Journal of Organometallic Chemistry, 61 (1973) 167–177

PREPARATION AND PROPERTIES OF SOME TRIMETHYLTIN-SUBSTITUTED BICYCLO[2.2.1] CARBOCYCLES, 3-NORTRICYCLYL-TRIMETHYLTIN AND NORBORN-2-EN-7-YLTRIMETHYLSILANES

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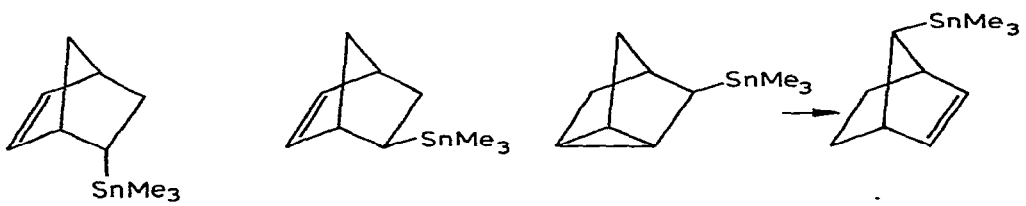
(Received March 21st, 1973)

SUMMARY

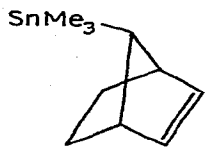
Methods of synthesis, spectral properties and some chemical properties of the following compounds are described: *endo*- and *exo*-2-norbornyltrimethyltins, *endo*- and *exo*-norborn-2-en-5-yltrimethyltins, *syn*- and *anti*-norborn-2-en-7-yltrimethyltins, norborna-2,5-dien-7-yltrimethyltin 3-nortricyclyltrimethyltin, *syn*- and *anti*-norborn-2-en-7-yltrimethylsilanes.

In the course of studies on the free radical addition of trimethyltin hydride to dienes[1,2] we observed that norbornadiene undergoes facile reaction to form a mixture of four isomeric products: *endo*-norborn-2-en-5-yltrimethyltin (In), *exo*-norborn-2-en-5-yltrimethyltin (Ix), 3-nortricyclyltrimethyltin (II), and *syn*-norborn-2-en-7-yltrimethyltin (IIIs)[2]. We have also reported on the electron impact fragmentation of these four compounds and the following related ones: *anti*-norborn-2-en-7-yltrimethyltin (IIIa), norborna-2,5-dien-7-yltrimethyltin(IV), *syn*-norborn-2-en-7-yltrimethylsilane (Vs), *anti*-norborn-2-en-7-yltrimethylsilane (Va), allyltrimethyltin and *cis*- and *trans*-trimethylcrotyltins[3]. In this paper we report preparative data and other information upon which structural and configurational assignments of these compounds have been made.

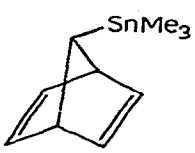


(In) (Ix) (II) (IIIs)

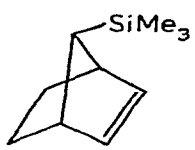
* The work done by F.L.P. was carried in the Department of Chemistry, University of New Hampshire and is reported in his Ph.D. Dissertation, 1968.



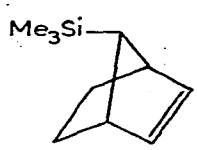
(IIIa)



(IV)



(Vs)



(Va)

A mixture of the adducts of trimethyltin hydride to norbornadiene[2] was hydrogenated over palladium on charcoal. Infrared bands due to the vinyl group at 3060 and 1570 cm^{-1} disappeared. Peaks in the gas chromatogram due to 6 and 6 appeared in the same area ratio, but at new retention times. Coinjection of authentic samples of *endo*-norborn-2-en-5-yltrimethyltin and *exo*-norborn-2-en-5-yltrimethyltin Ix separately increased these areas as expected.

A mixture of the 1,2-adducts could be separated from the rearranged products by GLPC on Apiezon L, and these, in turn, could be resolved on an analytical column of 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P. Enough of each isomer was obtained pure for infrared and NMR spectral measurements at 60 MHz. NMR spectra for these compounds are summarized in Table 1. They are highly similar in all respects to those of the corresponding trimethylsilyl analogs which have been discussed in detail[4]. The most striking characteristics are found in the signals from the vinyl and bridgehead protons. In Ix the vinyl protons appear as a pair of quartets centered 17 Hz apart; in In they appear as a narrow triplet. The bridgehead protons of Ix give signals separated by 13 Hz, whereas those of In appear to be superimposed.

