Aliphatic Semidiones. XX. Monoalkyl Glyoxal Radical Ions[1]

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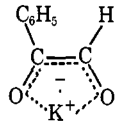
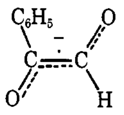
Abstract: A variety of alkylglyoxal radical anions have been prepared. The esr spectra indicate a mixture of cis and trans isomers. Bulky substituents favor the cis structure as do gegenions that can form chelates with the α-diketone moiety.

Phenylglyoxal radical ion has been prepared by disproportionation of ω-hydroxyacetophenone in dimethyl sulfoxide solution in the presence of potassium *tert*-butoxide.[3,4] The radical anion prepared in this manner has a doublet splitting by the aldehydic hydrogen of $a^H = 6.9$ G. It was subsequently realized that the electrolytic reduction of benzaldehyde in DMF solutions containing quaternary alkylammonium salts[5] produced a phenylglyoxalsemidione with $a^H = 5.53$ G.[4,6] It was suggested that in DMSO solutions containing potassium ions the cis structure predominated, whereas in DMF in the presence of tetraethylammonium ion the trans semidione was preferred.[7] It has since been shown that in DMSO solution containing cesium cations the trans structure predominates with $a^H = 5.59$ G.[6] It thus appears that the cis structure is favored by chelation but that in the absence of ion pairing the trans structure is thermodynamically preferred. A similar situation exists for 3,4,5-trimethoxyphenylglyoxalsemidione.[7] We now report data for a series of monoalkylglyoxals observed in DMSO solution in the presence of potassium cations.



cis

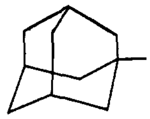


trans

Glyoxal radical anion **1a** can be prepared by treatment of glycolaldehyde dimer, or dibromoethylene carbonate with potassium *tert*-butoxide in DMSO. A flow system is preferable for its generation since the lifetime is short at room temperature ($t_{1/2} \approx 30$ sec). Only a single semidione with $a^H = 7.6$ G was observed. Electrolytic reduction of glyoxal in THF solution in the presence of tetraalkylammonium salts gave the same radical anion to which a trans structure was assigned.[8] Treatment of acetol with potassium *tert*-butoxide in DMSO produced a mixture of *cis*- and *trans*-**1b** ($t_{1/2} \approx$ 4–5 min) in which the trans isomer predominated (Table I). 1-Acetoxy-2-butanone gave a mixture of *cis*- and *trans*-ethylglyoxalsemidiones (**1c**) in nearly equal amounts ($t_{1/2} \approx$ 4–5 min). Isopropyl chloromethyl ketone, *tert*-butyl bromomethyl ketone, and 1-adamantyl bromomethyl ketone produced semidiones **1d**–**1f** upon treatment with base. The ratio of trans/cis semidiones decreased from isopropyl to *tert*-butyl to 1-adamantyl such that for the latter radical ion the cis isomer predominated over the trans isomer by more than tenfold. Semidiones **1d**–**1f** were much more stable than **1a**–**1b** in DMSO solution ($t_{1/2} \sim$ hours) and traces of water did not destroy the signals.

$RC(O\cdot){=}C(O^-)H$

1a, $R = H$
b, $R = CH_3$
c, $R = C_2H_5$
d, $R = (CH_3)_2CH$
e, $R = (CH_3)_3C$
f, R =



g, $R = C_6H_5$

In Figure 1 the spectrum of the mixture of *cis*- and *trans*-**1b** is given. The figure also shows the signal of *trans*-dimethylsemidione which is formed from methylglyoxal in DMSO solution (Scheme I).[4,9,10]

Scheme I

$$\begin{aligned}
&CH_3COCHO + CH_3SOCH_2^- \longrightarrow \\
&\qquad CH_3COCH(O^-)CH_2SOCH_3 \rightleftarrows \\
&\qquad CH_3C(O^-){=}C(OH)CH_2SOCH_3 \longrightarrow \\
&\qquad CH_3COC(OH){=}CH_2 + CH_3SO^- \rightleftarrows \\
&\qquad\qquad CH_3COCOCH_3 \longrightarrow CH_3C(O\cdot){=}C(O^-)CH_3
\end{aligned}$$

In Figure 2 the spectrum of a mixture of *cis*- and *trans*-**1d** is given. In this case further methylation of the glyoxal apparently occurs slowly if at all.

The variation in the trans/cis ratio observed reflects the relative extent of nonbonded interactions. Apparently a 1,5-hydrogen–oxygen interaction in a trans structure **2t** is not as severe as the 1,5 hydrogen–hydrogen plus 1,4 oxygen–oxygen interaction in **2c**.

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[2] National Defense Education Act Predoctoral Fellow, 1967–1968.

[3] G. A. Russell, R. D. Stephens, and E. R. Talaty, *Tetrahedron Lett.*, 1139 (1965).

