

in more planar structures. Calculations suggest that through-space orbital interactions<sup>29</sup> may play an important role in determining the spectroscopic properties of molecules.

The remaining result on which the calculations shed some light is the smaller positive  $\Delta\epsilon$  observed for the 2,4,9(11)-triene (**2g**) in comparison to the analogous 2,4-diene (**2e**) (+7.1; cf. +11.2). Both are essentially completely in the E conformation, according to the calculations on the model systems, and the calculated diene dihedral angle is in fact slightly greater for the triene. The position and intensity of the uv absorption maximum of the long wavelength  $\pi \rightarrow \pi^*$  band of the triene (**2g**) do not suggest any great degree of conjugation between the diene system and the homoallylic double bond (**2g**,  $\lambda$  267 nm,  $\epsilon$  5670; **2e**,  $\lambda$  265 nm,  $\epsilon$  6400). The calculated VESCF bond order between the C5  $\pi$  orbital and the C9  $\pi$  orbital when the 9(11) double bond is included in the  $\pi$  system is 0.03 (distance 2.529 Å) as against a bond order of 0.31 between the C3 and C4  $\pi$  orbitals. The dihedral angle between the 9–11 and 5–4 bonds is calculated to be  $-17.1^\circ$  for the model system. This is in the opposite sense to the chirality of the 2,4-diene system in this conformer. It seems reasonable that an interaction of this type should affect the vectorial rotational strength more than it affects the scalar oscillator strength. (This also holds true for the axial allylic bond effect.) The small  $\Delta\epsilon$  observed

(29) C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, *J. Chem. Soc., Perkin Trans. 2*, 210 (1973).

for the 2,4,9(11)-triene (**2g**) should thus be attributed to a specific electronic interaction rather than to a conformational change.

An alternative analysis of this observation might be made in terms of an allylic bond polarization rule.<sup>23</sup> However, such a rule as presently formulated would require that a  $\Delta 9(11)$  double bond and a  $10\beta$ -methyl group have a substituent effect of the same sign, contrary to observation.

Perhaps the most important insight provided by the calculations is that very different conformational situations can give rise to very similar Cotton effects. Thus according to our calculations, the small  $\Delta\epsilon$  observed for the  $10\beta$ -H, $9\alpha$ -H compound **2i** arises from an essentially conformationally homogeneous system and is attributable to the near planarity of the diene and the absence of substituent effects. However, the small  $\Delta\epsilon$  observed for the  $9\alpha,10\beta$ -dimethyl compound **2h** arises from the canceling Cotton effects of two conformers present in a near 1:1 ratio, which would each individually be expected to show a strong Cotton effect.

A more exact definition of the conformational properties of such flexible systems (and hence of the veracity of the calculated conformational preferences) must await further experimental data or advances in the quantitative theory of the Cotton effect. The value of force field calculations in providing insights into such complex conformational problems does seem clear, particularly in view of the difficulties in interpreting measurements of the Cotton effect.

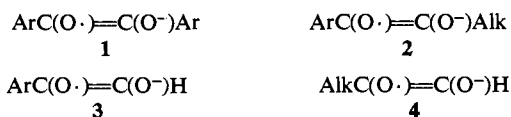
## Aliphatic Semidiones. XXII. Acyclic Dialkyl-1,2-semidiones<sup>1</sup>

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Ames, Iowa 50010. Received April 3, 1974

**Abstract:** Mixtures of cis and trans isomers have been detected by esr spectroscopy for the symmetrical semidiones  $RC(O\cdot)=C(O^-)R$  where  $R = CH_3, C_2H_5, n-C_3H_7, (CH_3)_2CHCH_2, (CH_3)_3CCH_2,$  and  $(CH_3)_2CH$  and for the series  $RC(O\cdot)=C(O^-)CH_3$  where  $R = C_2H_5, n-C_3H_7, (CH_3)_3CCH_2, (CH_3)_2CH,$  and  $(CH_3)_3C$ . Symmetrical semidiones with  $R = (CH_3CH_2)_2CH, (CH_3CH_2CH_2)_2,$  and  $(CH_3)_3C$  showed only a single (trans) isomer. When both cis and trans isomers were detectable the cis isomers were favored by the presence of smaller gegenions and solvents of lower polarity. Lowering the temperature seemed to have little effect on the conformation of alkyl groups such as  $(CH_3)_2CH$  or  $CH_3CH_2$  in the semidiones. Lower temperatures favored the trans isomers over the cis isomers and caused the semidiones to disproportionate into the diketone and enediol dianion.

**D**iarylsemidiones (**1**),<sup>4-7</sup> alkylarylsemidiones (**2**),<sup>8,9</sup> monoarylglyoxal radical anions (**3**),<sup>9-13</sup> and monoalkylglyoxal radical<sup>10,13,14</sup> anions (**4**) have been de-



scribed. Semidiones **1** and **2** prefer to exist in a trans

(1) This work was supported by grants from the National Science Foundation and the National Institutes of Health.

(2) National Defense Education Act Predoctoral Fellow, 1967–1968.

(3) National Institutes of Health Postdoctoral Fellow, 1965.

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(9) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1988 (1966).

