1971

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Recommended Citation

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71-21,954

LAWSON, David Francis, 1945-
SOME PHENOMENA OF SEMIDIONES IN SOLUTION.

Iowa State University, Ph.D., 1971
Chemistry, organic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

Some phenomena of semidiones in solution

by

David Francis Lawson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1971

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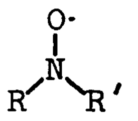
INTRODUCTION

Electron spin resonance (ESR) spectroscopy has been demonstrated to be a powerful tool for the study of conformational and structural phenomena in organic free radicals (1-8). Progress in this area has been nurtured to a great extent by the development of stable free radicals for spin-labels, and the refinement of techniques for studying transient free radical species.

Two important classes of stable neutral free radicals that have been studied extensively by ESR are the nitroxides, **1**, and substituted phenoxyls, **2**. From these investigations



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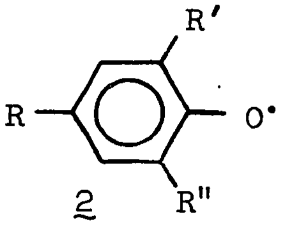

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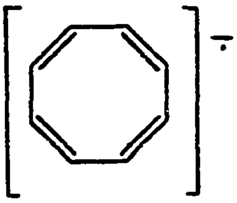
much information has been derived concerning molecular structure, motion and conformation, and organic and biochemical reactions. Other neutral radicals which are less stable have been studied by special techniques. Most impressive have been the investigations of alkyl free radicals performed by Fessenden and Schuler, using high energy irradiation techniques at low temperatures (9), and by Krusic and Kochi, who have generated alkyl free radicals with initiators by photoirradiation at low temperatures (10).

Relatively stable radicals may also be produced from neutral molecules by odd electron oxidation or reduction to give radical ions (2). A copious number of radical ions have been examined, such as hydrocarbon radical anions and cations, e.g. 3 and 4 (11, 12), nitroaromatic radical anions, 5 (13),



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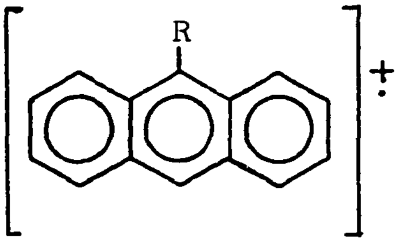

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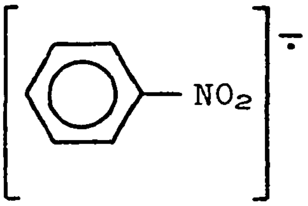

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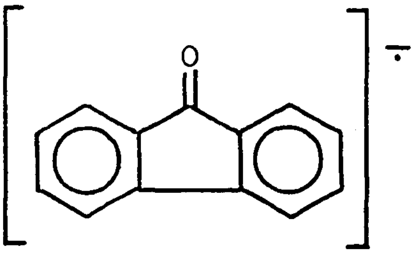
aliphatic and aromatic ketyl radical anions, e.g. 6 and 7 (14-16), and o- and p-benzosemiquinones, e.g. 8 and 9 (17, 18).

$$\left[\,(CH_3)_3CCH{=}CHCOC(CH_3)_3\,\right]^{\underset{\cdot}{-}}$$

6



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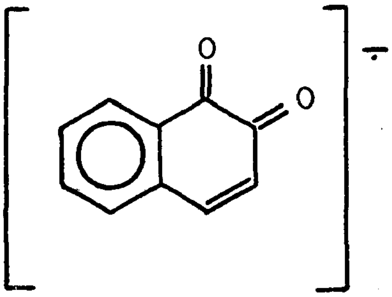

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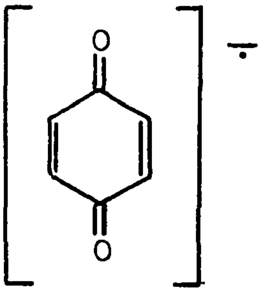

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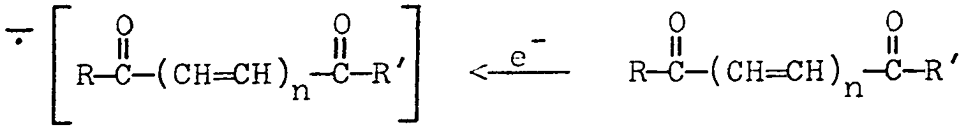
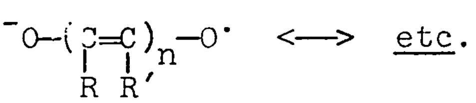
Another important class of radical anions related to semiquinones and ketyls, although distinct, are the semidiones, 10. A semidione may be formally considered as the one electron reduction product of an α-diketone, 11 (Reaction 1), (or



$$\overset{\cdot}{-}\left[R-\overset{O}{\overset{\|}{C}}-(CH{=}CH)_n-\overset{O}{\overset{\|}{C}}-R'\right] \xleftarrow{e^-} R-\overset{O}{\overset{\|}{C}}-(CH{=}CH)_n-\overset{O}{\overset{\|}{C}}-R' \qquad (1)$$

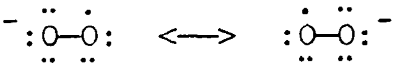
10a $n = 0, 1, 2...$ 11

vinylogues of α-diketones) or as a vinylogue of the stable superoxide ion, 12 (19). Semidiones have been known for some



$$^{-}O-(\underset{R}{\underset{|}{C}}=\underset{R'}{\underset{|}{C}})_n-O^{\cdot} \longleftrightarrow \text{etc.}$$

10b



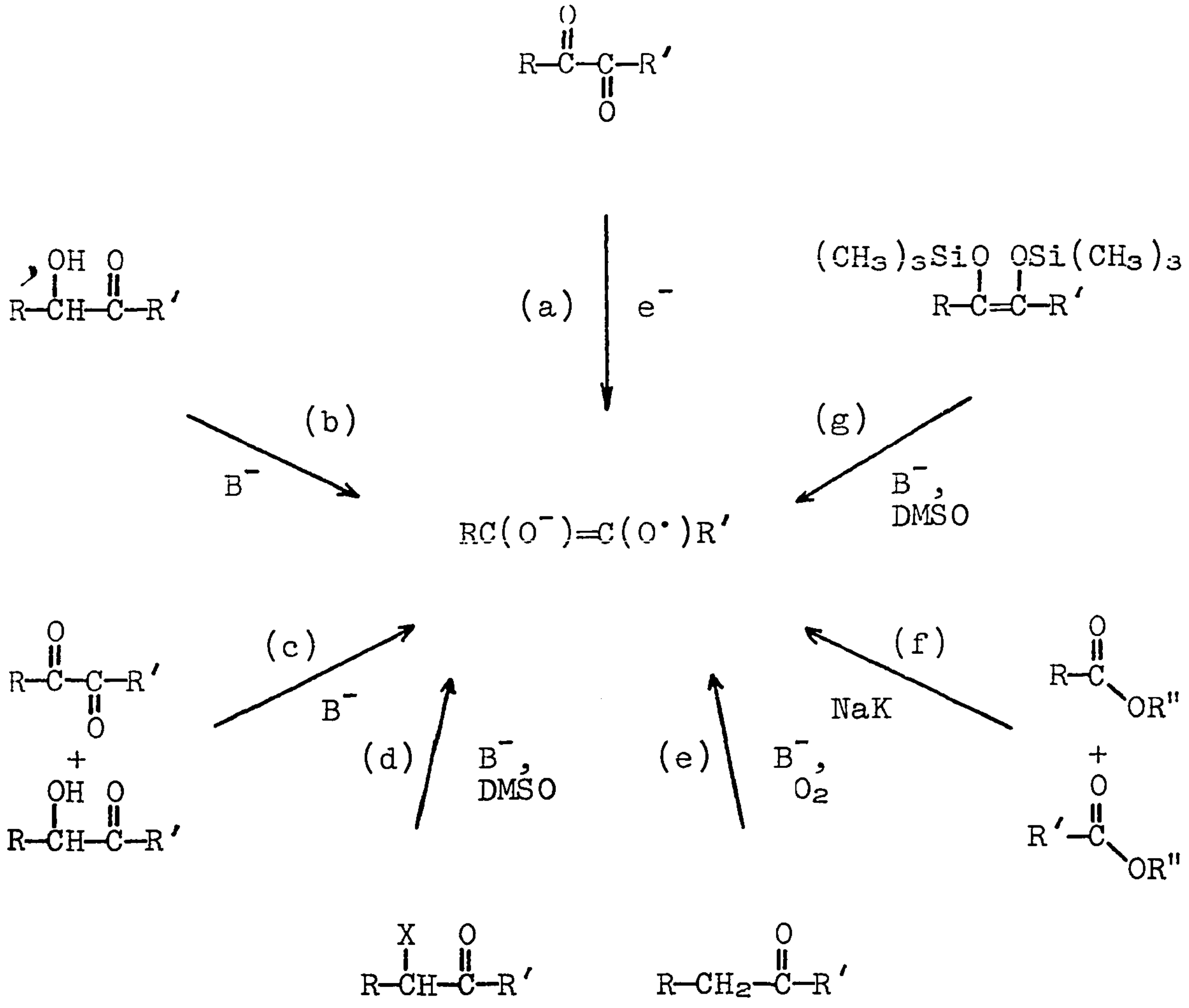
$$^{-}:\ddot{\underset{..}{O}}-\dot{\underset{..}{O}}: \longleftrightarrow :\dot{\underset{..}{O}}-\ddot{\underset{..}{O}}:^{-}$$

12

time (20) but were not studied by ESR until 1955 (21); since 1964 the semidiones have been investigated extensively by Russell and co-workers, with many interesting applications being made to chemical problems: structures of steroidal ketones (22), conformational analysis of various systems (23-25), reactions in solution (26,27), molecular rearrangements (28), long-range splittings (29), and valence isomerizations (30). Some of these subjects have been reviewed (31, 32).

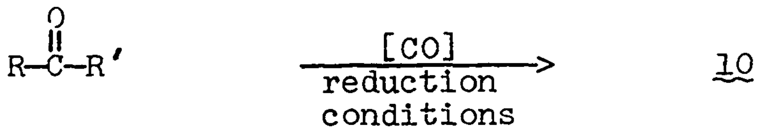
Much of the broad utility of the semidione as a spin label is derived from the variety of modes available for its generation in diverse systems (Scheme 1, a-g). Thus, in addition to the relatively limited (and seldom used) reduction of a diketone, (a), semidiones have been prepared by: (b), treatment of an α-hydroxy ketone with base, frequently in dimethyl sulfoxide (DMSO) solution; (c), electron-transfer between enediol dianion and diketone; (d), oxidation of an α-acetoxy- or α-halo ketone in basic DMSO, followed by one electron re-

Scheme 1.

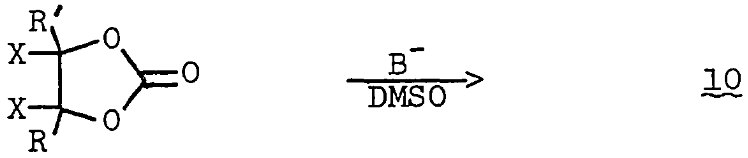


duction; (e), oxidation of a monoketone by molecular oxygen in basic solution; (f), in situ acyloin condensation of a mono- or dicarboxylic ester, usually in ether solution; and (g), cleavage of a bis(trimethylsiloxy)alkene, with electron transfer from the enediol dianion. Route (g) was developed as a portion of the research described in this thesis, and has since found successful applications (25, 33-36).

Two additional routes to semidiones were investigated in this work: the formation of semidiones from monoketones by incorporation of a CO moiety under reduction conditions, as in Reaction 2 (27); and the formation of semidiones from halogenated cyclic carbonates, e.g., Reaction 3. However, applications of these reactions have been quite limited.

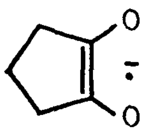


$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[\text{reduction conditions}]{[CO]} 10 \qquad (2)$$

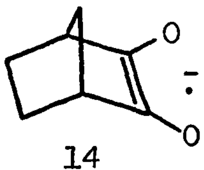


(3)

The semidiones may be divided into two major structural categories: When the semidione moiety forms a part of a ring system, the semidione is termed cyclic (or bicyclic, polycyclic), e.g. 13 and 14. When the carbons of the semidione moiety are not joined through a ring, e.g. 15, the semidione



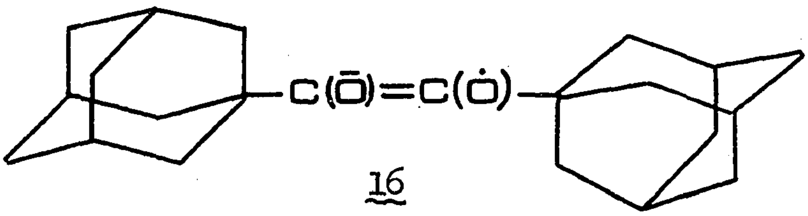
13



14

$CH_3C(O^-)=C(O\cdot)CH_3$

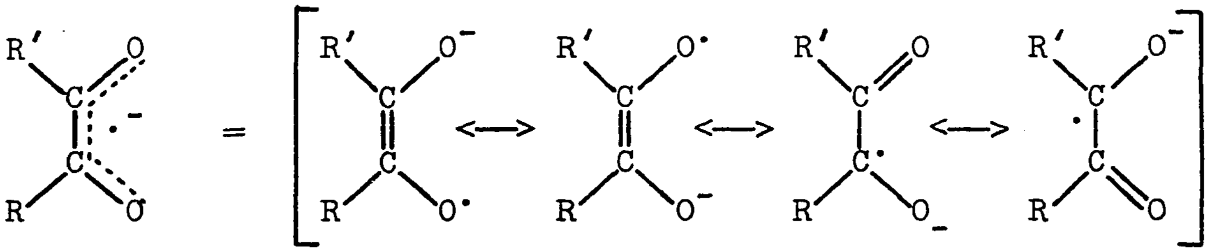
15



16

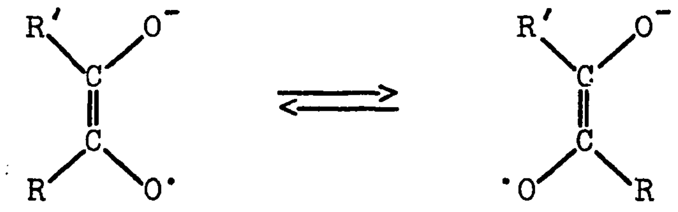
is *acyclic*; however, acyclic semidiones may also contain component ring systems, *e.g.*, **16**. Semidiones are properly named as derivatives of the parent hydrocarbons; thus, **13** is cyclopentane-1,2-semidione and **15** is butane-2,3-semidione. A more descriptive nomenclature is sometimes used for practicality; thus, **15** is frequently referred to as dimethyl semidione and **16** is bis(1-adamantyl)semidione. Both nomenclatures will be used in this thesis.

The 1,2-semidione has a four-atom, five-electron π-system and it may be represented by canonical structures **17** and **18**:



17a **17b** **18a** **18b**

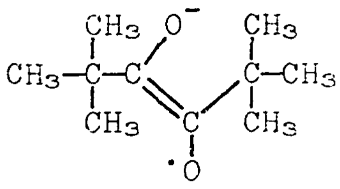
In cyclic semidiones, except for large rings, the semidione moiety is constrained in the *cis* geometry. This constraint is not present in acyclic semidiones, and if the CO-CO bond possesses sufficient double bond character (*e.g.*, Structure **17**), distinct *cis* and *trans* isomers are expected. Furthermore, the two isomers may be interchangeable (Equilibrium 4).



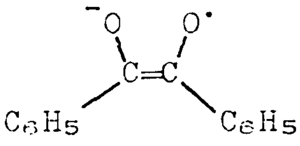
(4)

cis *trans*

Earliest ESR studies of acyclic semidiones failed to disclose the presence of both *cis* and *trans* isomers within a mixture. Luckhurst and Orgel (37) examined di-*t*-butylsemidione, **19**, with alkali metal ions in THF and observed only



19



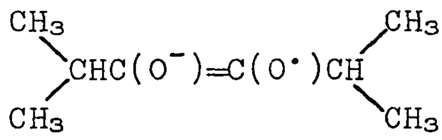
20

one species, to which they assigned the *trans* structure. The basis for their assignment was that steric repulsions between the *t*-butyl groups would be less severe with *trans* than with *cis* geometry. On the other hand, they observed that diphenyl semidione in THF solution gave a species exhibiting splitting by alkali metal and which was assigned the *cis* configuration **20**.

Heller (38) examined the photochemical generation of semidiones **19**, **21** and **22** in basic ethanol-water and observed only one configurational isomer in each case. About the same time,

$CH_3CH_2CH_3C(O^-)=C(O^\bullet)CH_2CH_2CH_3$

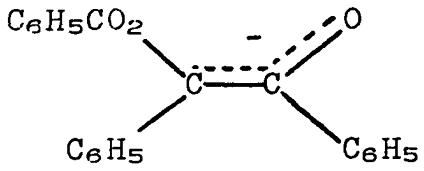
21

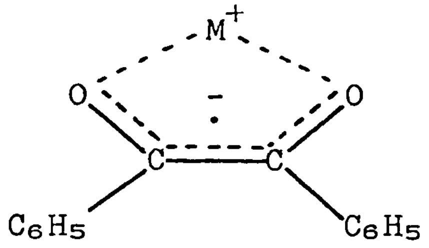


$(CH_3)_2CHC(O^-)=C(O^\bullet)CH(CH_3)_2$

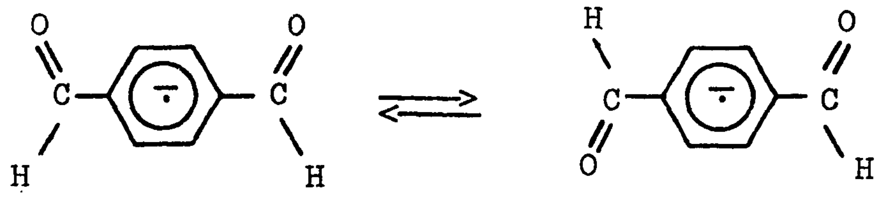
22

Bauld studied the configurational isomerism of benzil radical anion and dianion by trapping with benzoyl chloride to give isomeric bis(benzoyloxy)stilbenes (39). Bauld showed that the distribution of the isomeric esters should reflect the configurational distribution of the ions, since *cis*-*trans* isomerism of the intermediate enolate 23 is slow compared to the second benzoylation step in the presence of excess benzoyl chloride. He found that the *cis* configuration was favored, especially in poorly solvating media; however, a substantial amount of *trans* isomer was formed in some cases. Efficient coordination of a metal ion with both oxygen atoms in the *cis* configuration, *e.g.* 24, was believed responsible for overcoming the coulombic and steric repulsions imposed by that structure.

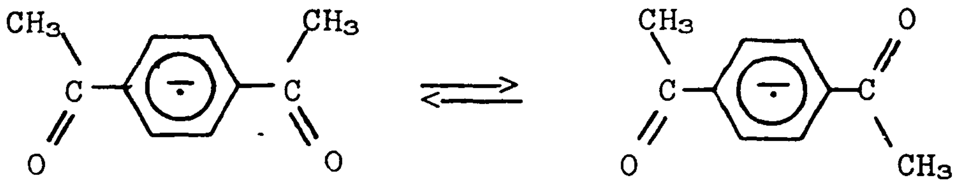

23


24

Maki (40) and Stone and Maki (41), and later Rieger and Fraenkel (42) and Steinberger and Fraenkel (43), studied what may be considered *p*-phenylogues of acyclic semidiones, 25 and 26, and observed mixtures of configurational isomers. A discussion of their results may be found in Reference 3.

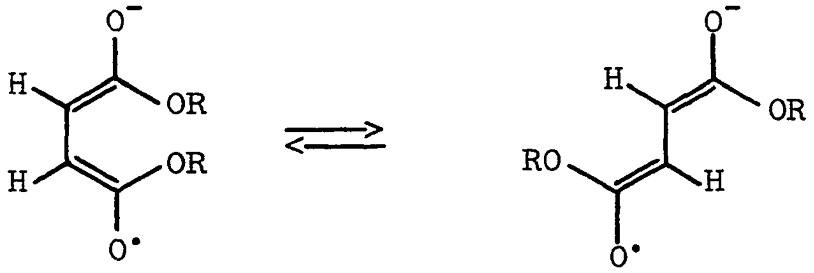

25a

25b



26a 26b

Nelsen (44) has generated the radical anions of maleic, fumaric and phthalic diesters electrolytically, observing mixtures of configurational isomers with the former two, e.g. 27.



27a 27b

Each of 27a and 27b can further differ in the disposition of its unsymmetrical ends. Nelsen found different hyperfine splitting constants (hfsc) and g-values for the two isomers, and the ratio of isomers was always less than 3:1.

Weyenberg, et al. (45), have examined the reduction and subsequent trapping of substituted 1,3-butadienes in the presence of chlorotrimethylsilane. They found that cis-1,4-bis(trimethylsilyl)butenes were the predominant products when the reducing agent was sodium in THF, lithium naphthalenide in THF or lithium in diethyl ether, whereas _trans_-1,4 addition was favored with lithium in THF. These results were taken to indicate a _cis_ configuration for the anion radical and a _trans_ configuration for the dianion.

Russell, _et al._ (26, 46, 47) studied some acyclic semidiones containing a single hydrogen substituent (alkylglyoxal radical anions); their results are summarized in Table 1.

Table 1. Hfs[a] of acyclic semidiones $RC(O^-)=C(O^\cdot)H$ in DMSO solution at 25°[b] (from Ref. 26).

Number	R	a_α^H	a_{CHO}^H
28	H[c]	...	7.7
29	CH_3	7.5	8.7
30	CH_3CH_2	5.6	8.4
31	C_6H_5	...	6.9

[a] In gauss.

[b] Potassium gegenion.

[c] Observed under flow conditions.

When R=H, configuration of the radical was unassigned; in the other cases the _cis_ configuration was assigned. These assignments were made by comparison with the dialkyl series. Tolles and Moore (48) have subsequently generated glyoxal semidione, $HC(O^-)=C(O^\cdot)H$, 28, electrolytically and observed only a single isomer, a_{CHO}^H = 7.63 G, which was assigned the *trans* configuration. Unfortunately, the ESR spectra of alkylglyoxal radical anions very often presented complex mixtures of radicals.

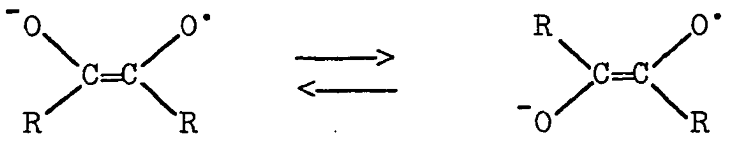
An Italian group (49) was able to prepare both *cis*- and *trans*(3,4,5-trimethoxy)phenyl semidione 32, finding the *cis* isomer to predominate under conditions where ion-pairing was favored. They confirmed Russell's speculation (26) that

$$(CH_3O)_3C_6H_2C(O^-){=}C(O^\bullet)H$$

32, *cis* and *trans*

phenyl-1,2-semidione was reported inadvertantly by Rieger and Fraenkel (42). They also observed that the *cis* and *trans* isomers had considerably different *g*-values: $\Delta g \sim 2.7\text{x}10^{-4}$.

Russell and Stephens (50) reported that the ESR spectra of acyclic dialkyl semidiones, 33, showed mixtures of both



33 - *cis*   33 - *trans*

cis and *trans* isomers. Their results are summarized in Table 2. They noted that when the potassium ion concentration was increased to 0.2 *M* for R=CH_3, the *trans*/*cis* ratio became 8:1, and with [Na^+]=0.2 *M*, the *trans*/*cis* ratio was *ca*. 3:1; addition of $LiClO_4$ decreased the *trans*/*cis* ratio to zero. The ESR spectrum obtained with R=CH_3 at low potassium ion concentrations is given in Figure 1. The configura-

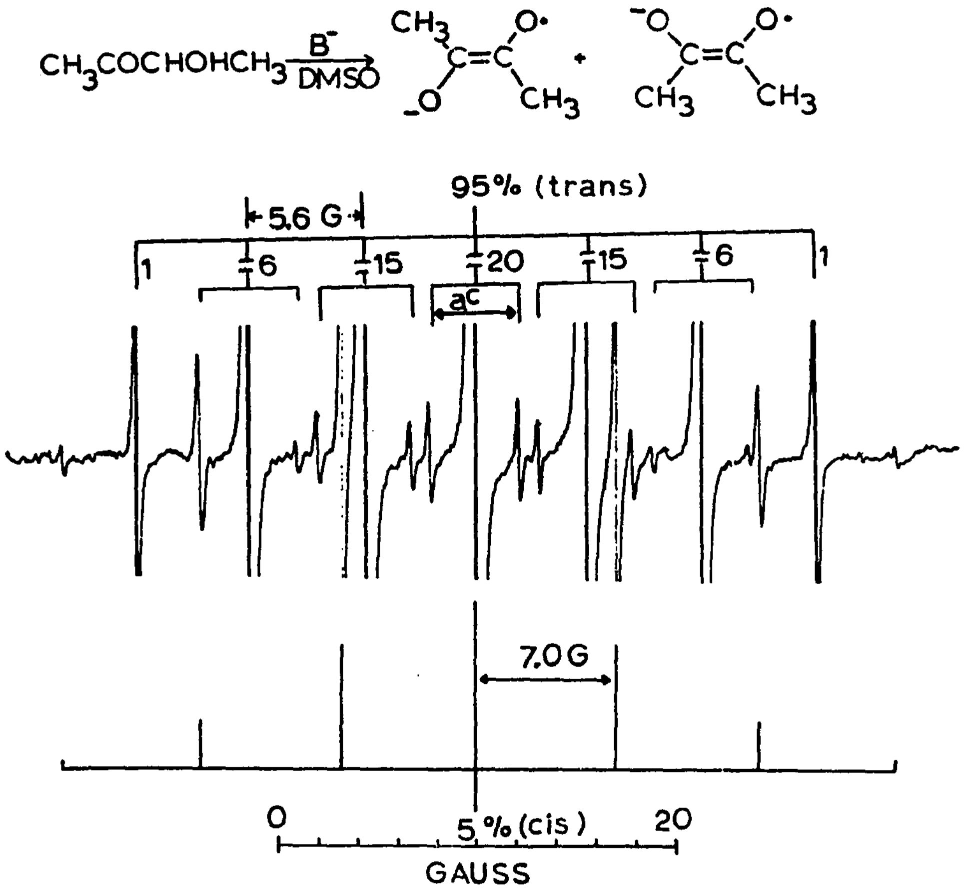


Figure 1. First derivative ESR spectrum of the mixture of radical anions obtained from disproportionation of acetoin in base-DMSO (from Reference 50).

Table 2. Hyperfine splitting constants[a] and *trans*/*cis* ratios of acyclic semidiones $RC(O^-)=C(O^\cdot)R$ at 25-28° in DMSO solution[b] (from Ref. 50).

R	$\underline{a}^H$ (*cis*)[c]	$\underline{a}^H$ (*trans*)[c]	$\underline{a}^C$ (*trans*)[d]	*trans*/*cis*
CH_3	7.0	5.6	4.5	20
CH_3CH_2	6.0	4.9	4.4	20
$CH_3CH_2CH_2$	5.6	4.6	4.4	30
$(CH_3)_2CH$	...	2.0	...	>100
$(CH_3)_2CHCH_2$	5.3	4.3	4.4	45

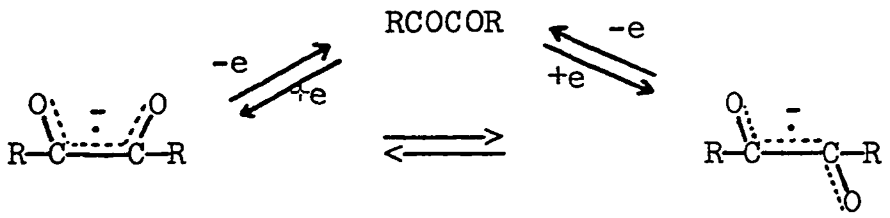
[a] In gauss.

[b] In the presence of quaternary alkylammonium ions or at low potassium ion concentrations.

[c] α-Hydrogens.

[d] Unassigned.

tions were assigned from elementary consideration of electron repulsions, which should lead to higher spin density at the carbonyl carbon atoms of the *cis* isomer. Observation of ^{7}Li hfs with *cis* was strong evidence their assignment was correct. The spectra were of a fine quality, permitting straightforward estimates of the relative concentrations of configurations and easy detection of ^{13}C hyperfine splitting. Russell and Stephens felt that the two isomers may be interconvertible by rapid electron transfer with neutral diketone, suggesting a thermodynamic equilibrium (Equilibrium 5); disproportiona-



(5)

tion of two semidiones to give neutral diketone and enediol dianion (Equilibrium 6) is likely under the experimental conditions.

$$2\ RC(O^-){=}C(O^\bullet)R \rightleftharpoons RCOCOR + RC(O^-){=}C(O^-)R \qquad (6)$$

The behavior of the cis-trans equilibrium suggested that ion pairing had a major role in the solution chemistry of semidiones, even in DMSO, and that further investigation of the acyclic semidiones might reveal information about ion pairing in their solutions. It was also reported that both the cis and trans isomers had identical g-values, causing the center lines of their spectra to be superposed.

It may be noted from Table 2 that the variation in a_α^H is consistent with a change in conformational preference of the alkyl groups. This point has been treated in detail by Malkus (51), who has also examined acyclic semidiones **34**-**36**; he found a mixture of isomers for **34**, with trans in very great predominance, and only a single isomer for **35** and **36**, presumably trans.

$[(CH_3)_3CCH_2CO]_2^{\bullet -}$ **34**

trans - a^H=3.5 G

cis - a^H=4.5 G

$[(CH_3CH_2)_2CHCO]_2^{\bullet -}$ **35**

a^H=1.09 G

$[(CH_3CH_2CH_2)_2CHCO]_2^{\bullet -}$ **36**

a^H=0.95 G

Norman and Pritchett (52) have studied semidiones and protonated semidiones generated in titanium(III)-hydrogen-peroxide-acyloin(or acylil)-water at intermediate pH ranges under flow conditions. Their results, summarized in Table 3, indicated to them that under their conditions the ratios of configurational isomers are kinetically determined, since: (1) the ratios were dependent upon precursor, and (2) addition of biacetyl to the reactants which yielded a non-equilibrium mixture of semidione radicals from acetoin failed to change the relative concentrations of radicals. They found electron transfer to be apparently slow under their conditions. Although they did not state it explicitly, Norman and Pritchett implicitly questioned the likelihood of a thermo-

Table 3. Hfsc[a] of semidiones $RC(O^-)=C(O^\cdot)R$ and their monoprotonated derivatives (from Ref. 52).

	Semidione		Protonated Semidione	
R	$\underline{a}^H$(*cis*)	$\underline{a}^H$(*trans*)	$\underline{a}^H$(*cis*)	$\underline{a}^H$(trans)
CH_3[b]	8.2	7.1	9.6	8.3
CH_3CH_2	5.7	5.0	7.7	5.5
$CH_3CH_2CH_2$	5.4	4.7	7.1	5.1
$(CH_3)_2CH$	2.45	1.7	3.0	2.25

[a] In gauss.

[b] *Trans*/*cis* *ca*. 1:1 when generated from acetoin.

dynamic equilibrium in Russell and Stephens' work. The marked disagreement of these two sets of results—including hyperfine splitting constants—called for very careful consideration.

A portion of the work reported in this thesis was concerned with investigating the configurational isomerism of acyclic semidiones in greater detail, with the prospect of characterizing the nature of semidiones in solution and, in so doing, studying ion-pairing and solvation phenomena in those solvent systems compatible with semidiones. In addition, the analysis of hyperfine splitting by nuclei other than ^{1}H was undertaken to further characterize spin distribution and conformational effects in semidiones.

Many of the early experiments and some of the ideas contained herein were originated by former members of the Russell group. Some are mentioned for the sake of completeness, and when discussed their origins are noted.

CIS-TRANS ISOMERISM AND ION-PAIRING IN ACYCLIC SEMIDIONES

Alkylglyoxal Radical Anions

The parent acyclic semidione is the radical anion derived from glyoxal, 37. As previously noted, this radical

$$HC(O^-)=C(O^\bullet)H$$

37

has been generated in the treatment of acetoxyacetaldehyde with DMSO-base under flow conditions (26, 32), and by electrolytic reduction of glyoxal in tetrahydrofuran (THF) in the presence of quaternary tetraalkylammonium salts (48). The same species, with $a^H = 7.6\text{-}7.7$ G, was apparently observed by ESR in each instance.

Treatment of glycolaldehyde dimer with potassium, cesium or sodium t-butoxide in DMSO or dimethoxyethane (DME) under flow or static conditions yielded the ESR spectrum of only a single identifiable species, $a_{CHO}^H = 7.6$ G, identical to that in Figure 2. Rationalizing that the isomeric distribution may be controlled by the precursor, a mixture of dibromoethylene carbonate and vinylene carbonate was treated with KOt-Bu (0.05 M)-KOH(saturated)-DMSO under flow conditions. The spectrum shown in Figure 2 (A) was obtained. Under no circumstances was a species with a^H other than 7.6-7.7 G observed in the generation of glyoxal semidione. The radical is short-lived ($t_{1/2} \approx 30$ sec) and reacts in DMSO to

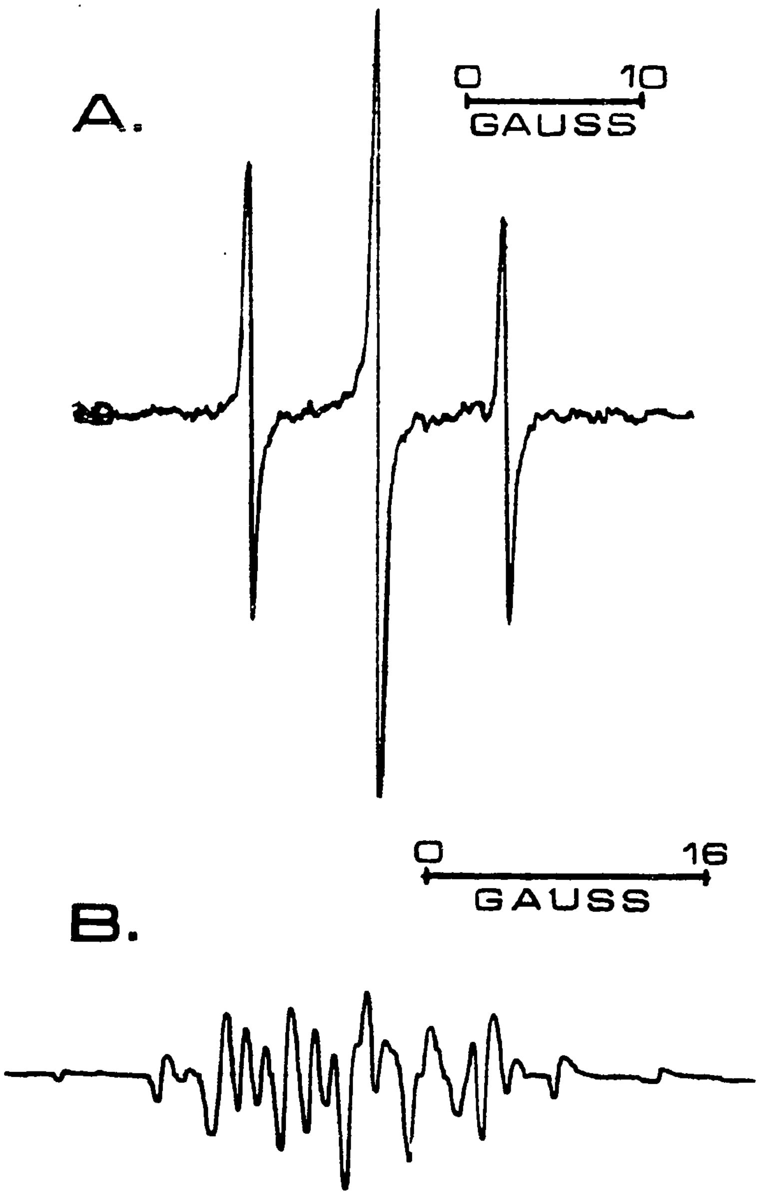


Figure 2. First derivative ESR spectra: (A) spectrum of glyoxal semidione ($HC(O^{-})=C(O\cdot)H$) generated from a mixture of dibromoethylene carbonate and vinylene carbonate in KO*t*-Bu-KOH-DMSO under flow conditions; (B) spectrum of the mixture obtained upon generation of glyoxal semidione from glycolaldehyde dimer under static conditions.

form methylated radicals and other unidentifiable products (Figure 2 (B)). Its ESR signal in DME solution is extremely weak. No ESR signal could be detected from pure vinylene carbonate under any of the above conditions. The structures of other alkylglyoxal radical anions studied here are given in Chart 1; their ESR data are listed in Table 4 and spectra are shown in Figures 2-9. The configurational assignments

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

37, R = H

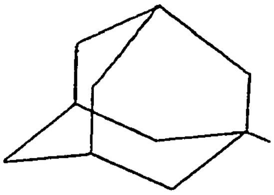
38, R = CH_3

39, R = CH_3CH_2

40, R = $(CH_3)_2CH$

41, R = $(CH_3)_3C$

42, R =



43, R = C_6H_5

Chart 1. Structures of alkylglyoxal radical anions.

were originally made by analogy with the dialkyl semidiones where $\underline{a}^H(cis)>\underline{a}^H(trans)$ (50).

Treatment of acetol with potassium t-butoxide in DMSO produced a mixture of cis- and trans-methylglyoxal radical anions, 38, with trans apparently predominating (Figure 3) under both flow and static conditions. The original radical anion was unstable ($t_{1/2}$ ~ 4-5 min) and a new signal, due to

Table 4. Proton hfsc[a], *g*-values and *trans*/*cis* ratios of semidiones containing a hydrogen substituent.[b]

Semidione	a_{CHO}^{H}	a_{α}^{H}	*trans*/*cis*	*g* ± 0.00005
37	7.6	...	∞	
38 (*trans*)	7.7	5.1	2	2.00515
38 (*cis*)	8.7	7.6		2.00505
39 (*trans*)	7.7	4.2	0.8	2.00521
39 (*cis*)	8.4	5.6		2.00509
40 (*trans*)	7.6	1.6	1.3	2.00530
40 (*cis*)	8.4	1.7		2.00520
41 (*trans*)	7.8	0.30[c]	<0.1	2.00568
41 (*cis*)	8.7	0.27[c]		2.00508
42 (*trans*)	7.7	0.19[d]	<<0.1[e]	
42 (*cis*)	8.7	--		
43 (*trans*)	6.0	--	--[f]	2.00520
43 (*cis*)	6.9	--		2.00493

[a] In gauss.

[b] DMSO-KO*t*-Bu solution, 25°.

[c] a_{β}^{H}.

[d] a_{γ}^{H} (3 equivalent hydrogen atoms).

[e] *Trans*/*cis* = 1-3 in presence of cesium ions.

[f] Not measurable due to complexity of spectrum.

trans-dimethyl semidione gradually grew in intensity under static conditions; however, the *trans*/*cis* ratio did not vary significantly with time.

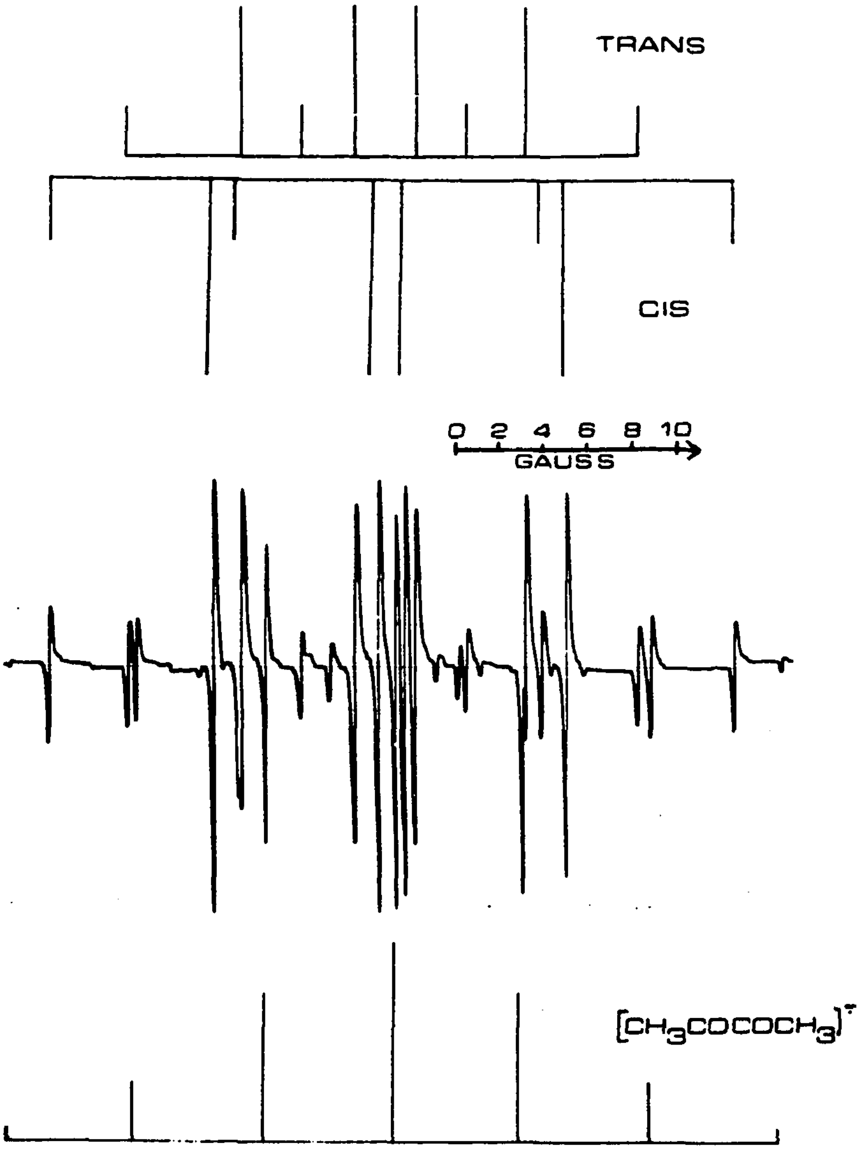
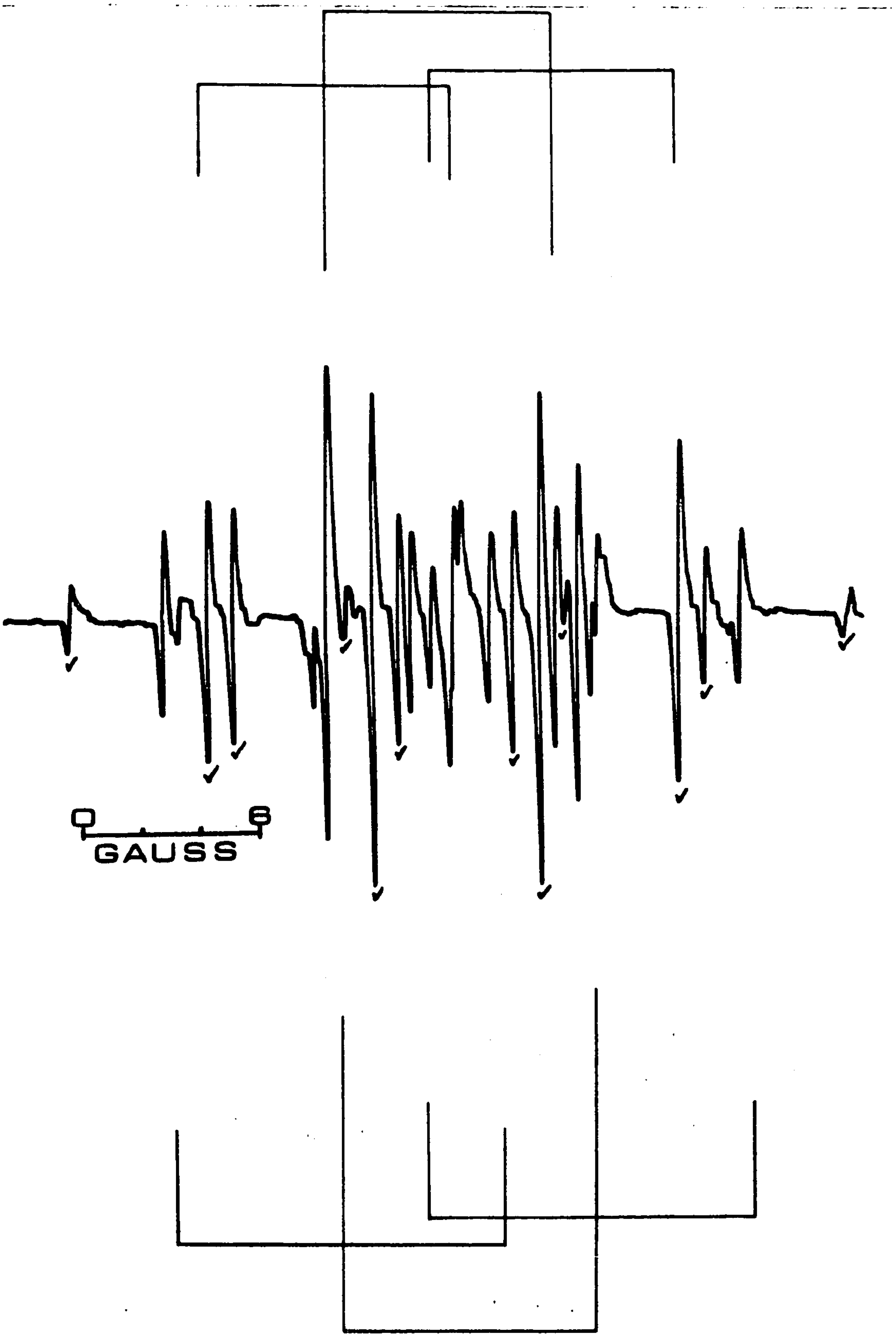


Figure 3. First derivative ESR spectrum of a mixture of *cis*- and *trans*-methylglyoxal radical anions generated from acetol in DMSO-potassium *t*-butoxide under static conditions; the spectrum of *trans*-dimethyl semidione is also clearly visible. Extraneous lines may be due to oxidation products.

