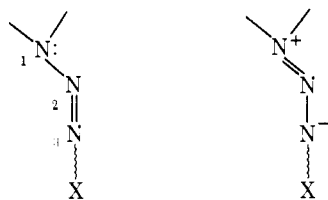
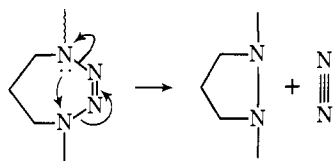


and then Seebach and co-workers,<sup>5</sup> prepared the first, authentic *cis* cyclic tetrazene, 1,4-dimethyl-1,4,5,6-hexahydro-1,2,3,4-tetrazine (**3**). Nelsen and Fibiger<sup>4</sup> studied the kinetics of the thermal decomposition of **3** and found, rather surprisingly, that it was relatively stable, ( $\Delta H^\ddagger = 38$  kcal/mol,  $\Delta S^\ddagger = 17$  eu). These values should be compared with those of tetramethyl-2-tetrazene, whose activation parameters in the gas phase were shown<sup>6</sup> to be  $\Delta H^\ddagger = 36.1$  kcal/mol,  $\Delta S^\ddagger = 4.7$  eu. Nelsen and Fibiger suggested that one possible explanation for this unexpected stability was the conformational restriction imposed by the cyclic structure, which increased the amino lone-pair interaction with the 2,3 bond. The larger ring size in



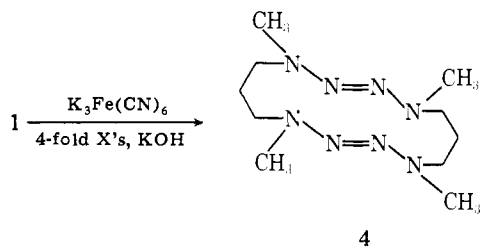
**2**, compared with that of **3**, might be expected to decrease the conformational rigidity of the cyclic *cis*-tetrazene, which would tend to decrease the lone-pair (2,3-bond) interaction. Thus it might be expected that **2** would decompose more readily than **3**. The data on the kinetics of the thermolysis of **2**, carried out by measuring the rate of nitrogen evolution in an automated, constant pressure device over the temperature range of 65–90 °C, are shown in Table I. The relative rate,  $k(2)/k(3)$ , at 90 °C is  $8.8 \times 10^4$ . These data demonstrate dramatically that, when the conformational restriction on the *cis* cyclic tetrazene is lifted, it becomes much less stable than the acyclic, *trans*-tetrazenes. In fact, the degree of the lowering of the enthalpy of activation in **2**, compared with that of tetramethyl-2-tetrazene ( $\Delta\Delta H^\ddagger \approx 17$  kcal/mol) is much greater than would have been predicted on the basis of comparison with *cis*- and *trans*-azoalkanes ( $\Delta\Delta H^\ddagger = 6$ –8 kcal/mol).<sup>4</sup> Interestingly, Roberts and Ingold<sup>3</sup> reported that the putative *cis*-tetraiso-propyl-2-tetrazene, which they suggested was the intermediate in the low temperature photolysis of the *trans*-tetrazene, decayed thermally with an activation energy of  $24 \pm 2$  kcal/mol.

A surprising result of the rate study was the negative entropy of activation. Although some negative entropies for azoalkane thermolyses have been reported,<sup>8</sup> the present result was unexpected. The possibility that the reaction was catalyzed by mercury vapor (from the kinetics apparatus)<sup>9</sup> was not checked specifically, but other kinetic studies of tetrazene decompositions, using the same apparatus,<sup>10</sup> failed to reveal any abnormalities. Thus, assuming that our entropy of activation value is correct, two rationales can be offered. One is that the equilibrium conformation of the tetrazene is different from the optimum geometry for decomposition. Therefore, the entropy may reflect the preequilibrium step. The other rationale is that the decomposition does not go through a 1,5 biradical, but rather is a concerted process leading directly to *N,N'*-dimethylpyrrolazine and nitrogen. In keeping with this mecha-



nism, the product of the reaction is the pyrrolazine, in better than 90% yield. The present data, however, do not allow us to distinguish between these possibilities (or, indeed, additional ones).

