Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME NOVEL BICYCLIC ORGANOTIN COMPOUNDS

C. H. W. JONES*, R. G. JONES, P. PARTINGTON AND R. M. G. ROBERTS**
Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex (Great Britain)

(Received April 22nd, 1971)

SUMMARY

A number of new bicyclic organotin compounds have been synthesised by treating the corresponding organic halide with (trialkyl- or triarylstannyl)sodium in liquid ammonia. *syn*-7-Bromo-2-norbornene yielded mainly the *anti*-7-trimethyltin derivative when treated with (trimethylstannyl)sodium, but gave a tricyclic compound on reaction with (triphenylstannyl)sodium. *anti*-7-Bromobenzonorbornadiene*** gave a *syn/anti* mixture of the trimethylstannyl analogue together with what appeared to be a tricyclic derivative. 7-Chloro-2,5-norbornadiene readily gave the corresponding 7-triphenylstannyl compound, but its trimethyltin analogue was formed only with difficulty and was unstable. The compounds were characterised by their PMR spectra, and the mechanism of formation is discussed. The addition of trimethyltin hydride to 2,5-norbornadiene resulted in a mixture of *exo* and *endo*-5-norbornenyl derivatives. ^{13}C NMR, Mössbauer and infrared spectroscopy were used in a search for donor–acceptor interactions between the tin atom and C–C double bonds situated in stereochemically favourable positions, *viz.* 7-(trimethyl- and triphenylstannyl)-2,5-norbornadiene, and also *endo*-5-(trimethylstannyl)-2-norbornene. None of the spectroscopic techniques used revealed any evidence for this effect.

INTRODUCTION

Relatively little is known of the chemistry of bridged organometallic compounds. Kreevoy[1] has studied the deoxymercuration of some (methoxynorbornyl)-mercury iodides, and Winstein has investigated the demercuration of nortricyclylmercury**** acetate[2] and di-4-bornylmercury[3] by perchloric acid. The reaction between the Grignard reagent obtained from *endo*-bromonorbornane and mercuric bromide has been shown to proceed with almost complete retention of configuration[4], as does *exo*-norbornyllithium with carbon dioxide, but inversion occurs when bromine

---

* Present address: Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada.

** To whom correspondence should be addressed.

*** *Chem. Abstr.* name: 9-bromo-1,4-dihydro-1,4-methanonaphthalene.

**** Nortricyclene = tricyclo[2.2.1.0^{2,6}]heptane.

is the electrophile[5]. The action of magnesium and lithium on *syn*-7-bromo-2-norbornene followed by carbonation led to a 2/1 mixture of the corresponding *anti*/*syn* carboxylic acids[6]. *exo*-5-Norbornene-2-boronic acid yields 3-(chloromercuri)nortricyclene with mercuric chloride in aqueous acetone some four hundred times faster than the *endo* isomer, anchimeric assistance to mercury–carbon bond formation by the carbon–boron bond being invoked[7]. [7-(*p*-Toluenesulphonyloxy)norbornadiene]-tricarbonyliron solvolyses in 80% acetone at least 10^6 times more slowly than the uncomplexed diene, suggesting marked inhibition of anchimeric assistance[8]. Kuivila has determined the stereochemistry of the 5-(trimethylsilyl)-2-norbornenes[9] formed from the addition of silanes to 2,5-norbornadiene, and has synthesised a number of (trimethylsilyl)norbornanones[10]. Seyferth *et al.*[11] have prepared some perhalo derivatives of 2-(trimethylstannyl)-2,5-norbornadiene. The Diels–Alder reaction has been used in a novel fashion to produce 7-(triphenylstannyl)-2,5-norbornadiene-2,3-dicarboxylic acid diethyl ester[12]. Recently a report has appeared on the structure and reactivity of some 7-metallanorbornadienes of Group IVB elements[13].

