

TRIMETHYLSTANNYL-2,4-CYCLOHEPTADIENE: A FLUXIONAL MOLECULE

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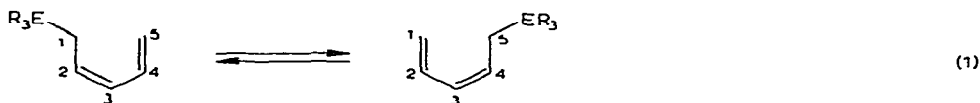
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SUMMARY

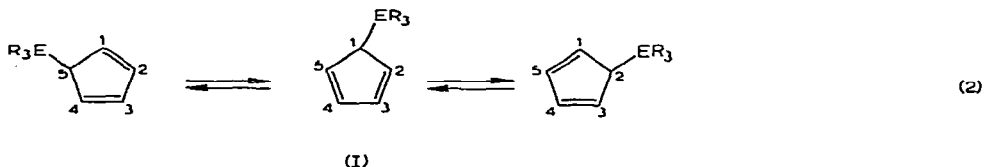
Trimethylstannyl-2,4-cycloheptadiene (II) was synthesized and shown to be fluxional on the NMR time scale. The activation energy for the [1,5] trimethyltin migration is estimated to be ca. 18 kcal/mole. This value is compared with estimated activation energies of 14 kcal/mole for trimethylstannylindene (IV) and 6 kcal/mole for cyclopentadienyltrimethylstannane (I, E = Sn). 1,1-Dimethyl-4-trimethylstannyl-2,5-cyclohexadiene (VIII) was also synthesized and was shown to be non-fluxional.

INTRODUCTION

The Group IV elements, Si, Ge, Sn, and Pb, when attached to 2,4-dienyl moiety exhibit fluxional behavior^{1,2,3,4}. Orbital symmetry arguments^{5,6} demand a [1,5] σ rearrangement, provided the reaction is concerted, the shift suprafacial, and involvement of *d* orbitals is negligible:



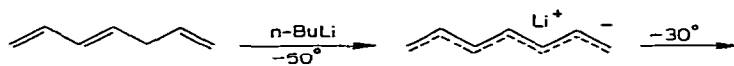
Most of the fluxional systems reported to date are based on cyclopentadienes in which the effects of [1,5] and [1,2] shifts are identical, *i.e.*, the [1,5] and [1,2] rearrangements are degenerate:



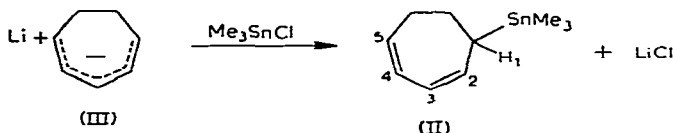
Larrabee⁷ has reported a fluxional tin-substituted cycloheptatriene in which the [1,5] shift is degenerate with a [1,4] shift. We therefore sought to demonstrate a [1,5] σ shift which would not be degenerate with other mechanisms, *e.g.* [1,2] or [1,4].

RESULTS AND DISCUSSION

Trimethylstannyl-2,4-cycloheptadiene (II) was readily prepared from 2,4-cycloheptadienyllithium (III) and trimethyltin chloride. The lithium reagent (III) was prepared by the procedure of Bates *et al.*⁸:



(3)



The product (II) was purified by vapor phase chromatography (VPC) and identified by its mass and NMR spectra. The NMR spectrum is temperature dependent (Fig. 1) and all changes are completely reversible. Although the spectrum is much too complex (even at 100 MHz) for complete analysis, the spectral changes are consistent with a rapid [1, 5] trimethyltin migration in which the magnetic environments of H-1 and H-5 become averaged.

