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Aliphatic Semidiones. XXX. Alkenyl and Cycloalkyl Substituted 1,2-Semidiones¹

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Abstract: The esr spectra of a series of cycloalkyl (C₃–C₈) substituted semidiones are reported and hyperfine splitting constants are assigned. The bisected conformation is highly preferred for cyclopropyl and other cycloalkyl substituted semidiones, including the anti(*n* + 3)-position derivatives of the bicyclo[*n*.1.0]alkanes. The rigid geometry of the latter radical anions gives rise to unusually large long range interactions involving 4 and 5 bonds in a zigzag coplanar arrangement with a carbon p_z orbital in the semidione spin label. Alkenyl semidiones with α,β-unsaturation have a high spin density at the β position ($\rho_{C-\beta} \approx 0.2$) and are highly reactive. However, cis–trans isomerization about α,β-conjugated double bonds cannot be detected.

Biscycloalkyl-1,2-semidiones. A series of acyloins (**1**) and semidiones (**2**) were prepared from the corresponding cycloalkanecarboxylic esters.

Somewhat simpler esr spectra were obtained from the methylcycloalkylsemidiones (**4**) obtained from the acyloins (**3**) prepared either by a mixed acyloin condensation (**3a, c**) or by addition of methylmagnesium bromide to the carboxaldehyde cyanohydrins.

Figure 1 gives typical esr spectra for **2c** and **4c**. The observed hfsc are collected in Table I.

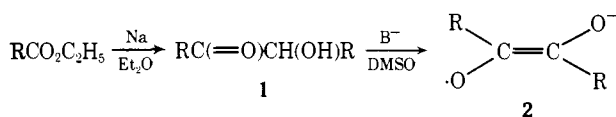
The semidiones **2** and **4** show several conformational effects as well as new examples of long range splitting. We

have commented previously on the highly preferred bisected conformation of cyclopropyl substituted semidiones³ and acyclic secondary alkyl substituted semidiones,^{4,5} where $a_{\alpha}^H \sim P_c \langle \cos^2 \theta \rangle$. Bulkier substituents (R' in **5**, Scheme I) cause a decrease in the value of a_{α}^H indicating a decrease in torsional motion ($\pm\theta$) as the bulk of R' is increased. The value of $\langle \cos^2 \theta \rangle$ appears to be quite constant for **2c–g** (or **4c–h**) and about equal to the value for *trans*-diisopropylsemidione, where $a_{\alpha} = 2.0$ G. There does seem to be an additional electronic factor leading to a lower value of a_{α}^H for the cyclopropyl substituted semidiones **2a, 4a, 2i, 2j, 4j** and **4k**. This interaction does not lead to an enhanced value of

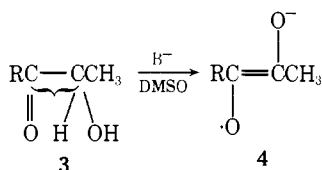
Table I. Observed Hfsc (G) for 2 and 4 in DMSO, 25°

Semidione	a_{R^H}					$a_{CH_3^H}$	$a_{unassigned^H}$
	α	β	β'	γ	γ		
2a	0.57 (2)	0.37 (4)	0.20 (4)				
4a	0.57	0.37 (2)	0.20 (2)			5.88	
2b	1.49 (2) ^a	0.65 (2)	0.10 (2)	0.27 (6)			
4b	1.49	0.65	0.09	0.27 (3)		5.79	
2c	2.22 (2)	0.45 (4)	0.23 (4)	0.08 (2)			
4c	2.11	0.44 (2)	0.23 (2)	<i>b</i>		5.55	
2d	1.92 (2)	0.44 (4)	0.22 (4)	0.11 (4)			
4d	1.92	0.44 (2)	0.22 (2)	0.11 (2)		5.77	
2e	1.88 (2)	<i>b</i>	<i>b</i>				
4e	1.73	0.30 (2)		0.30 (2)		5.73	0.08 (4)
2f	1.95 (2)	<i>b</i>	<i>b</i>				
2g	2.08 (2)	0.18 (4)		0.18 (4)			
4h	1.94					5.85	0.09 (4)
2i	0.75 (2)	0.20 (4)		0.95 (4)			
2j	0.52 (2)	0.27 (4)		0.78 (4)			0.48 (4)
4j	0.52	0.27 (2)		0.78 (2)		6.00	0.48 (2)
2k	0.48 (2)	0.13 (4)		0.37 (4)			0.37 (4)
2l	<i>b</i>						

^a In DMSO-*d*₆ H_α is exchanged to give $a^D = 0.24 (2) G$. ^b Not resolved,

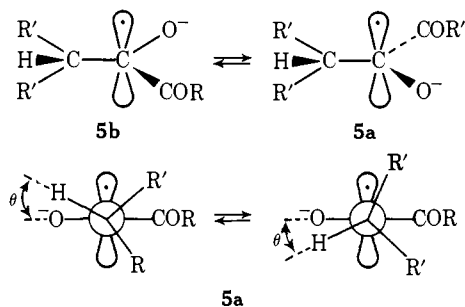


- a, R = cyclopropyl
 b, R = 2,2-dimethylcyclopropyl
 c, R = cyclobutyl
 d, R = cyclopentyl
 e, R = cyclohexyl
 f, R = cycloheptyl
 g, R = Δ⁴-cycloheptyl
 i, R = anti-6-bicyclo[3.1.0]hexyl
 j, R = anti-7-bicyclo[4.1.0]heptyl
 k, R = anti-8-bicyclo[5.1.0]octyl
 l, R = anti-9-bicyclo[6.1.0]nonyl



