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NONPLANAR ALLYL RADICALS. ESR STUDIES OF THE ADDITION OF SULFUR, SILICON AND TIN-CENTERED RADICALS TO ALLENES

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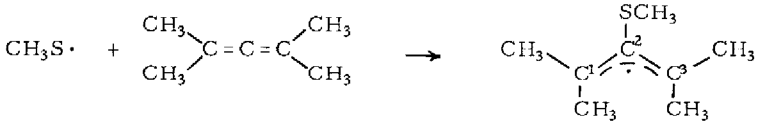
Allyl radical is planar, and the relatively high barrier to rotation about the two C-C bonds causes both pairs of protons at C-1 and C-3 to be inequivalent in its esr spectrum.[1] Similar differentiation of exo and endo positions pertains to other allylic radicals generated from various alkenes or allylic derivatives by processes involving either a hydrogen atom or a heteroatom transfer, respectively.[2] The introduction of bulky alkyl groups in the endo positions has recently been shown to induce nonplanarity in allylic radicals.[3]

We wish to report the formation of a novel series of nonplanar allylic radicals by homolytic addition to the central carbon of allenes. Thus, methylthiyl radical reacts with tetramethylallene (TMA) to form an adduct **I** in which all 12 methyl protons are equivalent as shown by the



I. (1)

tridecet splitting in Figure 1 with the expected binomial intensity ratios. The esr parameters of the adduct are listed in Table I, together with those of the analogous species from other sulfur, silicon and tin-centered radicals. In this study, the heteroatom radicals $R_nX\cdot$ were generated

Figure 1. Esr spectrum of methylthiyl adduct to tetramethylallene at + 15°C showing resolved ^{13}C splittings. Nmr field markers are in kHz.

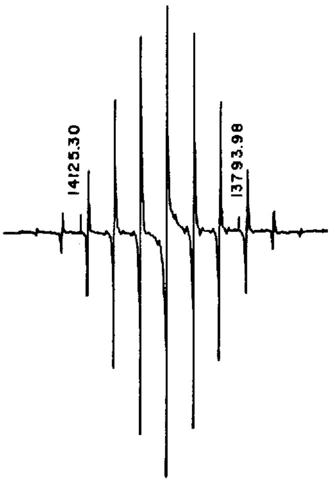


Table I. Esr Parameter of Heteroatom-Centered Adducts to TMA.[a]

Addend $R_nX\cdot$	Temp (°C)	$\langle g \rangle$[b]	Hyperfine Splitting, Gauss $a_H(CH_3)$[c]	a_X	$a_{^{13}C}(R)$	$a(R)$
$CH_3S\cdot$	+ 24	2.0029	13.02	(d) ^{33}S	7.95	(e)
	- 90		13.15	(d) ^{33}S	(e)	1.45 ^{1}H
$CF_3S\cdot$	+ 23	2.0030	13.02	(d) ^{33}S	(e)	1.19 ^{19}F
	- 26		13.19	(d) ^{33}S	(e)	1.07(f) ^{19}F
	- 58		13.29	(d) ^{33}S	(e)	1.07(g) ^{19}F
$CH_3CH_2CH_2S\cdot$	+ 15	2.0028	12.94	(d) ^{33}S	7.77	(e) ^{1}H
	- 85	2.0028	13.12	(d) ^{33}S	(d)	1.04(h) ^{1}H
$(CH_3)_3Sn\cdot$	- 5	2.0023	12.12	160 ^{119}Sn 153 ^{117}Sn	7.87	(e) ^{1}H
	- 60		12.31	152 ^{119}Sn 145 ^{117}Sn	(e)	(e) ^{1}H
$(CH_3)_3Si\cdot$	+ 20	2.0022	12.01	(j) ^{29}Si	(j)	(e) ^{1}H
	- 38	2.0023	12.06			

[a] In cyclopropane solutions. [b] Uncorrected. [c] Tridecet splitting. [d] Undetected. [e] Unresolved. [f] Broadened lines, partially resolved. [g] $M_I = \pm 1$, 2 lines split into 5 components (overlapping triplets), others are 4. [h] $M_I = \pm 1$ line split into 4 components, others are 3. [j] Overlapping lines.

by procedures previously employed in the homolytic additions of these radicals to simple alkenes, viz., photolysis of either dialkyl disulfides, hexamethyldistannane or a mixture of di-t-butyl peroxide and trimethylsilane.[4]

Hyperfine splitting by the heteroatom moiety R_nX in the esr spectra of the allylic radicals listed in Table I show further fine features, which help to identify the adduct. Thus, each line in the tridecet spectrum of the methylthiyl adduct is further split at -90°C into a quartet due to hyperfine coupling to the 3 protons on the methylthiyl addend. Similarly, the quartet splittings due to 3 fluorines are readily resolved in the esr spectrum of the trifluoromethyl adduct to TMA at even 23°C. Although hyperfine splitting due to $^{33}S(I = \frac{3}{2}$, 0.74% natural abundance) was too weak, the splittings due to ^{29}Si in the trimethylsilyl adduct, and both ^{117}Sn and ^{119}Sn in the trimethylstannyl adduct (Table I) could be observed.

