SEMIDIONE DERIVATIVES OF SILACYCLOALKENES[1]

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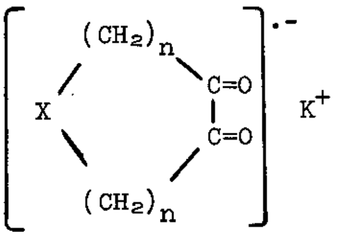
The structures of **1** ($X = CH_2$) and **2** ($X = Si(CH_3)_2$) have been studied by esr spectroscopy from -30 to +100°C. Ring inversion can be observed for the cis semidiones **2** (n = 2,3) and **1** (n = 3), but not for **1** with n = 2. Trans semidiones are observed for **2** (n = 3-5) and **1** (n = 4-6), but not for **1** with n = 3.

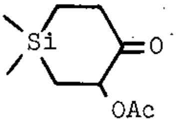
1,2-Semidiones are paramagnetic derivatives of alkenes from whose esr spectra information can be obtained on the occurrence of E,Z-isomers as well as conformational structure.[4] Herein we report the effect of substitution of $(CH_3)_2Si<$ for $CH_2<$ in cyclic 1,2-semidiones.



1, $X = CH_2$; **2**, $X = (CH_3)_2Si$
a, n = 2; **b**, n = 3; **c**, n = 4; **d**, n = 5

The expectation that the larger radius of silicon would increase the probability for conformational motion and facilitate the formation of a cyclic trans semidione has been realized.

The semidiones were formed by the treatment of the α-hydroxy ketones or bis(trimethylsiloxy)alkenes with potassium dimsylate in Me_2SO.[5] Solutions were diluted with THF for low temperature studies. For substrates with silicon β to the potential semidione function only acyclic semidiones could be observed, e.g.,

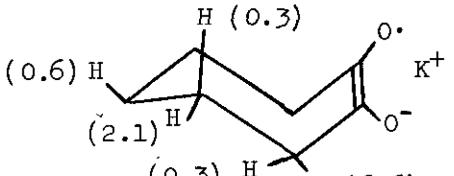


$$\xrightarrow[Me_2SO]{K^{+-}CH_2SOCH_3,} X\text{-}\overset{|}{\underset{|}{Si}}\text{-}CH_2CH_2C(\text{-}O\cdot)=C(\text{-}O^-)CH_3$$

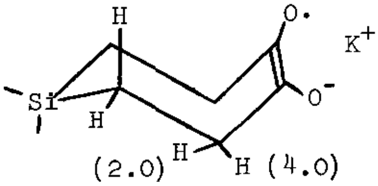
trans, $a^H = 5.74$ G (3H), 4.81 G (2H), $g = 2.00506$; cis, $a^H = 6.99$ G (3H), 5.98 G (2H), $g = 2.00495$

Semidiones with silicon γ or δ to the spin label had stabilities comparable to their carbocyclic analogues.

Cycloheptane-1,2-semidione (1a) exists as a staggered chair-like conformation up to 100°C with no indication of ring inversion, which would time average the quasi-axial and -equatorial hydrogen atoms ($E_a > 7$ kcal/mol).[6] The silicon analog 2a shows conformational motion over the entire temperature range investigated (-30° - +100°C). At +90° the spectrum is a pentet of pentets from four time-averaged α-hydrogen atoms ($a_{avg}^H = 3.08$ G) and four β-hydrogen atoms ($a_{avg}^H = 0.95$ G). Upon cooling to 25° the α-hydrogen atoms are no longer time-averaged ($a_{ax}^H = 4.0$ G, $a_{eq}^H = 2.0$ G). The β-hydrogen atoms whose a^H values are closer in magnitude are still in the fast exchange mode at 25° to -30°C with the 2nd and 4th peak of the pentet broadened. The observed hfsc for 2a are consistent with the chair-like conformation previously assigned to 1a.[6]



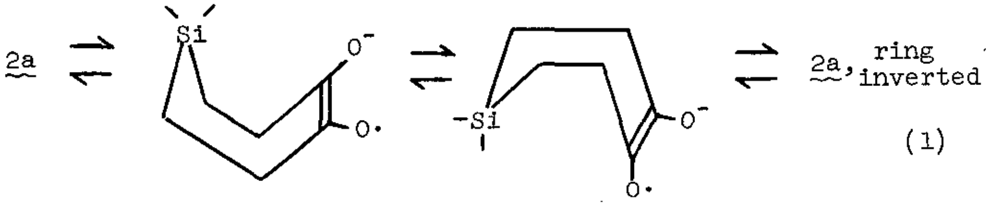
1a, a^H in Gauss $g = 2.00482$



2a, a^H in Gauss $g = 2.00495$

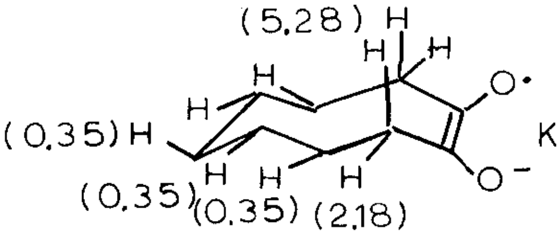
a_β^H (avg) $= 1.0$ G

From line broadening an E_a for ring inversion of 2a of 6.9 kcal/mol is calculated. However, the chair-like conformation of 2a cannot undergo the concerted ring flip which is possible for cyclohexane-1,2-semidione ($\Delta H^{\ddagger} = 4.0$ kcal/mol).[7] Dreiding models indicate that 2a, but not 1a, can be converted to the boat-like conformation which can undergo internal rotation to give ring inversion (Eq. 1).