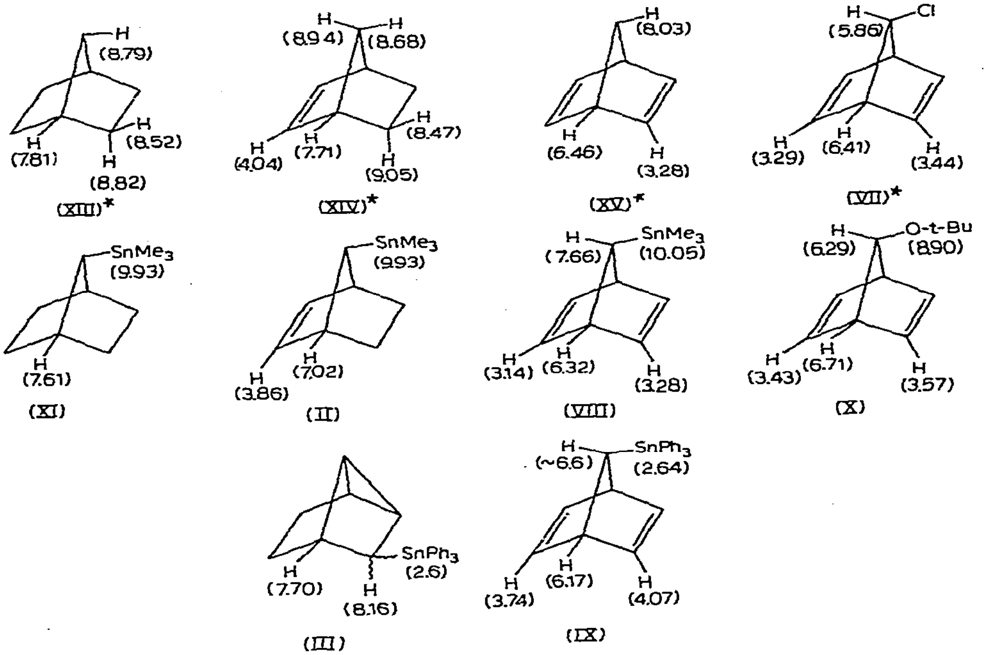


Fig. 1. Proton chemical shifts of some norbornane derivatives and their organotin analogues (τ values in parentheses).

It is the purpose of this paper to examine the structure of some norbornenyl and norbornadienyl derivatives of tin with special reference to the detection of donor–acceptor interactions between the tin atom and olefinic double bonds in these compounds using proton and carbon-13 nuclear magnetic resonance, Mössbauer, and infrared spectroscopy.

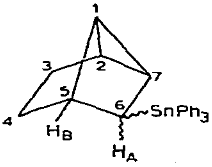
---

* Ref. 14.

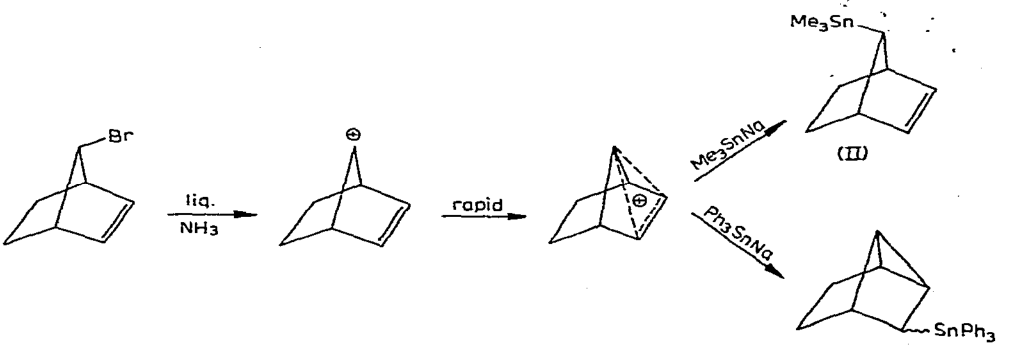
DISCUSSION AND RESULTS

1. *Proton magnetic resonance studies* (*Fig.* 1)

(*i*). *Reaction products in liquid ammonia. syn*-7-Bromo-2-norbornene (I), on reaction with (trimethylstannyl)sodium at room temperature, yielded mainly the *anti*-7-trimethyltin derivative (II). Its PMR spectrum showed no evidence of additional splitting of the triplet (J 1.7 Hz) at τ 3.86 ppm (olefinic H), suggesting the absence of an *anti* proton at C7 [14]. The methyl protons (9.93 ppm) were not shielded compared with tetramethyltin (9.93 ppm)[15] as might be anticipated for a *syn*-Me_3Sn group. Reaction of (I) with (triphenylstannyl)sodium under similar conditions yielded a compound whose PMR spectrum showed a multiplet at τ 2.3–2.9 ppm (Ph), a rather broad singlet at 7.70 ppm, a sharp singlet at 8.16 ppm with what appeared to be attendent tin satellites [$J(^{119,117}Sn-H) \sim 18.7$ Hz] and a complex absorption in the range 8.5–9.0 ppm. The corresponding measured proton ratios were 15.2/1/1/7. The spectrum is not consistent with the expected 7-(triphenylstannyl)-2-norbornene, and strongly resembles that anticipated for 6-(triphenylstannyl)tricyclo[3.2.0.$0^{2,7}$]heptane (III). We assign the absorptions at τ 8.16 and 7.70 ppm to protons H_A and H_B respectively. Protons at C1, C2, and C7 would appear at a higher field due to the anisotropy of the cyclopropane ring. H_B appears broader than H_A as a result of coupling with the adjacent methylene protons on C4. It is likely that the tin occupies the *exo* position in the structure. The difference in the nature of the products obtained using (trimethyl- and triphenylstannyl)sodium may be rationalised as follows. The reactions are carried out in a polar medium favouring an S_N1 mechanism.



