arguments that such activated complexes have reactant-like internal structures and solvent reorganization as their reaction coordinates have been based on p$K_a(\neq)$ and its temperature dependence.[17] A strikingly analogous conclusion about the reaction coordinate in cation-anion recombinations has been published recently by Ritchie.[18]

As alluded to above, rigorous deduction of the value of δ from observed values of k_1^H/k_1^D in MeCN and $TMSO_2$ requires knowledge concerning the values of ϕ_{OL^+} and ϕ_{OL} in those solvents. If $\phi_{OL^+} = \phi_{OL}$, then $k_1^H/k_1^D = 1.00$ (as observed) for all possible values of δ. Although we regard this alternative origin of k_1^H/k_1^D as unlikely, experiments designed to measured ϕ_{OL^+} relative to ϕ_{OL} in aprotic media are in progress.

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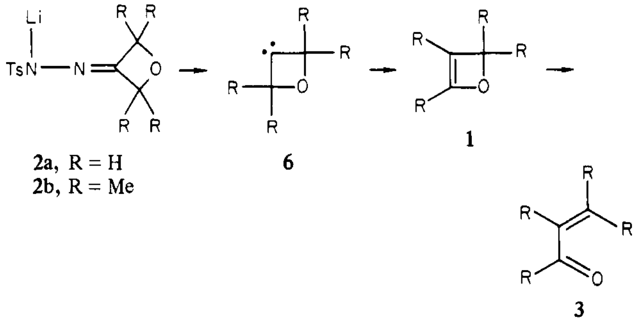
Oxetene: Synthesis and Energetics of Electrocyclic Ring Opening

Sir:

Although several substituted oxetenes have been synthesized,[1] the parent compound (1a) has not yet been prepared. We now report the synthesis of this unique strained ring compound and an investigation of the kinetics of its electrocyclic ring opening to acrolein.

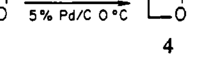
Hortman and Bhattacharjya[2] reported that pyrolysis of tosylhydrazone lithium salt **2b** leads to 3,4-dimethyl-3-penten-2-one (**3b**). Although tetramethyloxetene **1b** was not isolated in this reaction, the authors claim it is an intermediate. The rearrangement of **1b** to **3b** has been reported.[3] Accordingly, we have prepared the tosylhydrazone lithium salt **2a**[4] from 3-oxetanone.[5] Compound **2a** was flash pyrolyzed at 180-190 °C in vacuo, and volatile reaction products were collected at -196 °C. NMR analysis indicated acrolein and a compound thought to be oxetene were present in a 0.2-0.5:1 ratio. Oxetene could be further purified by trap to trap distillation from -110 to -196 °C. This procedure removed the majority of acrolein, leaving oxetene of >90% purity in the -110 °C trap. The only observable impurity was acrolein. The yield of **1a** was 11% on the basis of starting tosylhydrazone.



2a, R = H
2b, R = Me
6
1
3

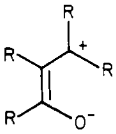
Spectral data are consistent with an assignment of the oxetene structure: NMR ($CDCl_3$, -25 °C) δ 5.27 (br s, 2 H), 5.73 (br s, 1 H), 6.70 (br s, 1 H); IR (gas phase, 25 °C) 3020 (w), 3000 (s), 2970 (m), 1565 (m), 1285 (m), 1025 (s), 920 (s), 880 (s), 665 (s), 425 (s) cm^{-1}. The IR band at 1565 cm^{-1} is assigned to the C=C stretch in analogy with the C=C stretch in cyclobutene which appears at 1566 cm^{-1}.[8,9]

The chemical reactivity of **1a** also provides evidence for its structure. Hydrogenation of **1a** to oxetane **4** was accomplished by reacting a gaseous mixture of **1a** and hydrogen over 5% Pd on activated charcoal at 0 °C. The IR spectrum of the product was identical with that of **4**. When a $CDCl_3$ solution of **1a** was allowed to stand at 25 °C, smooth rearrangement to acrolein (**3a**) occurred. Similarly, the gas-phase rearrangement of **1a** to **3a** at various temperatures was followed by IR spectroscopy. The kinetics of this gas-phase electrocyclic ring opening of **1a** to **3a** were measured at 35, 44.5, 57, and 86.2 °C. From these data, an activation enthalpy of 24.1 ± 1.5 kcal/mol and an activation entropy of 0.0 ± 3.1 eu were calculated. We have previously used the MINDO/3[10,11] molecular-orbital method to calculate a value of 30.7 kcal/mol for the activation enthalpy of this ring opening.



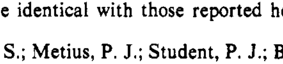
1a
4

The presence of the electronegative oxygen atom in **1a** raises the possibility of a polar transition state such as **5** for the electrocyclic ring opening. However, the fact that the $\Delta H^{\dagger}$ for the opening of **1a** in the gas phase is similar to that reported for **1b** in various solvents appears to preclude a polar transition state such as **5**. If this transition state was important, electron donation in **1b** would accelerate the rearrangement compared to that of **1a**. Friedrich and Schuster[3] have concluded there is little charge separation in the transition state for the ring opening of **1b**.