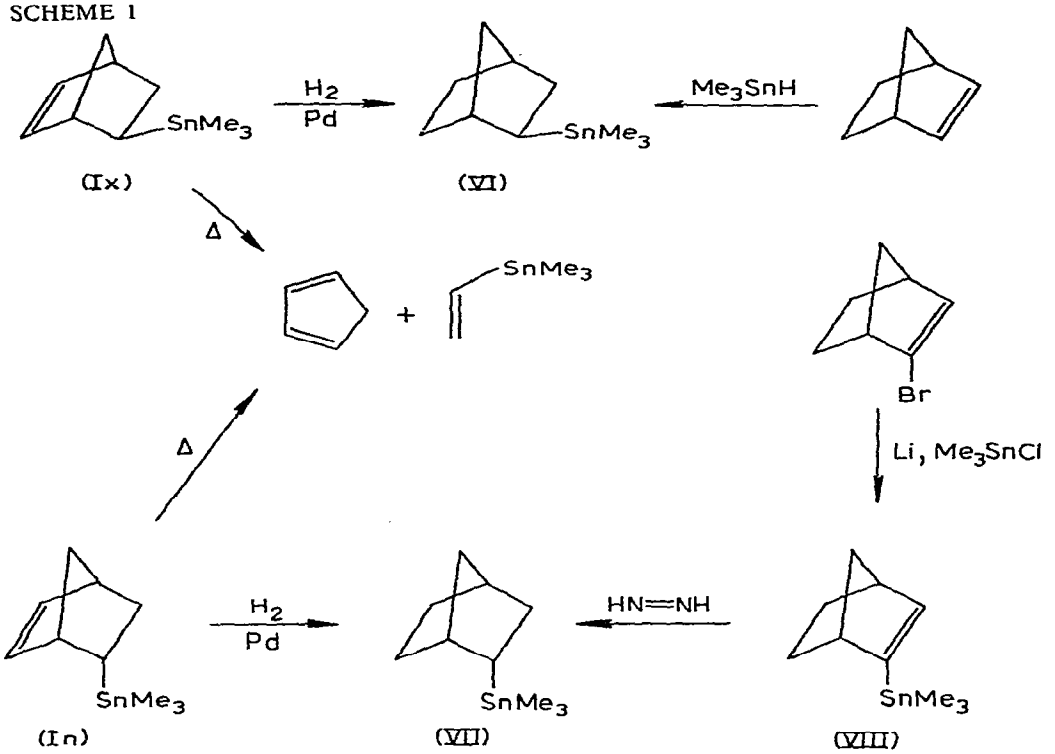
Injection of Ix and In into the gas chromatograph at an injection port temperature at 400° led to partial fragmentation into two detectable products. A retro-Diels–Alder reaction is indicated by the identity of retention time of one of the fragments with that of cyclopentadiene. Under conditions which led to decomposition of 50% of Ix only about 20% of In decomposed. This is consistent with greater strain in Ix due to non-bonded interactions between the *anti*-hydrogens in the 7-position of the ring and those on the methyl groups attached to tin (Also see below.)

TABLE 1

NMR SPECTRAL DATA FOR Ix AND In

	Chemical shift (ppm)	*Area*	*Multiplicity*	*Assignment*
Ix	6.10	1	unsym. quartet	H-2 or H-3
	5.81	1	unsym. quartet	H-3 or H-2
	2.90	1	broad singlet	H-1
	2.68	1	broad singlet	H-4
	0.17–1.85	5	complex	H-5,6,7
	0.02	9	singlet	$SnMe_3$
In	5.90	2	triplet	H-2,3
	2.90	2	broad singlet	H-1,4
	0.81–2.13	5	complex	H-5,6,7
	−0.13	9	singlet	$SnMe_3$

SCHEME 1



Their origins, spectral data and the chemical reactions shown in Scheme 1 provide the bases for assignment of the structures and configurations of Ix and In. The authentic *exo*-norborn-2-yltrimethyltin VI was obtained in high yield as the only isolated product of the addition of trimethyltin hydride to norbornene. Norborn-2-en-2-yltrimethyltin VIII was prepared from 2-bromonorborn-2-ene by treatment with lithium, followed by trimethyltin chloride. Reduction of VIII with diimide provided VII as the only reduction product indicating a high degree of selectivity. The assumption of *exo*-addition of trimethyltin hydride[5,6] and of reduction by diimide which is presumed to involve concerted *cis*-addition of the hydrogens[7] have ample precedence[8,9].

3-Nortricyclyltrimethyltin comprised about 11 % of the trimethyltin hydride–norbornadiene adduct mixture. Its infrared spectrum showed bands at 3070 and 806 cm^{-1} characteristic of nortricyclenes unsubstituted in the cyclopropane ring[10].