- a, R = cyclopropyl
 b, R = 2,2-dimethylcyclopropyl
 c, R = cyclobutyl
 d, R = cyclopentyl
 e, R = cyclohexyl
 h, R = cyclooctyl
 j, R = anti-7-bicyclo[4.1.0]heptyl

Scheme I



a_{β^H} and appears to be negated by the nonbonded interaction of *gem*-dimethyl substitution in the cyclopropyl ring (2a, 4b). Interaction 6 is a possible interpretation.

The larger β hfsc in the cyclopropylsemidiones can be identified with the trans hydrogen atom which is in the best

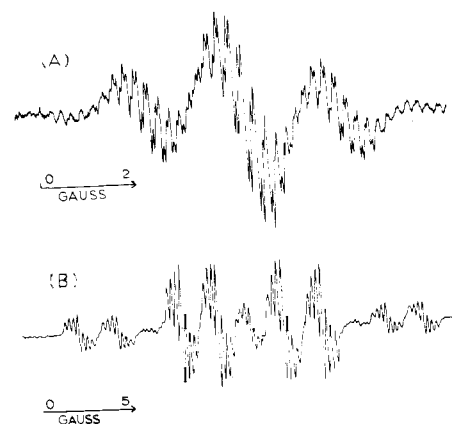
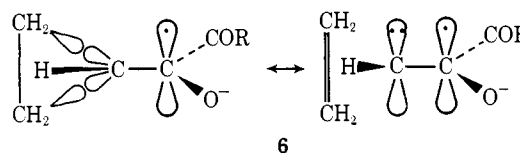
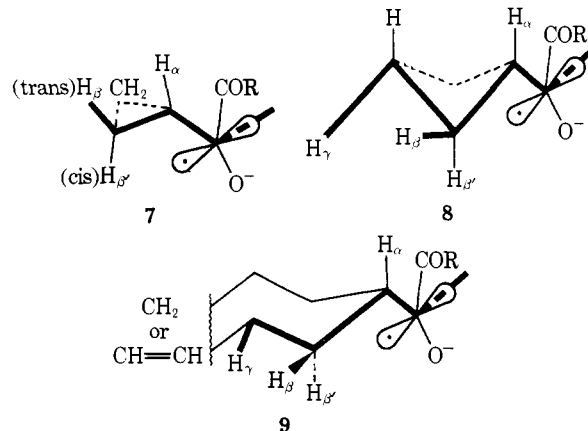


Figure 1. First-derivative esr spectra of the potassium salts of (A) dicyclobutylsemidione (2c) and (B) methylcyclobutylsemidione (4c) in DMSO at 25°.



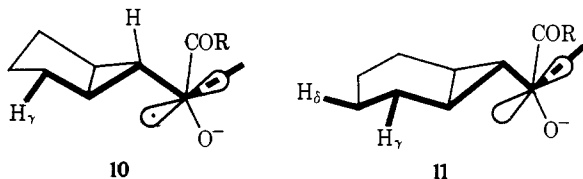
coplanar zigzag arrangement with the carbonyl carbon p_z orbital (7). Increasing θ in the bisected conformation 1a increases $a_{\beta\text{-trans}}^H$ (from 0.37 G in 2a to 0.65 G in 2b) and decreases $a_{\beta\text{-cis}}^H$ (from 0.20 G in 2a to 0.10 G in 2b).



The cyclobutyl- (2c, 4c) and cyclopentylsemidiones (2d, 4d) have somewhat larger values of a_{β^H} than the cyclopro-

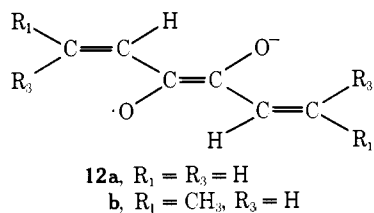
pyl derivatives, suggesting puckered rings with a more planar zigzag arrangement of bonds and orbitals. A 2.5 V interaction is now observed, undoubtedly for the cis γ hydrogen atom (**8**). For cyclohexyl and Δ^4 -cycloheptenyl substituted semidiones an excellent 2.5-V arrangement exists for the cis γ (equatorial) hydrogen atoms, and the values of a^H for β and γ equatorial hydrogen atoms are the same (**9**).

In the bicyclic derivatives **2i,j,k** and **4j**, excellent 2.5-V transoid arrangements of bonds and orbitals exist (**10, 11**). In addition, in **2i,k** and **4j**, a 3-V arrangement gives rise to significant (0.48, 0.37 G) values of a_3^H .



