Spectra. Before carrying out the kinetic measurements on the stop-flow apparatus, spectra of the diazonium ions and of the solutions in which the reactions were complete were obtained by the use of a Cary Model 14 spectrophotometer. These spectra were used to select the wavelengths to be used in the kinetic measurements. It was found that the wavelengths of maximum absorption of the diazonium ions and of the aryl azides were those where greatest change occurred.

Kinetic Measurements. The stop-flow apparatus used for the kinetic runs has been described in earlier work.[8] Runs in which the reactions were followed at the wavelength of maximum absorption of the diazonium ions were quite routine with the time scales selected to allow observation of at least 95% completion of the reactions. For the runs in which the reactions were followed at the λ_{max} of the aryl azide, one trace was obtained on the same time scale as used when the reactions were followed at the λ_{max} of the diazonium ions. The transmittance scale of the oscilloscope was then expanded by a factor of 5 and another trace was obtained on the slowest time scale available, 5 sec/division. For those reactions in which the second step was extremely slow, the oscilloscope reading was obtained at various times measured with a stop watch. Both the fast and slow traces for the reaction of *p*-benzoylbenzenediazonium ion, followed at 300 nm, are shown in Figure 2.

Apparent rate constants for all runs were obtained from the slopes of the usual plots of ln $(A - A_\infty)$ *vs.* time.

One kinetic run with the *p*-methoxybenzenediazonium ion was carried out with both diazonium ion and azide ion at concentrations of 4.0×10^{-5} *M*. The entire spectrum of the reaction mixture, from 220 to 400 nm, was recorded at various time intervals on the Cary Model 14 spectrophotometer. Under these conditions, the arylpentazole decomposes rapidly in comparison to the rate of the overall reaction. Isosbestic points at 275 and at 237 nm were observed for the reacting solutions. After completion of the reaction (8000 sec), the final spectrum showed an absorbance at 275 nm which was slightly lower (0.175 compared to 0.195) than had been shown by the solutions during the course of the reaction. This was undoubtedly caused by a small steady-state concentration of the arylpentazole.

Preparation of *p*-Methoxyphenylpentazole. The preparation closely followed the method described by Ugi[4] except that the diazonium fluoroborate was used in place of the chloride. This caused some solubility problems. The mixture of solutions of diazonium salt and sodium azide was stirred for *ca.* 30 min at −35° to allow for the difficult solubility. The pentazole was filtered off, washed with aqueous methanol followed by pentane, and stored at −70°. Solutions were prepared in methanol at −30°, and spectra were obtained with the cells thermostated at 0°. No attempts were made to prepare the solutions accurately since the concentration of pentazole could be obtained by allowing the solutions to decompose to aryl azide and measuring the absorbance.

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[8] C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Amer. Chem. Soc.*, **89**, 2063 (1967).

Ketyls of Cyclic α,β-Unsaturated Ketones[1]

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Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received August 3, 1970*

Abstract: Ketyls can be prepared from 2-cyclopentenone, 2-cyclohexenone, 2,4- and 2,5-cyclohexadienone, and their benzo derivatives provided all hydrogen atoms α to the π system are substituted by alkyl or aryl groups. Electrolytic reduction of the ketones in dimethylformamide solution at −60 to +25° yielded the ketyls from the alkylated enones but not from the enones containing α hydrogen atoms such as 2-cyclohexenone, 4,4-dimethyl-2-cyclohexenone, or 6,6-dimethyl-2-cyclohexenone.

Ketyls with two aromatic substituents have been recognized for 80 years.[2-4] More recently electrolytic reduction has yielded the radical anions of benzaldehyde, acetophenone, 1,4-diacetylbenzene, and 1,2-dimesitylbenzene detectable by esr spectroscopy.[5]

Favorsky prepared the ketyl of di-*tert*-butyl ketone by reduction of the ketone with potassium metal.[6] Stable ketyls containing an α hydrogen are rare, although *tert*-butyl isopropyl ketyl and *tert*-butyl 3-pentyl ketyl can be detected at room temperature by esr spectroscopy.[7] Also, *tert*-butyl methyl ketyl and trimethylsilyl methyl ketyl have been examined in DME by esr spectroscopy at −90 to −70° but decompose readily at higher temperatures.[8,9] The addition of

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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XXII. Supported by grants from the National Institutes of Health and the National Science Foundation.

[2] E. Beckmann and T. Paul, *Justus Liebigs Ann. Chem.*, **266**, 1 (1891); W. Schlenk and T. Weickel, *Chem. Ber.*, **44**, 1182 (1911).

[3] W. E. Bachmann, *J. Amer. Chem. Soc.*, **55**, 1179 (1933).

[4] E. Müller and W. Wiessemann, *Justus Liebigs Ann. Chem.*, **537**, 86 (1938); S. Sugden, *Trans. Faraday Soc.*, **30**, 18 (1934).

[5] N. Steinberg and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964); P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2811 (1962).

[6] A. Favorsky and I. N. Nazarow, *Bull. Soc. Chim. Fr.*, [5] **1**, 46 (1934).

[7] H. Hiroto and S. I. Weissman, *J. Amer. Chem. Soc.*, **82**, 4424 (1960).

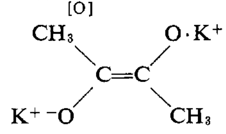
[8] P. R. Jones and R. West, *ibid.*, **90**, 6978 (1968).

