The Fluxionality of (*Z*)-6,6,6-Triphenyl-6-stannahexa-1,3-diene: Evidence for Symmetry-allowed Suprafacial [1,5]-Shifts in an Organometallic Compound †

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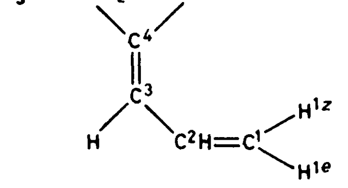
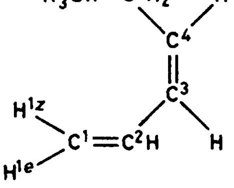
The ^{1}H and ^{13}C n.m.r. spectra of (*E*)- and (*Z*)-6,6,6-triphenyl-6-stannahexa-1,3-diene have been measured. The ^{1}H n.m.r. spectra have been fully assigned for the first time, but the ^{13}C n.m.r. spectrum was only partially assigned. By use of spin-saturation transfer and line-broadening in the ^{1}H n.m.r. spectra, it is shown that the *Z* isomer is fluxional with $\Delta G^‡ = 19.4$ kcal mol^{-1} and that there is no evidence for fluxionality in the *E* isomer or *E–Z* isomerism. The only reasonable interpretation of these data is a symmetry-allowed suprafacial [1,5]-shift.

The fluxionality of organometallic compounds has been discussed in terms of Woodward–Hoffmann sigmatropic shifts, especially suprafacial [1,5]-shifts.[1–4] However, for metal–σ-bonded systems, the range of organic ligands investigated is restricted to σ-allyl, σ-cyclopentadienyl, σ-cycloheptatrienyl, and σ-cyclohepta-1,3-dien-5-yl; the parent compounds of σ-penta-1,3-dien-5-yl have not been investigated. A kinetic investigation has appeared for both $Be(C_5H_7)_2$ and $Zn(C_5H_7)_2$ but the *E* and *Z* isomers are fluxional and an ionic or bimolecular mechanism is apparent.[5] The most thorough investigations have been performed on the SnR_3–σ-dienyl derivatives,[3,6] which showed [1,5]-shifts, but the parent system, $SnR_3(CH_2CH{=}CHCH{=}CH_2)$, has not been investigated. The preparations of the parent compounds $SnMe_3(CH_2CH{=}CHCH{=}CH_2)$ and $SnBu^n{}_3(CH_2CH{=}CHCH{=}CH_2)$ from SnR_3Cl and $C_5H_7^-$ have already been reported,[7,8] but these preparations yield a mixture of the *E* and *Z* isomers, (1), with a ratio of *ca.* 1 : 4. The fluxionality of these compounds was not investigated, although they are key compounds in establishing the [1,5]-shift mechanism. It is well established that SnR_3(σ-allyl)[9] and structure (2) (see below)[10] are not fluxional showing that [1,3]-shifts are unlikely to occur. Compounds *E*-(1) and *Z*-(1) provide a test of the dominance of suprafacial [1,5]-shifts. On this basis, the *Z* isomer, *Z*-(1), should be readily fluxional as the tin can approach the terminal olefinic CH_2 group permitting a symmetry allowed [1,5]-shift. In contrast, in the *E* isomer, *E*-(1), the constraints applied by the *trans*-double bond prevent a facile tin shift to the terminal olefinic CH_2 group. The alternative [1,3]-shift mechanism should be equally favoured in both the *Z* and *E* isomer and will interconvert these two isomers *via* the symmetric 3-triphenylstannylpenta-1,4-diene, (3). Hence, the $SnR_3(CH_2CH{=}CHCH{=}CH_2)$ system is important in establishing the mechanism of fluxionality.

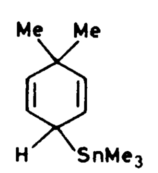


E - (1)

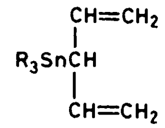


Z - (1)

R = alkyl



(2)



$$R_3Sn\overset{\displaystyle CH{=}CH_2}{\underset{\displaystyle CH{=}CH_2}{CH}}$$

(3)

Results and Discussion

The ^{1}H n.m.r. spectrum of $SnPh_3(CH_2CH{=}CHCH{=}CH_2)$ clearly shows the presence of two species in the ratio 1 : 3, see the Figure. The $Sn–C^5H_2$ protons occur as two readily assigned doublets of doublets at δ 2.297, ^3J(H–H) = 8.5 Hz (major isomer) and δ 2.405, ^3J(H–H) = 9.3 Hz. Decoupling experiments showed that these protons have a large ^3J(H–H) of *ca.* 9 Hz with the C^4H protons at δ 5.823 (major isomer) and δ 5.671. Similarly decoupling experiments were used to assign all substantial coupling constants and hence the associated protons. A complete assignment of all the dienyl protons was achieved, see Table 1. In the previous work on $SnMe_3(CH_2CH{=}CHCH{=}CH_2)$[7] and $SnBu^n{}_3(CH_2CH{=}CHCH{=}CH_2)$[8] only a partial assignment was achieved. The observation of $^3J(H^2–H^3)$ 15.0 Hz in the major isomer and 10.7 Hz in the minor isomer clearly shows that the major isomer has an *E*-olefinic bond [*E*-(1)], while the minor isomer has a *Z*-olefinic bond [*Z*-(1)].