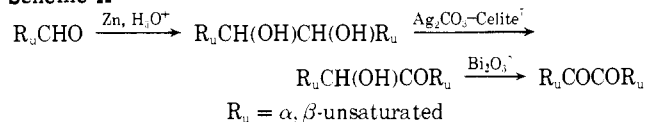
Other conformational effects could be involved for **2** and **4**. Cis-trans isomerization about the partial double bond of the semidione spin label could occur, but it seems likely that the observed semidiones have only the trans structure. Cisoid and transoid bisected conformations **5a** and **5b** could both be present (for **2** cisoid-cisoid, transoid-transoid, and cisoid-transoid conformations are possible), but it seems most likely that the preferred structure is **5a**. Finally, ring inversion of the cycloalkyl rings could be occurring. However, the observed hfsc's seem to best be rationalized with cycloalkyl rings (C_4 - C_7) locked with the semidione substituent in the equatorial-type position (**8, 9**). The quality of the observed esr spectra requires that if more than one conformation is involved rapid time averaging has occurred (with the exception of **2f** and **2l** where unresolved spectra were observed).

α,β -Unsaturated 1,2-Semidiones. Acyloin condensations of ethyl acrylate and crotonate gave crude products which failed to yield the expected semidiones (**12a, b**) upon treat-



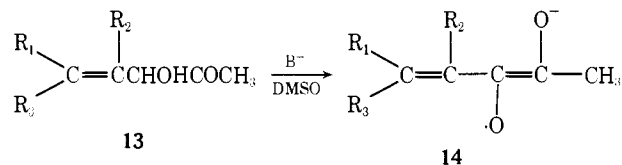
ment with base in DMSO. The appropriate hydroxy ketone and α -dione precursors to **12** have been reported (Scheme II).⁶ When applied to crotonaldehyde the dione was ob-

Scheme II

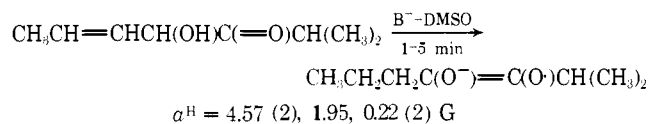


tained directly from the silver carbonate oxidation. Treatment with potassium *tert*-butoxide and DMSO in a flow system (a few seconds between mixing and detection) gave **12b** ($a^H = 5.28$ (6), 3.16 (2), 1.06 (2) G). Upon stopped flow, no esr signal could be detected after a few seconds. We were unable to synthesize the precursor to **12a** and turned attention to **13a-h**.

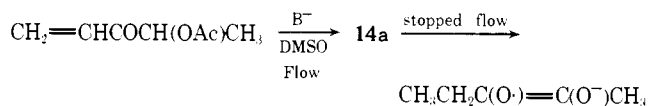
Reaction of the cyanohydrins of unsaturated aldehydes with methylmagnesium bromide gave a mixture of products. A further complication was the observation that although 2-methyl-4-hydroxy-5-hepten-3-one could be prepared in this manner the only paramagnetic product observed by esr in a static system was *n*-propylisopropylsemidione, previously observed.⁴ The known 4-hydroxyl-1-pen-



- 13** $\xrightarrow[BMSO]{B^-}$ **14**
- a, $R_1 = R_2 = R_3 = H$
 - b, $R_1 = R_3 = H; R_2 = CH_3$
 - c, $R_2 = R_3 = H; R_1 = CH_3$
 - d, $R_1 = R_2 = H; R_3 = CH_3$
 - e, $R_1 = R_3 = CH_3; R_2 = H$
 - f, $R_1 = R_2 = CH_3; R_3 = H$
 - g, $R_2 = R_3 = CH_3; R_1 = H$
 - h, $R_1, R_2 = -(CH_2)_4-; R_3 = H$

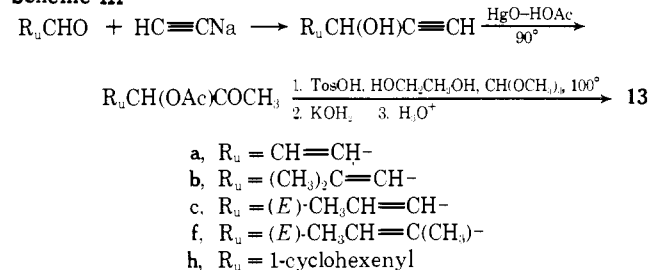


ten-3-one⁹ failed to give any esr signal when treated with potassium *tert*-butoxide in DMSO in either a static system or in a flow system wherein the esr signal could be observed 10-30 sec after mixing. On the other hand the acetate of 3-hydroxy-1-penten-4-one (**13a**)¹⁰ yielded an esr spectrum consistent with **14a** under the flow conditions but pentane-2,3-semidione under static or stopped-flow conditions. We



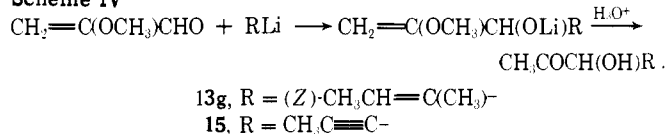
thus extended the reaction scheme used for the preparation of the acetate of **13a**¹⁰ to **13b, c, f, and h** (Scheme III). The additions of sodium acetylide to crotonaldehyde,¹¹ acrolein,¹² and 1-cyclohexenecarboxaldehyde¹³ have been previously reported, and the acetoxylation-hydration procedure of Mavrov and Kucherov¹⁰ worked smoothly for all the hydroxy enynes.

