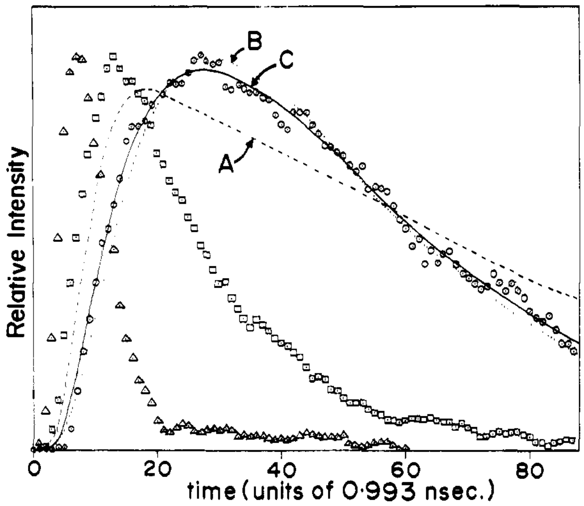

Figure 2. Fluorescence decay curves at 365 nm (▲), 470 nm (▣), and 620 nm (⊙) in the system 3,9-$(CN)_2P$ (10^{-3} M), *t*-An (0.22 M), and $PhNEt_2$ (4.0×10^{-3} M) in outgassed benzene. Data points at 620 nm are corrected for the contribution of the 3,10-$(CN)_2P$–*t*-An exciplex at this wavelength.

$(CN)_2P$-*t*-An exciplex (MQ_1), and a longer-lived emission shown by time-resolved spectroscopy[4] to have the same spectral shape as the 3,9-$(CN)_2P$-$PhNEt_2$ exciplex (MQ_2). These three emissions were monitored at 365 (pure M), 470 (pure MQ_1), and 620 nm, respectively (Figure 2). The long wavelength emission was incompletely resolved spectrally from MQ_1, but subtraction of the calculated modest MQ_1 contribution at 620 nm afforded the time profile of the new emission.

Using standard deconvolution techniques, and assuming a single-exponential decay, we attempted fits of the new emission to three different excitation functions: (1) M only, (2) MQ_1 only, and (3) a combination of M and MQ_1 (Figure 2). The best least-squares fit to M only is clearly unsatisfactory (Figure 2, A) and is much inferior to the fit to MQ_1 (Figure 2, B). The best fit (Figure 2, C) to a linear combination of M and MQ_1 occurs with 83 ± 9% excitation by MQ_1 and a lifetime determined to be 29.0 ± 2.4 ns. Since the lifetime of MQ_2 in the absence of anethole is 27.4 ± 2.0 ns, the spectral and lifetime comparisons strongly support the assignment of the new emission as MQ_2 itself and not to an excited termolecular complex[6] or *exterplex*[1b,7] ($MQ_1Q_2^*$). The results thus require S_{ex} as the major pathway for production of MQ_2 in the experiment above.

Steady-state data for several systems in which exciplex exchange occurs are given in Table I. As we have previously noted,[1b,2] the relative quenching efficiencies (k_{QT}) for a single exciplex correlate with the quencher ionization potentials. There is no obvious relationship between k_{QT} values for quenching of MQ_1 and $\Delta E = h\nu_{MQ_1}{}^{max} - h\nu_{MQ_2}{}^{max}$, a parameter which crudely[8] approximates $\Delta H°$ for eq 2. We expect exciplex exchange to be favored for large ΔE values. Unfortunately it is experimentally difficult quantitatively to study those cases where ΔE approaches zero. Whether S_{ex} results from collapse of a short-lived exterplex as intermediate or is itself an elementary process (i.e., the molecular analogue of the eternal triangle) remains to be determined.