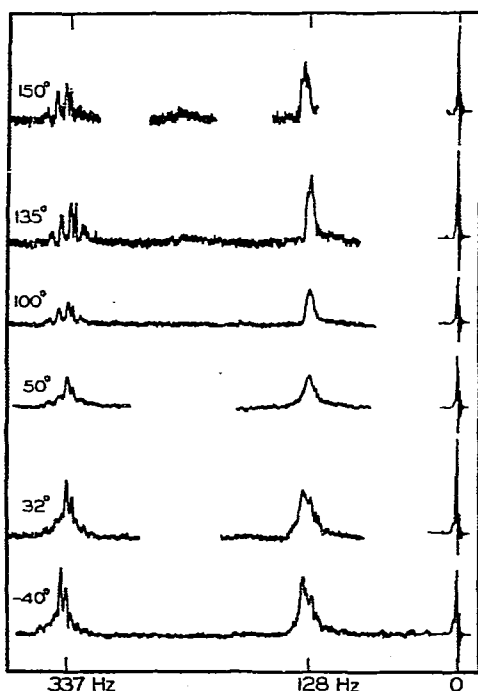
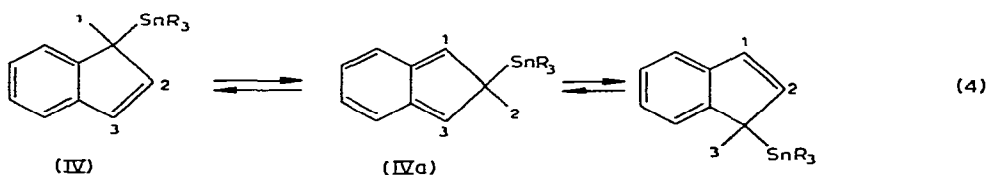


Fig. 1. 60 MHz NMR spectra of compound II, at various temperatures. Chemical shifts are *versus* the trimethylstannyl resonance.

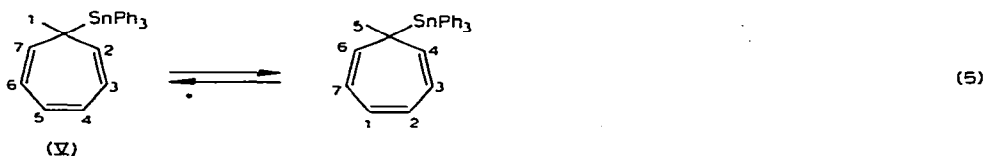
From -40° to -75° , no changes are observed in the spectrum. The -40° spectrum is therefore assigned to the static structure (II). As the temperature is increased (Fig. 1), the spin-coupling pattern of the 128 Hz peak broadens and collapses entirely at $+50^\circ$ *. Concomitantly, the fine structure on the 337 Hz peak broadens and then forms a new spin-coupling pattern. At 135° , some new fine structure appears on the 128 Hz peak, and a new peak at 238 Hz $((128 + 337)/2)$ appears. The H1 and H5 resonances are included in the 128 Hz and 337 Hz peaks, respectively; and upon averaging produce the 238 Hz peak.

The rate of the trimethyltin migration can be estimated from the data in Fig. 1. At coalescence, the rate of site exchange is approximately equal to the difference in resonance frequencies ($\Delta\nu$) of the protons undergoing averaging⁹. The activation energy for the exchange can be estimated if the value of the frequency factor, P_0 , is known, $P = P_0 \exp(-E_a/RT)$. For first-order reactions of this type, P_0 is practically always in the range 10^{12} – 10^{13} (sec^{-1})¹⁰. This range for P_0 gives an $E_a = 16$ – 19 kcal/mole allowing for an uncertainty in the coalescence temperature ($115 \pm 20^\circ$).

It is instructive to compare this estimated E_a with those reported in the literature for other fluxional molecules. Rakita and Davison³ find activation energies of ca. 14 kcal/mole for triorganostannylindenes (IV).



The activation energy for the corresponding silicon migration in trimethylsilylindene⁴ is 22.5 kcal/mole. The activation energy of I ($E = \text{Sn}$)³ is estimated to be 5–6 kcal/mole. Larrabee⁷ has found that the proton resonances of triphenylstannylcycloheptatriene (V) collapse to a single line below 100° due to a rapid $[1, 5]$ ($= [1, 4]$) trimethyltin migration. The activation energy for the process is 10.1 ± 0.8 kcal/mole.



