which absorbed in the carbonyl region only at 1745 cm^{-1} (five-membered ring ketone and ester carbonyl).

Inspection of models indicates that bicyclo[4.2.1]-non-1(8)-ene (**1**) is more strained than bicyclo[4.2.1]-non-1(2)-ene (**2**). We believe that the predominant production of the less stable isomer is the result of kinetic control during the Hofmann elimination. The Hofmann elimination has been shown to proceed by both *syn* and *anti* mechanisms.[9] Models of the quaternary ammonium hydroxide **12** indicate the alkenes **1** and **2** are most likely formed by *syn* elimination of the *exo* hydrogens at C-8 and C-2, respectively. Whereas the *exo* hydrogen at C-8 is held rigidly in a *syn* and coplanar orientation with respect to the trimethylammonium group, the *exo* C-2 hydrogen may be in various orientations due to the greater mobility of the four-membered bridge. Thus, kinetically preferred removal of the favorably oriented *exo* C-8 hydrogen should result in formation of the less stable isomer (**1**) in greater amount.

We are currently investigating the chemistry of this and other highly strained alkenes in our efforts to define the limits of Bredt's rule.[10]

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(9) (a) M. P. Cooke, Jr., and J. L. Coke, *J. Amer. Chem. Soc.* **90**, 5556 (1968); (b) J. L. Coke and M. C. Mourning, *ibid.*, **90**, 5561 (1968).

(10) This research was generously supported by Grants 916G and 3740A from the Petroleum Research Fund.

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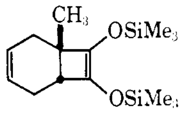
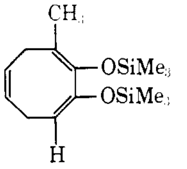
Application of Electron Spin Resonance Spectroscopy to a Study of Valence Isomerization and *cis–trans* Isomerization. Bicyclo[4.2.0]octane-7,8-semidione and Bicyclo[4.2.0]oct-3-en-7,8-semidione[1]

Sir:

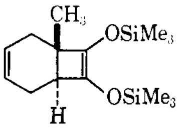
Treatment of **1**,[2] **2**,[2] or **3**[2] with a solution of potassium *t*-butoxide in dimethyl sulfoxide (DMSO) yields a single semidione[3] to which we assign structure **4**. Semidione **4**, when prepared from **1**, exchanges its α-hydrogen atom very slowly in DMSO-d_6 to give a_α^D = 2.1 G. The mixture of the deuterated and undeuterated semidiones could be easily analyzed by esr spectroscopy. Under standard conditions 50% hydrogen–deuterium exchange was found in 420 min. Under similar conditions, the semidione formed from **3** had undergone 95% exchange in 40 min, while the initial[4] semidione formed from **2** in DMSO-d_6 had exchanged 50% of the α-hydrogen atoms. These results suggest that **2a** and **3a** (or **2b** and **3b**) are rapidly interconverted by a conrotatory motion and that hydrogen–deuterium exchange occurs rapidly in one or the other. Orbital symmetries predict that the dianion **2a** should undergo a conrotatory ring closure more readily than the radical anion **2b**. We conclude that the reaction sequence of Chart I is involved wherein the concentrations of **2b** and **3b** are always less than 10% of **4**.