Acknowledgment. We thank the Robert A. Welch Foundation (Grants AT-532 and AT-562) and The University of Texas at Dallas Organized Research Fund for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

(1) (a) R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974); (b) D. Creed and R. A. Caldwell, *ibid.*, **96**, 7369 (1974).
(2) R. A. Caldwell, D. Creed, and H. Ohta, *J. Am. Chem. Soc.*, **97**, 3246 (1975).
(3) R. A. Caldwell and N. I. Ghali, unpublished results.
(4) D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 621 (1976).
(5) The system 3,9-$(CN)_2P$-*t*-An-$PhNEt_2$ was preferred over the 3,10-$(CN)_2P$-*t*-An-$PhNEt_2$ system for these time-resolved experiments. The shorter lifetime of the 3,9-$(CN)_2P$-$PhNEt_2$ exciplex (τ = 27.4 ns) compared to the 3,10-$(CN)_2P$-$PhNEt_2$ exciplex (τ = 100 ns) simplifies evaluation of the contribution of the direct vs. exciplex exchange mechanisms for the formation of MQ_2.
(6) (a) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968); (b) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, *J. Am. Chem. Soc.*, **97**, 5688 (1975).
(7) The name *triplex* has also been suggested[6b] for excited termolecular complexes.
(8) For reversible photoassociation,[9] $h\nu_M - h\nu_{MQ} = -\Delta H° + E_R$. We have ignored ground state repulsion terms (E_R).
(9) B. Stevens, *Adv. Photochem.*, **8**, 161 (1971).
(10) Fellow of the Robert A. Welch Foundation.

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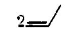
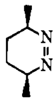
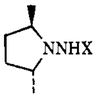
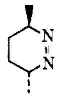
A Stereochemical Test of Similarly Substituted Tetramethylenediazene and Cyclic Azo Decompositions in the Gas Phase at the Same Temperature

Sir:

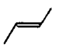
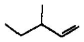
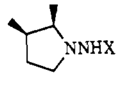
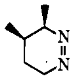
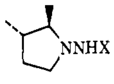
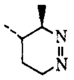
Valid comparisons of stereochemical tests directed toward an understanding of the behavior of 1,4-diradicals (**1**) generated by very different methods have been complicated by the lack of examples in the literature where the type of substituents, degree of substitution, and reaction conditions have been the same. We report here the first comparison of the product compositions from similarly substituted tetramethylenediazene[1] (**2**) and six-membered cyclic azo (**3**) thermal decompositions carried out in the gas

Table I. Percent Yields[a]

	T, °C[b]				
 (**4**)	120	77.6	5.0	17.1	0.3
	306	74.0	9.1	16.2	0.7
	439	72.8	9.3	15.8	2.1
 (**8**)	306	74.7	8.5	16.3	0.5
	439	72.9	9.7	16.3	1.1
 (**5**)	120	86.2	10.5	2.2	1.1
	306	79.7	13.1	6.2	1.0
	439	76.0	14.5	7.9	1.6
 (**9**)	306	80.5	12.7	5.7	1.1
	439	74.4	14.9	8.9	1.8

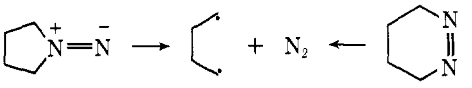
[a] Percent yield based on total hydrocarbon product. [b] Reactions at 120° (X = SO_2Ph) were carried out in *n*-octane with dry sodium methoxide for 30 min. Typical absolute yields of hydrocarbon products[11] are 38–73%. Reactions at 306 and 439° (X = SO_2Me) were carried out in the gas phase. Typical absolute yields of hydrocarbon products are 38–43%.

Table II. Percent Yields[a]

		T, °C[b]					
	(6)	120	1.9	86.5	1.2	10.4	—
		306	2.4	79.9	3.4	14.3	—
		439	3.1	80.7	3.2	12.6	0.4
	(10)	306	11.2	69.5	4.7	14.6	—
		439	11.4	64.4	8.2	16.0	—
	(7)	120	79.0	2.8	17.6	0.6	—
		306	66.6	3.3	26.5	3.4	0.2
		439	67.1	7.6	21.6	3.2	0.5
	(11)	306	69.7	4.3	23.4	2.6	—
		439	68.7	5.2	23.2	2.9	—

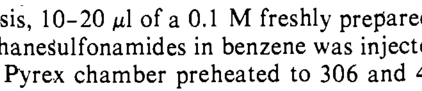
[a] Percent yield based on total hydrocarbon product. [b] Reactions at 120° (X = SO_2Ph) were carried out in *n*-octane with dry sodium methoxide for 30 min. Typical absolute yields of hydrocarbon products[11] are 38–73%. Reactions at 306 and 439° (X = SO_2Me) were carried out in the gas phase. Typical absolute yields of hydrocarbon products are 34–49%.

phase at the same temperature (306° and 439°). This stereochemical test bears on the important question of whether one can generate the same reactive species (e.g., 1,4-diradicals) by the extrusion of nitrogen by two very different methods and hence from two different points on an energy surface.