[9] Decomposition of trimethylsilyl methyl ketyl in the presence of potassium ion apparently leads to the *trans*-dimethylsemidione, rather than the dimeric molecule suggested by Jones and West.[8] Jones and West overlooked the fact that acyclic semidiones can exist as cis and trans isomers, and that the predominate isomer can vary with the gegenion.[10] Thus, the observation of Jones and West that treatment of bis-1,2-trimethylsiloxy-2-butene with sodium yielded a radical anion with $a_{CH_3}{}^H = 7.43$ (2) G, does not exclude the following scheme from occurring in the presence of potassium. Similarly, the ketyl of isopropyl trimethylsilyl ketone yielded diisopropylsemidione, $a_{CH}{}^H = 2.38$ (2) G at −40°.

$$2(CH_3)_3Si\dot{C}(O^-)CH_3 \longrightarrow$$

$$(CH_3)_3SiC(O^-)(CH_3){-}C(O^-)(CH_3)Si(CH_3)_3 \xrightarrow{-2e} \xrightarrow{o}$$

$$(CH_3)_3SiOC(CH_3){=}C(CH_3)OSi(CH_3)_3 \xrightarrow[{[O]}]{OH^-}$$



$$a_{CH_3}{}^H = 4.5\ (2);\ a^K = 1.3\ G$$

[10] G. A. Russell and R. D. Stephens (*J. Phys. Chem.*, **70**, 1320 (1966)) report $a_{CH_3}{}^H = 7.0$ and 5.6 G at 25° for *cis*- and *trans*-dimethylsemidione. *trans*-Diisopropylsemidione has $a_\alpha{}^H = 2.0$ G at 25° in DMSO solution.

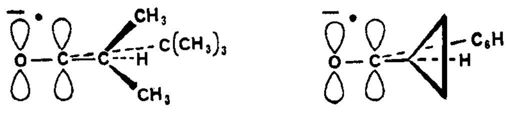


Figure 1. Preferred conformations for *tert*-butyl isopropyl ketyl and phenyl cyclopropyl ketyl.

sodium atoms to acetone, methyl ethyl ketone, diisopropyl ketone, cyclopentanone, and cyclohexanone at 77°K has been reported by Bennett, Mile, and Thomas.[11] These ketyls readily decompose upon warming to 140°K in a matrix to the keto alkyl radical, apparently with the formation of sodium hydride. Surprisingly, fluorinated ketyls such as the ketyl of perfluoroacetone or perfluorocyclobutanone are stable enough to be detected in solution at room temperature.[12]

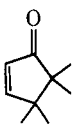
It is apparent that ketyls with α hydrogen atoms are inherently unstable[11] because of the high spin density on the carbonyl carbon. The stability of *tert*-butyl isopropyl ketyl or phenyl cyclopropyl ketyl is undoubtedly connected with a preferred conformation that places the α carbon–hydrogen in the nodal plane of the π system.[13] Thus $a_\alpha{}^H$ in *tert*-butyl isopropyl ketyl is 2.38 G[7] and that in phenyl cyclopropyl ketyl is <1 G (Figure 1).

In acetone ketyl[11] or pinacolone ketyl[8] the value of $a_{CH_3}{}^H$ is in the range of 15–16 G. Since $a_\alpha{}^H \cong 40\rho_C \cdot \langle\cos^2\theta\rangle$ for a radical ion,[14] ρ_C is $\sim$0.8 for a ketyl. For *tert*-butyl isopropyl ketyl the value of $\langle\cos^2\theta\rangle$ for the methine carbon–hydrogen bond must be $\sim$0.07, consistent with a value of θ of $\sim 0 \pm 15°$.

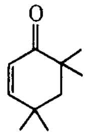
Ketyls of small ring ketones can also be unstable, even when the α hydrogens have been substituted. Thus, although 2,2,6,6-tetramethylcyclohexanone ketyl can be prepared, the reduction of 2,2,4,4-tetramethylcyclobutanone at $-80°$ with potassium metal gives a ketyl that at $-40°$ readily decomposes to yield 3,3,5,5-tetramethylcyclopentane-1,2-semidione.[15] A similar behavior has been noted for 7-ketobicyclo[2.2.1]heptene and its benzo derivative.[16] Alkali metal reduction of 2,2,4,4-tetramethylcyclobutanone-1,3-dione yields a paramagnetic substance assigned the ketyl structure.[17] However, the g value and a^C are more consistent with a semidione structure.[18,19]

Ketyls stable in solution at room temperature require either the absence of α hydrogen atoms or the presence of an α hydrogen atom which forms a dihedral angle with the carbon p_z orbital that stereoelectronically restricts interactions, either because of a rigid bridged geometry or because of a conformation preference.[20] Vinyl ketones represent a class of potentially stable ketyls, and in fact after this work was initiated, a report on the preparation of 2,2,6,6-tetramethyl-4-hepten-3-one ketyl appeared.[21] The *tert*-butyl hydrogens split by 0.27 and 0.39 G as opposed to the 11.67-G splitting from the β hydrogen. Since no splitting was observed for the α hydrogen, about half of the spin density resides on the β carbon and the other half on the carbonyl group. Interestingly, Ikegami and Seto[22] found very little spin density in the carbonyl group of the tropone ketyl since $\Sigma a^H = 27.5$ G ($Q_{CH}{}^H \approx -27$ G). The stable ketyls of tetraphenylcyclopentadienone[23] and some 2,6-di-*tert*-butyl-4,4-dialkylcyclohexadienones[24] are also reported.[25]

We now wish to report the synthesis of the unsaturated ketyls derived from ketones **1–4** and the appropriate benzo derivatives.