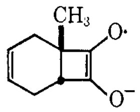
1



2



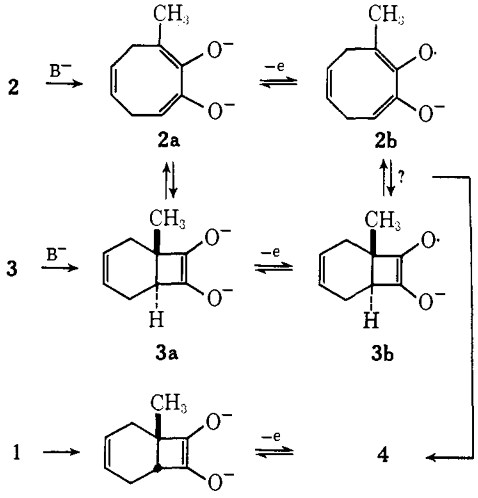
3



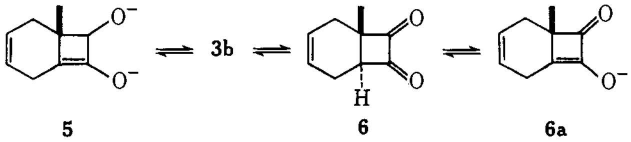
4

a^H = 13.5, 1.2, 0.4, 0.4 G
$a_{CH_3}^H$ = 0.2 G

Chart I

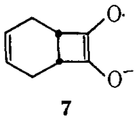


The process involved in the interconversion of **3b** to **4** and in the hydrogen–deuterium exchange may involve a radical dianion (**5**) or the diketone **6** and its enolate anion **6a**.



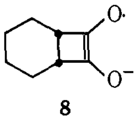
Alternately, protonation of **2a** will lead to hydrogen–deuterium exchange while a disrotatory ring closure of **2b** will yield **4**. A rapid but reversible conrotatory ring closure of **2a** or **2b** in competition with a slower but irreversible disrotatory closure to **4** is a distinct possibility.

We have previously demonstrated that, under the reaction conditions, the hydrogen–deuterium exchange of the α-methylene protons in bicyclo[3.1.0]hexane-2,3-semidione is highly stereoselective (the hydrogen *trans* to the cyclopropyl ring exchanges preferentially).[5] This observation is most consistent with a radical-dianion intermediate. Therefore, we examined **7**



7

a^H = 13.5, 13.5, 0.60, 0.60, 0.35, 0.35 G



8

a^H = 13.5, 13.5, 0.5, 0.5, 0.25, 0.25 G

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(1) Supported by the National Science Foundation.

(2) J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968).

(3) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967).

(4) Spectrum recorded 15 min after mixing of reagents.

(5) G. A. Russell, J. J. McDonnell, and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 5516 (1967).

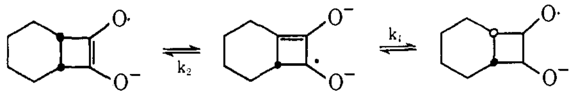
and **8**.[6] We expected that a radical-dianion mechanism might yield a one-deuterium exchange while a diketone mechanism should yield a two-deuterium exchange. Both **7** and **8** gave a fairly clean-cut two-deuterium exchange in DMSO containing potassium *t*-butoxide at 25° (Table I).

Table I. Hydrogen–Deuterium Exchange Data for **7** and **8** in DMSO-d_6[a]

Semidione	Exchange time, min	% d_0	% d_1	% d_2
8	30	61	11	28
8	60	46	9	45
8	150	14	8	78
7	450	50	18	32
7	1380	37	19	44

[a] 0.2 *M* $KOC(CH_3)_3$, 0.1 *M* bis(trimethylsiloxy)alkene.

It is possible to rationalize a two-deuterium exchange only by postulating an intermediate in which both α-hydrogen atoms are readily exchanged. The diketone is a likely candidate. However, it is also possible to rationalize the results in terms of the radical dianions and the *trans* isomers of **7** and **8** provided that the *trans* isomer is >10 times more acidic than the *cis* isomer and provided that there is a threefold preference for protonation of the radical dianion to yield the *trans*-semidione ($k_1/k_2 = 3$).



