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STEREOCHEMISTRY OF THE TIN–CARBON BOND

I. SYNTHESIS AND CHARACTERIZATION BY ^{13}C AND ^{119}Sn NMR OF A SERIES OF *exo*- AND *endo*-2-TRIORGANOSTANNYLNORBORNANES

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Summary

A series of *endo*- and *exo*-2-triorganostannylnorbornanes have been synthesized by various methods, some of them leading to pure stereoisomers. The 2-triorganostannylnorbornanes have been characterized by their ^{13}C and ^{119}Sn NMR spectra.

There have been only a few studies of the preparation of 2-triorganostannylnorbornanes, except for the trimethylstannyl derivatives [1,2] which were prepared by Kuivila et al. in pure *endo*- or *exo*-forms [1]. We describe below the results of our attempts to extend some initial findings [3] to the preparation of stereochemically pure 2-triorganostannylnorbornanes with other organic groups attached to the tin atom, as a preliminary to the study of the stereochemistry of the tin–carbon bond cleavage.

Two approaches were investigated or reinvestigated: the first, starting from norbornene, is based on hydrostannation; the second involves use of stannyl anions for substitution in the norbornyl system.

The structures of the various compounds were firmly established by ^{13}C and ^{119}Sn NMR studies.

A. Syntheses of a series of *endo*- and *exo*-2-triorganostannylnorbornanes

(1) Hydrostannation of norbornene

In an effort to extend Kuivila's synthesis [1] to other organotin hydrides we used

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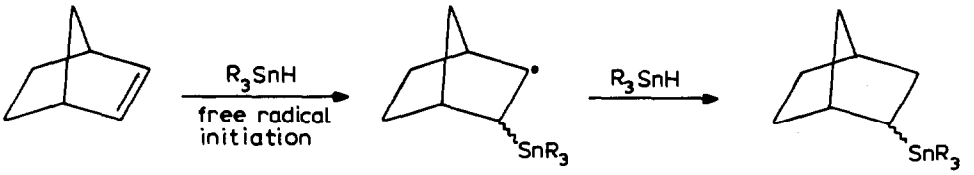
the following reaction:



(R = methyl, butyl, cyclohexyl or phenyl)

Our results are summarized in Table 1.

Lowering the reaction temperature to 0°C gave pure *exo*-isomers for R = Me or Bu, without a fall in yield. Since the *exo*-face is less hindered than the *endo*- one, a slight change in temperature is sufficient to inhibit the *endo*-approach for the organotin radical $R_3Sn^{\cdot}$ in the first step of the reaction.

Tricyclohexyltin hydride did not add to the double bond of norbornene under free radical conditions; this could be due to the large bulk of the hydride, but even under high pressure (a possible way to overcome steric hindrance [5]) no addition was observed.

Triphenyltin hydride gave the expected adducts when azobisisobutyronitrile (AIBN) was used as initiator. Unfortunately no addition was observed under UV

SCHEME 1

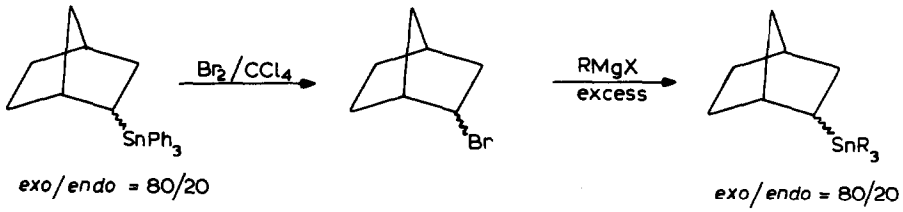


TABLE 1

HYDROSTANNATION OF NORBORNENE

R_3SnH	Conditions [a] (Temp. (°C))	*exo/endo* [b] ratio	Yield (%) [c]
R = Me	UV (60)	87/13	50
	UV (45)	95/5	49
	UV (0)	100/0	50
R = Bu	UV (45)	80/20	75
	UV (0)	99/1	70
R = C_6H_{11}	UV (60)		0
	AIBN (70)		0
	14 Kbar (50) [d]	polymers	0
R = Ph	AIBN (70)	80/20	87
	UV (60)		0

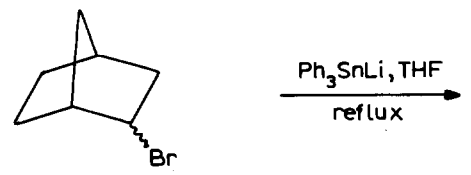
[a] All the experiments were run during 16 h without solvent. [b] ^{119}Sn NMR analysis. [c] ^{1}H NMR analysis. [d] See ref. 4.

irradiation, which means that temperature could not be lowered to favour the formation of the *exo*-isomer. 2-Triphenylstannylnorbornane is, in fact, a good precursor for other 2-triorganostannylnorbornanes as shown in Scheme 1 [6].