The ^{13}C n.m.r. spectrum of the *E–Z* mixture was also recorded and the results are given in Table 2. The assignment of the olefinic CH signals proved to be difficult and some of the signals were obscured by the aromatic signals. The assignment was assisted by single-frequency off-resonance decoupled spectra. The assignment of the phenyl carbon signals is based on previous assignments.[11]

The observation of substantial $^6J(^{117,119}Sn–H)$ and $^5J(^{117,119}Sn–^{13}C)$ coupling constants raised the possibility of a

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† *Non-S.I. units employed*: cal = 4.184 J; mmHg ≈ 13.6 × 9.8 Pa.

Table 1. Proton n.m.r. data for (*E*)- and (*Z*)-6,6,6-triphenyl-6-stannahexa-1,3-diene in [$^2H_8$]toluene [a]

Hydrogen atom	δ(H)/p.p.m.	^2J(H–H)/Hz	^3J(H–H)/Hz	J(H–H) [b]/Hz	J(^{117,119}Sn–H)/Hz
(*a*) *E* isomer					
H^{1e}	4.783	1.8 (d)	10.1 (d)	0.6 (t)	13.6
H^{1z}	4.900	1.9 (d)	16.9 (d)	0.6 (t)	12.4
H^2	6.155		10.2 (t), 16.9 (d)		
H^3	5.963		10.1 (d), 15.0 (d)	0.7 (t), 1.0 (t)	
H^4	5.823		8.4 (d), 15.0 (d)	0.6 (q)	11.5
H^5	2.297		8.5 (d)	0.8 (d)	74
(*b*) *Z* isomer					
H^{1e}	4.878	*ca.* 2 (d)	*ca.* 10 (d)		30
H^{1z}	4.996	2.2 (d)	16.8 (d)	0.8 (t)	10.2
H^2	6.585		10.2 (d), 11.1 (d), 16.7 (d)	1.0 (d)	
H^3	5.820		10.8 (t)	0.9 (t), 1.2 (t)	
H^4	5.671		9.4 (t), 10.7 (d)	0.8 (t), 1.5 (d)	
H^5	2.405		9.3 (d)	1.1 (d)	*ca.* 56

d = Doublet, t = triplet, and q = quartet. [b] Unassigned long-range couplings.

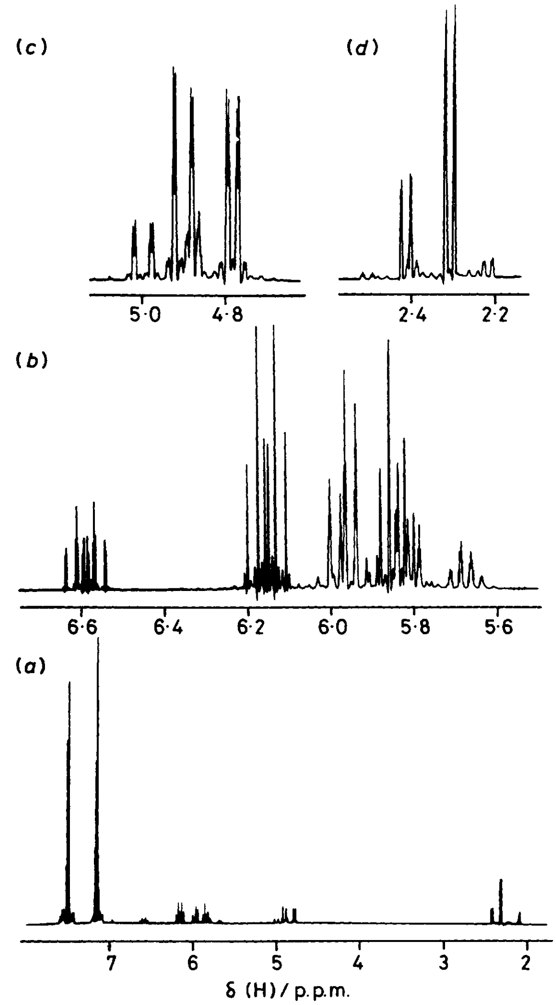


Figure. 400.13-MHz Proton n.m.r. spectrum of 6,6,6-triphenyl-6-stannahexa-1,3-diene in [$^2H_8$]toluene at *ca.* 23 °C. The spectrum is resolution enhanced using a Gaussian multiplication. (*a*) Complete spectrum, (*b*) the spectral region δ 5.5—6.7 showing the protons on C^2 to C^4, (*c*) the spectral region δ 4.6—5.1 showing the protons on C^1, and (*d*) the spectral region δ 2.1—2.6 showing the protons on C^5

