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ELECTRON SPIN RESONANCE STUDIES ON THE CYCLOPENTADIENYL RADICALS. ON THE ^{13}C HYPERFINE COUPLING CONSTANT AND SUBSTITUENT EFFECTS BY DEUTERIUM AND ALKYL GROUPS[1]

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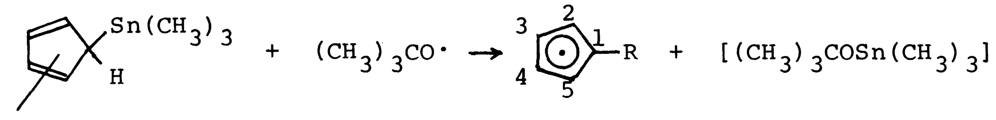
ESR spectra of parent and six substituted cyclopentadienyl radicals ($R\text{-}C_5H_4\cdot$; R=H, D, Me, Et, iso-Pr, t-Bu, Me_3SiCH_2), generated from the corresponding $R\text{-}C_5H_4\text{-}SnMe_3$ by an S_H2 attack on Sn with the photochemically generated t-butoxy radical, are recorded and discussed.

The parent cyclopentadienyl radical has been generated in solution by photolysis of a mixture of cyclopentadiene and di-t-butyl peroxide.[2] ESR spectra of alkyl-substituted cyclopentadienyl radicals are quite interesting and important in comparison with those of alkyl-substituted benzene anion radicals. However, generation of these radicals by hydrogen abstraction is not always easy except for silyl-substituted cyclopentadienyl radicals,[3] since additional signals due to an allylic radical resulting from addition of the t-butoxy radical to alkyl-substituted cyclopentadienes, as well as intrinsically low steady-state concentration of these cyclopentadienyl radicals, make the detailed investigation of ESR spectra of these radicals under the condition very difficult.

We have found that photolysis of a mixture of an alkyl-substituted cyclopentadienyltrimethylstannane and di-t-butyl peroxide at low temperature allows highly selective production of the corresponding alkyl-substituted cyclopentadienyl radical in high steady-state concentration through an S_H2 attack of the t-butoxy radical to Sn.[4,5] We have thus generated parent and six substituted cyclopentadienyl radicals by this novel method. Photochemically excited acetone can also be used for the production of these radicals.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3CO\cdot$$



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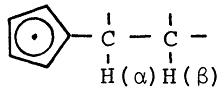
2a, R = H-
b, R = D-
c, R = CH_3-
d, R = C_2H_5-
e, R = $(CH_3)_2CH$-
f, R = $(CH_3)_3C$-
g, R = $(CH_3)_3SiCH_2$-

All the ESR spectra resolved with high S/N ratios, being enough to allow the detailed analysis. Table 1 lists hyperfine coupling constants (hfcc) and other ESR parameters of these radicals.

Table 1. ESR Parameters of Substituted Cyclopentadienyl Radicals

Radical	Temp/°C	hfcc/G					
		a_1^{*a}	$a_{2,5}$	$a_{3,4}$	$a_\alpha{}^b$	other	**R**[c]
2b	-92	5.86	6.19	5.99		a_D=0.90	
2c	-95	13.04	0.76	7.82	15.29		1.17
	-50	12.98	0.82	7.79	15.14		1.17
	24	12.72	1.00	7.73	14.80		1.17
2d	-95	12.74	0.94	7.79	15.99		1.26
	-50	12.80	1.00	7.70	15.33		1.20
	24	12.28	1.24	7.72	14.50		1.18
2e	-95	12.54	1.12	7.71	12.56	a_β=0.41[b]	1.00
	-50	12.66	1.15	7.62	12.28	0.42	0.97
	24	12.24	1.30	7.68	11.78	0.41	0.96
2f	-50	12.38	1.30	7.61		a_β=0.67	
	24	12.20	1.48	7.52		0.63	
2g	-95	14.04	0.50	7.58	10.40		0.74
	-50	14.00	0.48	7.62	10.49		0.75
	24	14.06	0.56	7.51	10.57		0.75

[a] $a_1^* = Q_H - \sum_{i=2}^{5} a_i$ (Q_H=30.20 G, see this text). [b]



[c] **R** = a_α / a_1^*

Table 2. Experimental and Calculated ^{13}C hfcc Values for Cyclic π Radicals (G)

Radical	Experimental (Temp/°C)	Calculated			Reference
		K-F[14)]	Y-K-K[15)]	INDO[16)]	
$C_5H_5\cdot$	2.66 ± 0.02 (-105)	1.56	2.04	4.1	this work
$C_6H_6^{\overline{\cdot}}$	2.8 ± 0.1 (-100)	1.30	2.23	4.0	ref. 17
$C_7H_7\cdot$	1.98 ± 0.02 (-105)	1.11	1.76	3.5	this work
$C_8H_8^{\overline{\cdot}}$	1.28 ± 0.05	0.98	1.43	3.0	ref. 18