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Table I. Dialkylsemidiones Observed in DMSO, 0.1 M K<sup>+</sup>, 25°

Substituents	$a_{\alpha}^H$	$a_{\beta}^H$	$a_{\alpha}^C$	$a_{\alpha'}^C$	$a_{\beta}^C$	$g$ value	[Trans]/[cis]
R = R' = H <sup>a</sup>							
Trans	7.6 <sup>b</sup>						
Cis	Not detected						> 50
R = R' = CH <sub>3</sub>							
Trans	5.6		4.5 <sup>c</sup>			2.00497	
Cis	7.0		5.2 <sup>c</sup>			2.00483	16
R = R' = CF <sub>3</sub> <sup>e</sup>							
Trans	8.24 <sup>f</sup>		4.52, 1.98			$\Delta g \cong 0.00004$	
Cis	11.53 <sup>f</sup>						> 100
R = R' = CH <sub>3</sub> CH <sub>2</sub>							
Trans	4.9	~0.02	~4.3		4.25 <sup>c</sup>	2.00485	
Cis	6.0					2.00487	6
R = R' = CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>							
Trans	4.6	0.20		4.4			
Cis	5.6						3.3
R = R' = (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>							
Trans	4.3	0.28		4.4		2.00493	
Cis	5.3					2.00487	~50
R = R' = (CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>							
Trans	3.5						
Cis	4.5						~100
R = R' = (CH <sub>3</sub> ) <sub>2</sub> CH							
Trans	2.0	~0.033	4.0 <sup>c</sup>		~4	2.00486	
Cis	2.4 <sup>g</sup>					2.00483	> 100
R = R' = (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> CH							
Trans	1.09	0.13		~3.5			
Cis	Not detected						> 100
R = R' = (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> CH							
Trans	0.95			~3.5			
Cis	Not detected						> 100
R = R' = (CH <sub>3</sub> ) <sub>3</sub> C <sup>h</sup>							
Trans		0.29	3.8 <sup>h,i</sup>		2.3 <sup>h</sup>		
Cis	Not detected						> 200
R = CH <sub>3</sub> , R' = H <sup>a</sup>							
Trans	7.6, <sup>b</sup> 5.1					2.00515	
Cis	8.7, <sup>b</sup> 7.6					2.00505	2
R = CH <sub>3</sub> , R' = CH <sub>3</sub> CH <sub>2</sub>							
Trans	4.85 (2), 5.75 (3)					2.00497	
Cis	6.10 (2), 7.05 (3)						12
R = CH <sub>3</sub> , R' = CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>							
Trans	4.6 (2), 5.6 (3)	0.15					
Cis	Not detected						> 20
R = CH <sub>3</sub> , R' = (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>							
Trans	4.4 (2), 5.6 (3)						
Cis	Not observed						> 50
R = CH <sub>3</sub> , R' = (CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>							
Trans	3.8 (2), 5.4 (3)					2.00497	
Cis	Not observed						> 50
R = CH <sub>3</sub> , R' = (CH <sub>3</sub> ) <sub>2</sub> CH							
Trans	2.0 (1), 5.8 (3)		~4.0, 4.6	3.75 <sup>a</sup>		2.00496	
Cis	2.5 (1), 7.0 (3)	0.15					~100
R = CH <sub>3</sub> , R' = (CH <sub>3</sub> ) <sub>3</sub> C							
Trans	5.6	0.29					
Cis	Not detected						~100

<sup>a</sup> Reference 13. <sup>b</sup>  $a_{CH_3O^H}$ . <sup>c</sup> <sup>13</sup>C isotopically enriched, reference 22. <sup>d</sup>  $a^O = 10.3$  G from <sup>17</sup>O isotopically enriched sample. <sup>e</sup> Reference 31. <sup>f</sup>  $a^F$ . <sup>g</sup> Observed in the presence of Na<sup>+</sup>. <sup>h</sup> Reference 25. <sup>i</sup>  $a^O = 10.5$  G.

as a result of lower planarity (*i.e.*, more strain in HOMO)<sup>25,26</sup> or of a more pronounced ion pairing (chelation) for the cis isomer. Values of  $\Delta g$  and  $\Delta a_{\alpha}^H$  were not particularly sensitive to the nature of the gegenion although the cis/trans ratios were highly dependent on the counterion.

The cis/trans ratios of Table I show the expected steric control in that when R becomes secondary alkyl or tertiary alkyl the trans isomer greatly predominates. Apparently in going from R = H to methyl, to ethyl, to *n*-propyl in the symmetrical semidiones the predominant nonbonded interaction is the alkyl-oxygen cisoid repul-

sion (in the trans isomer). Thus, the trans/cis ratio decreases from >50 (R = H, K<sup>+</sup>, and DMSO) to 16 (R = methyl) to 6 (R = ethyl), and to 3.3 (R = *n*-propyl). However, for R = secondary or tertiary alkyl groups apparently alkyl-alkyl repulsions now become the dominant factor by far and the trans/cis ratio becomes quite large as the bulk of R is increased.

The values of  $a_{\alpha}^H$  and  $a_{\beta}^C$  reflect conformational preferences of the alkyl groups and are determined mainly by hyperconjugation according to eq<sup>27</sup> 1 and 2 where

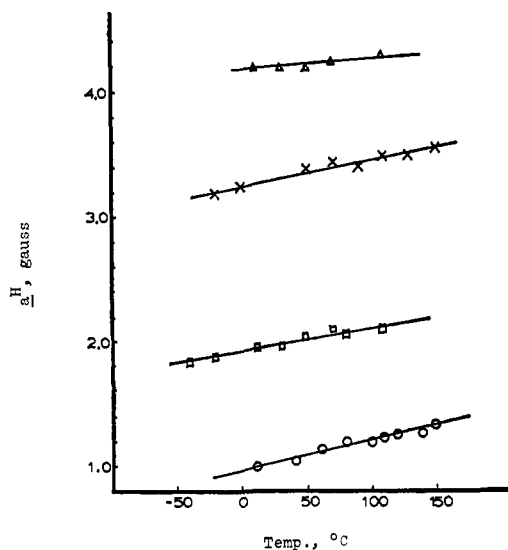
$$a_{\alpha}^H = B^H \rho_{\alpha}^{\pi} \langle \cos^2 \theta^H \rangle \quad (1)$$

$$a_{\beta}^C = B^C \rho_{\beta}^{\pi} \langle \cos^2 \theta^C \rangle \quad (2)$$

(25) G. A. Russell and G. R. Underwood, *J. Phys. Chem.*, **72**, 1074 (1968).