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[7] C. Corvaja, P. L. Nordio, and G. Giacometti, *J. Amer. Chem. Soc.*, **89**, 1751 (1967).

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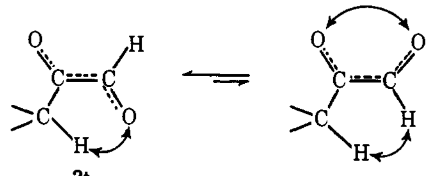
[9] G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

[10] A recent report by N. H. Anderson, A. J. Dobbs, D. J. Edge, R. O. C. Norman, and P. R. West (*J. Chem. Soc. B*, 1004 (1971)) utilizing flow techniques has appeared wherein spectra attributed to *cis*- and *trans*-**1b** in water at pH 5 are given. For *trans*-**1b** the reported values of a^H in water are 1.2 those observed in DMSO while for *cis*-**1b** the values of a^H in water are 1.1 those in DMSO, Δg (trans–cis) in water = 0.0003.

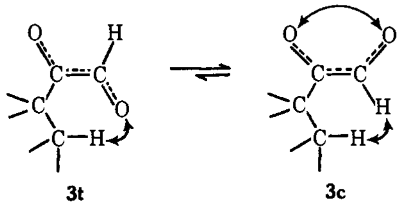
Table I. Proton Hyperfine Splittings and g Values of Glyoxalsemidiones in DMSO Solution at 25°

Semidione	Gegenion	a_{CHO}^H, G	a_α^H, G	Trans/cis (0.1 *M* K^+)	g (±0.00005)[a]
1a	K^+	−7.6		Cis not detected	
trans-**1b**	K^+	−7.7	+5.1	2	2.00515
cis-**1b**	K^+	−8.7	+7.6		2.00505
trans-**1c**	K^+	−7.7	+4.2	0.8	2.00521
cis-**1c**	K^+	−8.4	+5.6		2.00509
trans-**1d**	K^+	−7.6	+1.6	1.3	2.00530
cis-**1d**	K^+	−8.4	+1.7		2.00520
trans-**1e**	Cs^+	−7.8	0.30[b]	Trans detected but	2.00568
cis-**1e**	K^+	−8.7	0.27[b]	not measured[d]	2.00508
trans-**1f**	Cs^+	−7.7	0.19[c]		
cis-**1f**	K^+	−8.7		Trans not detected[d]	
trans-**1g**	Cs^+	6.00		*e*	2.00520
cis-**1g**	K^+	6.88			2.00493

[a] R. O. C. Norman and R. S. Pritchett, *Chem. Ind. (London)*, **50**, 22040 (1965). [b] a_β^H. [c] a_γ^H (3 hydrogen). [d] Approximately equal amounts of cis and trans isomers in the presence of Cs^+. [e] Spectral complexity makes concentration measurement difficult; Δg (trans–cis) = 0.0003.



2t **2c**



3t **3c**

However, when the α carbon is fully alkylated as in **1e** and **1f** a severe 1,6 hydrogen–oxygen interaction destabilizes **3t** relative to **3c**. Chelation of the gegenion by **2c** and **3c** is very important. Thus, when cesium *tert*-butoxide is used in place of potassium *tert*-butoxide the trans/cis ratio increases greatly and the two isomers are present at approximately equal concentrations for **1d**–**1f**. Potassium is more suitable for coordination with the cis semidione bidentate than is cesium. Moreover, the larger cesium gegenion may actually preferentially associate with the trans semidione.[11]

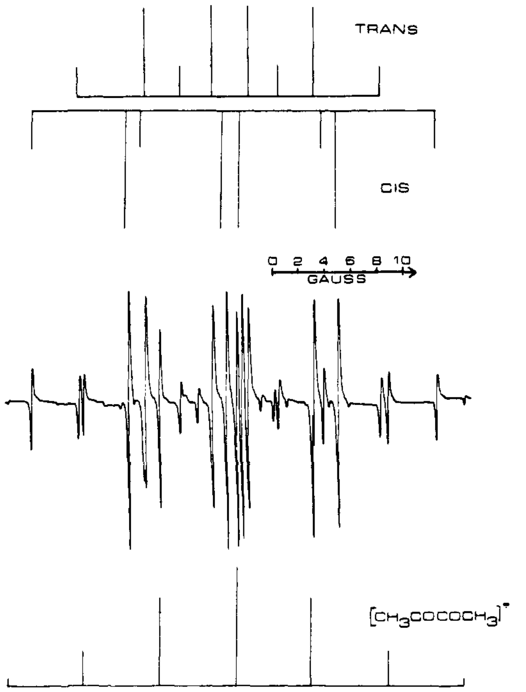


Figure 1. Esr spectrum of the mixture of radical anions seen upon treatment of acetol (CH_3COCH_2OH) with potassium *tert*-butoxide in DMSO solution. The signal assigned to the trans isomer of $CH_3C(O\cdot)=C(O^-)CH_3$ ($a_{CH_3}^H$ = 5.6 G) increased slowly with time while the relative intensities of the signals assigned to cis (a_{CHO}^H = 8.4, $a_{CH_3}^H$ = 7.6 G) and trans (a_{CHO}^H = 7.6, $a_{CH_3}^H$ = 7.6, $a_{CH_3}^H$ = 5.1 G) were constant.