1



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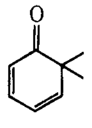

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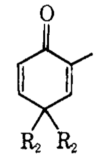
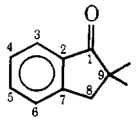
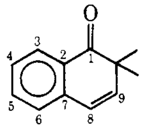


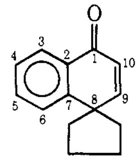
4a, $R_1 = H$; $R_2 = CH_3$
b, $R_1 = H$; $R_2 = C_6H_5$
c, $R_1 = R_2 = CH_3$



1b



3b



4b

Results

Cyclopentenone Ketyls. Electrolytic reductions of 2-cyclopentenone, 5,5-dimethyl-2-cyclopentenone, and 4,4-dimethyl-2-cyclopentenone[26] in DMF at -60 or $+25°$ gave no esr signal above the surface of a mercury pool electrode. The electrolytic reduction of **1** (10^{-2} *M*) yielded a well-resolved spectrum with lines of 100-mG width containing an 11.0-G doublet, 0.64-G septet, and a 0.45-G doublet proton splitting. The assignment of hyperfine splitting constants (hfsc) is made in Table I on the basis of Hückel and McLachlan[27] MO calculations, and by analogy with **5**.[21,28]

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[11] J. E. Bennett, B. Mile, and A. Thomas, *J. Chem. Soc. A*, 298 (1968).

[12] E. G. Janzen and J. L. Gerlock, *J. Phys. Chem.*, **71**, 4577 (1967); J. L. Gerlock and E. G. Janzen, *ibid.*, **72**, 1832 (1968).

[13] Although dicyclopropyl ketyl has been reported several times in the literature, we have been unable to reproduce these results using high-vacuum techniques.

[14] G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).

[15] G. A. Russell, D. F. Lawson, and L. Ochrymowycz, *Tetrahedron*, **46**, 4697 (1970).

[16] Private communication from the late Professor S. Winstein.

[17] R. L. Ward, *J. Chem. Phys.*, **36**, 2230 (1962).

[18] An aliphatic ketyl has a g value of 2.0038 and $a_{CO}{}^C \cong 50$ G, $a_\alpha{}^C \cong a_\beta{}^C = 5$–$8$ G. A semidione has $g = 2.0048$, $a_{CO}{}^C = 0.5$–1.5 G, $a_\alpha{}^C \cong a_\beta{}^C = 5$–$8$ G.[19]

[19] G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971).

[20] Bicyclic cyclopropanone ketyls may be an exception to this generality.

[21] K. W. Bowers, R. W. Giese, J. Grinshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

[22] Y. Ikegami and S. Seto, *Bull. Chem. Soc. Jap.*, **41**, 2225 (1968).

[23] W. Broser, H. Kurreck, P. Siegle, and J. Reusch, *Z. Naturforsch. B*, **24**, 685 (1969).

[24] A. I. Prokofev, S. P. Solodovnikov, A. A. Volodkin, and V. V. Ershov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1712 (1968).

[25] Reduction of diphenylcyclopropenone with alkali metals slowly yields biphenyl radical anions.[19]

[26] R. S. Rowe and W. E. Tyler, III, *J. Org. Chem.*, **26**, 3525 (1959).

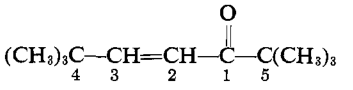
[27] A. D. McLachlan, *Mol. Phys.*, **3**, 223 (1960).

[28] Reductions in DMF solution can lead to complications, particularly at high potentials.[6] Benzaldehyde and acetophenone can yield phenylglyoxal or 1-phenylpropane-1,2-dione radical anions, apparently *via* reaction of the dianion of the ketone with DMF.[14,15] Unsaturated semidiones are easily distinguished from the ketyls by the mag-

Table I. Observed Hyperfine Splitting and Calculated Spin Densities for Ketyls of $1\cdot^-$, $2\cdot^-$, and **5**

	Obsd hfsc, a^H			Calcd spin densities	
Position	$1\cdot^-$	$2\cdot^-$	**5**	Hückel	McLachlan
C-1				0.3259	0.3581
C-2	0.45 ± 0.02	0.80 ± 0.03	0	0.0765	−0.1142
C-3	11.0 ± 0.1	11.80 ± 0.08	11.67	0.4662	0.7106
C-4[a]	0.64 ± 0.02	0.80 ± 0.03	0.39[b]		
C-5[a]		0.34 ± 0.02	0.27[b]		
O				0.1314	0.0455

[a] $a_{CH_3}{}^H$. [b] Our assignment.



$$(CH_3)_3\underset{4}{C}-\underset{3}{C}H=\underset{2}{C}H-\underset{1}{\overset{O}{\overset{\|}{C}}}-\underset{5}{C}(CH_3)_3$$

5

2,3-Benzo-5,5-dimethylcyclopentenone produced a strong esr signal upon electroreduction (Figure 2). The calculated spin densities and assignments are given in Table II. Indanone also produced a radical anion with similar coupling constants to that from **1b**, but with an additional triplet of 13.6 G (see Table II).

