Scheme I

Initiation

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

Propagation

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

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

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

Termination

I.

$$3 + SH \longrightarrow Ph_2\ddot{C}H + S\cdot \quad (5)$$

$$Ph_2\ddot{C}H + SH \longrightarrow Ph_2CH_2 + \bar{S}\cdot \quad (6)$$

II.

$$24 \rightleftarrows 5 + \underset{\mathbf{7}}{[Ph_2C{=}NN{=}CPh_2]^{2-}} \quad (7)$$

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

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

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

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.

Acknowledgments. This research was supported by the National Science Foundation (MPS-7502795 and CHE-76-01410). The assistance of K. L. Guyer and M. Asirvatham in several phases of the analytical work is gratefully acknowledged.

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 $E^0_{5/4}$ ($k_{minimum} = 10^3$ 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*-Bu)$_3$N was observed in all electrolyses using (*n*-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 $Ph_2CHN_2^+$, 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**.

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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

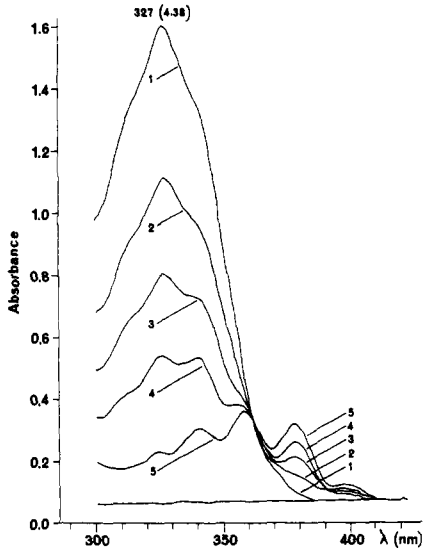
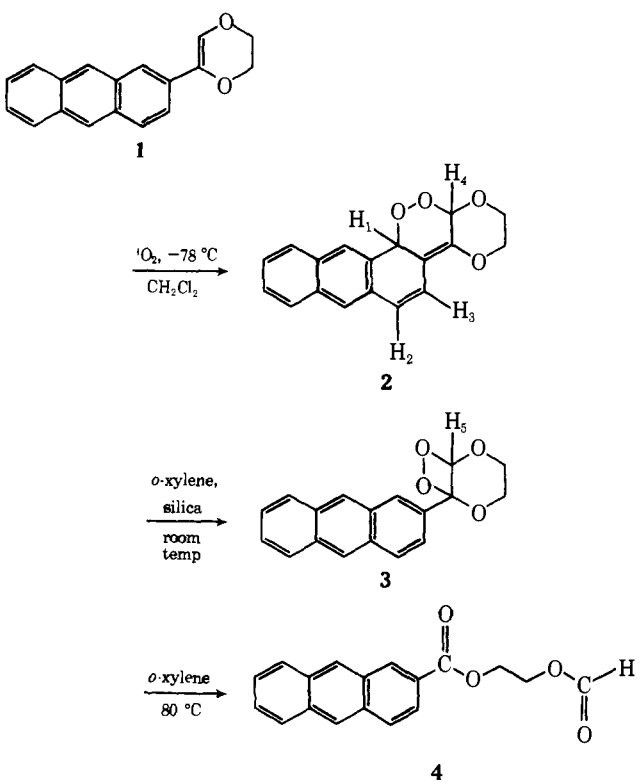


Figure 1. UV spectra of solutions of **2** in *o*-xylene (2.5 mL, 6.4×10^{-5} M) treated with silica gel and filtered. Curve 1 represents the initial solution. Curves 2–5 were obtained after stirring with silica gel for 0.2 (curve 2), 0.5 (curve 3), 1.0 (curve 4), and 2.0 (curve 5) min.



from the photooxygenation of 1,1-diphenyl-2-methoxyethylene,[7] 1-vinylnaphthalenes,[8] and 2-vinylthiophenes.[9]

Various endoperoxides have been found to undergo acid-catalyzed decomposition to carbonyl cleavage products, presumably via 1,2-dioxetane intermediates.[10] An investigation by Wilson[11] of the chemiluminescence which accompanies the acid-catalyzed decomposition of the endoperoxide of 1,4-dimethoxy-9,10-diphenylanthracene has provided indirect evidence for the intermediacy of a 1,2-dioxetane in that reaction.[12] LeRoux and Goasdoue[13] have recently prepared 1,2-dioxetanes from the acid-catalyzed rearrangement of polyarylfulvene endoperoxides. However, as 1,2-dioxetanes are readily cleaved by acids (Brönsted[14] and Lewis[15]), spectroscopic identification and/or isolation of intermediate 1,2-dioxetanes formed by the rearrangement of endoperoxides has not been possible in most cases. In contrast, we now describe the quantitative rearrangement of endoperoxide **2** to 1,2-dioxetane **3** at ambient temperature upon treatment with silica gel. The decomposition of **3** at 80 °C is attended by chemiluminescence and yields only the expected cleavage product **4**.