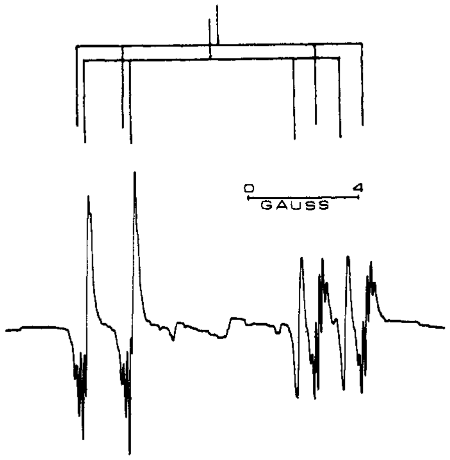


Figure 2. Esr spectrum of a mixture of *cis*- and *trans*-isopropylglyoxal radical anions. High field is to right. The differences in g values are clearly shown. The trans isomer (a_{CHO}^H = 7.6) absorbs at lower field than the cis isomer (a_{CHO}^H = 8.4 G), Δg = 0.0001.

Addition of lithium iodide to solutions of **1d** or **1e** destroyed the esr signal instead of giving a lithium chelate of *cis*-**1d** or *cis*-**1e** with a measurable a^{Li}. Lithium cations apparently shift equilibrium 1 far to the right by preferential association with the enediol dianion.

$$2[RCOCHO]\cdot^- \rightleftharpoons RCOCHO + RC(O^-)=C(O^-)H \quad (1)$$

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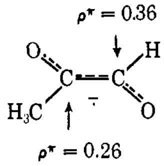
(11) G. A. Russell, J. L. Gerlock, and D. F. Lawson, *J. Amer. Chem. Soc.*, **93**, 4088 (1971).

The spin distribution in **1a** and **1b** can be estimated by the McConnell equations.[12,13] When applied to

$$a_{\mathrm{CH}}{}^{\mathrm{H}} = Q_{\mathrm{CH}}{}^{\mathrm{H}}\rho_{\mathrm{C}}{}^{\pi} \tag{2}$$

$$a_{\alpha}{}^{\mathrm{H}} = \mathrm{B}_{\rho_{\mathrm{C}}}{}^{\pi}\langle\cos^2\theta\rangle \tag{3}$$