(III)

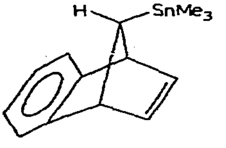


(II)

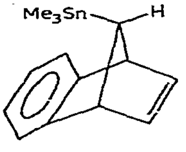
(III)

The resulting carbonium ion can be stabilised by homoallylic interaction generating either non-classical or rapidly equilibrating classical ions. The stereochemical effect of this interaction is to produce the inverted (*anti*) product preferentially. The approach of the nucleophile to form the more stable bicyclic system is more hindered than that for the formation of the less stable *exo*-tricyclic system, and hence with a large nucleophile the latter is formed preferentially.

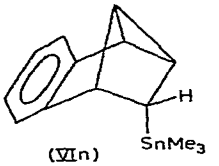
The reaction of *anti*-7-bromobenzonorbornadiene (IV) with (trimethylstannyl)sodium gave a low yield of a mixture of products whose PMR spectrum showed high field absorptions at τ 9.98, 10.27, and 10.42 ppm, each with attendant tin satellites. In view of the reactions above, four products are conceivable.



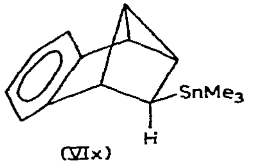
(Va)



(Vs)



(VIn)



(VIx)

The chemical shift of the Me_3Sn protons of (Va) and (Vs) were calculated from anisotropy data for the aromatic nucleus[16,17] and olefinic double bonds[18] by choosing the most favourable conformations of one methyl group with respect to (*a*) the aromatic or olefinic moiety and (*b*) the remaining groups attached to tin. The calculations gave τ values in the range 10.34–10.40 for (Vs). Weighting in less probable conformations always led to higher shifts, maximally 10.88 ppm. The most shielded protons (10.42 ppm) can therefore be reasonably assigned to (Vs). Values calculated for (Va) were in the range 10.0–10.1. Calculated τ values of greater than 10.6 were obtained for (VIn) which can be discounted. It is much less easy to decide between (Va) and (VIx) due to the lack of data concerning the anisotropy of the cyclopropane ring in tricyclic structures. In view of the shift observed for the norbornadienyl analogue (10.05), we tentatively assign the low field signal at 9.98 ppm to (Va). *Endo* attack to form (VIn) is again less probable[19], due to interactions between the incoming nucleophile and the aromatic nucleus. Products can again be accounted for in terms of rapidly equilibrating classical or non-classical ions[20].

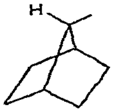
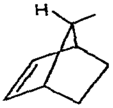
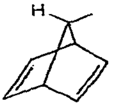
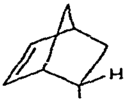
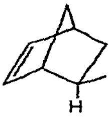
No substitution reaction was observed between 7-chloro-2,5-norbornadiene (VII), and (trimethylstannyl)sodium at room temperature, work-up of the reaction mixture leading to an inseparable 2/1 mixture of (VII) and hexamethyldistannane. However, on refluxing in 60–80 petroleum ether for 17 h, a very low yield of 7-(trimethylstannyl)-2,5-norbornadiene (VIII) was obtained. (VIII) was rather unstable, due perhaps to the destabilising influence of the neighbouring olefinic π electrons on what is, by virtue of electron release by the Me_3Sn group, an electron rich C7 atom. Significantly, the triphenyltin analogue (IX) was much more readily formed and more stable due to the ability of the phenyl groups to delocalise the negative charge on C7.

Although in the synthesis of (VIII), there was again some evidence for the formation of tricyclic derivatives, the amounts were small. The PMR spectrum of (VIII) showed absorptions at τ 3.14 (triplet, $J \sim 1.8$ Hz), 3.28 (triplet, $J \sim 1.9$ Hz), 6.32 (sextuplet), 7.66 [broad singlet with tin satellites, $J(^{119,117}Sn-H) \sim 21.0$ Hz] and 10.05 ppm (singlet) with corresponding proton ratios 4.09/1.98/1/9.2. The upfield triplet was broader than its neighbour, indicating some further splitting by the *anti* proton at C7. This enables the upfield triplet to be assigned[14] to the *syn* olefinic system by analogy with the 7-chloro (lowfield triplet $J \sim 2.2$ Hz) and 7-tert-butoxy (X, lowfield triplet

$J \sim 2.2$ Hz) derivatives, which both clearly show additional splitting ($J \sim 0.5$ Hz) of the upfield triplet. There is appreciable shielding of the methyl protons of (VIII) compared with both (II) and the parent saturated compound (XI). The C7 proton of (VIII) is deshielded relative to 2,5-norbornadiene, whereas shielding should occur both from the anisotropy of the olefinic double bond and electron release from tin. This anomaly is perhaps due to the anisotropy of the tin–carbon bonds which has not so far been unambiguously described. The PMR spectrum of 7-(triphenylstannyl)-2,5-norbornadiene (IX) was markedly different from the trimethyl analogue. In particular the olefinic protons appeared as two broad doublets at 3.74 and 4.07 ppm ($J \sim 2.7$ Hz). The three methine protons gave a complex multiplet at 6–7 ppm. This anomaly probably results from the very different anisotropy of the Ph_3Sn group compared with the Me_3Sn group.