The fourth product formed in the addition of trimethyltin hydride to norbornadiene has been shown to be *syn*-norborn-2-en-7-yltrimethyltin, IIIs. In order to establish its structure and to confirm the absence of the *anti*-isomer IIIa it was necessary to synthesize both isomers. Reaction of the lithium reagent prepared from 7-bromonorbornene with trimethyltin chloride provided 30 to 45 % yield of mixtures of IIIs and IIIa. One alternative procedure involved preparation of the Grignard reagent from the bromide by the method of Bank and Bank[11], who have found that certain Grignard reagents can be prepared by the reaction of halides with sodium naphthalene

in the presence of magnesium bromide (Eqn. 1 and 2). This procedure gave the

$$2\,Na^+\ C_{10}H_8^- + RX + MgBr_2 \rightarrow 2\,NaX + 2\,C_{10}H_8 + RMgBr \quad (1)$$

$$RMgBr + Me_3SnCl \rightarrow RSnMe_3 + MgClBr \quad (2)$$

desired products, but in only 9 % yield. A modification of this procedure, in which the formation of the Grignard reagent was by-passed (Eqn. 3) gave the norbornenyltins

$$2\,Na^+\ C_{10}H_8^- + RBr + Me_3SnCl \rightarrow 2\,C_{10}H_8 + RSnMe_3 + NaCl + NaBr \quad (3)$$

in 31 % yield. Separation of the isomers for further studies was effected by GLPC. This may indicate that trimethyltin chloride is a better "trap" for the anion R^- than is magnesium bromide.

NMR spectra of IIIs and IIIa were examined in some detail with the results shown in Table 2. The protons of the trimethyltin group of IIIa appear at a field 3.5 Hz

TABLE 2

NMR SPECTRAL PARAMETERS OF NEAT *syn*- AND *anti*-NORBORN-2-EN-7-YLTRIMETHYLTINS[a]

	Chemical shift (ppm) or coupling constant (Hz)	
	IIIs	*IIIa*
$\delta(SnMe_3)$ ($\pm$0.003)	−0.032	0.032
δ(H-7)	0.94	1.27
δ(H-5n, H-6n)	1.02	0.91
δ(H-5x, H-6x)	1.50	1.48
δ(H-1, H-4)	2.96[b]	2.90[b]
δ(H-2, H-3)	5.86[b]	6.07[c]
J(Sn–Me)[e] ($\pm$0.15)	51.1	50.25
J(Sn–H-1) = J(Sn–H-4)[e]	11.5 $\pm$ 0.3	10.1 $\pm$ 0.3
J(Sn–H-2) = J(Sn–H-3)[e]	$\leqslant$ ca. 2[d]	6.3
J(H-1–H-7) = 7(H-4–H-7)	$\leqslant$ 1.3	1.2
J(H-5n–H-7) = J(H-6n–H-7)	ca. 0.5[d]	2.4

[a] The NMR spectral parameters of IIIa are consistent with those reported by Roberts, *et al.*[23] Those for both IIIa and IIIs are consistent with those observed by Davis[24] although the arguments differ slightly. More recent ^{13}C–^{119}Sn coupling constants also confirm the assignments[25]. [b] Centrosymmetric multiplet. [c] Apparent triplet, J = 1.8 Hz. [d] Estimated. [e] ^{119}Sn.

lower than those of IIIs. This is in the direction anticipated due to the shielding of the *syn*-methylprotons by the double bond in IIIs. Examination of Dreiding models shows that the average position of the protons of the trimethyltin group is about 4.2 Å from the center of the double bond and the angle appropriate for calculating the shielding according to the McConnell equation is about 25°[12]. Neglecting other factors the calculated chemical shift difference in the two isomers would be about 7 Hz. The proton at C-7 *syn* to the double bond in IIIa appears at a lower field (δ 1.27 ppm) than does that which is *anti* to the double bond in IIIs (δ 0.94 ppm). The chemical shift difference (0.33 ppm) is of the same magnitude (0.29 p.p.m.) and in the same direction as observed with norbornene itself[13,14]. However, substitution at C-7 on occasion

reverses the relative chemical shifts of the *syn* and *anti* protons. This can be traced to the fact that the *syn*-7 proton in norbornene is near the boundary of the shielding cone of the double bond. *Anti* substituents can distort the shape of the molecule sufficiently to move this proton into the shielding cone and change its signal to a higher field than that of the *anti* proton in the *syn* substituted analog[13,14]. The absence of this effect due to the trimethyltin group in IIIa suggests that no significant distortion of the ring system is caused by its presence. Examination of a Dreiding model indicates that a small non-bonded interaction exists between the protons of the trimethyltin group and the *exo*-5 and *exo*-6 protons of the ring. The resultant strain can, however, be relieved most easily by bending of C–Sn bonds instead of C–H or C–C bonds because of the lower bending force constants of the former. Thus, little distortion of the ring need occur, and the *syn* C-7 proton in IIIa will be in essentially the same position relative to the double bond as it is in norbornene itself.