A necessary component in the oxidation of the dihydrazine<sup>11</sup>



**1** to the tetrazene **2** is a 20-fold excess of potassium hydroxide. When the amount of the base was lowered to a 4-fold excess, no **2** was formed; most of the reaction mixture consisted of intractable decomposition products. The workup of this mixture, however, did result in the isolation of small amounts (3–5%) of the solid, dimeric 14-membered-ring tetrazene, **4**. This material was analogous to the ditetrazene isolated by Nelsen and co-workers<sup>12</sup> in the oxidation *N,N'*-diamino-*N,N'*-dimethylethylenediamine. The ditetrazene **4** is completely stable and presumably has the *trans,trans* configuration.<sup>13</sup>

**Acknowledgment.** We are grateful to the NSF (CHE 76-24095) and to NIH (1-R01-CA22110) for generous support.

## References and Notes

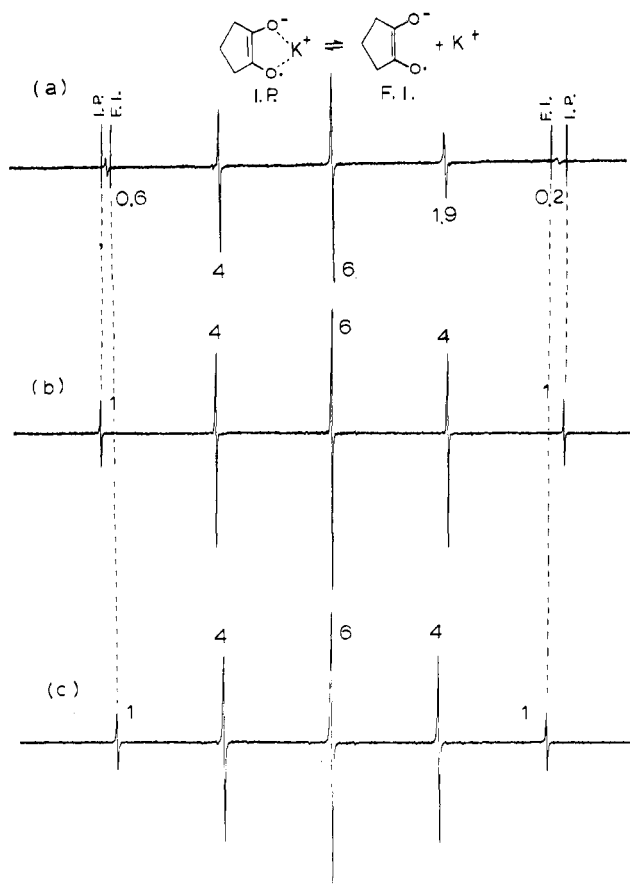
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- (13) This conclusion is based on the crystal structure of the 12-membered-ring ditetrazene: V. W. Day, S. F. Nelsen, and C. J. Michejda, unpublished work.
- (14) Address correspondence to the Frederick Cancer Research Center, P.O. Box B, Frederick, Md. 21701.

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## Ion-Pair Equilibria in Cyclic 1,2-Semidiones<sup>1</sup>

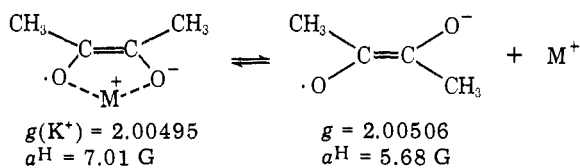
Sir:

The alkali metal salts of 1,2-semidiones can exist as ion pairs even in solvents as polar as dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ). For acyclic semidiones a mixture of *cis* ion-paired and *trans* free ion exists with sodium, potassium, or rubidium as the coun-



**Figure 1.** Cyclopentane-1,2-semidione: (a) mixture of free ion and ion pair observed in presence of 0.075 M  $K^+$ ,  $Me_2SO$ ; (b) ion pair observed in presence of 0.75 M KI; (c) free ion observed in presence of excess [2.2.2] cryptand.

terions<sup>2,3</sup> with lower  $g$  values observed for the ion-paired species.<sup>4</sup>



In the presence of an excess of the proper cryptand, counterions such as  $Li^+$ ,  $Na^+$ , or  $K^+$  can be complexed, and under these conditions only the more stable trans semidione can be detected (cis/trans, <0.01).<sup>2</sup> To study a cis semidione free of ion pairing, we have examined cyclic 1,2-semidiones. We have found that the rates of interconversion of the free ion and the ion pair are surprisingly slow.