This sequence of reactions was performed with R = isopropyl, neopentyl, and cyclohexyl (60, 49 and 43% yield), and ^{119}Sn NMR analyses confirmed the conservation of the isomer ratio (vide infra).

(2) Substitution on norbornyl derivatives

The stereochemistry of substitution of alkyl halides and tosylates with stannylanions has been extensively studied by several groups [7–15]. We attempted to use this type of reaction to prepare *endo*- or *exo*-2-triorganostannylnorbornane selectively. The *exo*-tosylate did not react with triphenyltinlithium in refluxing THF, but this result is not surprising in view of the very poor yield obtained by others in a similar reaction with 4-t-butylcyclohexyltosylate [16]. Use of *exo*- or *endo*-2-bromonorbornane led to the following mixtures of isomers:

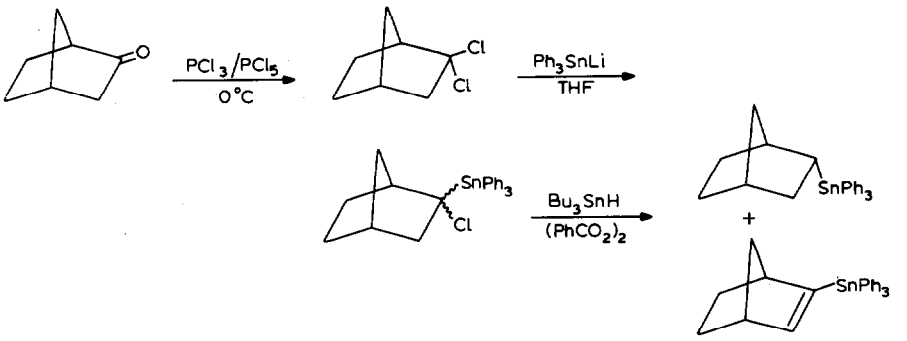


exo/endo = 100/0
exo/endo = 15/85

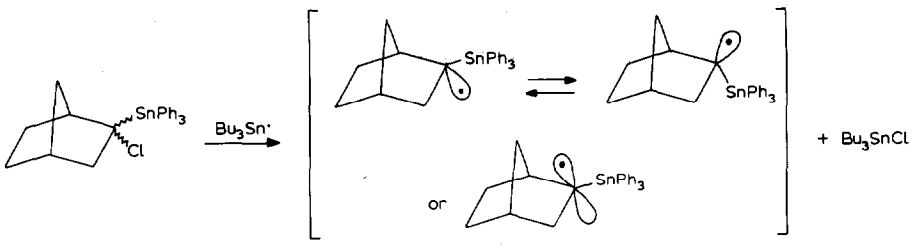
exo/endo = 35/65 (40% yield)
exo/endo = 73/27 (35% yield)

The poor stereochemistry of these reactions led us to devise a more convenient route, as shown in Scheme 2:

SCHEME 2



A subsequent reduction of the vinyltin derivative with diimide following Kuivila's procedure [1] increased the yield of *endo*-2-triphenylstannylnorbornane. The stereochemically determinant step is, in fact, the reduction by tributyltin hydride, which can be represented in the following way [17–19].



The hydrogen transfer occurs selectivity on the *exo*-side of the radical, and the structure of the chlorostannyl compound should have no influence on the final configuration.

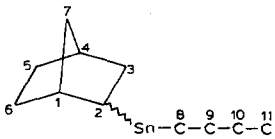
The route shown in Scheme 1, employing *endo*-2-triphenylstannylnorbornane, was used to prepare a series of analogous compounds: methyl, isopropyl and neopentyl derivatives were obtained by this procedure in the pure *endo*-form.