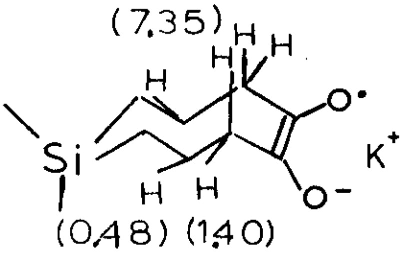


(1)

The C$_9$ carbocyclic semidione 1b is conformationally rigid on the esr time scale at 25°, and the rich hyperfine structure indicates a staggered chair-like conformation. Upon warming the hfs for β, γ, and δ hydrogen atoms are lost to give a triplet of triplets from the α-hydrogen atoms which coalesces to a pentet at 110°. From peak separation E_a for ring inversion of 5.6 kcal/mol is measured.



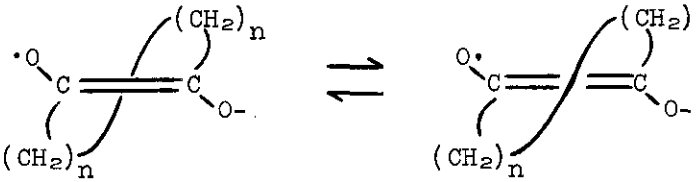
1b, a^H in Gauss, $g = 2.00493$



2b, a^H in Gauss, $g = 2.00494$

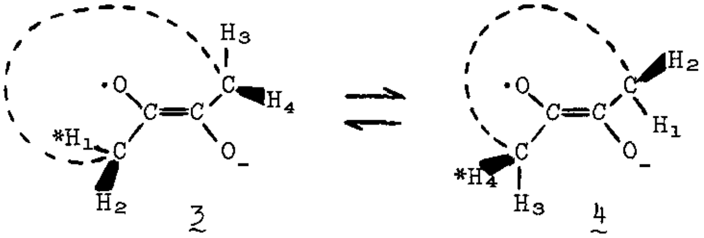
In the presence of 0.1 M K^+ a mixture of two semidiones is observed for the 9-membered ring silicon compound. These are identified as the Z ($g = 2.00494$) and E ($g = 2.00507$) isomers. Higher K^+ concentrations favor the ion-paired cis structure whose hfs pattern is consistent with a chair-like conformation. Warming causes a coalescence of the α-hydrogen atoms with $E_a = 2.9$ kcal/mol measured for ring inversion from peak positions.

The thermodynamically more stable trans isomer can be observed free of the cis isomer in the presence of an excess of [2.2.2]-cryptand, which prohibits stabilization of the cis structure by ion pairing.[8] The trans semidione shows hfs by two pairs of α-hydrogen atoms ($a^H = 3.6$, 2.3) at 50°. These hydrogens are not time averaged up to 100° excluding internal rotations (Eq. 2) as a facile process for trans-**2b**. Upon cooling the spectrum shows



(2)

selective line broadening with the wing peaks and center line remaining sharp to give a 1:2:1 spectrum at -30°. We can only explain this observation by the assumption that the trans semidione exists in a conformation containing four different α-hydrogen atoms, e.g., **3** and **4**, with a fortuitous overlap of intensity 2 at the center of the spectrum. Time averaging ($\underline{E}_a$ < 3 kcal/mol) of **3** and **4** (Eq. 3) will produce the triplet of triplets observed at 50°. Conformational motion is still occurring at -30°.



(3)

The 11- and 13-atom semidiones exist in the *E*-configurations even in the presence of 0.1 *M* K^+. However, even at 120°C the α-hydrogen atoms are not time averaged (Eq. 2) in 10^{-8} sec. Apparently one or more conformations with $\underline{C}_2$-symmetry are involved.

Table 1. Large Ring Semidiones (Me_2SO, K^+)

Semidione	Temp °C	$\underline{a}^H$ values (Gauss)	*g*-value
2c	25°	8.79 (2H), 1.39 (2H), 0.30 (4H)	2.00507
2d	25°	7.19 (2H), 1.60 (2H)	2.00509
1c	120°	5.81 (2H), 1.69 (2H)	-------
2d	120°	6.39 (2H), 1.38 (2H)	-------
1 (n=6)	25°	7.10 (2H), 1.93 (2H)	2.00508

There is some change in the conformational structure of the 11- and 13-membered rings with temperature since the larger hfsc increase and the smaller hfsc decrease and eventually disappear as the temperature decreases over the range + 120 to - 60° C.

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REFERENCES

1. Application of ESR Spectroscopy to Problems of Structure and Conformation. Part 31.
2. National Science Foundation Fellow, 1975-1978.
3. National Science Foundation Undergraduate Research Participant, June - August, 1978.
4. G. A. Russell, E. T. Strom, E. R. Talaty, K.-Y. Chang, R. D. Stephens, and M. C. Young, *Rec. Chem. Progress*, **27**, 3 (1966).
5. G. A. Russell and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 744 (1964).
6. G. A. Russell, R. G. Keske, G. Holland, J. Mattox, R. S. Givens, and K. Stanley, *J. Amer. Chem. Soc.*, **97**, 1892 (1975).
7. G. A. Russell, G. R. Underwood, and D. C. Lini, *J. Amer. Chem. Soc.*, **89**, 6636 (1967).
8. G. A. Russell, G. Wallraff, and J. L. Gerlock, *J. Phys. Chem.*, **82**, 1161 (1978).
9. W. P. Weber, R. A. Felix, A. K. Willard, and H. G. Boettger, *J. Org. Chem.*, **36**, 4060 (1971).
10. R. A. Benkeser and R. F. Cunico, *J. Org. Chem.*, **32**, 395 (1967).
11. P. Mazerolles and A. Faucher, *Bull. Soc. Chim. Fr.*, 2134 (1967); P. Mazerolles, A. Faucher, A. Laporterie, *ibid.*, 887 (1969).

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