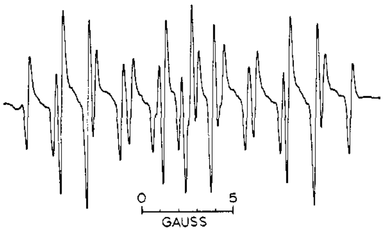


Figure 2. First-derivative esr X-band spectrum of **1b** in DMF solution.

Table II. Observed Hyperfine Splitting and Calculated Spin Densities for **1b** and Indanone Ketyls

	Assigned hfsc		Calculated spin densities	
	1b	Indanone		
Position′	a^H	a^H	Hückel	McLachlan
C-1			0.3634	0.4385
C-2			0.0636	0.234
C-3	5.54 ± 0.05	5.54 ± 0.05	0.1285	0.1681
C-4	<0.1	<0.1	0.0081	−0.0561
C-5	6.80 ± 0.05	6.82 ± 0.05	0.1593	0.2137
C-6	1.49 ± 0.05	1.64 ± 0.05	0.0081	−0.0561
C-7			0.1285	0.1681
C-8	1.87 ± 0.05	1.53 ± 0.05		
C-9		13.6 ± 0.1		
O			0.1404	0.1004

Cyclohexenone Ketyls. Electrolytic reduction of 2-cyclohexenone, 4,4-dimethyl-2-cyclohexenone,[30] or 6,6-dimethyl-2-cyclohexenone[31] failed to produce an esr signal at −60 or +25°. Reduction of **2** gave a well-resolved spectrum (Figure 3) at room temperature. Compound **2** with trideuteriomethyl groups at C-6 was synthesized and yielded a ketyl with an esr spectrum identical with that obtained from undeuterated **2**. The spectrum of $2\cdot^-$ requires a doublet splitting of 11.8 G, a triplet of 0.34 G, and an octet of 0.80 G. The splittings are assigned in Table I.

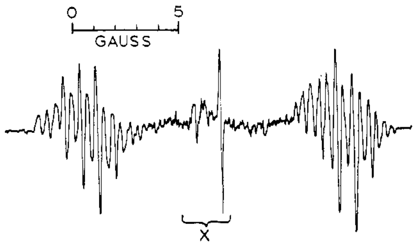


Figure 3. First-derivative esr X-band spectrum of **2** in DMF at 25°. Lines marked X are an impurity signal and were not observed reproducibly.

Both α-tetralone and 2,2-dimethyl-α-tetralone yielded strong esr signals upon reduction but neither system could be resolved.

Cyclohexadienone Ketyls. Electrolysis of 6,6-dimethylcyclohexadienone[32] gave a radical ion with 110-mG line width. The assignment of hfsc is given in Table III and the spectrum in Figure 4.

Table III. Observed Hyperfine Splitting and Calculated Spin Densities for $3\cdot^-$

		Calculated spin densities	
Position	a_H	Hückel	McLachlan
C-1		0.1974	0.1999
C-2	1.33 ± 0.05	0.0892	−0.0416
C-3	8.08 ± 0.05	0.1765	0.3864
C-4	1.33 ± 0.05	0.241	−0.1183
C-5	9.40 ± 0.05	0.3228	0.5385
C-6[a]	0.08 ± 0.01		
O		0.9000	0.0351

[a] $a_{CH_3}{}^H$.

2,3-Benzo-6,6-dimethylcyclohexadienone (**3b**)[33] gave a strong but not too well-resolved spectrum at −60°. Figure 5 gives the observed spectrum and the computer

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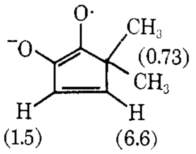
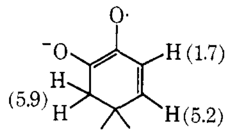
nitude of the hfsc. Thus, for **6** and **7** the following hfsc have been established.[29]



6



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(29) Unpublished results of Mr. R. Blankespoor, Mr. R. Penney, and Mr. C. Chung.

(30) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

(31) E. N. Marvell and E. Magoon, *J. Amer. Chem. Soc.*, **77**, 2542 (1955).

(32) K. Alder, F. H. Flock, and H. Lessenich, *Chem. Ber.*, **90**, 1709 (1957).

(33) E. N. Marvell and A. G. Geiszler, *J. Amer. Chem. Soc.*, **74**, 1259 (1952).

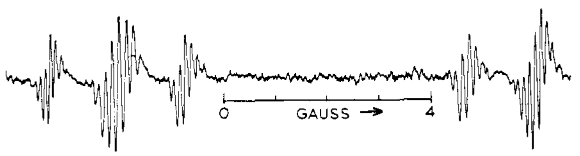


Figure 4. First-derivative esr X-band spectrum of **3** in DMF at 25°. Only the low-field half of the spectrum is shown.

simulation. Table IV lists the coupling constants and their assignment.