Table 2. Carbon-13 n.m.r. data for (*E*)- and (*Z*)-6,6,6-triphenyl-6-stannahexa-1,3-diene in [$^2H_8$]toluene

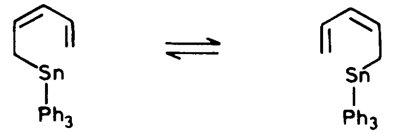
	E Isomer		*Z* Isomer	
Carbon atom	δ(^{13}C)/p.p.m.	J(^{117,119}Sn–^{13}C)/Hz	δ(^{13}C)/p.p.m.	J(^{117,119}Sn–^{13}C)/Hz
C^1H_2	17.15	315.9, 330.8	13.59	311.9, 326.4
	129.53	56.8	126.37	54.6
$C^{2,3,4}H$ *	132.38	56.2	130.39	13.3
			131.93	22.7
C^5H	112.91	21.4	115.49	17.9
ipso-C	138.36	471.5, 493.6	138.39	472.4, 494.4
ortho-C	137.03	35.1	137.03	35.1
meta-C	128.50	49.2	128.50	49.2
para-C	129.02	11.0	129.02	11.0

* Only some of the $C^{2,3,4}H$ signals were observed and assignments were not made.

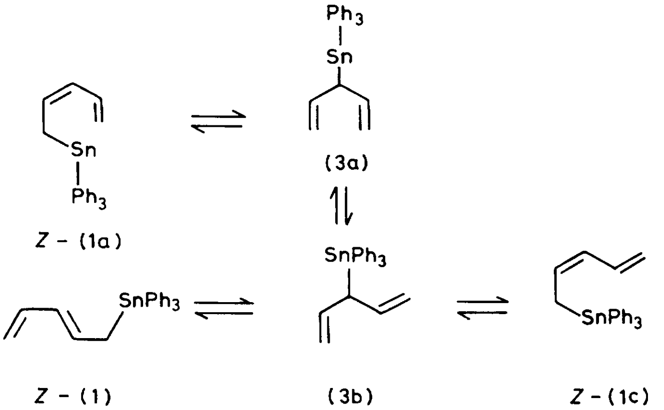
conformation permitting through-space coupling or co-ordination of the terminal olefinic bond to the tin. No evidence for the close proximity of the terminal olefinic group to the phenyl or C^5H_2 protons was found using nuclear Overhauser effect (n.O.e.) difference spectroscopy.

Although no fluxionality was found at room temperature, fluxionality occurs in [$^2H_8$]toluene at 77 °C and higher temperatures. At 77 °C irradiation of the *Z* isomer C^5H_2 protons produced spin-saturation transfer to the two different C^1H_2 protons, but irradiation of the *E* isomer C^5H_2 protons produced *no* spin-saturation transfer. There was no evidence of exchange between the *E* and *Z* isomers.

At 89.5 °C, the ^1H n.m.r. signals due to the C^1H_2, C^2H, C^4H, and C^5H_2 protons of the *Z* isomer broadened to 5 Hz while the other signals remained sharp. These observations show that there is a [1,5]-shift in the *Z* isomer, see Scheme 1, with an activation energy, $\Delta G^{\ddagger}$, of 19.4 kcal mol^{-1}. The lack of fluxionality of the *E* isomer is readily accounted for by the steric difficulties in placing the C^1H_2 group close to the tin. However the non-involvement of the *E* isomer rules out two sequential [1,3]-shifts which would interconvert the *E* and *Z* isomers, see Scheme 2. As the *E* isomer predominates in solution, if (3) is an intermediate then conversion into the *E* isomer would be expected to be faster than a further [1,3]-shift



Scheme 1.



Scheme 2.

to give the Z isomer. The observed [1,5]-shift for the Z isomer could pass through intermediate (3) without conversion to the E isomer only if the barrier to interconversion of (3a) and (3b) is higher than the barrier to a [1,3]-shift in (3). It is known that the barrier to rotation about unhindered carbon–carbon bonds is less than 8 kcal mol^{-1} [12] and there have been no reports of [1,3]-shifts occurring in tin allyls, putting this barrier in excess of 20 kcal mol^{-1},[9] making the above requirement improbable. It is probable that Z-(1) adopts conformation Z-(1b) for several reasons: there is no observed n.O.e. between

