(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

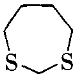
Sir:

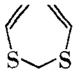
In the previous communication[1] we have described the synthesis of 2-*H*-1,3-dithiepin (**1**) and the characterization of its anion **2** a potentially 10π-heteroaromatic system.[2] While the ^{1}H NMR data obtained for the anion **2** indicated a certain delocalization of the negative charge over 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

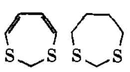
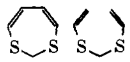

3


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	*t*-Bu-OD/*t*-Bu-OK $\longrightarrow$	24 h, 83° 4 h, 83°	1-d_4 1-d_2 1-d_3 (30%)	3-d_2 3-H_2 (32%) 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	*t*-Bu-OD/*t*-Bu-OK $\longrightarrow$	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.

B. Ganem, and Dr. C. Wilcox, Jr., for many helpful discussions. We are grateful to the Research Foundation of the City University of New York for financial support of this work (CUNY FRAP Awards 01769 N and 10190).

References and Notes

(1) C. Semmelhack, I-Ching Chiu, and K. Grohmann, *Tetrahedron Lett.*, in press.

(2) R. Breslow and E. Mohacsi, *J. Am. Chem. Soc.*, **85**, 431 (1963); R. Zahradnik in *Adv. Heterocycl. Chem.*, **5**, 1 (1963).

(3) (a) The synthesis of **1** is described in ref 1. Compound **3** was obtained from 1,4-butanedithiol and dibromomethane in presence of base.[4a] Bis(vinylmercapto)methane (**4**) has been synthesized from the reaction of vinyllithium and sulfur in tetrahydrofuran, followed by alkylation of the lithium vinyl thiolate[4b] with dibromomethane. (b) All new compounds have been fully characterized by their spectral and analytical data. Details will be reported in a full paper.

(4) (a) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427, 437 (1964); (b) L. Brandsma and P. J. W. Schuil, *Recl. Trav. Chim. Pays-Bas*, **88**, 30 (1969).

(5) The NMR analyses were carried out on the crude and distilled products.

(6) GC/mass spectra were obtained at the Cornell Mass Spec Facilities on a Finnegan 3300 instrument under the direction of Dr. J. Henion, whose help we gratefully acknowledge.

(7) A. Streitwieser, Jr., and S. P. Ewing, *J. Am. Chem. Soc.*, **97**, 190 (1975).

(8) For examples see D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, Chapter II; F. G. Bordwell, W. S. Mathews, and N. R. Vanier, *J. Am. Chem. Soc.* **97**, 442 (1975).

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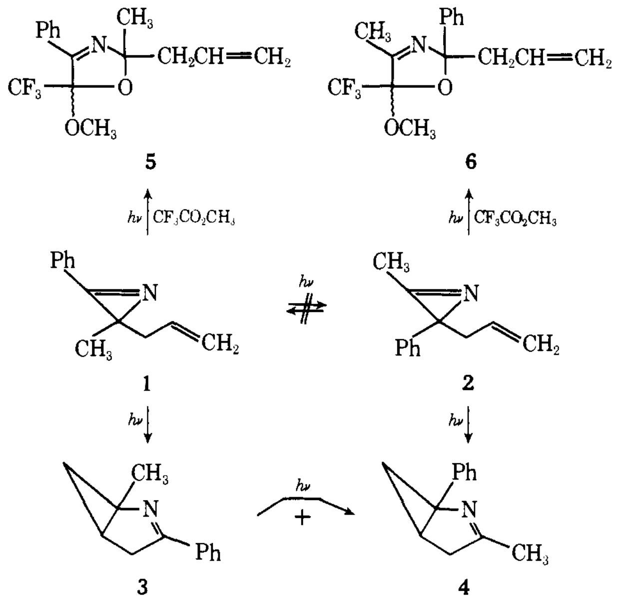
A Stepwise 1,3-Dipolar Cycloaddition Reaction[1]

Sir:

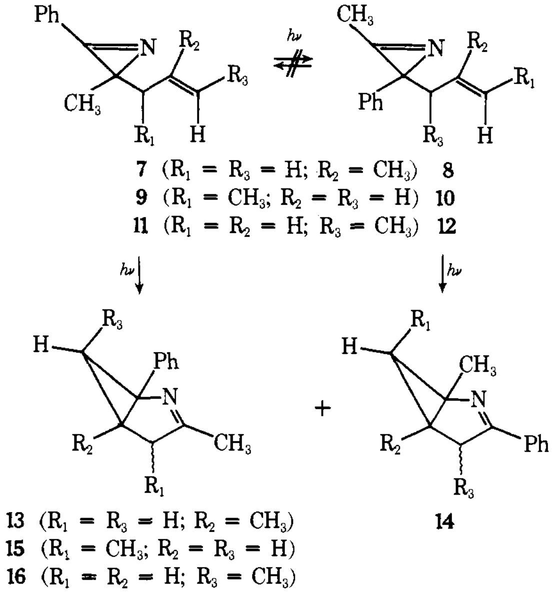
Substituted 2*H*-azirines undergo photochemical ring opening to form nitrile ylides.[2,3] These 1,3-dipoles can be intercepted with a variety of dipolarophiles to produce five-membered heterocyclic rings.[2,3] Salem has recently carried out some ab initio computations on the ground and excited state energy surfaces of the 2*H*-azirine molecule.[4] His calculations indicate that the ring-opened intermediate should be capable of dual reactivity when it is intercepted by an added dipolarophile. The behavior of the system was predicted to be dependent on the geometry of the transient intermediate generated from the photolysis. Opening of the ring to an intermediate with linear geometry will result in the formation of a 1,3-dipolar like species having closed-shell zwitterionic character. All of the photocycloadditions observed to date are in accord with such a species.[2,3] Salem's calculations also indicate that if the ring is opened to give an intermediate with bent geometry, a diradical state with partial dipolar character will be obtained. We now wish to report evidence which corroborates Salem's calculations and which also provides the first example of a stepwise 1,3-dipolar cycloaddition reaction.[5]

We recently reported that the irradiation of 2-phenyl-3-methyl-3-allylazirine (**1**) produced 2-azabicyclo[3.1.0]hex-2-ene (**4**) via an unusual 1,1-cycloaddition reaction[6] (Scheme I). In order to probe the generality of this internal cycloaddition reaction, we have examined the photochemical behavior of the isomeric 2-methyl-3-phenyl-3-allylazirine (**2**) system.[7] Irradiation of **2** in cyclohexane afforded a quantitative yield of azabicyclohexene (**4**). A control experiment showed that **1** and **2** were not interconverted by a Cope reaction under the photolytic conditions. Photolysis of **2** in the presence of the very reactive dipolarophile, methyl trifluoroacetate,[8] resulted in the trapping of a nitrile ylide and gave cycloadduct **6** in high yield.[9] Under these conditions, the formation of **4**, which is produced in quantitative yield in the absence of a trapping agent, is entirely suppressed. Photocycloaddition of **1** with added methyl trifluoroacetate resulted in the formation of cycloadduct **5** in high yield.[10] The isolation of **6** in the external trapping experiment eliminates a path by which **2** is partially isomerized to **1** which then rearranges to **4** on further excitation. This possibility was initially considered to be a reasonable one since the extinction coefficient of **1** at 254 nm (ϵ 8700) is much larger than that of **2** (ϵ 220). We have also found that the short term irradiation of **1** (20% conversion) produces a 1:1 mixture of azabicyclohexenes **3** and **4**.[11] On further irradiation, **3** was quantitatively isomerized to **4**. No significant quantities of **3** were found in the irradiation of **2**, however. This is probably related to the fact that **3** possesses a much larger extinction coefficient than **2** and is optically pumped to **4**, even at low conversions.

Scheme I



Scheme II



Support for this contention was obtained from a study of