5a, R = H
5b, R = Me

Pyrolysis of the tosylhydrazone salt **2a** undoubtedly proceeds via 3-oxacyclobutylidene **6a**. It is of interest that no evidence for ring contraction of **6a** to allene oxide **7** could be obtained. Although allene oxide is unknown, calculations suggest its rearrangement to cyclopropanone **8** is facile.[11] However, careful analysis of the pyrolysis products from **2a** revealed no **8** was



6a
7
8

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present. In contrast, cyclobutanylidene reacts primarily by ring contraction to give methylenecyclopropane along with smaller amounts of cyclobutene.[13] This diverse behavior of the two carbenes is probably ascribable to the fact that rearrangement of **6a** to **7** is less exothermic than is rearrangement of cyclobutanylidene to methylenecyclopropane. Hortman and Bhattacharjya did not find evidence for ring contraction of carbene **6b**.[2]

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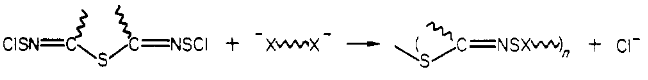
1,1-Dichloro-2,5-bis(*N*-chlorothioimino)-3,4-dicyanoselenophene

Sir:

Polymers with unsaturated sulfur (or selenium) and nitrogen and carbon backbones are of interest in regard to their potential electronic properties[1] because they are versatile extrapolations on the known inorganic superconducting polymer $(SN)_x$.

The SC=NSCl moiety, while relatively unknown,[3] could be used as an electrophile in condensation reactions as in eq 1.

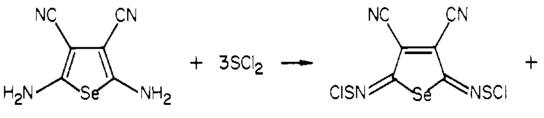


(1)

With this in mind, we designed the monomers **1**[4] and **3**; it was expected that the latter could be prepared from the unknown

1

diamine **2** by a procedure developed for the preparation of **1**, namely, eq 2.



2 **3**

4HCl + S (2)

Reductive selenation of TCNE (eq 3) was expected to produce the diamine **2** in analogy with the synthesis of 2,5-diamino-3,4-dicyanothiophene.[5]

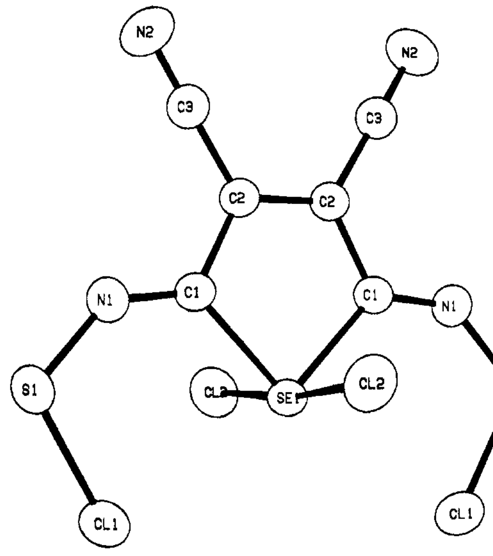
$$\text{TCNE} + 2\text{H}_2\text{Se} \rightarrow \mathbf{3} + \text{Se} \qquad (3)$$

Here we report the preparation, characterization, and solid-state structure of the title compound produced in an attempted synthesis of **3** via reaction 2.

Table I

	Bond Distances (Å)		
Se1-Cl1	3.110 (1)	N1-C1	1.266 (4)
Se1-Cl2	2.369 (1)	N2-C3	1.138 (4)
Se1-C1	1.970 (3)	C1-C2	1.445 (4)
Cl1-S1	2.041 (1)	C2-C3	1.427 (4)
S1-N1	1.585 (3)	C2-C2	1.362 (6)
	Bond Angles (Deg)		
Cl2-Se1-Cl2	173.46 (5)	S1-N1-C1	137.4 (3)
Cl2-Se1-C1	87.16 (9)	Se1-C1-N1	127.4 (2)
Cl2-Se1-C1	88.07 (9)	Se1-C1-C2	109.3 (2)
Cl2-Se1-C1	88.07 (9)	N1-C1-C2	123.3 (3)
Cl2-Se1-C1	87.16 (9)	C1-C2-C2	117.5 (2)
C1-Se1-C1	86.4 (2)	C1-C2-C3	120.3 (3)
Cl1-S1-N1	108.3 (1)	C2-C2-C3	122.2 (2)
		N2-C3-C2	179.2 (4)

[a] Numbers in parentheses are estimated standard deviations in the least-significant digits.



4

Figure 1. Molecular structure of 1,1-dichloro-2,5-bis(chlorothioimino)-3,4-dicyanoselenophene.

Reaction 3 did indeed produce the diaminoselenophene **2** in good yield as a salmon-colored solid[6] which was insoluble in most organic solvents and exhibited chemical properties similar to those of its sulfur analogue.[7] On the other hand, when **2** was exposed to sulfur dichloride under conditions identical with the preparation of **1**, compound **4** was produced instead of **3**. Since sulfur chlorides are known to disproportionate readily,[8] it was not surprising (after the fact) to isolate **4** instead of **3** because selenium is more electropositive than sulfur and can expand its valence octet more readily than sulfur[8] (cf. **1** which is devoid of chlorines in the 1-position).

Thus, **4** was produced in good yield as black prisms,[9] whose structure could not be determined solely on the basis of its spectral properties: IR (KBr) 2225 (vw), 1520 (m), 1490 (s), 1330 (s), 1227 (w), 849 (m), 812 (s) cm^{-1}; mass spectrum (MS), *m/e* 344 (P + 2), 342 (P), 307 (P − Cl), 272 ($\text{P} - \text{Cl}_2$), etc. Note that the elemental analysis was low on Cl for **4** and high for **3** and the MS was correct for **3**; furthermore, the IR spectra of **4** and **1** were practically identical which led us to believe that the product from reaction 2 was indeed **3**.[10] It was clear that in order to elucidate

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