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Preliminary communication

Temperature-dependent ^{13}C NMR spectra of trimethylstannylindene

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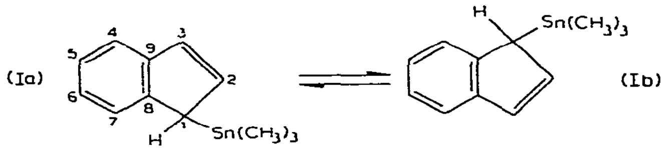
Earlier studies[1,2] of trimethylstannylindene (I) showed that this compound was subject to an intramolecular metallotropic rearrangement proceeding via an *apparent* 1,3 shift:



Two alternative explanations of this fluxional behavior may be proposed: (*i*) a true 1,3 shift; (*ii*) two successive 1,2 shifts[*]. Since the latter mechanism should proceed via an isoindenyl intermediate it should be possible to use the Diels–Alder reaction to isolate this and so resolve the problem unambiguously. By the formation of Diels–Alder-type adducts, the two-step migration course has been established for silicon indenyls[3], however, no Diels–Alder adduct has been reported for the tin indenyls[**].

A comparison of the free energy of activation $\Delta G^{\ddagger}$ for the indenyl system with that for the cyclopentadienyl system, as proposed by Cotton *et al.*[4], may help to solve the problem. If the value of $\Delta G^{\ddagger}$ for an indenyl compound is substantially higher than that for the corresponding cyclopentadienyl one, then the 1,2 shift mechanism will predominate in both cases. Although this approach is based on several vague assumptions[***], it has been found to be correct for the silicon migration[3,5].

The free energy of activation for the trimethylstannylcyclopentadiene system was reported to be 7.1 kcal/mole[6], but such measurements had not been performed for (I) since calculations of the rate constants from the PMR spectra of (I) are hindered by spin coupling effects[****].

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[*] A mixed type of migration may also exist but for the sake of simplification we exclude it here.

[**] Our attempts to isolate the isoindenyl intermediate of (I) by using tetracyanoethylene and acetylene dicarboxylate were unsuccessful (unpublished results).

[***] This approach includes the assumption that the migrations in both indenyl and cyclopentadienyl systems proceed via the same mechanism.

[****] Davison and Rakita[2] reported the value of $\Delta G^{\ddagger}$ (15.3 kcal/mole) for another tin indenyl: $C_9H_7Sn[(CH_3)_2Ph]$.

However, we have found the energy of activation for the metal migration from a study of the temperature dependence of the ^{13}C—{^{1}H} spectrum of (I) which avoids complications due to spin coupling effects. This approach was applied by us earlier to the cyclopentadienyl compounds[6].

The ^{13}C—{^{1}H} spectra (single scan) were measured on a JNM—4H—100 JEOL instrument at 25.14 MHz for carbon nuclei. Field sweep method was employed, so the saturating RF field frequency was swept synchronously with the field sweep. 8 mm o.d. sample tubes were used. Resolution was better than 0.8 Hz. The temperature was controlled with a JES-VT-3 unit accurate to ±1°C. Spectra were measured on the neat liquid.

Trimethylstannylindene was synthesised according to a procedure used by Jones and Lappert[7].

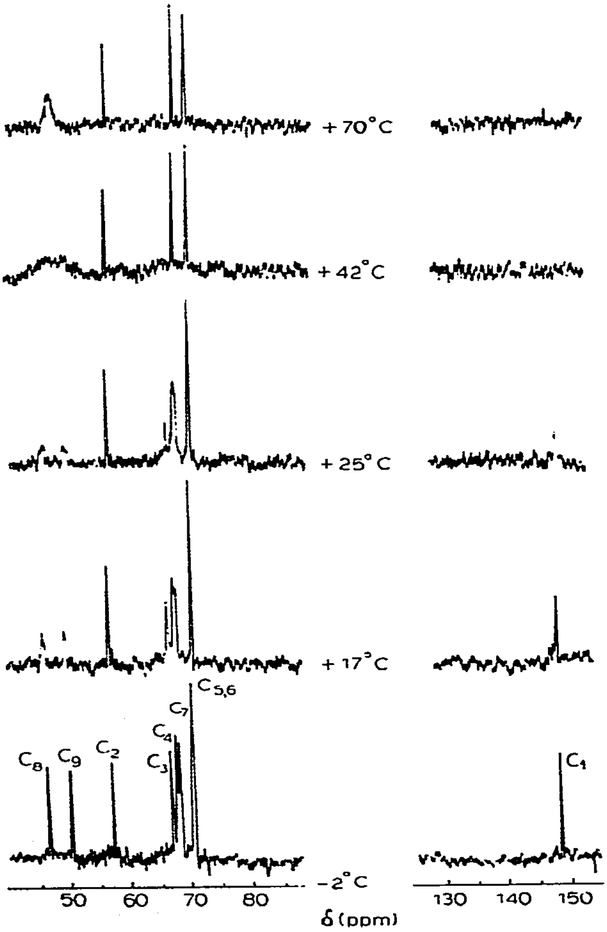

Fig. 1. ^{13}C—{^{1}H} spectra of the ring carbon atoms of trimethylstannylindene at various temperatures. Values in ppm relative to CS_2.