Figure 4. First derivative ESR spectrum of the mixture of *cis*- and *trans*-ethylglyoxal radical anions obtained upon treatment of 1-acetoxy-2-butanone with potassium-*t*-butoxide-DMSO under static conditions. Also visible are methylethyl- (checked lines) semidione and α-methylpyruvate radical dianion.


0
6
GAUSS

1-Acetoxy-2-butanone yielded a mixture of *cis*- and *trans*-ethylglyoxal radical anions, **39**, in approximately equal concentrations upon treatment with potassium *t*-butoxide-DMSO; the ESR spectrum of this mixture is given in Figure 4. Ethylglyoxal radical anion was also unstable ($t_{1/2}$ = 4-5 min), but it could be generated and observed under static conditions; signals due possibly to α-methyl pyruvate radical dianion and methylethyl semidione developed gradually.

i-Propyl chloromethyl ketone (1-chloro-3-methyl-2-butanone), *t*-butyl bromomethyl ketone (1-bromo-3,3-dimethyl-2-butanone) and 1-adamantyl bromomethyl ketone yielded semidiones **40**-**42** upon treatment with potassium *t*-butoxide-DMSO under static conditions; their ESR spectra are displayed in Figures 5-8. *i*-Propylglyoxal radical anion **39** gave a distinctively unsymmetrical spectrum (Figure 5) which readily shows the differences in *g*-values and hyperfine splitting constants of the two isomers; the low field lines of the two isomers (which are present in nearly equal concentrations) overlap, while the high field lines are separate. Low intensity satellites, probably due to ^{13}C in *trans* isomer, were detected, $a_1^{C} = 6.8$ G, $a_2^{C} = 4.8$ G (Figure 5 (B)); these could not be assigned with certainty.

Semidiones **41** and **42** in the presence of potassium ion showed only a single isomer with $a_{CHO}^{H} = 8.7$ G in each case (Figures 6 (A) and 7 (A)); when generated in cesium *t*-bu-

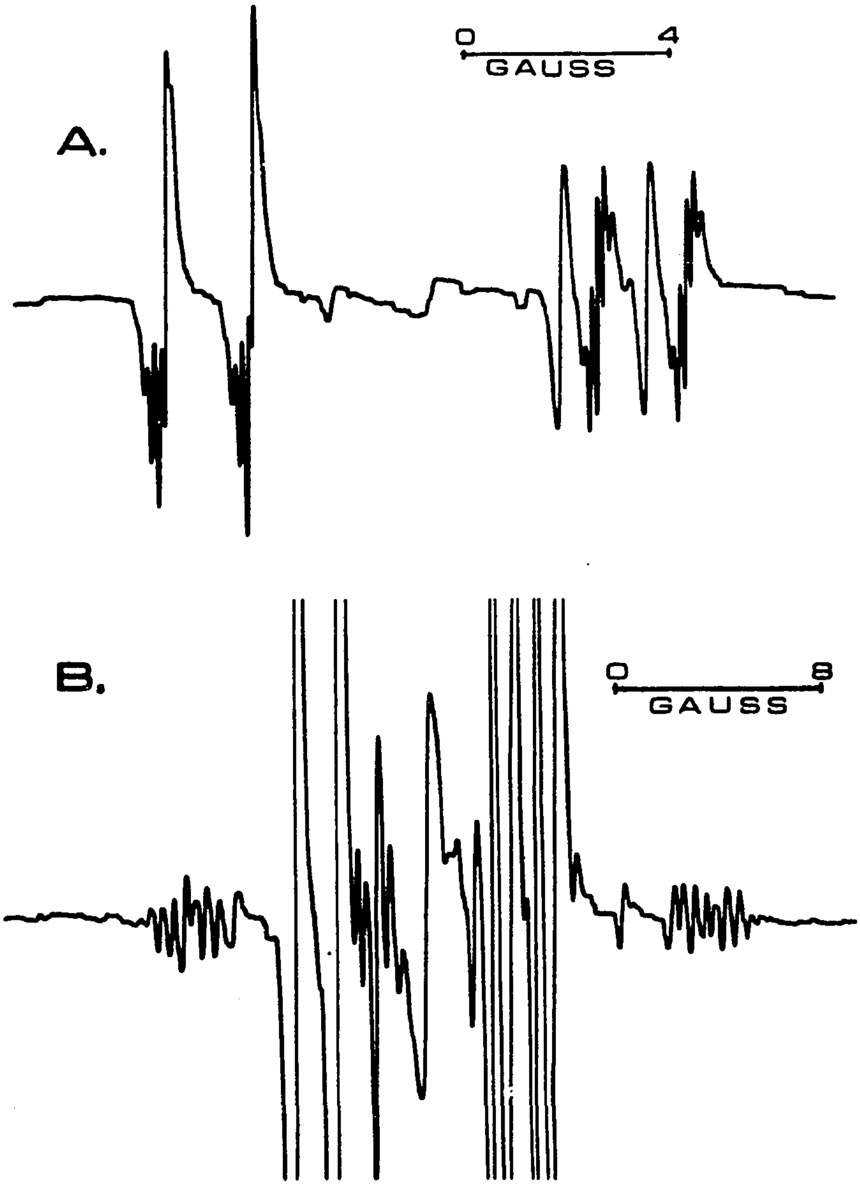


Figure 5. First derivative ESR spectra of the mixture of *cis*- and *trans*-isopropylglyoxal radical anions obtained upon treatment of isopropylchloromethylketone with potassium-*t*-butoxide-DMSO under static conditions (A) showing asymmetry of spectrum; (B) expanded, at high signal level, showing apparent ^{13}C satellites.

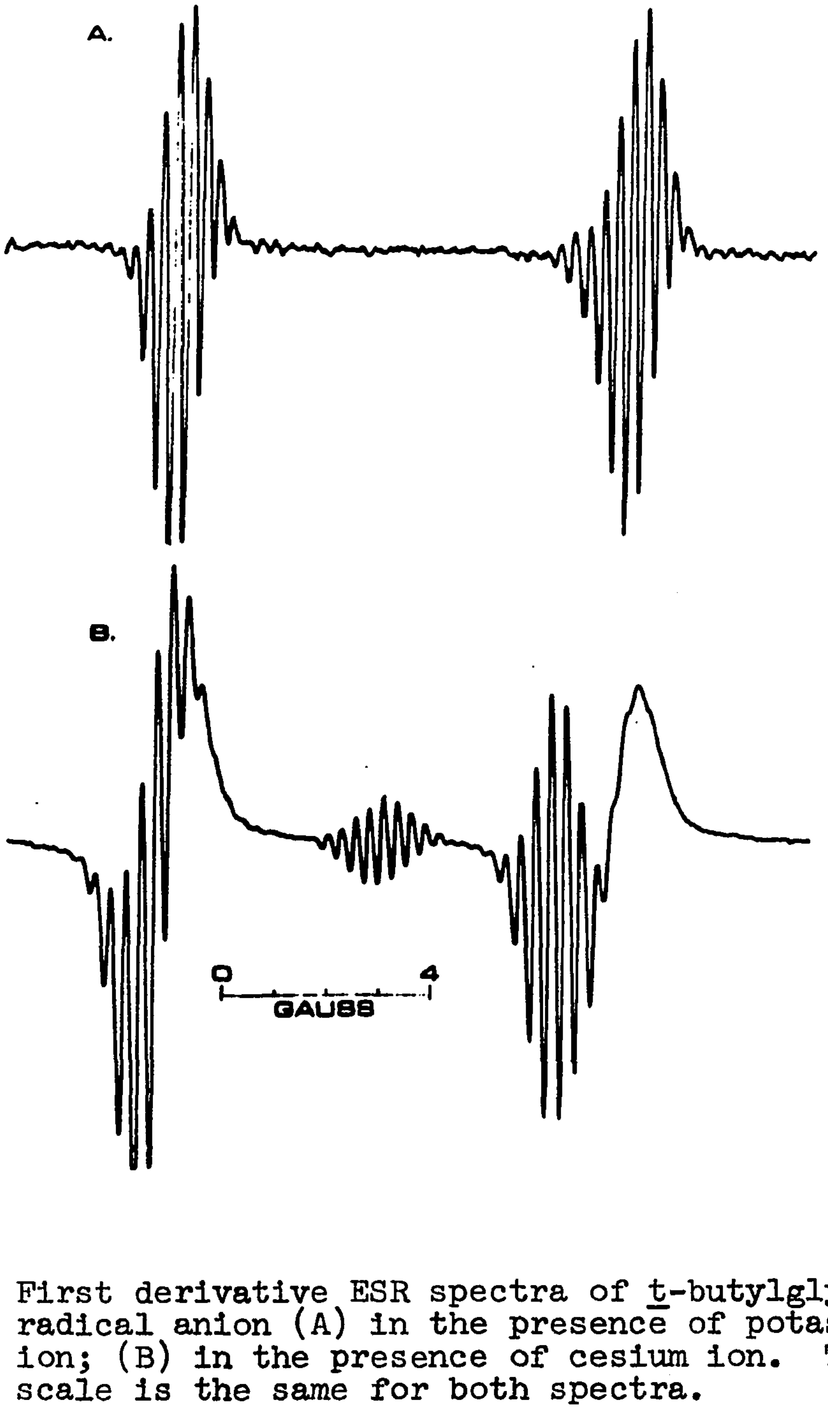


Figure 6. First derivative ESR spectra of t-butylglyoxal radical anion (A) in the presence of potassium ion; (B) in the presence of cesium ion. The scale is the same for both spectra.

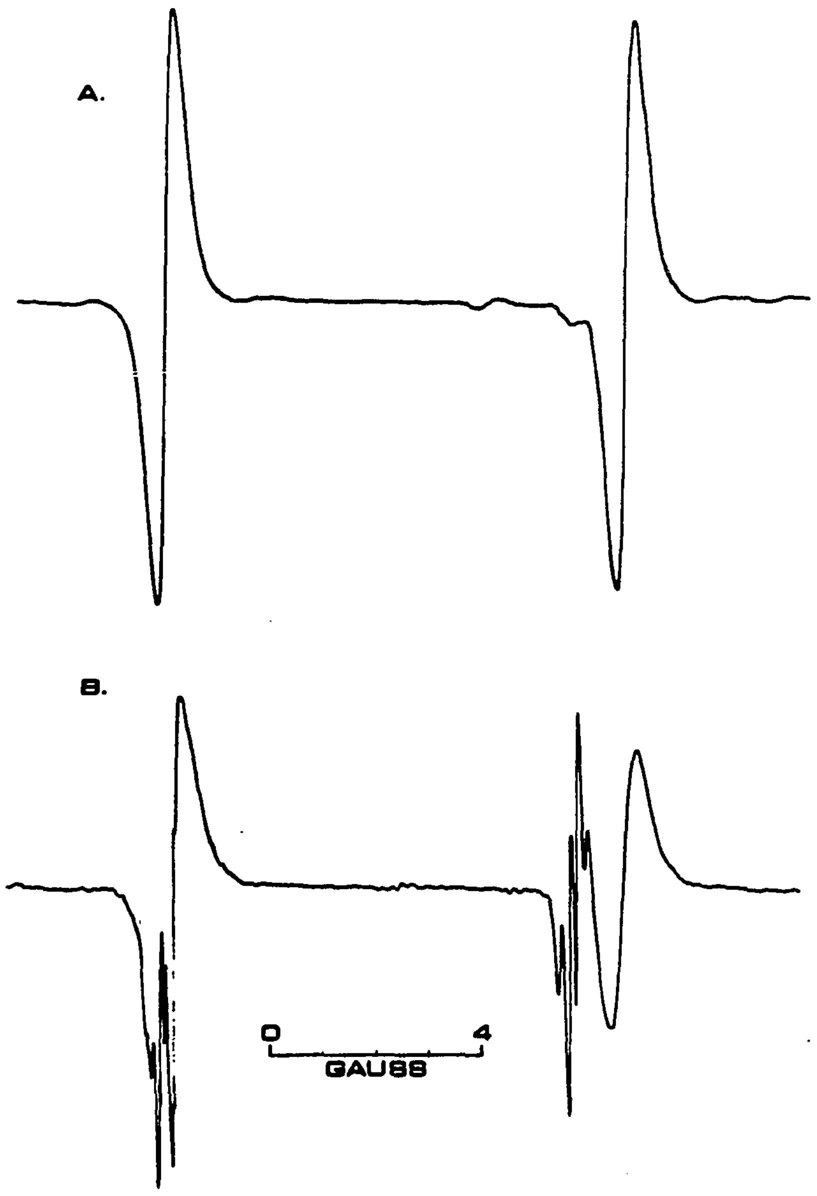


Figure 7. First derivative ESR spectra of 1-adamantylglyoxal radical anion: (A), in the presence of potassium ion; (B), in the presence of cesium ion.

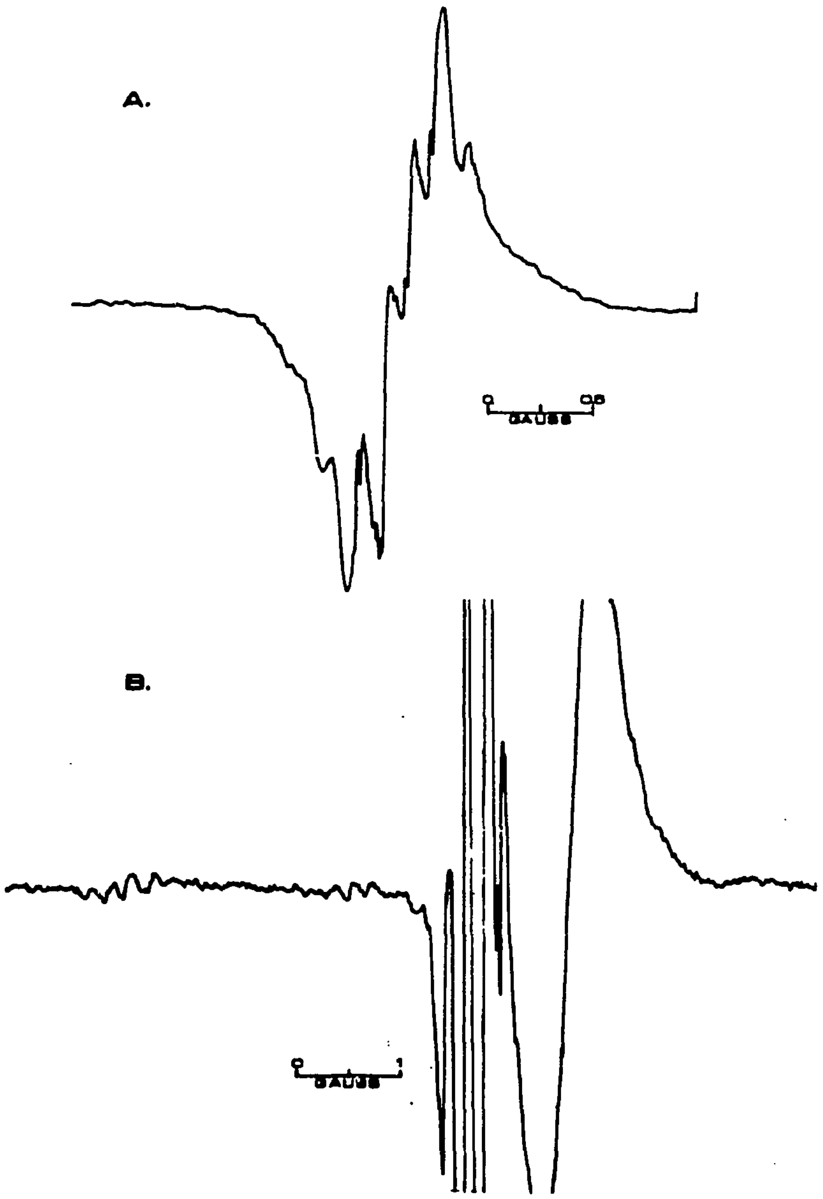
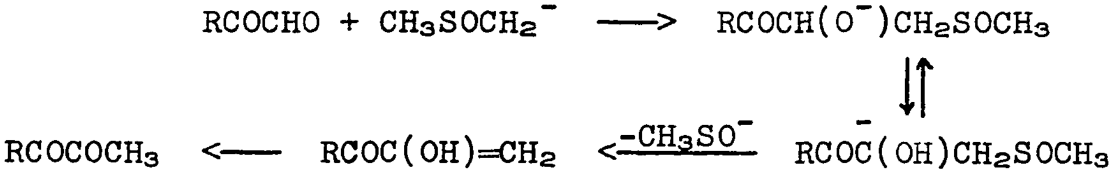


Figure 8. (A) Expansion of low-field portion of spectrum of Figure 7 (B), showing hyperfine structure; (B), expansion of high field portion of Figure 7 (B), showing high field lines of two isomers, plus low intensity (^{13}C?) satellite lines.

toxide-DMSO, mixtures of configurational isomers were observed by ESR (Figures 6 (B) and 7 (B)). Semidiones 40-42 were more stable than the simpler members of the series ($t_{1/2} \sim$ hours); in fact, 1-adamantylglyoxal radical anion 42 was unaffected by the addition of traces of water.

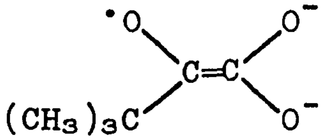
Methylation of 40-42 occurs slowly, if at all; this must be due in part to steric hindrance, since 37-39 methylate rapidly. A sequence of reactions has been suggested (46) to explain the methylation of glyoxals in DMSO-base (Scheme 2):

Scheme 2.



$$\begin{tikzcd}
 & RCOCHO + CH_3SOCH_2^- \arrow[r] & RCOCH(O^-)CH_2SOCH_3 \arrow[d, shift left] \\
RCOCOCH_3 & RCOC(OH){=}CH_2 \arrow[l] & RCO\bar{C}(OH)CH_2SOCH_3 \arrow[l, "-CH_3SO^-"'] \arrow[u, shift left]
\end{tikzcd}$$

The methylation products may then be further reduced to yield semidiones. However, semidiones 40-42 do react to give what appear to be the radical anions of their derivative α-keto-acids, *e.g.* 44; the simpler alkylglyoxals are thought to be-



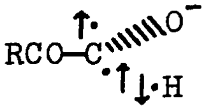
44

have analogously (46). Signals from a secondary radical di-anion are easily seen in Figures 5 (B) and 6 (B), and may also be present in Figure 7 (B).

The β- and γ-hydrogen hfsc for *t*-butyl- and 1-adamantylglyoxal radical anions, **41** and **42**, are worth noting. In **41**, $\underline{a}_{\beta}^{H}$ is slightly larger for the *trans* (lower $\underline{a}_{CHO}^{H}$) than for the *cis* isomer; in *trans*-**42**, $\underline{a}^{H}$ = 0.19 G, was observed due to three equivalent protons, evidently the γ-protons. In *cis*-**42**, an unresolved multiplet was observed, probably due to both β- and γ-protons.

Several semiempirical equations have been suggested to relate hyperfine splitting to spin densities. For a spin-polarization interaction, such as one might expect for the aldehydic proton of a glyoxal radical anion, *e.g.* **45a**, a relationship such as Equation 1 is preferred, where $\underline{Q}_{CH}^{H}$ = -22.5 G and ρ_{C}^{π} is the π-spin density at carbon (53).

spin polarization:

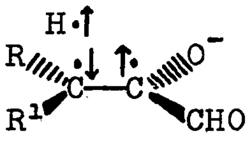


45a

$$\underline{a}_{CH}^{H} = \underline{Q}_{CH}^{H}\rho_{C}^{\pi} \qquad (1)$$

Equation 2 applies to hyperconjugative interactions, as might occur in a system with α-protons, *e.g.* **45b**. Since B_0 is small

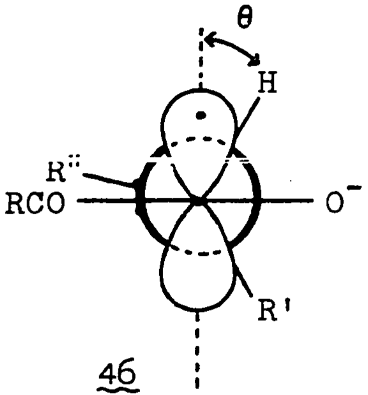
hyperconjugation:



45b

$$\underline{a}_{\alpha}^{H} = (B_0 + B\langle\cos^2\theta\rangle)\rho_{C}^{\pi} \qquad (2)$$

and B is large (~40 G), Equation 2 may be simplified to Equation 3 (54, 55) where B = 40 G, ρ_C^{π} is the π-spin density at carbon, and $\langle\cos^2\theta\rangle$ is determined by the conformational preferences of the alkyl group, θ being the dihedral angel between the carbon p_z orbital and the C_α—H_α bond, vis. 46:

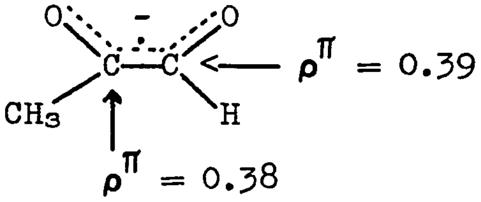


46

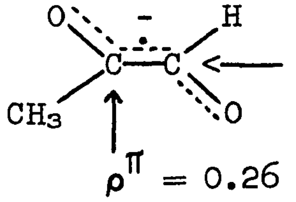
$$\underline{a}_{\alpha}^{H} = B\langle\cos^2\theta\rangle\rho_C^{\pi} \tag{3}$$

For a "freely rotating" methyl group, $\langle\cos^2\theta\rangle = 0.5$.

Application of Equations 1 and 3 to the results in Table 4 for cis-methylglyoxal radical anion (cis-38) yields estimates of $\rho_C^{\pi} = 0.39$ and 0.38 for the aldehydic and acetyl carbons, respectively. However, application to trans-38



cis-38

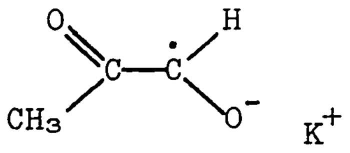


trans-38

leads to estimates of grossly different values of ρ_C^{π} for the two carbonyl atoms; $\rho_C^{\pi} = 0.36$ and 0.26 for the aldehydic and acetyl carbonyls, respectively, in trans-38. That the cis configuration should have a higher spin density at carbon than *trans* may be rationalized naively by considering electron repulsions in both configurational isomers. These forces should be lower in the *trans* isomer, allowing the unpaired electrons to move out onto the oxygen atoms to a greater extent, reducing ρ_C^{π}. However, this explanation does not explain the large difference in ρ_C^{π} observed for the two carbonyl positions of *trans*-38. The actual reason is probably that ion pairing occurs to a higher degree with the *cis* structure; thus, with the increased charge density at the coordinating oxygen atoms, the spin density on oxygen decreases and the spin density on carbon increases. The same argument has been used by Hirota (56) to explain the temperature dependence of hyperfine splitting constants in ketyl radical anions.

Further evidence for an effect of this sort might be found in the *g*-values. For 38-40 $\Delta g \sim 1\times10^{-4}$; in 41, $\Delta g = 6\times10^{4}$, an extraordinary difference. The difference found for 43 (2.7×10^{-4}) is identical to that observed for 3,4,5-trimethoxyphenylglyoxal radical anion (49). Larger *g*-values are always associated with the *trans* isomers, which have higher ρ_O^{π} and lower ρ_C^{π}; *g* is known to increase with increasing spin density at oxygen (57). The large Δg observed for *t*-butylglyoxal radical anion 41 may be caused by a steric interference with solvation or ion pairing occurring only in the *trans* configuration.

The disparity in values of ρ_C^{π} for the two carbonyl carbon atoms in trans-38 suggests that a structure such as 47 may be important, whereby the radical anion undergoes association with a potassium ion preferentially at the aldehydic oxygen atom. Alternatively, a differential solvation of the semidione moiety may be indicated. Addition of lithium iodide to solutions of 38 and 40-42 completely destroyed the ESR signals instead of forming lithium chelates of the cis structures with measurable $\underline{a}^{Li}$. The lithium cations apparently shift the disproportionation equilibrium (Reaction 6) far to the right by preferential association with enediol dianion.



47

Treatment of α-bromoacetophenone or mandelaldehyde dimer with potassium t-butoxide-DMSO produced the cis isomer of phenylglyoxal radical anion 43 (Figure 9, top). The ESR spectrum of this species was the same as previously observed in similar preparations (26, 46). When the radical anion was generated in the presence of cesium t-butoxide, the ESR spectrum given at the bottom of Figure 9 was observed; this spectrum is consistent with the trans isomer of 43, and the splitting constants are similar to those found by Rieger and Fraenkel (42) in quaternary alkylammonium ion-N,N-dimethyl-

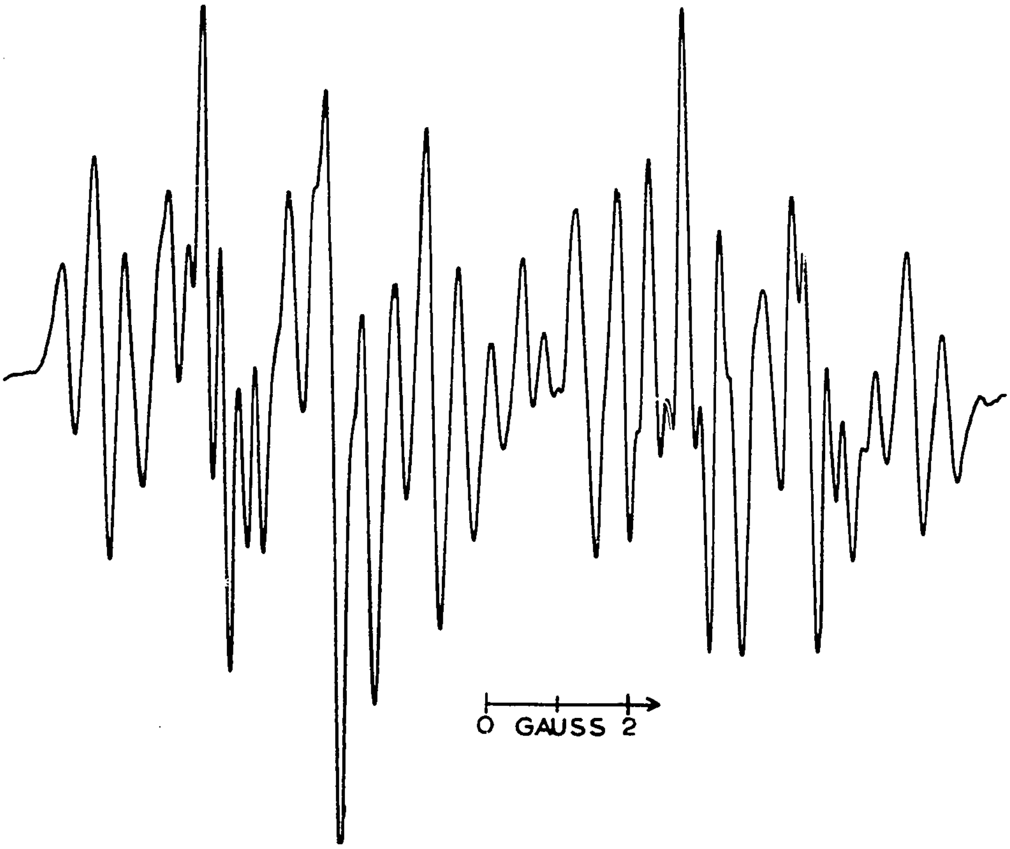


Figure 9a. First derivative ESR spectrum of <u>cis</u>-phenylglyoxal radical anion generated from mandelaldehyde dimer in potassium <u>t</u>-butoxide-DMSO under static conditions.

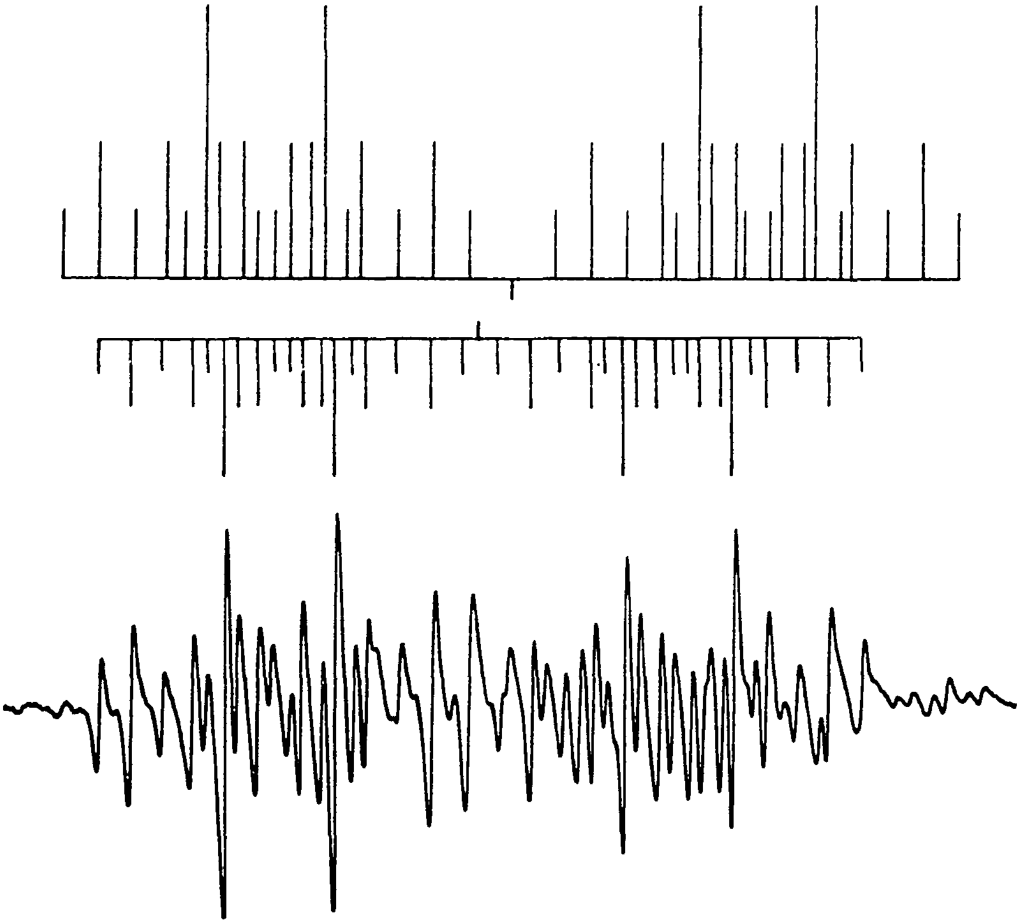


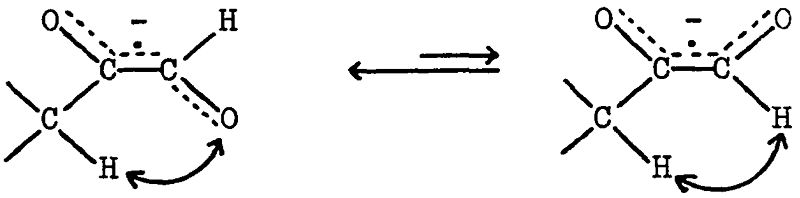
Figure 9b. First derivative ESR spectrum of trans-phenylglyoxal radical anion generated from mandelaldehyde dimer in cesium t-butoxide-DMSO, static conditions; stick diagrams show relative spectra of cis and trans isomers and g-value differences.

formamide (DMF) solutions. Attempts to generate 43 from phenylglyoxal, or from mandelaldehyde dimer with Triton B as the base, in DMSO resulted in very rapid methylation to form methylphenyl semidione (1-phenylpropane-1,2-semidione), 48.

$$C_6H_5C(O^-)=C(O^\bullet)CH_3$$

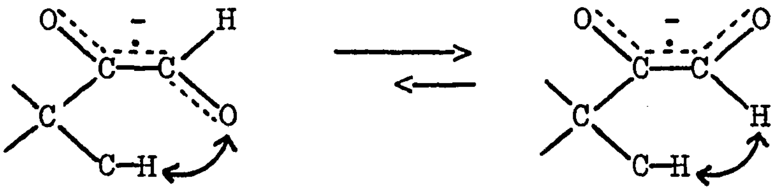
48

The foregoing experiments confirm that configurational isomers do indeed exist for alkylglyoxal radical anions. Moreover, the configurational distribution is determined primarily by the steric requirements of the semidione and by the nature of the counterion. Apparently a 1,5-hydrogen-oxygen interaction in a <u>trans</u> structure 49 is not as severe as the com-



49 50

bination of 1,5-hydrogen-hydrogen and 1,4-oxygen-oxygen interactions in a <u>cis</u> structure 50. However, when the α-carbon is fully alkylated a severe 1,6-hydrogen-oxygen interaction destabilizes 51 relative to 52; association of the



51 52

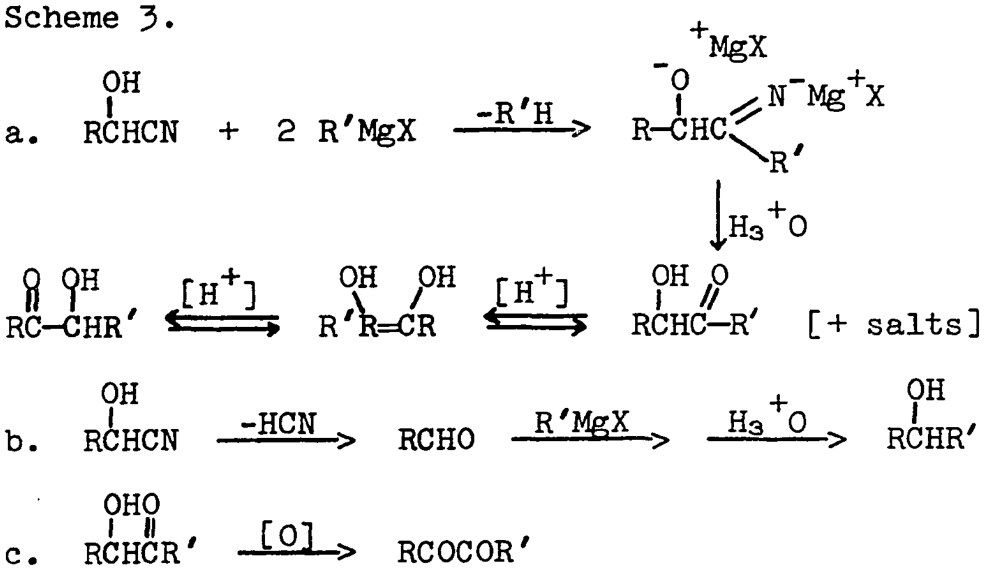
counterion (as a chelate?) may further stabilize the cis structures. Similar considerations may also provide an explanation for the isomeric distribution of isoprene, where the cisoid conformation is favored ca. 6:1 at 50°C (58).

Dialkyl Semidiones

A variety of routes were available for the preparation of precursors for acyclic semidiones (see Scheme 1 for generation of semidiones). Symmetrical semidiones were generated easily from symmetrical acyloins, prepared by the acyloin condensation or one of its modifications. Thus, bis(trimethylsiloxy)-alkenes were synthesized by acyloin condensations in the presence of $(CH_3)_3SiCl$ (59), and could be cleaved by base-DMSO to give semidiones. Ketones with a single active methylene group could be oxidized in base-DMSO to yield semidiones, although mixtures of radicals and weak ESR signals were sometimes observed.

Several unsymmetrical acyloins were prepared by addition of a Grignard reagent to a cyanohydrin, then hydrolysis (60), Scheme 3. Although convenient, this route was not wholly satisfactory since the acyloins were obtained as mixtures with starting cyanohydrin, products of side reactions (e.g. b, Scheme 3) and oxidation products as impurities. Analyses indicated that purification, even by VPC, was incomplete in several cases.

Scheme 3.



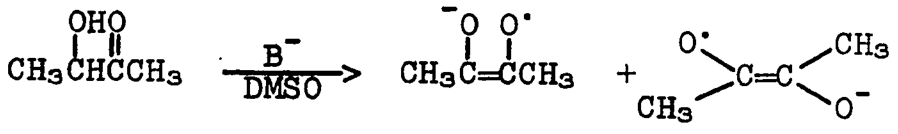
Nature of the cis-trans equilibrium

Previous investigations of acyclic semidiones raised a number of questions. It has been shown that cis and trans isomers exist for most acyclic semidiones, but the nature of the cis-trans equilibrium is still shrouded. Norman and Pritchett (52) have pointed out that the distribution of isomers in their flow systems was kinetically determined—that is, dependent upon the mode of generation. Furthermore, they presented evidence that electron exchange with neutral diketone occurred slowly—at odds with the suggestion by Russell and Stephens that rapid exchange with neutral diketone produced a thermodynamic mixture of isomeric semidiones (50). Bauld (39) has shown that cis- and trans-diphenylsemidione produced by the reduction of benzil with alkali metal exist in thermodynamic equilibrium by electron transfer with benzil. In addition, he brought up the possibility that the isomeric semidiones may also be interconvertible in the absence of neutral diketone.

The nature of the equilibrium may be dependent upon the conditions employed in the generation of semidiones and both viewpoints may be correct. Thermodynamic equilibrium may be slowly attained (~1 to 60 min) and not observed on Norman and Pritchett's timescale (<1 sec). To investigate this situation further, the trans/cis ratios of dimethyl semidione mixtures generated from several different precursors—under identical conditions of solvent, counterion and concentration—were measured. Dimethyl semidione 53 was chosen because it represented the simplest of the stable acyclic semidiones; moreover, this radical anion was ideally suited for other studies (see below) which could provide an overlap of information.

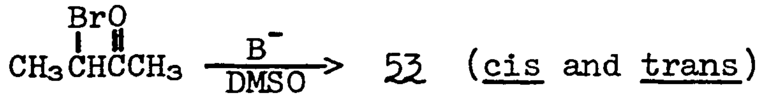
Four precursors were chosen: 3-hydroxy-2-butanone (acetoin), 3-bromo-2-butanone, 2-butanone and 2,3-bis(trimethylsiloxy)-2-butene. The latter compound was used both as a mixture of geometric isomers and as the VPC-isolated isomeric components. The modes of generation were routes (b), (d), (e) and (g) of Scheme 1, namely:

(b)

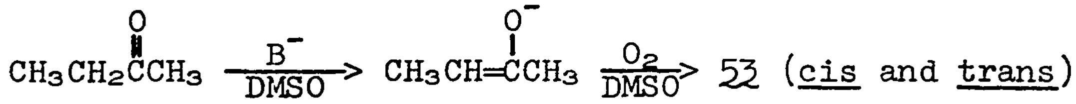


cis trans

53

(d) 

$CH_3\overset{Br}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[DMSO]{B^-}$ **53** (*cis* and *trans*)

(e) 

$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[DMSO]{B^-} CH_3CH{=}\overset{O^-}{\overset{|}{C}}CH_3 \xrightarrow[DMSO]{O_2}$ **53** (*cis* and *trans*)

(g) 

$CH_3\overset{(CH_3)_3SiO}{\overset{|}{C}}{=}\overset{OSi(CH_3)_3}{\overset{|}{C}}CH_3 \xrightarrow[DMSO]{B^-}$ **53** (*cis* and *trans*)

cis and/or *trans*

Route (b) is postulated (50) to involve disproportionation of the acyloin into *vic*-diol and α-diketone, which can then accept an electron from the enediol dianion to give semidione (Scheme 4). Route (d) very likely involves oxidation of bromoketone by DMSO displacement of bromine (46) and route (e) may involve reaction of molecular oxygen with an enolate ion to give diketone, which can be reduced to the semidione by electron transfer from enolate ion (19). Route (g) is apparently the cleavage of a labile Si-O bond by base to give enediol dianion; one-electron oxidation (facile in DMSO?) gives the semidione.

Scheme 4.

$$2\ CH_3CH(OH)COCH_3 \overset{B^-}{\rightleftharpoons} CH_3CH(OH)CH(OH)CH_3 + CH_3COCOCH_3$$

$$CH_3CH(OH)COCH_3 \overset{B^-}{\rightleftharpoons} CH_3C(O^-){=}C(O^-)CH_3$$

$$CH_3C(O^-){=}C(O^-)CH_3 + CH_3COCOCH_3 \rightleftharpoons 2\ \mathbf{53}$$ (mixture of *cis* and *trans*)

The results, together with experimental conditions, are listed in Table 5. Treatment of 3-bromo-2-butanone with potassium *t*-butoxide-DMSO under various conditions resulted in only a very weak ESR signal of dimethyl semidione, showing a *trans/cis* ratio of >5. Little difference was observed in the *trans/cis* ratios, and all were apparently identical within

Table 5. *Trans/cis* ratios of dimethyl semidione produced from various precursors.

Precursor (conditions)[a]	*trans/cis*
I. (0.15 *M* potassium *t*-butoxide-DMSO)	
A. 2,3-bis(trimethylsiloxy)-2-butene: mixture of *cis* and *trans* isomers	12.0 ± 0.5
cis isomer[b]	11.9 ± 0.5
trans isomer[b]	12.4 ± 0.5[c]
B. acetoin	12.5 ± 1.0
II. (0.2 *M* potassium *t*-butoxide-DMSO)	
A. 2,3-bis(trimethylsiloxy)-2-butene, mixture of *cis* and *trans* isomers	8.5 ± 0.5
B. acetoin	8.3 ± 0.5
C. 2-butanone	8.5 ± 0.5

[a] Static measurements, made at least 10 min after mixing, 25°.

[b] Probable assignment of geometry.

[c] After 45 min; *trans/cis* ~13:1, 5 min after mixing.

experimental error at their respective concentrations. (It should be noted that experimental error, large in many cases, can be attributed primarily to instrument noise and recorder peculiarities; the error diminishes as *trans/cis* approaches unity.) It might be concluded, therefore, that since the *trans/cis* ratio of dimethyl semidione in the presence of DMSO and strong base is independent of starting material, the ratio observed should be thermodynamically determined; for example, through rapid electron transfer between semidione and neutral diketone. Dr. G. R. Underwood has estimated the enthalpy change in the disproportionation of diisopropyl semidione **54** to give enediol dianion **55** and diketone **56** to be -9.6 kcal.

$$2\ \underset{\mathbf{54}}{RC(O^-){=}C(O^\cdot)R} \overset{k_d}{\rightleftharpoons} \underset{\mathbf{55}}{RC(O^-){=}C(O^-)R} + \underset{\mathbf{56}}{RCOCOR} \quad (R = (CH_3)_2CH)$$

The presence of diketone is thus possible, even though it is not introduced with the starting material. The acyclic semidiones behave similarly, since their overall ESR signal intensities decrease with decreasing temperature. Still another possibility exists: that routes (b), (e) and (g) have a common intermediate which determines the configurational distribution of the semidione. The likelihood of this explanation has not been determined, but it seems remote. If semidione or diketone is the common species, then a thermodynamic equilibrium is likely. From these considerations, the *cis-trans* distribution of dimethyl semidione seems to be thermodynamically determined and dependent upon temperature, concentration, counterions and solvent, but not upon precursor.

Further scrutiny of Norman and Pritchett's results (Table 3) reveals a startling ambiguity: $\underline{a}_{CH_3}{}^{H}$ = 8.2 G for cis-dimethyl semidione and 7.1 G for the trans isomer (in contrast with observations in these laboratories that $\underline{a}_{CH_3}{}^{H}$(cis) = 7.0 G and $\underline{a}_{CH_3}{}^{H}$(trans) = 5.6 G, in DMSO-strong base) while for the monoprotonated semidione, $\underline{a}_{CH_3}{}^{H}$(cis) = 9.6 G and $\underline{a}_{CH_3}{}^{H}$(trans) = 8.3 G. Disagreement of results, together with the similarities between $\underline{a}^{H}$ in Norman and Pritchett's "semidiones" and protonated semidiones, suggest that mixtures of cis semidione and trans monoprotonated semidione, rather than cis and trans semidiones, may have actually been observed. In such instance, conclusions about the cis-trans equilibrium are meaningless.

The effect of light on the cis-trans distribution was studied, with inconclusive results. A solution of dimethyl semidione, generated from acetoin-potassium-t-butoxide-DMSO, was monitored by ESR while intermittently exposed to a high-pressure mercury lamp. Although the overall concentration of semidione increased twofold during periods of illumination, the trans/cis ratio did not change greatly, varying between 10.2 ± 0.5 when dark and 9.3 ± 0.5 when illuminated. Considerable error was introduced by measurement of the trans/cis ratio (K_{TC}) while the radical concentration was changing.