TABLE 1

TIN–PROTON COUPLING CONSTANTS [$J(^{119}Sn{-}CH_3)$, $J(^{117}Sn{-}CH_3)$ in Hz] FOR VARIOUS TRIMETHYLALKYL- AND -ALKENYLTIN COMPOUNDS (Me_3SnR)

R	$J(^{119}Sn{-}CH_3)$	$J(^{117}Sn{-}CH_3)$
$-CH_3$	54.4	52.0
$-CH_2CH{=}CH_2$	53.7	52.2
$-(CH_2)_2CH{=}CH_2$	53.0	50.8
$-(CH_2)_3CH{=}CH_2$	52.2	50.9
$-(CH_2)_4Ph$	50.9	49.5
$-(CH_2)_2CO_2Me$	52.9	52.5
	50.4	50.1
	50.6	50.2
	51.4	49.1[a]
	50.8	48.4
	50.8	48.4

[a] $J(^{119,117}Sn{-}C{-}H) \sim 21.0$ Hz.

(*ii*). *Products from addition reactions.* The free radical addition of trimethyltin hydride to 2,5-norbornadiene resulted in a 1.22/1 mixture of *exo*- and *endo*-5-(trimethylstannyl)-2-norbornene (XIIx, n). No evidence was obtained for any tricyclic products as observed by Kuivila and Warner[9] in the corresponding chloroplatinic acid catalysed addition of trimethylsilane. The PMR spectrum of (XIIx, n) exhibited sharp singlets at 9.94 and 10.04 ppm which we assign to the *exo* and *endo* isomers respectively (*cf.* 10.00 and 10.10 ppm for the silicon analogues[9]). The stereochemical course of the hydrostannation reaction reflects the easier approach of the radical in the *exo* direction[19], whereas in the hydrosilation reaction a silane/olefin/catalyst complex[21] is formed by coordination at the *endo* side of the molecule.

(*iii*). *J(Sn–C–H) coupling constants.* Values of these constants appear in Table 1. The most significant feature is the low value obtained for the J(Sn–C–H) on the bridge position compared with $J(\text{Sn–CH}_3)$. A correlation has been established between $J(\text{Sn–CH}_3)$ and %s character in the Sn–C bond[22] but the bridging-proton–tin coupling constants do not fit this. An empirical correlation may exist for the $J(\text{Sn–C–HR}_2)$ case similar to that found for $J(\text{Sn–CH}_2)$[23] but at present we have insufficient data to formulate the relationship.

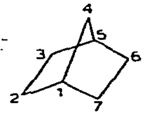
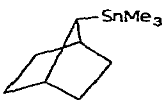
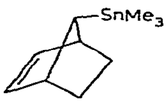
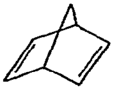
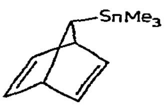
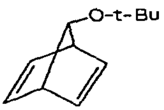
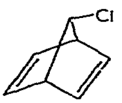
2. *Carbon-13 nuclear magnetic resonance studies*

The experimental C-13 chemical shifts are compiled in Table 2. The primary purpose of this work has been to try to detect evidence for donor–acceptor interactions between the tin atom and a C–C double bond situated in a stereochemically favourable position. The carbon-13 chemical shifts should be more sensitive than proton chemical shifts to this kind of interaction, which must, if present lead to significant changes in the molecular orbitals of the π system. The contribution of the paramagnetic term to the C-13 screening constant shows an inverse relationship to a mean excitation energy involving the ground state and lower lying excited electronic states of the molecule. This term in the Ramsey formula[24] may become very large when there is an asymmetric distribution of p and d electrons close to the nucleus when these electrons have low lying excited states. The paramagnetic term is dominant in determining the chemical shifts of nuclei other than hydrogen. The order of magnitude of the ^{13}C shift expected as a result of d_π–p_π overlap is not known, a priori, but some indication is provided by an examination of ^{119}Sn chemical shifts measured by Hunter and Reeves[25] for tetramethyltin (0.0), trimethylvinyltin (35.4 ppm) and dimethyldivinyltin (79.4 ppm). The ^{13}C data relevant to the d_π–p_π problem will now be evaluated; other ^{13}C data listed in Table 2 will be discussed more comprehensively in a later paper.