Figure 1 shows the $^{13}C-\{^1H\}$ spectra of the ring carbon atoms of compound (I) at various temperatures. At –2° the spectrum corresponds to a rigid structure. Table 1 summarises the assignments based on (i) the off-resonance technique[8], (ii) the selective saturation of protons[9], (iii) the shape of the temperature-dependent spectra, and (iv) the regularities observed for σ-cyclopentadienyl compounds[6].

TABLE 1

CHEMICAL SHIFTS OF CARBON ATOMS IN $C_9H_7Sn(CH_3)_3$ [a]

Carbon atom	C_1	C_2	C_3	C_4	C_7	C_5, C_6	C_8	C_9	CH_3
Shift	147.9	58.4	67.0	68.0	68.5	70.7	46.2	49.9	201.9

[a] The shifts are in ppm from CS_2 (external reference) and are accurate to ±0.2 ppm. The shifts were measured at 0°C.

Figure 1 demonstrates that, unlike the proton spectra, the carbon spectra contain no spin-spin multiplicity and are characterised by a rather wide range of chemical shifts, so they allow the study of exchange processes for both five-membered and for aromatic rings★. The processes may be considered as concerted two-position exchanges for the pairs C_1/C_3, C_4/C_7, C_8/C_9, C_5/C_6.

Thermodynamic parameters (E_a = 13.8±0.8 kcal/mole, ln$A$ = 11.7±0.8) have been obtained by studying the temperature dependence of the C_8/C_9 and C_4/C_7 signals★★ from

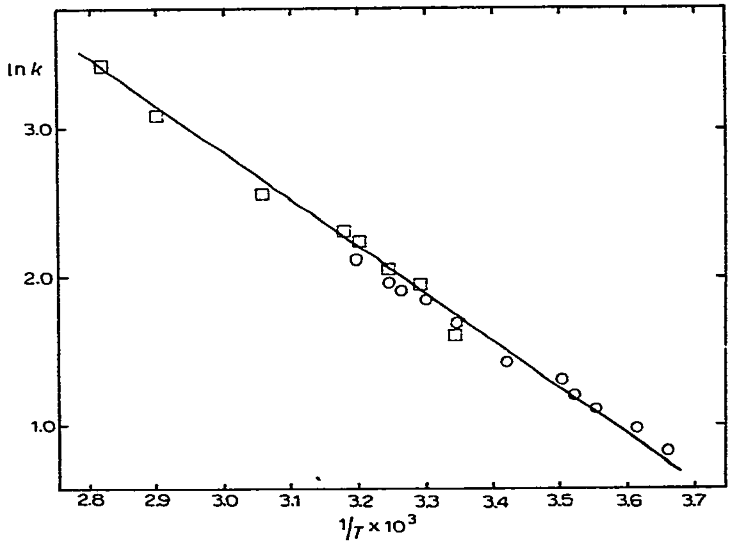

Fig. 2. ln *k* *vs.* $1/T$ obtained from the $^{13}C-\{^1H\}$ spectra of trimethylstannylindene. □ denotes ln *k* obtained from the analysis of the C_8/C_9 spectra; ○ denotes the same for the C_4/C_7 spectra.

★Some advantages of carbon-13 spectra in the study of dynamic phenomena have been recently demonstrated by D.K. Dalling *et al.*[10].

★★The C_5 and C_6 signals coincide even at slower rates of exchange. The C_1/C_3 signals are difficult to use since the difference in their chemical shifts is high.

0–82°. The ln k *vs.* $1/T$ plot is shown in Fig. 2. The parameters were estimated by collating the experimental and calculated spectra. The calculations of line shapes were performed using a BESM-6 computer. The spin-spin relaxation time, T_2, was taken as 0.3 sec. Chemical shift differences for the signals in the slow exchange limit were equal to 12.3 and 94.0 Hz for C_4/C_7 and C_8/C_9, respectively.

Thus, the free energy of activation for the tin indenyl derivative differs from that for the tin cyclopentadienyl derivative by 8.2 kcal/mole. This may be real evidence in favour of the mechanism consisting of the successive 1,2 shifts.

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