Table I. ^{13}C NMR Resonances of the Diazo Carbons of **3** and **6**

R	**3**, δ^a (J_{CP})	**6**, δ^b (J_{CP})
a, Et_2NSO_2	60.9 (152 Hz)	59.4 (216 Hz)
b, *i*-Pr_2O_3P	37.9 (147, 200 Hz)0137.6 (204 Hz)	
c, Me_2NCO	55.0 (165 Hz)	49.7 (220 Hz)

[a] In D_2O, pH > 9, dioxane as internal reference (δ 66.5). [b] In $CDCl_3$, referenced to $CDCl_3$ as δ 77.0.

Table II. λ_{max} (log ϵ) of Diazo Derivatives

R	**6**^{a}	**3**^{b}	**10**^{b}
a, Et_2NSO_2	227 (3.85)	233 (3.85)	226 (3.93)
	373 (1.65)	393 (1.64)	390 (1.78)
b, (*i*-PrO)$_2$PO	227 (3.83)	238 (3.85)	225 (4.09)^c
	337 (1.08)	367 (1.71)	365 (1.14)^c
c, Me_2NCO	244 (3.86)	263 (4.17)	254 (4.35)
	357 (1.58)	381 (1.81)	376 (1.36)

[a] Spectra run in H_2O. [b] Spectra run in 0.2 M phosphate buffer, pH 9. [c] Log ϵ for the dimethyl ester.

Table III. Half-Lives for the Decomposition of **3** → **9** at 21-22 °C

Derivative	pH^a	$t_{1/2}$
a, R = Et_2NSO_2	6.0	5 h
	7.5	>5 days
b, R = (*i*-PrO)$_2$PO	6.0	20 h
	7.5	>5 days
c, R = Me_2NCO	7.5	<5 min^b
	9.0	40 min

[a] 0.2 M potassium phosphate. [b] $t_{1/2}$ = 3 min in 0.01 M potassium phosphate, pH 7.5.

by TLC, UV, and by its rate of decomposition at pH 6.0. The UV spectrum of the compound extracted from the decomposition of **3b** was very similar to that of authentic dimethyl diazomethylphosphonate.[10a] Although an authentic sample of *N,N*-diethyldiazomethanesulfonamide (**10a**) prepared by another method was not available for comparison, the IR and UV spectra of the material extracted from the decomposition of **3** were fully consistent with the assigned structure. Decomposition of the monomethyl ester of diazomalonic acid occurs similarly at pH > 3, with loss of CO_2 and formation of ethyl diazoacetate.[15b] In the decomposition of **3a**-**3c**, loss of metaphosphate from the diazonium zwitterion **9** is strictly analogous. We have not attempted to determine the structure of the final, UV-inactive products.

The half-lives for the decomposition of the diazophosphonic acids via loss of phosphate are indicated in Table III. Both the sulfamoyl- and phosphono-stabilized diazomethylphosphonic acids are moderately stable even at pH 6.0, and exceedingly stable at pH 7.5. In this respect they are the first examples of this class of compounds to show real promise as photoaffinity labeling groups. Their stability is in marked contrast to that of the carbamoyl derivative **3c** and the α-diazobenzylphosphonate dianion.[9] The latter compounds decompose within minutes at neutral pH in buffers commonly employed for biochemical work, and could be applied only to protein systems which have sufficient stability at much higher pH.

The relative instability of carbonyl- and phenyl-stabilized compounds would be a definite limitation for the design of possible photoaffinity labels incorporating the α-diazophosphonic acid moiety. Nonetheless, a variety of useful compounds based on sulfonyl- and phosphono-stabilized structures can still be envisaged. We are currently investigating the photochemistry of compounds **3a** and **3b** as further evaluation of their potential for photoaffinity labeling.

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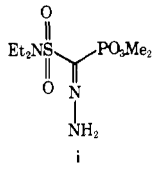
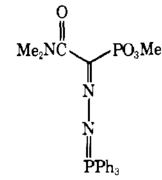
(11) Satisfactory microanalysis and spectral data were obtained for this compound.