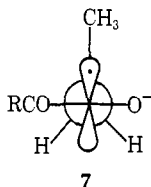
(26) A. J. Stone, *Mol. Phys.*, **6**, 509 (1963); *ibid.*, **7**, 311 (1964).

(27) H. C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).



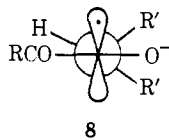
**Figure 1.** Effect of temperature of  $a_{\alpha}^H$  for *trans*-dialkylsemidiones in DMF solutions in the presence of potassium *tert*-butoxide;  $\Delta$ , diisobutylsemidione;  $\times$ , dineopentylsemidione;  $\square$ , diisopropylsemidione;  $\circ$ , di-4-heptylsemidione.

$B^H \sim 40$  for a semidione,<sup>9</sup>  $B^C \sim 20$ ,<sup>22,28</sup> and  $\rho_0^{\pi} \sim 0.25$ .<sup>9</sup> The values of  $a_{\alpha}^H$  decrease from methyl (no conformational preference,  $\langle \cos^2 \theta^H \rangle = 1/2$ ) to ethyl to isopropyl. At the same time  $a_{\beta}^C$  decreases from ethyl to isopropyl to *tert*-butyl (no conformational preference,  $\langle \cos^2 \theta^C \rangle = 1/2$ ). The values of  $a_{\alpha}^H$  and  $a_{\beta}^C$  for diethylsemidione suggest that conformation 7 ( $\langle \cos^2 \theta^H \rangle = 1/4$ ) is pre-



ferred. As the bulk of the  $\beta$ -alkyl group is increased the value of  $a_{\alpha}^H$  decreased from (trans isomers) 4.9 G (ethyl) to 4.6 G (*n*-propyl), to 4.3 G (isobutyl), and to 3.5 G (neopentyl) suggesting a higher population of 7, or less vibrational movement in 7.<sup>29</sup>

For the secondary alkyl groups conformation 8 is

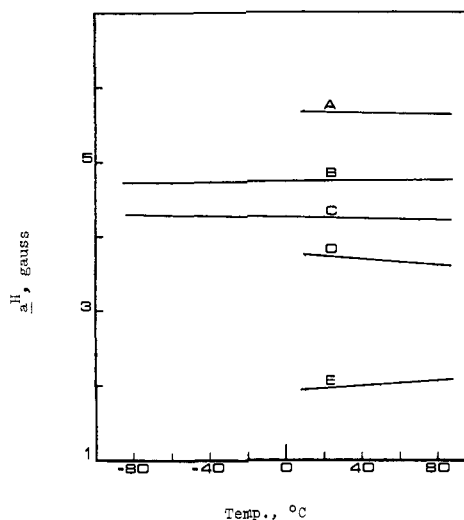


indicated. The value of  $\langle \cos^2 \theta^H \rangle$  is low and becomes lower as  $R'$  becomes more bulky,  $a^H = 2.0$  ( $R' = \text{CH}_3$ ), 1.1 ( $R' = \text{C}_2\text{H}_5$ ), and 0.95 ( $R' = n\text{-C}_3\text{H}_7$ ). The effect of decreasing temperature for  $R = \text{isopropyl}$  is to cause a small decrease in  $a_{\alpha}^H$  and slightly increase  $a_{\beta}^C$  (Figure 1). However, for an ethyl group no significant temperature effect was noted (Figure 2) although for diisobutylsemidione  $a^H$  decreased from 100 to 0° at the rate of  $1 \times 10^{-3}$  G/°C and for dineopentylsemidione  $a^H$  decreased at the rate of  $2.2 \times 10^{-2}$  G/°C (Figure 1).

The hfsc of Table I (in DMSO solution) are in good

(28) H. Lemaire, A. Rassat, P. Servoz-Gavin, and G. Berthier, *J. Chim. Phys. Physiochim. Biol.*, 1247 (1962).

(29) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 37, 1326 (1962); *ibid.*, 38, 1254 (1963).



**Figure 2.** Effect of temperature on  $a^C$  and  $a^H$  in *trans*-1-<sup>13</sup>C-hexane-3,4-semidione in DMF and *trans*-1-<sup>13</sup>C-2-methylpentane-3,4-semidione in DMSO containing potassium *tert*-butoxide: (A)  $a_{(C-6)H_3}^H$ , (D)  $a_{C-1}^C$ , (E)  $a_{(C-2)H}^H$  in 2-methylpentane-3,4-semidione; (B)  $a_{CH_2}^H$ , (C)  $a_{CH_3}^C$  in hexane-3,4-semidione.

agreement with the hfsc reported for semidione radical anions in aqueous solution<sup>20</sup> with one exception (Table II). From Table II it appears most likely that in the