Table IV. Observed Hyperfine Splitting and Calculated Spin Densities for **3b**·⁻

		Calculated spin densities	
		Hückel	McLachlan
Position	a^H	ρ_i	ρ_i
C-1		0.2764	0.3301
C-2		0.0716	0.0446
C-3	1.20 ± 0.05	0.0774	0.0884
C-4	0.35 ± 0.02	0.0256	−0.0195
C-5	3.10 ± 0.05	0.1157	0.1509
C-6	0.82 ± 0.02	0.0008	0.0637
C-7		0.1232	0.1622
C-8	0.35 ± 0.02	0.0256	−0.0484
C-9	6.75 ± 0.07	0.1705	0.2703
O		0.1132	0.0851

4,4-Dimethylcyclohexadienone (**4a**) gave a triplet of triplets, a^H = 7.08 and 1.14 G. The methyl groups were not seen even though the lines were very narrow, ~60 mG. 4,4-Diphenylcyclohexadienone (**4b**) gave a ketyl with a^H = 7.02 (2) and 1.01 (2) G but with a line width of ~0.5 G, presumably from unresolved phenyl hydrogen splittings. 2,4,4-Trimethylcyclohexadienone (**4c**) gave a ketyl with a^H = 7.28, 6.66, and 1.16 G and $a_{CH_3}{}^H$ = 1.44 G. This confirms the assignments made in Table V for **4** on the basis of spin density calculations.

Table V. Observed Hyperfine Splitting and Calculated Spin Densities for **4**·⁻

	Observed hfsc		Calculated spin densities	
Position	**4**·⁻	**5**·⁻	Hückel	McLachlan
C-1			0.2470	0.2696
C-2	1.14 ± 0.05	1.01 ± 0.05	0.0255	−0.1075
C-3	7.05 ± 0.05	7.02 ± 0.05	0.2958	0.4452
O			0.1104	0.0550

4,4-Tetramethylene-2,3-benzocyclohexadienone (**4b**)[34] gave a partially resolved spectrum. The assignment of hfcs is shown in Table VI.

Tropone Ketyls. Tropone yielded radical ion **8** as reported by Ikegami and Seto,[22] with hfsc as shown. The assignment of the small hfsc to the position β to the carbonyl group is in accord with McLachlan calculations[22] which yield values of spin density at the α, β, and γ carbon atoms of 0.3722, −0.0202, 0.1843, respectively. 2,7-Dimethyltropone gave a spectrum consistent with **6** with $a_\beta{}^H$ = 0.48, $a_\gamma{}^H$ = 4.77, and $a_{CH_3}{}^H$ = 8.76 (2) G. 2,6-Di-*tert*-butyltropone gave only a triplet of broadened lines with a^H = 2.14 G, apparently from the γ hydrogen atoms. We conclude that the conformation of the di-*tert*-butyltropone is grossly different from tropone itself.

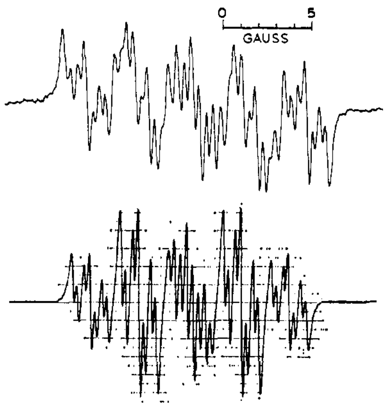
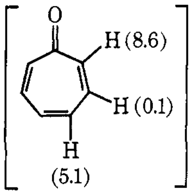


Figure 5. First-derivative esr X-band spectrum of **3b** in DMF at −60°: top, observed; bottom, calculated, with 0.11-G line width.



8[22]

Cyclopropyl Ketyls. We were unable to detect any esr signal upon electroreduction at −60°, or upon reaction with potassium in dimethoxyethane, for dicyclopropyl ketone, umbellulone, bicyclo[3.1.0]hexen-2-one, 4,4-dimethylbicyclo[4.1.0]hept-3-en-2-one, bicyclo[5.1.0]octa-2,5-dien-4-one, or 6,6-dimethyltricyclo[5.1.0.0^{3,5}]octan-2-one. Phenyl cyclopropyl ketone or phenyl α-deuteriocyclopropyl ketone gave a spectrum upon electrolytic reduction in DMF with $a_p{}^H$ = 6.5 and $a_o{}^H$ = 3.9 G. Acetophenone ketyl[5] has $a_p{}^H$ = 6.60, $a_o{}^H$ = 4.25 G, while aromatic semidiones have $a_p{}^H \approx$ 1.8, $a_o{}^H$ = 1.6 G.[14]

Table VI. Observed Hyperfine Splittings and Calculated Spin Densities for **4b**·⁻

		Calculated spin densities	
Position	a^H	Hückel	McLachlan
C-1		0.2640	0.3073
C-2		0.0179	−0.0182
C-3	1.4 ± 0.1	0.0773	0.0983
C-4	<0.2	0.0021	−0.0368
C-5	3.3 ± 0.1	0.0856	0.1073
C-6	1.4 ± 0.1	0.0021	−0.0368
C-7		0.0773	0.0983
C-8	0.64,[a] 0.20[a]		
C-9	6.9 ± 0.1	0.3256	0.5116
C-10	3.3 ± 0.1	0.0324	−0.1133
O		0.1156	0.0824

[a] Two equivalent hydrogen atoms in cyclopentane ring.

Divinyl Ketyl, Cyclopentadienone Ketyl. Attempted reduction of divinyl ketone gave only a polymer. The Diels–Alder dimer of cyclopentadienone[35] was reduced

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(34) R. T. Arnold, J. J. Buckley, Jr., and R. M. Dodson, *J. Amer. Chem. Soc.*, **72**, 3150 (1950).