2 1 3

To our knowledge, there is no method reported in the literature for the thermal decomposition of 1,1-dialkydiazenes in the gas phase.[5] The study of the thermal reactions of substituted tetramethylenediazenes, potential precursors of 1,4-diradicals, has thus far been consigned to relatively low temperature solution chemistry (base induced α-eliminations and oxidation of *N*-amino precursors with HgO or $Pb(OAc)_4$ at 25–120°).[2-4] We describe here reactions in the gas phase (306–439°) of stereospecifically labeled *N*-methanesulfonamidopyrrolidines which on thermal decomposition afford hydrocarbon products consistent with the intermediacy of 1,1-diazenes.[2-4] Treatment of *N*-amino-*cis*-(and *trans*-)2,3-(and 2,5-)dimethylpyrollidines (each >99.5% isomeric purity)[7] with 1 equiv of methanesulfonyl chloride and triethylamine in methylene chloride (−78°) afforded the corresponding methanesulonamides (**4–7**).[8]



For pyrolysis, 10–20 µl of a 0.1 M freshly prepared solution of the methanesulfonamides in benzene was injected into an evacuated Pyrex chamber preheated to 306 and 439°. The hydrocarbon products were collected in a trap at −196°.[9] In order to provide information on the sensitivity of product ratios to differences in temperature and phase, we also report here the thermal decomposition of the *N*-benzenesulfonamido-*cis*-(and *trans*-)2,3-(and 2,5-)dimethylpyrrolidines in solution (120°) in the presence of base. Product ratios were determined by electronically Integrated analytical vapor phase chromatography (VPC) analysis. Conditions and results of the pyrolysis are listed in Tables I and II together with the corresponding product distributions from the thermal decomposition of *cis*-(and *trans*-)3,4-(and 3,6-)dimethyl-3,4,5,6-tetrahydropyridazines (**8–11**)[10] carried out in the gas phase (306 and 439°).

The data for the thermal decomposition of the dimethylpyrollidines (**4–7**) and cyclic azo compounds (**8–11**) show a similarity in product distributions at 306 and 439° in the gas phase. The symmetrically substituted cases (**4** and **8**, **5** and **9**) are in remarkable close agreement. This stereochemical test has provided at least permissive evidence that similar reactive species are generated in the gas phase from cyclic azo and 1,1-dialkyldiazene thermal decompositions at the same temperature and that these species can be thought of in part as 1,4-diradical intermediates.[12] Since cyclic 1,1-dialkyldiazene decompositions behave much like cyclic azo decompositions in the gas phase at the same temperatures (306 and 439°) and yet appear *more stereospecific* in solution at lower temperatures (120°), these experiments provide an opportunity for determining the relative importance of reaction conditions and temperature on the behavior of reactive species (e.g., 1,4-diradicals) generated by different methods.

Acknowledgment. The authors are grateful to E. I. du-Pont de Nemours and Co., Research Corporation and the National Science Foundation (MPS75-06776) for their generous support.

References and Notes

(1) 1,1-Diazenes are also known as aminonitrenes or *N*-nitrenes. Unlike their more stable azo isomers, the highly reactive 1,1-diazenes have not yet been isolated or characterized by physical means, but rather are assumed intermediates based on a substantial body of chemical evidence (e.g., several independent methods of generation, chemical trapping, and decomposition products).[2-4]

(2) D. M. Lemal in "Nitrenes", W. Lwowski, Ed., Interscience, New York, N.Y., 1970, Chapter 10; D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Am. Chem. Soc.*, **85**, 1943 (1963).

(3) B. V. Ioffe and M. A. Kuznetsov, *Russ. Chem. Rev. (Engl. Transl.)*, **41**, 131 (1972).