**Table II.** Values of  $a_{\alpha}^H$  (G) for Symmetrical Semidiones in Water and in DMSO

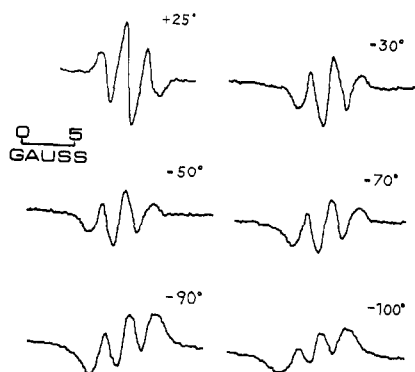
R	Radical anion		Neutral radical <sup>20</sup> H <sub>3</sub> O <sup>+</sup>
	H <sub>2</sub> O <sup>20</sup>	DMSO	
CH <sub>3</sub>	Cis	8.2 <sup>a</sup>	9.6
	Trans	7.1 <sup>b</sup>	8.3
C <sub>2</sub> H <sub>5</sub>	Cis	5.7	7.7
	Trans	5.0	5.5
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Cis	5.4	7.1
	Trans	4.7	5.1
Isopropyl	Cis	2.5	3.0
	Trans	1.7	2.3

<sup>a</sup> Trans neutral radical (?). <sup>b</sup> Cis radical anion (?).

aqueous flow experiments with acetoin a mixture of the cis radical anion,  $a^H = 7.1$  G, and trans neutral radical ( $\text{CH}_3\dot{\text{C}}(\text{OH})\text{COCH}_3 \rightleftharpoons \text{CH}_3\text{CO}\dot{\text{C}}(\text{OH})\text{CH}_3$ ),  $a^H = 8.2\text{--}8.3$  G, was actually observed.

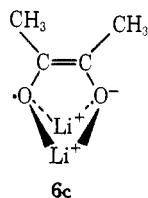
**Effects of the Gegenions on [Trans]/[Cis] Ratios.** Table III presents data on the value of  $a_{\alpha}^H$ ,  $a^M$ , and [trans]/[cis] for three semidiones. Typical spectra for dimethylsemidione are given in Figure 3. Little effect on  $a_{\alpha}^H$  is observed by variation of the counterion although some variation in  $a_{\beta}^H$  and  $a_{\text{CO}}^C$  is observed (Tables I and III). The trans/cis ratios for all three semidiones as measured by relative peak heights increase drastically as the gegenion is varied from lithium (only cis detected) to sodium to potassium to rubidium and to cesium (only trans detected). For dimethylsemidione tetramethylammonium ethoxide gives a trans/cis ratio (35:1) between potassium and rubidium while with diethylsemidione benzyltrimethylammonium ion gives a ratio (8:1) very similar to potassium. It is of interest to





**Figure 4.** ESR spectra observed upon reduction of isobutyryl on a potassium mirror in THF (84%)–DME (16%).

butoxide in 2 ml of acetonitrile a mixture of the cis ( $a_{\text{CH}_3^{\text{H}}} = 7.01$  G) and trans ( $a_{\text{CH}_3^{\text{H}}} = 5.71$  G) semidiones was observed in which the trans isomer greatly predominated. Addition of 0.3–1.0 mmol of lithium iodide in 1 ml of acetonitrile gave spectra in which only the cis isomer could be detected with  $a^{\text{Li}} = 0.55$  G and  $a_{\text{CH}_3^{\text{H}}} = 7.63$ . Increasing the lithium iodide concentration to 3–5 mmol completely removed the hfs by lithium and increased  $a_{\text{CH}_3^{\text{H}}}$  to 8.00 G. It can be inferred that lithium is still tightly associated with the cis semidione not only from the value of  $a^{\text{H}}$  but also from the fact that no trans isomer can be detected. The increase in  $a_{\alpha^{\text{H}}}$  for **6** from 7.63 to 8.00 as the lithium ion concentration is increased may indicate the existence of a new species at high  $\text{Li}^+$  concentrations, possibly **6c**. Mixtures of DMSO and THF showed a similar



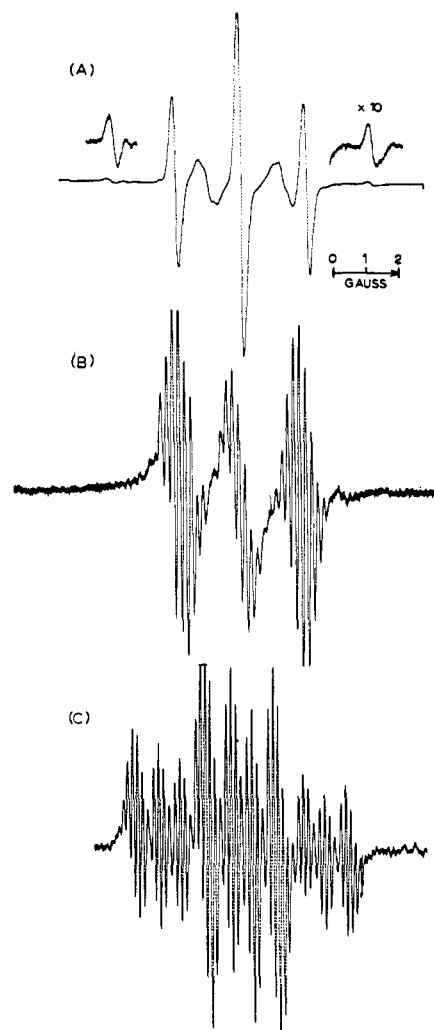
effect. Treatment of 0.05 mmol of acetoin with 0.11 mmol of potassium *tert*-butoxide in 2 ml of DMSO with 0.33 mmol of lithium iodide in 1 ml of THF gave **6** with  $a^{\text{H}} = 7.53$  and  $a^{\text{Li}} = 0.59$ . Increasing the lithium iodide concentration to 5 mmol caused  $a^{\text{Li}}$  to disappear and  $a^{\text{H}}$  to increase to 7.82 G.