(35) C. H. DePuy and C. E. Lyons, *ibid.*, **82**, 631 (1960).

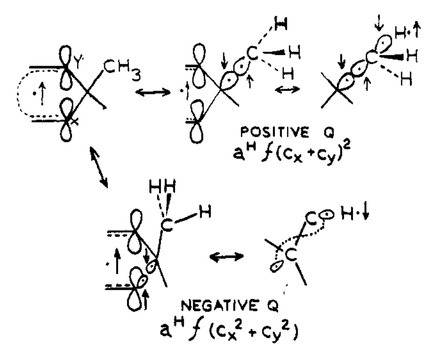


Figure 6. Spin-delocalization mechanisms.

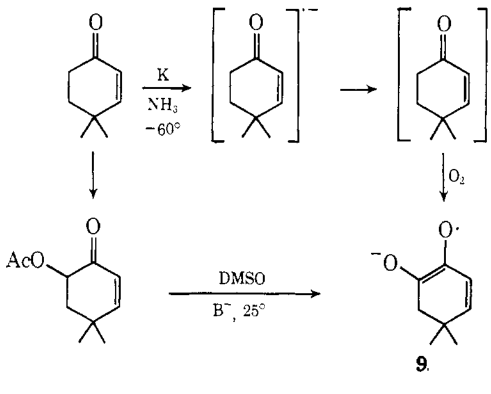
in hope of observing a reverse Diels–Alder to give cyclopentadienone ketyl. However only polymeric material lacking an esr signal was observed. Indenone also gave a polymer without esr signal. Cyclohepta-2,6-dienone and 4,5-homotropone gave only polymers under reductive conditions successful for 4,4-dialkylcyclohexa-2,5-dienone.

Discussion

Stable radical anions of α,β-unsaturated ketyls are observed only when allylic and enolic protons have been substituted. Benzo substitution increases the stability of the enone radical ions greatly so that α hydrogen atoms can be present but greater stability is still observed when these hydrogen atoms are replaced.

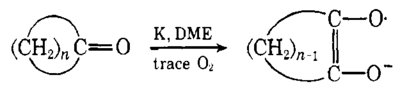
The report of Bersohn and Chen[36] that the ketyl of 4,4-dimethylcyclohexenone can be detected at −60° by reduction with potassium in liquid ammonia requires comment. The spectrum assigned by Bersohn and Chen to the ketyl is actually the semidione **9** which we have been able to prepare from the acetoxy ketone,[29] Scheme I. Semidione **9** has a lifetime of only a few seconds at 25°.

Scheme I

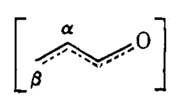


Other unsaturated ketyls mentioned by Bersohn and Chen[36,37] are either the semidiones or the semiquinones formed by oxidation of the enolate radicals or anions.

These results recall the reports of Lown[38] that a variety of cycloalkanone ketyls could be prepared at room temperature by potassium reduction. The reported ketyls are in fact the oxidation products, the semidiones.[39]



HMO calculation for a carbonyl group in conjugation with a double bond indicates a high spin density (about half) in the β position and the other half in the carbonyl group leaving the α position with little or no spin density. This is experimentally confirmed by 4,4,6,6-tetramethylcyclohexenone, 4,4,5,5-tetramethylcyclopentenone, and 2,2,6,6-tetramethylhepten-3-one



where the β proton has $a^{\mathrm{H}} = 11\text{–}12$ G and the α proton has $a^{\mathrm{H}} < 1$ G. The methyl splittings in **1** or **2** indicate that the carbonyl carbon must have a much lower spin density than the β carbon atom since only the C-4 methyls give hfs.

The lack of methyl hfs in 4,4-dimethylcyclohexadienone is rather surprising, particularly since hyperconjugation with the spin on C-3 and C-5 should take the form, $a_{\mathrm{CH_3}}{}^{\mathrm{H}} = Q_{\mathrm{CC(CH_3)}}{}^{\mathrm{H}}(c_3 + c_5)^2$ where c_3 and c_5 are the MO coefficients at C-3 and C-5.[40] The value of $(c_3 + c_5)^2$ is ~0.8 (Table V) for **4**$\cdot^-$. On the other hand, for **3**$\cdot^-$, where $a_{\mathrm{CH_3}}{}^{\mathrm{H}} = 0.08$ G, $(c_1 + c_5)^2$ is ~0.5. A possible explanation is that there are two mechanisms involved for methyl splitting in **1**–**4** with opposite signs for Q: a hyperconjugative effect with $a^{\mathrm{H}} \int (c_x + c_y)^2$ and a spin polarization–delocalization mechanism with $a^{\mathrm{H}} \int (c_x^2 + c_y^2)$.[41] Thus, bicyclo[4.1.0]heptene-2,5-semidione shows hfs by the cyclopropylmethylene hydrogen atoms even though $c_x = -c_y$. A mechanism where $a^{\mathrm{H}} \int (c_x^2 + c_y^2)$ must be involved. Specific mechanisms involving carbon–carbon bond hyperconjugation (process A) and spin polarization with hydrogen hyperconjugation (process B) are shown explicitly in Figure 6.

