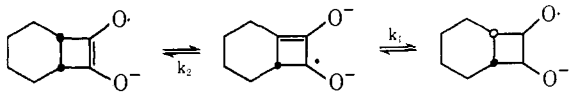
and **8**.[6] We expected that a radical-dianion mechanism might yield a one-deuterium exchange while a diketone mechanism should yield a two-deuterium exchange. Both **7** and **8** gave a fairly clean-cut two-deuterium exchange in DMSO containing potassium *t*-butoxide at 25° (Table I).

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.

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

$$\mathrm{H^+}\downarrow\uparrow\mathrm{-H^+}$$

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

9

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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.

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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	$\sin^2\theta_{\mathrm{obsd}} \times 10^5$	$\sin^2\theta_{\mathrm{calcd}} \times 10^5$	$I/I_0 \times 100$
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
221 116	12,242	12,253 12,247	100
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.

Table II. Ta$_6$S

hkl	$\sin^2 \theta_{obsd} \times 10^5$	$\sin^2 \theta_{calcd} \times 10^5$	$I/I_0 \times 100$
002	1,388	1,392	10
200	1,524	1,519	5
−311	4,871	4,867	1
−312		4,886	
004	5,561	5,569	1
311	6,923	6,914	1
020	8,480	8,499	25
021	8,863	8,848	60
312	8,992	8,982	25
−315	9,118	9,123	70
−115	9,508	9,498	20
−513	9,621	9,631	25
204	9,818	9,818	20
022	9,885	9,896	20
−511	10,263	10,258	100
−514	10,375	10,359	80
−602	10,951	10,968	55
−223	11,110	11,104	85
023	11,631	11,636	90
313	11,743	11,748	60
006	12,523	12,529	1
−224	12,854	12,854	1
115	12,919	12,913	50
−423	13,617	13,611	70
−606	13,912	13,906	5
024	14,082	14,069	1

the *b* axes in both Ta$_2$S and Ta$_6$S. The average Ta–Ta distance from the central Ta atom to one on the pentagonal antiprisms is 2.91 Å in Ta$_2$S and 2.93 Å in Ta$_6$S. The distance from one central Ta atom to the next such atom is 2.79 Å in Ta$_2$S and 2.64 Å in Ta$_6$S. Thus, in both structures, each central Ta atom is surrounded by 12 Ta atoms in a slightly distorted icosahedron.

In the Ta$_2$S structure the chains of Ta antiprisms are bridged in the *a* and *c* directions by two types of sulfur atoms. The first type is bonded to six Ta atoms forming faces of each of two antiprisms with an average Ta–S distance of 2.56 Å. The second type of sulfur atom is bonded to three Ta atoms forming the face of one antiprism and to a Ta atom at the corner of another antiprism with an average Ta–S distance of 2.47 Å.

In Ta$_6$S, the Ta chains are bridged in the *a* and *c* directions by one sulfur atom bonded to six Ta atoms forming a distorted trigonal prism with an additional Ta atom capping one of the rectangular faces. The average Ta–S distance in Ta$_6$S is 2.49 Å.

Each of these structures is a new type and exhibits a very different type of metal coordination than is found in other known transition metal sulfides, such as Hf$_2$S,[3] Ti$_2$S,[4] V$_3$S,[5] and Nb$_{21}$S$_8$[6] or related phosphides such as Ta$_2$P[7] or Nb$_7$P$_4$.[8] In all of these structures, with the exception of Hf$_2$S, there exist remnants of body-centered structures of the metal.[9] The interpenetrating icosahedral arrangement of Ta atoms in Ta$_6$S and Ta$_2$S is unique to these compounds among known structures. These are the only metal-rich compounds of those mentioned above in which there exist metal atoms which do not have nonmetal near neighbors. The coordination about the sulfur in Ta$_6$S is similar to that found about the nonmetal atoms in Hf$_2$S, V$_3$S, Ti$_2$S, Nb$_{21}$S$_8$, Ta$_2$P, and Nb$_7$P$_4$, namely trigonal prismatic. However, the two sulfur atoms in Ta$_2$S are not found in a trigonal-prismatic coordination. A relatively large hole surrounded by sulfur (the shortest S–S distance is 2.86 Å) separates four chains of interpenetrating icosahedra in Ta$_2$S. This unusual structural feature is unique among the metal-rich sulfides and phosphides.

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(3) H. F. Franzen and J. Graham, *J. Inorg. Nucl. Chem.*, **28**, 377 (1966).

(4) J. P. Owens, B. R. Conrad, and H. F. Franzen, *Acta Cryst.*, **23**, 77 (1967).

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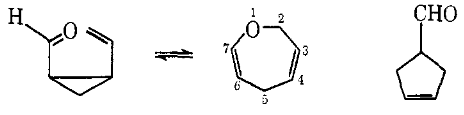
Valence Tautomerism in *cis*-2-Vinylcyclopropanecarboxaldehyde. 2,5-Dihydrooxepin

Sir:

Among the valence isomers of *cis*-2-vinylcyclopropanecarboxaldehyde (I), the retro-Claisen rearrangement product, 2,5-dihydrooxepin (II), might reasonably be expected to exist in equilibrium with the parent substance at ordinary temperatures.[1] Earlier workers[2] sought to observe such behavior without success; I was reported to show "surprisingly high thermal stability," resisting change up to 400°, at which temperature it rearranged to 3-cyclopentenecarboxaldehyde (III). We wish to report that I, in fact, is quite thermolabile and may be diverted quantitatively to II under mild conditions.[3]



I II III

Compound I was prepared from *cis*-2-vinylcyclopropanecarboxylic acid chloride[4] by conversion to the acylaziridine and LiAlH$_4$ reduction of the latter.[5] The crude product (bp 40–50° (10 mm)) was purified by preparative glpc. The structure of I follows from its method of preparation and its spectral properties. A molecular weight of 96 is obtained mass spectrally; the infrared spectrum confirms the presence of the

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(1) Evidence for the phenomenon in the closely related system

has been presented by M. Rey and A. S. Dreiding, *Helv. Chim. Acta*, **48**, 1985 (1965).

(2) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

(3) Under more energetic conditions (∼200–300°), I interconverts with its *trans* isomer and with its valence isomer, 2-vinyl-2,3-dihydrofuran, while proceeding irreversibly to III. We hope to report quantitative data on these processes soon (unpublished experiments, R. D. Cockroft).

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