In this work we have never obtained evidence for the independent existence of the free cis semidione (**5**) and the 1:1 ion pair (**6**). Time averaging between these two species seems to be quite rapid. There is a report in the literature that under kinetically controlled conditions in aqueous solution the free ion and the magnesium chelate of biacetylsemidione can be observed simultaneously in a flow system.<sup>30</sup> However, as illustrated in Table II, we feel that in water the assignment of hfsc to the neutral radical and the radical anions needs further investigation.

Perfluorobiacetyl radical anion provides an example of ion pairing between lithium, sodium, or potassium and the trans semidione in solvents such as THF at 25° as evidenced by line width alternation.<sup>21,31</sup> This ion pairing results in a magnetic nonequivalence of the

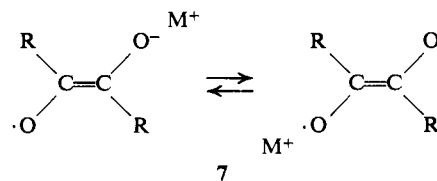
(30) A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 2053 (1972).

(31) G. A. Russell and J. L. Gerlock *J. Amer. Chem. Soc.*, **96**, 5838 (1974).



**Figure 5.** ESR of diisopropylsemidione: (A) trans isomer ( $a^{\text{H}} = 2.02$  G) showing  $a^{\text{C}}$  (natural abundance) = 3.9 in DMSO containing potassium *tert*-butoxide; (B) spectrum attributed to trans isomer ( $a^{\text{H}} = 1.9$  G) showing line width alternation and  $a_{\text{CH}_3^{\text{H}}} = 0.2$ , lithium in THF (65%)–HMPA (35%); (C) cis isomer,  $a^{\text{H}} = 2.25$  G, with  $a^{\text{Li}} = 0.65$  and  $a_{\text{CH}_3^{\text{H}}} = 0.16$  G observed with lithium *tert*-butoxide or potassium *tert*-butoxide and lithium iodide in DMSO solution.

trifluoromethyl groups as illustrated in **7**. Attempts to



prepare biacetylsemidione in ethereal solvents have so far been unsuccessful. However, reduction of isobutyryl on a potassium mirror in THF (84%)–DME (16%) yielded a 1:2:1 triplet at 25° which was consistent with the diisopropylsemidione. Cooling caused the central peak to broaden until at –100° a 1:~1:1 triplet resulted (Figure 4). This effect is consistent with the modulation of  $a_{\alpha^{\text{H}}}$  predicted by **7**. In another study reaction of 2,2,4,4-tetramethylcyclobutane-1,3-dione with lithium metal in THF (65%)–HMPA (35%) and a trace of oxygen gave a spectrum also consistent with **7** wherein a 2:~1:2 triplet ( $a^{\text{H}} = 1.90$  and  $a_{\beta^{\text{H}}} = 0.20$ ) was observed at 25° (Figure 5). The bicyclobutane **8** may be an intermediate in eq 4.

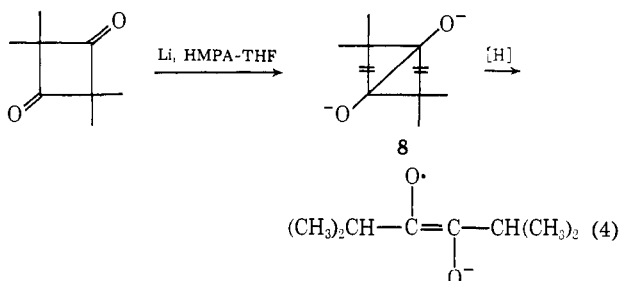
Table IV. [Trans]/[Cis] at Various Temperatures for Dialkylsemidiones (5) in DMSO

Subst	[Trans]/[Cis]						
	13°	23°	38°	53°	63°	78°	93°
R = CH <sub>3</sub> , 0.10 M K <sup>+</sup>		17.5	14.8		11.6	9.6	
R = CH <sub>3</sub> , 0.05 M K <sup>+</sup>		20.7	17.1	16.4	13.9	11.7	11
R = CH <sub>3</sub> , 0.025 M K <sup>+</sup>		23.7	20.3	17.6	17.2		
R = CH <sub>3</sub> , 0.20 M K <sup>+</sup> and DMF	6.1			4.0			2.3
R = CH <sub>3</sub> , 0.10 M Rb <sup>+</sup>		41	32	27	23	20	18
R = CH <sub>3</sub> CH <sub>2</sub> , 0.10 M K <sup>+</sup>	6.9		4.8	3.4	3.3	3.0	
R = CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> , 0.10 M K <sup>+</sup>	4.1		2.6	2.6	2.4	2.0	

Table V. [Trans]/[Cis] for Dimethylsemidione at 25°, 0.1 M Potassium Gegenion

Solvent	ε	[Trans]/[Cis]			
		100% <sup>c</sup>	80% <sup>a</sup>	50% <sup>a</sup>	20% <sup>a</sup>
DMSO	49 <sup>b</sup>	17.5 (6.2) <sup>c</sup>	17.5	17.5	17.5
DMF	37 <sup>d</sup>	7.8 (4.6) <sup>e</sup>	8.7	12.6	15
CH <sub>3</sub> OH	33 <sup>e</sup>				~10
HMPA	30 <sup>f</sup>	3.0	5.2	7.9	9.8
Pyridine	12 <sup>e</sup>	<0.1 (0.1) <sup>e</sup>	1.8	7.7	14
<i>t</i> -BuOH	12 <sup>e</sup>	<0.06	1.4	10	13
THF	7.4 <sup>g</sup>	<0.05 <sup>h</sup> (<0.05 <sup>h</sup> ) <sup>e</sup>			
DME	7.2 <sup>g</sup>	<0.05 <sup>h</sup> (<0.05 <sup>h</sup> ) <sup>e</sup>	0.7	4.5	11
CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub>		0.10			
CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> CH <sub>3</sub>		0.25	1.7	5.9	12
CH <sub>3</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>4</sub> CH <sub>3</sub>		0.25	3.4	8.6	19

