

Preliminary communication

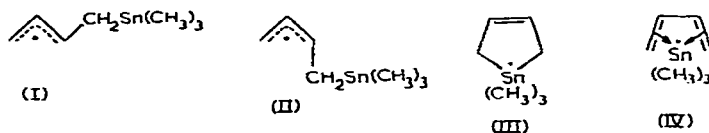
Electron spin resonance study of the adduct of trialkylstannyl radical to butadiene

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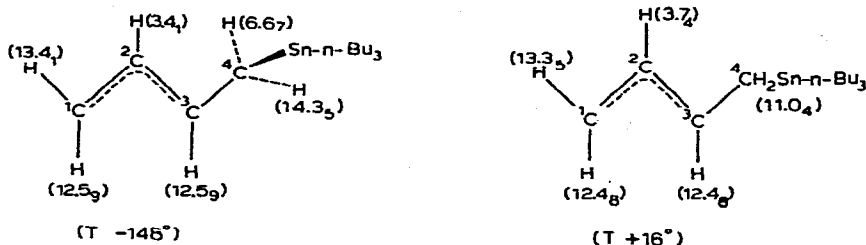
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The radical chain addition of trimethylstannane to 1,3-butadiene was reported by Kuivila and coworkers to afford *cis*-crotyltrimethyltin rather than the *trans* isomer as the major product¹. To explain this unusual result they suggested the presence of a bridged radical III or a π -complex species IV in equilibrium with the open-chain allylic isomers I and II.

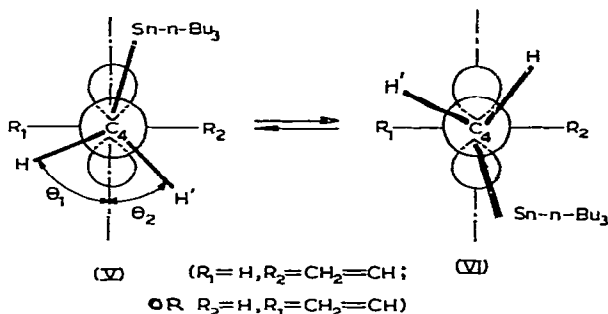


In order to pursue this interesting proposal, we examined the electron spin resonance (ESR) spectrum of the adduct of tributylstannyl radical to butadiene. Trialkylstannyl radicals for these studies were readily generated *in situ* either by reaction of tributylstannane and *t*-butoxy radicals produced photolytically from di-*t*-butyl peroxide or by direct photolysis of hexamethyldistannane². The ESR spectrum of only one paramagnetic species was observed under these conditions, the temperature variation of which is shown in Fig. 1. The analysis of the spectrum observed at -148° showed four sets of doublets (14.3₅, 13.4₁, 6.6₇ and 3.4₁ G) further split into a 1/2/1 triplet of 12.5₉ G. When the temperature was raised to $+16^\circ$, the spectrum changed to one consisting of a pair of doublets (13.3₅ and 3.7₄ G) split further into two sets of triplets (12.4₈ and 11.0₄ G). The phenomenon was reversible, and doubtlessly involved a temperature dependent dynamic change. The ESR spectra observed at both temperatures were clearly associated with allylic radicals, and the coupling constants shown below were assigned on the basis of comparisons with other substituted allyl radicals^{2,3}.

These results are consistent with earlier studies which showed that (a) radical additions generally occurred to the *S-trans* conformation of butadiene and (b) the allylic adduct was configurationally stable under these conditions (at least at temperatures between 0° and -150° ^{2,3}).



The spectra shown in Fig. 1 also exhibit selective line broadening due to hindered internal rotation around the C_3-C_4 bond (*i.e.*, a dynamic equilibrium between conformations V and VI).



