

perconjugative mechanism for the electron-releasing metal-methyl substituents.^{10,11} This conclusion is based on good experimental evidence that for structurally similar compounds the chemical shift of C₄ is not influenced by steric, compressional, and related factors but reflects changes in local π -charge density.¹² The para (C₄) ¹³C SCS for **1**, **5**, and **7** (Table II) parallels the ¹⁹F SCS (ppm) for *p*-fluorobenzyltrimethylstannane (2.60), **6** (2.14), and **8** (2.15).¹³

Secondly, the coupling constant data in Table I for entries **1–4** demonstrate the generality that ⁵J_{C₄-X} is uniformly larger than ⁴J_{C₃-X} for benzyl-metallic systems. That this phenomenon has its origin in carbon-metal (σ - π) hyperconjugation, and is a ground state property of some significance, is clearly exemplified by a comparison of the coupling data for compound **10** with the data for compound **5**. Note that in **10** where the dihedral angle (θ) is zero, ⁵J_{C₄-Sn} is less than 5 Hz, whereas in **5** where $\theta \approx 60^\circ$, ⁵J_{C₄-Sn} is 15.4 Hz! This striking result suggests that the long-range coupling is being determined predominantly by a π -electron contribution to the coupling mechanism which is enhanced when direct access to the tin s orbitals is possible via σ - π interactions. Interestingly, the similar value of ⁵J_{C₄-Sn} for **1** and **5** implies that the average or effective dihedral angle (θ) in the mobile monocyclic species ArCH₂Sn(CH₃)₃ must approach 60°. This was expected, for if C-Sn hyperconjugation is important, it must tend to increase this angle in order to maximize the resulting stabilization.¹⁴

Finally, the similar values of ⁵J_{C₄-Sn} for **7** (15.7 Hz) and **5** (15.4 Hz) indicate that the effective dihedral angle (θ) for the conformationally mobile tetralin system must also be $\approx 60^\circ$. This can only be achieved if the predominant conformation has the Sn(CH₃)₃ group axially orientated.⁴ The magnitude of the vicinal coupling constant ³J_{C₉-Sn} (19.2 Hz) unambiguously confirms this conclusion.¹⁵ These conclusions are strongly supported by the appropriate relative chemical shifts (¹³C and ¹⁹F).

Further studies on other model systems are in progress and these will be reported on shortly.

Acknowledgments. This research was supported in part by the Australian Research Grants Committee.

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- The conclusion is equivocal since a comparison of relative coupling constants in different systems through a different number of intervening bonds is highly questionable. Further, relative magnitudes can be complicated by the sign of the σ and π contributions to the coupling mechanism.
- All new compounds (**5–8**) gave satisfactory analyses, and their other properties (including their proton nmr spectra) were in accordance with the assigned structures.
- Model systems **5** and **9** have been successfully employed in other studies concerning the origin of the electronic effect of metallomethyl substituents (see ref 10a and 10b). An examination of Dreiding models indicates that the angle between the CCSn plane and the aromatic ring (dihedral angle θ) in the rigid systems **5** or **6** and **10** is approximately 60 and 0°, respectively. However, in **7** or **8** the alicyclic ring is potentially mobile, there being two possible conformations in which the Sn(CH₃)₃ group can occupy either an equatorial ($\theta \approx 30^\circ$) or an axial ($\theta \approx 70^\circ$) position. A consideration of nonbonding interactions and hyperconjugative stabilizing interactions suggests the axial conformer should be favored.
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- Utilizing the correlation line generated between para ¹³C SCS and σ^+ (see ref 12e) the following approximate values of σ^+ can be obtained: -CH₂Si(CH₃)₃ (-0.4, ref 6), -CH₂Sn(CH₃)₃ (-0.45), -CH₂Pb(CH₃)₃ (-0.52), -CH₂HgCH₂C₆H₅ (-0.50). On this correlation $\sigma^+_{\text{OCH}_3} = -0.65$. However, these σ^+ values are significantly less than those derived from reactivity and charge transfer measurements. See W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).
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- The fluorine nmr spectra of **6** and **8** were measured in benzene with a Varian A56/60 operating at 56.4 MHz. The value for p-FC₆H₄CH₂Sn(CH₃)₃ in cyclohexane was taken from a previous report; A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, **92**, 6140 (1970). The SCS quoted are upfield relative to *p*-fluoroethylbenzene, 5-fluorindan (ref 10c), and 6-fluorotetralin (ref 10c), respectively.
- The effective dihedral angle (θ) for mobile electron-deficient species, where presumably electronic demands on the C-Sn σ -bond are much larger than the neutral ground state (see ref 10b and 11), must therefore approach 90° (the most favored orientation for maximum σ - π interactions).
- A Karplus relation has been established between ³J_{C₉-C₅Sn} and the dihedral angles (ϕ) about the C-C bond (see ref 9). When Sn(CH₃)₃ is equatorial ϕ is 180°, when Sn(CH₃)₃ is axial $\phi \approx 70^\circ$. Note that in **10**, where ϕ is 180°, ³J_{C₉-Sn} is 41.3 Hz.