(12) The diazo esters **6** were all oily materials. Treatment of **6a** with Ph_3P followed by chromatography and concomitant hydrolysis on silica gel afforded a crystalline hydrazone (i),[11] mp 83-84 °C (*i*-Pr_2O). Treatment of **6b** with Ph_3P afforded a crystalline phosphazene (ii),[11] mp 155-157 °C dec (ethanol/*i*-Pr_2O). A crystalline derivative of **6b** was not obtained, but the ^{1}H NMR, ^{13}C NMR, IR, and UV spectral properties were in complete accord with the assigned structure, as was the exact mass spectral determination (found: *m/e* 314.0791).


i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Paul A. Bartlett,* Karen P. Long
Department of Chemistry, University of California
Berkeley, California 94720

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Hypovalent Radicals.[1] 1. Electrochemical Generation of Diphenylcarbene Anion Radical

Sir:

Nine possible substituted carbon molecular fragments, either neutral or bearing unit charge, may be derived from tetracovalent carbon species, R_4C, by stepwise loss of R:$^-$, R·, or

Table I. Coulometric Data and Product Analysis for Controlled Potential Reduction of Diphenyldiazomethane[a]

Run no.	[Ph_2CN_2], mM (**1**)	Applied potential, V	*n* value[d]	Products, % yield[b,c] Ph_2CH_2 (**6**)	$Ph_2C{=}NN{=}CPh_2$ (**5**)	Ph_2CHNH_2 (**9**)
1	2.20	−1.6 to −1.8	0.5	6 (7)	64 (76)	4 (5)
2	1.37	−1.7 to −1.8	0.6	11 (13)	50 (60)	7 (8)
3	1.32	−1.68	1.16	33 (40)	44 (52)	10 (12)
4	1.20	−1.94	1.50	42 (51)	21 (24)	9 (11)
5	0.72	−2.0 to −2.2	2.0	41 (49)	18 (21)	6 (7)
6	4.70	−1.75	0.25	3 (4)	69 (82)	6 (7)
7	4.43	−1.68	0.5	11 (13)	66 (79)	5 (6)
8	4.18	−1.68	1.0	19 (23)	50 (59)	8 (10)
9	4.79	−1.68	1.0	28 (34)	56 (67)	6 (8)
10	5.15	−1.94	1.0	40 (49)	36 (43)	9 (11)

[a] Controlled potential electrolyses were performed in DMF with 0.1 M $(n\text{-Bu})_4N^+ClO_4^-$ as the supporting electrolyte; working electrode, Pt gauze; reference electrode, SCE. [b] Typical recoveries of the above products from known mixtures were 83 ± 3% **6**, 84 ± 6% **5**, and 83 ± 3% **9**. $(n\text{-Bu})_3N$, the product resulting from proton abstraction from the supporting electrolyte, was the only other product detected in substantial amount. Yields in () were obtained by dividing the absolute yields by the recovery factor. [c] Tetraphenylethane and tetraphenylethene were found only in trace amounts (<0.5%). [d] Controlled potential electrolyses were terminated arbitrarily at this point. Azine **5** is electroactive at the applied potential.

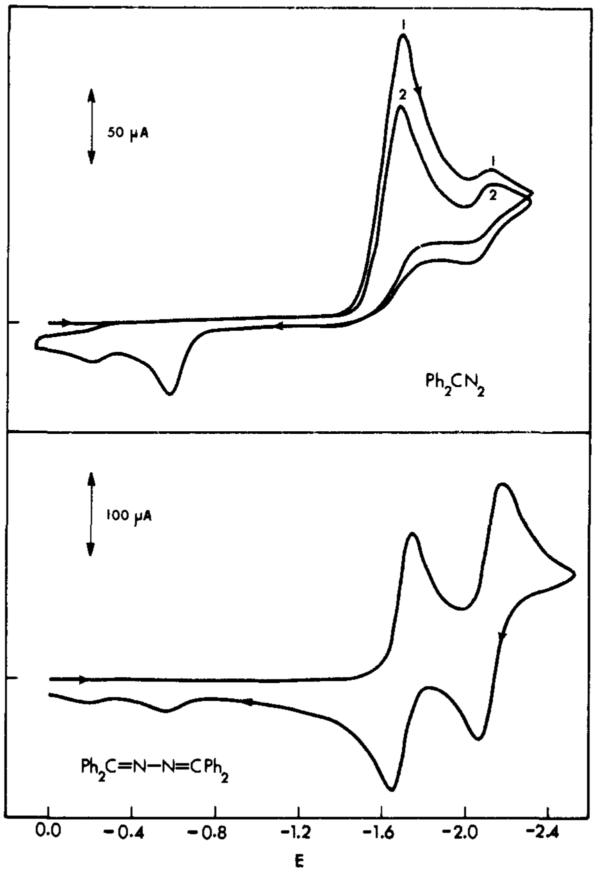

Figure 1. Scan rate, 0.2 V/s; working electrode, 0.25 cm^2 planar platinum button; reference electrode, aqueous, saturated calomel electrode; supporting electrolyte-solvent system, 0.1 M $Et_4N^+ClO_4^-$-DMF: (upper) 2.66×10^{-3} M **1** (numbers 1 and 2 denote first and second cycles, respectively); (lower) 3.10×10^{-3} M **5**.