At the lowest temperatures studied, the two hydrogens at carbon-4 were inequivalent and the splitting consisted of two doublets. As the temperature was raised the "inner" two lines of the pair of doublets began to broaden (Fig. 1b), this portion of the spectrum then collapsed to a triplet with a broadened center line (Fig. 1c) and finally at the highest temperature achieved of $+16^\circ$, the center line ($M_1 = 0$) became sharper and this multiplet clearly approached a 1/2/1 triplet (Fig. 1d).

The first-order lifetime, τ , for the hindered rotation around the C_3-C_4 bond can be estimated by Eq. (1) when the splitting due to two protons consists of two sets of doublets, and Eq. (2) when the splitting is a triplet (the notations have their usual significance)⁴.

$$\tau^{-1} = T_2'^{-1} - T_2^{-1} \quad (1)$$

$$\tau = 8 (T_2'^{-1} - T_2^{-1})(\omega_1 - \omega_2)^{-2} \quad (2)$$

The ratio of T_2 to T_2' is proportional to the square root of the ratio of peak heights of the outer and inner lines. The values of T_2' were, thus, measured relative to T_2 from these peak height ratios. The lifetimes were calculated at various temperatures using values of $T_2 = 1.46 \times 10^{-7}$ sec and $\omega_1 - \omega_2 = 1.35 \times 10^8$ rad \cdot sec⁻¹ obtained from the spectrum at -148° . The linearity of the Arrhenius plot is shown in Fig. 2, from which the energy barrier and the frequency factor are estimated to be 5 kcal/mole and 10^{13} sec⁻¹, respectively.

The preferred conformation in V or VI can be deduced from the values of the

*The measurement of correlation times by line shape analysis is in progress⁵.

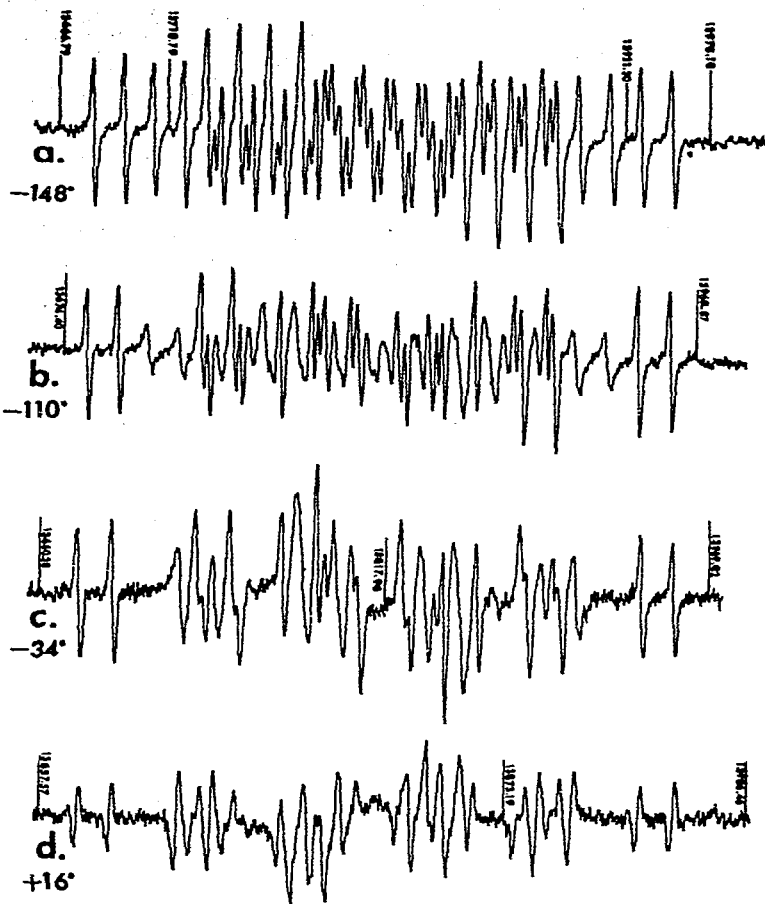


Fig. 1. The electron spin resonance spectrum of the adduct of tri-*n*-butylstannyl radical to 1,3-butadiene. The proton NMR field markers are in kilohertz.