Effect of structure

It is apparent from Table 2 that a major determining factor in the cis-trans distribution of acyclic dialkyl semidiones is the bulkiness of the alkyl groups. Thus, whereas dimethyl- and diethyl semidiones often have T/C ≤ 20, cis-di-t-butyl semidione, 19, has apparently never been observed (37, 51). Prohibitively severe alkyl-alkyl interactions are expected in this semidione.

Spin density at the carbonyl carbon atoms of dimethyl semidione may be estimated using Equation 3 with the observed proton hfsc of Table 2. For the cis isomer, $\rho_C^\pi = 0.35$, and since the semidione moiety here is symmetrical, $\rho_O^\pi = 0.15$; the trans configuration has $\rho_C^\pi = 0.28$, $\rho_O^\pi = 0.22$. Estimates for the more highly substituted acyclic semidiones are not so straightforward, because $\langle\cos^2\theta\rangle$ may assume an indeterminate value. It also cannot be assumed a priori that ρ_C^π is the same as in dimethyl semidione, since inductive effects and/or steric requirements of the alkyl substituent may alter ρ_C^π. A series of acyclic semidiones with a single methyl substituent was examined to monitor ρ_C^π; the results for the trans isomers are given in Table 6. The ESR spectra of 58-62 are given in Figures 10-14.

Table 6. Hfsc[a] for acyclic semidiones $RC(O^-)=C(O^\cdot)CH_3$ with a single methyl substituent.[b]

Number	R	a_α^H	a_β^H	$a_{CH_3}^H$
53,	CH_3[c]	5.6	---	5.6
57,	C_2H_5[d]	4.8	---	5.6
58,	$CH_3CH_2CH_2$	4.6	0.1-0.2	5.6
59,	$(CH_3)_2CH$[e]	2.0	---	5.8
60,	$(CH_3)_3C$	---	0.29	5.6
61,	$(CH_3)_3CCH_2$[f]	3.8	---	5.4
62,	$(CH_3)_2CHCH_2$	4.4	---	5.6

[a] In gauss.

[b] 0.1 M potassium t-butoxide-DMSO, 25°.

[c] Trans isomer.

[d] $g = 2.00497 \pm 0.00005$.

[e] $g = 2.00496 \pm 0.00005$; cis isomer observed in low concentration, $a_\alpha^H = 2.5$ G, $a_\beta^H = 0.15$ G, $a_{CH_3}^H = 7.0$ G.

[f] $g = 2.00497 \pm 0.00005$.

Generally, little variation was detected in $a_{CH_3}^H$, implying that ρ_C^π is constant through the acyclic semidiones. Minor (~4%) variation was noted for $a_{CH_3}^H$ in 59 and 61, and the cause of this may be an unsymmetrical distortion of the semidione π-system, e.g., in 61a, or a change in planarity of the π-system (24). Malkus' assumption that ρ_C^π is invariant

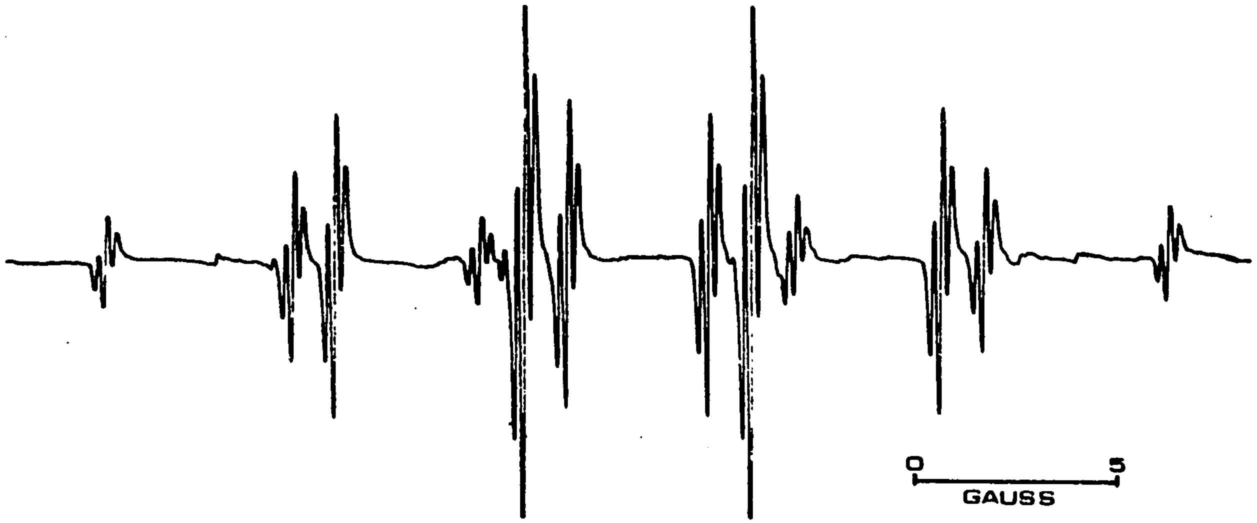


Figure 10. First derivative ESR spectrum of *n*-propyl methyl semidione in potassium *t*-butoxide-DMSO solution, 25°; semidione generated from crude acyloin mixture.

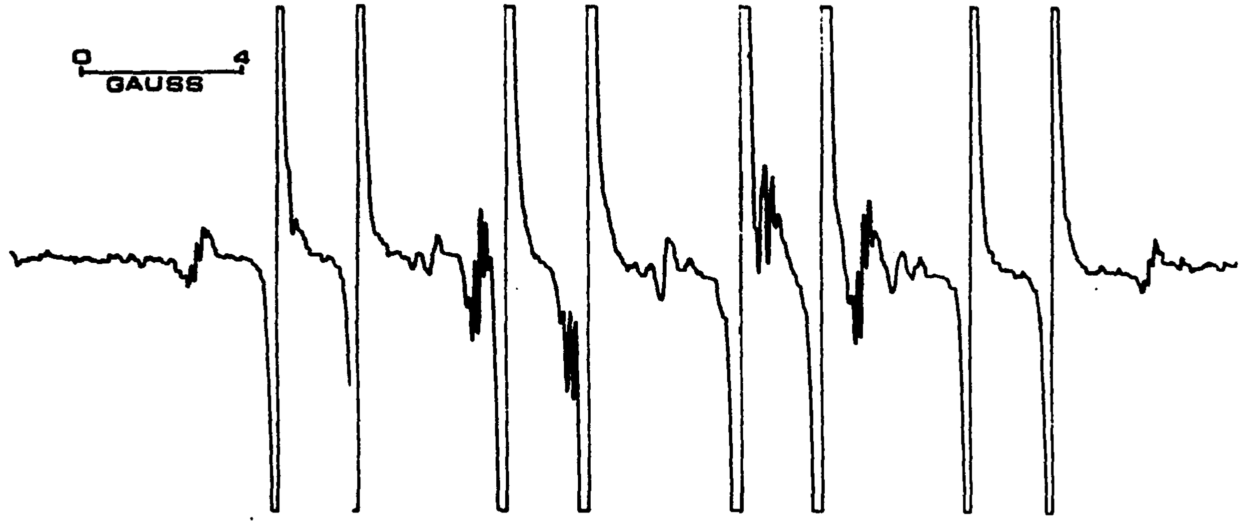


Figure 11. First derivative ESR spectrum at high signal level of isopropyl methyl semidione in potassium t-butoxide-DMSO solution, 25°, showing cis isomer in low concentration and natural abundance ^{13}C satellites; semidione generated by oxidation of methyl isobutyl ketone.

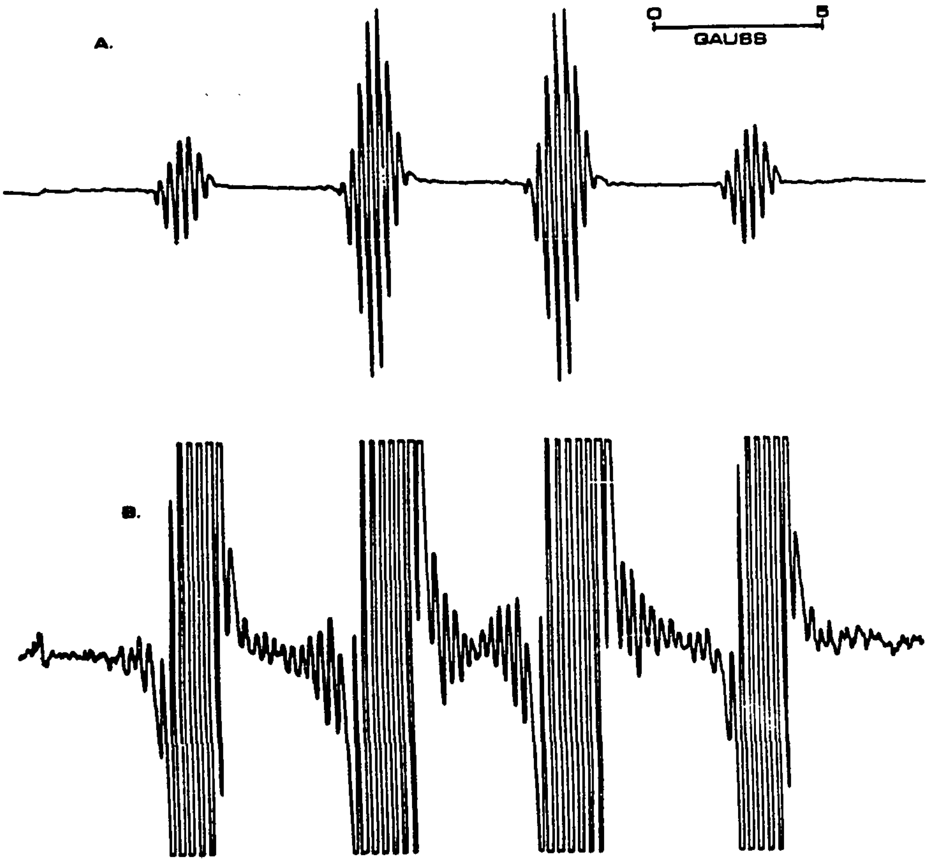


Figure 12. First derivative ESR spectra of t-butyl methyl semidione in potassium t-butoxide-DMSO, 25°; (A) at normal signal level; (B), at high signal level, showing natural abundance ^{13}C satellites; semidione generated by oxidation of methyl neopentyl ketone.

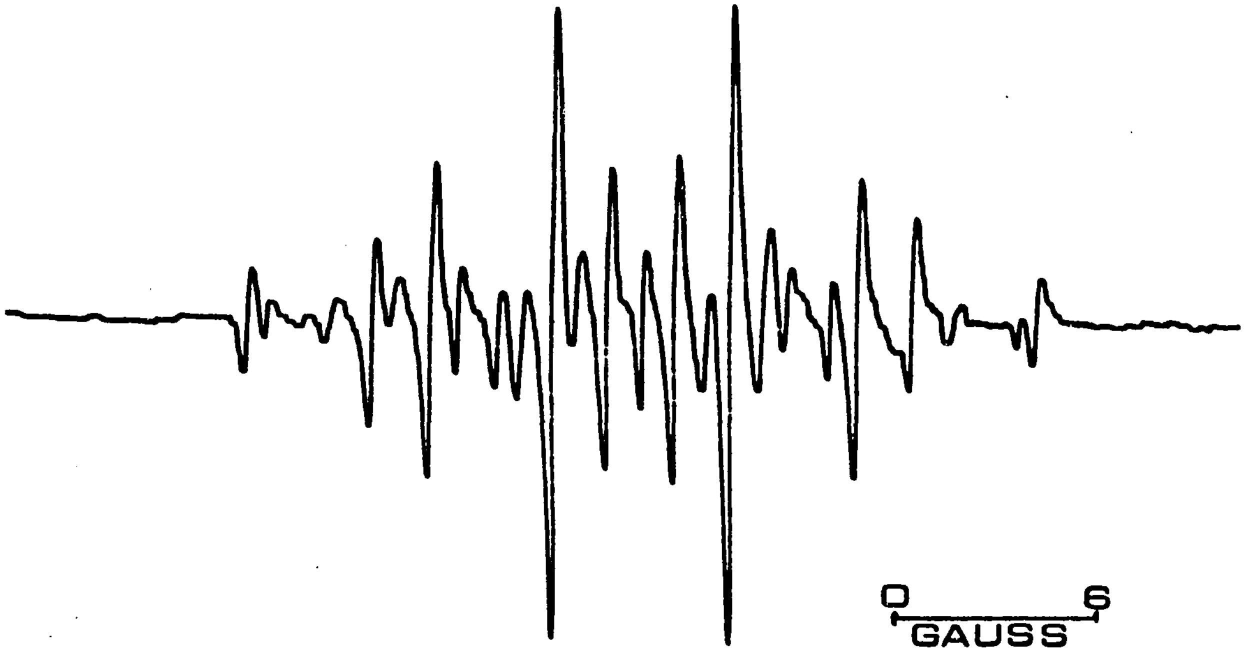


Figure 13. First derivative ESR spectrum of neopentyl methyl semidione in potassium t-butoxide-DMSO solution, 25°; extraneous lines due to an impurity at lower concentration are also detectable; semidione generated from crude acyloin mixture.

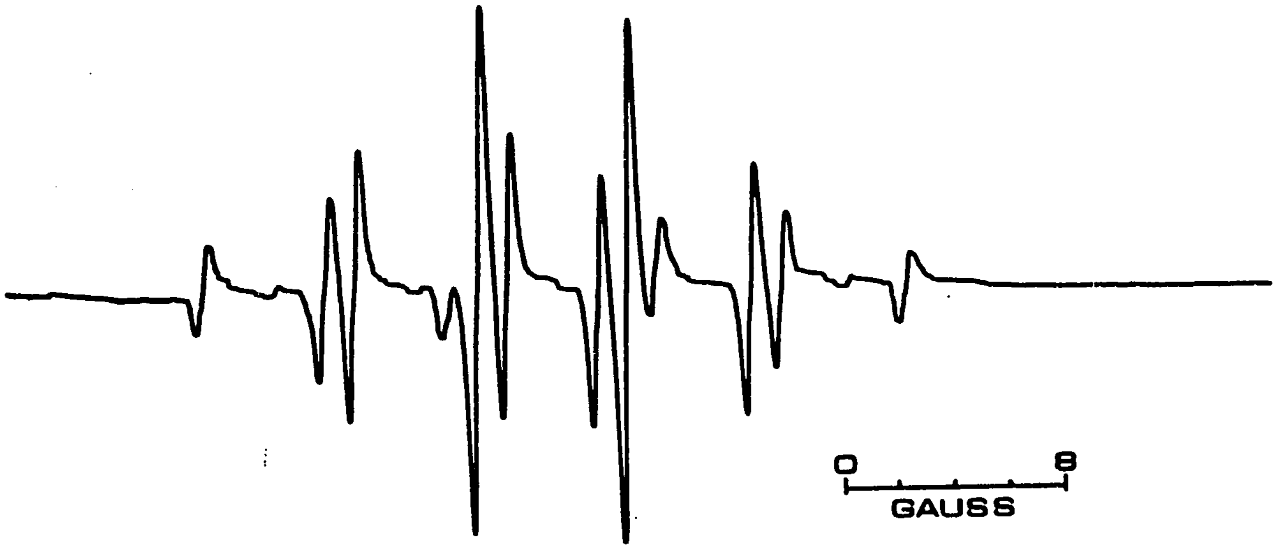
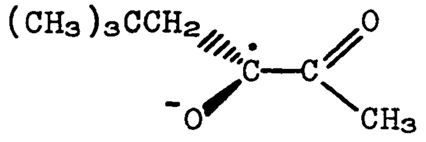


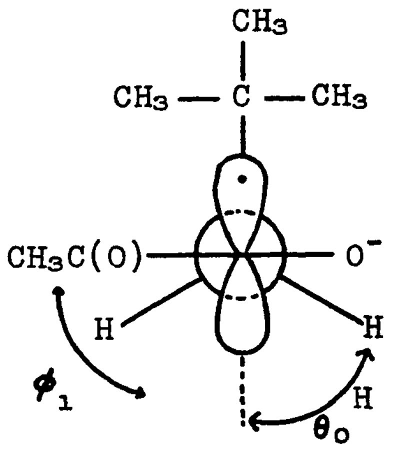
Figure 14. First derivative ESR spectrum of isobutyl methyl semidione in potassium t-butoxide-DMSO solution, 25°; semidione generated by oxidation of 5-methyl-2-hexanone.



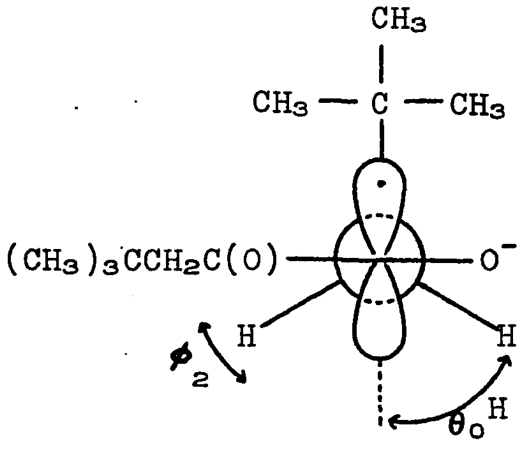
61a

(51) appears correct. Alkyl splittings ($\underline{a}_\alpha^H$) of the methyl-substituted semidiones agree well with the symmetrically substituted analogues. Variations occur in 61 and 62 and are presumably the result of increased torsional oscillation in these radical anions, due to a reduced interaction with the opposing group.

This effect may be better understood after consideration of Newman projections 63 and 64. θ_0^H is the equilibrium di-



63



64

hedral angle for hydrogen, identical in both 67 and 68; the value of $\underline{a}^H$ is proportional to $\langle\cos^2\theta\rangle$ which approaches ½ when φ (torsional oscillation) becomes large. For $\theta = 60^\circ$ the value of $\cos^2\theta$ will be ¼. A higher amplitude of torsional motion (φ) will result in a value of $\langle\cos^2\theta\rangle$ closer to ½.

Since $\varphi_1 > \varphi_2$, the value of $\langle \cos^2\theta \rangle$ for 63 should be greater than for 64.

Except for 59, only a single configurational isomer was detected in the monomethyl semidiones. The size of $a_{CH_3}^{H}$ indicated that isomer was of the trans structure; no attempt was made to obtain evidence for a second configuration.

g-Values for the dialkyl semidiones examined by Russell and Stephens (50) are given in Table 7. As noted for mono-

Table 7. g-Values for acyclic dialkyl semidiones $RC(O^-)=C(O^\cdot)R$.[a]

R	g[b] (cis)	g[b] (trans)
CH_3	2.00483	2.00497
CH_3CH_2	2.00478	2.00485
$(CH_3)_2CH$	2.00483	2.00486
$(CH_3)_2CHCH_2$	2.00487	2.00493

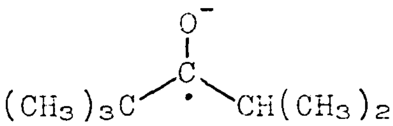
[a] Determined by Dr. G. R. Underwood; DMSO solution, potassium counterion, 25°.

[b] ± 0.00005.

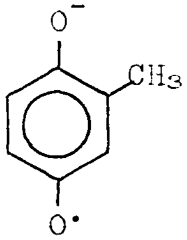
alkylglyoxal semidiones, a greater g-value was found for the semidione of trans configuration. The similarity in g-values between cis and trans isomers, together with the great dissimilarity of concentrations, probably led to earlier reports of identical g-values (50). g-Values are characteristic of radical structure and can be useful for identification of unknown radicals. Chart 2 lists the approximate g-values for some organic radicals; it can be seen that the results for

$CH_3\cdot$

65, g = 2.0026 (9)



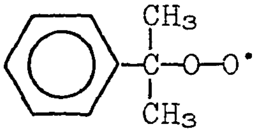
66, g = 2.0036 (61)



67, g = 2.0046 (62)

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

68, g = 2.0049



69, g = 2.0155 (63)

Chart 2. g-Values.

dialkyl semidiones fit quite well. A major factor determining the g-value magnitude in this series is the total spin density on oxygen. Methyl is comparable to most hydrocarbon radicals and radical ions which generally have g = 2.002-2.003, and g is found to increase with increasing ρ_O^π. The g-value may thus be used—with reservation—for a rough estimate of ρ_O^π. The $\Sigma\rho_O^\pi$ for semidiones of 0.3-0.4 indicates that for aliphatic ketyls, e.g. 66, ρ_O^{π} ~0.2. Caution must be used, however, since wide g differences exist between di- and monoalkyl semidiones, and even between configurational isomers, e.g. 41 and 43. In addition, Stone (64, 65) has pointed out that the g-value may be more precisely related to the energy level of the highest (singly) occupied molecular orbital, which can in turn be affected by ion pairing and/or solvation, as well as the presence of non-bonded electrons (57). Solvent shifts for g-values have been observed (6, 66-68).

Effect of gegenion and anion

The effect of gegenion on the proton hfsc and configurational distribution of two representative dialkyl semidiones is indicated in Table 8; data for diethyl semidione were obtained by Dr. Graham Underwood. A dramatic and significant change occurs between lithium and cesium: the isomeric distribution reverses completely. Results with quaternary tetraalkylammonium ions are similar to those for potassium in diethyl semidione and rubidium in dimethyl semidione. A most noticeable feature of the ESR spectra of dimethyl- and diethyl semidiones in the presence of lithium or sodium ions was the presence of hyperfine splitting due to metal ions.

Table 9 shows the effect on the cis-trans equilibrium of dimethyl semidione generated from acetoin by varying anion; no change in $a_{CH_3}^{H}$ was detected. Little effect of anion was noted, and the minor deviations observed were small compared to cation effects.

Table 8. Hfsc[a] and *trans*/*cis* ratios of dimethyl- and diethyl semidione with various counterions.[b]

	M^+	a_α^H (*cis*)	a_α^H (*trans*)	*trans*/*cis*[c]
Dimethyl semidione:				
	Li[d]	7.4 ± 0.1	---	0
	Na	7.1 ± 0.1	5.7 ± 0.05	1.8
	K	7.0 ± 0.05	5.6 ± 0.05	16
	Rb	"	"	40
	Cs	---	"	>200
	R_4N[e]	6.9 ± 0.05	"	35
Diethyl semidione:				
	Li[d]	6.1	4.85 ± 0.05	0.25
	Na	6.0	"	4
	K	5.9 ± 0.1	"	7
	Rb	"	"	100
	Cs	---	"	>200
	R_4N[f]	5.9 ± 0.1	"	8

[a] In gauss.

[b] 0.1 *M* M^{+-}O*t*Bu in DMSO, 25°.

[c] ± 5-10%.

[d] By addition of LiI-DMSO to semidione solution.

[e] $(CH_3)_4N^{+-}OC_2H_5$.

[f] Triton *B*.

Table 9. Dependence of dimethyl semidione K_{TC} on counteranion.[a]

Base	K_{TC}	Base	K_{TC}
$NaOCH_3$	1.7	$KOCH_3$	12.6 ± 0.1
$NaOCH_2CH_3$	2.3	$KOCH_2CH_3$[b]	10.8 ± 2
$NaOC(CH_3)_3$	1.7	$KOC(CH_3)_3$	14.8 ± 1
NaDMSO	1.6	KDMSO	13.8 ± 1

[a] 0.1 *M* in DMSO, 25°.

[b] 0.2 *M*.

Hyperfine splitting by alkali metals

Addition of a saturated solution of lithium iodide-DMSO to a DMSO solution of dimethyl semidione and potassium ion produced a radical ion with $a_{CH_3}^{H} = 7.4\text{-}7.5$ G (6H) and $a^{Li} = 0.58$ G (1 Li, Figure 15). No other configurational isomer could be detected by ESR. Similarly, diethyl semidione gave a lithiated species with $a_{CH_2}^{H} = 6.2$ G (4H) and $a^{Li} = 0.65$ G (1 Li); a second species in low concentration without a^{M}, $a_{CH_2}^{H} = 4.8$ G (4H), could also be detected (Figure 16). Malkus (51) has generated lithium diisopropyl semidione by this method and obtained a spectrum that he felt could be interpreted in several ways: 1) $a_{CH}^{H} = 2.08$ G (2H), $a^{Li} = 0.65$ G (1 Li), $a^{Li} = 0.15$ G (2 Li) [a quadruple ion?] or 2) $a_{CH}^{H} = 2.08$ G (2H), $a_{CH_3}^{H} = 0.15$ G (12H), $a^{Li} = 0.65$ G (1 Li). The

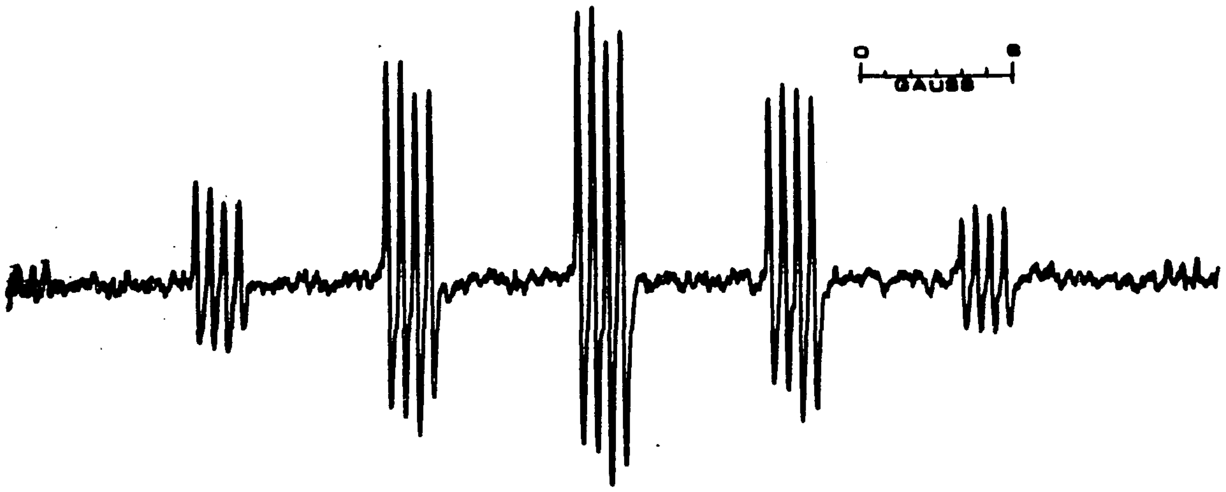


Figure 15. First derivative ESR spectrum of lithium dimethyl semidione, produced by the addition of lithium iodide-DMSO to a solution of dimethyl semidione - 0.1 M potassium t-butoxide-DMSO.

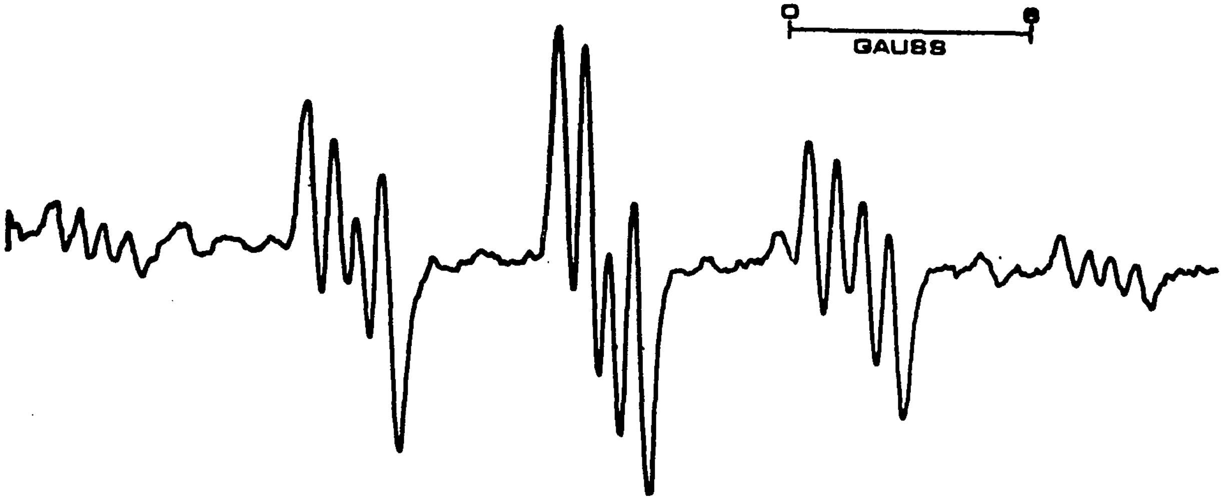


Figure 16. First derivative ESR spectrum of lithium diethyl semidione produced by the addition of lithium iodide-DMSO to a solution of diethyl semidione -0.1 M potassium t-butoxide-DMSO.

latter interpretation seems more consistent with results for dimethyl- and diethyl semidiones. Repetition of Malkus' experiment produced a semidione whose ESR spectrum is given in Figure 17, $\underline{a}_{CH}{}^{H} = 2.2$ G (2H), $\underline{a}_{CH_3}{}^{H} = 0.16$ G (12H), $\underline{a}^{Li} = 0.64$ G (1 Li). Attempts by this worker to obtain lithium di-*t*-butylsemidione failed, as did attempts to generate lithiated alkylglyoxal radical anions; attempts to generate lithiated semidiones using lithium alkoxides or by the addition of lithium perchlorate-DMSO generally yielded poor quality spectra. All spectra of semidiones in the presence of lithium ions were marked by lower intensities and poorer resolution than those with potassium ions. This is presumably because lithium ions shift Equilibrium 6a to the right by association with enediol

$$2\ \pi^{\overline{\cdot}} \rightleftharpoons \pi^{=} + \pi \qquad (6a)$$

dianion $\pi^{=}$. Electron transfer between $\pi^{\overline{\cdot}}$ and $\pi^{=}$ (and/or π) may be responsible for the line broadening observed.

Generation of dimethyl or diethyl semidione from the acyloin in 0.1 *M* sodium *t*-butoxide-DMSO gave radical anions which displayed ^{23}Na hfs with the *cis* configuration; these results are summarized with the above results in Table 10. Observation of hfs by lithium and sodium is strong evidence that the semidiones exist as contact ion pairs with these cations (69, 70); the fact that alkali metal splitting is observed in the isomer thought to be of *cis* configuration suggests the contact ion pair may have a *chelate* structure, *e.g.* **70**. Bauld

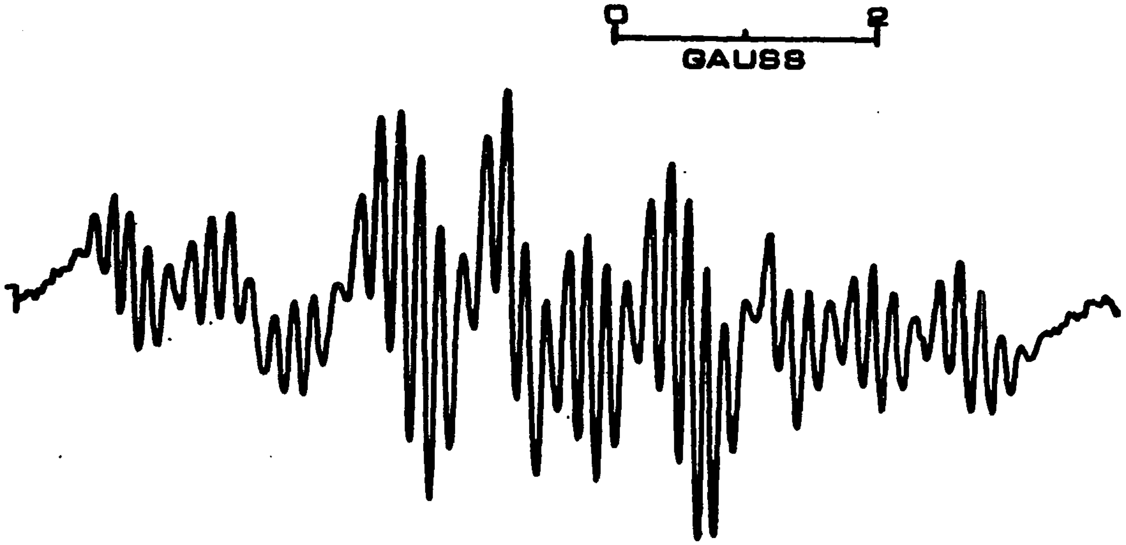


Figure 17. First derivative ESR spectrum of lithium diisopropyl semidione produced by the addition of lithium iodide-DMSO to a solution of diisopropyl semidione -0.1 <u>M</u> potassium <u>t</u>-butoxide-DMSO.

Table 10. Hfsc[a] and *trans*/*cis* ratios of metalated dialkyl semidiones.[b]

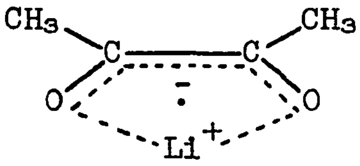
Semidione, M^+	$\underline{a}^M$	$\underline{a}_\alpha^H$	$\underline{a}_\beta^H$	*trans*/*cis*
dimethyl				
Li	0.58	7.4 ± 0.1	---	0
Na	0.23	7.1	---	1.80
diethyl				
Li	0.65	6.1	<0.1[c]	0.25
Na	0.4	6.0	"	4.0
diisopropyl				
Li	0.64	2.2	0.16	*ca.* 0
Na	---[d]	2.4 ± 0.1	0.13	*ca.* 10

[a] In gauss.

[b] DMSO solution, 25°.

[c] Unresolved.

[d] No ^{23}Na hfs detected.



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has previously suggested a similar structure to explain the surprising stability of *cis*-benzil radical anion and dianion (39). Supporting the chelated ion pair notion are the observations 1) that $\underline{a}^M$ decreases from lithium to sodium (increasing ionic radius), although the atomic hyperfine coupling constant increases (Table 11), and 2) that hyperfine splitting by rubidium or cesium was not detected; ^{39}K hfs in 1,2-semidiones has never been substantiated. The larger alkali metals, especially rubidium and cesium, are less suitable for coordination within the small semidione bidentate. Thus, the cis configurations of monoalkylglyoxal radical anions, though disfavored greatly by dipolar repulsions, are stabilized by coordination—possibly to the extent of chelation—with a potassium ion. With cesium ion this particular stabilization does not take place, and considerable amounts of the trans configuration may be formed in spite of severe non-bonded interations.

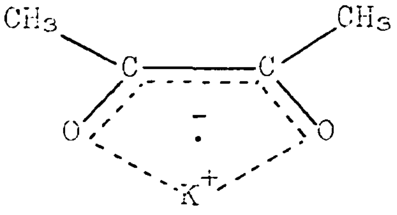
Table 11. Atomic hyperfine splitting constants (a_0^M),[a] nuclear spins (I) and cation radii (r) of some alkali metals.

Atom(%abund.):	^{7}Li(92)	^{23}Na(100)	^{39}K(93)	^{85}Rb(73)	^{123}Cs(100)
a_0^M :	143.3	316.2	82.4	362	820.1
I :	3/2	3/2	3/2	5/2	7/2
r, Å[b] :	0.60	0.96	1.33		1.66

[a] In gauss.

[b] In THF, 25°, Ref. 71.

Failure of semidiones to exhibit ^{39}K hfs was at first puzzling. The size of a potassium ion should not prohibit its coordination with a cis-semidione to form the five-membered chelate structure 71—although potassium ion may be farther



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from oxygen than are the lithium and sodium analogues. In dimethyl semidione, $a^{Li} \sim 0.6$ G, $a^{Na} \approx 0.23$ G, permitting estimates of spin density on the metal ions from Equation 4 (70)

$$\rho^{M} = a^{M}/a_{0}^{M} \qquad (4)$$

of $\rho^{Li} \approx 0.0045$ and $\rho^{Na} \approx 0.0007$. Since the magnitude of these spin densities apparently depends on cation size (as could be expected for a chelate ion pair of this type), the spin density on potassium ion should be no greater than on sodium, at the very most. Thus, a maximum a^{K} of 0.05 G is indicated, with the actual value probably much below this limit. It can be concluded that ^{39}K hfs should not be observed for chelated ion pairs of 1,2-semidiones, i.e. 71. This does not exclude the possibility of observing a^{K} if other structures are involved; in fact, quite large alkali metal hfsc have been observed for 1,4-semidiones. Herold, et al. (72), examined the alkali metal ion pairs of o-dimesitoylbenzene radical anion 72; their results are outlined in Chart 3. Calculated ρ^{M} are proportional to the inverse of

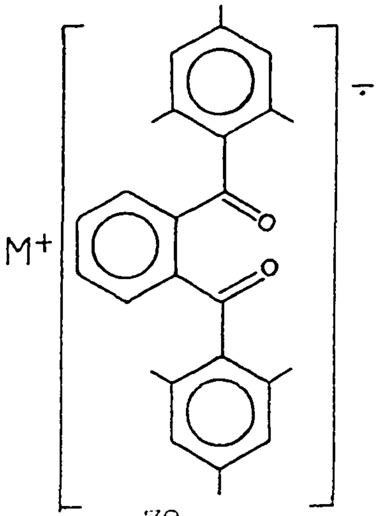
$\underline{a}^{Li} = 3.75$ G, $\rho^{Li} = 0.026$

$\underline{a}^{Na} = 6.95$ G, $\rho^{Na} = 0.022$

$\underline{a}^{K} = 1.33$ G, $\rho^{K} = 0.016$

$\underline{a}^{Cs} = 10.2$ G, $\rho^{Cs} = 0.012$

Chart 3. Ion-pair results.



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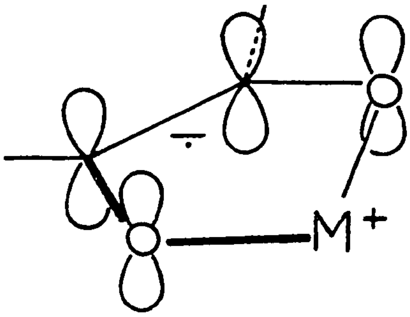
the cation radii, suggesting that coordination with the semidione is weaker for the larger cations. The cation-anion interactions are strong overall, however, and it was suggested that this is the result of chelation; the large $\underline{a}^M$ may be due to the elimination of interference from solvent.

It appears unlikely to this worker that a strong coplanar, seven-membered chelate structure with alkali metal between oxygen atoms should be formed. 1,2-Semidiones probably form chelate structures with alkali metals, and low $\underline{a}^M$ are observed. The difference between contact ion pairs of 1,2-semidiones and those of 1,4-semidiones is very likely that metal ion occupies a position within the nodal plane of the 1,2-semidione π-system, *e.g.* 73, whereas the metal ion is located above the 1,4-semidione π-system, *e.g.* 74.

Takeshita and Hirota (73) investigated several representative radical anions by ESR and NMR to determine the signs of metal ion hfsc. They found that $\underline{a}^{Li}$ in 2,2-dipyridyl radi-



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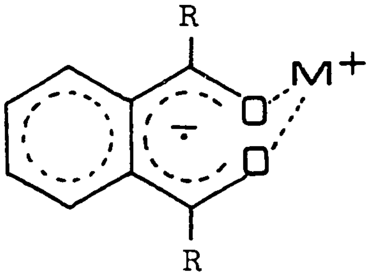
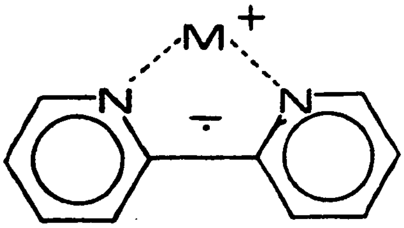


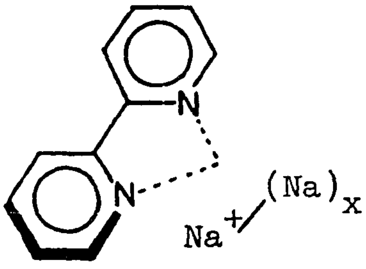
74

cal anion 75 was insensitive to changes in temperature or solvent, supporting a tightly coordinated ion pair. $\underline{a}^{Li}$ was low and negative, indicating that Li^+ was covalently bound



75

within the nodal plane of the π-system, and hyperfine splitting occurred by indirect spin polarization. Structures should be much the same for cis-1,2-semidiones and o-benzosemiquinones. Hfs by sodium ion was negative in highly polar solvents or at low concentrations, but positive and variable in poorly solvating media. This change was explained by a change in the structure of the ion pair, with a concomitant change in hyperfine splitting mechanism. Ionic aggregates, e.g. 76, are formed with sodium in less polar solvents and hyperfine splitting can occur by a direct transmission of


(Na$^+$ not in nodal plane of radical anion.)

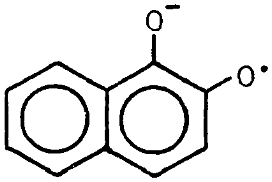
76

spin when the metal ion is located above the π-system. Metal hfs in "non-dentate" radical anions such as anthracenide and naphthalenide (and 1,4-semidiones?) probably occurs by a single mechanism: direct transmission. Symons (74) has discussed the various mechanisms to explain metal hyperfine splitting.

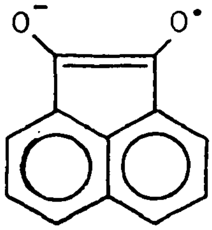
Keske (36) has used the notion of a chelated 1,2-semidione to modify molecular orbital calculations, whereby inclusion of a potassium orbital in the semidione basis set produces good agreement between calculated and experimental results. No experimental evidence directly supports this assumption (in fact, $a_{CH_3}^{H}$ for dimethyl semidione shows little effect with varying alkali metal, except in the case of lithium ion), but the compatibility between calculated and experimental splitting constants is gratifying.

Other investigations concerning the nature of ion-pairing in semidiones and related radical anions have been reported. Warhurst and Wilde (17) have investigated ion pairing in 1,2-

naphthosemiquinone 77 and acenapthoquinone 78; some of their results are shown in Table 12.



77



78

Table 12. Metal hyperfine splitting constants[a] (Ref. 17).

	a^M					
Radical anion	Li	Na	K	^{87}Rb	^{85}Rb	Cs
77[b,c]	0.53	0.69	0.09	0.87	0.27	0.29
78[b,d]	0.54	0.49	0	0.29	0.10	0.56

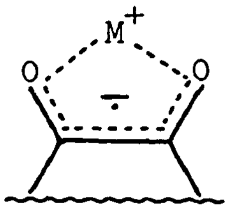
[a] In gauss.

[b] DME solution.

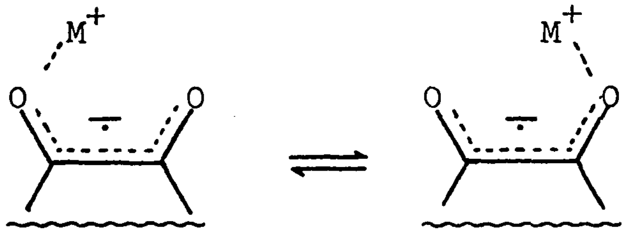
[c] +20°.

[d] -1°.

Although hyperfine splitting due to potassium, rubidium and cesium ions could be detected, the characteristics of these semiquinones were very similar to those of the cis acyclic semidiones. Thus, as the size of the associated alkali metal decreased, the charge density on oxygen increased, and the disproportionation equilibrium shifted towards diamagnetic species. The ratios of observed a^M to a_0^M (atomic) were found to be roughly proportional to the inverse of the cation radius; similarities between their results and those of Herold, *et al.* (72), were pointed out. (Whereas, it has been indicated here that great differences exist between 1,2- and 1,4-semidiones.) The actual nature of the contact ion pair was in doubt, but two possibilities were thought to exist. The metal ion could be firmly chelated directly between the two oxygen atoms, as in 79a, or "jumping" rapidly between the two sites, *e.g.* 79b-c. No linewidth alternation could be detected between -80° and +20°, but the authors felt there was rapid averaging of structures such as 79b and 79c.



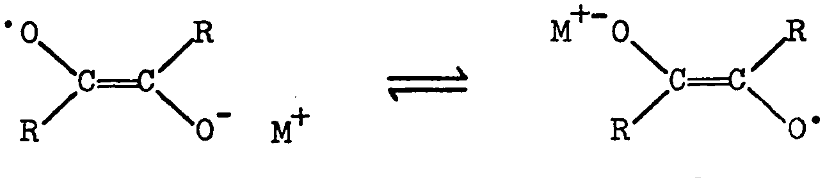
79a



79b 79c

Observation of a^M in Warhurst's and Wilde's work may be due in part to the extended π-systems of their semidiones. Metal cations might be able to assume an average position above the nodal plane of the π-system. The very low (or zero) a^K observed is probably a characteristic of *cis*-1,2-semidiones as opposed to 1,4-semidiones. The problem of distinguishing between 79a and 79b-c for cis-1,2-semidiones is difficult and by no means settled.

Experimental evidence for cation migrations is more likely to be found in trans-1,4- or trans-1,2-semidiones, where the oxygen atoms are farther apart than in cis-1,2-semidiones. In fact, Oakes and Symons (75) have examined the ESR spectra of substituted p-benzosemiquinone anions as a function of solvent, cation and temperature and obtained evidence for migration of cations between the oxygen atoms. No such information concerning a similar equilibrium for trans-1,2-semidiones, e.g. 80a ⇌ 80b, has been derived in this work.