(4) C. G. Overberger, M. Valentine, and J. P. Anselme, *J. Am. Chem. Soc.*, **91**, 687 (1969).

(5) Recent producedures[6] for generating acyl-substituted 1,1-diazenes from *N*-aminosulfoximines at high temperatures in the gas phase have not been successfully applied to 1,1-dialkyldiazenes, apparently due to the difficulty in trapping dialkyldiazenes with dimethyl sulfoxide.

(6) C. W. Reese and M. Yelland, *Chem. Commun.*, 377 (1969).

(7) Successive treatment of each of four isomeric diols (*d,l*-, and *meso*-2,5-hexanediol and *threo*- and *erythro*-3-methylpentane-1,4-diol) with methanesulfonyl chloride and hydrazine hydrate afforded stereospecifically the four *N*-amino dimethylpyrollidines (~97% isomerically pure). These were further purified (≥99.5% isomerically pure) by preparative vapor phase chromatography (VPC) on a 10 ft × 0.25 in. glass column, Pennwalt-223 amine packing.

(8) The methanesulfonamides gave satisfactory C, H analyses and spectral data.

(9) Chamber pyrolysis: 30 s at 306 ± 2°, estimated pressure >25 mm; 5 s at 439 ± 2°, estimated pressure >31 mm. Product ratios were insensitive to changes in surface area. Control experiments show that the cyclobutane products are stable under the pyrolysis conditions. *cis*-2-Butene was shown to isomerize to some extent (3.5 and 1.5%, at 439 and 306°, respectively) and product ratios are corrected accordingly. *trans*-2-Butene was stable under the pyrolysis conditions.

(10) P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).

(11) 1,1-Diazenes are known to typically undergo three different reactions: (a) diazene–hydrazone isomerization, (b) diazene–tetrazene dimerization, and (c) diazene decomposition with the extrusion of nitrogen.

(12) To our knowledge this is the first examination of the stereochemistry of the cleavage reaction in tetramethylenediazene decompositions. Analysis of the diazene data permits the intermediacy of diazene-generated 1,4-diradical precursors to both cleavage and closure products and suggests some direct diazene fragmentation to olefins with retained stereochemistry.

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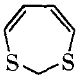
1,3-Dithiepin Anion. A 10π-Heteroaromatic System

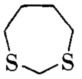
Sir:

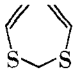
In the previous communication[1] we have described the synthesis of 2-*H*-1,3-dithiepin (**1**) and the characterization of its anion **2** a potentially 10π-heteroaromatic system.[2] While the ^{1}H NMR data obtained for the anion **2** indicated a certain delocalization of the negative charge over the ring, because of the complexity of the factors affecting the chemical shifts (diamagnetic ring current, charge distribution, anisotropy, and geometry at the heteroatom), no clear decision concerning the aromaticity of **2** could be made. An alternative experimental approach toward answering the question as to whether **2** is an aromatic system consists, according to Breslow, of establishing a greater stabilization by π-electron delocalization in **2** compared to a suitable model lacking this cyclic delocalization.[2] An indication of the stability of the 1,3-dithiepinyl anion (**2**) as compared with other compounds would be the relative acidity of its conjugate acid **1**. On this basis Breslow and Mohacsi had investigated the kinetic and thermodynamic acidity of 2-carbomethoxydibenzo [*d,f*][1,3]dithiepin and of the acyclic model ethyl bis(phenylmercapto)acetate.[2] Their results did not indicate any detectable additional stability (aromaticity) of this heavily substituted derivative of **2**.

In this communication, we wish to report our results concerning the relative acidities of the parent 2-*H*-1,3-dithiepin (**1**) as compared with the saturated 1,3-dithiacycloheptane (**3**) and the open chain model bis(vinylmercapto)methane (**4**).[3,4]


1


2

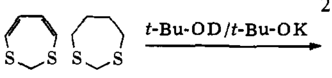
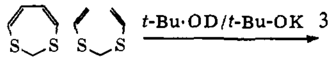

3


4

Compounds **1**, **3**, and **4** were subjected to competitive H/D exchange in *tert*-butyl alcohol-OD with a catalytic amount of potassium *tert*-butoxide. The reactions were carried out at constant temperatures, and the workup involved quenching with ice water and extraction with ether, followed by vacuum distillation. The products were analyzed by NMR and gas chromatography/mass spectroscopy.[5,6] The results are summarized in Table I.