Shaking 1 mL of a 7.5×10^{-3} M solution of endoperoxide **2** in benzene-d_6 with 41 mg of silica gel (Baker, 60–200 mesh) for 4 min followed by filtration gave a solution containing the 1,2-dioxetane **3** as evidenced by absorptions in the ^{1}H NMR spectrum at δ 3.54 (m, 2 H, CHCH), 4.10 (m, 1 H, methylene CH), 4.59 (m, 1 H, methylene CH), 5.96 (s, 1 H, H_5), 7.20 (m, 2 H, aromatic), 7.80 (m, 4 H, aromatic), 8.09 (s, 2 H, aromatic), and 8.46 (s, 1 H, aromatic). After heating for 60 min at 80 °C, the solution exhibited only absorptions of **4**.[6]

The silica gel-catalyzed rearrangement of **2** to **3** is conveniently monitored by UV spectroscopy (Figure 1). Solutions of **2** (2.5 mL, 6.4×10^{-5} M) in *o*-xylene were stirred with 100 mg of silica gel (Baker, 60–200 mesh) for various times and filtered. The half-life for the rearrangement of **2** to **3** under these conditions was approximately 30 s. The final solution (Figure 1, curve 5) contained essentially pure 1,2-dioxetane **3**.[16] An isosbestic point for the conversion of **2** to **3** was observed at 363 nm. On heating solution 5, the UV spectrum changed to that of **4**.[6]

Thermolysis of endoperoxides generally results in either the evolution of singlet oxygen with concomitant regeneration of the aromatic hydrocarbon[17] or the resrrangement of the endoperoxide to a bisepoxide.[18] However, heating **2** in *o*-xylene at 80 °C for 12 h gave **4** quantitatively. The thermal rearrangement of **2** to **4** also contrasts with the spontaneous rearomatization of a structurally similar endoperoxide prepared by Foote and co-workers from 1,1-diphenyl-2-methoxyethylene.[7] Although only **2** and **4** were detectable by ^{1}H NMR, the thermolysis of **2** was accompanied by chemiluminescence with a kinetic form indicating the slow buildup of a light-producing intermediate.[19] The chemiexcitation quantum yield (singlet excited **4**) for the thermolysis of **2** at 80 °C was determined to be 0.8%; the value for solutions containing only 1,2-dioxetane **3** was 0.9%. Therefore, the thermal rearrangement of **2** to **4** involves **3** as the major, if not the only, intermediate with no alternate, nonluminescent pathway.

We had observed that protracted contact of 1,2-dioxetane **3** with silica gel resulted in decomposition to **4**. Subsequent investigations have shown that silica gel also catalyzes the cleavage of **3** to **4** at ambient temperature. However, in contrast to the nonluminescent, catalyzed decomposition of 1,2-dioxetanes with transition metals,[20] amines,[21] and electron-rich olefins,[21] the conversion of **3** to **4** in the presence of silica gel is accompanied by a greatly enhanced chemiexcitation quantum yield. These results will be described shortly.

In summary, we have found that silica gel can be used to advantage as a heterogeneous catalyst for the rearrangement of an endoperoxide to a 1,2-dioxetane. The relatively unstable 1,2-dioxetane **3** can be "stored" as **2** and generated when needed. This system therefore has the potential for a practical chemical light source. Studies of the rearrangement of endoperoxides with various heterogeneous catalysts are in progress.

Acknowledgment. Support from the U.S. Army Research Office-Durham and the National Science Foundation is gratefully acknowledged. We also thank Dr. Michael Albright for his assistance in obtaining the ^{1}H NMR spectra.

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(5) Whether the formation of **3** and **4** is the result of 1,2-cycloaddition of $^1O_2$ to **1** or of rearrangement of **2** to **3** under the reaction conditions is still under investigation.
(6) Yellow solid; mp 137–139 °C; UV (*o*-xylene) λ_{max} (log ϵ) 325 (3.39), 340 (3.61), 358 (3.68), 378 (3.69), and 398 nm (3.67); IR (KBr) 1701 and 1719 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 4.71 (s, 4 H, $(CH_2)_2$), 7.63 (m, 2 H, aromatic), 8.16 (m, 4 H, aromatic), 8.32 (s, 1 H, CHO), 8.54 (s, 1 H, aromatic), 8.67 (s, 1 H, aromatic), and 8.94 (s, 1 H, aromatic); satisfactory analysis.
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(16) The UV spectrum of **3** is identical with that of 2-methylanthracene.
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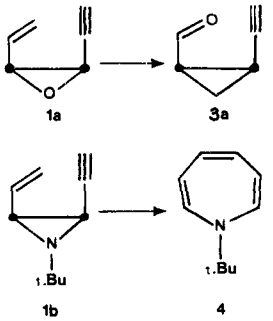
A New Valence Tautomerism: Thermal Rearrangement of *cis*-2-Vinyl-3-ethynyl Three-Membered Heterocycles