The difference in chemical shift between the 2,3- and 5,6-carbons of 7-(trimethylstannyl)norbornane is 1.3 ppm reflecting the magnetic anisotropy and steric effects of the Me_3Sn group. For *anti*-7-(trimethylstannyl)-2-norbornene, where no d_π–p_π overlap occurs, the chemical shift of the olefinic carbon atoms, is 54.9 ppm upfield from reference CS_2. The most favourable case for d_π–p_π overlap occurs for 7-(trimethylstannyl)-2,5-norbornadiene and if present should result in a marked chemical shift difference between 2,3- and 5,6-carbons. However, the two carbon pairs absorb at 46.4 and 47.5 ppm. The difference is therefore less than in the fully saturated analogue. The overall low-field shift relative to the norbornenyl compound can be attributed to steric strain. A similar difference in shifts has been observed between norbornene and norbornadiene[26]. These data suggest that there is no d_π–p_π overlap in the norbornadienyl compound in agreement with other results in this paper. This conclusion is further reinforced by the uniformity of the chemical shifts observed

TABLE 2

^{13}C CHEMICAL SHIFTS[a] OF SOME BICYCLIC COMPOUNDS AND THEIR ORGANOTIN ANALOGUES

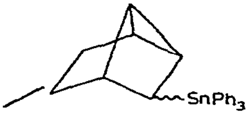
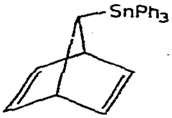
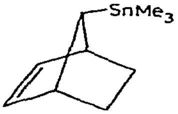
Compound	C1	C2	C3	C4	C5	C6	C7	Me_3Sn
	156.0	162.7	162.7	156.0	162.7	162.7	154.1	
	153.3	162.1	162.1	153.3	163.4	163.4	154.9	203.7[b]
	150.0 (150.6)[c]	58.3 (57.3)	58.3 (57.3)	150.0 (150.6)	167.2 (167.3)	167.2 (167.3)	143.4 (144.0)	
	146.2	54.9	54.9	146.2	166.5	166.5	140.7	201.0
	143.8 (141.9)[c]	50.1 (49.4)	50.1 (49.4)	143.8 (141.9)	50.1 (49.4)	50.1 (49.4)	118.5 (117.4)	
	[d]	46.4	46.4	[d]	47.5	47.5	[d]	203.0
	138.5	53.6	53.6	138.5	56.5	56.5	88.9	
	137.0	51.5	51.5	137.0	55.1	55.1	107.7	

[a] Relative to CS_2, ±0.2 ppm. [b] Me_4Sn 202.0. [c] Ref. 26. [d] Could not be accurately measured due to low concentrations employed. [e] CO 120.9, $(CH_3)_3$ 166.3; *cf.* t-BuOH: CO 124.8, $(CH_3)_3$ 162.3 ppm.

for the carbons of the trimethyltin group in these compounds and also in 4-(trimethylstannyl)-1-butene (203.9 ppm) methyl 3-(trimethylstannyl)propionate (204.0 ppm) and 1-phenyl-4-(trimethylstannyl)butane (204.1 ppm).

TABLE 3

ISOMER SHIFTS (δ), LINE WIDTHS (Γ) AND QUADRUPOLE SPLITTING (Δ) FOR VARIOUS ALKYL AND ARYL TIN COMPOUNDS

Compound	δ^a (mm/sec)	2Γ (mm/sec)	Δ
Ph_4Sn	−0.80	1.12	0
	−0.90	1.23	0
	−0.77	1.13	0
$(CH_3)_3SnCH{=}CH_2$	−0.82	0.98	0
$(CH_3)_3SnCH_2CH{=}CH_2$	−0.785	1.05	0
$(CH_3)_3Sn(CH_2)_2CH{=}CH_2$	−0.80	1.4	0
$(CH_3)_3Sn(CH_2)_3CH{=}CH_2$	−0.78	1.15	0
$(CH_3)_3Sn(CH_2)_2CO_2CH_3$	−0.82	1.17	0
	−0.79	1.09	0

[a] δ quoted with reference to $\delta(Sn_\alpha)$ = 0.00 mm/sec.

3. *Mössbauer spectroscopy*

The relevant data from Mössbauer studies on a number of organotin compounds appear in Table 3. In all cases studied single narrow lines were observed indicating the absence of any appreciable quadrupole interaction. The isomer shifts (δ) are almost constant over a fairly wide range of structure. Unfortunately it was not possible to obtain spectra for (VIII) owing to its marked instability. It would appear therefore that in the ground state at least no appreciable bonding occurs between tin and the olefinic moiety in these compounds. This supports the findings of Clark and Poller[27] and other results quoted in this paper. However, π bonding seems to play a relatively minor role in producing quadrupole splitting, the dominant effect being one of change in σ bond polarity about the tin atom[28].