The magnetic equivalency of all 12 protons in the esr spectrum of **I** indicates that the structure of this adduct is not a planar allyl radical. Thus, previous esr studies of a series of methylated allyl radicals have shown that the proton hfs of methyl groups attached to the allyl radical in the endo and exo positions differ by at least a gauss or more;[2] and the difference in hfs is apparent in an INDO molecular orbital calculation carried out in Table II for a planar hydrocarbon model of **I**, i.e., 1,1,1,3,3-tetramethylallyl radical. We induced distortion from planarity

Table II. Effects of Nonplanarity on the Hfs of 1, 1, 1, 3, 3-Tetramethylallyl Radical Calculated by the INDO MO Method.[a]

θ_1[b]	θ_2[b]	Hyperfine Splitting, Gauss							
		a_{CH_3}				a_{C^2}	a_{H_2}	a_{C^5}	a_{C^6}
(deg.)	(deg.)	H_4	H_5	H_6	H_7				
0	0	20.1	20.1	16.2	16.2	-14.5	5.6	-9.5	-7.3
0	90	0.42	0.89	23.8	23.8	-13.8	53.7		
90	90	22.3	22.3	22.3	22.3	29.9	-18.3		
-45	+45	17.4	17.2	17.1	16.8	-27.1	70.0	-10.7	-9.9
-45[c]	+45	16.7	16.8	16.6	16.4	-27.0	84.3	-10.4	-9.9

[a] d(CH) = 1.08 Å, d(CC) = 1.38 Å, $<C^4C^3C^2$ = 120°. [b] Rotation of terminal group in the direction of arrow is +. [c] $<C^4C^3C^2$ = 130°.

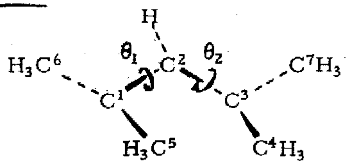


Figure 2. A model for nonplanar allyl radical.

in this model by varying the torsional angles θ_1 and θ_2 about the C^1-C^2 and C^2-C^3 bonds, respectively, as depicted in Figure 2. The INDO MO calculations show that the proton hfs's of both exo and endo methyl groups become more or less equal in a model in which $\theta_1 \sim -45°$ and $\theta_2 \sim +45°$. Variation in the internal angles CH_3-C^1-C^2 and CH_3-C^3-C^2 also improve the fit to the experimental values. As a result of such a distortion from planarity, the calculations indicate that the spin density at C-2 becomes more negative and the hfs increases. Unfortunately we were unable to measure the ^{13}C (natural abundance) hfs to verify this prediction. However, the observation of the unusually large ^{117}Sn and ^{119}Sn hfs in the trimethylstannyl adduct to TMA is consistent with this expectation.[5]

Molecular models also support a formulation in which nonplanarity relieves steric strain imposed by a bulky substituent on the central carbon. Such a "twisted" allyl radical loses in part the delocalization energy inherent in a planar allyl system,[6] and the resulting structure is expected to be less rigid than its planar counterpart. Indeed, we find that the esr spectrum of **I** exhibits a rather pronounced line broadening effect as the temperature is lowered. (Over the same temperature range, the esr spectra of planar allyl radicals show no detectable line broadening.) Only at the low temperature limit are the broadened lines in the spectrum of **I** resolved into a quartet (vide supra). Line broadening due to the modulation of the hfs by motional averaging has been treated theoretically.[7] The added complexities in the spectrum of **I** involving both the allyl framework as well as hindered internal rotation about the C^2-SCH_3 bond complicate a detailed lineshape analysis of the broadening which must await further studies.

Only a weak esr spectrum was observed when the sterically hindered di-t-butyl disulfide was photolyzed in the presence of TMA. We surmise that methyl radicals generated from the photolysis of diacetyl peroxide also did not react with TMA at any appreciable rate, since only the characteristic esr spectrum of methyl radical was observed. Allenes such as TMA are not only susceptible to homolytic addition but also undergo hydrogen atom transfer. Thus, t-butoxy radicals react with TMA exculsively by the latter route under these conditions, and only the esr spectrum of $(CH_3)_2C=C=C(CH_3)\dot{C}H_2$ is obtained.[8] There is no evidence for the presence of t-butoxy adducts to TMA. The preference for abstraction is in accord with the known propensity of t-butoxy radicals to react with simple olefins preferentially by hydrogen atom-transfer rather than by addition.[9] On the other hand, the facile addition of sulfur, silicon and tin-centered radicals to TMA in competition with hydrogen transfer is also in agreement with the behavior of these radicals toward simple alkenes.[4] We have observed homolytic addition to other allenes such as 1, 1-dimethylallene, 1, 1-di-t-butylallene, 1-t-butyl-3, 3-dimethylallene and tri-t-butylallene. However, there is some ambiguity as to the degree of regiospecificity in the addition of the heteroatom-centered radicals to these allenes, since chemical studies[10] have shown that addition to the terminal carbons becomes more important as the number of alkyl substituents decreases. Spectral studies of these complex systems will be presented in due course.[11]

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