B. Characterization

We were unable to separate the *endo*- and *exo*-isomers by GLC for the methyl or butyl derivatives or by HPLC for the phenyl derivative. However, the ^{13}C NMR spectra are different for the two isomers; the data are listed in Table 2, and include

TABLE 2

^{13}C NMR CHEMICAL SHIFTS (ppm) FOR SOME 2-TRIORGANOSTANNYLNORBORNANES ($^{3}J(^{119}Sn-^{13}C)$ [a] (Hz) are given in brackets; int. reference TMS)

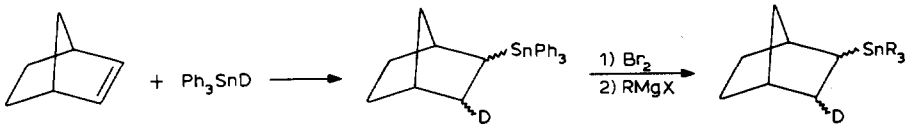


		1	2	3	4	5	6	7	8	9	10	11
R = Me [b]	*exo*	40.1	27.5	34.8	37.4	29.4	33.4	38.5	−10.9			
		(9.8)	(387–407)	(23.4)	(12.7)	(n.o.)	(67.4)	(n.o.)	(292–306)			
	endo	40.5	28.5	33.7	36.7	30.1	30.0	40.5	−10.3			
		(10.0)	(432)	(n.o.)	(23.4)	(n.o.)	(36.0)	(56.6)	(293–306)			
R = i-Pr [b]	*exo*	40.7	26.9	36.4	37.9	29.5	34.7	39.4	14.3	22.6		
		(10.0)	(284–296)	(21.5)	(12.7)	(n.o.)	(55.8)	(n.o.)	(294–306)	(15.2)		
	endo	41.4	29.0	34.4	36.6	30.9	31.5	40.4	14.7	22.7		
		(9.1)	(296–311)	(6.0)	(23.3)	(6.3)	(25.3)	(53.0)	(296–311)	(15.2)		
R = neopentyl [b]	*exo*	40.7	29.5	36.7	37.8	29.1	35.0	38.7	31.8	32.1	33.8	
		(13.0)	(299–304)	(21)	(n.o.)	(n.o.)	(60.7)	(n.o.)	(273–285)	(n.o.)	29.5	
	endo	41.4	34.3	30.5 [d]	37.1	29.5 [d]	30.5 [d]	41.1	32.4	32.2	33.8	
		(9.7)	(222–248)	(n.o.)	(27.0)	(n.o.)	(n.o.)	(60.8)	(283–303)	(n.o.)	(31.9)	
R = Ph [c]	*exo*	40.1	29.1	35.2	37.4	29.1	33.8	38.7	139.2	137.3	128.3	128.6
		(10.6)	(407–397)	(n.o.)	(13.7)	(n.o.)	(n.o.)	(n.o.)	(450–460)	(28.4)	(42.5)	(n.o.)
	endo	40.5	29.6	33.7	36.2	29.6	31.3	40.1	139.6	137.1	128.3	128.6
		(10.9)	(396)	(n.o.)	(25.8)	(13)	(36.7)	(68.0)	(437–457)	(38.9)	(46.2)	(n.o.)

[a] Absolute values; for ^{1}J, $^{1}J(^{119}Sn-^{13}C)$ follows $^{1}J(^{117}Sn-^{13}C)$. [b] Solvent C_6D_6. [c] Solvent $CDCl_3$. [d] Most probable assignment.

the trimethylstannyl derivative for which data were already available in the literature [2].

Secondary and quaternary carbons were identified by off-resonance noise decoupling. The introduction of deuterium at C(3) (vide infra) allows this atom to be identified. The coupling between tin and carbon is also of use in determining *exo–endo* stereochemistries. In the case of C(6) and C(7) the absolute values of the coupling constants to tin are a function of the dihedral angle θ = Sn–C–C–C. This Karplus like relation [2] indicates that coupling between C(6) and Sn must be strong in the *exo*-isomer ($\theta \simeq 170°$) and weak in the *endo*-isomer ($\theta \simeq 35°$). The position is reversed for C(7) for which $\theta \simeq 85°$ in the *exo*-isomer and $\theta \simeq 160°$ in the *endo*-isomer. Although ^{13}C NMR is suitable for establishing the structures of these norbornyl derivatives, it does not provide a very accurate measure of the isomer ratios. Greater accuracy can be achieved by using a recently developed method which shows a Karplus like relation between the absolute value of the coupling constant ^3J(Sn–D) and the dihedral angle Sn–C–C–D [3]. To take advantage of these data we synthesized deutero-analogs of the compounds described in part A, using 3-deuterio-2-triphenylstannylnorbornane as a precursor.

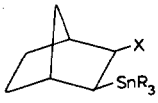
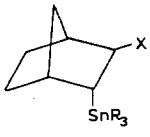


Derivatives with R = methyl, n-butyl, isopropyl, neopentyl and cyclohexyl were prepared in this way. Their ^{119}Sn NMR spectral data are listed in Table 3.