Sir:

In recent years, there has been a considerable interest in the Cope rearrangement of 2,3-divinyl[1] and 2,3-diethynyl[2] three-membered rings. Our continuing interest in the thermolytic behavior of 1,5-enynes[3a,b] and the recently published rearrangement of *cis*-1-ethynyl-2-vinylcyclopropane,[3c] prompt us to report on our study of the valence isomerization of *cis*-1-ethynyl-2-vinyloxirane (**1a**) and *cis*-*N*-*tert*-butyl-2-ethynyl-3-vinylaziridine (**1b**).

The desired starting material **1a** was prepared by treatment of 3,4-dihydroxy-1,5-hexenyne[4] (erythro + threo) with 2 equiv of sodium hydride, and 1 equiv of *p*-toluenesulfonyl chloride in ether. A mixture of *cis*- and *trans*-**1a** was obtained (52% yield, cis:trans 1:0.7) and separated by preparative vapor phase chromatography. Deuterated **1c** was prepared by stirring **1a** with BaO in a large excess of D_2O.[5] Aziridine **1b** was prepared conveniently by aminolysis of *cis*-**1a** (46% yield), followed by cyclization of the intermediate threo amino alcohol[6] with Ph_3PCl_2 at room temperature[7] (31% yield). The structures of **1a,b** were established by NMR spectroscopy.[8]

Scheme I



Thermal rearrangements were conducted in sealed tubes in inert solvents (C_6H_6, CCl_4) over the temperature range 80–130 °C. These reactions gave rise to a single product: *cis*-1-carboxaldehyde-2-ethynylcyclopropane (**3a**) and *N*-*tert*-butyl-1*H*-azepine (**4**), respectively, from *cis*-**1a** and *cis*-**1b**. The structure of *cis*-**3a** was established by its straightforward spectral characteristics: ^1H NMR (60 MHz, C_6H_6, δ_{Me_4Si}) O═^{5}—^{4}∇$_6$^{3}—^{2}≡^{1} 9.22 (m, 1 H, H_5), 2.02 (d, 1 H, J = 1.6 Hz, H_1), 1.85–1.50 (m, 2 H, H_4 and H_3) 1.46–0.8 (m, 2 H, H_6); ^{13}C NMR (15.08 MHz, $CDCl_3$, δ_{Me_4Si}) 69.1 (d, C_1), 81.0 (d, C_2), 8.7 (d, C_3), 27.7 (d, C_4), 200.7 (d, C_5), 14.4 (t, C_6); IR ($CHCl_3$, cm^{-1}), 3200, 2100, 1705; MS (70 eV, *m/e*, rel intensity %) 94 (M^+, 5), 65 (100), as well as by its facile conversion to *trans*-**3a**[9] by thermolysis in a flow system[10] at 350 °C.

The structural assignment of **4** was based on its ^1H NMR spectrum (60 MHz, CCl_4, δ_{Me_4Si}) 5.87 (t, 2 H, H-C_4), 5.30 (d, 2 H, J = 7.5 Hz, H-C_2) 4.95 (2t, 2 H, H-C_3), 1.12 (s, 9 H, *t*-Bu); the ethylenic part of the spectrum is very similar to that of *N*-carbalkoxy-1*H*-azepines.[11] The ^{13}C NMR spectrum (15.08 MHz, $CDCl_3$, δ_{Me_4Si}) 26.5 (methyls) 52.4 (quater, C) 114.4, 132.1, and 135.8 (C_2, C_3, and C_4) confirmed this structural assignment.

The rearrangement of **1a** is stereospecific and follows a clean first-order rate law[12] (up to 70% reaction) with respect to starting material. The calculated rate constants ($\times 10^3$ mn) were determined by least-squares analysis of the experimental data: k(102°.8) = 2.70, k(110°.5) = 5.64, k(113°.6) = 7.83, k(116°8) = 10.58, k(120°6) = 14.61, k(130°6) = 29.10. The activation parameters ($\Delta H^{\ddagger}$ = 25.1 ± 1.7 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −3 ± 3 eu) are compatible with a Cope rearrangement. The enthalpy of activation for this rearrangement is only 2.4 kcal mol^{-1} higher than that for the rearrangement of *cis*-divinyloxirane.[1i]

The following mechanism (Scheme II) is proposed to ac-

Scheme II