Scheme III



Alcohol **13g** and $CH_3C\equiv CH(OH)COCH_3$ (**15**) were synthesized *via* Scheme IV.¹⁴ Hydrogenation of **15** over Pd-C in methanol (33%)-quinoline (67%) gave **13d**.

Scheme IV



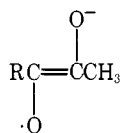
Under very slow flow (several minutes after mixing) or under static conditions hydroxy or acetoxy ketones **13a-d, f, g, and h** gave rise to the corresponding saturated semidiones (**16**) when treated with potassium *tert*-butoxide in DMSO.

Semidione **14e** was observed upon treatment of the acetate¹⁵ of 5-hydroxy-2-methyl-2-hexen-4-one¹⁶ with base in DMSO under static or flow conditions. The other unsaturated semidiones could be observed only under flow conditions. Only one isomer was observed and this has been assumed to be the trans semidione. Table II lists the observed hfsc **14a-h**.

Table II. Hyperfine Splitting Constants for 14

System	Precursor	a_1^H (trans)	a_3^H (cis)	a_2^H	$a_{CH_3^H}$
a	Acetate	4.90	5.00	1.25	2.88
b	Alcohol	3.90	4.13	(1.23) ^a	3.40
c	Alcohol	(4.89) ^a	4.60	1.46	3.41
d	Alcohol	4.80	(5.10) ^a	1.78	3.28
e	Acetate	(4.32) ^a	(4.56) ^a	1.97	3.60
f	Alcohol	(4.10) ^a	3.50	(1.16) ^a	3.34
h	Alcohol	(5.45) ^b	3.43	(1.41) ^b	4.07

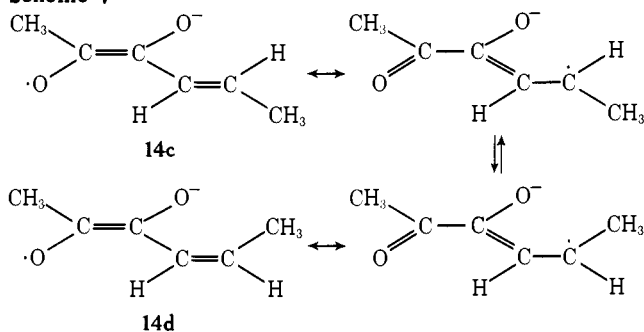
^a $a_{CH_1^H}$, ^b $a_{CH_2^H}$.



- 16a, R = CH₃CH₂; a^H = 5.70 (3), 4.60 (2) G
 b, R = (CH₃)₂CH; a^H = 5.70 (3), 1.95 G
 c(d), R = CH₃CH₂CH₂; a^H = 5.70 (3), 4.63 (2), 0.21 (2) G
 f(g), R = (CH₃)(C₂H₅)CH; a^H = 5.73 (3), 1.69 G
 h, R = cyclohexyl; a^H = 5.75 (3), 1.88, 0.31 (4) G

The data of Table II present a consistent picture of the extent of spin delocalization. First, the value of $a_{CH_3^H}$ is decreased from 5.7 G for the biacetyl radical anion to 3–4 G for 14a–h. This corresponds to a decrease in spin density in the semidione spin label of ~40%. This spin is delocalized to C_β of the vinyl substituent where about 0.2 of an unpaired spin is found using the relationships $a_{CH^H} = -22.5 \rho_c$ or $a_{CC^H} = +20 \rho_c$.¹⁷ The spin delocalization from a semidione group to a vinyl group is somewhat less than from the semidione group to a benzene ring.¹⁷ For 1-phenylpropane-1,2-semidione the value of $a_{CH_1^H}$ is 3.43 G while the aromatic ring spin density ($\Sigma a_{o,p-CH^H} = 4 \text{ G}$)¹³ is ~0.2. The high spin density on C_β in 14 makes cis–trans isomerization in the vinyl groups a real possibility (Scheme V). However, 13c yielded only 14c while 13d gave exclusively 14d (Figure 2). During a chemical lifetime of a few seconds there was no detectable cis–trans isomerization at 25°.