R^+ units. Of these, only four ($R_3C{:}^-$, $R_3C\cdot$, R_3C^+, and $R_2C{:}$) have received much attention by chemists in condensed and gas phase experiments. As our first report on the synthesis and chemistry of the five remaining carbon fragments (hypovalent radicals),[1] we wish to describe our preliminary results on the formation and certain reactions of diphenylcarbene anion radical (**3**).

Our approach to the synthesis of **3**[2-4] was electrochemical reduction of diphenyldiazomethane (**1**) in DMF solution. The cyclic voltammetric behavior of **1** is illustrated in Figure 1. We attribute the principal redox process near −1.68 V to the chemically irreversible reduction of **1** to its radical anion **2**. Since no anodic wave was seen for the reoxidation of **2** at scan rates up to 100 V/s, a lower limit of 10^3 s^{-1} can be assigned to its unimolecular decomposition rate constant. The relatively small size of the reversible couple near −2.14 V indicates that the species responsible for this process is only a minor product in the cyclic voltammetric reduction of **1**. The material was identified by both electrochemical and chromatographic methods to be benzophenoneazine (**5**), a compound which is reduced reversibly first to its radical anion, **4**, at −1.68 V, and then to its dianion, **6**, at −2.12 V (Figure 1). Because **5** is formed in relatively low yield under these conditions, the **5**/**4** redox couple near −1.68 V is masked by the much larger cathodic wave due to the reduction of **1**.[5]

The chronoamperometric $it^{1/2}/C$ value obtained for the reduction of **1** was diffusion controlled (1 ms < t < 3 s) at any potential in the range from −1.96 to −2.4 V (i.e., $E_{\text{applied}} \ll E_{\text{p,c}}$). From comparison of the experimental data with those from other known electrochemical systems, we conclude that one electron is transferred per molecule of **1**. In contrast, controlled potential electrolysis of **1** can give an *n* value which is substantially less than one (Table I)[6] In addition, we observed that the product yields were a function of *n* value and mass transfer rate (runs 1-5 and 6-8), concentration (runs 3 and 8), and applied potential (runs 9 and 10). The larger yields of azine **5** were obtained when electrolysis was effected near the half-wave potential ($E_{\text{p/2,c}} = -1.68$ V), whereas the larger yields of diphenylmethane (**6**) were obtained when electrolyses were conducted at a potential more negative than $E_{\text{p,c}}$. The third principal product obtained from these electrolyses, diphenylmethylamine (**9**), was found in separate controlled electrolysis experiments to be the final reduction product of **5**.[6] Neither **9** nor **6** is electroactive in this potential range. Only trace amounts of tetraphenylethene and tetraphenylethane were formed; these were detected by chromatographic methods.

We believe that these results are consistent with the radical chain process shown in Scheme I. Propagation of the chain involves coupling of the carbene anion radical **3** with diazoalkane **1** to give azine anion radical **4** (reaction 2), followed by electron transfer between **1** and **4** to produce azine **5** and **2** (reaction 3).[7] Loss of nitrogen from the latter species regenerates **3**, the chain-carrying species.

Termination of the chain occurs principally by reactions 5 and 6. When the concentration of **1** at the electrode surface is small, **3** abstracts a hydrogen atom from a component of the

Scheme I

Initiation

$$\underset{\mathbf{1}}{Ph_2CN_2} + e^- \longrightarrow \underset{\mathbf{2}}{[Ph_2CN_2]^{\cdot -}} \xrightarrow{\text{fast}} \underset{\mathbf{3}}{Ph_2C^{\cdot -}} + N_2 \qquad (1)$$