The assignment of the signals of *exo*- and *endo*-isomers cannot be made solely on the magnitudes of the chemical shifts, but becomes possible by using the values of ^3J(Sn–D) [3]. Quantitative analysis confirms that there is no change in the *exo/endo* ratio during successive substitution (Scheme 1). Since isotopic effects are very small (Table 3) [20] it therefore becomes possible to analyse the nondeuterated *exo/endo* mixture directly.

TABLE 3

^{119}Sn CHEMICAL SHIFTS (ppm) FOR SOME 3-DEUTERIO-2-TRIORGANOSTANNYLNORBORNANES ^3J(Sn–D) (Hz) are given in brackets. Solvent C_6D_6. External reference (Me_4Sn)

	R =	Me [a]	n-Bu [a]	i-Pr	Neopentyl	C_6H_{11}	Ph
	X = D	+3.3	−13.5	−41.1	−44.2	−81.4	−103.1 [b]
		(16.8)	(15)	(13.3)	(15.3)	(13.3)	(17.7)
	X = H	+3.0	−13.6	−41.0	−44.2	−81.0	−103.3
	X = D	−0.5	−12.4	−31.8	−45.4	−71.2	−96.8 [c]
		(5.9)	(5)	(4.5)	(5.6)	(–)	(6.1)
	X = H	−0.7	−12.4	−31.8	−45.4	−71.2	−96.8

[a] Ref. 3. [b] Isomeric compound with *endo*-deuterium has not been detected. [c] Isomeric compound with *exo*-SnR_3 has not been detected.

Experimental

NMR spectra were recorded on a Perkin–Elmer R12 (^1H), Bruker WP 60 (^{13}C) and Bruker WH 90 (for ^{119}Sn) spectrometers. Mass spectrometric analyses were carried out on a VG-Micromass 16F Spectrometer using an 80/20 *exo/endo* mixture. HPLC analyses were performed on a Varian 5000 Liquid chromatograph equipped with columns Si-10, C18 (normal or reverse phase) and NH_2 bonded phase (normal or reverse). A Philips HPK 125 lamp was used for UV irradiation. Tetramethylsilane was the reference for ^{13}C and ^1H NMR and tetramethyltin for ^{119}Sn NMR. Chemical shifts are given in ppm.

(a) Hydro- and deutero-stannation

Organotin hydrides or deuterides were prepared according by standard procedures [21–23].

A typical procedure for hydrostannation under UV light is as follows. A mixture of trimethyltin hydride (1.5 g, 9 mmol) and norbornene (0.86 g, 9 mmol) was irradiated at 0°C in a Pyrex flask. Distillation gave trimethylstannylnorbornane (1.2 g) (b.p. 60°C/10 Torr. 50% yield). The same procedure was used at other temperatures and for deutero-stannation.

(b) 2-Trimethylstannylnorbornane

Data for the hydrogeno-derivative were as follows: ^1H NMR (CCl_4): 0.2 (Me_3Sn, s, 9H), 1 to 2 (br, 9H), 2.3 (s, 2H). MS for the deutero-compound: [ion, relative intensities] 246 [$Me_2SnC_7H_{10}D^+$,41], 165 [Me_3Sn^+,98], 152 [Me_2SnD^+,26], 151 [Me_2SnH^+,19], 150 [Me_2Sn^+,12], 135 [$MeSn^+$,23], 96 [$C_7H_{10}D^+$,100], 68 [$C_5H_6D^+$,18], 67 [$C_5H_7^+$,15].

(c) 2-Tributylstannylnorbornane

For the hydrogeno-derivative, b.p. 125°C/0.01 Torr. Yield 72%. ^1H NMR (CCl_4): 0.8–2.1 (br, 36H), 2.2 (s,2H). MS for the deutero-compound: 330 [$Bu_2SnC_7H_{10}D^+$,54], 291 [Bu_3Sn^+,41], 274 [$BuHSnC_7H_{10}D^+$,59], 236 [Bu_2SnD^+,27], 235 [Bu_2SnH^+,64], 218 [$H_2SnC_7H_{10}D^+$,63], 216 [$SnC_7H_{10}D^+$,50], 180 [$BuSnDH^+$,37], 179 [$BuSnH_2^+$,87], 177 [$BuSn^+$,89], 96 [$C_7H_{10}D^+$,100], 68 [$C_5H_6D^+$,24], 67 [$C_5H_7^+$,15], 57 [Bu^+,32].