We conclude that for **4a**$\cdot^-$ processes A and B cancel each other. Apparently for **3**$\cdot^-$, where A would be relatively less important than B, the observed $a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ is the result of a predominance of process B; for **4a**$\cdot^-$ $c_3^2 + c_5^2 = 0.40$, $(c_3 + c_5)^2 = 0.81$; for **3**$\cdot^-$ $c_1^2 + c_5^2 = 0.33$ (20% less than **4a**$\cdot^-$), $(c_1 + c_5)^2 = 0.55$ (32% less than **4a**$\cdot^-$).

Experimental Section

General Technique. The X-band esr spectra were recorded with a Varian 4500 epr spectrometer with a 12-in. magnet. Temperature was regulated with a Varian V-4500 variable temperature controller. Ketyls were generated directly in the esr cavity in DMF using tetra-*n*-butylammonium perchlorate as the supporting electrolyte in a Varian flat-fused silica electrolytic cell with mercury cathode and platinum anode. At −60° the mercury cathode was, of course, a solid. The emf across the electrodes was increased until an esr signal could be detected. Reduction potentials were not measured.

The spectra were simulated by use of Lorentzian line shapes using a Japanese Electron Optics Corporation HNM-RA-1 spectrum accumulator. Molecular orbital calculations employed the parameters, $\alpha_{\mathrm{O}} = \alpha_{\mathrm{C}} + 1.8\beta_{\mathrm{CC}}$, $\beta_{\mathrm{CO}} = 1.4\beta_{\mathrm{CC}}$.

Reagents. 4,4,5,5-Tetramethylcyclopentenone (1) was prepared from 2.5 g of 4,4-dimethylcyclopentenone,[26] 5.5 g of NaH, and 22 g of methyl iodide. The reaction mixture was refluxed for 24 hr in 50 ml of ether under a N_2 atmosphere. After cooling, 50 ml of

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[36] H.-L. J. Chen and M. Bersohn, *Mol. Phys.*, **13**, 573 (1967).

[37] We are indebted to Professor Bersohn for supplying us with the pertinent spectra and data from the thesis of Dr. Chen.

[38] J. W. Lown, *Can. J. Chem.*, **43**, 2571, 3294 (1965); J. W. Lown, *J. Phys. Chem.*, **70**, 591 (1969).

[39] G. A. Russell and E. R. Talaty, *J. Amer. Chem. Soc.*, **87**, 4867 (1965).

[40] D. H. Whiffen, *Mol. Phys.*, **6**, 224 (1963).

[41] G. A. Russell, T. Ku, and G. Lokensgard, *J. Amer. Chem. Soc.*, **92**, 3833 (1970).

water was added and the organic layer was dried ($MgSO_4$). Evaporation of the ether and distillation of the residue at 15 Torr gave 1.5 g of material, bp 70–74°, that was further purified by preparative glpc on a QX-1 column at 110°; nmr (CCl_4) δ 0.93 (s, 6), 1.05 (s, 6), 5 9 (d, 1, J = 10 Hz), 7.4 (d, 1, J = 10 Hz).

Anal. Calcd for $C_9H_{14}O$: C, 78.12; H, 10.14. Found: C, 78.11; H, 10.30.

4,4,6,6-Tetramethylcyclohexenone (2) was prepared by the bromination–dehydrobromination of 2,2,4,4-tetramethylcyclohexanone[42] and by the methylation of 4,4-dimethylcyclohexenone.[30] The enone (5 g) was refluxed in 100 ml of ether with 3 equiv wt of $NaNH_2$ for 1 hr. Methyl iodide (3 equiv wt) was then added and the mixture refluxed for 24 hr. After cooling, 50 ml of water was added and the organic layer was dried ($MgSO_4$). Distillation at 15 Torr gave 1 g of product, bp 82–84°, which was purified by glpc on a QX-1 column at 110°; pmr (CCl_4) δ 1.17 (s, 6), 1.24 (s, 6), 1.7 (s, 2), 5.7 (d, 1, J = 10 Hz), 6.6 (d, 1, J = 10 Hz).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.95; H, 10.52. Found: C, 79.13; H, 10.60.

The use of trideuteriomethyl iodide (99%, Merck Sharp and Dohme of Canada, Ltd.) gave **2** with trideuteriomethyl groups at C-6. By pmr the isotopic purity was >97%.

2,3-Benzo-5,5-dimethylcyclopentenone (1b)[43] was prepared by the methylation of 1-indanone (Eastman Organic Chemicals) by treatment with $NaNH_2$ followed by methyl iodide; pmr (CCl_4) δ 1.2 (s, 6), 2.9 (s, 2), 7.2–7.7 (m, 4).

Bicyclo[3.1.0]hex-3-en-2-one was prepared by the methylation of cyclopentenone by trimethylsulfoxonium ylide to yield bicyclo[3.1.0]hexan-2-one in 70% yield. The bicyclic ketone (2 g) in 25 ml of ethylene glycol was treated with 3.4 g of bromine at 0°. After a few minutes the mixture was poured into a mixture of 7 g of Na_2CO_3 in 50 ml of pentane. The pentane layer was dried (Na_2SO_4) and evaporated to yield an oil which was added to 3.5 g of sodium methoxide in 45 ml of DMSO at <30°. The mixture was stirred for 20 hr at 25° before the addition of 200 ml of water. The mixture was extracted five times with 50 ml of pentane and the pentane extracts were dried (Na_2SO_4). Distillation at 28 Torr gave 2 ml of the ethylene ketal of bicyclo[3.1.0]hex-3-en-2-one, bp 89–95°. The ketal was shaken with 3 ml of 3% sulfuric acid for 10 min. The acid solution was extracted with ether and the dried ether solution evaporated to yield the enone which was purified by glpc on a 6-ft 20% DEGS on 60–80 Chromosorb W column at 140° (retention time, 8 min). The 100 mg of the enone collected had the following pmr spectral data: (CCl_4) δ 1.2 (m, 1), 1.5 (m, 1), 2.1 (m, 1), 2.5 (h, 1, J = 3 Hz), 5.5 (d, 1, J = 6 Hz), 7.6 (q, 1, J = 3 and 6 Hz). The multiplets due to the four cyclopropyl hydrogen atoms were completely separated from each other at 100 MHz.