two coupling constants due to H_4 and H_4' . Thus, the dihedral angles θ_1 and θ_2 which describe the two C_4-H bonds relative to the odd electron orbital at C_3 can be obtained from the general expression⁶:

$$\theta = \cos^{-1} (a_{H\beta} Q / a_{H\alpha} B)^{1/2}, \text{ where } |B/Q| = 2.401 \quad (3)$$

by invoking a simple $\cos^2 \theta$ dependence of the β coupling,

$$a_{H\beta} = B \rho \cos^2 \theta \quad (4)$$

and the McConnell relationship for the α -proton coupling,

$$a_{H\alpha} = Q \rho \quad (5)$$

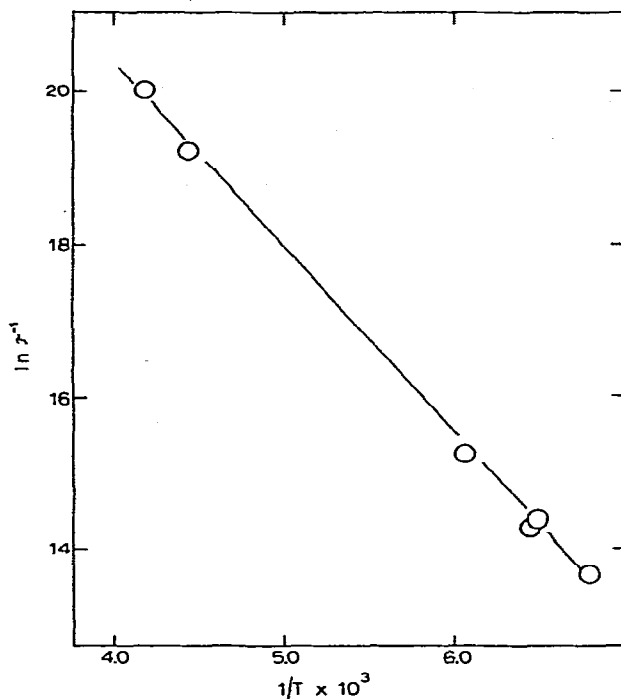


Fig. 2. The Arrhenius plot of the hindered internal rotation around the C_3-C_4 bond in the adduct of tri-*n*-butylstannyl radical to 1,3-butadiene. The line shows the relationship, $\tau^{-1} = 1.2 \times 10^{13} \exp(-4.83 \text{ kcal/mole}/RT)$.

At the most stable conformation, the values of θ_1 and θ_2 obtained in this manner are 63° and 47° , respectively. The dihedral angle between the C_4-Sn bond and the p -orbital is estimated to be only 7.5° .

The principal adduct of trialkylstannyl radicals to butadiene, thus, is a *trans* α -substituted allylic radical I. We could find no evidence for the presence of the *cis* isomer II or the tin-centered radicals III or IV. The most stable conformation adopted by I is an interesting one in which the tin atom is optimally located with respect to the π -orbitals. The fairly large energy barrier (5 kcal/mole) involved in displacing the tin atom from this position compared to the barrier of approximately 1 kcal/mole for hydrocarbon radicals^{2,7} may be due to a hyperconjugative interaction between the π system and the carbon-tin bond and/or delocalization of the π electrons onto the d -orbitals of tin. A similar situation but of reduced magnitude, also pertains to the sulfur substituted allylic analog².

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Note added in proof: The earlier studies may be accommodated if the products were isomerized under reaction conditions. For example, if large amounts of α -methallyltrimethyltin (2,1-adduct) were formed initially, recent experiments have shown that it is readily isomerized to *cis*-crotyltrimethyltin, which isomerizes further, but quite slowly, to the *cis-trans* mixture in which the *trans*-isomer predominates. (Private communication, Dr. H.G. Kuivila).

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