We were led to the investigation of ion pairing in cyclic 1,2-semidiones by the observation that in some cyclic semidiones the high field lines of the ESR spectrum show line broadening. This suggests the presence of two species with different  $a^H$  and  $g$  values, for example **1** and **2**, wherein  $a^H$  increases as the  $g$  value decreases.

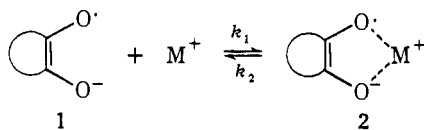


Figure 1a illustrates the line broadening observed for cyclopentane-1,2-semidione (0.075 M  $K^+$ ,  $Me_2SO$ )<sup>5</sup> where both the high- and low-field lines of the 1:4:6:4:1 pentet are broadened with the high-field broadening being most pro-

**Table I.** Values of  $a^H$  and  $g$  for Cycloalkane-1,2-semidiones ( $Me_2SO$ , 25 °C<sup>a</sup>)

counterion	$g$ value	$a^H$ (4 H), G <sup>b</sup>	1/2
Cyclobutane			
$K^+$ , [2.2.2] cryptand	2.005 09	13.85	>20
$K^+$ , 0.075 M	2.005 08	13.90	~10 <sup>c</sup>
$K^+$ , excess	2.005 00	14.13	>0.05
Cyclopentane			
$K^+$ , [2.2.2] cryptand	2.005 10	12.93	>20
$(C_2H_5)_4N^+$	2.005 08	12.94	>20
$K^+$ , 18-crown-6; excess	2.005 00 <sup>d</sup>	13.33 <sup>d</sup>	<0.05
$K^+$ excess	2.00494	13.62	<0.05
$K^+$ , 0.075 M	2.005 00	13.30	0.72 <sup>c</sup>
$Na^+$ , excess	2.004 88	13.84 <sup>e</sup>	<0.05
$Li^+$ , excess	2.004 72	14.52 <sup>f</sup>	<0.05
Cyclohexane			
$K^+$ , [2.2.2] cryptand	2.005 10	9.50 <sup>g</sup>	>20
$K^+$ , 0.050 M	2.004 96	9.80	~0.5 <sup>c</sup>
$K^+$ , excess	2.004 91	10.01	<0.05

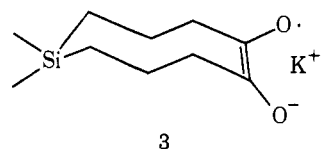
<sup>a</sup> The concentration of counterion or complexing agent was increased until only a single species was present as judged by the observation of a 1:4:6:4:1 pentet with constant values of  $a^H$  and  $g$ . <sup>b</sup> Measured between the center line and first upfield line. Second-order splitting can be resolved for cyclopentane-1,2-semidione. <sup>c</sup> Apparent values of  $K$  for ion-pair formation (liters/mole) increase from <1.5 ( $C_4$ ) to 18 ( $C_5$ ) and ~40 ( $C_6$  and  $C_7$ ). <sup>d</sup> Crown-complexed ion pair. <sup>e</sup>  $\lambda^{Na} = 0.52$  G. <sup>f</sup>  $a^{Li} = 0.55$  G,  $a_{\beta}^H = 0.14$  G (2 H). <sup>g</sup>  $a_{\beta}^H = 0.09$  G (4 H).

nounced (intensity ratios are shown in Figure 1a). Figure 1b shows the dramatic effect of adding excess KI to give a solution containing only **2**. The intensities are now 1:4:6:4:1 even though the viscosity of the solution has increased considerably. On the other hand, addition of an excess of [2.2.2] cryptand (Figure 1c) gives a species with a higher  $g$  value and a lower  $a^H$  which we attribute to the free ion (**1**). With  $K^+$  as the counterion we find that over a 4000-fold dilution range that  $a^H$  and  $g$  value are related by  $a^H$  (gauss) =  $-5.0546 \times 10^3 g + 10\,147.84$ .<sup>6</sup> Thus, Figure 1a represents a 42:58 mixture of **1** and **2**. Data for  $Li^+$  and  $Na^+$  show a similar trend between  $a^H$  and  $g$  with  $a^H$  increasing from  $K^+$  to  $Na^+$  to  $Li^+$  (Table I).