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[42] H. A. Smith, B. J. L. Huff, W. J. Powers, and D. Caine, *J. Org. Chem.*, **32**, 2851 (1967).

[43] J. H. Burckhalter and R. C. Fuson, *J. Amer. Chem. Soc.*, **70**, 4184 (1948).

Organic Sulfur Chemistry. X. Selective Desulfurization of Disulfides. Scope and Mechanism[1]

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Contribution from the Department of Chemistry, McGill University, Montreal, Canada. *Received August 15, 1970*

Abstract: Organic disulfides undergo facile desulfurization to the corresponding sulfides on treatment with aminophosphines. This reaction is applicable to alkyl, aralkyl, and alicyclic disulfides and is compatible with a wide variety of common functional groups. The desulfurization process is stereospecific in that inversion of configuration occurs at one of the carbon atoms α to the disulfide group. The reaction was found to follow second-order kinetics. The rates of desulfurization are enhanced in solvents of high polarity. Activation parameters were measured and were found to be consistent with a mechanism involving nucleophilic scission of the disulfide bond in the rate-controlling step. A thermally labile phosphonium salt intermediate was observed in the desulfurization of di-2-benzothiazole disulfide (**14**).

The disulfide linkage is found in a large number of natural products[3,4] and contributes to the tertiary structure of enzymes[4] and hormones.[5] Since radiation damage to biologically important compounds may occur by scission of sulfur–sulfur bonds,[6] the cleavage of disulfides by radicals and nucleophiles has become a topic of considerable current interest.[7] In contrast to the behavior reported for a number of phosphines[8,9] and phosphites,[10,11] we have found that disulfides are

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[1] For Part IX, see D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971).

[2] NRCC Scholarship Holder, 1968–1970.

[3] L. Young and G. A. Maw, "The Metabolism of Sulphur Compounds," Wiley, New York, N. Y., 1958.

[4] R. F. Steiner, "The Chemical Foundations of Molecular Biology," Van Nostrand, Princeton, N. J., 1965.

[5] K. G. Stern and A. White, *J. Biol. Chem.*, **117**, 95 (1937); K. Jost, V. Debabov, H. Nesvabda, and J. Rudinger, *Collect. Czech. Chem. Commun.*, **29**, 419 (1964).

[6] R. Shapira and G. Stein, *Science*, **162**, 1489 (1968); G. Stein in "Energetics and Mechanisms in Radiation Biology," G. O. Phillips, Ed., Academic Press, New York, N. Y., 1968; L. K. Mee, G. Navon, and G. Stein, *Biochim. Biophys. Acta*, **104**, 151 (1965); G. Navon and G. Stein, *Israel J. Chem.*, **2**, 151 (1964); G. O. Phillips, Ed., "Energetics and Mechanisms in Radiation Biology," Academic Press, New York, N. Y., 1968; K. Dose in "Physical Processes in Radiation Biology," L. Augenstein, R. Mason, and B. Rosenberg, Ed., Academic Press, New York, N. Y., 1964; W. Snipes, Ed., "Electron Spin Resonance and the Effects of Radiation on Biological Systems," National Academy of Science, National Research Council, Washington, D. C., 1966.

[7] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 2731 (1970); J. L. Kice, "Mechanism of Reactions of Sulfur Compounds," Vol. 3, Wiley, New York, N. Y., 1968, p 91; N. Kharasch and A. J. Parker, *Quart. Rep. Sulfur Chem.*, **1**, 285 (1966); N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press, Elmsford, N. Y., 1961; A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 589 (1959).

[8] Only acyl, thioacyl, and vinylogous acyl "disulfides" desulfurize with triphenylphosphine, whereas benzyl and diethyl disulfides (among others) failed to react.[9] *p-N,N*-Dimethylamino phenyl disulfide was reported to desulfurize;[9b] however, in our hands, this substance failed to undergo desulfurization. Alkylidine alkyl disulfides have been desulfurized but undergo allylic type rearrangement *en route*.[9d]

[9] (a) A. Schönberg, *Chem. Ber.*, **68**, 163 (1935); (b) A. Schönberg and M. Barakat, *J. Chem. Soc.*, 892 (1949); (c) F. Challenger and D. Greenwood, *ibid.*, 26 (1950); (d) C. Moore and B. Trego, *Tetrahedron*, **18**, 205 (1962).

[10] When phosphites are used in this reaction, either irradiation is necessary for the reaction to take place,[11c,d,j] Arbuzov rearrangement occurs ($RSSR + (EtO)_3P \rightarrow RSEt + (EtO)_2P(O)SR$),[11a,b,d,f–h,j] or,