80a

80b

In hopes of finding evidence for the equilibrium 80a ⇌ 80b, the temperature dependence of the potassium salt of diisopropyl semidione in THF-DME was investigated by ESR. This semidione was prepared by reduction of isobutyril on a potassium metal mirror; the results are shown in Figure 18. It was hoped that the spectra might show the effect of slower cation migration or exchange upon cooling—such as linewidth alternation at lower temperatures. Only a single triplet was observed over the range -120° to +25°, but the relative intensities of the three (rather broad) lines varied over this

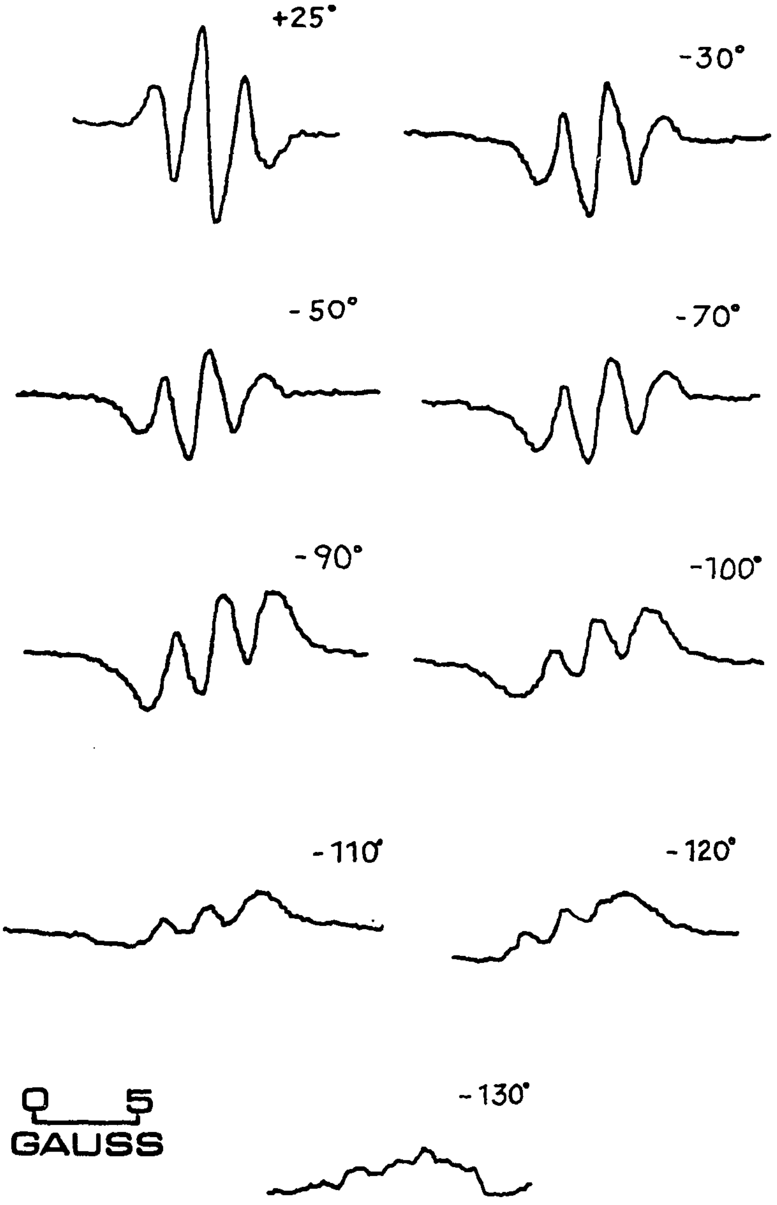


Figure 18. First derivative ESR spectra at various temperatures of the semidione obtained by reduction of isobutyril on a K metal mirror in 5:1 THF-DME.

range. Thus, while the triplet had the expected 1:2:1 intensities at higher temperatures, it had approximately 1:1:1 intensities at -100°. However, the outer lines as well as the center peak were extensively broadened. The broad-lined triplet may be due to two isomers in similar concentrations with very similar g-values and proton hfsc; temperature variations then change the configurational distribution and a_{CH}^{H}, as well as cation motion and conformation disposition. A detailed interpretation is not apparent; variable temperature studies of diisopropylsemidione in DMF-DMSO showed little variation in a_{CH}^{H} and no linewidth alternation, discounting the likelihood of contributions from conformational effects.

Effect of cation, concentration, temperature and solvent

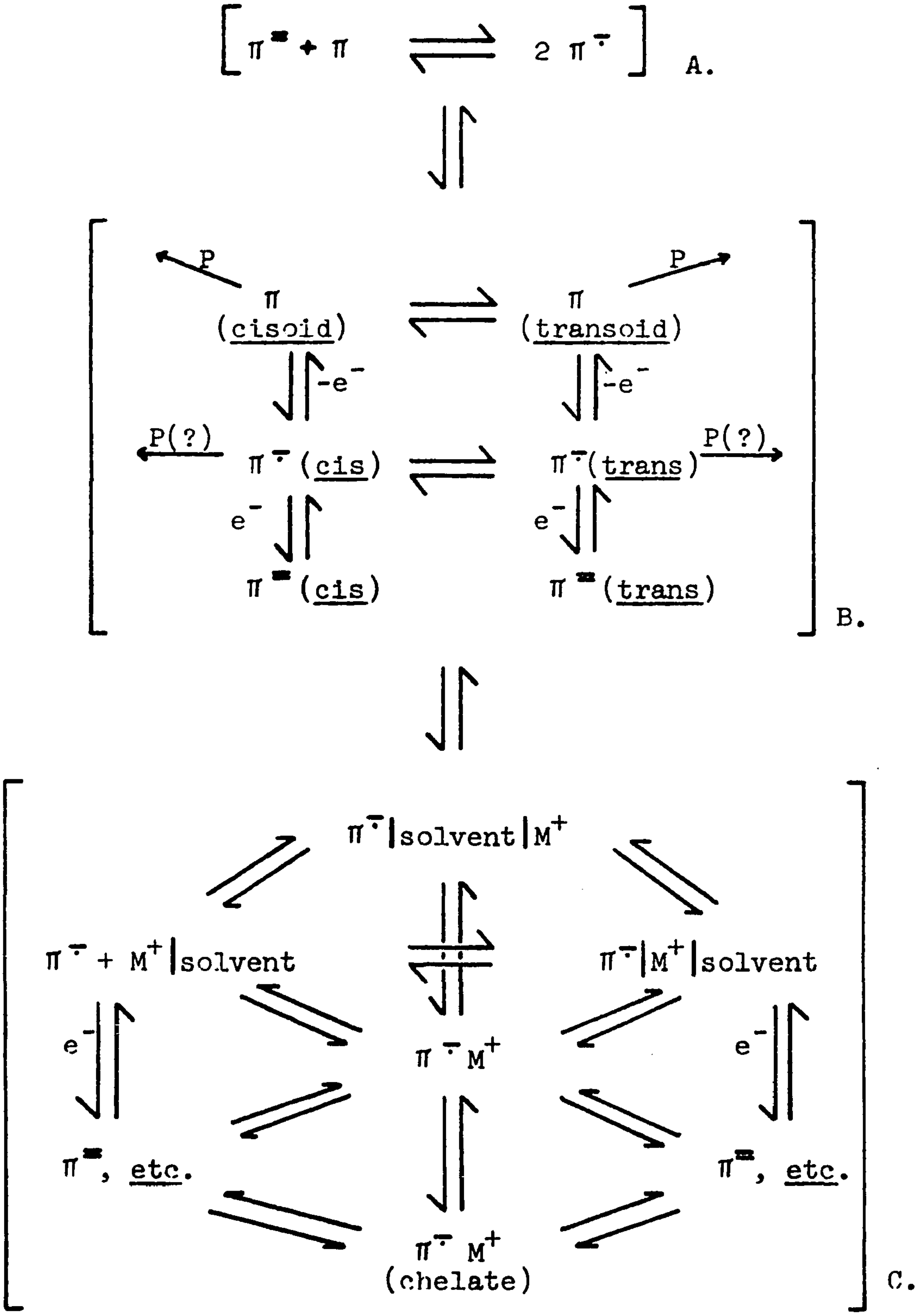
That lithium acyclic semidiones exist predominantly as contact ion pairs in DMSO is unquestionable; however, whether semidiones exist as the free ions or form ion pairs with cesium in DMSO is not clear. If the ions are "free" (that is, separated by large distances on the average in solution) then the trans/cis ratio probably reflects a minimization of dipolar repulsions and non-bonded interactions in the semidione. If ion pairing occurs, the high trans/cis ratio may be the result of a tendency of cesium ion to associate with large or diffuse (trans) anions, rather than coordinate with the cis bidentate. Two cesium ions may associate with a semidione to form a triple ion; trans may be favored in such a situation.

Alternatively and perhaps most likely, a still more complicated situation may arise with free ions and one or more type of ion pair existing simultaneously in solution.

The situation is even less clear in the intermediate cases where both cis and trans isomers are observed; sodium obviously forms a contact ion pair with cis semidione, but a number of questions are raised: 1) Are ion pairs other than the cis-chelate present in solution? 2) Why is alkali metal splitting never observed for the trans isomer? Does this imply a "free" ion? 3) What species and equilibria are involved? A more detailed examination of acyclic semidiones with intermediate-sized cations will address itself to these and similar questions.

Many reactions or equilibria may be postulated to occur, at several different "levels" of consideration, in solutions of acyclic semidiones. Taking the disproportionation of acetoin in potassium-t-butoxide-DMSO as an example, the reactions in Scheme 4 may occur initially. Comproportionation of enediol dianion and diketone can give semidiones. The semidiones can then isomerize, undergo electron transfer or react further to give non-radical products; furthermore, ion pairing may occur at various stages, and a host of additional equilibria are possible (76, 77) between "free ions", "contact" ion pairs and "loose" ion pairs, to list a few (78-81). Some of these possibilities are more graphically depicted in Scheme 5.

Scheme 5.


$\pi^{=} + \pi \rightleftharpoons 2\,\pi^{\overline{\cdot}}$
A.
P
π (cisoid)
π (transoid)
P
$-e^-$
$-e^-$
P(?)
$\pi^{\overline{\cdot}}$ (cis)
$\pi^{\overline{\cdot}}$(trans)
P(?)
e^-
e^-
$\pi^{=}$ (cis)
$\pi^{=}$ (trans)
B.
$\pi^{\overline{\cdot}}$|solvent|M^+
$\pi^{\overline{\cdot}}$ + M^+|solvent
$\pi^{\overline{\cdot}}$|M^+|solvent
e^-
$\pi^{\overline{\cdot}}M^+$
e^-
$\pi^{=}$, etc.
$\pi^{=}$, etc.
$\pi^{\overline{\cdot}}$ M^+
(chelate)
C.

With time, only the comproportionation-disproportionation equilibrium of Scheme 4 is likely to be of any importance among the "radical-forming" reactions at level A (where diketone is represented by π, semidione, by $\pi^{\overline{\cdot}}$, etc.). Once formed, the semidiones may enter into oxidation-reduction equilibria (considered distinct from the disporportionation equilibrium as a formality), interconvert configurations (perhaps *via* electron transfer equilibria), or be destroyed by "product formation", P, all at level B. Bauld has pointed out that the direct interconversion of *cis* and *trans* dianion is unlikely, at least for benzil dianion, and that direct interconversion of *cis* and *trans* semidiones may or may not occur (39). With rapid, reversible electron transfer and rapid interconversion of diketone conformations, the equilibrium constant for *cis* $\rightleftharpoons$ *trans* semidione interconversion, K_{TC}, is well approximated by [*trans*-$\pi^{\overline{\cdot}}$]/[*cis*-$\pi^{\overline{\cdot}}$]; relative concentrations of isomers are easily estimated by ESR measurements. Each of the equilibria cited in levels A and B is in turn affected—directly or indirectly—by the ion-pairing equilibria of level C. All previous experiments indicate that the concept of ion pairing is important to an understanding of semidione phenomena. Unfortunately, various ion pair equilibria (of which only a few of the more likely are shown) are not easily discerned by single, direct ESR measurements unless hyperfine splitting by metal ions can be detected, thereby revealing the presence of contact ion pairs.

For this reason, systematic investigation of the dimethyl semidione radical anion under a variety of conditions was undertaken as a means of providing a clearer account of the more abstruse phenomena. Dimethyl semidione, as noted, is the simplest stable acyclic semidione; its symmetry and lack of obvious conformational or steric peculiarities make it the ideal representative of acyclic semidiones. Presumably, ideas derived from studies of dimethyl semidione may be applied to the more complex mono-, poly-, and acyclic semidiones. Specifically, the effects of factors important in ion-pairing equilibria—counterions, concentration, temperature and solvent—were examined by ESR using dimethyl semidione as a probe. Results of these studies are found with some discussion in the pages immediately following.

Table 8 shows the effects of various alkali metal _t_-butoxides in DMSO on dimethyl and diethyl semidiones. The presence of large cations favors _trans_-semidione, whereas _cis_-semidione is increasingly favored in the presence of smaller cations. Results with quaternary tetraalkylammonium ions appear to be anomalous, but may actually represent a situation with "free" or completely solvated ions.

The dependence of the _cis_-_trans_ equilibrium of dimethyl semidione on cation concentration and temperature was examined. Solutions of 10 μl acetoin and metal _t_-butoxide in DMSO were degassed separately, then mixed, and the resultant semidione mixtures were analyzed by ESR. It was generally found that although the trans isomer always predominated, the cis isomer was increasingly favored at higher temperatures. Exceptions to this generalization were found with 0.05 M sodium t-butoxide-DMSO, where K_{TC} goes through a maximum at 38-53°, and cesium t-butoxide-DMSO, where no cis isomer was ever observed. The results are given in Table 13. Temperature dependence of lithium ion-dimethyl semidione or tetraalkylammonium ion-dimethyl semidione was not determined since satisfactory ESR signals were not observed under these conditions. Experimental error in the measurements was considerable and attributable in part to the signal-to-noise ratio, made lower by use of the variable temperature insert. The temperature range studied (~20°-100°) reflects the approximate range in which solutions of DMSO-base are liquid and stable. The proton hfsc of either isomer was not greatly affected over the temperature range (proton hfsc are noted in Table 8). As originally noted by Russell and Stephens (50), higher trans/-cis ratios were generally observed at lower cation concentrations, very likely indicative of cis isomer favored by ion-pairing.

To eliminate the possible interference of aggregation differences in the metal t-butoxides, the temperature and concentration dependence of dimethyl semidione in freshly prepared solutions of sodium and potassium dimsylate was examined

Table 13. Temperature dependence of the configurational distribution of dimethyl semidione with several metal *t*-butoxides in DMSO solution.

Metal *t*-butoxide, concentration	K_{TC} 23°	38°	53°	63°	78°	93°
A. sodium[a]						
0.1 *M*	1.80±0.12	1.74±0.02	1.72±0.01	1.67±0.1	1.54±0.04	1.30±0.08
0.05 *M*	1.51±0.09	1.62±0.02	1.62±0.03	1.55±0.02	1.47±0.04	1.19±0.01
B. potassium[b]						
0.1 *M*	17.5±1.0	14.8±0.8	21.7±0.7	11.6±0.7	9.58±0.05	---
0.05 *M*	20.7±0.4	17.1±0.1	16.4±0.05	13.9±0.3	11.7±0.1	11±1
0.025 *M*	15.9±2.2	17±3.6	12.9±0.7	15.3±0.7	16.4±2.5	12.1±1
C. rubidium[b,c,d]						
0.1 *M*	40.7	32.3	26.6	23.2	19.6	18.5
0.05 *M*	65.3	43.9	--	32.4	24.9	--
0.025 *M*	--	31.0	27.0	27.5	24.3	26.0
D. cesium			(>200)[e]			
E. potassium (DMF)[f]	13° 6.14	43° 5.25	53° 4.0	73° 3.55	93° 2.33	

[a] Linewidth of *cis* isomer greater than that of *trans*.

[b] *Cis* and *trans* linewidths apparently equal.

[c] K_{TC} uncorrected for contribution from ^{13}C satellite lines.

[d] Error of ± 10%

[e] Only *trans* isomer detectable at all temperatures and concentrations.

[f] Determined by Dr. G. R. Underwood in ~0.2 *M* potassium *t*-butoxide-DMF.

the results are found in Table 14. Although K_{TC} is generally lower here than in Table 11, the gross observations are similar, with two notable exceptions: K_{TC} steadily increases with T in 0.1 M sodium ion-DMSO and [cis] reaches a minimum at 38° in 0.05 M sodium ion-DMSO. The lower trans/cis ratios, if significant, probably reflect the absence of competition of t-butoxide anions for metal cations.

Table 14. Temperature dependence of the configuration distribution of dimethyl semidione in methylsulfinyl carbanion-alkali metal ion-DMSO.

	K_{TC}				
Metal ion, concentration	23°	38°	53°	63°	78°
A. sodium[a]					
0.1 M	1.38±0.1	1.56±0.07	1.50±0.02	1.46±0.05	1.29±0.14
0.05 M	1.26±0.03	1.59±0.16	1.80±0.13	1.90±0.06	2.00
B. potassium[b]					
0.1 M	13.8±1	10.9±0.85	9.58±0.45	8.56±0.41	8.35±0.15
0.05 M	13.5±1	11.5±0.74	9.77±0.56	9.61±0.64	9.00±0.5
0.025 M	23.7±4.7	20.3±1.33	17.6±2.04	17.2±2.8	---

[a] Linewidth of cis isomer greater than that of trans.

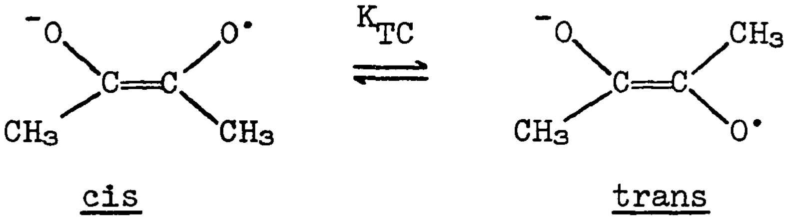
[b] Cis and trans linewidths apparently equal.

It is possible to estimate some thermodynamic parameters for the configurational interconversion of cis and trans dimethyl semidione using Equations 5 and 6, where ΔG^{o} repre-

$$\Delta \underline{G}^{o} = -\underline{R}T \ln K_{TC} \tag{5}$$

$$\frac{d(\ln K_{TC})}{dT} = \frac{\Delta H}{\underline{R}T^{2}} \tag{6}$$

sents the change in G accompanying the transformation of one mole of cis-semidione into a mole of trans-semidione (82); ΔH is the change in enthalpy for the transformation as written:



and K_{TC} is taken as the trans/cis ratio. Integration of Equation 6 (identical to van't Hoff's equation) gives Equation 7, which assumes that ΔH is constant over the tempera-

$$\ln\left[\frac{K_2}{K_1}\right] = \frac{\Delta H}{\underline{R}}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{7}$$

ture range in consideration; the validity of this assumption in the case of dimethyl semidione is uncertain. A plot of ln K_{TC} against 1/T yields a straight line (if ΔH is constant) whose slope equals ΔH/R. Data in Table 14 were treated by this method; straight lines could obviously not be fitted to plots for sodium ion, but were fitted for potassium ion although ΔH was not necessarily constant. The resultant graphs are shown in Figure 19 and 20. From Figure 20, the following values of ΔH were estimated: 0.1 M K^{+}, ΔH = -1.5 kcal/mole

Figure 19. Temperature dependence of K_{TC} for dimethyl semidione in Na^{+-}DMSO-DMSO.

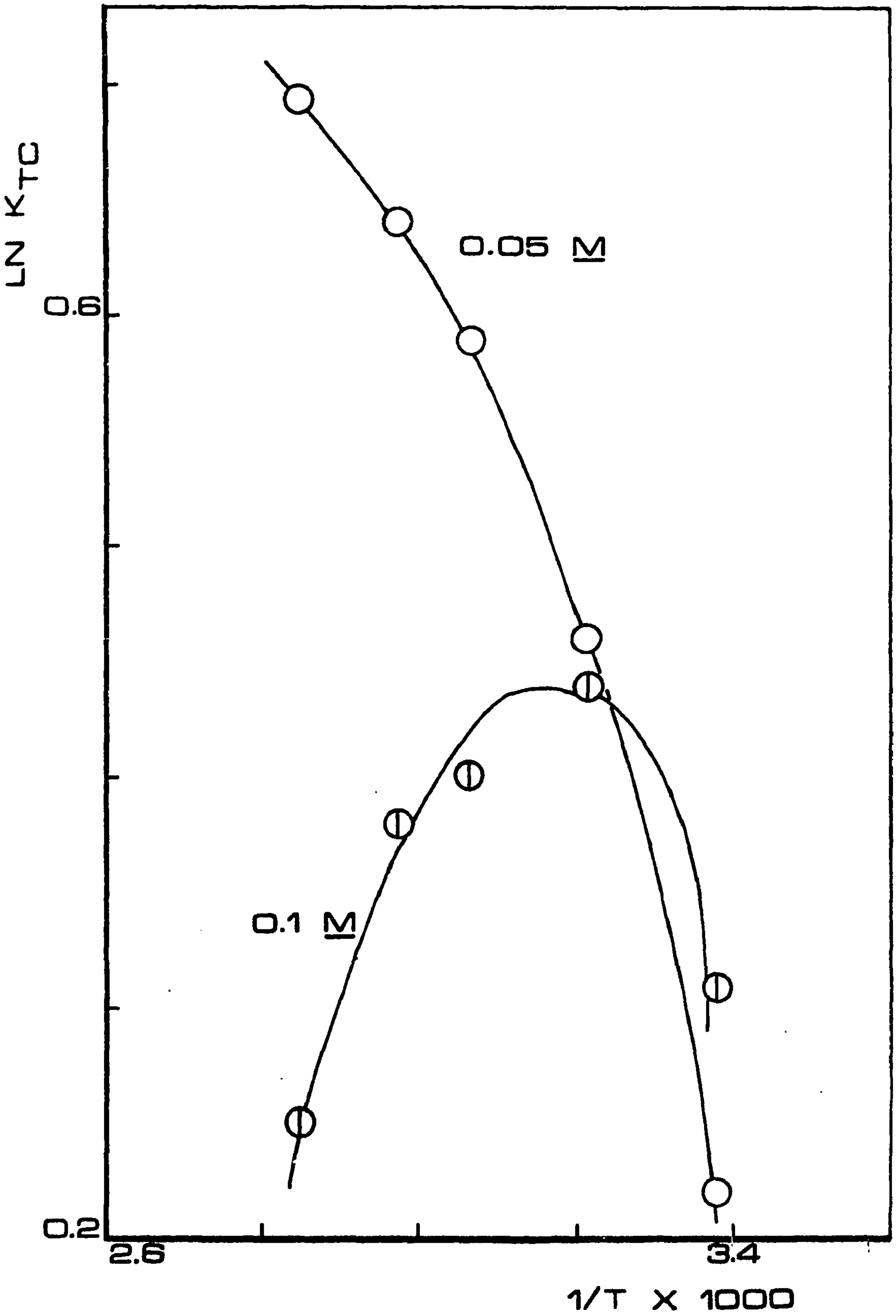
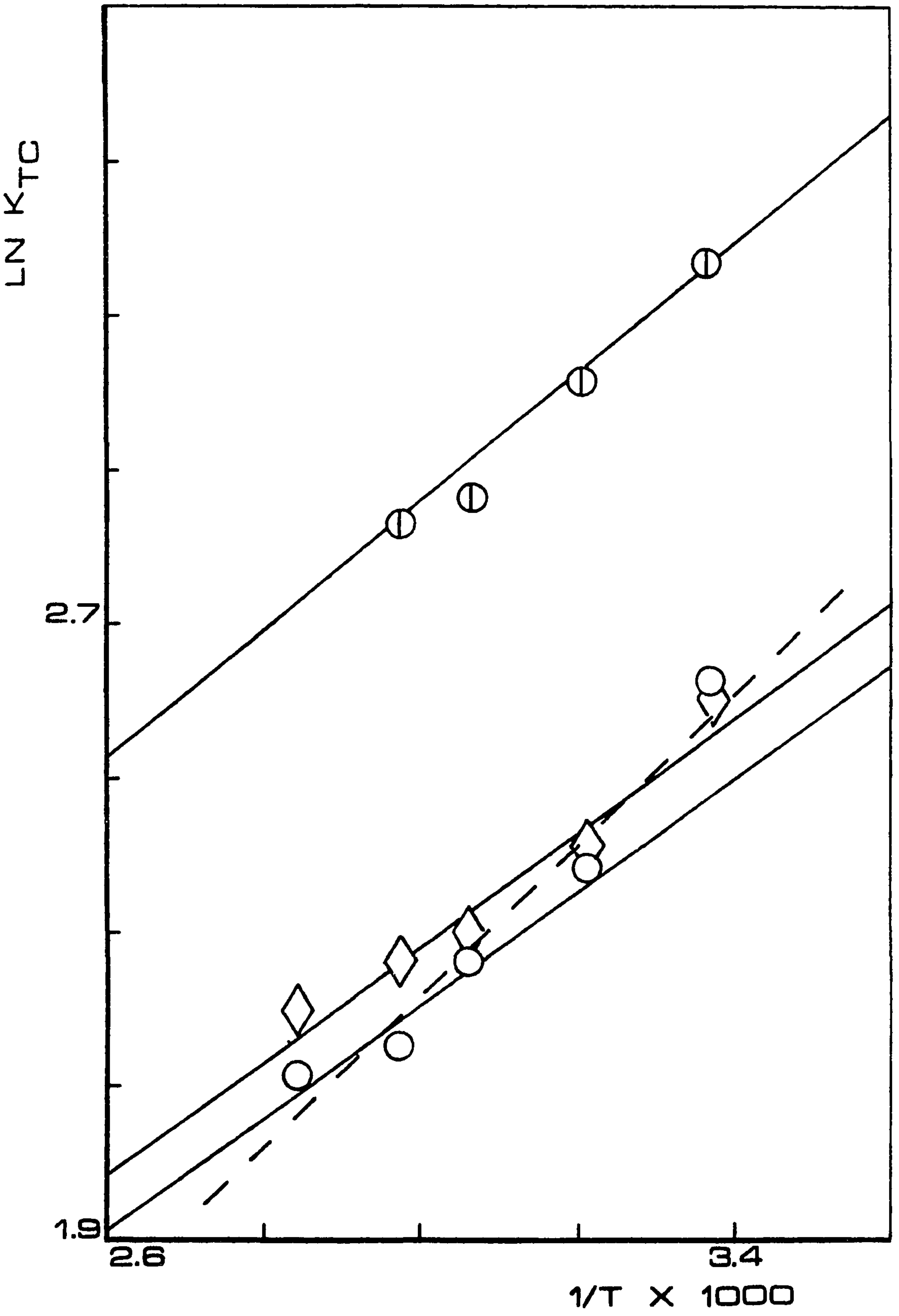

LN K$_{TC}$
0.6
0.2
2.6
3.4
1/T X 1000
0.05 M
0.1 M

Figure 20. Temperature dependence of K_{TC} for dimethyl semidione in K^+-DMSO-DMSO; dashed line is the result of including K_{TC} at 23° in 0.10 M K^+-DMSO. Legend: $[K^+]$ = 0.1 M, circles; $[K^+]$ = 0.05 M, diamonds; $[K^+]$ = 0.025 M, filled circles.


LN K_{TC}
2.7
1.9
2.6
3.4
1/T X 1000

(heavy line), ΔH = -1.9 kcal/mole (dotted line); 0.05 M K^+, ΔH = -1.5 kcal/mole; 0.025 M K^+, ΔH = -1.7 kcal/mole. At each concentration of K^+ the conversion *cis* → *trans* is apparently exothermic; a similar situation exists with Rb^+, although numerical values for ΔH were not estimated. A negative and variable ΔH might be explained by an increase in ion-pairing at higher temperatures favoring formation of the *cis* isomer. Ion-pairing is known to increase with decreasing solvating ability at higher temperatures (83).

The temperature dependence of diethyl- and di-*n*-propyl semidione *cis*-*trans* equilibria were determined in 0.1 M potassium *t*-butoxide-DMSO. These data are listed in Table 15

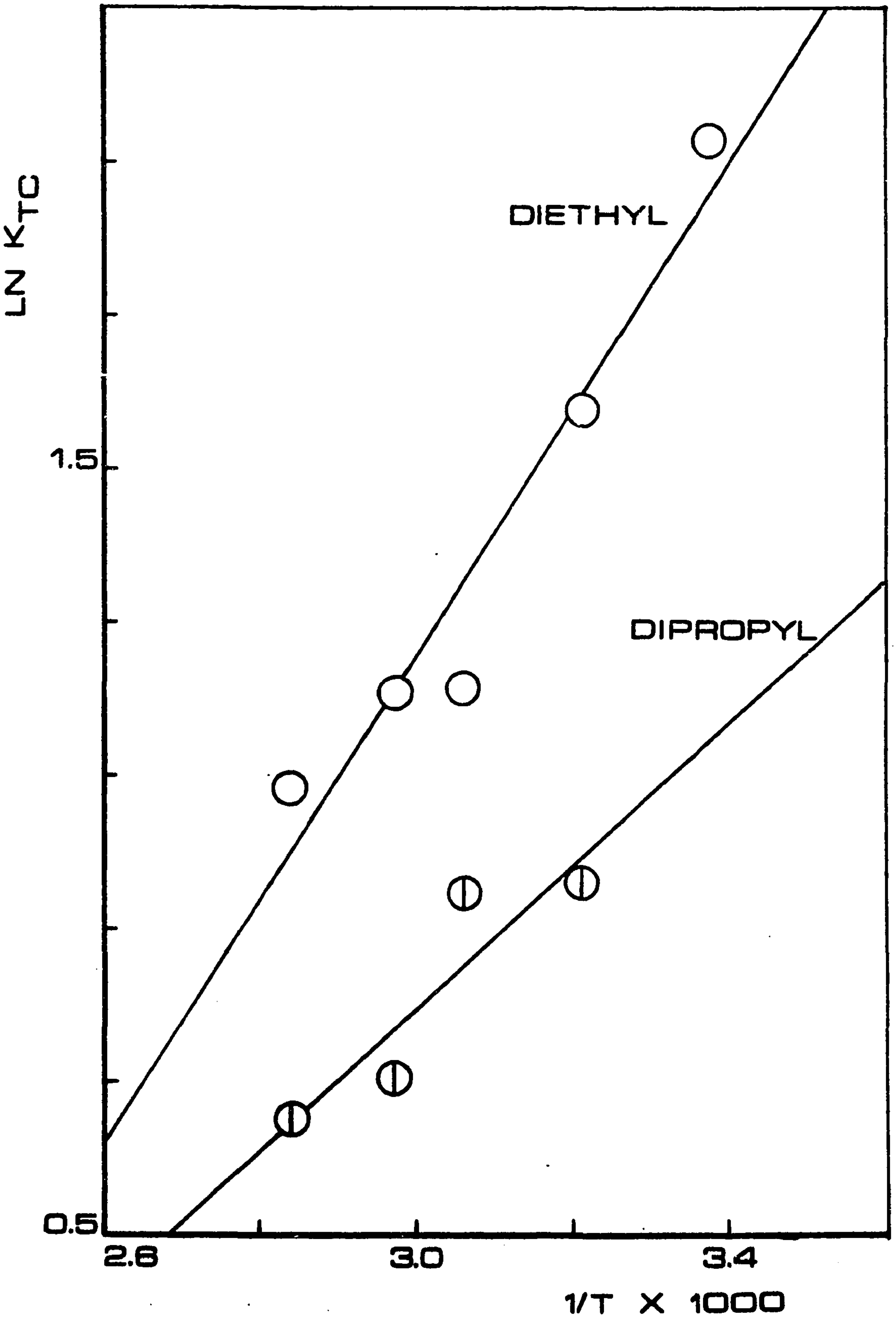
Table 15. Temperature dependence of K_{TC} for diethyl- and di-*n*-propyl semidiones.[a]

	K_{TC}				
semidione	13°	38°	53°	63°	78°
diethyl	6.87±0.94	4.83±0.42	3.36±0.42	3.34±0.58	2.95±0.40
di-*n*-propyl	4.11±0.48	2.62±0.09	2.58±0.07	2.36±0.08	2.02±0.06

[a] 0.1 M potassium *t*-butoxide-DMSO.

and plotted in Figure 21; ΔH = -2.3 kcal/mole for diethyl semidione and ΔH = -1.9 kcal/mole for di-*n*-propyl semidione. Comparable to the enthalpy change found for dimethyl semi-

Figure 21. Temperature dependence of K_{TC} for diethyl- and di-*n*-propyl semidiones in the presence of 0.1 *M* potassium *t*-butoxide-DMSO.


LN K_{TC}
DIETHYL
DIPROPYL
1.5
0.5
2.6
3.0
3.4
1/T X 1000

dione, ΔH is probably determined primarily by differences in π-electron energy levels between cis and trans semidiones, in the common counterion-solvent. Variation in the determined values, if significant, may be due to a difference in steric effects. It should be noted that the error for these and the preceding enthalpy values are large, and great reservation must accompany their use.

It appears that ion pairing is significant for dimethyl semidione, even in DMSO-potassium t-butoxide, and a value of K_{TC} representing a situation with no ion pairing is difficult to guess. Complete solvation and no chelation is expected for semidiones with tetraalkylammonium counterions. However, K_{TC} for dimethyl semidione in the presence of R_4N^+ is approximately the same as that observed in the presence of rubidium ion, and much lower than K_{TC} with cesium ion. Having values of K_{TC} for dimethyl semidione at several different $[K^+]$, it should be possible to extrapolate to zero metal ion concentration to determine K_{TC} for "free" semidione ions. A value of $K_{TC} = 30$-40, or about that observed with Rb^+ or R_4N^+, is indicated. K_{TC} with Cs^+ is extraordinarily high by comparison (>200), suggesting that ion pairing does indeed occur here—but to favor the trans configuration. In ion pair formation (whether contact or solvent-separated) the large cesium ion might be expected to prefer a large counterion, such as that presented by a trans-semidione. Tight coordination of two

Table 16. Configurational distribution of dimethyl semidione in various pure and mixed solvents.[a]

Solvent	Dielectric constant[b]	K_{TC}			
		100%	80% (20%DMSO)	50% (50%DMSO)	20% (80%DMSO)
DMSO	48.9[c]	17.5±1	---	---	---
DMF	36.7[d]	7.8±0.55	8.7 ±0.09	12.6±0.9	15.0±1.1
MeOH[e]	32.6	---	---	---	≥10
HMPA[f]	29.6[g]	2.95	5.16±0.21	7.9±0.64	9.8±0.74
Pyridine	12.3	<0.1	1.75±0.04	7.7±0.36	13.6±1.6
t-BuOH[h]	12.2	<0.06	1.41±0.03	9.97±0.31	12.9±0.9
DME	7.2[i]	~0	0.66±0.03	4.48±0.36	11.4±0.7

[a] 0.1 M potassium t-butoxide, 0.06 M acetoin, 25°; percentages indicate v:v proportions of solvent.

[b] Ref. 84.

[c] At 20°, Ref. 85.

[d] Ref. 86.

[e] Methanol.

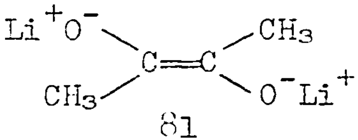
[f] Hexamethylphosphoramide.

[g] Ref. 87.

[h] t-Butyl alcohol.

[i] Ref. 88.

lithium ions with a trans enediol dianion 81 may partially explain the shift of Equilibrium 6 towards diamagnetic species and the complete absence of trans semidione in that system.



81

If ion pairing is, as suspected, a significant factor in the configurational distribution of acyclic semidiones, then the trans/cis ratios should be affected greatly by solvent. To ascertain the effect of solvation on configurational isomerism, solutions of dimethyl semidione were prepared in a variety of pure and mixed nonaqueous solvents and analyzed by ESR. The results are given in Table 16, and a sample spectrum obtained in 80% pyridine-20% DMSO (v:v) is shown in Figure 22. It was observed that virtually any ratio of configurational isomers could be obtained by proper choice of solvent or solvent mixture. In addition, the free energy difference (α ln K_{TC}) was found to have a roughly linear relationship with the dielectric constant of the solvent, as well as with the approximated dielectric constants of the solvent mixtures. This was surprising in view of the fact that the solvents examined are not ideal, continuous and structureless media; Chan and Smid (89) have shown that other factors besides dielectric constants are important to solvating ability. For the most part these solvents consist of highly ordered dipolar molecules, the dipoles due mainly to non-bonded elec-

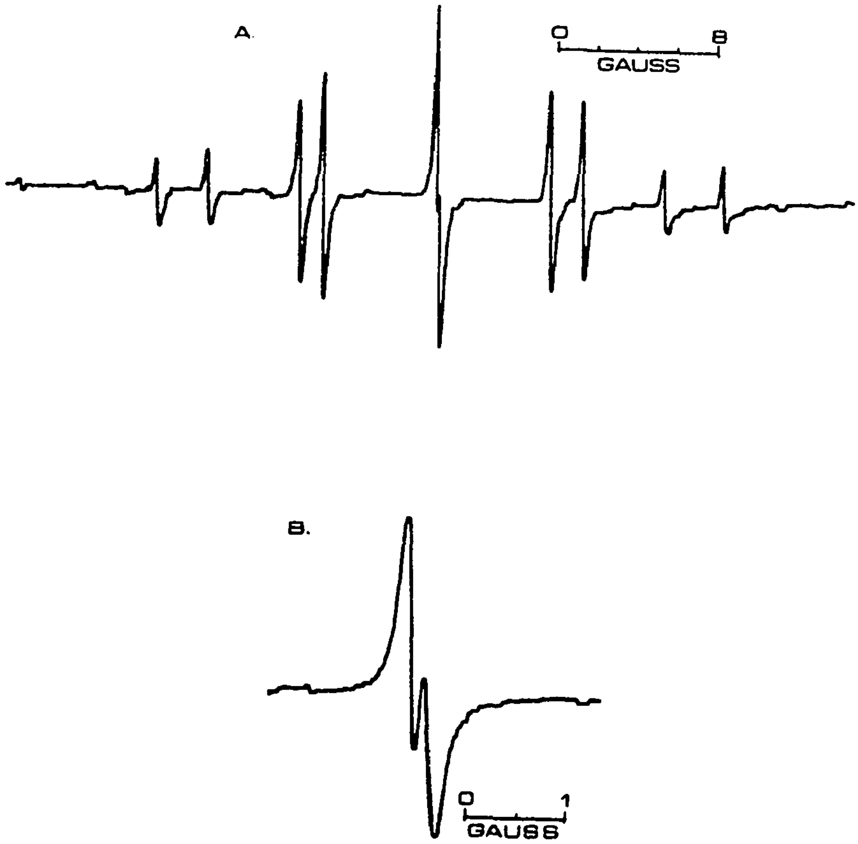


Figure 22. First derivative ESR spectrum: (A) of a solution of dimethyl semidione generated from acetoin in 80% pyridine -20% DMSO (v:v) with 0.1 *M* potassium *t*-butoxide, with *cis* and *trans* isomers in comparable concentration (*cf*. Figure 1); (B) expansion of the nearly overlapping central lines of (A), readily showing a difference in *g*-factors.

trons on oxygen or nitrogen atoms, and the solvents are mainly cation-solvating; exceptions are the protic solvents methanol and t-butyl alcohol, which can solvate both cations and anions. Appropriately, deviations from the overall linearity were most prominent for t-butyl alcohol and its mixtures.

Considerable variation of $a_{CH_3}{}^H$ with solvent was observed, as noted in Table 17. In general, $a_{CH_3}{}^H$ increased with decreasing K_{TC} (or increased ion pairing, where the effective increase of charge density on oxygen raises $\rho_C{}^\pi$ and $a_{CH_3}{}^H$). Large variations were found in protic media, where both ion pairing and hydrogen bonding can occur to increase the charge density on oxygen. It should also be noted that both cis and trans isomers suffer a significant increase in $a_{CH_3}{}^H$ in protic solvents, whereas only the cis isomer is affected to any great extent where the increase is caused solely by ion-pairing. This may be regarded as further evidence that the

Table 17. Proton hfsc (in gauss) of dimethyl semidione with various solvents (25°, potassium t-butoxide).

$a_{CH_3}{}^H$	100% DMSO	80% HMPA	20% MeOH	80% t-BuOH	80% Pyridine	80% DME
(cis)	7.0	7.0	--	7.5	7.0	7.2
(trans)	5.6	5.7	6.0-6.3	6.2	5.7	5.9

cis structure is important in ion pairing, at least with small or intermediate-sized cations.

Effect of solvent on the configurational distribution of diethyl semidione has been examined by Dr. G. R. Underwood; his results are contained in Table 18. The observations are similar to those for dimethyl semidione.

Table 18. Configurational distribution of diethyl semidione (0.1 *M* potassium *t*-butoxide, 25°.)[a]

Solvent:	DMSO	DMF	Pyridine	DME	THF
K_{TC}	6.2	4.6	0.11	~0	~0

[a] Results of Dr. G. R. Underwood, 1967.

The foregoing suggest the occurrence of several interdependent equilibria, of which three likely examples are depicted in Scheme 6. Effective solvation of K^+ (large K_C) should shift Equilibrium (*a*) of Scheme 6 to the right if K^+ is not rigidly bound in the *cis*$^{\cdot-}$ K^+ pair; Equilibrium (*b*) is known to favor *trans*$^{\cdot-}$. Hence, K_{TC} should increase with increasing cation-solvating ability of the solvent, as observed. By studying the variation of K_{TC} with [DMSO], Dr. G. R. Underwood has determined a coordination number for DMSO-K^+ of *n* $\approx$ 2. Higher values of *n* were indicated in some of the other solvents studied.

Scheme 6.

(a) $\underline{\text{cis}}^{\bar{\cdot}}\ \text{K}^+ \xrightleftharpoons{K_a} \underline{\text{cis}}^{\bar{\cdot}} + \text{K}^+$

82

(b) $\underline{\text{cis}}^{\bar{\cdot}} \xrightleftharpoons{K_b} \underline{\text{trans}}^{\bar{\cdot}}$

(c) $\text{K}^+ + n\ (\text{solvent}) \xrightleftharpoons{K_c} \text{K}^+\ (\text{solvent})_n$

Solvents such as DMSO and DMF are relatively effective for cation solvation; however, formation of ion pairs by lithium, sodium and potassium cations with dimethyl semidione still occurs in these media. Chelation of the metal ion by cis semidione is apparently a very favorable process. Dimethoxyethane is, of the simple ethers, also a relatively good cation-solvating agent, but the cis isomer of dimethyl semidione is greatly favored in its solutions.

DME is the simplest member of a series of acyclic polyethers known as "glymes"; it is occasionally referred to as "glyme-2", a shorthand notation indicating a glyme with two oxygen atoms. Glyme-2 is a bidentate solvating agent, with a probable coordination number $n = 2$ (85); it is less polar than DMSO or DMF and not as effective in cation solvation. Higher members of the glyme series, diethyleneglycol dimethyl ether (glyme-3) and triethyleneglycol dimethyl ether (glyme-4) are similar to glyme-2 in solvating properties. Tetraethyleneglycol dimethyl ether (glyme-5) has been shown to have a coordination number $n = 1$ with sodium or potassium ion (90);

glyme-5 produces a glyme-separated ion pair when added to THF solutions of triphenylenesodium in a 1:1 ratio (91). The effect of various glymes and glymated mixtures on the dimethyl semidione cis-trans distribution was examined by ESR spectroscopy; results of this investigation are summarized in Table 19. Proton hfsc did not vary significantly throughout the glyme-DMSO mixtures ($\underline{a}_{CH_3}{}^{H} = 5.6, 7.0$ G) but were 3-4% higher in pure glymes.

Table 19. Effect of glymes on K_{TC} of dimethyl semidione (acetoin, 0.1 M potassium t-butoxide, 25°).

	K_{TC}			
Glyme	100%	80%(20%DMSO)[a]	50%(50%DMSO)[a]	20%(80%DMSO)[a]
Glyme-2	~0	0.66	4.5	11.4
Glyme-3	0.1	1.92	6.6	12.8
Glyme-4	0.25	1.72	5.9	12.0
Glyme-5	0.25	3.35	8.64	18.6

[a] Volume:volume.