Scheme V



Scheme VI

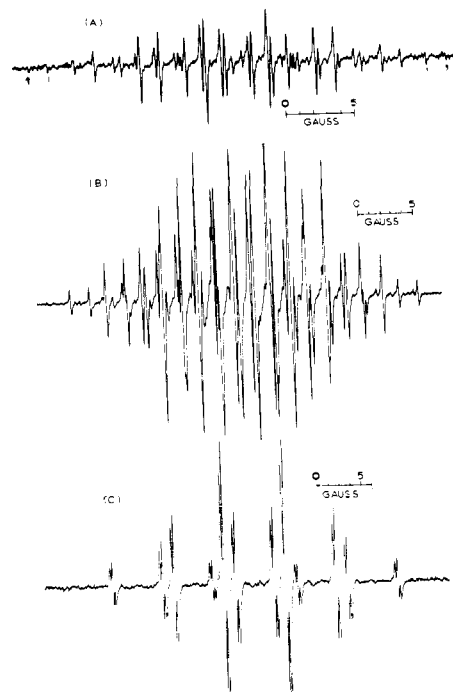
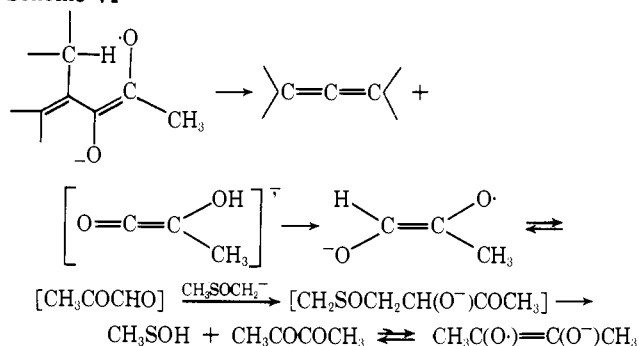
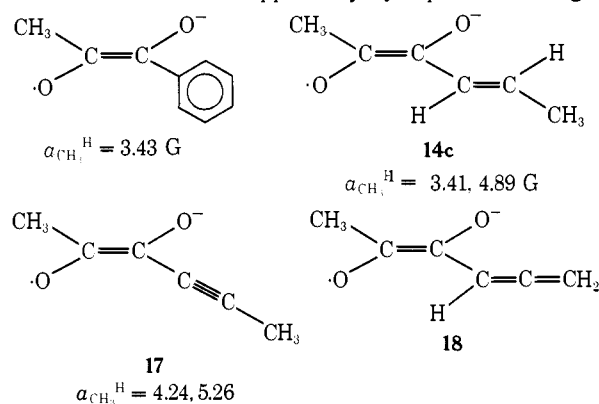


Figure 2. ESR spectra observed upon treatment of 3-acetoxypent-4-en-2-ones (13c,d) with potassium *tert*-butoxide in DMSO solution: (A) semidione (14c) from the trans isomer in a flow cell, (B) semidione (14d) from the cis isomer in a flow cell, (C) methyl propyl semidione (16c) observed at stopped flow from 13c or 13d.

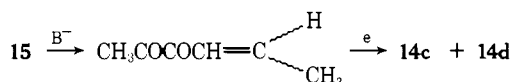
Stopped flow with hydroxy ketones 13b, 13f, and 13h in KOC(CH₃)₃-DMSO gave in addition to 16b, f, and h a mixture of cis and trans biacetyl radical anions ($a^H = 5.65 \text{ G}$ (trans), 7.00 G (cis)). The structural requirement of a saturated C_β-H bond suggests the process of Scheme VI. The conversion of methylglyoxal or phenylglyoxal to biacetyl radical anion and 1-phenylpropane-1,2-semidione by methylsulfinylmethide ion has been previously documented.^{18,19}

Acetylenic and Allenic Conjugated Semidiones. The series 1-phenylpropane-2,3-semidione, 14c, 17, and 18, provide a model series for measuring spin delocalization.

Treatment of 15, the acyloin precursor to 17, with potassium *tert*-butoxide in DMSO under flow conditions gave a mixture of 14c and 14d apparently by a process analogous



to the formation of saturated semidiones from 13 upon stopped flow. Conversion of 15 to the acetate followed by



reaction with base in DMSO in a flow system gave a mixture of two radicals; one with $a^H = 3.51 \text{ G}$ for six equivalent hydrogens and one with $a_{CH_3^H} = 4.24, 5.26 \text{ G}$. The radi-

Table III. Cycloalkyl Acyloins

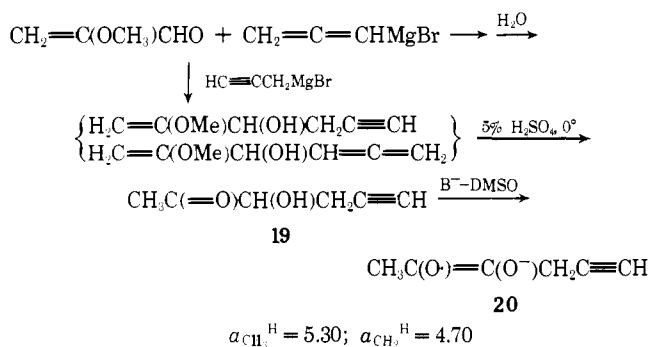
$$\begin{array}{c} \text{R}-\text{C}-\text{C}-\text{R}' \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{O} \quad \text{H} \quad \text{OH} \end{array}$$