The rates of hydrogen–deuterium exchange of **7** and **8** are greatly increased by the addition of D_2O to the DMSO-d_6. A rate acceleration of approximately 100-fold was observed by the addition of 2% of D_2O. This undoubtedly involves an increase in the concentration of an intermediate that can undergo exchange of the α hydrogen. The diketone seems reasonable but the neutral radical **9** cannot be excluded.

$$2{>}CHC(O\cdot){=}C(O^-)CH{<} \rightleftharpoons {>}CHCO{-}COCH{<} + {>}CHC(O^-){=}C(O^-)CH{<}$$

$$H^+ \downarrow\uparrow -H^+$$

$$\underset{\mathbf{9}}{2{>}CHO(O\cdot){=}C(OH)CH{<}} \rightleftharpoons {>}CHCO{-}COCH{<} + {>}CHC(OH){=}C(OH)CH{<}$$

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[6] Prepared by treatment of the isolated bis(trimethylsiloxy)alkenes[2] with potassium *t*-butoxide in DMSO solution. The semidiones are also conveniently prepared by performing an acyloin condensation in dimethoxyethane with 1:1 sodium–potassium alloy[3] followed by dilution of a filtered aliquot with an equal volume of 0.2 *M* potassium *t*-butoxide in DMSO.

[7] National Aeronautical and Space Administration Predoctoral Fellow, 1965–1968; Petroleum Research Fellow, 1968–1969.

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Two New Subsulfides of Tantalum[1]

Sir:

A new clustering of metal atoms has been observed in two new metal-rich sulfides, Ta_2S[2a] and Ta_6S.[2b] The sulfides were prepared by annealing samples in a tungsten container at about 1600° under high vacuum. The crystal structures of both phases were determined using the direct method to solve the phase problem. The Ta_2S structure has Pbcm space group symmetry, and the Ta_6S structure has C2/c space group symmetry; there are 12 and 18 formula units per unit cell of Ta_2S and Ta_6S, respectively. The cell parameters, obtained by least-squares treatment of Guinier powder data using Cu Kα radiation, λ 1.5405 Å, are: for Ta_2S, $a = 7.381 \pm 2$ Å, $b = 5.574 \pm 1$ Å, $c = 15.195 \pm 3$ Å; for Ta_6S, $a = 14.158 \pm 4$ Å, $b = 5.284 \pm 1$ Å, $c = 14.789 \pm 5$ Å, $\beta = 118.01 \pm 0.02°$. Calculated and observed $\sin^2\theta$ values, λ 1.5405 Å, are listed in Tables I and II, respectively, for Ta_2S and Ta_6S.

Table I. Ta_2S

hkl	$\sin^2\theta_{obsd} \times 10^5$	$\sin^2\theta_{calcd} \times 10^5$	$I/I_0 \times 100$
002	1,032	1,028	50
100	1,085	1,089	50
102	2,124	2,116	10
004	4,116	4,112	10
211	6,521	6,521	15
114	7,106	7,110	10
212	7,295	7,295	18
021	7,887	7,896	80
213	8,573	8,577	80
121	8,789	8,784	35
006	9,244	9,249	25
115	9,416	9,421	80
300	9,792	9,802	25
023	9,943	9,953	40
106	10,354	10,338	50
302	10,826	10,832	50
123	11,033	11,038	100
310	11,726	11,709	40
221	12,242	12,253	100
116		12,247	
215	12,680	12,691	5
206	13,593	13,605	40
313	14,027	14,021	20
223	14,307	14,307	20
125	15,148	15,154	5
216	15,532	15,519	35
314	15,817	15,824	25
008	16,440	16,446	10
225	18,419	18,419	15
132	19,286	19,300	5
230	21,565	21,543	18
134	22,389	22,389	15
232	22,593	22,571	15
218	23,732	22,710	10

Least-squares treatments of both structures resulted in values of $R = \Sigma||F_o| - s|F_c||/\Sigma|F_o|$, with s a scale factor, equal to 0.096 for 443 observed reflections for Ta_2S and equal to 0.066 for 668 observed reflections for Ta_6S.

The Ta atoms in both structures are all contained in chains of slightly distorted body-centered pentagonal antiprisms sharing faces. The chains run parallel to

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[1] This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2500.

[2] (a) H. F. Franzen and J. G. Smeggil, *Acta Cryst.*, in press; (b) H. F. Franzen and J. G. Smeggil, submitted for publication.