It can be seen that the distributions of configurational isomers in glyme-3 and glyme-4 solutions are similar to those in DME solutions. The trans/cis ratio decreases with increasing concentration of glyme because the average solvating ability (gauged by dielectric constant?) decreases. Addition of glyme-5 to DMSO solutions of dimethyl semidione does not have as great an effect on K_{TC} as addition of lower glymes. In these experiments the added glymes may be thought of as external complexing agents and provide further insight into the equilibria of Scheme 6. Thus in 100% glyme-5—superior among the glymes studied for cation solvation and known to completely solvate K^+ in other ion-pairing studies (91)—K_{TC} is quite low, indicating among several possibilities, 1) energy gained in glymation of K^+ is less than that lost by dissociation of *cis*$^{\cdot-}$ K^+ and/or 2), if glymation occurs, additional equilibria may be involved (*e.g.*, Equilibria 7-10), raising

$$\underset{\mathbf{82}}{\underline{\text{cis}}^{\overset{-}{\cdot}}\ K^+} + \underline{n}(\text{glyme}) \overset{K_d}{\rightleftharpoons} \underset{\mathbf{83a}}{\underline{\text{cis}}^{\overset{-}{\cdot}}\ K^+\ (\text{glyme})\ \underline{n}} \tag{7}$$

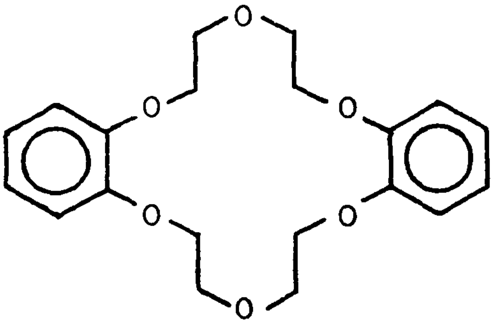
$$\underset{\mathbf{83a}}{\underline{\text{cis}}^{\overset{-}{\cdot}}\ K^+\ (\text{glyme})\ \underline{n}} \overset{K_e}{\rightleftharpoons} \underset{\mathbf{83b}}{\underline{\text{cis}}^{\overset{-}{\cdot}}/\underline{n}\ (\text{glyme})\ /\ K^+} \tag{8}$$

$$\underline{\text{trans}}^{\overset{-}{\cdot}} + K^+\ (\text{glyme})\ \underline{n} \overset{K_f}{\rightleftharpoons} \underline{\text{trans}}^{\overset{-}{\cdot}}\ K^+\ (\text{glyme})\ \underline{n} \tag{9}$$

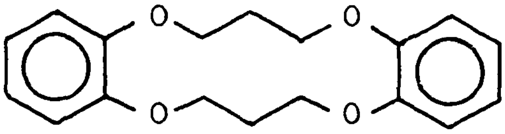
$$\underline{\text{trans}}^{\overset{-}{\cdot}}\ K^+\ (\text{glyme})\ \underline{n} \overset{K_g}{\rightleftharpoons} \underset{\mathbf{83a}}{\underline{\text{cis}}^{\overset{-}{\cdot}}\ K^+\ (\text{glyme})\ \underline{n}} \tag{10}$$

the possibility of several distinct types of ion pairs. Formation of solvent-separated pairs may favor the *cis* isomer **83a** (large K_g) if glymated cations can coordinate with the *cis* semidione bidentate. (Equilibrium 8 may or may not be trivial, depending on fine distinctions in solvent-separated pair structures 83a and 83b.) Hence, although cations are glymated, they may still form pairs.

Pedersen has prepared macrocyclic polyethers, which were shown to be most effective for complexation with cations (92-96). Showing great selectivity for sodium and potassium ions was 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene 94, more handily referred to as "dibenzo-18-crown-6"



84, Dibenzo-18-crown-6



85, Dibenzo-14-crown-4

for obvious reasons. This crown-polyether has a 4.0 Å "hole" surrounded by six oxygen atoms, ideally suited for coordination with sodium or potassium cations (90). 2,3,9,10-Dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene 85 (dibenzo-14-crown-4), with a 1.8 Å hole shows high selectivity for lithium ions (92). Addition of dibenzo-18-crown-6 in a 1:1 molar ratio with metal cation to solutions of acetoin in DMSO produced a remarkable change in K_{TC} of the semidione generated (Tabel 20). Addition of 85 to DMSO solutions of lithium dimethyl semidione had little noticeable effect.

Table 20. Configurational distribution of dimethyl semidione with added dibenzo-18-crown-6 (DMSO, 25°, acetoin).

	K_{TC}	
Cation	DMSO-0.1 M-t-butoxide	DMSO-0.1 M-t-butoxide-0.1 M dibenzo-18-crown-6
potassium	~18	~40
sodium	1.7	7.2

The results were revealing; generation of dimethyl semidione in the presence of crown polyether-potassium ion raised K_{TC} to the value observed with tetraalkylammonium or rubidium ions—and approximately that expected for "free" semidione ions. Crown polyether, replacing solvent, thus shifts Equilibria a and c of Scheme 6 far to the right by efficient competition with semidione for K^+ initially. (It should be pointed out that K_{TC} decreases with time to ca. 30, as K^+ is leached from the ether by semidione.) In the presence of crown polyether—sodium ions K_{TC} increased but did not approach a value expected for free semidione ions, not surprising in view of the fact that ^{23}Na hfs was clearly visible (Figure 23). Moreover, the ^{23}Na quartets were better resolved and a^{Na} was slightly greater ($a^{Na} \sim 0.3$ G) than in the absence of dibenzo-18-crown-6.

A possible explanation for these observations is suggested, involving at least two types of ion pairs: Contact ion pairs,

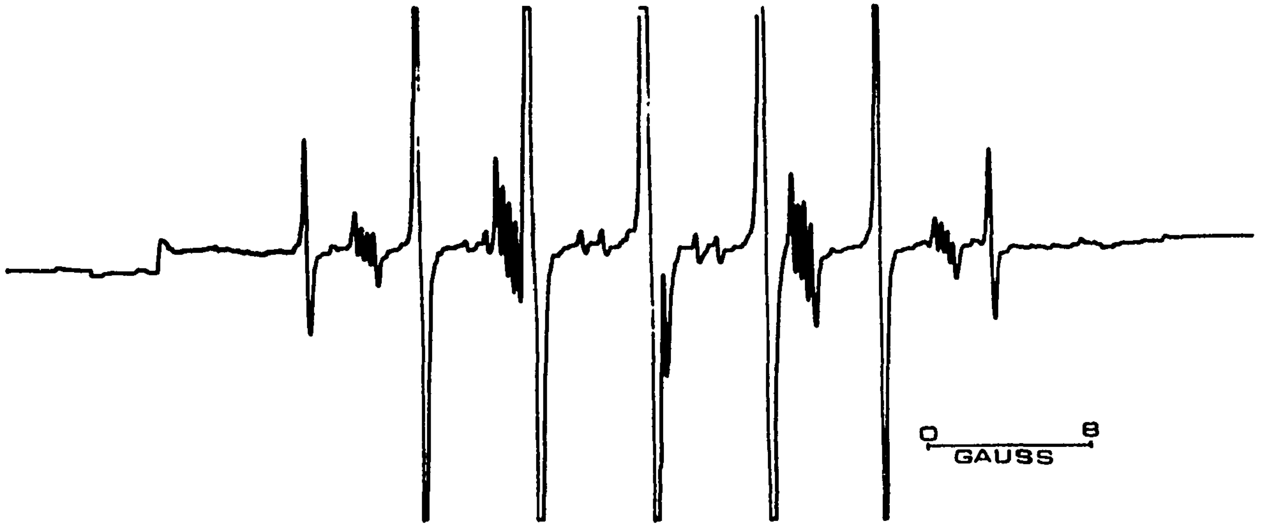


Figure 23. First derivative ESR spectrum of dimethyl semidione in the presence of DMSO -0.1 *M* sodium *t*-butoxide-0.1 *M* dibenzo-18-crown-6, showing hyperfine splitting by sodium ion (I = 3/2) in the *cis* configuration. Center five lines of the *trans* septuplet are off scale.

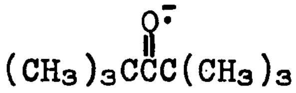
"loose" (*e.g.* solvent-separated) ion pairs and free ions are formed in the dimethyl semidione-Na^+-DMSO system. The *cis* structure is favored by both types of ion pair, although not necessarily to the same extent, and the *trans* configuration is favored for the free ions (minimizing dipolar repulsions). Complexation of Na^+ by dibenzo-18-crown-6 eliminates most "loose" ion pairs, leaving only contact ion pairs and free ions; thus, broadening of ^{23}Na hyperfine lines from equilibrium 11 is eliminated. Tight binding of Na^+ within a *cis*-

$$\underset{\text{contact}}{\underline{\textit{cis}}^{\overline{\cdot}}\ Na^+} \rightleftharpoons \underset{\text{loose}}{\underline{\textit{cis}}^{\overline{\cdot}}//Na^+} \qquad (11)$$

semidione moiety prevents the elimination of chelated ion pairs. A slightly different situation exists for the dimethyl semidione-K^+-DMSO system, where binding within a $\underline{\textit{cis}}^{\overline{\cdot}}\ K^+$ chelate is probably weaker and contact ion pairs, if formed, do not exhibit ^{39}K hfs. Solvent-separated and contact ion pairs with K^+ are both likely to be relatively labile and disrupted by addition of dibenzo-18-crown-6.

CARBON-13 AND OXYGEN-17 HYPERFINE SPLITTING IN SEMIDIONES

The investigations described thus far have been based largely upon measurements from proton and metal ion hyperfine splitting constants. However, ESR spectra of semidiones are of an uncommonly fine quality which permits detection of hyperfine splitting due to natural abundance ^{13}C (1.1%, $I = \frac{1}{2}$) in many instances. Thus, Heller (38) was able to observe $\underline{a}^{C} \sim 4$ G (natural abundance) in diisopropyl semidione and identify some of the low intensity lines of the di-*t*-butyl semidione signal as ^{13}C satellites; assignments of the splitting constants were not made. Strom and Russell (97) observed a natural abundance ^{13}C-hyperfine splitting constant of 4.9 G in the ESR spectrum of cyclohexane-1,2-semidione. This was assigned to the carbonyl carbon atoms by analogy with the natural abundance results of Hirota and Weissman (15) and Ward (98), who reported no $\underline{a}_{\alpha}^{C}$ in 86 or 87, respectively. Hfs by ^{13}C in natural abundance was also detected in the dialkyl acyclic semidiones listed in Table 2 (50), as well as in the

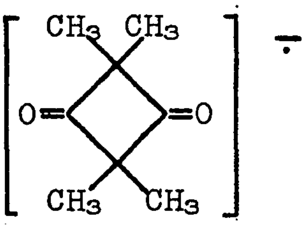


$(CH_3)_3C\overset{O^{\overline{\cdot}}}{\overset{\|}{C}}C(CH_3)_3$

$\underline{a}_{CO}^{C} = 49.6$ G

$\underline{a}_{CH_3}^{C} = 7.7$ G (15)

86

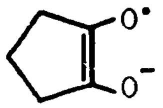


$\underline{a}_{CO}^{C} = 5.0$ G

$\underline{a}_{CH_3}^{C} = 7.6$ G (98)

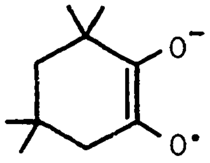
87

cyclic semidiones 88 and 89 (24, 99). Only a single $\underline{a}^C$ was



$\underline{a}^C = 5.6$ G (99)

88

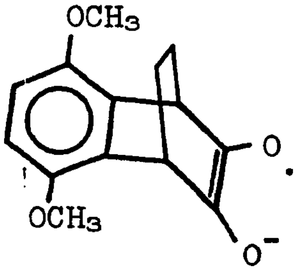


$\underline{a}^C = 4.42$ G (24)

89

detected in each instance, and a definite assignment was not made. The semidione observations were apparently in agreement with Ward's results (98); however, Ward's results differed considerably from those of Hirota and Weissmann (15) for hfs by carbonyl carbon atoms. If $\underline{a}_{CO}{}^{C}$ in 87 were to follow 86, a value ~25 G might be expected.

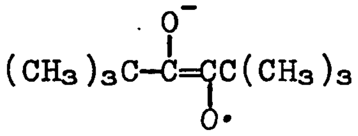
Russell and Underwood (100) examined ^{17}O hfs and natural abundance ^{13}C hfs in carbonyl-^{17}O-enriched semidiones 90 and 91 and ketyl 86. The observation of $\underline{a}_{\alpha}{}^{C}$ and $\underline{a}_{\beta}{}^{C}$ in 91 was the



$\underline{a}^C = 6.15$ G

$\underline{a}^O = -9.95$ G

90



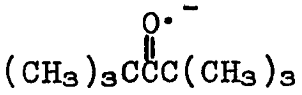
$(CH_3)_3C\text{–}\overset{O^{-}}{\overset{|}{C}}=\underset{\dot{O}}{\underset{|}{C}}C(CH_3)_3$

$\underline{a}_{\alpha}{}^{C} = 3.8$ G (2C)

$\underline{a}_{\beta}{}^{C} = 2.4$ G (6C)

$\underline{a}^O = -10.5$ G

91



$(CH_3)_3C\overset{O\cdot^{-}}{\overset{\|}{C}}C(CH_3)_3$

$\underline{a}^O = -11.1$ G

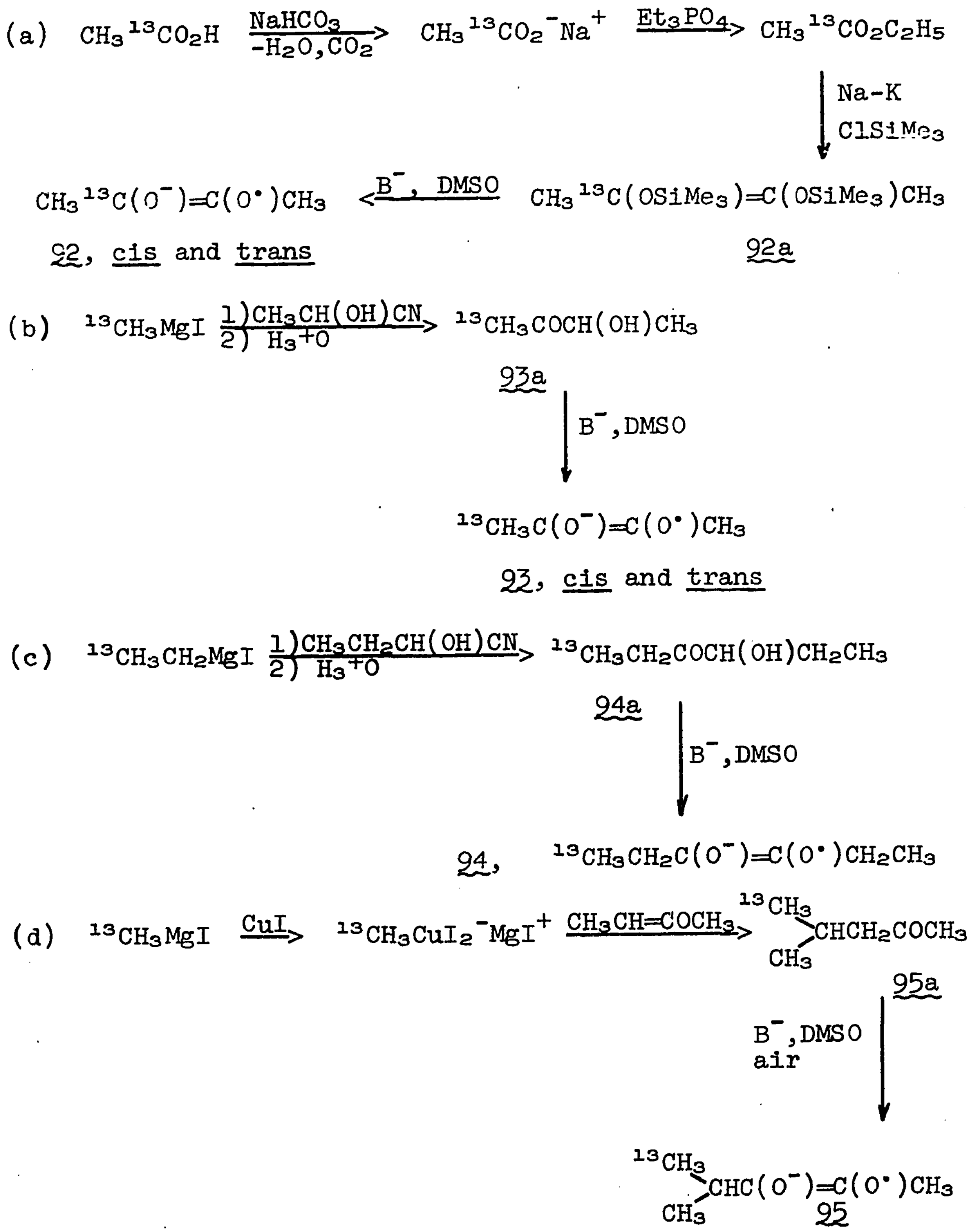
86

first example known of two distinct ^{13}C hyperfine splitting constants in a semidione. A determination of the sign of $\underline{a}^{C}$ by line broadening studies (101) was not possible for the natural abundance ^{13}C lines. It was concluded that $\underline{a}_{CO}{}^{C}$ was not observed in **90** and **91**, unlike **86** and **87**, with the implication that $\underline{a}^{C}$ observed in other semidiones might also be due to the α- or β-carbon atoms; alternatively, $\underline{a}_{CO}{}^{C}$ might equal $\underline{a}_{\alpha}{}^{C}$ or $\underline{a}_{\beta}{}^{C}$.

The purpose of the work reported in this section was to undertake a detailed investigation of hfs by nuclei other than ^{1}H in semidiones and related radical anions. The study had the multiple objectives of: 1) providing unambiguous assignments of ^{13}C splittings; 2) corroborating conclusions about spin delocalization and structure made from proton hfsc; and 3) explaining the variations and discrepancies in $\underline{a}^{C}$ among ketyl and semidione radical anions. The most unequivocal approach to definitive assignments of $\underline{a}^{C}$ involves the synthesis of compounds isotopically enriched at specific sites; therefore, a series of aliphatic semidiones enriched with ^{13}C at various positions was examined.

^{13}C-enriched semidiones **92**-**95** were prepared by the sequences of Scheme 7. ^{13}C-containing acetic acid and alkyl iodides (~50-60% ^{13}C) were obtained from Merck, Sharp and Dohme of Canada, Ltd.; syntheses were planned so that the final semidione had at least 10% ^{13}C in the desired position.

Scheme 7.



(a) $CH_3{}^{13}CO_2H \xrightarrow[-H_2O,\,CO_2]{NaHCO_3} CH_3{}^{13}CO_2^-Na^+ \xrightarrow{Et_3PO_4} CH_3{}^{13}CO_2C_2H_5$

$CH_3{}^{13}CO_2C_2H_5 \xrightarrow{Na\text{-}K,\ ClSiMe_3} CH_3{}^{13}C(OSiMe_3){=}C(OSiMe_3)CH_3$ 92a

$CH_3{}^{13}C(OSiMe_3){=}C(OSiMe_3)CH_3 \xrightarrow{B^-,\ DMSO} CH_3{}^{13}C(O^-){=}C(O^\bullet)CH_3$ 92, *cis* and *trans*

(b) ${}^{13}CH_3MgI \xrightarrow[2)\ H_3{}^+O]{1)\ CH_3CH(OH)CN} {}^{13}CH_3COCH(OH)CH_3$ 93a

${}^{13}CH_3COCH(OH)CH_3 \xrightarrow{B^-,\ DMSO} {}^{13}CH_3C(O^-){=}C(O^\bullet)CH_3$ 93, *cis* and *trans*

(c) ${}^{13}CH_3CH_2MgI \xrightarrow[2)\ H_3{}^+O]{1)\ CH_3CH_2CH(OH)CN} {}^{13}CH_3CH_2COCH(OH)CH_2CH_3$ 94a

${}^{13}CH_3CH_2COCH(OH)CH_2CH_3 \xrightarrow{B^-,\ DMSO}$ 94, ${}^{13}CH_3CH_2C(O^-){=}C(O^\bullet)CH_2CH_3$

(d) ${}^{13}CH_3MgI \xrightarrow{CuI} {}^{13}CH_3CuI_2^-MgI^+ \xrightarrow{CH_3CH{=}COCH_3} ({}^{13}CH_3)(CH_3)CHCH_2COCH_3$ 95a

$({}^{13}CH_3)(CH_3)CHCH_2COCH_3 \xrightarrow[air]{B^-,\ DMSO} ({}^{13}CH_3)(CH_3)CHC(O^-){=}C(O^\bullet)CH_3$ 95

After repeated unsuccessful attempts to hydrolyze **92a** to acetoin in good yield, it was found that **92a** was cleaved in base-DMSO to give a moderately strong ESR signal from the semidione. Figures 24 and 25 show the ESR spectra of butane-2,3-semidione-2-^{13}C, **92** (~10% ^{13}C); both *cis* and *trans* isomers were observed in potassium *t*-butoxide-DMSO, having a_{CO}^{C} = 1.14 and 0.58 G, respectively. The carbonyl carbon splitting constant was cation-dependent; thus, a_{CO}^{C} = 0.7 G (*trans*) and ~1.4 G (*cis*) in sodium *t*-butoxide-DMSO, and a_{CO}^{C}= 1.8 G (*cis*) in LiI-potassium-*t*-butoxide-DMSO (Figure 26). Butane-2,3-semidione-1-^{13}C, **93**, yielded a mixture of *cis* and *trans* isomers with $a_{CH_3}^{C}$ = 5.2 and 4.5 G, respectively (Figure) 27); variation of $a_{CH_3}^{C}$ with cation was not determined. A preliminary report of semidiones **92** and **93** appeared as a footnote in Reference 100.

Hexane-3,4-semidione-1-^{13}C, **94**, also yielded a mixture of *cis* and *trans* isomers in potassium-*t*-butoxide-DMSO, but only the *trans* isomer was present in sufficient concentration to reveal $a_{CH_3}^{C}$ = 4.25 G (Figure 28). Likewise, the *trans* isomer of 2-methylpentane-3,4-semidione-1-^{13}C exhibited $a_{CH_3}^{H}$= 3.74 G (Figure 29).

Since the spectrum of di-*t*-butyl semidione, **86**, was extremely complicated (100), bis(1-adamantyl)semidione, **96**, was examined to confirm the ^{13}C hfsc assignments made for **86**. The *in situ* acyloin condensation (33) of 1-carboethoxy adaman-

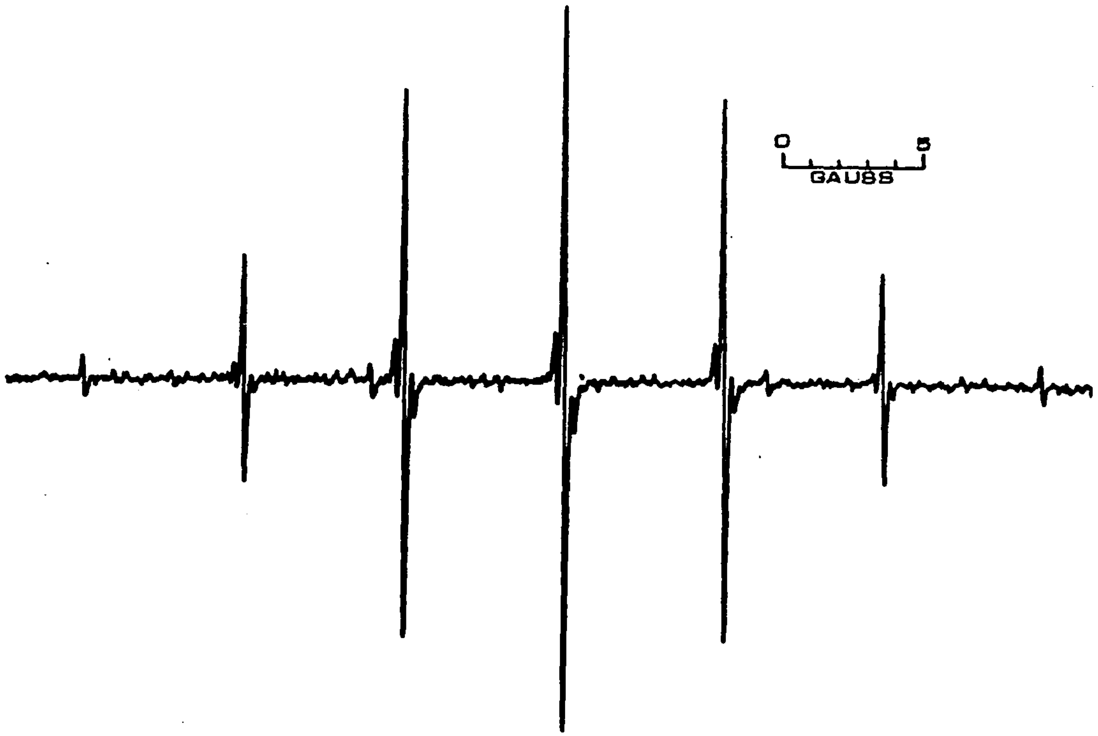


Figure 24. First derivative ESR spectrum of butane-2,3-semidione-2-^{13}C (~10% ^{13}C) in DMSO-potassium *t*-butoxide at 25°C, at normal signal intensity, showing ^{13}C-satellites for lines of *trans* isomer.

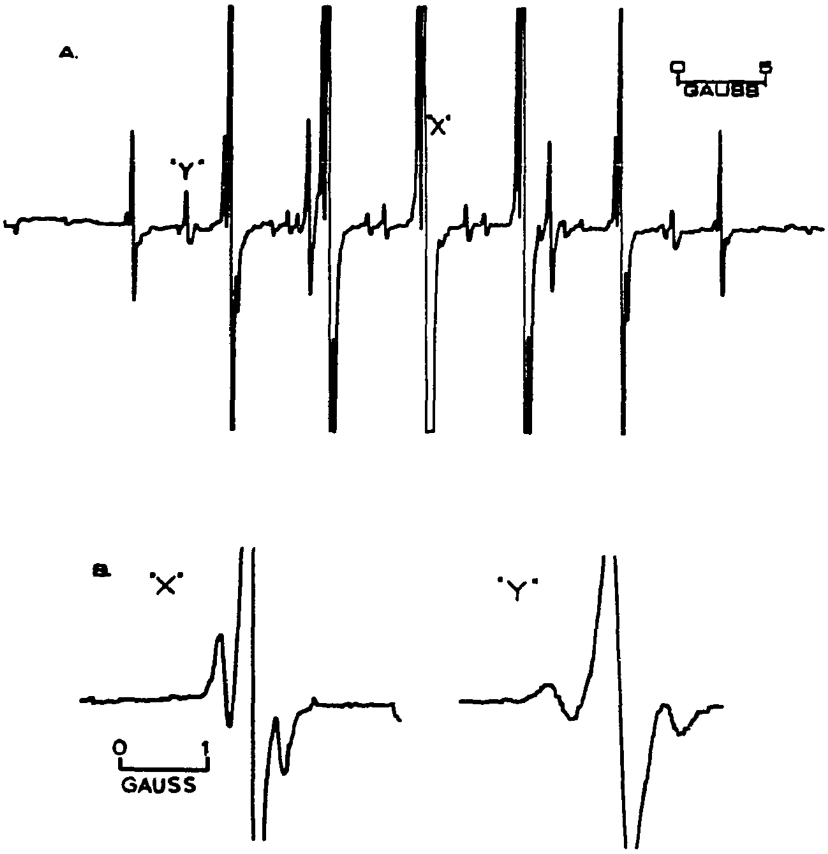


Figure 25. First derivative ESR spectrum of butane-2,3-semidione-2-^{13}C (~10%) in DMSO-potassium t-butoxide: (A) at high signal level; (B) at high signal level, expanded, showing peaks "X" (*trans*, degeneracy 20), and "Y" (*cis*, degeneracy 6) of spectrum A, with ^{13}C-satellites.

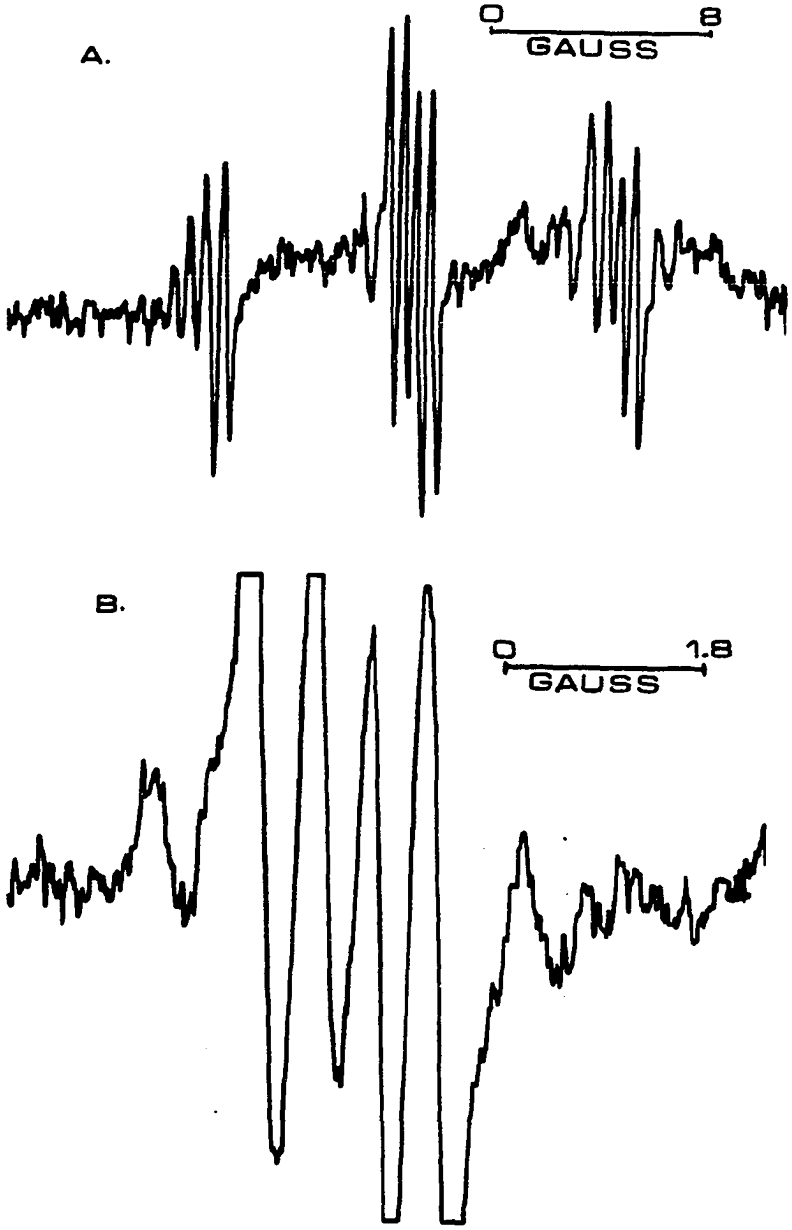


Figure 26. First derivative ESR spectrum of butane-2,3-semidione-2-^{13}C (~10% ^{13}C) in DMSO-potassium *t*-butoxide-LiI at 25°C showing: (A) central three lines of spectrum, with ^{7}Li hfs; (B) expanded central line, with $\underline{a}^{Li}$ and $\underline{a}^{C}$ visible.

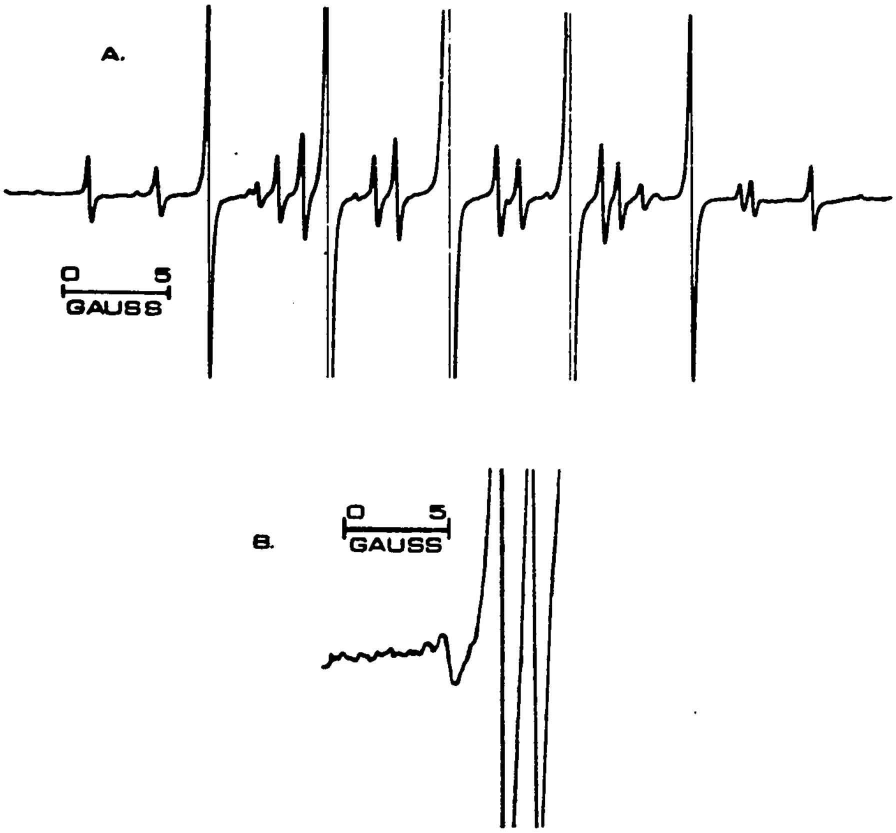
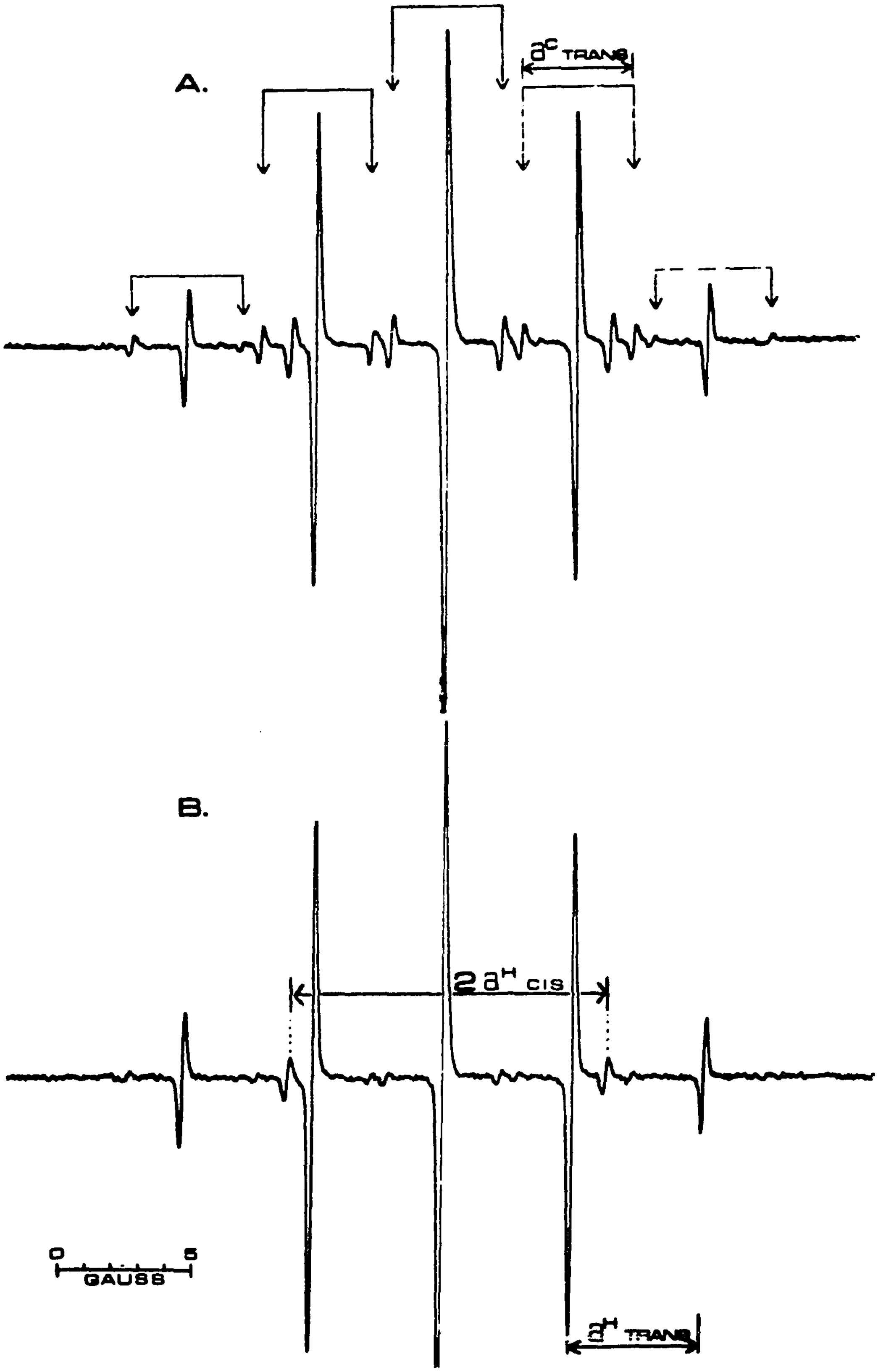


Figure 27. First derivative ESR spectrum of butane-2,3-semidione-1-^{13}C (~10% ^{13}C) in DMSO-potassium *t*-butoxide at 25°C showing: (A) $\underline{a}^C$ in *trans* isomer at high signal level; (B) $\underline{a}^C$ in *cis* isomer (degeneracy 1 line), expanded at high signal level.

Figure 28. First derivative ESR spectra (DMSO-potassium *t*-butoxide, 25°C) of: (A) hexane-3,4-semidione-1-^{13}C (~10% ^{13}C), showing *a*^{C} for *trans* isomer; (B) unlabeled hexane-3,4-semidione.


A.
a^{C}_{TRANS}
B.
$2a^{H}_{CIS}$
0
5
GAUSS
a^{H}_{TRANS}

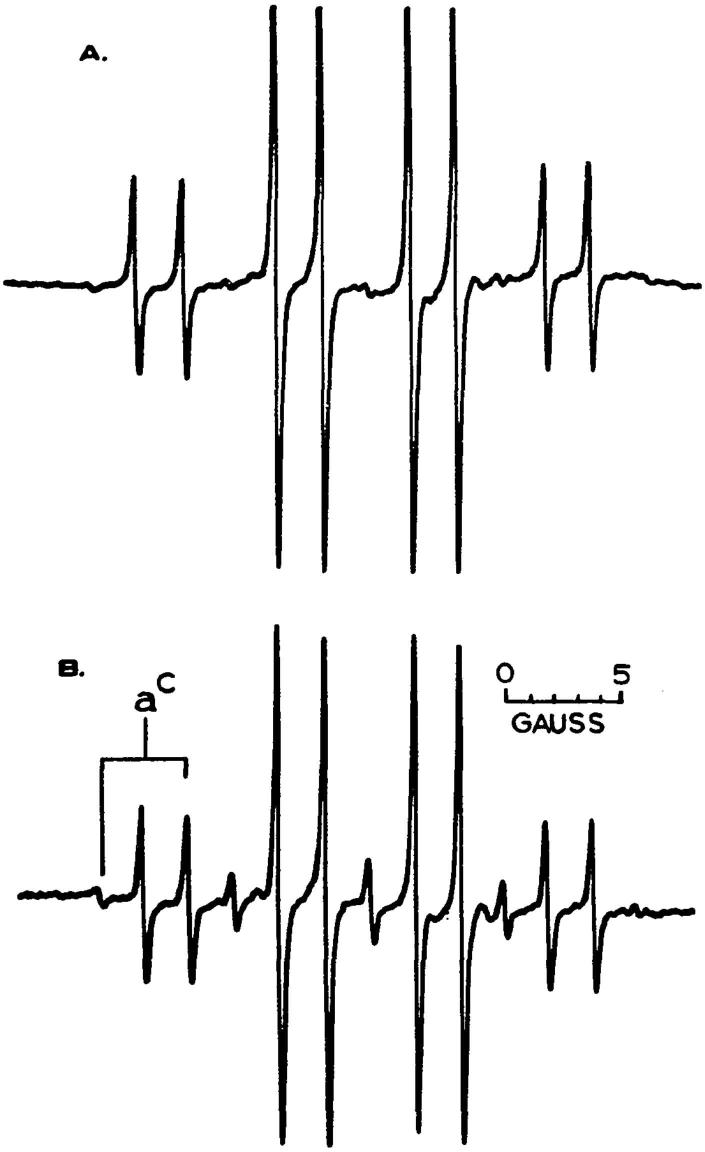
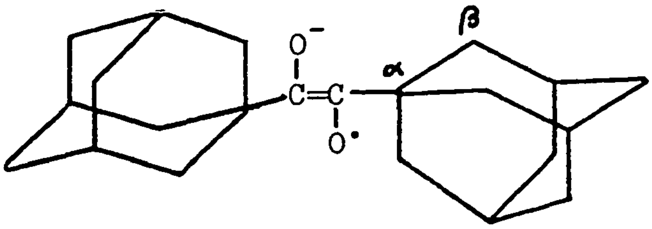


Figure 29. First derivative ESR spectra (DMSO-potassium t-butoxide, 25°C) of: (A) unlabeled 2-methyl-pentane-3,4-semidione; (B) 2-methylpentane-3,4-semidione-1-^{13}C (~10% ^{13}C), showing a^C for trans isomer.



96

tane in DME gave 96 in good yield; two sets of splittings due to ^{13}C in natural abundance were revealed, $a_{\alpha}^{C} = 3.8$, $a_{\beta}^{C} = 2.3$ G, in an intensity ratio of 1:3 (Figure 30).

Table 21 contains a summary of the preceding results along with those of Malkus (51), who examined a^{C} in several ^{13}C-enriched diisopropyl- and di-t-butyl semidiones 97 and 98 in a complementary study; and Gerlock, who has observed a^{C} due to natural abundance ^{13}C in bis(trifluoromethyl)semidione, 99. All a^{C} values were measured at room temperature; the signs of the splitting constants were not determined experimentally.

From Table 21 the following generalizations can be made: 1) $a_{\alpha}^{C} > a_{CO}^{C}$; 2) a_{CO}^{C} increases as the bulk of the alkyl substituent increases; 3) a_{α}^{C} decreases as the number of substituents at the α-carbon increases; 4) a_{β}^{C} decreases in the order: ethyl>isopropyl>t-butyl. Interpretation of these generalizations can be made in terms of accepted mechanisms and semiempirical relationships for ^{13}C hfs, revealing detailed features of semidione structure and spin distribution.

Figure 30. First derivative ESR spectrum of bis(1-adamantyl)-semidione in DME-NaK alloy at 25°C: (A) at normal signal level, showing $\underline{a}^{H}$; (B) at high signal level, showing two sets of natural abundance ^{13}C hfsc.

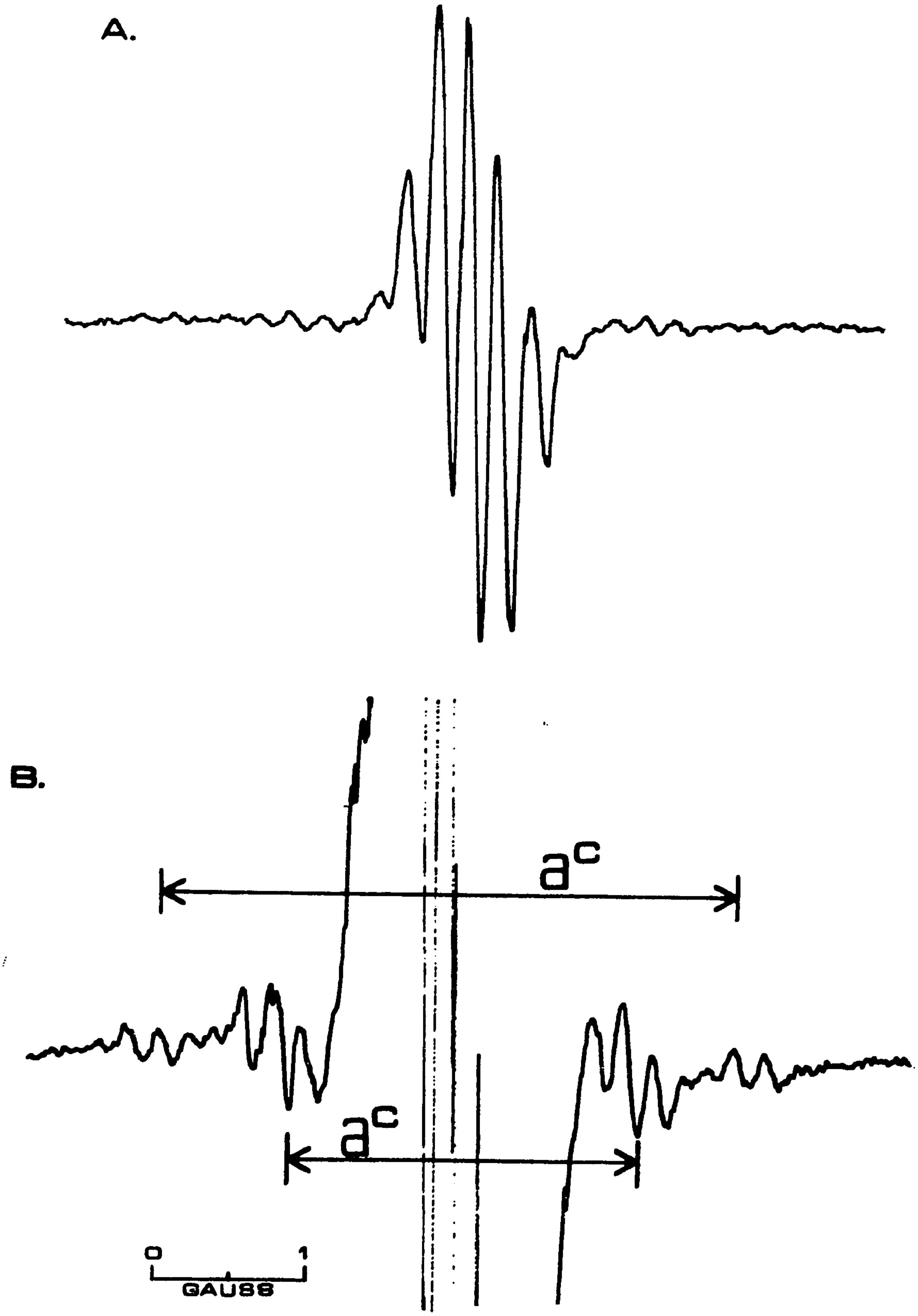
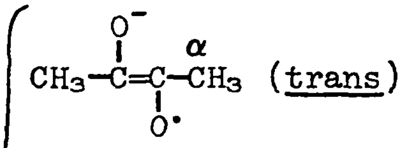
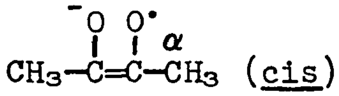
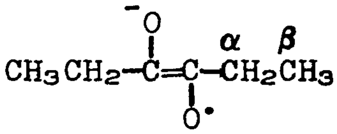
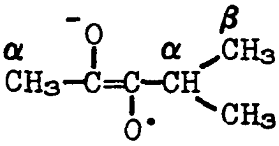

A.
B.
a^c
a^c
0
1
GAUSS

Table 21. ^{13}C hfsc[a] of acyclic semidiones (DMSO-potassium *t*-butoxide, 25°C).