4. *Infrared spectroscopy*

All the trimethyltin compounds displayed strong absorptions at 770 cm^{-1} characteristic of the Me_3Sn group. Norbornenyl derivatives (II) and (XIIx, n) showed weak signals at 1570 and 1572 cm^{-1} respectively which could be assigned to the ν(C=C) mode (*cf.* 1570 cm^{-1} for norbornene) and very strong sharp peaks due to γ(CH) modes at 732 and 720 cm^{-1} respectively (*cf.* 705 cm^{-1} for norbornene). (VIII) showed two bonds of medium intensity at 1548 (sharp) and 1590 cm^{-1} (broad) compared with those observed in the Raman spectrum of norbornadiene[29] itself. *viz.*

1549, 1575, 1601 cm^{-1}. The corresponding γ(CH) modes appeared at 695, 740 cm^{-1} for (VIII) and 660, 730 cm^{-1} for norbornadiene. Thus there is no strong evidence for a shift of ν(C=C) to lower wavenumber in (VIII) and thus little likelihood of significant d_π–p_π bonding. The ν(C=O) of methyl 3-(trimethylstannyl)propionate (1736 cm^{-1}) lies in the range observed for the unsubstituted propionates and again seems to preclude any donor acceptor interactions in the ground state. We may therefore conclude that the application of a variety of spectroscopic techniques has failed to produce any unambiguous evidence for d_π–p_π bonding in olefinic tin compounds in the ground state even in stereochemically favourable circumstances.

EXPERIMENTAL

(1) *Preparations*

1-Bromo-4-phenylbutane was prepared by converting 4-phenylbutyric acid to ethyl 4-phenylbutyrate[30], followed by reduction to 4-phenyl-1-butanol[31], and subsequent treatment with hydrogen bromide[32]. *exo-cis*-2,7-Dibromonorbornane was obtained in 55% yield on brominating 2-norbornene. Treatment of the dibromide with potassium tert-butoxide in tert-butanol gave 41% *syn*-7-bromo-2-norbornene (I)[33] which on catalytic hydrogenation using PtO_2 in ether at 4 atm yielded 7-bromonorbornane (92%). 7-tert-Butoxy-2,5-norbornadiene (X) was synthesised by the method of Story[34] and converted into the 7-chloro analogue (VII) in 61% yield by bubbling dry HCl through an ethereal solution of the tert-butoxy derivative[35]. *anti*-7-Bromobenzonorbornadiene (IV) was prepared by dehydrobromination of *exo*-5-*anti*-7-dibromobenzonorbornene using potassium tert-butoxide in pure DMSO[36]. (KO-t-Bu was prepared from potassium metal and tert-butanol under nitrogen[37] and the excess solvent removed at 100°/0.5 mm.)

Trimethyltin hydride[38], hexamethylditin[39], and trimethyltin bromide[40] were prepared by conventional methods. Triphenyltin bromide was obtained in 90% yield by treatment of triphenyltin chloride with excess sodium bromide in dry acetone.

Preparation of 7-(trimethylstannyl)norbornane (XI). Me_3SnBr (8.00 g, 0.033 mole) was added dropwise by means of a heated Pasteur pipette to a solution of Na (1.15 g, 0.066 g-atom) in liquid NH_3 (50 ml) under an argon atmosphere at −78°. Carbon dioxide was excluded by means of a soda lime guard tube. On addition of Me_3SnBr, the original blue colour of the solution was dispersed to give a pale yellow suspension. A solution of 7-bromonorbornane (5.75 g, 0.033 mole) in dry (60–80°) pet. ether (50 ml) was added dropwise with vigorous stirring and the mixture allowed to warm to room temperature overnight. After treatment with satd. NH_4Cl (50 ml), followed by ether extraction of the aqueous phase, the combined ethereal extracts were dried, the ether removed under reduced pressure and the residue distilled under 8 mm to give a main fraction boiling at 71–72°.

Any contaminating $(Me_3Sn)_2$ was removed by precipitation at 0° giving 36% 7-(trimethylstannyl)norbornane (nc); n_D^{20} 1.5127. (Found: C, 46.4; H, 7.72. $C_{10}H_{20}Sn$ calcd.: C, 46.6; H, 7.62%.) The following compounds were prepared by this method. 7-(Triphenylstannyl)2,5-norbornadiene (IX) (17%) (nc); m.p. 79°. (Found: C, 67.9; H, 5.18. $C_{25}H_{22}Sn$ calcd.: C, 68.0; H, 5.00%.) *anti*-7-(Trimethylstannyl)-2-norbornene (II) (43%) (nc); b.p. 66–68° (6 mm); n_D^{20} 1.5135. (Found: C, 46.4; H, 7.08. $C_{10}H_{18}Sn$ calcd.: C, 46.6; H, 7.00%.) 6-(Triphenylstannyl)tricyclo[3.2.0.0^{2,7}]heptane (III) (8%)

(nc); m.p. 89°. (Found: C, 67.9; H, 5.34. $C_{25}H_{24}Sn$ calcd.: C, 67.8; H, 5.42%.) 1-Phenyl-4-(trimethylstannyl)butane (48%) (nc); b.p. 112° (2 mm); n_D^{20} 1.5225. (Found: C, 52.5; H, 7.27. $C_{13}H_{22}Sn$ calcd.: C, 52.6; H, 7.41%.) Trimethyl-n-butyltin (43%); b.p. 42–43° (12 mm); n_D^{20} 1.4570. Trimethyl-n-pentyltin (52%) b.p. 173–174° (755 mm); n_D^{20} 1.4600.