<sup>a</sup> Vol % of solvent in DMSO. <sup>b</sup> H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960). <sup>c</sup> For diethylsemidione. <sup>d</sup> G. R. Leader and F. Gormley, *J. Amer. Chem. Soc.*, **73**, 5751 (1951). <sup>e</sup> A. A. Marriott and E. R. Smith, *Nat. Bur. Stand. Circ.*, No. 514 (1951). <sup>f</sup> J. Dubois and H. Viellard, *J. Chem. Phys.*, **62**, 699 (1965). <sup>g</sup> C. Corvajal, K. J. Tölle, J. Smid, and M. Swzarc, *J. Amer. Chem. Soc.*, **87**, 5548 (1965). <sup>h</sup> Trans not detected.



**Temperature Effect on the [Trans]/[Cis] Ratio.** The relative concentrations of trans and cis isomers of dimethylsemidione were measured from peak heights between 23 and 93° with several different gegenions in DMSO. The results with sodium were complex with plots of  $\log K$  vs.  $1/T$  showing curvature (0.05 M) or a maximum (0.1 M) although the overall effect of temperature was not large. No corrections were applied for obvious line width differences (from unresolved sodium hfs in the cis isomer) which undoubtedly were temperature dependent themselves. With potassium or rubidium as the gegenions no difference in line width was obvious and a gradual decrease in the ratio [trans]/[cis] was observed upon raising the temperature while plots of  $\log K$  vs.  $1/T$  gave good linear plots. It was thus estimated that the trans isomers are more stable than the cis isomers (0.1 M K<sup>+</sup> and DMSO) by  $1.5 \pm 0.5$  kcal/mol for R = methyl,  $2.3 \pm 0.5$  kcal/mol for R = ethyl, and  $1.9 \pm 0.5$  kcal/mol for R = *n*-propyl. Even if the extent of ionic association is itself independent of temperature, the observed values of  $\Delta H$  cannot reflect the true thermodynamic difference between the cis and trans form of 5 but rather a  $\Delta H$  affected by preferential ionic association of the cis isomer. Table IV lists some representative data.

#### Effect of Solvent on [Trans]/[Cis] Ratios for Dimethyl-

semidione. The [trans]/[cis] ratios (potassium gegenion) are quite sensitive to solvents, with solvents of low dielectric constants favoring the cis structure, undoubtedly as a consequence of increased ion pairing. Table V presents some representative data.

The effect of tri- and tetraglyme seems to be consistent with their known complexing ability for potassium cations.<sup>32</sup>

#### Experimental Section

**Precursors to Semidiones.** Dimethylsemidione was prepared from 3-acetoxy-2-butanone or commercial acetoin (Aldrich Chemical Co.) which had been extracted from aqueous solution by chloroform, dried over Na<sub>2</sub>SO<sub>4</sub>, and distilled (75–80° at 25–30 Torr); mass spectrum (70 eV) *m/e* (rel intensity) 91 (nil), 90 (1), 89 (10.6), 88 (100), 87 (16.3), 86 (4.15). Purified acetoin was stored over molecular sieves prior to use. 3-Hydroxy-2-butanone-*l*-<sup>13</sup>C was prepared from 10% isotopically pure iodomethane-<sup>13</sup>C (Merck Sharp and Dohme of Canada, Ltd.) and lactonitrile according to a literature procedure<sup>33</sup> to give material with a pmr of  $J_{CH} = 129$  Hz, mass spectrum, *m/e* (rel intensity) 88 (100), 89 (18.3), 90 (4.3). Dimethylsemidione was also prepared from 2,3-bis(trimethylsiloxy)-2-butene prepared from ethyl acetate and ethyl acetate-*l*-<sup>13</sup>C<sup>34</sup> by acyloin condensation with Na–K alloy in the presence of trimethylchlorosilane.<sup>35,36</sup> Distillation of the reaction product gave a fraction bp 65–75 at 12 Torr from which the cis and trans siloxybutenes were separated by glpc on a 20% SF-96 column at 155°. *cis*-2,3-Bis(trimethylsiloxy)-2-butene, retention time 10 min, gave a parent and principal ion at *m/e* 232 (70 eV): pmr (CCl<sub>4</sub>)  $\delta$  0 (s, 18), 1.57 (6); ir (neat) 2950, 1685, 1385, 1280, 1220, 1060, 1003 (cis C=C), 890, 843 cm<sup>-1</sup>.

*Anal.* Calcd for C<sub>10</sub>H<sub>24</sub>Si<sub>2</sub>O<sub>2</sub>: C, 51.67; H, 10.41; Si, 24.16. Found: C, 51.14; H, 10.28; Si, 23.01.

The minor (trans) isomer had a retention time of 12 min, pmr (CCl<sub>4</sub>) of  $\delta$  1.56 (s, 6) and 0 (s, 18), and mass spectrum (70 eV) of *m/e* 232 for parent and principal peak. The cis and trans isomers

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were not separated for the bis(trimethylsiloxy)butene prepared with  $^{13}\text{C}$  at the vinyl carbon atoms.