Semidione	a_{CO}^{C}	a_{α}^{C}	a_{β}^{C}	a^{H}
92  $CH_3-C(O^-)=C(O^\bullet)-CH_3$ (*trans*)	0.58[b] 0.7[b,c]	4.5[b]	---	5.6
93  $CH_3-C(O^-)=C(O^\bullet)-CH_3$ (*cis*)	1.14[b] ~1.4[b,c] 1.8[b,d]	5.2b	---	7.0
94  $CH_3CH_2-C(O^-)=C(O^\bullet)-CH_2CH_3$	---[e]	(4.3)	4.25[b]	4.8
95  $CH_3-C(O^-)=C(O^\bullet)-CH(CH_3)_2$	---[e]	(4.0, 4.6)	3.74[b]	2.0, 5.7
96	---[e]	(3.8)	(2.3)	0.2[f]

[a] In gauss.

[b] Isotopically enriched.

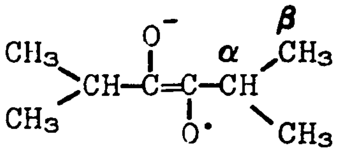
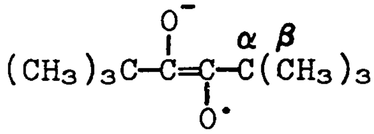
[c] Sodium gegenion

[d] Lithium gegenion.

[e] Could not be detected from natural abundance.

[f] Due to six protons.

Table 21. (Continued)

Semidione		a_{CO}^{C}	a_{α}^{C}	a_{β}^{C}	a^{H}
97		$0.8^{b,g}$	$4.0^{b,g}$	(~ 3.9)	1.9
98	 $(CH_3)_3C-\overset{O^-}{C}=\underset{O\cdot}{C}-\overset{\alpha\ \beta}{C}(CH_3)_3$	$1.41^{b,g}$	$(3.8)^{h}$	$(2.4)^{h}$	0.31
99	$CF_3COCO\overset{\alpha}{C}F_3^{\cdot -}$	$(1.9)^{i}$	$(4.5)^{i}$		$---^{i}$

[g] Reference 51.

[h] Reference 100.

[i] Result of Dr. John L. Gerlock, $a^F = 8.3$ G.

Both a_{CO}^{C} and a_{α}^{C} are higher in cis-dimethyl semidione than in the trans isomer, apparently consistent with the observation from proton hfsc that the cis semidione possesses a higher ρ_C^{π}. It is possible to estimate ρ_C^{π} from a_{α}^{C} by use of Equation 8, assuming a spin-polarization interaction, where

$$a_{\alpha}^{C} = Q_{CC'}^{C'}\rho_C^{\pi} \qquad (8)$$

$Q_{CC'}^{C'}$ can be evaluated as -15 G from the ethyl radical, $a_{\alpha}^{C} = 13.57$ G (102). Thus, ρ_C^{π} for dimethyl semidione is estimated to be 0.30 (trans) and 0.345 (cis) by Equation 8; this can be compared with $\rho_C{}^\pi$ estimated from $\underline{a}_\alpha{}^H$ (50) of 0.28 (trans) and 0.35 (cis). The sign of $\underline{a}_\alpha{}^C$ in semidiones is probably negative. As the structure changes from dimethyl to di-t-butyl semidione, either $\rho_C{}^\pi$ changes or the magnitude of $\underline{Q}_{CC'}{}^{C'}$ changes. Little change was noted in $\underline{a}_{CH_3}{}^H$ through the alkylmethyl semidiones; hence, it is possible that $\underline{Q}_{CC'}{}^{C'}$ could drop from 15 G for $C' = CH_3$ to 13.5 G for C' = central carbon atom of t-butyl.

On the other hand, the increase observed in $\underline{a}_{CO}{}^C$ from 0.58 G in trans-92 to 1.4 G in di-t-butyl semidione (also presumably of trans configuration) may be explained in the value of $\underline{Q}_{CC'}{}^C$ in Equation 9 (103). Often referred to as the

$$\underline{a}^C = (S^C + \sum_{i=3}^{1} \underline{Q}_{CX_i}{}^C)\rho_C{}^\pi + \sum_{i=3}^{1} \underline{Q}_{X_iC}{}^C \rho_{X_i}{}^\pi \qquad (9)$$

Karplus-Fraenkel equation, Equation 9 predicts the value of $\underline{a}^C$ for a carbon atom within a π-system (including alkyl radicals), taking into account contributions to the observed splitting constant from: 1) polarization of 1s electrons (S^C); 2) spin density on C, which is attached directly to X_i, through the 2s orbital ($\underline{Q}_{CX_i}{}^C$); and 3) spin density on neighboring atoms X_i, through the 2s orbital of C ($\underline{Q}_{X_iC}{}^C$), where $\rho_{X_i}{}^\pi$ is the spin density at the neighboring atom. For a symmetrical semidione, Equation 9 simplifies to Equation 10, since for the two carbonyl carbon atoms $\underline{Q}_{CC^2}{}^C \approx -\underline{Q}_{C^2C}{}^C$,

$$\underline{a}_{CO}^{C} = (S^{C} + \underline{Q}_{CC'}^{C} + \underline{Q}_{CO}^{C})\rho_{C}^{\pi} + \underline{Q}_{OC}^{C}(0.5-\rho_{C}^{\pi}) \tag{10}$$

$\rho_{C^1}^{\pi} \approx 0$, and $\rho_{O}^{\pi} = \frac{1}{2}(1-2\rho_{C}^{\pi})$. Values of $S^{C} = -12.7$ (103), $\underline{Q}_{OC}^{C} = -27.1$ (104) and $\underline{Q}_{CO}^{C} = +17.7$ G (104) have been used successfully in the past.[1] Using $\rho_{C}^{\pi} = 0.28$ for *trans*-**92**, **97** and **98** yields $\underline{Q}_{CC'}^{C} = 18$, 19 and 21 G for $C' =$ methyl, isopropyl and *t*-butyl, respectively, if all $\underline{a}_{CO}^{C}$ are positive.

A value of $\underline{Q}_{CC'}^{C} = +16$ G ($C' = CH_3$) is estimated for the ethyl radical (102). Using this as invariant, Equation 10 may be solved for ρ_{C}^{π}; Table 22 indicates the results obtained if $\underline{a}_{CO}^{C}$ is taken to be negative and if it is taken to be positive. If the values of $\underline{a}_{CO}^{C}$ are either all positive or all negative, and the other parameters of Equation 10 are correct, then all ρ_{C}^{π} are similar and within ± 0.03. However, results from $\underline{a}_{\alpha}^{C}$ and $\underline{a}_{\alpha}^{H}$ indicate that ρ_{C}^{π} (*cis*) is generally considerably higher than ρ_{C}^{π} (*trans*); furthermore, the ratio of $\underline{a}^{F}$ (=34.7 G) in hexafluoroacetone ketyl (109) to $\underline{a}^{F}$ (=8.3 G) in bis(trifluoromethyl)semidione, **99**, of 4.2:1 indicates that ρ_{C}^{π} in **99** is certainly not greater than 0.25. Therefore, it

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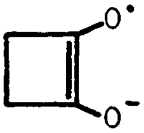
[1] Alternative values have also been suggested at various times. Gilbert and Kreilick (105) were able to calculate $\underline{a}_{CO}^{C}$ in several phenoxyl radicals using $\underline{Q}_{OC}^{C} = 10.4$ G and $\underline{Q}_{CO}^{C} =$ 8.9 G, the difference being attributed to charge effects. Broze and Luz (106) have surveyed a number of oxygen-containing radicals and radical anions, including semidiones, and suggest use of $\underline{Q}_{CO}^{C} = 36$ G and $\underline{Q}_{OC}^{C} = -24.3$ G in the Karplus-Fraenkel expression; they observed, however, that $\underline{a}_{CO}^{C}$ for semidiones and ketyls could not be reproduced using their values. Modifications and extensions of the Karplus-Fraenkel treatment have appeared (107).

Table 22. Calculated spin densities for semidiones.

	ρ_C^{π}	
Semidione	(a_{CO}^{C} positive)	(a_{CO}^{C} negative)
trans-92	0.295	0.270
cis-92, K$^+$	0.306	0.258
" " , Li$^+$	0.320	0.246
97	0.299	0.266
98	0.312	0.254
99	0.322	0.244
100:[a] 	0.312	0.254

[a] a_{CO}^{C} = 1.4 G (natural abundance), Reference 108.

is likely that a_{CO}^{C} between *cis* and *trans* semidiones might be opposite in sign, where a_{CO}^{C} (*cis*) is positive, ρ_C^{π} (*cis*) $\geq$ 0.31, and a_{CO}^{C} (*trans*) is negative, ρ_C^{π} (*trans*) $\leq$ 0.28, for the radicals examined.[1] Expected variations in $Q_{CC'}^{C}$ may account for further differences. Unfortunately, experimental determination of the signs of a_{CO}^{C} was not possible.

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[1] In light of these results, the recent assignment to the carbonyl carbon atom of a^C = 5.2 G in monoprotonated dimethyl semidione (110) may be questioned.

As a further probe into semidione spin distribution, ^{17}O-enriched dimethyl semidione was examined. The semidione was generated from acetoin which had been treated with ^{17}O-enriched water (Yeda Research Laboratories, Inc., Rehovot,

$$CH_3CH(OH)COCH_3 \xrightarrow{H_2{}^{17}O} \xrightarrow{B^-,DMSO} CH_3C(O^-)=C(^{17}O^\cdot)CH_3$$

Israel). The ESR spectrum of the trans isomer (Figures 31 and 32) revealed $\underline{a}^O = (-)\ 10.3$ G, quite consistent with $\underline{a}^O$ previously observed by Russell and Underwood (100), who have suggested that $\underline{a}^O$ may be predicted by Equation 11, with $Q_{OC}{}^C =$

$$\underline{a}^O = Q_{OC}{}^C \rho_O{}^\pi \qquad (11)$$

-40 to -50 G. Using $Q_{OC}{}^C = -44.9$ G (111), a $\rho_O{}^\pi$ of 0.23 is calculated, in perfect agreement with $\rho_C{}^\pi = 0.27$ calculated above from ^{13}C hfsc.

The values observed for $\underline{a}_\beta{}^C$ in 94, 95, 98 and 96 appear to be reasonable and consistent with $\underline{a}_\beta{}^H$ and the notion of preferred conformations of the alkyl substituents. Semidiones 96 and 98 may be taken to represent a "free rotation" limit (or equal populations of conformations) with $\langle \cos^2\theta^C \rangle = ½$, where θ^C is defined as the dihedral angle between the $\underline{p}_z$ orbital of the carbonyl carbon atom and the C^α-C^β bond. A hyperconjugation mechanism has previously been suggested to explain β-^{13}C hfsc (112), where $\underline{a}_\beta{}^C$ may be predicted by a relationship such as Equation 12; a value of $B^C \approx 20$ G is pre-

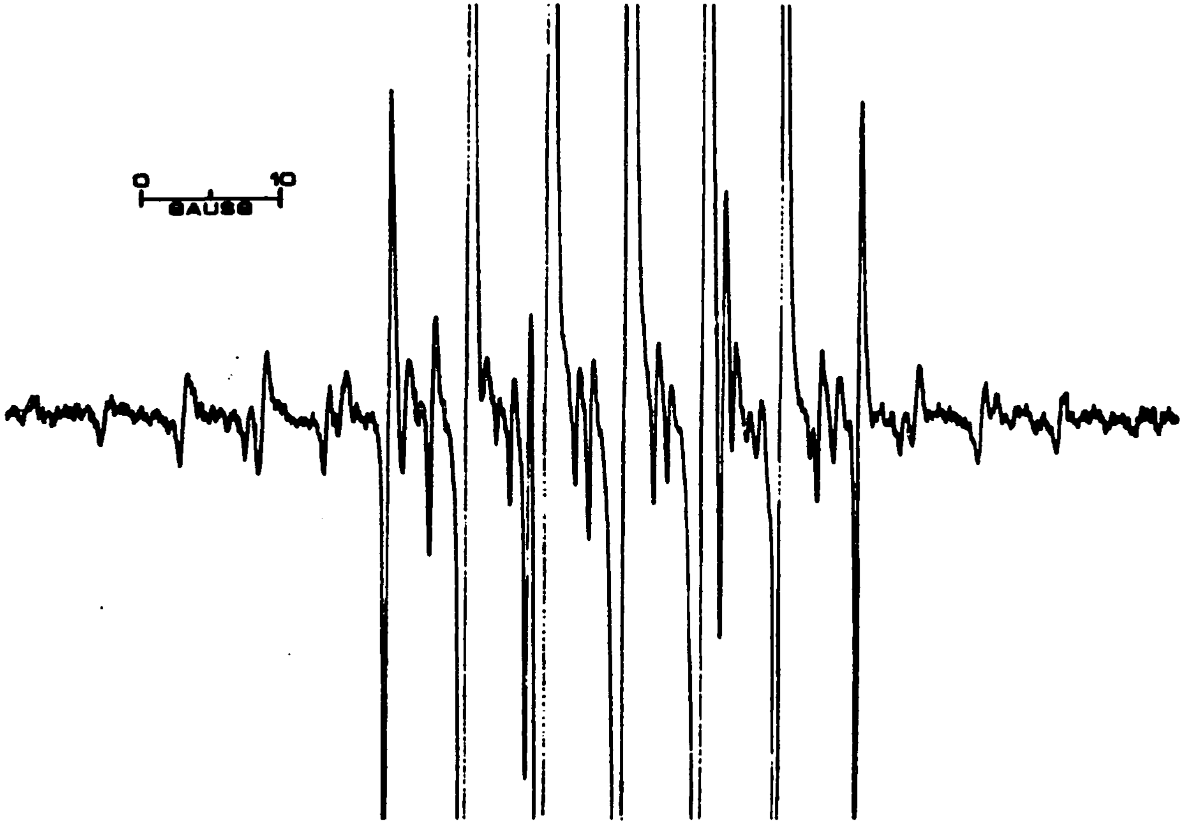


Figure 31. First derivative ESR spectrum of butane-2,3-semidione-^{17}O (~1% ^{17}O) in DMSO-potassium *t*-butoxide (25°C) at high signal level, showing ^{17}O satellites.

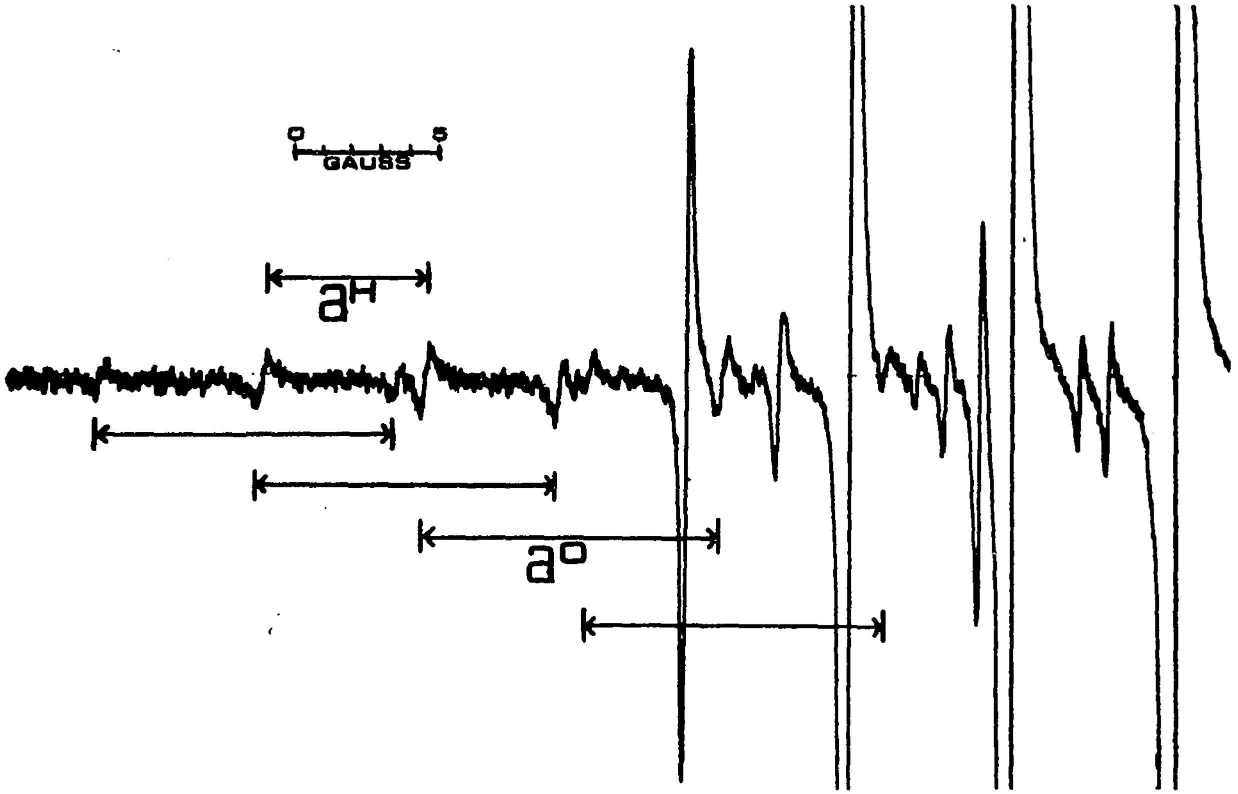


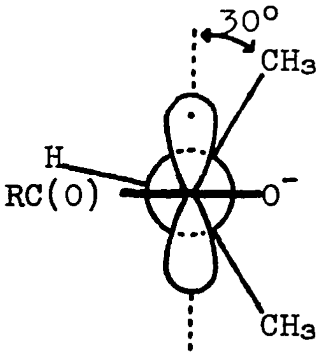
Figure 32. First derivative ESR spectrum of butane-2,3-semidione-^{17}O (~1% ^{17}O), expanded, at high signal level.

$$a_{\beta}^{C} = B^{C}\langle\cos^{2}\theta^{C}\rangle \tag{12}$$

ferred (112-114). Using ρ_{C}^{π} of 0.27 for **98** leads to $B^{C} = 18$ G in Equation 12; using ρ_{C}^{π} of 0.25 leads to the expected value for $B^{C} = 19\text{-}20$ G.

A conformation such as **101** might be expected for an isopropyl semidione, *e.g.* **95** (50), if semidiones assume the preferred conformations suggested by Stone and Maki (115). In conformation **101**, $\langle\cos^{2}\theta^{C}\rangle$ should be 0.75 if no torsional

101:



$$a_{\beta}^{H} = 40\rho\langle\cos^{2}\theta^{H}\rangle \tag{13}$$

motion occurs; taking $a_{\beta}^{C} = 2.4$ G in **98** where $\langle\cos^{2}\theta\rangle = 0.5$, a value of $a_{\beta}^{H} = 3.6$ G is predicted for **101**. The observed value of $a_{\beta}^{C} = 3.74$ G is thus apparently in very good agreement. The low value of a_{CH}^{H} (*ca.* 2.0 g) indicates a low (but not zero) $\langle\cos^{2}\theta^{H}\rangle$. The temperature dependence of a_{β}^{C} and $a_{CH}^{CH_3}$ is shown in Figure 33; little variation was detected in either value from 0° to 90°. It may be concluded, therefore, that over this temperature range only a single vibrational level with a low torsional oscillation (φ, figure 2 in Reference 115) or a high barrier to rotation (V_0, figure

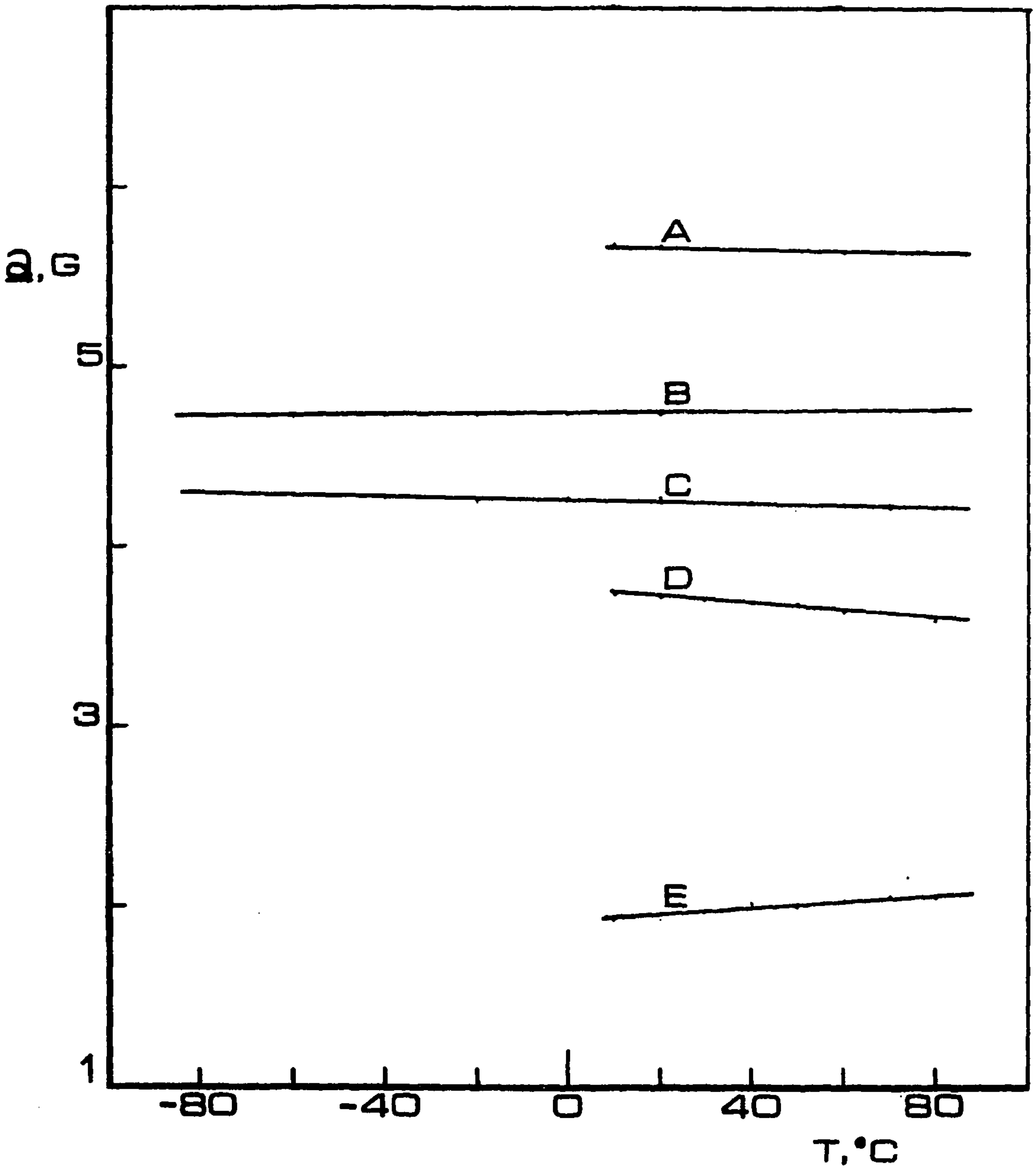


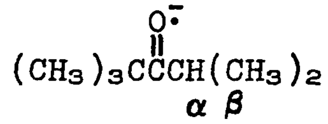
Figure 33. Temperature dependence of hfsc in semidiones: (A) $\underline{a}_{CH_3}{}^{H}$, (D) $\underline{a}_{\beta}{}^{C}$, (E) $\underline{a}_{CH}{}^{H}$ in 2-methylpentane-3,4-semidione-1-^{13}C; (B) $\underline{a}_{CH_2}{}^{H}$, (C) $\underline{a}_{\beta}{}^{C}$ in hexane-3,4-semidione-1-^{13}C.

r

3 in Reference 115) must be populated by 95. However, no fit can be made to the figures in Reference 115 using $\langle \cos^2\theta^C \rangle$ calculated for 95 on the basis of $\langle \cos^2\theta^C \rangle = 0.5$ for 98, indicating either failure in the theory, or an anomaly in observed $a_\beta{}^C$ (possibly in $a_\beta{}^C$ for 98).

If it is assumed that the β-substituents are separated by 120° and that $B^C = 20$ G, it is possible to solve Equations 12 and 13 simultaneously, where now $\langle \cos^2\theta^C \rangle = \frac{1}{2}[\cos^2(\theta^H + 120°) + \cos^2(\theta^H - 120°)]$ for an isopropyl group. A plot of the solutions of Equation 12 and 13 is given in Figure 34. Taking observed values of $a_\beta{}^H$ and $a_\beta{}^C$ for 96 from Table 21 yields $\langle \cos^2\theta^H \rangle = 0.18$, $\theta^H = 65°$ and $\rho_C{}^\pi = 0.28$.[1] From the figures in Reference 115, values of $\varphi = 36°$ and $V_0 = 1.25$ kcal/mole are estimated for 95, $(\theta_0{}^H = 90°)$.

The same approach may be followed for 102 (15) and 103 (116, 117), for which the values of both $a_\beta{}^H$ and $a_\beta{}^C$ are known, since these also have an isopropyl substituent at the radical center. For 102 values of $\langle \cos^2\theta^H \rangle = 0.067$, $\theta^H = 75°$



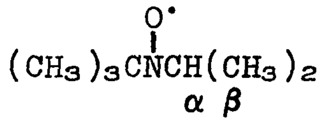
$(CH_3)_3C\overset{O^{\dot{-}}}{\overset{\|}{C}}CH(CH_3)_2$

$\alpha\ \beta$

$a_\alpha{}^H = 2.38$ G

$a_\beta{}^C = 13.0$ G

102



$(CH_3)_3C\overset{O^{\cdot}}{\overset{|}{N}}CH(CH_3)_2$

$\alpha\ \beta$

$a_\alpha{}^H = 1.8$ G

$a_\beta{}^C = 6.8$ G

103

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[1] A value of $\theta^H = 63°$ has been estimated from $a_\beta{}^H$ in phenylisopropyl semidione (26).

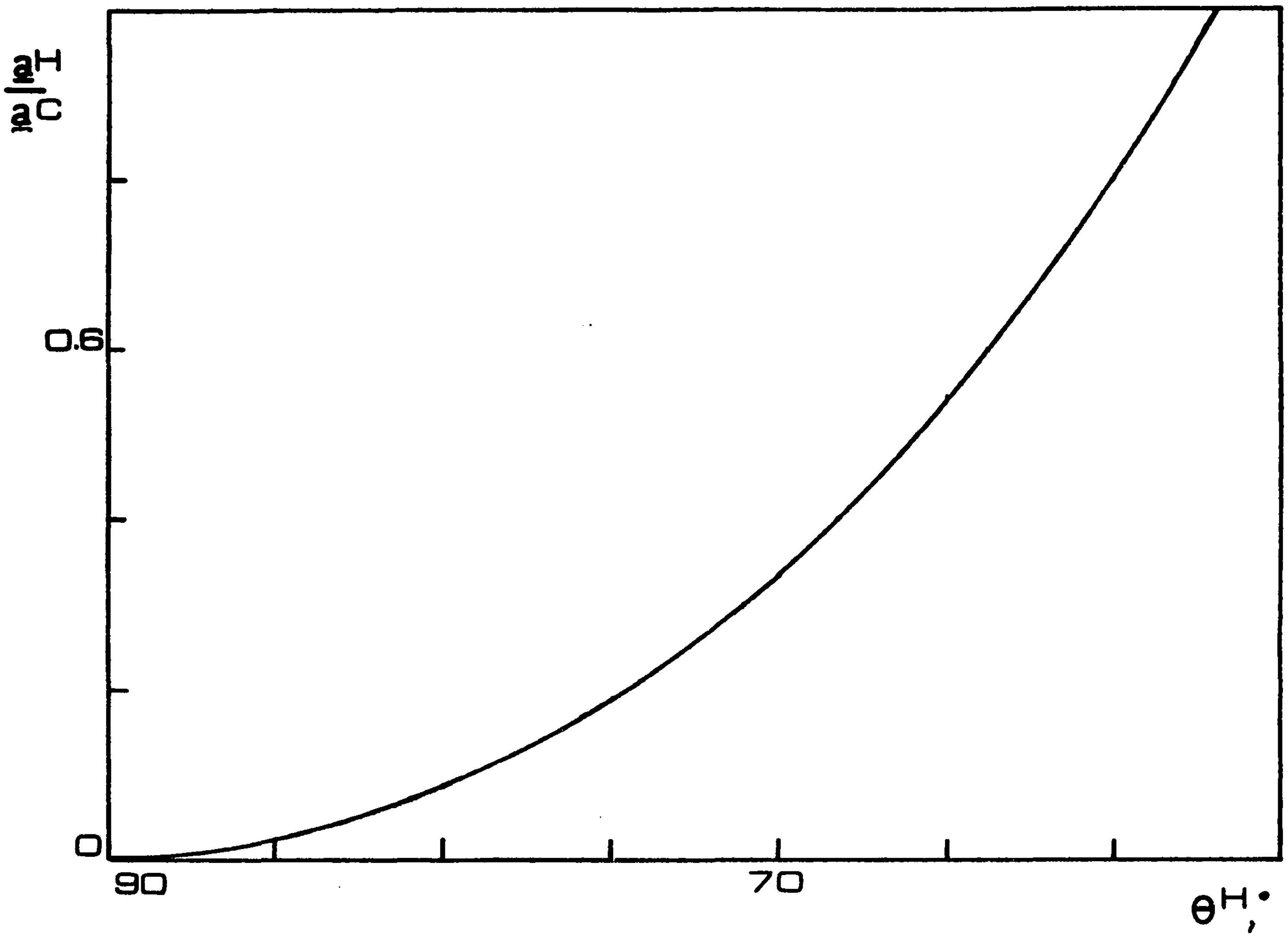
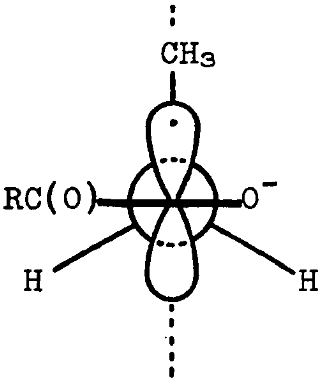


Figure 34. Angular dependence of $\underline{a}^H/\underline{a}^C$ for isopropyl-like substituents.

and $\rho = 0.89$ were found; values of $\varphi = 19^\circ$ and $V_0 \approx 3.9$ kcal/mole were derived from Reference 115. In **103**, $\langle\cos^2\theta^H\rangle = 0.106$, $\theta^H = 72^\circ$ and $\rho = 0.42$; φ and V_0 were determined to be 27° and 2.5 kcal/mole, respectively. For both **102** and **103**, θ_0^H was taken to be 90°.

The situation encountered when the alkyl group under consideration is ethyl may be more complex. If diethyl semidione were to follow the predictions of Stone and Maki based upon nitroethane radical anion (115), bisected conformation **104** should be preferred. In this conformation, $\theta_0^H = 60^\circ$



104

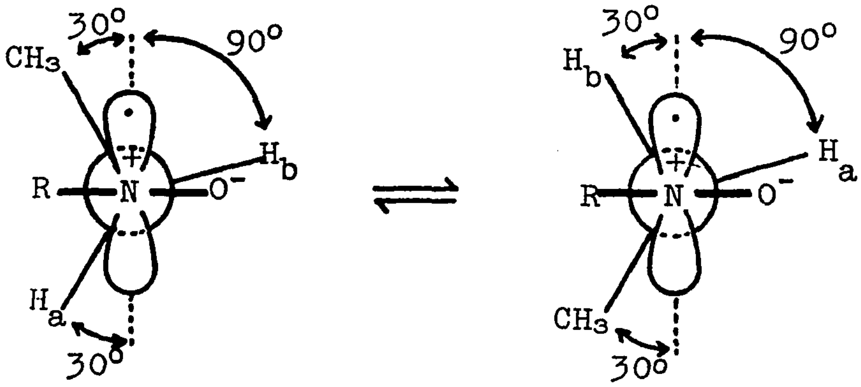
$(\cos^2\theta_0^H = 0.25)$ and $\theta_0^C = 0^\circ$ $(\cos^2\theta_0^H = 1)$; the observed values for trans-diethyl semidione, **94**, based on trans-**92** and **98**, were $\langle\cos^2\theta^H\rangle = 0.43$ and $\langle\cos^2\theta^C\rangle = 0.86$. These values differed from reference values presumably because of torsional motion (see figure 2, Reference 115). Both values could be fitted to Stone and Maki's treatment, but a wide discrepancy was noted. Estimates for φ of 55° and 33°, and for V_0 of 0.5 and 2.0 kcal/mole were made from $\langle\cos^2\theta^H\rangle$ and

$\langle \cos^2\theta^C \rangle$, respectively. Since 98 may be anomalous as a standard for β-^{13}C-hfsc, the observed values of a^H and a^C for 94 were fitted to the set of simultaneous solutions of Equation 14, which applies to an ethyl group (Figure 35). Through

$$a^H/a^C = \frac{[\cos^2(\theta^C + 120^\circ) + \cos^2(\theta^C - 120^\circ)]}{\cos^2\theta^C} \qquad (14)$$

this treatment, estimates of $\langle \cos^2\theta^C \rangle = 0.703$, $\theta^C = 35^\circ$ and $\rho_C^{\pi} = 0.30$ were made; φ and V_0 were estimated as 50° and 0.5 kcal/mole, respectively, by use of Reference 115.

Another possibility exists for the conformation of an ethyl group attached to a spin label. The staggered conformations 105 and 106 have been suggested as the preferred conformations in ethyl-substituted nitroxides, R = alkyl, as well



105 106

as nitroethane radical anion, R = O$^-$ (117). Equilibrium of equally populated conformations 105 and 106 at room temperature should lead to $\langle \cos^2\theta^C \rangle = 0.75$ and $\langle \cos^2\theta^H \rangle = 0.375$; torsional motion will make these values upper and lower

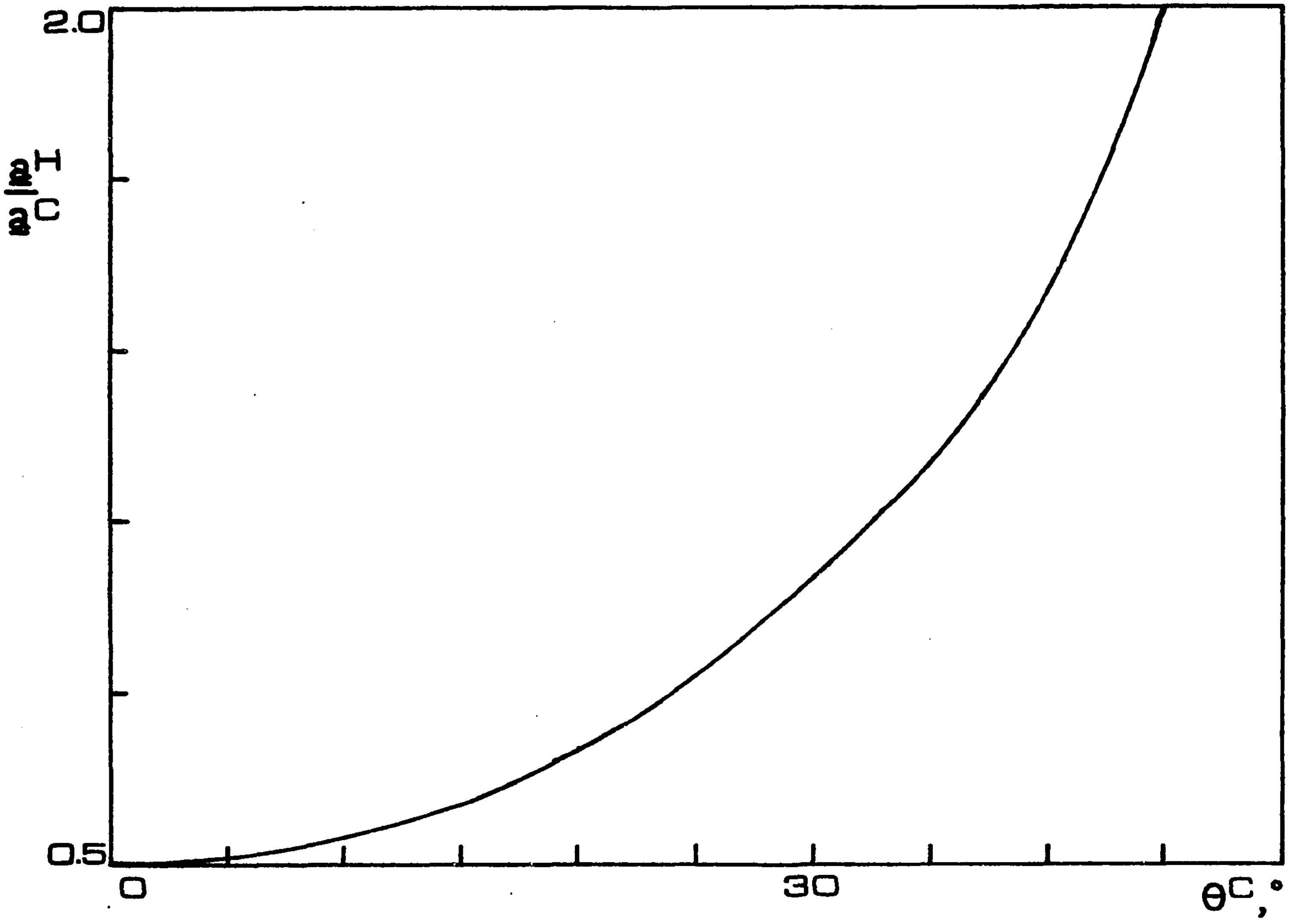
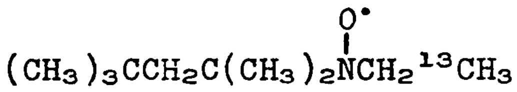


Figure 35. Angular dependence of $\underline{a}^H/\underline{a}^C$ for ethyl-like substituents.

limits, respectively. Values of $\langle \cos^2\theta^C \rangle = 0.71$[1] and $\langle \cos^2\theta^H \rangle = 0.44$ for t-octylethyl nitroxide, 107 (117), have been observed. (^{13}C results were kindly communicated by Professor Rassat.) Although $\langle \cos^2\theta^C \rangle$ for diethyl semidione



$(CH_3)_3CCH_2C(CH_3)_2\overset{O^\bullet}{\overset{|}{N}}CH_2{}^{13}CH_3$

107

$a_{CH_3*}{}^C = 6.25$ G

$a_{CH_2}{}^H = 10.7$ G

94 is certainly greater than 0.75, indicating the bisected conformation, the similarity between expected values of $\cos^2\theta^H$ for the bisected and staggered conformations renders an experimental distinction between the two based on proton hfsc difficult. In fact, $\langle \cos^2\theta^H \rangle$ and $\langle \cos^2\theta^C \rangle$ for 107 are consistent with either a staggered or a bisected conformation. Thus, good fit is obtained with Reference 115 for $\varphi = 48°$ and $V_0 = 0.6$ kcal/mole. Using Equation 14, the unlikely values $\langle \cos^2\theta^C \rangle_{av} = 0.552$, $\theta^C = 42°$, $\rho_N{}^\pi = 0.56$, $\varphi = 63°$ and $V_0 =$ 0.1 kcal/mole were found. However, whereas 107 exhibits nonequivalence of the α-hydrogen atoms at low temperatures (117)—consistent with 105, 106 and/or some preferred conformation of the t-octyl group—94 shows little effect of temperature (Figure 33). The latter is consistent with a bisected conformation in 94, with a low barrier to rotation and high tor-

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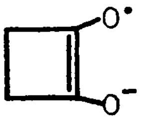
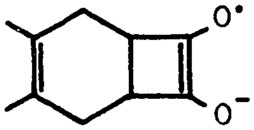
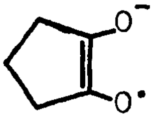
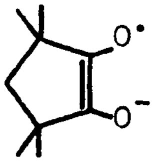
[1] Based upon $a_\beta{}^C = 4.35$ G observed for di-t-butyl nitroxide (112) where $\langle \cos^2\theta^C \rangle$ is taken as ½.

sional amplitude.

It thus appears that ^{13}C hfsc in semidiones may be explained by existing semiempirical relationships. Assignments of natural abundance ^{13}C-hfsc in other semidiones can be made by analogy; these are summarized in Table 23.

Table 23. Hfsc[a] in various semidiones (potassium-*t*-butoxide-DMSO, 25°C).

Semidione	a_{CO}^{C}	a_{α}^{C}	a_{β}^{C}	a^{H}	Ref.
	1.4	5.4	---	13.6	108
	1.5	5.0	7.9	13.0, 0.7	108
	--[b]	5.6	--[b]	13.1	99
	--[b]	(5.9± 0.1)[c]	(5.9± 0.1)[c]	--[d]	This work

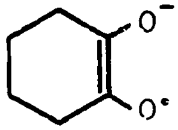
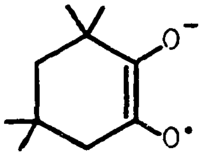
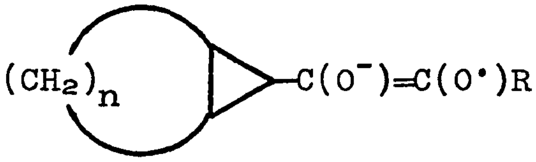
[a] In gauss.

[b] Not detected in natural abundance.

[c] Actual assignment uncertain.

[d] Not resolvable under experimental conditions.

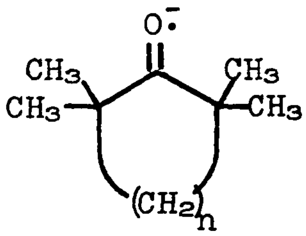
Table 23. (Continued)

Semidione	$\underline{a}_{CO}^{C}$	$\underline{a}_{\alpha}^{C}$	$\underline{a}_{\beta}^{C}$	$\underline{a}^{H}$	Ref.
	--^{b}	4.9	--^{b}	9.8	97
	--^{b}	$(\sim 4.4)^c$	$(\sim 4.4)^c$	8.9	24
$(CH_3)_2CHCH_2C(O^-)=$ - $C(O^\bullet)CH_2CH(CH_3)_2$	--^{b}	$(4.4)^c$	$(4.4)^c$	4.3	50
$(CH_3)_3CC(O^-)=C(O^\bullet)CH_3$	--^{b}	4.5,--^{b}	3.2	5.6, 0.27	This work
					
n = 0	--^{b}	4.5	8.1		51
n = 3	--^{b}	--^{b}	8.7		51
n = 4	--^{b}	--^{b}	8.7		51
n = 5	--^{b}	--^{b}	8.2		51
n = 6	--^{b}	5.4	9.6		51

CARBON-13 HYPERFINE SPLITTING IN KETYL RADICAL ANIONS

The magnitude of a^C for a carbon atom bearing an unpaired electron has been used as a criterion for establishing geometry at that site (102, 118-122). Thus, it has been suggested (121) that the high value of $a_{CO}^C \approx 50$ G in di-*t*-butyl ketyl, **86**, is a manifestation of non-planarity due to steric factors.

To explore this possibility further, a series of cyclic ketyls, **108**-**111**—completely substituted at the α-positions for stability—was prepared and examined by ESR spectroscopy.



108, n = 1
109, n = 2
110, n = 3
111, n = 4

If steric reasons were a major factor in increasing a_{CO}^C, considerable variation in a_{CO}^C for **108**-**111** might be expected. The range of a_{CO}^C observed was 43.9-50.2 G (Table 24); the ESR spectrum of **110**, typical of **109** and **111**, is shown in Figure 36.

The range observed is probably due to the stereochemistry of the rings; however, the variation is much less than would be expected if the effect of nonplanarity on a_{CO}^C in di-*t*-butyl ketyl were as great as suggested. In fact, the observed values of a_{CO}^C are in fair agreement with the Karplus-

Table 24. Hfsc[a] of cyclic ketyl radical anions (THF solution, potassium gegenion).

Ketyl	a_{CO}^{C}	$a_{C^1}^{C}$ [b]	Comments
108	50.2	13.4	$a_{CH_2}^{H} = 0.67$, $a_{CH_3}^{H} = 0.1$ G;-60°C
109	43.9	14.2	25°C[c]
110	47.3	10.25	25°C[c]
111	47.2	10.4	25°C[c]

[a] In gauss.