The rate of time averaging of **1** and **2** can be slow on the ESR time scale. In the spectrum of Figure 1a the line broadening leads to a value of  $k_1(M^+ = K^+_{total}) = 4.4 \times 10^8$  L/(mol·s) and  $k_2 = 2.4 \times 10^{-7}$  s<sup>-1</sup>. Sometimes both **1** and **2** can be observed independently ( $k_1 < 10^6$  s<sup>-1</sup>). When slightly less than stoichiometric quantities of [2.2.2] cryptand are added to cyclohexane-1,2-semidione ( $K^+$ ), the high-field peaks can be resolved for the free ion and the ion pair. Similarly for the cyclopentane-1,2-semidione system the high-field lines of **1** and **2** can be resolved for  $M^+ = Li$  and  $Na$  (well-resolved  $a^M$  for **2**) when deficient quantities of these cations are added to the  $K^+$  [2.2.2] cryptand salt.<sup>7</sup>

As judged from the values of  $a^H$ ,  $g$ , or  $a_{CO}^C$ ,<sup>8</sup> tighter ion pairing increases the spin density on the carbonyl carbon in the semidione system (e.g., the  $g$  value for a carbon radical is 2.002 and for an oxy radical 2.015). One might have expected the reverse for a symmetrical ion pair (ion pairing giving an increase in charge and spin density on oxygen). Apparently the effect of ion pairing on the charge distribution for the filled MO's of the semidione system is appreciable and must be taken into account.

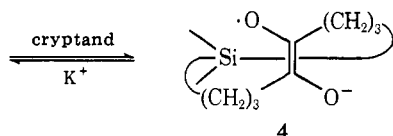
Manipulation of ion pairing in 1,2-semidiones extends the utility of this spin probe for conformational and structural analysis. For example, it provides a tool for addressing the question of cis-trans isomers in large-ring semidiones.<sup>9</sup> Thus, we have been able to identify *cis*- and *trans*-6,6-dimethyl-6-



$$a_{\alpha}^H = 7.33 \text{ (2 H)}, 1.40 \text{ (2 H) G}$$

$$a_{\beta}^H = 0.48 \text{ (2 H) G}$$

$$g = 2.00494$$



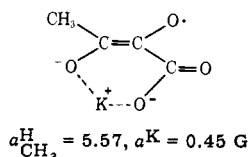
$$a_{\alpha}^H = 3.6 \text{ (2 H)}, 2.3 \text{ (2 H) G}$$

$$g = 2.00507$$

silacyclononane-1,2-semidiones as the ion-paired (**3**) and free ion (**4**), respectively.

## References and Notes

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- (6) Experiment performed by Mr. B. Graether.
- (7)  $a^K$  is not observed for 1,2-semidiones even in the presence of crown ethers (which for  $\text{Na}^+$  greatly reduces the rate of the exchange; semidione $^-$ ,  $\text{Na}^+$  +  $^*\text{Na}^+ \rightleftharpoons$  semidione $^-$ ,  $^*\text{Na}^+$  +  $\text{Na}^+$ ).<sup>2</sup>  $a^K$  can be observed in  $\text{Me}_2\text{SO}$  for semidione radical dianions (unpublished work with Mr. T. Takano), such as that shown.



- (8)  $a_{\text{CO}}^C$  in *cis*-dimethylsemidione increases from 1.1 ( $\text{K}^+$ ,  $\text{Me}_2\text{SO}$ ) to 1.4 ( $\text{Na}^+$ ,  $\text{Me}_2\text{SO}$ ), 1.8 ( $\text{Li}^+$ ,  $\text{Me}_2\text{SO}$ ), 1.9 ( $\text{K}^+$ , *tert*-butyl alcohol). In  $\text{Me}_2\text{SO}$   $a^H$  increases from 7.0 ( $\text{K}^+$ ) to 7.1 ( $\text{Na}^+$ ) to 7.4 ( $\text{Li}^+$ ).<sup>3</sup>
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- (10) National Science Foundation Fellow, 1975–1978.