R, R'	Pmr (CCl ₄) (δ)	Analysis			
		Found % C	Found % H	Calcd % C	Calcd % H
Cyclopropyl	3.93 (d, 1, <i>J</i> = 6 Hz), 3.21 (s, 1), 2.35–1.88 (m, 1), 1.30–0.75 (m, 5), 0.75–0.15 (m, 4)	68.17	8.80	68.45	8.62
2,2-Dimethylcyclopropyl	3.72 (s, 1), 3.62 (d, 1, <i>J</i> = 5.5 Hz), 1.26–1.17 (m, 6), 1.10 (s, 6), 2.3–0.3 (m, 6)	73.33	10.11	73.45	10.28
Cyclobutyl	3.96 (d, 1, <i>J</i> = 3.8 Hz), 3.38 (s, 1), 3.2–1.5 (m, 14)	71.25	9.67	71.30	9.60
Cyclopentyl	4.89 (s, 1), 4.21 (d, 1, <i>J</i> = 4 Hz), 3.40–2.90 (m, 1), 2.90–1.00 (m, 17)	73.40	10.28	73.07	10.31
Cyclohexyl	4.10 (d, 1, <i>J</i> = 1 Hz), 3.20 (s, 1), 2.70–2.20 (m, 1), 2.20–0.90 (m, 21)	74.77	10.65	74.85	10.76
Cycloheptyl	4.08 (d, 1, <i>J</i> = 1.5 Hz), 3.75 (s, 1), 3.00–2.00 (m, 2), 2.00–1.00 (m, 24)	76.15	11.18	76.40	11.34
Δ ⁴ -Cycloheptenyl	5.8–5.6 (m, 4), 4.11 (d, 1, <i>J</i> = 2.4 Hz)	76.55	9.65	77.23	9.51
Methyl, cyclopropyl	4.29 (q, 1, <i>J</i> = 7 Hz), 4.05 (s, 1), 2.21 (s, small) and 1.37 (d, large, <i>J</i> = 7 Hz) total area 3, 2.16–0.20 (m, 5)	63.02	8.72	63.08	8.85
Methyl, cyclobutyl	3.80–3.35 (m, 1), 3.33 (s, 1), 2.20 (s, small) and 1.15 (d, larger, <i>J</i> = 5.5 Hz) total area 3, 2.10–1.60 (m, 7)	65.19	9.41	65.60	9.45
Methyl, 2,2-dimethylcyclopropyl	3.72 (s, 1), 3.62 (d, 1, <i>J</i> = 5.5 Hz), 1.26–1.17 (m, 6), 1.10 (s, 6), 2.30–0.30 (m, 6)	73.33	10.11	73.45	10.28
Methyl, cyclopentyl	4.20–3.95 (m, 1), 3.20 (s, 1), 2.11 (2) and 1.30 (d, <i>J</i> = 7 Hz) total area 3, 2.00–1.20 (m, 9)	67.42	10.06	67.50	9.93
Methyl, cyclohexyl	3.63–3.30 (m, 1), 2.5 (s, 1), 1.96 (s, small) and 1.10 (d, large, <i>J</i> = 6.25 Hz) total area 3, 2.10–0.90 (m, 11)	69.64	10.13	69.30	10.30
Methyl, cyclooctyl	4.06 (d, 1, <i>J</i> = 3.5 Hz), 3.26 (s, 1), 2.12 (s, large) and 1.12 (d, small, <i>J</i> = 6.25 Hz) total area 3, 2.5–1.0 (m, 15)	71.37	11.25	71.75	10.87
<i>anti</i> -6-Bicyclo[3.1.0]hexyl	5.40 (s, 1), 3.66 (d, 1, <i>J</i> = 8 Hz), 3.20–0.70 (m, 18)	76.55	9.34	76.37	9.23
<i>anti</i> -7-Bicyclo[4.1.0]heptyl	3.28 (s, 1), 3.35 (d, 1, <i>J</i> = 6.7 Hz), 2.30–0.50 (m, 22)	77.23	9.57	77.25	9.74
<i>anti</i> -8-Bicyclo[5.1.0]octyl	4.52 (s, 1), 3.0–0.50 (m, 27)	78.29	10.17	78.21	10.21
<i>anti</i> -9-Bicyclo[6.1.0]nonyl	3.78 (d, 1, <i>J</i> = 7 Hz), 3.28 (s, 1), 3.20–0.50 (m, 28)	78.88	10.36	78.90	10.59
Methyl, <i>anti</i> -7-bicyclo[4.1.0]-heptyl	5.3 (s, 1), 2.8–0.20 (m, 14)	71.40	9.70	71.30	9.59

cal with two methyl groups would be quite consistent with **17** with $a_{\text{C}\equiv\text{CCH}_3}^{\text{H}} = 5.26$ G. If this assignment is correct the delocalization of spin into phenyl, vinyl, and ethynyl groups is about equal. The nature of the radical (anion) with six equivalent hydrogens is obscure. The radical ion of 3-hexyne-2,5-dione is a possible candidate which could conceivably be formed from **15** and might have a^{H} in the range of 3.5 G.

In an attempt to prepare a possible precursor to **18**, allenylmagnesium bromide²¹ was substituted in the reaction of Scheme IV. However, hydrolysis with water yielded the propargyl derivative which could be further hydrolyzed to propargylmethylacyloin (**19**) which upon treatment with potassium *tert*-butoxide in DMSO yielded methylpropargylsemidione, **20** (Scheme VII).