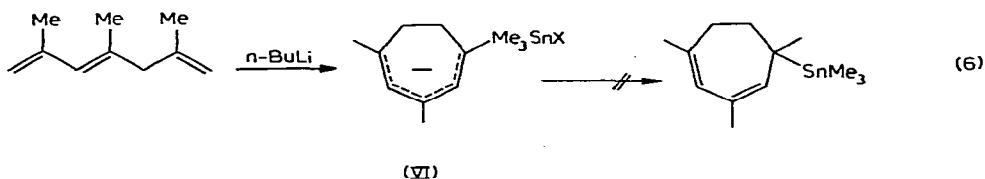
Thus, the activation energies for trimethyltin migrations increase in the order $I < V < IV < II$. The low activation energy of the $[1, 5] = [1, 2]$ shift in I arises from the low vibrational amplitude required of the tin group to shift to the adjacent carbon and the delocalization energy of the cyclopentadienide moiety. The high activation energy for the $[1, 2]$ shift in IV arises from the loss of delocalization energy in the intermediate IVa. The required vibrational amplitudes are presumably nearly equal

* Chemical shifts expressed in Hz are downfield from the tin-methyl resonance which occurred at $\tau \approx 0 \pm 0.1$ vs. external TMS at 30° . τ values are vs. TMS.

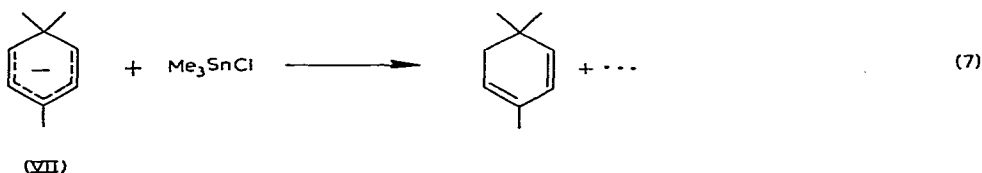
in II and V, but the intermediate, Va, undoubtedly has more delocalization energy than the intermediate, IIa:



Many attempts were made to prepare other pentadienyltin compounds which would have NMR spectra less complex than II. The 1,3,5-trimethylcycloheptadienide ion⁸ (VI) reacted with trimethyltin chloride or bromide to give complex mixtures from which pure organotin derivatives could not be obtained even by GLC. The primary product appeared to be a mixture of isomers of trimethylcycloheptadienes (*m/e* 136 in mass spectrum).

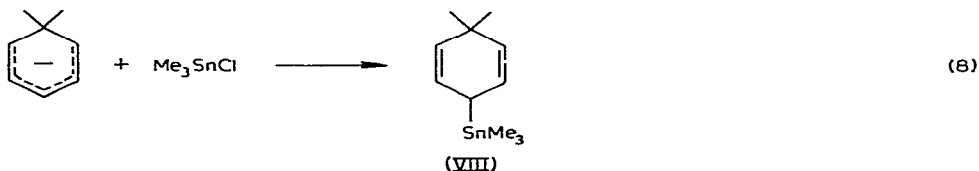


Trimethyltin chloride reacted with the 1,1,4-trimethylcyclohexadienide ion (VII) to give 1,1,4-trimethyl-2,4-cyclohexadiene as the only olefinic compound.



Apparently these highly substituted, delocalized anions are not sufficiently nucleophilic to displace halide from tin. Instead, one-electron exchange¹¹ occurs to give radicals which abstract H atoms from the solvent, or dimerize. The fate of the trimethyltin group was not established in the reaction (eqn. 7).