Propagation

$$\mathbf{1} + \mathbf{3} \longrightarrow \underset{\mathbf{4}}{[Ph_2C{=}NN{=}CPh_2]^-} \qquad (2)$$

$$\mathbf{4} + \mathbf{1} \overset{K<1}{\rightleftharpoons} \underset{\mathbf{5}}{Ph_2C{=}NN{=}CPh_2} + \mathbf{2} \qquad (3)$$

$$\mathbf{2} \xrightarrow{\text{fast}} \mathbf{3} + N_2 \qquad (4)$$

Termination

$$\text{I.}\quad \mathbf{3} + SH \longrightarrow Ph_2\bar{\ddot{C}}H + S\cdot \qquad (5)$$

$$Ph_2\bar{\ddot{C}}H + SH \longrightarrow \underset{\mathbf{6}}{Ph_2CH_2} + \bar{S}\!: \qquad (6)$$

$$\text{II.}\quad 24 \rightleftharpoons \mathbf{5} + \underset{\mathbf{7}}{[Ph_2C{=}NN{=}CPh_2]^{2-}} \qquad (7)$$

$$\mathbf{7} + 2H^+ \longrightarrow \underset{\mathbf{8}}{Ph_2C{=}NNHCHPh_2]} \qquad (8)$$

$$\mathbf{4} + H^+ \longrightarrow [Ph_2CHNN{=}CPh_2]\cdot \xrightarrow{e^-;\ H^+} \mathbf{8} \qquad (9)$$

$$\mathbf{8} + 4H^+ + 4e^- \longrightarrow \underset{\mathbf{9}}{2Ph_2CHNH_2} \qquad (10)$$

solvent-electrolyte system to give diphenylmethyl anion. Protonation of this anion then affords **6**.[9,10] A second, minor chain termination pathway is plausible when an appreciable concentration of **1** remains at the electrode surface (e.g., when the applied potential is more positive than $E_{p,c}$ for **1** during controlled potential electrolysis). Instead of reaction 3, **4** may either disproportionate and be protonated (reactions 7 and 8, or be protonated and further reduced (reaction 9).[10] Reduction of **8** occurs at the applied potential and affords **9** as product.[6,11,12]

We conclude that carbene anion radical **3** behaves primarily as a radical species in its reaction producing hydrocarbon **6**.[9] Likewise, dimerization of **3** is ruled out as an important reaction channel under the present conditions.[2b] Studies of solvent effects, structural changes in R of $R_2C^{\cdot -}$, radical vs. anion trapping experiments, and chemical generation of carbene anion radicals are in progress.

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References and Notes

(1) The term "hypovalent radicals" is used to describe a neutral or charged radical species containing *less* than the number of attached substituents found in the uncharged, free radical system normally associated with the central atom in the radical; e.g., triplet $H_2\dot{C}\cdot$ and $H\dot{C}$: are neutral carbon hypovalent radicals.

(2) (a) G. D. Sargent, C. M. Tatum, and S. M. Kastner, *J. Am. Chem. Soc.*, **94**, 7174 (1972), and (b) G. D. Sargent, C. M. Tatum, and R. P. Scott, *ibid.*, **96**, 1602 (1974), have reported that carbene anion radicals were produced by reduction of *gem*-dihalides with sodium naphthalene.

(3) T. Kauffmann and S. M. Hage, *Angew. Chem., Int. Ed. Engl.*, **2**, 156 (1963), reported that diazoalkane **1** was reduced to $[Ph_2CN_2]^{\cdot -}Na^+$ by sodium in ether.

(4) Reduction of CH_2N_2 in the gas phase has been shown to give $H_2C^{\cdot -}$; P. F. Zittel, G. B. Ellison, S. V. ONeil, E. Herbst, W. C. Lineberger, and W. P. Reinhardt, *J. Am. Chem. Soc.*, **98**, 3732 (1976).

(5) The anodic peaks near −0.6 and −0.2 V are also seen in the cyclic voltammogram of **4** (Figure 1 (lower)) and arise from decomposition products from the solvent-electrolyte system.

(6) Precise *n* values cannot be reported, since **5**, one of the principal products of the exhaustive reduction of **1**, is electroactive at the applied potential. Although the corresponding anion radical (**4**) appears to be stable on the cyclic voltammetric and chronoamperometric time scales, coulometric reduction of **5** at −1.94 V for 150 min results in the consumption of approximately four electrons per molecule of **5** and affords **9** in 51% yield. Twenty-three percent of **5** was recovered unchanged. The reaction pathway (reactions 7 and 8, Scheme I) proposed here for the reduction of **5** to **9** is identical with the route demonstrated by Lund for the reduction of the closely related benzalazine: H. Lund, *Acta Chem. Scand.*, **13**, 249 (1959). Alternatively, the formation of **8** may arise from **4** by a CEC process involving protonation, electron transfer, and further protonation (reaction 9).