Scheme VII



Since propargyl ketones can be isomerized to the allenic isomers by base,²¹ attempts were made to oxidize **19** to the ketone by chromium trioxide–dipyridine or activated manganese dioxide without success. Compound **19** itself was not

isomerized to the allenic analog by potassium carbonate in THF.

Experimental Section

Esr Measurements. The esr spectra were obtained using a Varian Associates E-3 spectrometer. Static experiments were performed by mixing deoxygenated solutions of the acyloin or α -acetoxy ketone (~0.01 *M*) with an equal volume of 0.1 *M* potassium *tert*-butoxide in DMSO. For flow experiments solutions were mixed in a three-way stopcock before entering the flat-fused silica esr cell. There was approximately 2 ml of volume between the points of mixing and detection. Flow rates of 5–10 ml/min were satisfactory for the detection of alkenyl semidiones with faster flow rates resulting in decreased signal intensities.

Synthesis of Acyloins. Acyloin condensations of ethyl carboxylates by sodium in xylene at 105–110° followed the general procedure of McElvain.²² The products were isolated by distillation, crystallization, and glpc where necessary. An alternative acyloin synthesis employed for the synthesis of dicyclopropylacyloin (**1a**) involved decanting the xylene from the cooled sodium sand and performing the condensation with the sodium sand in refluxing ether solution. After destruction of the sodium and distillation of the solvent, the acyloin was isolated by glpc on a silicone 550 column at 150°. Other analytical details are given in Table III. In a similar fashion **1b**, bp 50–55° (0.5 Torr) was synthesized in 13% yield. Dicyclobutylacyloin (**1c**) was isolated in 9% yield (glpc, propylene glycol column at 150°) from the condensation in ether. Dicyclopentylacyloin, bp 83–87° (1 Torr) and dicyclohexylacyloin, mp 43.5°, were prepared in xylene in yields of 9 and 45%, respectively. Dicycloheptylacyloin was isolated in 40% yield by distillation from xylene, bp 127–130° (2 Torr). Δ⁴-Cycloheptenylacyloin was isolated from the xylene solution by distillation and elution from silical gel with benzene (80%)–ether (20%) in 5% yield.

Mixed methylcycloalkylacyloins (**3**) were prepared in low yield by mixed acyloin condensation and glpc isolation. Methylcyclopropylacyloin (**3a**) was isolated from ether by glpc with a silicone 550

column at 135° in 0.4% yield. In a similar fashion **3c** was prepared in 1%.

2,2-Dimethylcyclopropanecarboxylic acid chloride (0.05 mol) was added dropwise to a solution of equimolar amounts of ethyl-eneimine and trimethylamine in 50 ml of ether at -5°. After 4 hr at 25° the trimethylammonium chloride was removed by filtration and the ether solution dried over MgSO₄ before treatment with a 60% excess of lithium aluminum hydride at -5°. The product was hydrolyzed with 3 *N* hydrochloric acid saturated with ammonium chloride and the ether extract washed with aqueous sodium bicarbonate before drying over MgSO₄. The ether solution of the aldehyde was treated with 50 ml of aqueous sodium bisulfite, and the addition product was treated with 1.5 equiv of sodium cyanide in 25 ml of water for 2 hr before extraction of the cyanohydrin with ether. The dry (MgSO₄) ether extract was added to 2 equiv of methylmagnesium iodide in ether over a 1-hr period. After 4 hr of reflux the solution was hydrolyzed and the ether extract dried (Na₂SO₄) and distilled to give acyloin **3b**, bp 50–55° (0.05 Torr) in 13% yield.

Bromocyclopentane was converted to the Grignard reagent which was treated with triethyl orthoformate to yield the aldehyde. The aldehyde was converted to its sodium bisulfite addition product and then to the cyanohydrin from which 28% of **3d** was isolated, bp 25–26° (0.13 Torr). Similarly cyclohexanecarboxaldehyde was converted to **3e**, bp 100–110° (13 Torr) in 20% yield. Cyclooctanecarboxaldehyde gave 16% of **3h** isolated by glpc.

Cyclopentene, cyclohexene, cycloheptene, and cyclooctene were treated with ethyl diazoacetate²³ in the presence of a zinc-copper catalyst²⁴ to yield the corresponding ethyl cyclopropylcarboxylates. Ethyl *anti*-6-bicyclo[3.1.0]hexanecarboxylate,²⁵ bp 89° (15 Torr) underwent acyloin condensation in xylene to give 6% of **1i** distilled by a Toepler still at 0.05 Torr. Ethyl *anti*-7-norcaranecarboxylate, bp 107–108° (15 Torr), lit.¹⁹ bp 108–110° (18 Torr), gave 35% of the acyloin, bp 135° (0.03 Torr).

Cycloheptene yielded the ethyl 8-bicyclo[5.1.0]octanecarboxylate, bp 138–141° at 15 Torr; pmr (CCl₄) δ 4.02 (q, 2, *J* = 7 Hz) 1.20 (t, 2, *J* = 7 Hz), 2.45–0.80 (m, 13).

Anal. Calcd for C₁₁H₁₈O₂: C, 72.48; H, 9.96. Found: C, 72.51; H, 9.88.