The 1,1-dimethylcyclohexadienide anion does displace chloride from trimethyltin chloride to give 1,1-dimethyl-4-trimethylstannyl-2,5-cyclohexadiene (VIII):



Compound VIII was unambiguously identified from its mass and NMR spectra. The NMR spectrum (Fig. 2) definitely establishes C-4 as the point of attachment of the Me₃Sn group. The H-4 resonance appears as a triplet of triplets ($J_{2,4} = 1.2$ Hz, $J_{3,4} = 4.0$ Hz) 152 Hz downfield from the Me₃Sn peak. The vinylic proton resonances

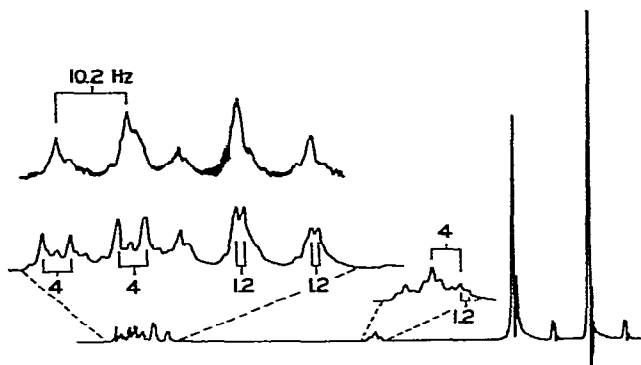


Fig. 2. 60 MHz NMR spectrum of compound VIII. Expanded insets are 100 Hz full scale. In the top vinyl pattern, H-4 has been decoupled (CCl_4 solvent).

appear as a complex (AA'BB'X) pattern 320 Hz downfield from the Me_3Sn peak. Decoupling H-4 causes the vinyl pattern to collapse to a perturbed AB quartet with approximate parameters: $J_{2,3} \approx 10$ Hz; $\Delta\delta_{2,3} \approx 24$ Hz. The lowest field resonance is most strongly coupled to H-4 and is assigned to H-3. In accord with the expectations of theory^{5,6} and the behavior of allyltrimethylstannane², compound VIII does not exhibit fluxional behavior on the NMR time scale at room temperature.

Several attempts were made to prepare unsubstituted cyclohexadienyl derivatives. 1,3- or 1,4-Cyclohexadiene appeared to be metalated by *n*-butyllithium at low temperatures, but upon reaction with trimethyltin chloride only intractable oils were obtained under a variety of conditions.

EXPERIMENTAL

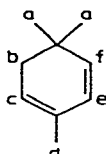
Mass spectra were obtained on an AEI MS902 spectrometer. Variable temperature NMR spectra were recorded on a Varian A-60 equipped with the Varian variable temperature unit. The temperature regulation dial was calibrated against methanol peak separations at low temperature and against a thermometer at temperatures above ambient. Toluene-*d*₈ was used as solvent in the temperature dependence studies. Chemical shifts were measured from the chart paper. Other NMR spectra were obtained on a Varian T-60 equipped with a spin decoupling unit. Schlenk tube techniques were used to handle all air sensitive compounds.

Trimethylstannyl-2,4-cycloheptadiene (II). Lithium cycloheptadienide was prepared in THF by the method of Bates *et al.*⁸ from 1.0 g of 1,3,6-heptatriene and 6.3 ml of *n*-BuLi (1.6 M in hexane). After this mixture had been kept at -30° for 1 h, excess (ca. 4 g) of trimethyltin chloride was added, causing an immediate precipitate of LiCl. The mixture was quenched with water and the organic and aqueous phases separated. The aqueous phase was washed three times with 30 ml portions of ethyl ether and the washings and the organic layer were combined. After washing with water, the ether was dried over sodium sulfate. Following removal of the ether, the residue was purified by VPC on a 5 ft. column (15% silicone on Chromosorb 20M) at 170° . The mass spectrum of the purified material exhibited peaks at (^{120}Sn) 258 (P), 243 (P-15), 229 ($\text{C}_8\text{H}_{13}\text{Sn}^+$), 211 ($\text{C}_7\text{H}_7\text{Sn}^+$), 185 ($\text{C}_5\text{H}_5\text{Sn}^+$), 165 (Me_3Sn^+),

151 (Me_2SnH^+), 150 (Me_2Sn^+), 135 (MeSn^+), 121 (SnH^+), 120 (Sn^+), 93 (C_7H_9^+), 91 (C_7H_7^+), 77 (C_6H_5^+), 65 (C_5H_5^+), 53 (C_4H_5^+), 51 (C_4H_3^+), 41 (C_3H_5^+), 39 (C_3H_3^+). (Found: C, 46.84; H, 7.28. $\text{C}_{10}\text{H}_{18}\text{Sn}$ calcd.: C, 46.77; H, 7.02%.)