[b] Tentatively assigned to the methyl carbon atoms.

[c] No a^{H} resolved.

Fraenkel equation using $\rho_C^{\pi} = 0.9$, $\rho_O^{\pi} = 0.1$, $S^C = -12.7$, $Q_{CC'}^{C} = 21$, $Q_{CO}^{C} = 17.7$ and $Q_{OC}^{C} = -27.1$ G, which yields a calculated value of $a_{CO}^{C} = 42$ G. The values of $\rho_C^{\pi} = 0.9$ and $Q_{CC'}^{C} = 21$ G were indicated in the foregoing discussion of ^{13}C hfsc in semidiones. A value of $Q_{CC'}^{C} > 21$ G (C' = *t*-butyl) would give very good agreement with experimental a_{CO}^{C} in these aliphatic ketyls.

The possibility that steric effects upon a_{CO}^{C} in these ketyls are relatively constant or that a_{CO}^{C} reflects factors other than steric effects should not be overlooked. Several examples bear out the latter possibility. The highly hindered —and expectedly "puckered"—ketyls 112 and 113 were generated

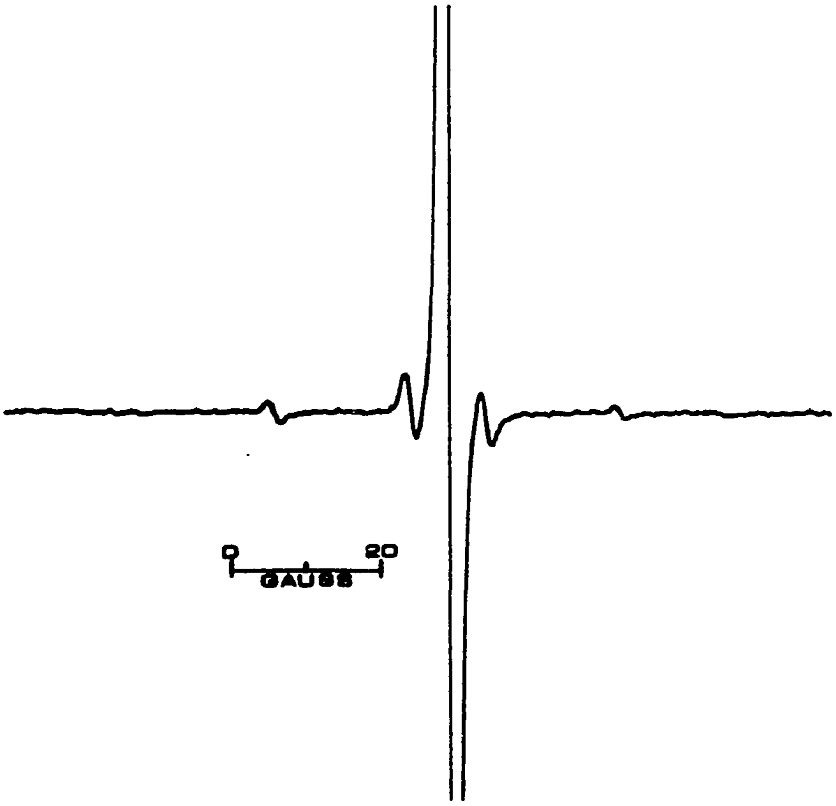
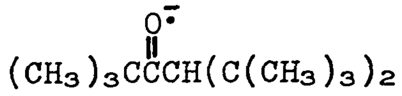


Figure 36. First derivative ESR spectrum of 2,2,6,6-tetramethylcyclohexan-1-one radical anion in DME-NaK alloy (25°C), at high signal level, showing two sets of ^{13}C satellites.

by reduction of the corresponding ketones at low temperatures in DME on a potassium mirror. The results suggest that 112 and 113 are not puckered—their a_{CO}^{C} being compatible with expectations for planar ketyl radical anions (102, 121). Differences in a_{CO}^{C} between ketyls 112, 114 and ketyls 87, 108-111 may be caused by association of less hindered ketyl anions with metal cations, raising either the spin density at carbon or Q_{CO}^{C} in Equation 10.



$(CH_3)_3C\overset{O^{\overline{\cdot}}}{\overset{\|}{C}}CH(C(CH_3)_3)_2$

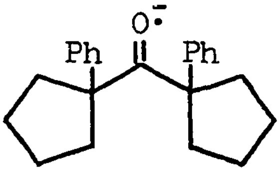
(-80°)

$a_{CO}^{C} = 34.0$ G

$a^{C} = 8.8$ G, 15.8 G

$a_{CH}^{H} \leq 1.8$ G

112



(-80°)

$a_{CO}^{C} = 40$ G

$a^{C} = 12$ G

113

Further evidence might be seen in hexafluoroacetone ketyl, 114, where Knolle and Bolton (123) have observed an apparently low $a_{CO}^{C} = 23.3$ G from the electrolytic reduction of hexafluoroacetone in the presence of quaternary tetra-

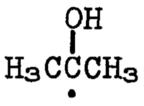
$F_3C\overset{O^{\overline{\cdot}}}{\overset{\|}{C}}CF_3$

$a^{F} = 34.5$ G

$a_{CO}^{C} = 23.3$ G

$a_{\alpha}^{C} = 8.0$ G

114



$H_3C\underset{\bullet}{\overset{OH}{\overset{|}{C}}}CH_3$

$a_{\alpha}^{C} = 5.35$ G (108)

$a_{CO}^{C} = 65.05$ G (108)

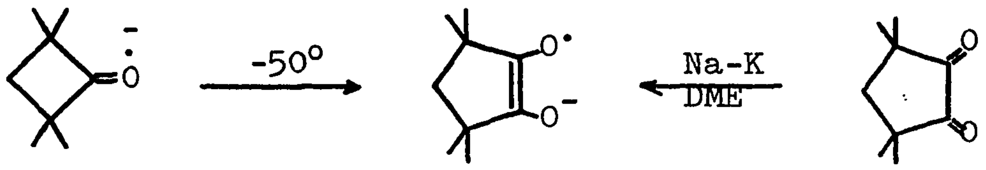
(=52.8 G (120))

115

alkylammonium salts. Here the ions are probably unassociated and ρ_C^{π} is not increased; however, $Q_{CC'}^{C}$ may also vary between C' = hydrocarbon and $C' = CF_3$. Radical **115**, derived from 2-propanol, should not be very different from **114** in its steric requirements, yet $a_{CO}^{C} = 52.8\text{-}65.05$ G have been reported (108, 120). Thus, the a_{CO}^{C} in certain ketyl radical anions appear to be less steric than electronic in nature, and the non-planarity indicated in many oxygen-substituted radicals may be the result of factors other than bulky alkyl substituents.

SEMIDIONES AS PRODUCTS OF KETONE REDUCTIONS

During the course of this work it was observed that ketyl 108 was unstable and decomposed to a more stable radical at ambient temperatures (27). 2,2,4,4-Tetramethylcyclobutanone could be reduced on a potassium mirror in THF at -80°C to give ketyl 108 (Figure 37), with the splitting constants listed in Table 24. The g-value at -80° was 2.00374 ± 0.00005. Upon warming to -50°C, the ketyl decomposed (Figure 38), $t_{1/2} \approx 2$ min, and was replaced by a broad singlet (linewidth = 0.6 G), $g = 2.00493$. The singlet had a lone $a^{C} = 5.9 \pm 0.1$ G at +30°C (Figure 39); it was identified as 3,3,5,5-tetramethylcyclopentane-1,2-semidione, 116, since reduction of 3,3,5,5-tetramethylcyclopentane-1,2-dione, 117, in DME with Na-K alloy gave



$a^{H} = 0.68(2H), 0.1(>6H)$ G
$a^{C} = 50.2(1C), 13.4(>4C)$ G
$g = 2.00374$

108

$a^{C} = 5.9 \pm 0.1$ G
$g = 2.00493$

116

117

a radical whose ESR spectrum was identical, with $g = 2.00493$. Semidione 116 was the only ESR signal observed: 1) when 2,2,4,4-tetramethylcyclobutanone was reduced with Na-K alloy in

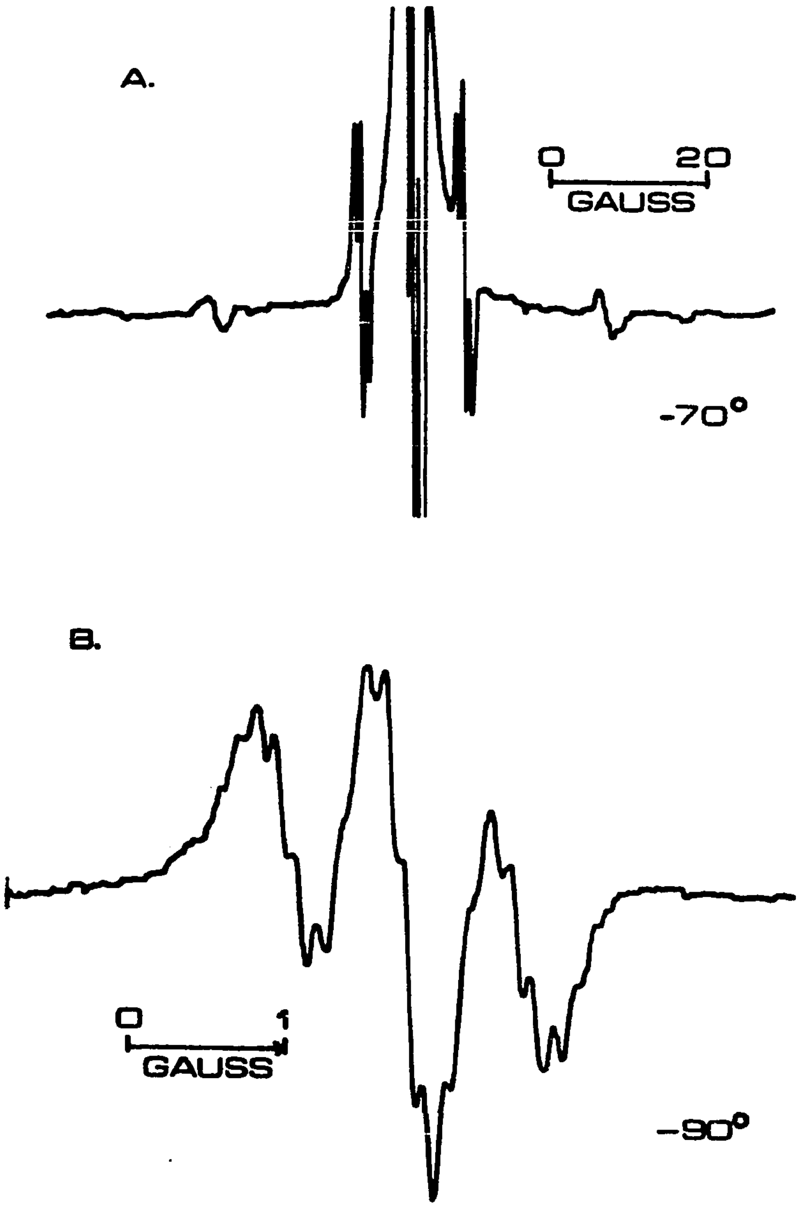


Figure 37. First derivative ESR spectrum of 2,2,4,4-tetramethylcyclobutanone radical anion (THF, potassium gegenion): (A) at high signal level, -70°, showing two sets of natural abundance ^{13}C satellites; (B) expanded, at normal signal level, -90°, showing proton hfs.

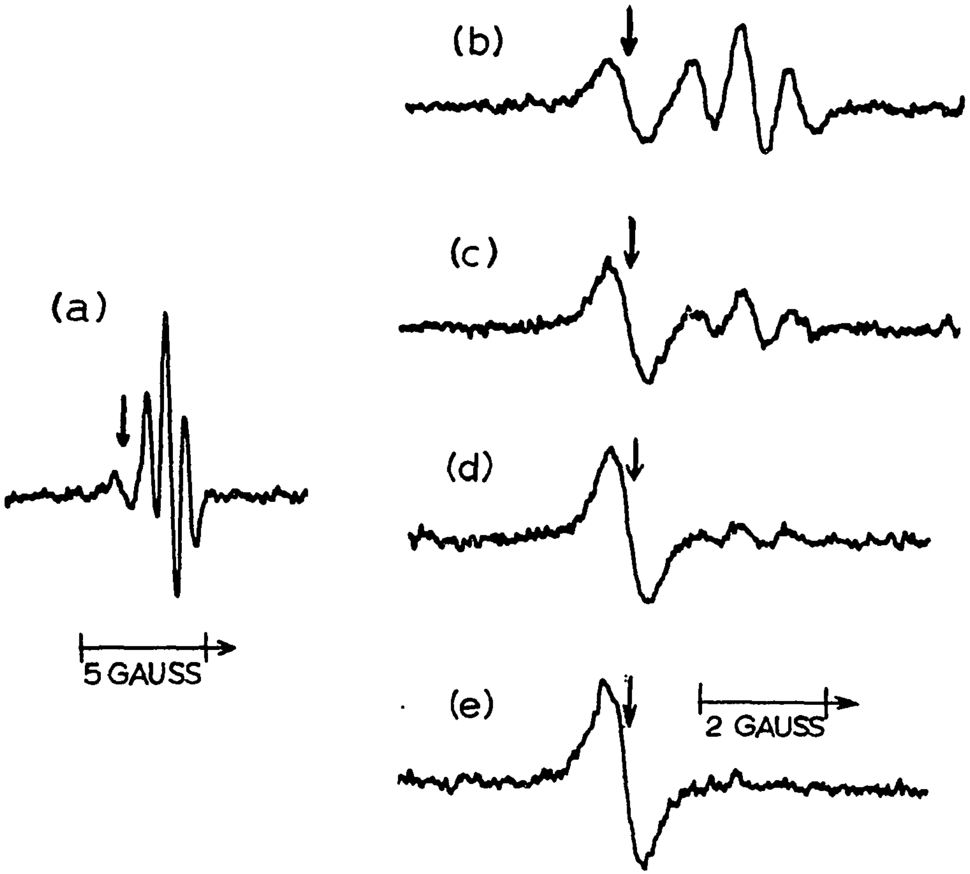


Figure 38. First derivative ESR spectra obtained upon warming 2,2,4,4-tetramethylcyclobutanone ketyl to -50°C; (a) initial spectrum, arrow indicating new signal developing; (b-e) elapsed-time spectra at 2.5, 5.0, 7.5 and 10.0 min, respectively.

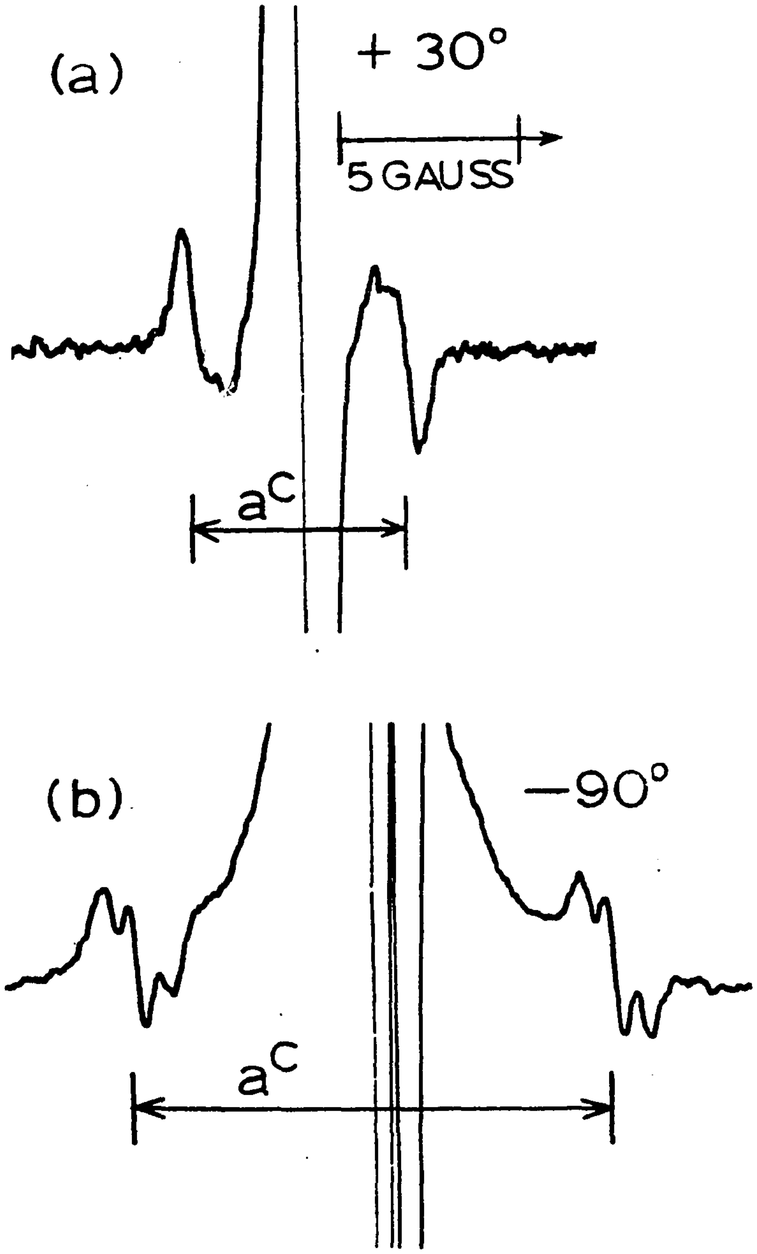


Figure 39. First derivative ESR spectra, at high signal levels, of: (A) 3,3,5,5-tetramethylcyclopentane-1,2-semidione at +30°C in THF; (B) 2,2,4,4-tetramethylcyclobutanone ketyl at -90°C in THF.

DME at 25°C; 2) when 2,2,4,4-tetramethylcyclopentan-1-one was oxidized in basic dimethyl sulfoxide solution. Ketyls **109**-**111** failed to undergo a similar transformation and were stable at room temperature. Ketyls **112** and **113** were unstable at room temperature, but yielded no paramagnetic products. The decay of **108** was apparently a first-order process, since a plot of $\ln([108]_0/[108])$ vs. time was linear (slope, $k = 5.7 \times 10^{-3}$ sec^{-1}); thus, loss of **108** *via* pinacol formation does not appear to be a major process at this temperature.

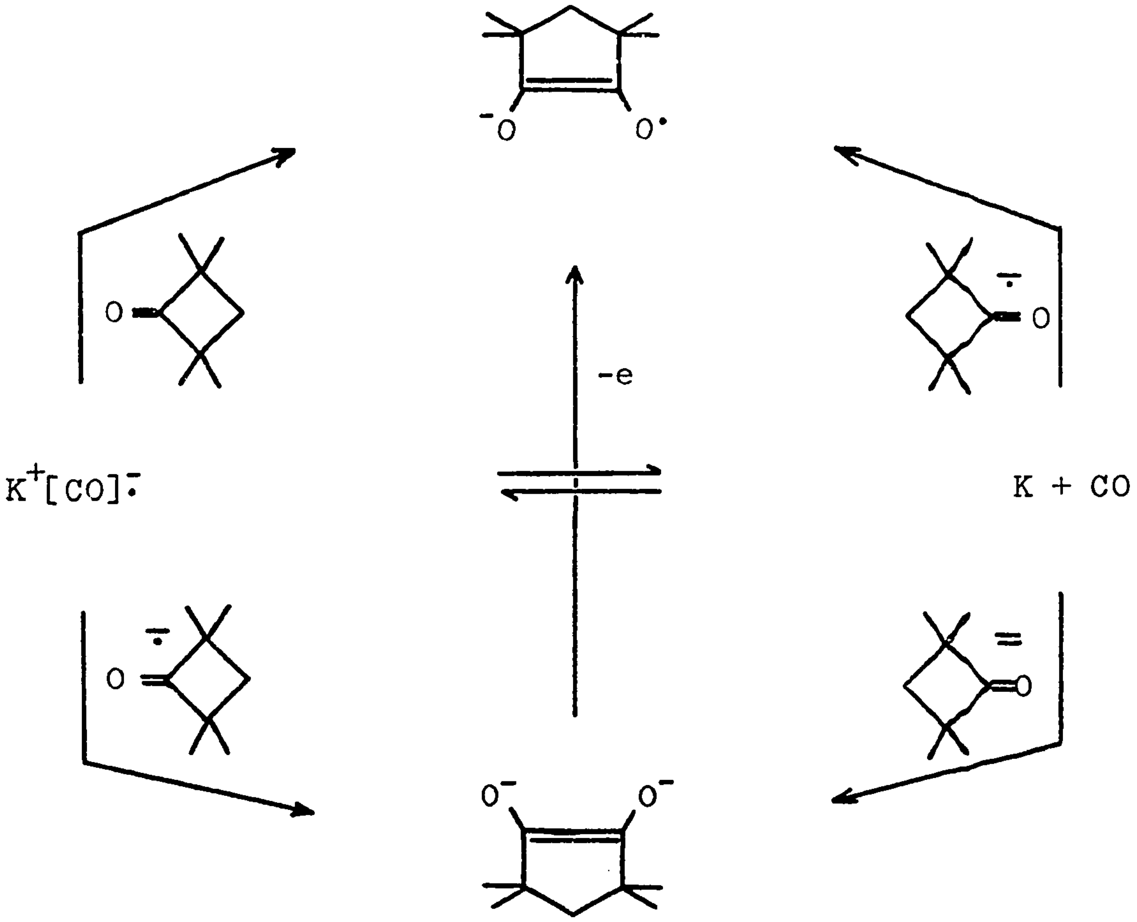
A possible explanation for this behavior is that a strained ketyl decomposes to yield CO or $K^{+}\,[CO]^{\cdot -}$ (Reactions 12 and 13); these might then undergo one of several insertion

$$R_2CO^{\cdot -}\,K^{+} \longrightarrow R{-}R + K^{+}\,[CO]^{\cdot -} \qquad (12)$$

$$R_2CO^{\cdot -}\,K^{+} \longrightarrow [R_2]^{\cdot -}\,K^{+} + CO \qquad (13)$$

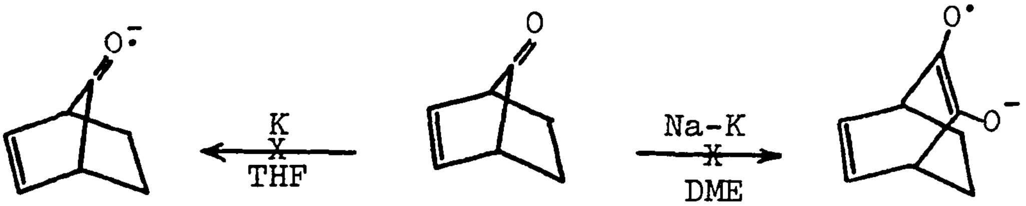
reactions with the ketone or ketyl to yield a diketone derivative (Scheme 8). Choice of the actual mechanism may be difficult, although the reaction bears some similarity to the rearrangement of α-hydroxy aldehydes observed in basic solution (27). A carbonyl insertion reaction was first communicated by the late Professor S. Winstein, who with his students observed that 7-ketobenzonorbornene **118** yielded benzobicyclo-[2.2.2]octane-2,3-semidione, **119**, upon reduction with alkali metal; semidione **119** had also been prepared by Russell, *et al.* (24). Attempts to observe the transformation of **120** into

Scheme 8.



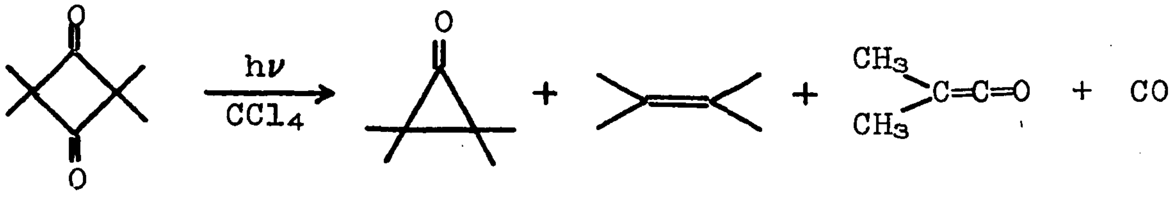
semidione 121 by ESR spectroscopy during alkali metal reduction were unsuccessful, in both this laboratory and Winstein's laboratory, and no radical identifiable as 122 could be observed.

118 119



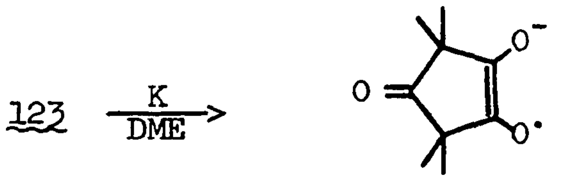
122 120 121

Expulsion of CO from strained ketones is a known photochemical process (124, 125); in particular, the photochemical decomposition of tetramethylcyclobutane-1,3-dione, 123, is a well-known reaction (125), and an efficient means of preparing tetramethylcyclopropanone, 124 (126, 127). Thus, the loss of CO or K^{+} $[CO]^{\overline{\cdot}}$ from 108 is not surprising.



123 124

An explanation to the observation of Ward (98) concerning the reduction of tetramethylcyclobutane-1,3-dione, 123, by alkali metal at 25°C in DME is also apparent now. The reported values of a^C (7.57, 5.0 G) are those expected for a semidione—and not a ketyl—on the basis of semidione ^{13}C-labeling experiments. By analogy with tetramethylcyclobutanone ketyl 108 and the photochemical reactions of 123, it appears that 123 might react to eventually yield 3,3,5,5-tetramethyl-1,2,4-cyclopentanesemitrione, 125. The likelihood of this explanation was supported by several observations besides the reaction analogy and a^C measurements: 1) An ESR spectrum identical to that reported by Ward, except for the absence of metal hfsc, was obtained by stirring 123 with Na-K alloy in DME—diethyl ether containing chlorotrimethylsilane, then removing an aliquot and mixing it with 20% *t*-butyl alcohol—80% DMSO containing a trace of potassium *t*-butoxide and recording its spectrum. Stability of an aliphatic ketyl radical anion under these conditions would be surprising. 2) Reduction of 123 with Na-K alloy in DME at room temperature yields the same radical obtained by the *in situ* acyloin condensation (33) of

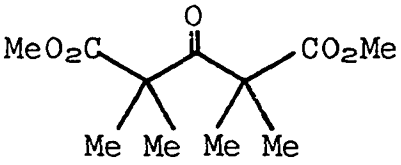


125

$a_\alpha^C = 5.0$ G
$a_\beta^C = 7.57$ G
$g = 2.00477$

dimethyl 2,2,4,4-tetramethyl-3-ketoglutarate 126 with Na-K alloy in DME at 25°C, $\underline{a}^{C} = 5.0, 7.6$ G ($\underline{a}^{M}$ not observed). Of

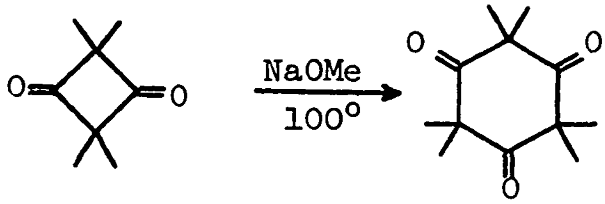
$$123 \xrightarrow[\text{DME}\ 25^{\circ}]{\text{Na-K}} R^{\dot{-}} \xleftarrow[\text{DME}\ 25^{\circ}]{\text{Na-K}}$$



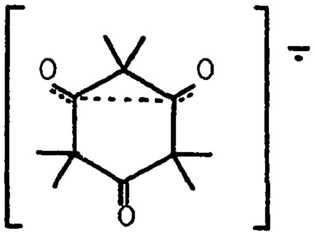
126

course, any conclusions about conjugation or electron transfer in 87 based on Ward's observations become meaningless.

A second structural possibility was also considered for the radical observed by Ward. Tetramethylcyclobutane-1,3-dione has been shown to yield hexamethylcyclohexane-1,3,5-trione, 127, in the presence of base at elevated temperatures



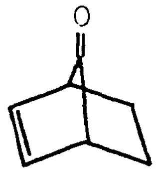
123 127



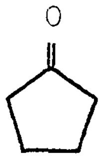
128

(128). Radical anion 128 has been postulated as an intermediate in the lithium-ammonia reduction of 127, where vic-cyclopropanediol derivatives were obtained (129). However, reduction by this worker of 127 in THF on a potassium mirror, either at room temperature or -80°C, produced no detectable ESR signal.

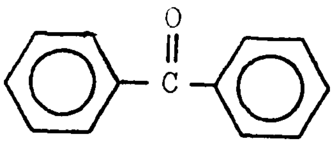
In an attempt to elucidate the carbonyl insertion mechanism further and possibly extend the utility of this reaction, the reactions of a variety of ketones with carbon monoxide under reduction conductions were investigated. Only compounds theoretically capable of giving a stable semidione product were examined, the reactions being monitored by ESR spectroscopy; the compounds studied are listed in Chart 4. Of these, only diisopropyl ketone, 131, yielded a product thought to



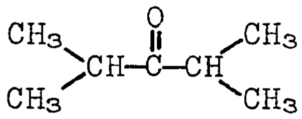
120



129



130

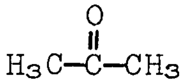


$$(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-CH(CH_3)_2$$

131

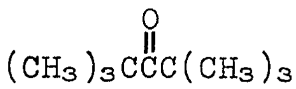
$(CH_3)_3CCHO$

132



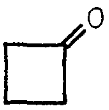
$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

133

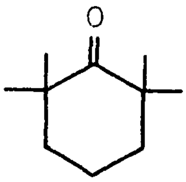


$$(CH_3)_3C\overset{O}{\overset{\|}{C}}C(CH_3)_3$$

134



135



136

Chart 4. Ketones treated with carbon monoxide.

possess a semidione structure when it was treated with Na-K alloy in DME at 25° while passing carbon monoxide through the solution at atmospheric pressure. The ESR spectrum of the resulting semidione was superimposable with that of authentic diisopropyl semidione (Figure 40). Diisopropyl ketone and Na-K alloy in DME at 25° in the absence of CO failed to give a detectable ketyl ESR signal. Other techniques attempted unsuccessfully were 1) reduction of carbon monoxide by potassium in liquid ammonia, followed by addition of DME, evaporation of NH_3, then treatment with a solution of the ketone in DME, and 2) generation of the ketyl radical anions, then reaction with carbon monoxide (for 130, 134 and 136) at atmospheric pressure.

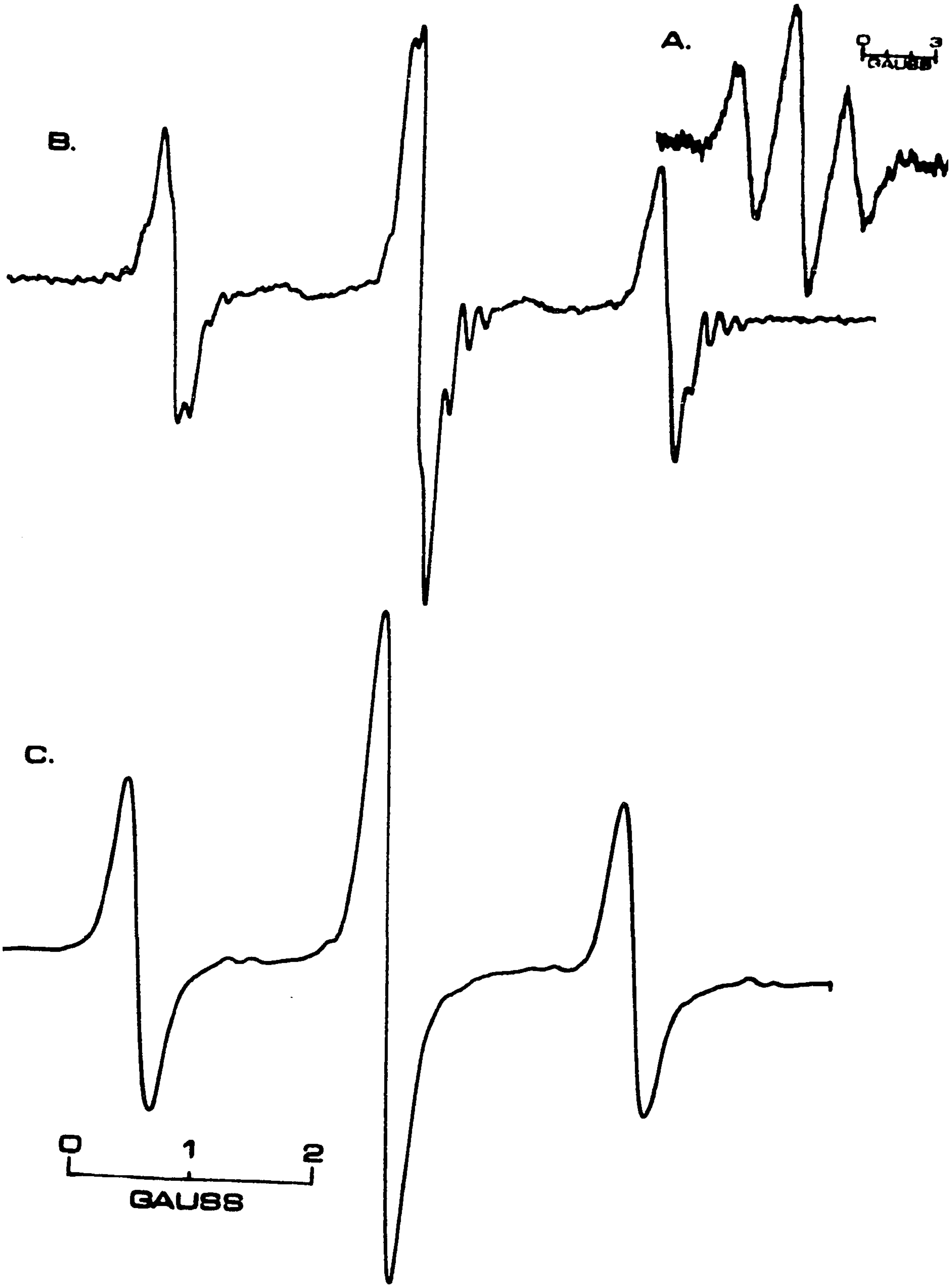
The reduction of CO by alkali metals is recognized to give potassium carbonyl (130) which dimerizes rapidly to form an ethynediol dianion, 137. Further condensation products

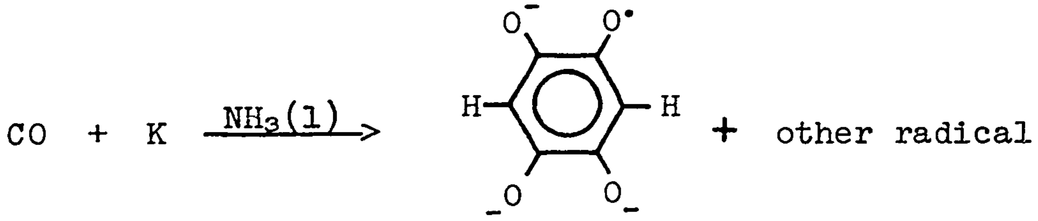
$$CO + K \xrightarrow{NH_3(l)} [OCCO]^{2-} \quad 2\ K^+$$

137

have been reported (131) and the solid compounds from the reaction between CO and K in liquid ammonia have been shown by ESR to contain a low concentration of two radicals (132). One of these radicals was identified as the potassium salt of 2,5-dihydroxy-1,4-benzosemiquinone, 138, while the other was thermally unstable and believed to be an open-chain radi-

Figure 40. First derivative ESR spectra of: (A) the radical anion obtained upon treatment of diisopropyl ketone with CO in DME-NaK alloy at room temperature, after 6 hrs; (B) the radical anion producing (A), upon dilution with dimethyl sulfoxide; (C) diisopropyl semidione, at high concentration, in DME-DMSO-potassium _t_-butoxide.


A.
0
3
GAUSS
B.
C.
0
1
2
GAUSS



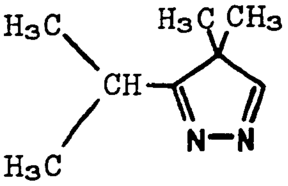
$\underline{a}^H = 0.8$ G

138

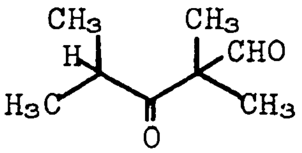
cal (132). This rapid formation of polymeric products makes questionable the likelihood of intervention by $K^+ [CO]^{\overset{\bullet}{-}}$ in the carbonyl insertion reaction, although it may have an appreciable lifetime and importance in very dilute solutions.

The ketyls of 130, 134 and 136 did not react with CO to produce semidiones, but the presence of an excess of CO destroyed their ESR signals. This was not surprising, since these ketyls are relatively stable at room temperature and have little apparent steric driving force for the formation of semidiones, unlike 108 or 87. However, ketone 131 also has little apparent driving force for the insertion of CO; its reaction was surprising.

The reaction of diisopropyl ketone with potassium naphthalenide in DME in the presence of carbon monoxide has been reported (133). The product, after quenching with acetic acid and treatment with hydrazine hydrate, was thought to be 3-isopropyl-4,4-dimethylpyrazole, 139, indicating that formylation of diisopropyl ketone occurred to give 140. No actual structural proof for 139 or 140 was given, other than inference



139

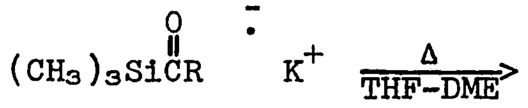


140

from the mass spectrum of 139. It is not obvious whether 140 or its derivatives are involved in the observed insertion of CO into 131, although such involvement may explain the failure of fully-substituted ketones to undergo insertion. The reactions of 108 and 87 are not explained at all by an α-formyl intermediate.

Considerably more work is necessary to clarify this chemistry, including study of the insertion reaction under a wide range of conditions. Product analyses may be of particular value in choosing a mechanism.

Yet another example of a ketone reduction eventually yielding a semidione has appeared (unrecognized) in the literature. Jones and West (61) have examined the ESR spectra of several trimethylsilyl ketyls, 141; at low temperature, the



$$(CH_3)_3Si\overset{O}{\overset{\|}{C}}R^{\overset{\cdot}{-}}\quad K^+ \xrightarrow[\text{THF-DME}]{\Delta}$$

$g \approx 2.0038$

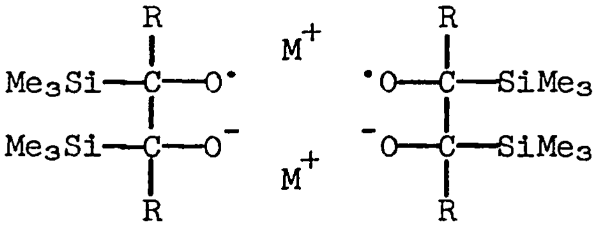
141

Secondary species:

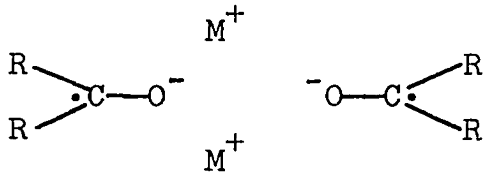
a) $a^H = 4.5(6H)$, $a^K = 1.3$ G($2K^+$), $g = 2.00459$ ($R = CH_3$).

b) $a^H = 2.38$ G(2H), $g = 2.00486$ ($R = CH(CH_3)_2$).

spectra were unquestionably due to structure 141. At higher temperatures, however, 141 disappeared and a new spectrum due to a secondary species was observed. The authors assigned to these radicals structure 142, largely by analogy with Hirota (56), who has shown evidence for the formation of ion quadruplets, 143, in ketyl solutions at elevated temperatures.



142



143

The assignment of structure 142 to the secondary species appears improbable for several reasons: 1) unlike 143, the secondary species does not revert to ketyl upon lowering the temperature; 2) pinacolate radical structures such as 142 might be expected to behave similarly to alkoxy radicals, RO•, which should have large, variable *g* and be impossible to detect in the liquid phase by ESR[1]; and 3) a^H in the secondary species are considerably larger than would be expected for a structure such as 142.

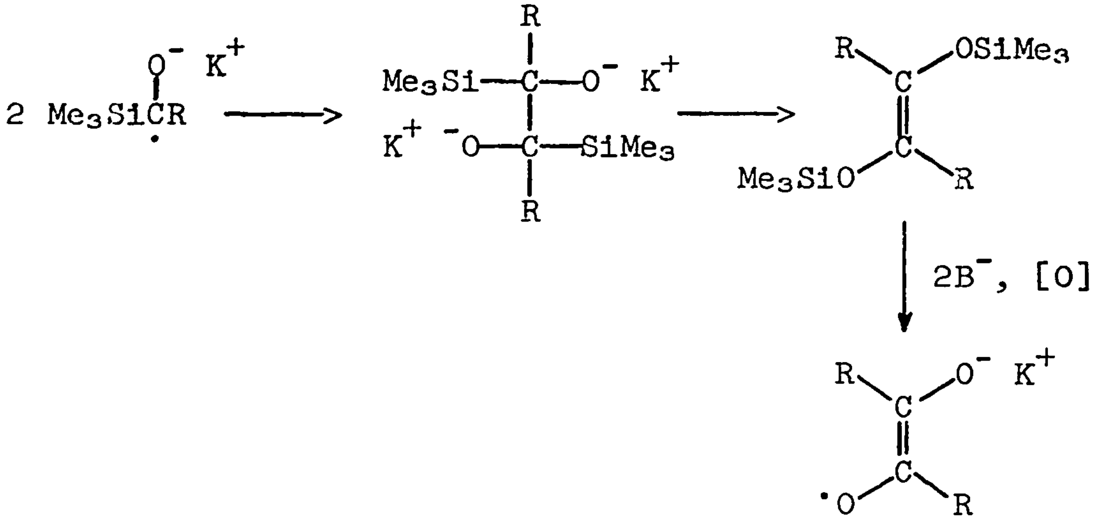
---

[1] Symons (134, 135) has commented upon various reports of ESR spectra from alkoxy radicals in solution and dismissed the likelihood of such observations.

The implication is strong that the secondary species may actually be a semidione, at least when R = $CH(CH_3)_2$. A *g*-value identical to that measured for diisopropyl semidione (Table 7) was observed, and the hfsc ~2.4 G is also consistent with either *cis*- or *trans*-diisopropyl semidione in an ethereal solvent. When R = CH_3, *cis*-dimethyl semidione appears unlikely, but a structure derived from dimethyl semidione (and/or biacetyl), such as the potassium salt of 2,5-dimethyl-1,4-benzosemiquinone, is possible; alternatively, potassium-*trans*-dimethyl semidione triple ion may be involved.

The authors considered the possibility that the secondary species in (a) was a rearranged dimer of methyl trimethylsilyl ketyl, and tested this hypothesis by reducing 2,3-bis-(trimethylsiloxy)-2-butene under identical conditions. A seven-line ESR spectrum, $\underline{a}^H = 7.4$ G (6H) was observed which was attributed to the siloxy olefin radical anion. The spectrum is recognized by this worker to be that of *cis*-dimethyl semidione, and an explanation for the formation of a secondary species is suggested (Scheme 9).

Scheme 9.



SUMMARY

Cis-*trans* isomers have been shown by ESR spectroscopy to exist for many acyclic aliphatic semidiones; the isomers generally differ in their hyperfine splitting constants, *g*-values and association with alkali metal ions. The ratio of *cis*- to *trans*-dimethyl semidione in static systems is apparently thermodynamically determined. Major factors affecting the *cis*-*trans* distribution of acyclic semidiones are alkyl-alkyl and alkyl-oxygen non-bonded interactions and ion-pairing/solvation effects. At least two distinct types of ion-pairs appear to be involved in semidione solutions. The *cis* semidione moiety presents a unique chelating anion, and contact ion pairs displaying metal hyperfine splitting are observed with small cations, even in highly polar solvents. Loose- and solvent-separated ion pairs probably occur with intermediate-sized cations.

Specific ^{13}C-labeling experiments have provided unambiguous assignments of a^{C} in acyclic semidiones, and detailed inferences of spin distribution and conformational phenomena are drawn from a^{C} and a^{O} using known semiempirical relationships.

Reactions of several cyclobutanones with reducing agents were shown to yield the cyclopentane semidiones as a product. Diisopropyl ketone in the presence of carbon monoxide and potassium also yielded the semidione.

EXPERIMENTAL

Methods

The ESR spectra in this work were obtained using either a Varian V-4502 spectrometer with 100 KHz field modulation and a 9-inch magnet, equipped with a Fieldial magnetic field regulator and V-4520 temperature controller, or by a Varian E-3 spectrometer with 4-inch magnet and 100 KHz field modulation. $\underline{g}$-Values were determined by placing a solution of Fremy's salt in a capillary alongside the sample in the spectrometer cavity (57). Splitting constants and field differences were measured with the Fieldial and calibrated against Fremy's salt, $\underline{a}^H = 13.00$ G, $\underline{g} = 2.00550 \pm 0.00005$.