The acyloin (**1k**) was formed in xylene in 22% yield isolated by distillation in a Toepler still at 0.05 Torr.

Cyclooctene gave 10% of ethyl 9-bicyclo[6.1.0]nonanecarboxylate: bp 143.5–144.5° (18 Torr), lit.²⁶ bp 100–105° (3 Torr), pmr (CCl₄) δ 4.03 (q, 2, *J* = 7.2 Hz) 1.20 (t, 3, *J* = 7.2 Hz), 2.25–0.85 (m, 15).

Anal. Calcd for C₁₂H₂₀O₂: C, 73.45; H, 10.28. Found: C, 73.25; H, 10.38.

The acyloin (**1l**) was formed in 6.5% yield in xylene and purified by Toepler distillation at 0.03 Torr.

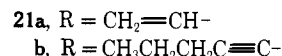
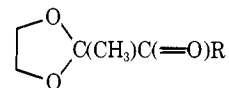
7-*anti*-7-Norcaranecarboxylic acid chloride was converted to the amide and reduced to the aldehyde as described in the synthesis of **3b**. Conversion to the cyanohydrin and then to the methylacyloin gave an overall yield of 4% of **3i**, mass spectrum (70 eV) *m/e* 168 (parent ion), 166.

Addition of isopropylmagnesium chloride to the cyanohydrin of crotonaldehyde²⁷ gave an 18% yield of 2-methyl-4-hydroxy-5-hepten-3-one: pmr (CCl₄) δ 1.05 (d, 3, *J* = 7 Hz) 1.10 (d, 3, *J* = 7 Hz), 1.75 (q, 3, *J* = 6.1 Hz), 2.88 (h, 1, *J* = 7 Hz), 4.10 (broad s, 1), 4.57 (q, 1, *J* = 7, 1 Hz) 5.08–6.18 (m, 2).

Anal. Calcd for C₈H₁₄O₂: C, 67.60; H, 9.94. Found: C, 67.61; H, 9.76.

The syntheses and physical properties of acyloins **13b–d**, **13f–g**, **15**, and **19** and acetates of **13a–c**, **13f**, **13h**, and **15** have been described elsewhere.¹⁴

In an unsuccessful series of experiments, we attempted to prepare precursors to **13a** and **15** from pyruvic ester derivatives in which the α-keto group was protected by the ethylene ketal linkage. 2-Ethoxycarbonyl-2-methyl-1,3-dioxolane²⁸ reacted with vinylolithium or 1-pentynyllithium to give the expected products **21**, identifiable by pmr and mass spectral evidence. Compound **21a**, bp 70–72° at 8 Torr had a pmr of δ 1.38 (s, 3), 3.98 (m, 4), 5.66 (q, 1, *J* = 3.5 and 9.5 Hz), 6.7 (m, 2). Hydrolysis with toluenesulfonic acid in refluxing acetone gave only tars or recovered starting material. Compound **21b**, bp 110–111° at 4 Torr was prepared in 68%



yield: pmr δ 1.07 (5, 3 λ, *J* = 6 Hz), 1.42 (s, 3), 1.20–1.95 (m, 2), 2.36 (t, 2, *J* ≈ 6 Hz), 3.97 (s, 4). The ketal was not hydrolyzed by THF (7%)–20% aqueous sulfonic acid (33%) at 10° or by Dowex 50 (acid form) in acetone (67%)–water (37%) at 25°.

trans,trans-2,6-Octadiene-4,5-dione was prepared in 32% yield by refluxing 7.11 g (50 mmol) of dipropenylethylene glycol (prepared by the duplicative reduction of crotonaldehyde²⁹) with a suspension of 100 g of Fetizon's reagent³⁰ (174 mmol of silver carbonate) in 700 ml of benzene under a Dean-Stark trap for 3 hr. Distillation yielded material with the following characteristics; bp 84–89° at 8 Torr; pmr (CCl₄) δ 1.97 (d, 6, *J* = 6 Hz), 6.4–7.4 (m, 4); *m/e* (calcd for C₈H₁₀O₂, 138.068075) 138.068072. We were unable to prepare 1,5-hexadiene-3,4-dione by a similar technique from divinylethylene glycol.²⁹

Dodeca-4,8-diyne-6,7-dione, which was prepared by the addition of 100 mmol of oxalyl chloride in 100 ml of ether to 200 mmol of 1-pentynyllithium at -80°, yielded 5.3 g (28%); bp 109–111° at 3.5 Torr; pmr δ 1.06 (t, 3, *J* = 6 Hz), 1.68 (m, 2), 2.37 (t, 2, *J* ≈ 6 Hz); *m/e* (calcd for C₁₂H₁₄O₂, 190.099; C₁₁H₁₄O, 162.104, C₉H₁₀O, 134.073; C₆H₇O, 25.0497) 190.1016, 162.1048, 134.074, 95.0472. Treatment of the dione with potassium *tert*-butoxide in DMSO in the presence or absence of propiophenone³¹ failed to yield a resolved esr signal under static or flow conditions similar to those which were satisfactory for **13** or **15**.

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