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## Conversion of Allyl Alcohols to Dienes by Sulfoxide and Selenoxide Syn Elimination. Synthesis of PCB Arene Oxides

Sir:

Of the many procedures and reagents available for the dehydration of alcohols, few work well for the conversion of allyl alcohols to dienes, and even fewer provide for regiospecific dehydration. We report here a new procedure (Scheme I,  $\text{Y} = \text{S}, \text{Se}$ ) for the 1,4 dehydration of allyl alcohols, and application of this method as a key step in the synthesis of chlorinated and brominated biphenyl oxides.

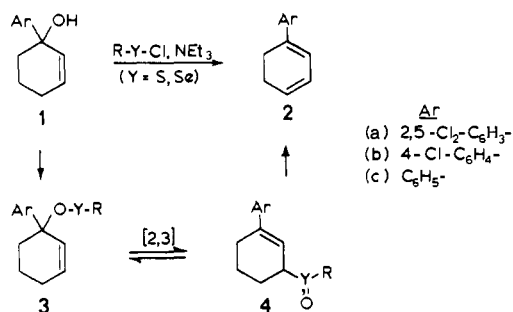
Treatment of alcohol **1a** with 2-nitro-4-methylbenzeneselenenyl chloride in refluxing dichloromethane leads to diene

**Table I.** 1,4-Dehydration of Allyl Alcohols Using 2,4-Dinitrobenzenesulfonyl Chloride-Triethylamine

run	allyl alcohol	diene	yields, % <sup>a</sup>
1	<b>1a</b>	<b>2a</b>	83 <sup>b</sup>
2	<b>1b</b>	<b>2b</b>	66 <sup>b</sup>
3	<b>1c</b>	<b>2c</b>	79 <sup>b</sup>
4			68 <sup>c</sup>
5			77 <sup>c</sup>
6			71 <sup>c</sup>
7			<10 <sup>c</sup>
8			75 <sup>b</sup>
9			58 <sup>b</sup>
10			74 <sup>b</sup>
11			73 <sup>b</sup>
12			54 <sup>c, d</sup>

<sup>a</sup> Reactions were carried out on 1–10 mmol of allyl alcohol; products were purified chromatographically or by distillation. <sup>b</sup> Reaction in  $\text{CH}_2\text{Cl}_2$  at 25–40 °C. <sup>c</sup> Reaction in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  at 80 °C. <sup>d</sup> The diene was a 60:40 mixture of *E,E* and *E,Z* isomers.

## Scheme I



**2a** (65% yield). The reaction must proceed by [2,3]-sigmatropic rearrangement of selenenyl ester **3** to the allyl selenoxide **4**, which fragments to diene.<sup>1</sup> There are several reported examples of allyl selenoxide to selenenyl rearrangements,<sup>2,5</sup> but this is the first demonstration of the allyl selenenyl to selenoxide conversion.

In the course of attempting to generalize the process described above a number of readily available selenenyl ( $\text{PhSeCl}$ ,  $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SeBr}$ ) and sulfonyl ( $\text{CCl}_3\text{SOCl}$ ,  $2\text{-NO}_2\text{C}_6\text{H}_4\text{SOCl}$ ,  $2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3\text{SOCl}$ ) halides were examined. It was hoped that the powerful electron-attacking substituents in the sulfonyl halides, together with the acceleration provided by the allylic nature of the sulfoxide intermediate,<sup>6</sup> would lead to sufficiently fast sulfoxide syn elimination<sup>6</sup> to accommodate the mild reaction conditions desirable for the synthesis of reactive dienes. 2,4-Dinitrobenzenesulfonyl chloride is the reagent currently showing the most promise. Of a variety of reaction conditions tried, treatment with 2.4 equiv<sup>7</sup> of the sulfonyl chloride and 3 equiv of triethylamine in dichloromethane (–30 to 40 °C) or 1,2-dichloroethane (20 to 80 °C) gave the highest yields. Table I presents several examples using these conditions.<sup>8</sup> At its current stage of development, the reaction proceeds in acceptable yield for a variety of allyl alcohols. One