Z - (1b)

the C^1H_2 and the C^5H_2 or phenyl groups; the coupling constant $^3J(H^2-H^3)$ is *ca.* 10.7 Hz; [13] and experimental evidence indicates a *trans* arrangement is normally adopted for the butadiene residue.[14] Hence conformation Z-(1c) is more probable than Z-(1a), but a [1,3]-shift to (3b) would lead directly to the E isomer, E-(1). Hence the [1,3]-shift mechanism is highly improbable, leaving only the [1,5]-shift mechanism. In contrast to the $\Delta G^\ddagger$ of 15.4 kcal mol^{-1} for (σ-cycloheptatrienyl)triphenyltin and 15.8 kcal mol^{-1} for (σ-cyclohepta-1,3-dien-5-yl)triphenyltin, the activation energy for (Z)-6,6,6-triphenyl-6-stannahexa-1,3-diene is 19.4 kcal mol^{-1}. For (σ-cycloheptatrienyl)triphenyl tin, the X-ray structure has shown that the molecule adopts a conformation which is close to that required for a [1,5]-shift, but it is probable that (Z)-6,6,6-triphenyl-6-stannahexa-1,3-diene adopts a conformation Z-(1b) and part of the 4 kcal mol^{-1} energy difference is used in adopting conformation Z-(1a). A tin–secondary carbon bond will be stronger than the corresponding tin–tertiary carbon bond, for example, D[SnMe$_3$-Et] 64 and D[SnMe$_3$-Pr^i] 60 kcal mol^{-1},[15] which will also lead to a higher activation energy.[1]

In conclusion the observation of fluxionality in (Z)-6,6,6-triphenyl-6-stannahexa-1,3-diene provides strong evidence for [1,5] sigmatropic shifts.

Experimental

The ^1H and ^{13}C n.m.r. spectra were recorded using a Bruker WH-400 n.m.r. spectrometer. Chemical shifts are referenced to internal SiMe$_4$ using the IUPAC approved sign convention that high frequency is positive.[15] Accurate temperature calibration was achieved by using a Comark series 5000 electronic thermometer attached to a copper–constantan thermocouple in an n.m.r. tube containing toluene. The mass spectrum was recorded on a Kratos MS-25 and the analysis was performed by the departmental analytical service.

Preparation of 6,6,6-*Triphenyl*-6-*stannahexa*-1,3-*diene*.—A 100 cm^3 three-necked, round bottom flask was thoroughly flushed with nitrogen, then charged with potassium shot (1 g, 26 mmol) in tetrahydrofuran (thf) (20 cm^3). After cooling to -78 °C triethylamine (2.6 g; 3.5 cm^3, 26 mmol) and penta-1,3-diene (mixed isomers) (1.8 g; 2.6 cm^3, 26 mmol) were added. The mixture was stirred vigorously for *ca.* 3 h while it was allowed to warm to room temperature. The resulting yellow-orange solution of ' potassium dienyl ' was recooled to -78 °C and triphenyltin chloride 4.9 g (13 mmol) was added dropwise in thf solution (20 cm^3). This was stirred and allowed to return to room temperature over *ca.* 2 h. Ethanol (10 cm^3) was added and stirred vigorously for 15 min after which the mixture was reduced to dryness under reduced pressure (0.1 mmHg, 25 °C). The residue was extracted with light petroleum (b.p. range 40—60 °C) (3 × 50 cm^3) and the volume was reduced to *ca.* 5 cm^3 which was transferred to a short (2-in) silica gel column and eluted with light petroleum (b.p. 40—60 °C)–Et$_2$O (1 : 1) (250 cm^3). The collected eluant was reduced in volume and chromatographed using preparative scale t.l.c. (Kiesel gel G.F. 254) with light petroleum (b.p. 40—60° C)–Et$_2$O (9 : 1) as eluant. The product bands were identified by use of a u.v. lamp. The upper of the two observed bands at R_f *ca.* 0.8 was identified by ^1H n.m.r. as organic side-products. The band at R_f 0.6—0.7 was extracted with CH$_2$Cl$_2$ and recrystallised from hot light petroleum (b.p. 40—60 °C, *ca.* 20 cm^3) to yield 6,6,6-triphenyl-6-stannahexa-1,3-diene, a white slightly air-sensitive material, yield 1.33 g (3.2 mmol, 35% w.r.t. SnPh$_3$Cl), m.p. 40—41 °C (Found: C, 65.8; H, 5.45. Calc. for $C_{23}H_{22}Sn$: C, 66.35; H, 5.30%). Mass spectrum M^+ (maximum intensity peak in a characteristic tin containing envelope): m/e 418, requires $^{12}C_{23}{}^1H_{22}{}^{120}Sn$.

Acknowledgements

We wish to thank the S.E.R.C. for financial support (to M. J. H. and C. M. S.) and for access to the high-field n.m.r. service in Sheffield.

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Received 30*th July* 1982; *Paper* 2/1320