Reaction of Me_3SnNa with *anti*-7-bromobenzonorbornadiene yielded a waxy low melting solid whose NMR spectrum indicated a mixture of isomers and a large preponderance of unreacted bromide.

7-(Trimethylstannyl)-2,5-norbornadiene (VIII). A solution of Me_3SnNa in liquid NH_3 (100 ml) was made under argon from Me_4Sn (19.0 g, 0.100 mole) and sodium metal (4.6 g, 0.200 g-atom). 7-Chloro-2,5-norbornadiene (10.0 g, 0.079 mole) in dry (60–80°) pet. ether (100 ml) was added dropwise and the mixture allowed to reach room temperature, after which it was refluxed under argon for 17 h. After working up in the usual manner a crude residual oil (5.2 g) was obtained. This on fractional distillation gave 7-(trimethylstannyl)-2,5-norbornadiene (nc); 0.64 g (3.2%); b.p. 50–55° (1 mm); n_D^{20} 1.5310. Owing to the instability of the compound, no C/H analyses could be obtained, but the structure of the product was confirmed by its PMR spectrum. The compound was stored at 0° under nitrogen.

The main reaction product was a brown, apparently polymeric powder (7.5 g; m.p. >280°) which awaits characterisation.

4-(Trimethylstannyl)-1-butene. To the Grignard reagent made from 4-bromo-1-butene (10 g, 0.074 mole) and Mg (2.18 g, 0.090 g-atom) in dry THF (100 ml) was added dropwise a solution of Me_3SnBr (17.0 g, 0.070 mole) in THF (50 ml). The mixture was refluxed for 10 h then decomposed with satd. NH_4Cl. After drying and removing the solvent the residue was distilled under reduced pressure to give 7.2 g (47%) 4-(trimethylstannyl)-1-butene; b.p. 44–45° (13 mm); n_D^{20} 1.4680. 5-(Trimethylstannyl)-1-pentene (30%) was similarly prepared; b.p. 34° (1.5 mm).

Addition of Me_3SnH to 2,5-norbornadiene. The reaction was carried out according to the method of Neumann[38] using Me_3SnH (4.8 g, 0.029 mole), 2,5-norbornadiene (5.4 g, 0.058 mole) and α,α'-azobisisobutyronitrile (0.53 g, 3.2 mmole). Distillation of the reaction mixture after filtration yielded 2.3 g of a colourless oil; n_D^{20} 1.5155; b.p. 53–57° (3.5 mm). The PMR spectrum showed the product to be a mixture (1.22/1) of *exo-* and *endo-*5-(trimethylstannyl)-2-norbornene. A similar reaction of Me_3SnH with methyl acrylate yielded methyl 3-(trimethylstannyl)propionate (nc); 3.7 g (40%); b.p. 194–195° (758 mm); n_D^{20} 1.4673. (Found: C, 33.6; H, 6.56. $C_7H_{16}O_2Sn$ calcd.: C, 33.5; H, 6.38%.) Attempts to prepare 1-bromo-3-(trimethylstannyl)propane by this method were not successful.

(2). *Spectroscopic methods*

(i). PMR and ^{13}C NMR spectroscopy. PMR spectra were run on 20% CCl_4 solutions of the compounds using a Varian A60A instrument.

The carbon-13 spectra have been obtained using neat liquid samples, without enrichment, in 8 mm sample tubes. The spectrometer used was a JEOL Co., Ltd., JNM C60HL operated in the external lock (H_2O) mode at 15.1 MHz. The spectra were obtained in most cases from single scans using the JNM SDHC Heteronuclear Spin Decoupler by noise modulating the proton irradiation frequency. The JNM-IS-60 attachment maintained the proton decoupling condition over large carbon-13 sweep ranges (up to 135 ppm) by synchronising the irradiation frequency with the magnetic field sweep in a field/frequency sweep mode. The spectra of some of the compounds prepared later in the series were obtained by accumulation using a PDP8/I computer with interfacing[41] and software[42] developed at the University of Essex.

(*ii*). *Mössbauer spectroscopy*. The spectra were obtained as 2 × 256 channel mirror image spectra using a constant acceleration transducer driven by a triangle function generated from the mid-channel binary output of an N.D. 2200 series 512 channel analyser.

The absorbers were held at liquid N_2 temperature and the source was ^{119m}Sn in a Sn/Pd matrix held at room temperature.

A thin NaI(Tl) scintillation detector was used.

The compounds which were liquid at room temperature were transferred from their ampoules under nitrogen to a thin window lucite container and frozen under nitrogen to form a solid film. The container was sealed with a thin lucite disc and o-ring. The frozen sample was then immediately transferred to the cold-finger of the spectrometer.

The solid compounds were compressed into discs between mylar foil, sealed and then mounted in the cold finger.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. D. I. Rawson and Mr. I. Capstick for their assistance with some of the synthetic work and also Dr. P. Vasuder for running the Mössbauer spectra. The award of an S.R.C. Research Studentship to one of us (P.P.) is gratefully acknowledged.