semidiones the values of $Q_{\mathrm{CH}}{}^{\mathrm{H}} = -22.5$ and $\mathrm{B} = 40$ G are appropriate.[4] This leads to $\rho_{\mathrm{C}}{}^{\pi} = 0.34$ in **1a** and 0.38 for both carbon atoms in *cis*-**1b**. Values of a^{H} in these and other semidiones are not particularly sensitive to the gegenion and the observed variation in $\rho_{\mathrm{C}}{}^{\pi}$ between cis and trans isomers cannot be explained by ionic association. On the other hand, the trans isomer of **1b** leads to grossly different values of $\rho_{\mathrm{C}}{}^{\pi}$ for the two carbonyl carbon atoms, *i.e.*, **4**. The aldehydic carbon in **4** has a spin density (0.36) approximately like the carbonyl carbon atom in **1a** (0.34) and *cis*-**1b** (0.38), whereas the acyl carbon atom has a spin density like that of *trans*-biacetylsemidione (0.27)[4] and considerably less than in **1a**. A possible explanation of these effects is that **4** undergoes association with the potassium gegenion and other solvation preferentially at the aldehydic oxygen atom, *e.g.*, **4a**. Structures similar to **4a** are possible for both oxygens in **1a**. *cis*-**1b** has a value of $\rho_{\mathrm{C}}{}^{\pi}$ of 0.38 at both carbonyl carbon atoms, about the same as in *cis*-biacetylsemidione (0.35)[4] suggesting that solvation and/or chelation effects are about the same at all the carbonyl groups in these cis radical anions. The chelation suggested, as well as the variations in spin density, must be responsible to some degree for the differences in *g* values observed where the trans isomers (higher $\rho_{\mathrm{O}}{}^{\pi}$ and lower $\rho_{\mathrm{C}}{}^{\pi}$) always have a greater *g* value.[7,14] It has been noted that the *g*-value difference between *cis*- and *trans*-3,4,5-trimethoxyphenylglyoxal radical anions is much greater in DMSO with K^+ gegenion than in DMF with $\mathrm{Et_4N^+}$ and the suggestion was made[7] that the presence of the metal counterion greatly modified the n–π* excitation energies which control the orbital mixing responsible for the deviation of the *g* factor from the free-electron value.[15] Other factors are also involved. Values of Δ*g* (trans–cis) for dialkylsemidiones ($\mathrm{RC(O\cdot){=}C(O^-)R}$) with K^+ gegenion in DMSO solution vary from 0.00014 for R = $\mathrm{CH_3}$ to 0.00006 for R = isobutyl, 0.00008 for R = trifluoromethyl, and 0.00003 for R = isopropyl. There seems to be a correlation with the trans/cis ratios of the semidiones (0.1 *M* $\mathrm{K^+}$, DMSO) which vary from 18 (R = $\mathrm{CH_3}$) to 45 (R = isobutyl), to 120 (R = trifluoromethyl), and >100 for R = isopropyl. The trans/cis ratios are determined by steric factors such that a high trans/cis ratio probably reflects considerable nonbonded interaction in the cis structure. This strain apparently causes an increase in the *g* factor of the cis isomer so that the intrinsic difference in *g* values between the cis and trans structures practically disappears when the trans/cis ratio is high. The differences in *g* values for the monoalkylglyoxal radical ions (potassium salts in DMSO) also seem to be at least partially connected with steric effects. Thus, Δ*g* (trans–cis) increases from 0.0001 for methyl, ethyl, and isopropyl to 0.0006 for *tert*-butylglyoxal radical anion. This parallels the drastic change in trans/cis ratios from ~1 for R = methyl, ethyl, and isopropyl to <0.1 for R = *tert*-butyl. It thus appears likely that the same factor which destabilizes the trans structure for R = *tert*-butyl (**3t**) is responsible for the considerable shift to a higher *g* value for this isomer, presumably by affecting the n–π* excitation energy. The absolute *g* values (Table I) are in accord with this analysis since *g* is essentially constant for the *cis*-glyoxal radical ions with R = methyl or *tert*-butyl. Deviations from planarity for cis dialkylsemidione or trans monoalkylsemidiones with bulky substituents apparently effects the n–π* excitation energy and hence the *g* value.



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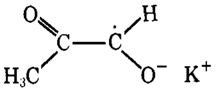

4a

Experimental Section

Glycolaldehyde, 1-adamantyl bromomethyl ketone (Aldrich Chemical Co., Inc.), **1-acetoxy-2-butanone** (Alfred Bader Chemical Co.), **acetol** (Jefferson Chemical Co.), potassium, and cesium *tert*-butoxides (Mine Safety Appliance Research Corp.) were obtained commercially.

1-Chloro-3-methyl-2-butanone[16] and **1-bromo-3,3-dimethyl-2-butanone**[17] were prepared by standard procedures.[18,19]

Dibromoethylene Carbonate. Vinylene carbonate (5 g, 0.058 mol, Aldrich Chemical., Inc.) was stirred with 200 ml of carbon tetrachloride, and bromine (9.3 g) was added dropwise. After stirring overnight, the solvent and excess $\mathrm{Br_2}$ were removed under vacuum. The resulting crude mixture was shown by pmr (60 MHz) to contain 60% dibromoethylene carbonate ($\delta_{\mathrm{CDCl_3}}$ 6.79) and 40% vinylene carbonate ($\delta_{\mathrm{CDCl_3}}$ 7.21). The mixture was used directly for esr experiments.

Esr Measurements. Esr spectra were obtained using a Varian V-4500 spectrometer with 100-kHz field modulation and a 9-in. magnet, equipped with a Fieldial magnetic field regulator and V-4520 temperature controller, or by a Varian E-3 spectrometer. Flat-fused silica cells (Varian V-4548 aqueous solution cells) were used with inverted U-shape mixing cells[20] for stable semidiones. A fused silica mixing cell (Varian V-4549) was employed in flow experiments with unstable radicals. Here, solutions of sample and base were degassed separately in large bottles, then continuously mixed in the spectrometer cavity while spectra were obtained. *g* values were determined by placing a solution of Fremy's salt in a capillary alongside the sample in the spectrometer cavity.[21] Splitting constants and field differences were measured with the Fieldial and calibrated against Fremy's salt, $a^{\mathrm{N}} = 13.00$ G, $g = 2.00550 \pm 0.00005$.

Analysis of Data. Ratios of isomers within a mixture were taken to be the ratio of their first-derivative peak heights, between extrema, for lines of the same degeneracy. Ratios are the averages of at least three separate measurements. It was assumed that both isomers had identical line widths and line shapes; this assumption implies that trans/cis represents a maximum limit in situations where cis lines are broader than the trans lines.

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(21) See Table I, footnote *a*.