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Hot 1,4-Biradicals from the Photodecomposition of 3-Ethyl-2-propylthietane Vapor¹

Sir:

Biradicals are important intermediates in the photochemical and thermal decompositions of many classes of compounds, including the cyclic ketones,² the cyclic azo compounds,³ those alkanones with γ -hydrogen atoms,⁴ and the cyclic ethers and thioethers.⁵ In many of the photochemical studies of these systems it has been suggested that "hot" biradicals may be involved and the consequences of the vibrational and rotational disequilibrium which exists in such species has been a subject of great interest and some controversy.^{4c,d,e}

3-Ethyl-2-propylthietane (EPT), prepared according to Searles, *et al.*,⁶ was purified and separated into *cis* and *trans* isomers by preparative gas chromatography. Samples of pure *cis*-EPT or pure *trans*-EPT at pressures of 0.5 Torr were allowed to come to thermal equilibrium with mercury vapor at 25.0 \pm 0.1° and were illuminated with 253.7-nm

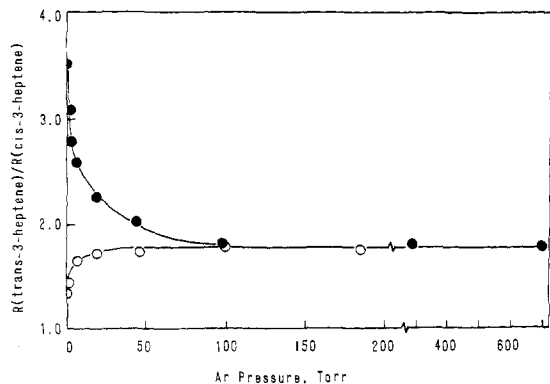
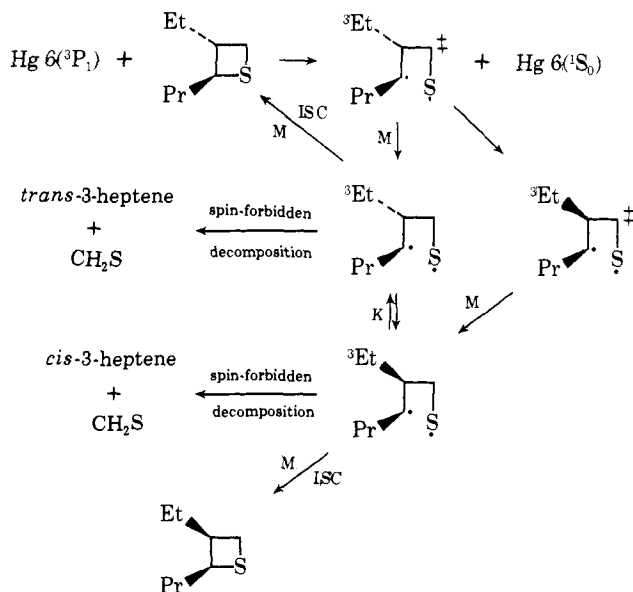


Figure 1.

radiation from a filtered low-pressure mercury lamp. Products resulting from 30 to 60 min of photolyses of either EPT isomer were 1-butene, *cis*- and *trans*-3-heptene, isomerized EPT, and, by inference, thioformaldehyde and thiobutyraldehyde, although these two latter products could not be measured.⁷ The same products, but in different relative yields, were found on direct photolysis of EPT at 313 nm.^{5c}