REFERENCES

1 M. M. KREEVOY, J. W. GILJE, L. T. DITSCH, W. BATOREWICZ AND M. A. TURNER, *J. Org. Chem.*, 27 (1962) 726.
2 S. WINSTEIN, E. VOGELFANGER AND K. C. PANDE, *Chem. Ind. (London)*, (1962) 2061.
3 S. WINSTEIN AND T. G. TRAYLOR, *J. Amer. Chem. Soc.*, 78 (1956) 2597.
4 F. R. JENSEN AND K. L. NAKAMAYE, *J. Amer. Chem. Soc.*, 88 (1966) 3437.
5 D. E. APPLEQUIST AND G. N. CHMURNY, *J. Amer. Chem. Soc.*, 89 (1967) 875.
6 R. R. SAUERS AND R. M. HAWTHORNE JR., *J. Org. Chem.*, 29 (1964) 1685.
7 D. S. MATTESON AND M. L. TALBOT, *J. Amer. Chem. Soc.*, 89 (1967) 1119.
8 D. F. HUNT, C. P. LILLYA AND M. D. RAUSCH, *J. Amer. Chem. Soc.*, 90 (1968) 2561.
9 H. G. KUIVILA AND C. R. WARNER, *J. Org. Chem.*, 29 (1964) 2854.
10 H. G. KUIVILA AND G. L. GRADY, *J. Organometal. Chem.*, 21 (1970) 303.
11 D. SEYFERTH, A. B. EVNIN AND D. R. BLANK, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 181.
12 H. GILMAN AND L. A. GIST JR., *J. Org. Chem.*, 22 (1957) 250.
13 J. G. ZAVISTOSKI, *Diss. Abstr. B*, 29 (1968) 526.
14 B. FRANZUS, W. C. BAIRD JR., N. F. CHAMBERLAIN, T. HINES AND E. I. SNYDER, *J. Amer. Chem. Soc.*, 90 (1968) 3721.
15 M. P. BROWN AND D. E. WEBSTER, *J. Phys. Chem.*, 64 (1960) 698.
16 C. E. JOHNSON JR. AND F. A. BOVEY, *J. Chem. Phys.*, 29 (1958) 1012.
17 J. W. EMSLEY, J. FEENEY AND L. H. SUTCLIFFE, *High Resolution NMR Spectroscopy*, Vol. 1, Pergamon Press, Oxford, 1st Ed. 1965, p. 595.
18 J. W. APSIMON, W. G. CRAIG, P. V. DEMARCO, D. W. MATHIESON, L. SAUNDERS AND W. B. WHALLEY, *Tetrahedron*, 23 (1967) 2357.
19 J. MEINWALD, Y. C. MEINWALD AND T. N. BAKER III, *J. Amer. Chem. Soc.*, 85 (1963) 2513.

20 M. Brookhart, A. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, 88 (1966) 3133, 3135.
21 J. W. Ryan and J. L. Speier, *J. Amer. Chem. Soc.*, 86 (1964) 895.
22 J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 83 (1961) 3903.
23 M. Gielen, M. De Clercq and J. Nasielski, *Bull. Soc. Chim. Belg.*, 78 (1969) 237.
24 N. F. Ramsey, *Phys. Rev.*, 78 (1950) 699; 86 (1952) 243.
25 B. K. Hunter and L. W. Reeves, *Can. J. Chem.*, 46 (1968) 1399.
26 J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith and J. D. Roberts, *J. Amer. Chem. Soc.*, 92 (1970) 7107.
27 H. C. Clark and R. C. Poller, *Can. J. Chem.*, 48 (1970) 2670.
28 R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, (1969) 2145.
29 V. T. Aleksanyan and E. Sterin, *Chem. Abstr.*, 53 (1959) 21159*d*.
30 *Org. Syn.*, 18 (1938) 26.
31 H. Normant, *C.R. Acad. Sci.*, 226 (1948) 733.
32 W. E. Truce and J. P. Milionis, *J. Amer. Chem. Soc.*, 74 (1952) 974.
33 H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, 76 (1954) 4072.
34 P. R. Story, *J. Org. Chem.*, 26 (1961) 287.
35 S. C. Clarke and B. L. Johnson, *Tetrahedron*, 24 (1968) 5067.
36 S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, 32 (1967) 3727.
37 *Org. Syn.*, 45 (1965) 33, 89.
38 W. P. Neumann, G. Burkhardt and R. Sommer, *Justus Liebigs Ann. Chem.*, 659 (1962) 27.
39 H. L. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, 82 (1960) 1888.
40 D. Seyferth and F. G. A. Stone, *J. Amer. Chem. Soc.*, 79 (1957) 515.
41 B. W. Ready, unpublished work.
42 P. Partington, Ph. D. Thesis, University of Essex, 1971.