(d) 2-Triphenylstannylnorbornane

The adduct crystallized from ethanol, m.p. 90°C, yield 87%. ^1H NMR (CCl_4): 1.2–2.6 (br, 11H), 7.0–7.6 (br, 15H). MS for the deutero-compound: 370 [$Ph_2SnC_7H_{10}D^+$,1.7], 351 [Ph_3Sn^+,100], 275 [Ph_2SnH^+,2], 197 [$PhSn^+$,16] 122 [DSn^+,1.6], 96 [$C_7H_{10}D^+$,13], 77 [Ph^+,3], 68 [$C_5H_6D^+$,3], 67 [$C_5H_7^+$,3].

Brominative cleavage of the phenyl groups in 2-triphenylstannylnorbornane was by the procedure described in ref. 6.

(e) 2-Triisopropylstannylnorbornane

Prepared from 2-triphenylstannylnorbornane following Scheme 1 [6]. B.p. 115°C/2×10^{-3} Torr. Yield 60%. ^1H NMR (CCl_4): 0.6–1.9 (br, 30H), 2.3 (s,2H). MS for the deutero-compound: 302 [i-$Pr_2SnC_7H_{10}D^+$, 45], 260 [i-PrHSn-$C_7H_{10}D^+$,38], 249 [i-Pr_3Sn^+,60], 208 [i-Pr_2DSn^+,40], 166 [i-PrHDSn$^+$,21], 121 [HSn^+,37], 96 [$C_7H_{10}D^+$,100], 68 [$C_5H_6D^+$,18], 67 [$C_5H_7^+$,14], 43 [$C_3H_7^+$,30].

(f) 2-Trineopentylstannylnorbornane

Prepared from 2-triphenylstannylnorbornane following Scheme 1 [6]. M.p. 140°C, yield 60%. ^{1}H NMR (CCl_4): 0.8 (s,27H), 0.9–2.6 (br, 17H). MS for the deutero-compound; 358 [$Neopent_2SnC_7H_{10}D^+$,100], 333 [$Neopent_3Sn^+$,97], 264 [$Neopent_2DSn^+$,26] 263 [$Neopent_2HSn^+$,26], 96 [$C_7H_{10}D^+$,58], 71 [$Neopent^+$,32].

(g) 2-Tricyclohexylstannylnorbornane

Prepared from 2-triphenylstannylnorbornane following Scheme 1 [6]. M.p. 220°C, yield 49%. ^{1}H NMR (CCl_4): 1–2.6 (br). MS for the deutero compound: 382 [$(C_6H_{11})_3SnH_{10}D^+$,100], 369 [$(C_6H_{11})_3Sn^+$,17], 288 [$(C_6H_{11})_2DSn^+$,14], 287 [$(C_6H_{11})_2HSn^+$,29], 206 [$C_6H_{11}DHSn^+$,19], 205 [$C_6H_{11}H_2Sn^+$,37], 96 [$C_7H_{10}D^+$,70], 83 [$C_6H_{11}^+$,32].

(h) endo-2-Triphenylstannylnorbornane

Triphenyltinlithium was prepared during 8 h under nitrogen from Ph_3SnCl (11.6 g, 0.03 mol) and lithium chips (0.07 g, 0.1 mol) in THF (30 ml) at 20°C. After filtration, the solution was added to 2,2-dichloronorbornane (b.p. 93°C/25 Torr [24]), (4.45 g, 0.027 mol) in THF (10 ml) and the mixture was refluxed for 4 h. Hydrolysis and removal of solvent gave crude 2-chloro-2-triphenylstannylnorbornane, to which was added Bu_3SnH (8.8 g, 0.033 mol) and a catalytic amount of $(t\text{-}C_4H_9O)_2$. After 2 h at 70°C the mixture was treated with KF (2.3 g, 0.04 mol) in 1/1 H_2O/acetone (80 ml). The white precipitate of tributyltin fluoride was filtered off. After extraction with ether and solvent evaporation, the solid was crystallized from ethanol to yield 7.1 g *endo*-2-triphenylstannylnorbornane (75%, $\delta(^{119}Sn)$ −96.6 ppm in C_6D_6) and 2-triphenylstannylnorbornene (25%, $\delta(^{119}Sn)$ −137 ppm in C_6D_6).

Hydrogenation of the norbornene derivative was performed as follows. A solution of the mixture of saturated and unsaturated compound (7.1 g) in 120 ml dry dioxane was cooled to 0°C under argon and 14.4 g dry potassium azodicarboxylate (prepared as in ref. 25) was added with stirring. Acetic acid was then added until no colour remained. The mixture was extracted with ether, and the ether was washed, and dried over magnesium sulfate. After solvent evaporation and recrystallization from ethanol, 7.1 g (9.2×10^{-3} mol, 58%) pure *endo*-2-triphenylstannylnorbornane (T 90°C) was obtained.

Acknowledgements

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