeffel Instrument Corp. Model SF-770 UV-vis spectrophotometer; the wavelength used in these analyses was 254 nm . Calibration curves for standards of all products were constructed daily.

Chemicals. Dimethylformamide (Burdick and Jackson) was purified by passage through a column of alumina (80–200 mesh, Brockman activity 1, activated at 600°C overnight) and was collected over a mixture of activated Davison 4A molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag.

Diphenylmethane (Matheson, Coleman and Bell) was vacuum distilled with the purity being checked chromatographically (GC and high-performance LC). Diazodiphenylmethane,²² benzophenone azine,²³ benzophenone hydrazone,²⁴ and fluorenone azine²⁵ were synthesized according to known procedures. Several recrystallizations were performed until sharp melting points were obtained. All other compounds were commercially available. Purities were verified chromatographically (GC and/or high-performance LC) and spectroscopically.

Benzophenone benzhydrylhydrazone was prepared by the electrochemical reduction of benzophenone azine (1.63 g , 4.53 mmol) in 40 mL of $0.1\text{ F Et}_4\text{NClO}_4\text{-DMF}$ in the presence of diethyl malonate (3.11 g , 19.5 mmol). The reduction was performed at -0.75 V and 25°C ; the electrolysis was terminated ($Q = 940\text{ coulombs}$, $n = 2.2$) when the azine had been fully consumed, as determined by cyclic voltammetry. Upon completion of the electrolysis, the DMF was removed under vacuum. The resultant residue was dissolved in hot absolute methanol. When the solution was cooled to 0°C , the benzophenone benzhydrylhydrazone slowly crystallized. A second recrystallization from absolute methanol gave white crystals: 1.46 g , 89% yield; mp $90.5\text{--}91^\circ\text{C}$, reported mp 91°C .²⁵ The ^{13}C NMR and UV-vis absorption spectra confirm that this compound is benzophenone benzhydrylhydrazone and not the isomeric azo compound. The purity was verified by high-performance LC.

Reaction of $\text{Ph}_2\text{C}=\text{NNH}^{\cdot-}$ with Ph_2CN_2 . The conjugate base of benzophenone hydrazone, $\text{Ph}_2\text{C}=\text{NNH}^{\cdot-}$, was generated in situ in DMF- 0.1 F ($n\text{-Bu}$)₄ NClO_4 by the addition of a slight excess of Me_4NOH ($270\text{ }\mu\text{mol}$) to $\text{Ph}_2\text{C}=\text{NNH}_2$ ($238\text{ }\mu\text{mol}$). Addition of Ph_2CN_2 ($234\text{ }\mu\text{mol}$) to this mixture resulted in the immediate evolution of nitrogen and the appearance of the distinctive purple color of the azine anion radical. After acidification with DEM, three major products were identified and quantitated by high-performance LC: $(\text{Ph}_2\text{C}=\text{N})_2$ ($115\text{ }\mu\text{mol}$), $\text{Ph}_2\text{C}=\text{NNH}_2$ ($181\text{ }\mu\text{mol}$), and Ph_2CH_2 ($55\text{ }\mu\text{mol}$).

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged. F.M.T. is the recipient of the Phillip's Petroleum Fellowship for the 1979–1980 academic year.

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