As we have reported in a previous paper,[3] the Q_H value defined by the McConnell relationship[6] can be assumed to be constant for substituted cyclopentadienyl radicals and a_1^* (= $Q_H - \sum_{i=2}^{5} a_i$) is defined as the imaginary proton splitting constant corresponding to the spin density at position 1. Within the limit of this assumption, a_1^* offers a measure of the electronic effect of a substituent. Since the hfcc of the cyclopentadienyl radical (**2a**) is 6.04 G and temperature independent, the Q_H is 30.20 G.[3] The value of a_1^* should be larger than 6.04 G for a cyclopentadienyl radical substituted with an electron-donating substituent, while a_1^* should be less than 6.04 G for a substituted cyclopentadienyl radical with an electron-accepting group.[3]

Judging from a_1^* values of alkyl-substituted cyclopentadienyl radicals, electron-donating ability of alkyl groups is:

$$(CH_3)_3SiCH_2- > CH_3- > C_2H_5- > (CH_3)_2CH- > (CH_3)_3C-$$

Evidently, the trimethylsilylmethyl group is the strongest electron donor due to the extensive σ(C-Si)-π conjugation.[7] A similar Baker-Nathan order of the electron donating ability of alkyl groups has been found for benzene anion radicals,[8] and cycloheptatrienyl ones.[9,10]

Since a_α is approximately equal to $B < \cos^2\theta > \rho_1$ and $a_1{}^*$ is $Q_H\rho$, where B is a constant and θ is the angle between the C_1-C_α-H plane and the axis of the p orbital on the trigonal C_1 atom, the **R** value defined as $R = a_\alpha/a_1{}^*$ is equal to $(B/Q_H) < \cos^2\theta >$ and can be used for an extent of the conformational preference of an alkyl group. Table 1 contains these **R** values. Being freely rotating, the methyl group in **2c** gave a constant **R** (=1.17) in a temperature range over 100°C, irrespective of varying $a_1{}^*$ values. The small and constant **R** value for **2g** is another indication of the extensive σ(C-Si)-π conjugation. The trimethylsilyl group of **2g** eclipses preferably the p orbital on the C_1 atom throughout the temperature range studied.[11]

Two types of perturbing effects for deuterium substitution on a cyclic π radical, _i.e._ resonance-integral and Coulomb-integral perturbation, have been suggested previously.[12] The HMO perturbation theory predicts that the unpaired electron in the benzene-_d_ anion radical ($C_6H_5D^{\bar{\cdot}}$) should occupy predominantly the antisymmetric orbital in the antibonding orbitals by both two perturbations, as found experimentally. However, in cyclopentadienyl-_d_ radical (**2b**) it should be expected that the symmetric orbital between the degenerate highest occupied orbitals of the parent cyclopentadienyl radical should be stabilized and destabilized by resonance-integral and Coulomb-integral perturbation, respectively. Therefore, the unpaired electron should be located in the antisymmetric orbital if the resonance-integral perturbation would be dominant while it should be located in the symmetric orbital if the Coulomb-integral perturbation would be the determining factor. Although considerable contribution from the excited electronic configuration is expected because of thermal mixing and vibronic coupling, the ratio of $a_1{}^*$ to a_H of **2a** (= **r**) can be regarded as a proper criterion for discriminating the predominant perturbation. Thus, we can decide resonance-integral perturbation to be dominant if $a_1{}^*/a_H$ is less than unity, while Coulomb-integral perturbation to be the major effect if $a_1{}^*/a_H > 1$.

The spectrum of **2b** shows that the twofold degeneracy of the ground state electronic configuration of the cyclopentadienyl radical is lifted by deuterium substitution. Thus, two sets of triplet (intensity ratio 1:2:1) of 6.19 ±0.02 G and 5.99 ±0.02 G, which are further split into a triplet (1:1:1) of 0.90 ±0.01 G, are observed. Our sample of $(CH_3)_3SnC_5H_4D$ contained unlabeled compound and this was rather prosperous since the spectrum of **2b** was superimposed with that of **2a** and the latter served as an internal standard for precise determination of **r**. The ratio, **r**, is 0.969 ±0.008 from 12 measurements, which indicates that the unpaired electron resides predominantly in the antisymmetric orbital.[13]

The carbon-13 hyperfine constant for $C_5H_5\cdot$ was measured from the satellites of **2a** as 2.66 ±0.02 G at -105°C. Table 2 lists ^{13}C hfcc values of cyclic π radicals together with calculated hfcc values by three different methods.

Well-known Karplus-Fraenkel treatment[14] of ^{13}C hfcc did not give good agreement with these experimental splittings not only quantitatively but also qualitatively. Although the theory predicts that ^{13}C hfcc should increase with decreasing ring size, rather smaller ^{13}C hfcc of $C_5H_5\cdot$ than that of $C_6H_6^{\overline{\cdot}}$ was observed. On the other hand, Yonezawa-Kawamura-Kato treatment,[15] an alternative method for estimating ^{13}C hfcc from π-AO spin density matrix, gives rather good agreement with experiments. The latter treatment fully predicts the drop of ^{13}C hfcc from $C_6H_6^{\overline{\cdot}}$ to $C_5H_5\cdot$ due to the effect of off-diagonal elements of the π-AO spin density matrix included in the theory. Related works are in progress.

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