The products of greatest interest are the isomeric 3-heptenes since the relative rates of their formation indicate the stereochemical course of the decomposition which results from initial C₂-S cleavage.⁸ Starting with *trans*-EPT substrate, the ratio of the rate of formation of *trans*-3-heptene to that of *cis*-3-heptene, $R(\textit{trans}\text{-}3\text{-heptene})/R(\textit{cis}\text{-}3\text{-heptene})$, is 3.61 ± 0.07 , substantially smaller than the value of 6.88 obtained from direct photolysis at 313 nm. Starting with *cis*-EPT substrate, $R(\textit{trans}\text{-}3\text{-heptene})/R(\textit{cis}\text{-}3\text{-heptene}) = 1.30 \pm 0.02$ for the mercury photosensitized decomposition compared with 0.51 for direct photolysis at 313 nm. The variation in $R(\textit{trans}\text{-}3\text{-heptene})/R(\textit{cis}\text{-}3\text{-heptene})$ as a function of the pressure of added Ar is shown in Figure 1.⁹ Regardless of which isomer is being decomposed, the same value of $R(\textit{trans}\text{-}3\text{-heptene})/R(\textit{cis}\text{-}3\text{-heptene})$, 1.75 ± 0.05 , is obtained at high pressure. By comparison, in direct photolysis the addition of up to 1 atm of CO₂ had no effect on this ratio.

These results indicate that "hot," "triplet"¹⁰ biradicals which can decompose rather stereospecifically in the ab-

Scheme I. Reactions of thermalized triplet 1,4-Biradicals^a

^a For simplicity, only initial C₂-S cleavage of *trans*-EPT is shown.

sence of deactivating collisions and which can be deactivated by moderate pressures of Ar result from the interaction of EPT with triplet mercury atoms. Scheme I is consistent with experiments under conditions where deactivation is the only important process involving the initially formed hot triplet biradical, *i.e.*, for $P_{\text{Ar}} > 100$ Torr.

The fact that the same value of $R(\textit{trans}\text{-}3\text{-heptene})/R(\textit{cis}\text{-}3\text{-heptene})$ is obtained at high pressure regardless of which EPT isomer is decomposed is conclusive evidence that thermal equilibrium among the biradical rotamers is attained at high pressure. In other systems^{4d,11} ring closure of photolytically derived singlet 1,4-biradicals has been shown to be fast relative to the time required for multiple rotations about C-C bonds. If the same is true in this system, equilibrium must be established among triplet, not singlet, biradical rotamers. The rate determining step in the decomposition and/or ring closure of these 1,4-biradicals may therefore be their triplet-singlet intersystem crossing, in agreement with previous suggestions.^{2a,4d,e} The thermodynamic equilibrium constant, K (*cf.* Scheme I), is equal to 1.75 ± 0.05 at 25°. Thus, the average standard free energy of those triplet biradical rotamers which lead to *trans*-3-heptene is 330 ± 20 cal/mol smaller than the average standard free energy of those rotamers which lead to *cis*-3-heptene. As expected, the *transoid* rotamers are somewhat more stable than those having a *cisoid* conformation.

It is energetically feasible for the triplet biradical to undergo several additional reactions at low pressures when it retains a substantial fraction of its initial complement of excess internal energy.¹² From the standpoint of Scheme I, the most important of these additional reactions is the direct decomposition of the hot triplet into 3-heptene and CH_2S in its $^3(n, \pi^*)$ excited state since such a reaction would provide a rapid pathway which circumvents the slow spin-forbidden decomposition step. Preliminary experiments have failed to reveal any evidence for CH_2S in its $^3(n, \pi^*)$ state, however.

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- (9) Due to competitive quenching of excited mercury atoms, the rates of formation of the individual decomposition products decrease slightly with increasing Ar pressure. However, neither this nor pressure broadening should affect the values of $R(\textit{trans}\text{-}3\text{-heptene})/R(\textit{cis}\text{-}3\text{-heptene})$.
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Received June 1, 1974