$^{17}\text{O}$  was incorporated into acetoin by heating 30  $\mu\text{l}$  of acetoin and 15  $\mu\text{l}$  of  $^{17}\text{O}$ -labeled water (15.5%  $^{17}\text{O}$ , Yeda Research Laboratories, Inc.) for 3 days at 150°. Under these conditions acetoin and  $^{18}\text{O}$ -enriched water (80%  $^{18}\text{O}$ ) yielded material with a mass spectrum (70 eV) of  $m/e$  (rel intensity) 93 (2.8), 92 (31), 91 (9.9), 90 (100), 89 (9.9), 88 (92), 87 (2.8), 86 (25.4) consistent with 30%  $\text{C}_4\text{H}_8\text{O}_2$ , 48%  $\text{C}_4\text{H}_8\text{O}^{18}\text{O}$ , and 22%  $\text{C}_4\text{H}_8^{18}\text{O}_2$ . The exchanged acetoin was isolated by glpc on a 20% DEGS column at 100°. The possibility of oxygen exchange with DMSO and base DMSO was investigated by use of the  $^{18}\text{O}$ -labeled sample. After 2 hr in DMSO (2  $\mu\text{l}$  of acetoin/2 ml of DMSO) the acetoin had a mass spectrum (70 eV) of  $m/e$  (rel intensity) 93 (4.1), 92 (36.8), 91 (10.2), 90 (100), 89 (10.2), 88 (95), 87 (2), 86 (24.5) while in the presence of a trace of potassium *tert*-butoxide the mass spectrum (70 eV) was  $m/e$  (rel intensity) 93 (2.1), 92 (23.2), 91 (8.5), 90 (8.5), 89 (8.5), 88 (100), 87 (4.3), and 86 (29.8).

2,7-Dimethyl-5-hydroxy-4-octanone (isovaleroin) was prepared from ethyl isovalerate by acyloin condensation using sodium in xylene<sup>37</sup> giving 62% of material, bp 98–100° at 45 Torr (lit.<sup>38</sup> bp 94–97 (12–13 Torr)). 2,2,7,7-Tetramethyl-5-hydroxy-4-octanone (dineopentylacyloin) was synthesized in a similar fashion to give 33% of a yellow oil that was purified by glpc: pmr ( $\text{CCl}_4$ )  $\delta$  1.02 (s, 18), 1.39 (q, 2,  $J = 2.7$  and 9.1 Hz), 2.30 (s, 2), 3.10 (broad s, 1), 4.02 (q, 1,  $J = 2.7$  and 9.1 Hz); mass spectrum (70 eV)  $m/e$  200 (molecular ion).

Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{O}_2$ : C, 71.99; w, 12.08. Found: C, 71.92; H, 12.36.

4-Hydroxy-3-hexanone and 5-hydroxy-4-octanone were prepared by the acyloin condensation of ethyl propionate and ethyl butyrate. 4-Hydroxy-3-hexanone- $I$ - $^{13}\text{C}$  was prepared from 1 g of 56% 2- $^{13}\text{C}$ -iodoethane (Merck Sharp and Dohme of Canada, Ltd.) diluted with 2 g of ordinary ethyl iodide. To the Grignard reagent (0.02 mol) was added 0.77 g (0.01 mol) of propionaldehyde cyanohydrin (City Chemical Corp.) to yield 0.5 g of the acyloin, bp 50–60° (10 Torr), purified by glpc on a 20% Carbowax column at 150°: pmr ( $\text{CCl}_4$ )  $\delta$  0.9–1.1 (t,  $\sim 5.4$ ,  $J = 7$  Hz); d of t,  $\sim 0.6$ ,  $J = 7$  Hz,  $J_{\text{CH}}$  = 125 Hz), 1.63 (m, 2,  $J = 7$  Hz), 2.45 (q, 2,  $J = 7$  Hz), 3.45 (s, 1), 4.02 (t, 1); mass spectrum (70 eV)  $m/e$  (rel intensity) 114 (100), 115 (32.1), 116 (90.4), 117 (19.3). Unlabeled propionin gave a mass spectrum (70 eV) of  $m/e$  (rel intensity) 114 (100), 115 (12.8), 116 (71), 117 (5.45).

2-Pentanone, 4,4-dimethyl-2-pentanone, and 5-methyl-2-hexanone from Aldrich Chemical Corp. were oxidized to the semidiones in basic DMSO solution. 2-Hydroxy-3-hexanone was prepared by the reaction of *n*-propylmagnesium iodide with acetaldehyde cyanohydrin to yield 83% of material bp 90–103° (15 Torr). Three components were present by glpc analysis, presumably 2-hydroxy-3-hexanone, 3-hydroxy-2-hexanone, and hexane-2,3-dione.

Anal. Calcd for  $\text{C}_6\text{H}_{12}\text{O}_6$ : C, 62.02; H, 10.42. Found: C, 60.01; H, 10.21.

5,5-Dimethyl-2-hydroxy-3-hexanone was prepared from neopentylmagnesium chloride and acetaldehyde cyanohydrin which yielded 55% of material bp 95–105° (15 Torr). A mixture of the isomeric acyloins and the diketone was separated by glpc from 2,2-dimethyl-4-butanol.

2-Methyl-4-pentanone- $I$ - $^{13}\text{C}$  was prepared from the reaction of labeled methylmagnesium iodide (0.034 mole) from 1 g of 50.6% methyl- $^{13}\text{C}$  iodide and 3.8 g of unlabeled material with 0.033 g of cuprous iodide and 0.022 mol of 3-penten-2-one<sup>39</sup> at  $-80^\circ$  according to a literature procedure.<sup>40</sup> The product had a bp of 115–123° (lit.<sup>40</sup> 119°) with a pmr spectrum identical with methyl isobutyl ketone except for  $\sim 10\%$  of  $^{13}\text{C}$  satellites of  $J_{\text{CH}} = 175$  Hz at  $\delta$  0.93 ( $\text{CCl}_4$ ).