(7) The effect of the rapid loss of nitrogen from anion radical **2** is to shift the peak reduction potential of **1** in the positive direction. Since the magnitude of this shift is 30 mV per tenfold increase in the decomposition rate constant, $E^0{}_{1/2}$ is at least 0.1 V more negative than $E^0{}_{5/4}$ ($k_{\text{minimum}} = 10^3$ s^{-1}).[8]

(8) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(9) The sequence of carbene anion radical **3** acquiring H and H^+ to yield **6** remains unknown. However, if the sequence were **3** + $H^+ \rightarrow Ph_2\dot{C}H$, we would expect dimerization and/or reduction of the benzhydryl radical. The former pathway would give tetraphenylethane (trace amount observed), while the latter process should give **6** in an overall two-electron process. Neither prediction is observed electrochemically.

(10) The fate of solvent-electrolyte derived radicals (S·) and anions ($S:^-$) in Scheme I has not been investigated. $(n\text{-Bu})_3N$ was observed in all electrolyses using $(n\text{-Bu})_4N^+ClO_4^-$ as the electrolyte. The amine was probably formed by a Hofmann-type elimination from the quaternary salt.

(11) The redox behavior of **1** has been examined previously by electrochemical methods. Elofson et al.[12] report that reduction of **1** in sulfolane produces a 40% yield of **6**, a 20% yield of **9**, and nitrogen. The decomposition of **2** was suggested to occur by protonation to give $Ph_2CHN_2\cdot$, which then either loses nitrogen to give benzhydryl radical and ultimately **6**, or couples with benzhydryl radical to give azodiphenylmethane. Reduction of this azo compound (see ref 6, however) was postulated to give amine **9**.

(12) R. M. Elofson, F. F. Gadallah, A. A. Cantu, and K. F. Schulz, *Can. J. Chem.*, **52**, 2430 (1974).

Richard N. McDonald,* J. R. January
K. J. Borhani, M. Dale Hawley*
Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

Received September 17, 1976

Silica Gel-Catalyzed Rearrangement of an Endoperoxide to a 1,2-Dioxetane

Sir:

Singlet molecular oxygen undergoes 1,2-cycloaddition to vinyl ethers, vinyl sulfides, enamines, and tetraalkyl-substituted olefins to yield 1,2-dioxetanes.[1] The chemiluminescent decomposition of 1,2-dioxetanes has been the subject of considerable study recently.[2] We now describe the silica gel-catalyzed rearrangement of an isolable endoperoxide to a 1,2-dioxetane in quantitative yield. The use of a heterogeneous catalyst for the rearrangement facilitates the separation of the catalyst from the sensitive 1,2-dioxetane. The endoperoxide is obtained via the Diels-Alder reaction of singlet oxygen with a vinyl-substituted anthracene, in which the aromatic system functions as part of the diene.

2-(2′-Anthryl)-1,4-dioxene (**1**)[3] was photooxygenated at −78 °C in CH_2Cl_2 using polymer-bound rose bengal[4] as sensitizer with two 500-W tungsten-halogen lamps and a UV-cutoff filter. ^1H NMR analysis of the reaction solution indicated a mixture of endoperoxide **2** (31%), 1,2-dioxetane **3** (16%), diester **4** (23%), and unknown material (30%).[5] Column chromatography of this mixture on silica gel with $CHCl_3$ at ambient temperature resulted in an intense bluish chemiluminescence with subsequent isolation of only **4**[6] in 70% yield. However, chromatography of the reaction mixture at −55 °C followed by recrystallization from cold $CHCl_3$–pentane gave pure **2** as a pale yellow solid in 26% yield: mp 141–142 °C dec; UV (*o*-xylene) λ_{max} (log ϵ) 327 nm (4.38); ^1H NMR (100 MHz, C_6D_6) δ 3.36 (m, 4 H, $(CH_2)_2$), 5.27 (s, 1 H, H_1), 6.28 (AB d, 1 H, J = 10 Hz, H_2 or H_3), 6.43 (s, 1 H, H_4), 6.71 (AB d, J = 10 Hz, 1 H, H_3 or H_2), 7.12 (m, 3 H, aromatic), 7.43 (m, 2 H, aromatic), and 7.93 (s, 1 H, aromatic); satisfactory analysis. Endoperoxides analogous to **2** have also been obtained