When trimethyltin chloride was added to 1,3,5-trimethylcycloheptadienide⁸. LiCl precipitated immediately. The above workup procedure gave a mixture which exhibited an overlapping series of four peaks on GLC. A mass spectrum of this mixture had a strong parent peak at m/e 136. No heavier peaks were observed, and no peaks contained the tin isotope pattern.

1,1,4-Trimethyl-2,4-cyclohexadiene. This diene was prepared by the method of Crossly and LeSueur¹² from 1,1,4-trimethyl-3,5-cyclohexadione¹³. The diene is easily recognized from its very characteristic NMR spectrum (multiplicity and J -values in parentheses): τ_a 9.05 (1); τ_d 8.30 (4, $J_{bd} \simeq J_{cd} = 1.8$ Hz); τ_b 8.00 (6, $J_{bc} = 4.0$, $J_{bd} = 2.0$ Hz); $\tau_{c,e,f}$ 4.55 (multiplet). The addition of an equimolar amount of *n*-BuLi to the diene in THF at -20° gave a pale yellow color. The addition of trimethyltin chloride did not cause precipitation of LiCl until the solution was warmed to 45° .



The THF was removed and the residue treated with ether. The ether extracts were washed with water, dried and evaporated. An NMR spectrum of the resulting residue gave peaks due to starting diene and a methyl-tin resonance at τ 9.80. No butyltrimethylstannane could be detected in the mixture. That the diene was in fact metalated by *n*-BuLi is shown by the observation that *n*-BuLi reacts immediately with Me_3SnCl to give Me_3SnBu and LiCl precipitate under identical conditions.

1,1-Dimethyl-2,4-cyclohexadiene. 5,5-Dimethyl-3-oxocyclohexene¹⁴ was reduced with AlH_3 in ethyl ether¹⁵ to give an 80% yield of 5,5-dimethyl-3-hydroxycyclohexene, b.p. $48-49^\circ/0.5$ mm. Treatment of the alcohol with conc. H_3PO_4 gave a 20% yield of the desired diene; b.p. $111-112^\circ$ (lit.¹², 111°).

1.1 g (10 mmoles) of this diene in THF was treated with 10 mmoles of *n*-BuLi. After stirring at 25° for 0.5 h, 2.0 g (10 mmoles) of trimethyltin chloride was added and the mixture stirred for 2 h. The THF was then replaced with ether which was washed with water, dried, and removed. The residue was purified by VPC (silicone column). A mass spectrum of the purified liquid gave a parent peak at m/e 272 (^{120}Sn). Fragments were observed at $P-15$ and $P-30$, followed by a series of overlapping peaks at 231, 229 and 227. Other fragment peaks are 185 ($\text{C}_5\text{H}_5\text{Sn}^+$); 165, 150, 135 and 120 (Me_nSn^+ $n=3, 2, 1, 0$); 107 ($\text{C}_8\text{H}_{11}^+$); 91 (C_7H_7^+); 79 (C_6H_7^+); 77 (C_6H_5^+); and 65 (C_5H_5^+). (Found: C, 48.92; H, 7.50. $\text{C}_{11}\text{H}_{20}\text{Sn}$ calcd.: C, 48.78; H, 7.39%.)

In diethyl ether, *n*-BuLi does not react with dimethyl-2,4-cyclohexadiene. The products isolated were unreacted diene and *n*-butyltrimethylstannane.

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