2,5-Dimethyl-4-hydroxy-3-hexanone (isobutyroin) was prepared from the reaction of ethyl isobutyrate, sodium sand, and trimethylchlorosilane in ether.<sup>36</sup> Hydrolysis yielded 85% of isobutyroin, bp 73° (15 Torr) (lit.<sup>41</sup> bp 66–70° (12–13 Torr)). Isobutyroin-3- $^{13}\text{C}$  was

prepared in a similar fashion from ethyl isobutyrate- $I$ - $^{13}\text{C}$  prepared by carbonating<sup>42</sup> isopropylmagnesium chloride and esterifying the sodium isobutyrate- $I$ - $^{13}\text{C}$  with triethyl phosphate.<sup>43</sup> Isobutyroin was also prepared by the addition of isopropylmagnesium chloride to isobutyraldehyde cyanohydrin, bp 160° (15 Torr) (lit.<sup>44</sup> bp 106 (22 Torr)), prepared by hydrocyanation.<sup>46</sup> This procedure was used for the synthesis of isobutyroin-2- $^{13}\text{C}$  from 2-chloropropane-2- $^{13}\text{C}$  (Volk Radiochemical Co., 40%  $^{13}\text{C}$ ). 3,6-Diethyl-5-hydroxy-4-octanone (di-3-pentylacyloin) was synthesized from 2-ethyl butyrate<sup>46</sup> in 10% yield by sodium in xylene,<sup>37</sup> bp 107–110° (15 Torr): pmr ( $\text{CCl}_4$ )  $\delta$  0.70–1.75 (m, 21), 2.60 (p, 1,  $J = 6.25$  Hz), 3.95 (d, 1,  $J = 4.5$  Hz), 4.26 (s, 1); mass spectrum (70 eV)  $m/e$  200 (parent ion).

Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{O}_2$ : C, 71.98; H, 11.98. Found: C, 72.41; H, 11.70.

4,7-Di-*n*-propyl-6-hydroxy-5-decanone was prepared in a similar fashion from ethyl 2-propylvalerate<sup>47</sup> in 70% yield, bp 120° (15 Torr): pmr,  $\delta$  0.63–2.20 (m, 29), 2.20–3.00 (m, 1), 3.10 (s, 1), 4.15 (s, 1); mass spectrum (70 eV)  $m/e$  at 256 (parent ion).

Anal. Calcd for  $\text{C}_{18}\text{H}_{32}\text{O}_2$ : C, 75.23; H, 12.62. Found: C, 74.94; H, 12.36.

Pivaloin was synthesized from ethyl pivalate in 58% yield,<sup>37</sup> mp 78° (lit.<sup>48</sup> mp 81°). Pivaloin-3- $^{13}\text{C}$  was synthesized from *tert*-butylmagnesium chloride and carbon- $^{13}\text{C}$  dioxide wherein the resulting ethyl pivalate- $I$ - $^{13}\text{C}$  was diluted with unlabeled ethyl pivalate to give material containing  $\sim 10\%$   $^{13}\text{C}$  at the carboxyl group.

**Other Reagents.** 2,3:11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene was prepared by method X of Pederson.<sup>49</sup> The compound was sublimed at 150–160° (0.75 Torr) to give material with mp 164° (lit.<sup>49</sup> mp 164°): pmr ( $\text{CDCl}_3$ )  $\delta$  4.1 (m, 16), 6.87 (s, 8); mass spectrum (70 eV)  $m/e$  at 360 (parent ion). Commercial potassium *tert*-butoxide (Mine Safety Appliance Research Corp.) was sublimed at 150° (0.25 Torr) before use. Lithium alkoxides were prepared by the reaction of *sec*-butyllithium with the alcohol in *n*-hexane and sodium alkoxides from reaction of the metal and alcohol in refluxing toluene. Commercial cesium and rubidium *tert*-butoxides (Mine Safety Appliance Research Corp.) were used as received. Benzyltrimethylammonium methoxide in methanol (J. T. Baker Chemical Co.) was evaporated to dryness and then dissolved in DMSO. DMSO, HMPA, and DMF were distilled and stored over molecular sieves. THF and DME were distilled from potassium and then lithium aluminum hydride and stored over Na-K alloy under nitrogen. Diethylene, triethylene, and tetraethylene glycol dimethyl ethers (Ansul Chem. Co.) were distilled from calcium hydride under vacuum and stored over molecular sieves.

**Esr Techniques.** The esr spectra were recorded with a Varian Associates V-4502 spectrometer equipped with 100-kHz field modulation, a Fieldial Magnetic field regulated 9-in. magnet and a V-4520 temperature controller (calibrated to  $\pm 3^\circ$ ) or by a Varian E-3 spectrometer. The spectrometers were calibrated against Fremy's salt,  $g^{\text{H}} = 13.00$  G.<sup>50a</sup>  $g$  values were measured by placing a capillary of Fremy's salt in water ( $g = 2.00550$ ) adjacent to the sample cell in the spectrometer cavity.<sup>50b</sup>

The dialkylsemidiones were prepared in flat fused silica cells (Varian V-4548) by use of inverted U-type mixing cells.<sup>51</sup> Variable temperature spectra were obtained with a V-4548-1 cell.

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