Flat fused-silica cells (Varian V-4548 aqueous solution cells) were used with inverted U-type mixing cells, as in Figure 41, for ESR measurements of stable semidiones by methods previously described (136). Variable temperature spectra of stable semidiones were obtained using a Varian V-4548-1 cell and a U-type mixing cell; temperatures are accurate within ±3°C of the reported values. A fused-silica mixing cell (Varian V-4549) was employed in flow experiments with unstable semidiones. A diagram of the flow system is given in Figure 42 (A). Solutions of sample and base were degassed separately in large bottles, then run into the mixing cell through polyethylene tubing containing needle-valve regulators (Fisher and Porter Company); continuous mixing took

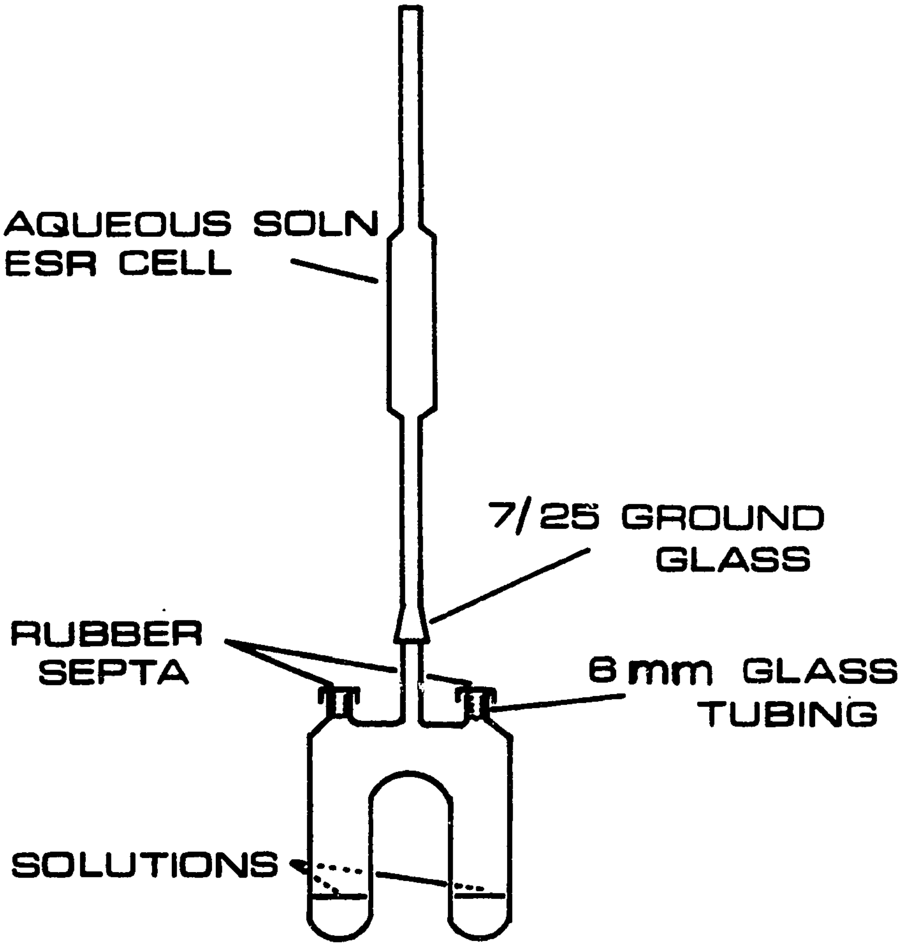


Figure 41. ESR cell and U-type mixing cell used with solvents of high dielectric constant.

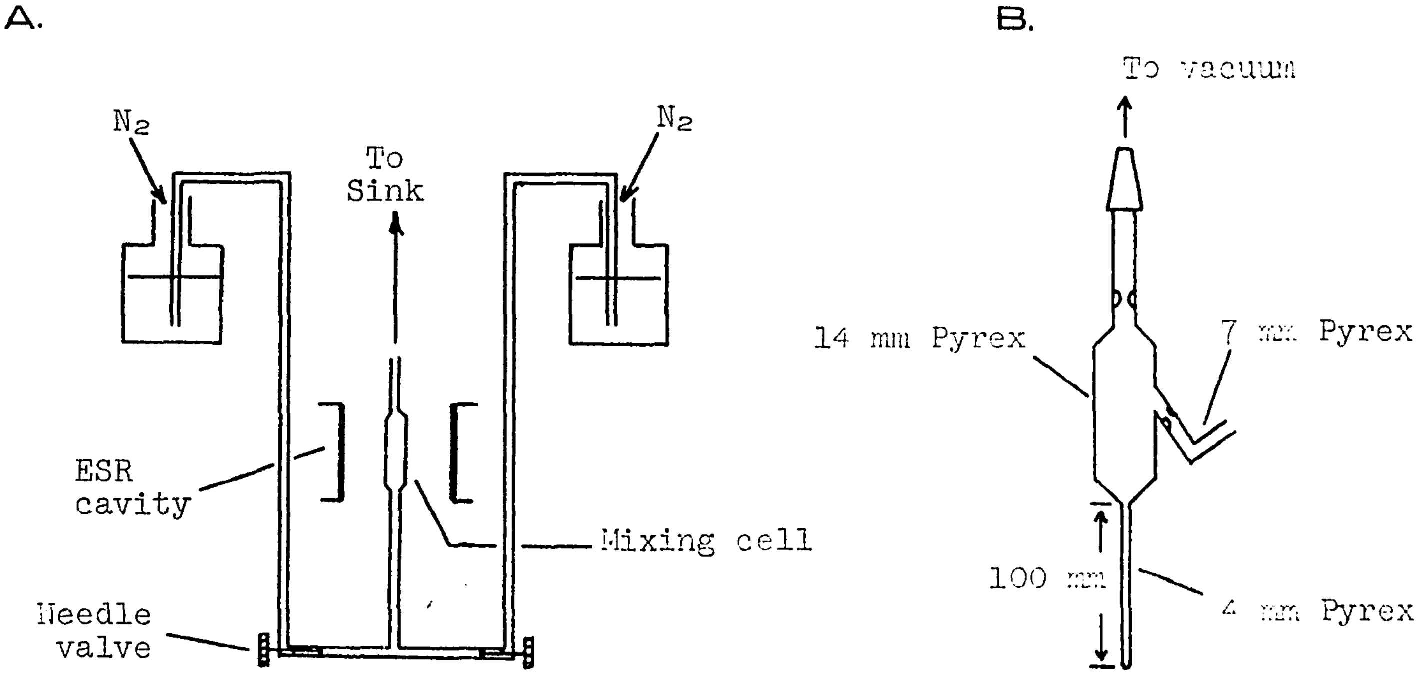


Figure 42. Apparatus for radical anion generation: (A) schematic diagram of flow system used with unstable semidiones; (B) low-temperature reduction vessel.

place within the spectrometer cavity. A technique similar to this has been described by Dixon and Norman (137).

Low temperature alkali metal reductions were performed by use of a 14 x 100 mm tube fitted with a 4 x 100 mm Pyrex sidearm and a 7 x 75 mm open sidearm (Figure 42 (B)). A small pellet of alkali metal was added to the open sidearm, which was then sealed. Ketone was placed into the 4 mm tube and cooled to -80°C. The apparatus was evacuated to 10^{-6} Torr and the metal distilled to form a mirror in the main reaction tube. The 75 mm sidearm was removed and solvent vacuum-transferred from Na-K alloy into the vessel to give a final ketone concentration $\sim 10^{-3}$M. The vessel was then sealed, removed from the vacuum line, cooled to -80°C and inverted to mix the ketone and the solvent over the metal mirror. The radical anion solution was returned to the 4 mm tube and the tube inserted into a spectrometer cavity pre-cooled to -80°C.

IR spectra were obtained using a Perkin-Elmer Model 21 Double Beam Infrared Spectrophotometer; some routine spectra were recorded with a Perkin-Elmer "Infracord" Spectrophotometer. NMR spectra were obtained using either a Varian A-60 NMR spectrometer or Perkin-Elmer/Hitachi R-20B NMR Spectrometer with a ^{1}H probe. Mass spectra were obtained with an Atlas CH-4 spectrometer. An Aerograph Model A-90-P Manual Temperature Programmer Gas Chromatograph was used for vapor phase chromatography (VPC). Melting points were determined with a Meltemp apparatus in capillary tubes and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc.

Analysis of Data

Ratios of isomeric radicals within a mixture were taken to be the ratio of their first-derivative peak heights, between extrema, for lines of the same degeneracy when the linewidths and lineshapes were very similar. Thus, trans/cis represents a maximum limit where cis lines are slightly broader than trans lines, as in some semidiones with sodium gegenion. When one isomer's lines were noticeably broader, the isomeric ratio was taken as the ratio of (peak height) x $(\text{linewidth})^2$ for lines of the same degeneracy. With semidione mixtures having extremely disparate isomeric concentrations, lines of the same degeneracy could not be compared; instead, the isomeric ratio was taken as the ratio of (peak height) ÷ (degeneracy) for the lines compared. Ratios are the averages of at least three separate measurements.

g-Values were calculated from Equation 15, where ΔH is

$$g = 2.00550\ (1 - \frac{\Delta H}{3370}) \qquad (15)$$

the field difference between the center of spectra of Fremy's salt and the unknown, taken to be positive when the unknown occurs at higher field.

Computer linear least squares calculations and plots were obtained with programs of the Iowa State University Chemistry Department, using the University's computation facilities.

Materials

Solvents

General solvents were used as obtained commercially, without further purification. Solvents for which high purity was required were dried and purified by appropriate methods and stored over Linde Type 4A Molecular Sieves in glass-stoppered vessels. THF and DME to be used for solutions of radical ions were distilled once from potassium, then from lithium aluminum hydride onto Na-K alloy under nitrogen. This mixture was degassed under vacuum and stirred until a blue color appeared; it was subsequently stored and transferred under high vacuum.

Reagents

Commercial acetoin was obtained as an 85% aqueous solution and purified by extraction with chloroform, drying over sodium sulfate, then vacuum distillation (bp 75-80° at 25-30 Torr). The purified acetoin was stored over Linde Type 4A Molecular Sieves. Semidione solutions approximately 0.057 M in acetoin were prepared from this reagent. Sodium and potassium alkoxides were prepared by reaction of the metal and alcohol in refluxing toluene, followed by removal of solvent and vacuum drying. Lithium alkoxides were prepared from the reaction of sec-butyllithium with the alcohol in n-hexane. Commercial potassium t-butoxide was sublimed (150° at 0.25 Torr) and stored in a desiccator. Cesium- and rubidium t-butoxides were stored in a desiccator and used without further treatment. Na-K alloy was prepared by mixing the pure metals, in the desired ratio by weight, in refluxing DME. The alloy was transferred by means of a pipette and stored in a glass-stoppered vessel under DME which had been distilled from lithium aluminum hydride. Tetramethylcyclobutane-1,3-dione was sublimed before use.

2,3,11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6)

The macrocyclic polyether was prepared by Method X of Pedersen (92). Crude crystals (mp 160-162°, containing sodium chloride) were sublimed (150°-160° at 0.75 Torr) to give pure compound, mp 164° (lit (92) mp 164°); PMR ($CDCl_3$) δ 6.87 (s, 8), 4.1 (m, 16); Mass Spectrum (70 eV) mol wt 360; found M^+ = 360.

2,3,9,10-Dibenzo-1,4,8,11-tetraoxacyclotetradeca-2,9-diene (dibenzo-14-crown-4)

Pedersen's Method W was followed (92, 138), yielding white crystals, mp 149-150° (lit (92) mp 150-152°); the compound was vacuum-dried before use.

1-Chloro-3-methyl-2-butanone

This compound was prepared by the procedure of Asinger, *et al*. (139), following the general method of Eistert (140); bp 62-66° at 15 Torr (lit (139) bp 56-58° at 9 Torr); PMR (CCl_4) δ 4.25 (s, 2), 2.98 (m, 1, $J = 6$ Hz), 1.16 (d, 6, $J = 6$ Hz); IR (neat) 3.4, 5.7, 8.4, 8.7, 13.22 μ; Mass Spectrum (70 eV) mol wt 120; found $M^+ = 120$, Cl isotope at 122.

1-Bromo-3,3-dimethyl-2-butanone

This compound was prepared by the procedure of Charpentier-Morize (141), according to the method of Jackman, *et al*, (142); bp 78-85° at 15 Torr (lit (141) bp 85-57° at 20 Torr); PMR (CCl_4) δ 4.17 (s, 2), 1.14 (s, 9) (lit (143) PMR (CCl_4) δ 4.23 (s, 2), 1.22 (s, 9)).

2,5-Dihydroxy-3,6-diphenyl-1,4-dioxacyclohexane (mandelaldehyde dimer)

This compound was prepared from the methyl mercaptal of phenylglyoxal by the method of Russell and Ochrymowycz (144); mp 136-137° (lit (144) mp 137-138°).

Dibromoethylene carbonate

To a stirred mixture of 5 g (0.058 mole) vinylene carbonate and 200 ml CCl_4 was added 9.3 g bromine. After stirring overnight, the solvent and excess bromine were removed under vacuum. The resulting crude mixture was shown to containe 60% dibromoethylene carbonate, PMR ($CDCl_3$) δ 6.79; IR (mixture, neat) 3.17, 13.9 μ and 40% vinylene carbonate, PMR ($CDCl_3$) δ 7.21; IR (mixture, neat) 3.30 μ. The mixture was not purified, but was used directly for ESR experiments.

2-Hydroxy-3-hexanone

Unsymmetrical acyloins could be prepared by the reaction of Grignard reagents with cyanohydrins (60).

A 100 ml round-bottomed flask, fitted with an efficient condenser, dropping funnel, magnetic stirrer and nitrogen inlet was flame-dried and charged with 1.2 g (0.05 mole) magnesium turnings. The metal was covered with 10 ml anhydrous ether, and a small portion of 1-iodopropane (8.5 g, 0.05 mole) was added to initiate the reaction. The remainder of the 1-iodopropane was diluted with 20 ml ether and added at a rate sufficient to maintain a reflux. After addition the mixture was refluxed for three hours, cooled, and 1.7 g (0.025 mole) acetaldehyde cyanohydrin (lactonitrile) was added slowly.

After refluxing overnight, the salts were hydrolyzed with a 10% aqueous H_2SO_4 solution, the organic layer was separated, and the aqueous solution was extracted twice with 50 ml portions of $CHCl_3$. The combined organic phases were washed three times with 25 ml portions of saturated sodium chloride. After drying (Na_2SO_4) and removal of solvent under vacuum, the residue was distilled under vacuum. A major fraction of 2.5 g (83% of theor., based on cyanohydrin) was collected, bp 90-103° at 15 Torr. This fraction was analyzed by VPC

(15% DEGS, 5' x ¼" column, 140°) and found to contain at least three components. PMR and IR of the crude mixture suggested the presence of 2-hydroxy-3-hexanone, its isomer, 3-hydroxy-2-hexanone, and the oxidation product, hexane-2,3-dione. IR (mixture, neat) 2.92, 3.40, 5.86, 6.85, 8.95 μ; Mass Spectrum (70 eV) mol wt 116; found $M^+-2=114$; Calc. for $C_6H_{12}O_2$: C, 62.02%; H, 10.42%; found: C, 60.01%; H, 10.21%.

5,5-Dimethyl-2-hydroxy-3-hexanone

The procedure was essentially the same as in the preparation of 2-hydroxy-3-hexanone. The Grignard reagent was prepared from 1-chloro-2,2-dimethylpropane (neopentyl chloride). Yield of crude acyloin, 55%; bp 95-105° at 15 Torr (bp 145° at 742 Torr). The product was analyzed by VPC (15% QF-1; 5' x ¼" column, 100°) and found to contain a mixture of the desired product, its isomer, 5,5-dimethyl-3-hydroxy-2-hexanone, and the product of oxidation, 5,5-dimethylhexane-2,3-dione, plus a considerable amount of 2,2-dimethyl butan-4-ol arising from reaction of the Grignard reagent with decomposed acetaldehyde cyanohydrin. A mixture of isomeric acyloins and α-diketone was separated from the alcohol by VPC, but was not purified further. IR (mixture, neat) 2.93-3.05, 3.40, 5.87 (shoulders, 5.83, 5.90) μ; Mass Spectrum (70 eV) mol wt 144; found $M^+-2=142$, base peak at m/e = 57.

2,3-bis(Trimethylsiloxy)-2-butene

The procedure followed for this compound was a modification of the methods of Rühlmann, *et al*. (59, 145). Anhydrous ether (15 ml), 1.8 ml sodium-potassium alloy (1:5, w/w) and 5.7 ml freshly distilled chlorotrimethylsilane were stirred under nitrogen at 0° in a 50 ml flask. Ethyl acetate (2.0 g, 0.023 mole) in twice its volume of anhydrous ether was added dropwise with stirring, and stirring at 0° was continued for 25 min after addition.

The suspension was filtered, taking care to keep the salts from becoming dry. Solvent and low-boiling components were removed under vacuum; distillation of the residue gave a 2.5 g fraction, bp 65-75° at 12 Torr (lit (59) bp 69-73° at 12-13 Torr). This fraction was found to contain three components, which were separated by preparative VPC (20% SF 96, 13' x $\frac{3}{8}$", 150-160°): fraction A (ret. time, 5 min) *unidentified*, Mass Spectrum, $M^+ = 220$; fraction B (ret. time, 10 min), *cis-2,3-bis(trimethylsiloxy)-2-butene*, PMR (CCl_4, 1% benzene std.) δ -5.56 (s, 6), -7.14 (s, 18); IR (neat) 3.41, 5.94, 7.23, 8.04 (shoulder, 7.96), 8.21, 8.92, 9.97 (*cis* C=C), 11.23, 11.90, 13.2-13.4 μ; Mass Spectrum (70 eV) mol wt 232; found $M^+ = 232$ (M^+ = base peak), other significant peak at m/e = 217 ($M^+ - 15$); Calc. for $C_{10}H_{24}Si_2O_2$: C, 51.67%; H, 10.41% Si, 24.16%; found: C, 51.14%; H, 10.28%, Si 23.01%; fraction C (ret. time, 12 min), *trans(?)-2,3-bis(trimethylsiloxy)-2-butene*, PMR (CCl_4, 1% benzene std.) δ -5.56, -7.12;

Mass Spectrum (70 eV) mol wt 232; found $M^+ = 232$ (M^+ = base peak), significant peak at $m/e = 217$ ($M^+ - 15$). The ratio of fraction B to fraction C was approximately 19:1. The pure compounds could be stored in a desiccator in tightly sealed glass bottles for an indefinite period of time; however, exposure to moist air for several days caused hydrolysis of the ethers, yielding a mixture of acetoin, biacetyl and silicon-containing residues.

2,3-bis(trimethylsiloxy)-2-butene-2-^{13}C

Ethyl acetate-1-^{13}C was prepared from acetic acid-1-^{13}C (51.5% ^{13}C) by the method of Ropp (146). A solution of 3.6 g (0.043 mole) $NaHCO_3$ in 10 ml water was stirred in a 25 ml pear-shaped flask, and 2.5 g (0.042 mole) acetic acid (composed of 0.5 g acetic acid-1-^{13}C and 2.0 g unlabeled acetic acid) in 5 ml ether was added cautiously. When the effervescence ceased, the mixture was heated at 150° until dry. Xylene was added and distilled 10 times in 5 ml portions to azeotropically dry the salt. The salt was dried further by heating under vacuum at 200° for 30 min.

The salt was cooled, and 12.5 g (0.069 mole) triethylphosphate was added. A fractionating column was placed on the flask, and the flask was heated to 180°. Collection of ethyl acetate-1-^{13}C over one hour gave 3.0 g, 81.5%, bp 76°; PMR (neat) $J_{C-H} = 7$ Hz, intensity indicating ~10 atom % ^{13}C (only J_{CH} observed).

The acyloin condensation in the presence of chlorotrimethylsilane was performed as previously described for unlabeled 2,3-bis(trimethylsiloxy)-2-butene. A low yield (less than 1 g) of the 2-^{13}C-diether was obtained and the 65°-75° fraction was used for ESR experiments without further purification.

3-Hydroxy-2-butanone-1-^{13}C (acetoin-^{13}C)

This compound was prepared by Gauthier's method (60). Trial syntheses using unlabeled materials gave a product identical in all respects to authentic acetoin.

A flame-dried 100 ml round-bottomed flask fitted with an efficient condenser, dropping funnel, nitrogen inlet and a powerful magnetic stirrer was charged with 0.85 g (0.0354 mole) magnesium turnings. Anhydrous ether sufficient to cover the turnings was added, and the reaction was initiated by the addition of five drops unlabeled methyl iodide. The remainder of the methyl iodide, consisting of a mixture of 1.0 g $^{13}CH_3I$ (50.6 atom % ^{13}C) and 4.0 g unlabeled CH_3I (total 5 g CH_3I, 0.0352 mole), was diluted with 2.5 ml anhydrous ether and added to the flask at a rate sufficient to maintain a moderate reflux. The mixture was refluxed with stirring for one hour after addition was complete.

The mixture was cooled, and 1.35 g (1.35 ml, 0.0176 mole) lactonitrile in an equal volume of anhydrous ether was added slowly. The mixture was refluxed for three hours, then cooled. The salts were hydrolyzed cautiously with 20 ml 3 N HCl. The ether layer was separated, and the aqueous phase extracted four times with 25 ml $CHCl_3$. The chloroform extracts were combined with the ether layer, washed once with 25 ml saturated NaCl, and filtered through Na_2SO_4 to dry. After removing solvent, the residue was distilled under vacuum to give 1.1 g (70%) acetoin-1-^{13}C, bp 70-80° at 25-30 Torr; PMR (neat) J_{C-H} = 128-130 Hz, estimated 10.9 atom % ^{13}C; Mass Spectrum (70 eV) m/e (relative intensity): unlabeled, 88 (100), 89 (7.9), 90 (3.9); 1-^{13}C, 88 (100), 89 (18.3), 90 (4.3), indicating 10.4 atom % ^{13}C.

4-Hydroxy-3-hexanone-1-^{13}C (propioin-^{13}C)

A procedure identical to the preparation of acetoin-1-^{13}C was followed, substituting the following reagents: iodoethane (3.12 g, 0.02 mole, composed of a mixture of 1.0 g iodoethane-2-^{13}C, 56% ^{13}C, and 2.12 g unlabeled iodoethane), 0.5 g (0.02 mole) magnesium turnings, 0.77 g (0.01 mole) propionaldehyde cyanohydrin. The synthesis yielded 0.5 g propioin-1-^{13}C (43% yield based on cyanohydrin), bp 50-60° at 10 Torr (lit (59) bp 60° at 12-13 Torr). The product was identical to an authentic sample of propioin. Analytical samples were prepared by VPC (20% Carbowax, 6' x ¼", 150°); PMR (CCl_4) 4.02 (t, 1, broad), 3.43 (s, 1), 2.45 (q, 2, J = 7 Hz), 1.63 (m, 2, J_A = 7 Hz), 1.08 (t, 3, J = 7 Hz, J_{C-H} = 125 Hz), 0.9 (t, J = 7 Hz); Mass Spectrum (70 eV) mol wt 116; unlabeled, found (rel. intensity): 114 (100, M^+ -2), 115 (12.8), 116 (79, M^+), 117 (5.45); propioin-1-^{13}C, found (rel. intensity): 114 (100, M^+ -2), 115 (32.1), 116 (90.4, M^+), 117 (19.3), base peak = 59. Estimated 15-20% ^{13}C.

2-Methyl-4-pentanone-1-^{13}C

This compound was prepared from 3-penten-2-one (147) by the method of House, et al. (148). Methyl magnesium iodide-^{13}C was prepared as described in the synthesis of acetoin-^{13}C from 1.0 g $^{13}CH_3I$ (50.6 atom % ^{13}C), 3.8 g unlabeled CH_3I (combined, 0.034 mole) and 1.2 g magnesium turnings. Upon generation, the Grignard reagent was added to a slurry of 6.3 g (0.033 mole) cuprous iodide in anhydrous ether at -80° via a stainless steel tube. All reactions and transfers were performed under prepurified nitrogen. This mixture was stirred well for 10 min until it became a uniform canary yellow, then 1.94 g (0.022 mole) of 3-penten-2-one was added rapidly. The mixture was allowed to stir for 15 min at -80°, then for one hour at 0°.

The reaction was quenched by the addition of cold methanol-water at 0°, and neutralized by the addition of cold, saturated NH_4Cl until a salt separated. The ether was decanted and the salts were washed twice with 25 ml ether. The combined extracts were dried ($MgSO_4$), then distilled through a 150 cm Vigreaux column to give 1.0 g (0.01 mole, 45%) 2-methyl-4-pentanone-1-^{13}C, bp 115-123° (lit (148) bp 119°).

The PMR spectrum of the product was identical to that of an authentic sample of methyl isobutyl ketone, with ^{13}C satellites in evidence about the doublet at δ (CCl_4) 0.93, J_{C-H} = 125 Hz; estimate 8-10% ^{13}C.

1-Carboethoxyadamantane

This ester was prepared quantitatively from the acid chloride by refluxing in absolute ethanol for two days, bp 70-80° at 2 Torr, PMR (CCl_4) δ 4.05 (q, 2), 1.72-1.88 (broad, m, 15), 1.21 (t, 3); IR (neat) 3.46, 5.81, 6.89, 8.12, 9.32 μ; Mass Spectrum (70 eV) mol wt 208; found M^+ = 208, other predominant peaks at m/e 179, 135 (base peak); Calc. for $C_{13}H_{20}O_2$: C, 74.96%; H, 9.68%; found: C, 74.85%; H, 9.64%.

3-Hydroxy-2-butanone-^{17}O (acetoin-^{17}O)

Exchange studies with ^{18}O (149, 150). The incorporation of ^{18}O into 3-hydroxy-2-butanone was studied in some detail before experiments with ^{17}O were attempted. Since a sample of ^{17}O-enriched H_2O (15.5% $H_2{}^{17}O$) was available, exchange in the system acetoin-water was chosen for the incorporation technique. In a thick-walled capillary tube was placed 35 μl acetoin and 15 μl $H_2{}^{18}O$ (80% $H_2{}^{18}O$); after sealing, the tube was immersed in a 150° bath for three days. Upon cooling, the tube was opened and its contents were separated by VPC (20% DEGS, 5' x ¼", 100°, 25 μl injections), yielding approximately 6 μl acetoin-^{18}O; Mass Spectrum (20 eV) 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); blank, 93-91 nil, 90 (1), 89 (10.6), 88 (100), 87 (16.3), 86 (41.5); (16 eV): m/e 93 (2.41), 92 (29.3), 91 (9.8), 90 (100), 89 (9.8), 88 (92.6), 87 (2.4), 86 (24); blank, 93-91 nil, 90 (0.72), 89 (10), 88 (100), 87 (14.3), 86 (37.2). Mass spectral data were consistent with acetoin containing the following amounts of ^{18}O: 30% 0-^{18}O, 48% 1-^{18}O, 22% 2-^{18}O. Interpretation of mass spectra by Dr. T. H. Kinstle, Iowa State University, is most gratefully acknowledged.

The possibility of rapid oxygen exchange between semidione and dimethyl sulfoxide was investigated by mass spectral analysis of mixtures of acetoin-^{18}O/DMSO and acetoin-^{18}O/DMSO/potassium t-butoxide. A 2 μl portion of acetoin-^{18}O prepared above was mixed with 2 μl DMSO and allowed to stand two hrs; Mass Spectrum (20 eV) mixture, 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); neat acetoin-^{18}O, 93 (2.8), 92 (31), 91 (9.9), 90 (100), 89 (9.9), 88 (92), 87 (2.8), 86 (25.4). A second 2 μl portion of acetoin-^{18}O was mixed with 2 μl DMSO containing a trace of potassium t-butoxide and allowed to stand two hours; Mass Spectrum (20 eV) mixture, m/e (rel. intensity), 93 (2.1), 92 (23.2), 91 (8.5), 90 (85), 89 (8.5), 88 (100), 87 (4.3), 86 (29.8); neat acetoin-^{18}O blank, 93 (2.8), 92 (31), 91 (9.9), 90 (100), 89 (9.9), 88 (92), 87 (2.8), 86 (25.4); unlabeled mixture, 93-90 nil, 89 (7.3), 88 (100), 87 (4.9), 86 (42.6), indicating considerable oxygen loss to solvent.

Oxygen-17-incorporation. Into a thick-walled capillary tube was placed 30 μl acetoin and 15 μl $H_2{}^{17}O$ (15.5% ^{17}O). The tube was sealed and heated at 150° for three days. After cooling, the tube was opened and samples of acetoin were prepared by VPC (see above) directly into H-type mixing cells. ESR experiments indicated satisfactory isotopic incorporation; the relative intensity of ^{17}O satellites to ^{1}H hyperfine lines diminished gradually with time.

2,2,4,4-Tetramethylcyclobutanone

This compound was prepared in 20% yield by the method of Herzog and Buchman (151) through the incomplete Wolff-Kishner reduction of 2,2,4,4-tetramethylcyclobutane-1,3-dione bis-semicarbazone. The ketone had bp 120-128° (lit (151) bp 128.5-129°); IR (neat) 3.35, 5.60, 6.84, 7.30, 9.75 μ; PMR (CCl_4) δ 1.17 (s, 12), 1.75 (s, 2); Mass Spectrum (70 eV) mol wt 126; found $M^+ = 126$. The ketone gave a 2,4-dinitrophenylhydrazone derivative with mp 114-115° (lit (151) mp 115-116°); Mass Spectrum (70 eV), found $M^+ = 306$.

2,2,6,6-Tetramethylcyclohexanone

A modification of the procedure of Haller and Cornubert (152) was used to prepare this compound. A 500 ml round-bottomed flask, fitted with reflux condenser, dropping funnel, magnetic stirrer and nitrogen inlet was flame-dried and charged with 3.5 g (0.09 mole) of sodium hydride in 150 ml of anhydrous ether. The suspension was stirred and 3.9 g (0.04 mole) of freshly distilled cyclohexanone in 10 ml of anhydrous ether was added rapidly; upon addition, the mixture was refluxed for 2 hrs. After cooling, a solution of 12.1 g (0.086 mole) of CH_3I in 10 ml anhydrous ether was added rapidly and the mixture was refluxed for 2.5 hrs. Upon cooling another 3.5 g (0.09 mole) of sodium amide was added and the mixture was refluxed for 5 hrs; then 12.1 g (0.086 mole) of CH_3I in 20 ml anhydrous ether was added, and the mixture was refluxed for 24 hrs.

The suspension was poured into 200 ml of ice-water and the layers were separated. The organic phase was washed three times with 15 ml of 10% H_2SO_4, three times with 15 ml of 10% $NaHCO_3$, and finally with water. The aqueous phase was extracted with methylene chloride, and the extracts washed as described. The combined extracts were dried ($MgSO_4$) and solvent was removed under vacuum. Chromatography of the residue (silica gel, 3 chloroform: 1 hexane, v:v) gave 6.0 g (93%) of desired product. Distillation under vacuum gave a colorless liquid, bp 102-104° at 60 Torr (lit (152) bp 100° at 57 Torr); PMR (CCl_4) δ 1.70 (s, 6), 1.07 (s, 12); IR (neat) 3.44 (shoulder, 3.50), 5.92, 6.83, 9.73 μ; Mass Spectrum (70 eV) mol wt 154, $M^+ = 154$, other significant peaks at m/e = 82 (base peak), 56.

2,2,5,5-Tetramethylcyclopentanone

The procedure followed in the preparation of this compound was that of Conia (153). A low yield (<10%) of the ketone was obtained after fractional distillation, bp 155°. Samples for ESR experiments and analyses were prepared by VPC (15% Carbowax 1500, 5' x ¼", 160°); PMR (CCl_4) δ 1.74 (s, 4), 1.00 (s, 12) (lit (154) PMR: δ 1.02, 1.73); IR (neat) 3.37, 3.48, 5.74, 6.83 9.76 μ (lit (154) IR: 5.74 μ); Mass Spectrum (70 eV) mol wt 140; found $M^+ = 140$, other significant peaks at m/e 72, 69 (base peak), 57. A yellow 2,4-dinitrophenylhydrazone derivative was prepared, mp 136-138°.

2,2,7,7-Tetramethylcycloheptanone

This ketone was prepared by the procedure described for 2,2,6,6-tetramethylcyclohexanone (152), bp 124-126° at 59 Torr; PMR (CCl_4) δ 1.62 (s, 8), 1.12 (s, 12); IR (neat) 3.38 (shoulder, 3.51), 5.95, 6.78, 6.89, 7.24, 9.51 μ. Samples for ESR experiments and microanalyses were prepared by VPC (20% QF-1, 5' x ¼", 130°); Mass Spectrum (70 eV) mol wt 168; found $M^+ = 168$; Calc. for $C_{11}H_{20}O$: C, 78.50%; H, 11.99%; found: C, 78.35%; H, 11.86%.

3,3,5,5-Tetramethylcyclopentanedione

A mixture of 25 ml isopropenyl acetate, 0.1 g of p-toluenesulfonic acid and 2.9 g (0.02 mole) of 2,2,4,4-tetramethylcyclopentan-1-one was heated at 90° with stirring; acetone was distilled as it formed. When acetone formation ceased, the remaining isopropenyl acetate was removed by distillation and the residue was fractionally distilled to give 3.0 g of the crude enol acetate, bp 70-90° at 20 Torr; PMR (CCl_4) δ 5.33 (s, 1), 2.15 (s, 2), 2.08 (s, 3), 1.08-1.11 (m, 12) (the presence of ca. 25% unreacted starting ketone was also indicated, PMR (CCl_4) δ 2.14 (s, 2), 1.75 (s, 2), 1.10 (s, 6), 1.06 (s, 6)). The crude distillate was dissolved in 150 ml $CHCl_3$, and bromine was added dropwise to the heated $CHCl_3$ solution until its color persisted. The solvent and excess bromine and HBr were removed under vacuum, and the residue was dissolved in 100 ml of dry DMSO and stirred vigorously for 2 days. The solution was then diluted to 700 ml with water and extracted four times with 100 ml of ether. The combined ether extracts were washed twice with brine, then dried ($MgSO_4$).

The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, 1 CH_2Cl_2/4 hexane, v/v) to give 0.32 g of orange diketone, mp 91-92° (lit (155) mp 92-93°).

Dimethyl 2,2,4,4-tetramethyl- -ketoglutarate

This diester was prepared according to the procedure of Murin, *et al.* (156). bp 88-89° at 2 Torr (lit (156) bp 93-94° at 3 Torr); PMR (CCl_4) δ 3.65 (s, 6). 1.32 (s, 12).

2,2,4,4,6,6-Hexamethylcyclohexane-1,3,5-trione

A mixture of 10 g (0.07 mole) of 2,2,4,4-tetramethylcyclobutane-1,3-dione, 15 ml of toluene and 0.5 g of sodium methoxide was heated to 85-90° slowly. The mixture was then refluxed for two hours and distilled to give three fractions: A, 1.5 g, bp <210°, mp 65-73°; B, 2.3 g, bp 210-230°, mp 72-78°; C, 2.5 g, bp 235-245°, mp 78-80° (lit (128) mp 78-80°). Recrystallization of fraction C from ethanol gave needles, mp 79° (lit (128) mp 80°).

Bicyclo[2.2.1]hept-2-en-7-one

This ketone was prepared from hexachlorocyclopentadiene by the method of Gassman and Marshall (157), bp 90-95° at 107 Torr (lit (157) bp 96-100° at 115 Torr; PMR (CCl_4) δ 1.17 (m, 2), 1.91 (m, 2), 2.72 (m, 2), 6.49 (m, 2). Samples were prepared by VPC (20% SF 96, 5' x ¼", 100°) for ESR experiments.

Sources of Chemicals

Metal *t*-butoxides: Mine Safety Appliance Research Corporation. Acetoin, glycolaldehyde, vinylene carbonate, 4,4-dimethyl-2-pentanone, 5-methyl-2-hexanone, 1-adamantyl bromomethyl ketone, 1-adamantane carboxylic acid chloride, lactonitrile: Aldrich Chemical Company, Inc. 1-Acetoxy-2-butanone: Alfred Bader Chemical Company. Acetol: Jefferson Chemical Company. Triton B: J. T. Baker Chemical Company. Propionaldehyde cyanohydrin: City Chemical Company.

Methyl iodide-^{13}C, ethyl iodide-2-^{13}C, acetic acid-1-^{13}C; Merck, Sharp and Dohme of Canada, Ltd. $H_2{}^{18}O$: Miles Laboratories, Inc. $H_2{}^{17}O$: Yeda Research Laboratories, Inc.

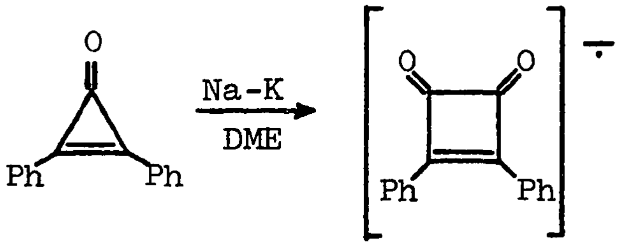
3,3,5,5-Tetramethylcyclopentane-1,2-dione: Dr. G. R. Underwood. 2,2,4,4-Tetramethylcyclopentan-1-one: Dr. E. J. Panek. 4-t-Butyl-2,2,5,5-tetramethyl-3-hexanone: Dr. T. T. Tidwell. bis(1-Phenylcyclopentyl)ketone: Dr. J. W. Wilt. Diphenylcyclopropenone, diphenylacetylene: Dr. T. J. Barton and Miss Joanne Johnson. Propioin, butyroin: Dr. R. D. Stephens. Isobutyroin, isobutyril, pivaloin, pivalil: Dr. H. L. Malkus, Phenylglyoxal methyl mercaptal: Dr. L. A. Ochrymowycz.

APPENDIX

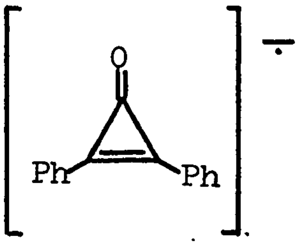
Alkali Metal Reduction of Diphenylcyclopropenone

When it became apparent that 2,2,4,4-tetramethylcyclobutanone ketyl, 108, disproportionated to form 3,3,5,5-tetramethylcyclopentane-1,2-semidione, 116, it was hoped that this reaction might be applicable to the generation of other semidiones of theoretical interest. Of particular interest were cyclobutenesemidiones, formally considered to be derivatives of elusive cyclobutadiene (158). Alkali metal reduction of diphenylcyclopropenone, 144, might be expected to yield the corresponding cyclobutenesemidione, 145, if the intermediate ketyl 146 were to disproportionate CO.

When a 5 mg sample of diphenylcyclopropenone, 144 (159),



144 145



146

was treated with 0.05 ml Na-K alloy (1:3, w/w) in 2 ml DME at 25°C, no ESR signal was detected within one hour. After 18 hrs, the signal shown in Figure 43 (A) was observed: $\underline{a}^{H}$ = 2.65 G (4H), 0.50 G (4H), 5.30 G (2H). This signal—incompatible with calculations for 145 or 146—persisted for at least two hours; its identity was not readily apparent. The

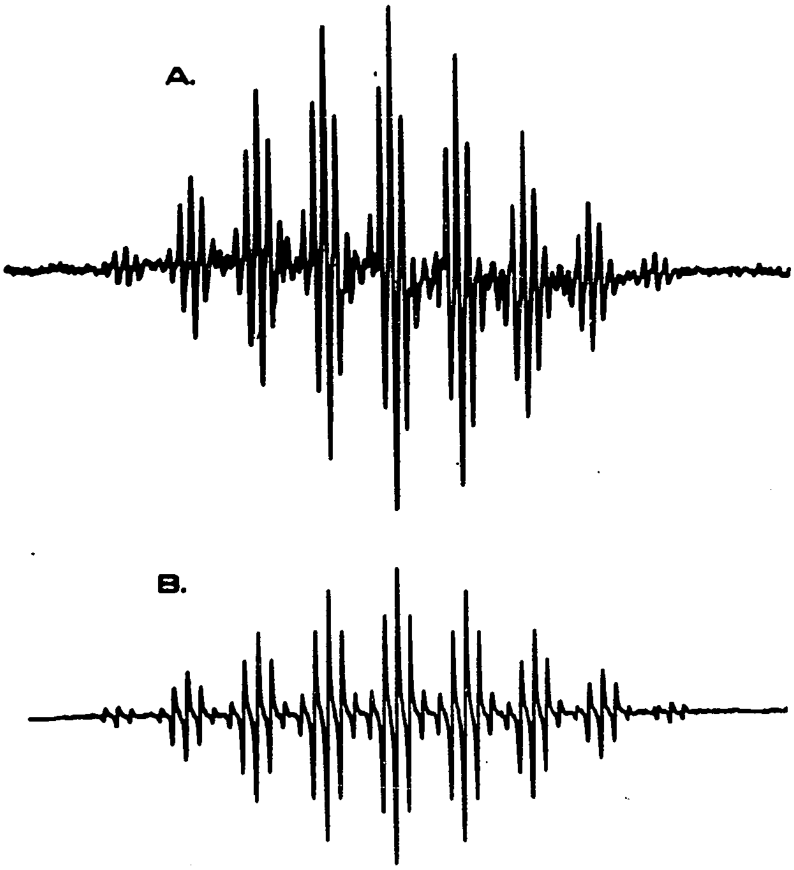
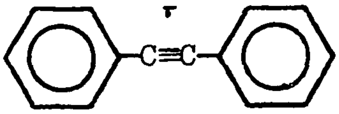


Figure 43. (A) First derivative ESR spectrum of radical obtained from the reduction of diphenylcyclopropenone with Na-K alloy in DME at 25°C. (B) Computer simulation (different scale) of A, using values in text.

spectrum was similar to that reported for diphenylacetylene radical anion, 147 (160, 161), but not identical. Preparation of 147 from authentic diphenylacetylene under conditions identical to those for the reduction of diphenylcyclopropenone gave a different ESR signal: $a^H = 2.65$ G (4H), 0.65 G (4H), 4.8 G (2H). Furthermore, the signal decayed within two hours.

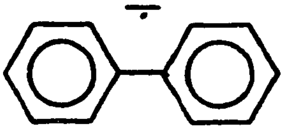


147

a) $a^H = 2.8$ G (4H), 0.6 G (4H), 5.08 G (2H), at -40° in DMF $-R_4N^+I^-$ (160).

b) $a^H = 2.68$ G (4H), 0.62 G (4H), 4.75 G (2H), at R.T. in ether-K metal (161).

The spectrum of Figure 43 is most consistent with biphenyl radical anion, 148, previously reported by Carrington and coworkers (162). Such a product might be explained if 144 or 146 were to lose phenyl, possibly at the surface of the alloy; phenyl could then be reduced to phenyl anion by the metal and couple with another phenyl radical to give 148. The actual order of processes could be reversed. A similar phenomenon may also have been responsible for the unidentified ESR spectrum observed by Thomson and Kilcast (163) in the reduction of pentaphenylphosphole; the spectrum is very similar to that of

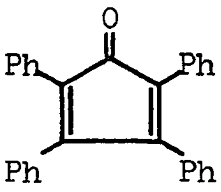


148

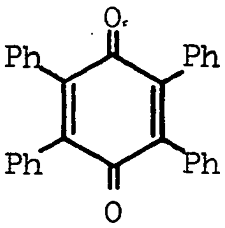
$a^H = 2.73$ G (4H), 0.43 G (4H), 5.46 G (2H) (162).

biphenyl radical anion.

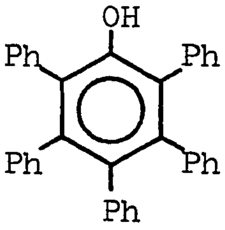
Several other possible structures for the reduction product of 144 have been considered, in light of recent reports concerning the reduction of 144 with other dissolving metals. Treatment of 144 with Mg-$\mathrm{MgI_2}$ in refluxing ether benzene had been reported to yield tetraphenylcatechol as the major product, with small amounts of tetraphenylcyclopentadienone, 149, and tetraphenyl-p-benzoquinone, 150 (164). A later communication (165) describing the reduction of 144 by Al-Hg in refluxing benzene-ethanol showed that the "tetraphenylcatechol" previously reported was actually tetraphenylresorcinol, 151, which is known to decompose to 149 (166).



149



150



151

The ESR spectrum of the radical anion of 149 was only 8 G wide, with $a^H \sim 0.14$ G (167, 168). Likewise, hfsc for the radical observed from 144 are larger than those expected for radicals related to 150 or 151, and the splitting patterns are different; however, structures 150 and 151 cannot be fully discounted without generation of authentic radicals.

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ACKNOWLEDGMENTS

I must thank Professor Glen Russell for his patient direction in all phases of this work, his inspiration, his support and his friendship. Particularly relished were his thoughtful-but-loose rein on events in the lab and shared moments of savoir-faire.

Thanks also to: Professor Phil Hogan for his early instruction and his brotherly counseling; Professors T. Barton, J. Espenson, H. Franzen, T. Kinstle, D. Metzler, E. Meyer and W. Trahanovsky for their gracious helpfulness; innumerable members of the Russell group and their families, for technical assistance and social rapport—particularly the Malkuses, the Underwoods, the Stevensons, the Whittles, the Mattoxes, the Paneks and the Bolton; my parents, parents-in-law, family and friends for loving encouragement.

A special word of love and gratitude to my wife, Readith, for her seemingly infinite capacity to love, understand, proofread and do whatever else keeps me alive. She made even Ames quite enjoyable.

I am indebted to Miss Marlene Collins for typing this manuscript. Finally, I am grateful for support from the following: NDEA, Title IV Fellowship, 1967-1968; Mobil Chemical Company Fellowship, 1969; and research assistantships funded by the National Science Foundation and National Institutes of Health.