As is apparent from Table I, the three compounds investigated show very different kinetic acidities under the conditions employed. In refluxing *tert*-butyl alcohol, compound **1**, the 2-*H*-1,3-dithiepin, exchanges completely both protons in position 2 within 10 min. The saturated model **3** under the same conditions does not exchange at all. The same results are obtained after 2 h at 83°, while after 24 h at 83° both **1** and **3** completely exchange their protons in position 2. On basis of these results one can estimate a minimum value of the relative acidity for **1** and **3** of ca. 150:1, or, in other words, the 1,3-dithia-4,6-cycloheptadiene (**1**) is at least 150 times as acidic as its saturated model **3**. This relative rate ratio for **1**/**3** of 150 corresponds to an approximately 3 kcal/mol stabilization of the 1,3-dithiepin anion **2** as compared with the saturated anion derived from **3**. We should like to interpret these results as follows: the increased acidity of **1** is an indication of the increased stability (aromaticity) of the planar 1,3-dithiepinyl anion **2**, stabilized by π-electron delocalization with a "resonance energy" of at least 3 kcal/mol.

Table I. Base Catalyzed H/D—Exchange Results for Compounds 1, 3, and 4

Compounds	Conditions	Products	
 **1** **3**	24 h, 83°	1-d_4	3-d_2
	4 h, 83°	1-d_2	3-H_2 (32%)
		1-d_3 (30%)	3-d_1 (50%) 3-d_2 (18%)
	2 h, 83°	1-d_2	3-H_2
	10 min, 83°	1-d_2	3-H_2
	30 min, 35°	1-d_2 (50%) 1-d_1 (41%) 1-H_2 (8%)	3-H_2
 **1** **4**	30 min, 50°	1-d_2 (95%)	4-H_2 4-d_1 (traces)

However, in view of a recent publication by Streitwieser and Ewing,[7] who attribute the stability of a carbanion next to sulfur to polarization at the heteroatom, one could argue that the increased stability of the unsaturated anion **2** as compared with the saturated anion derived from **3** is the result of better polarization at the sulfur in **2**, due to the presence of polarizable π-electrons at the adjacent carbon atoms. The anion of model compound **4** should exhibit the same or an even greater polarizability than the cyclic unsaturated anion **2**. Therefore, if 2-*H*-1,3-dithiepin (**1**) and bis(vinylmercapto)methane (**4**) show different acidities, the difference should clearly establish stabilization through π-electron delocalization in **2** and thus characterize anion **2** as a 10π-heteroaromatic system. As apparent from Table I, after 30 min at 50°, **1** has nearly completely exchanged its protons at position 2, while **4** has exchanged hardly at all.

In view of uncertainties associated with the interpretation of kinetic exchange data,[2,8] we studied the equilibrium acidity of **1**, **3**, and **4**. Metalation of **3** as well as **4** with *n*-butyllithium in tetrahydrofuran gave the corresponding anions, which were quenched with trimethylsilyl chloride.[3b] Addition of an equimolar amount of the diene **1** to the *colorless* solution of the anion derived from **3** at −45°, then holding the reaction mixture at 0° for 2 h, produced a *deep red* solution of the anion **2**.[1] Quenching of this solution at −45° with freshly distilled trimethylsilyl chloride gave exclusively the 2-trimethylsilyl-1,3-dithia-4,6-cycloheptadiene[1] and no trimethylsilyl derivative from the saturated anion. The experiment with bis(vinylmercapto)methane (**4**) had the same result. The stronger acid **1** is metalated completely by the stronger bases derived from **3** or **4** to give the more stable anion **2** (as lithium ion pair of unknown aggregation) and the weaker acids **3** or **4**.

It appears from these results that the 1,3-dithiepin anion **2** represents a 10π-heteroaromatic system, although the degree of aromaticity seems to be small.

Acknowledgment. We thank Dr. M. F. Semmelhack, Dr.