Previous studies on norbornenes have revealed that *syn*-protons on C-7 show couplings of 1.7 to 2.3 Hz with the 1- and 4-protons, and couplings of 2.0 to 3.1 Hz with the *endo*-5 and -6 protons, but no significant coupling with the C-2 and C-3 vinyl protons[13–18]. *Anti*-protons on C-7 exhibit couplings of 1.3 to 1.7 Hz with the C-1 and C-4 protons, and couplings of 0.3 to 0.8 Hz with the C-2 and C-3 vinyl protons, but no significant coupling with the C-5 and C-6 protons. We have obtained the normal 100 MHz spectra of IIIa and IIIs and those in which the 1- and 4-protons were decoupled. Results for IIIa are shown in Figs. 1 and 2, for the region containing signals from the C-5, C-6 and C-7 protons. Although the magnetic anisotropic effects of the norbornene skeleton are not yet well understood, it is generally recommended that the signals due to *syn*- and *anti*-7-proton resonances be assigned on the basis of these couplings, rather than on the basis of relative chemical shifts[13]. Decoupling of the 1,4-protons of norbornene itself results in a spectrum in which the *anti*-7-proton signal appears as a broadened doublet [J(7a–7s) = 7.7 Hz; J(2–7a) = J(3–7a) = 0.5 Hz], and in which the *syn*-7-proton signal is a doublet of triplets [J(7a–7s) = 7.7 Hz; J(5n–7s) =

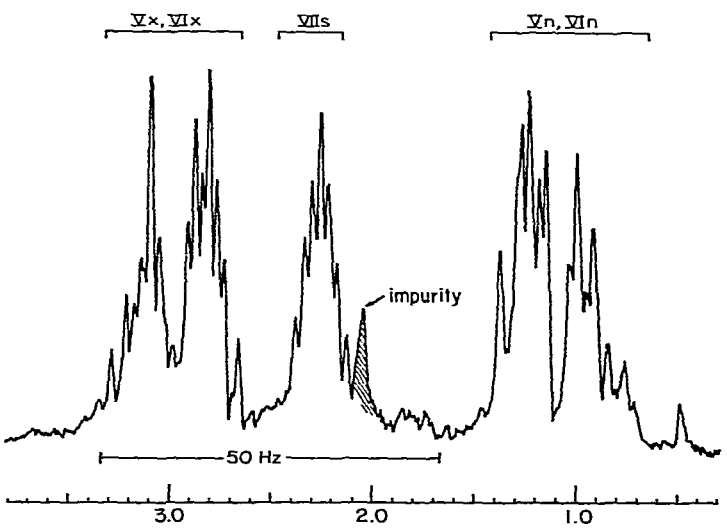


Fig. 1. Undecoupled 100 MHz NMR spectrum of the 5-, 6-, 7-protons of compound IIIa.

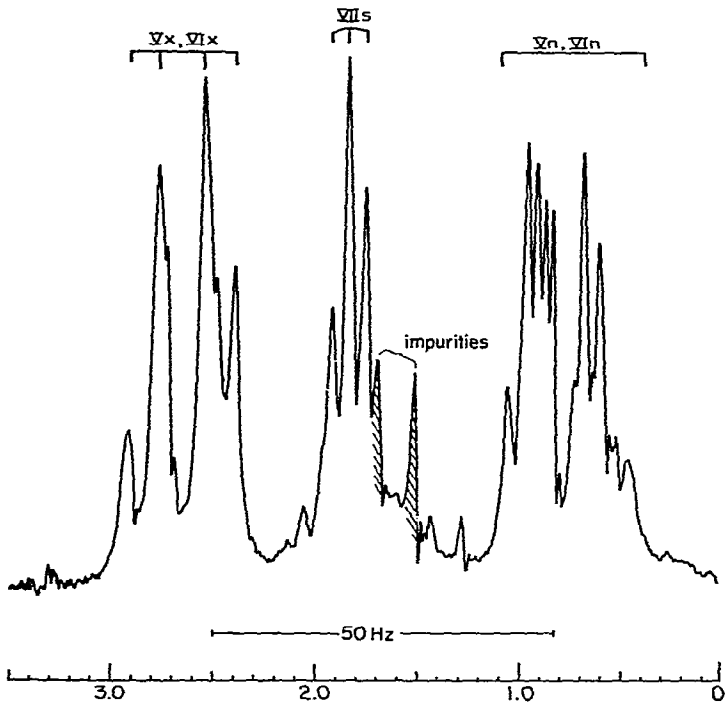


Fig. 2. 100 MHz NMR spectrum of the 5-, 6-, 7-protons of compound IIIa with 1,4-protons decoupled.

J(6n–7s) = 2.2 Hz]. The spectra shown in Figs. 1 and 2 for IIIa can be seen to conform with these expectations. In particular the 7-proton displays a triplet of triplets [J(1–7s) = J(4–7s) = 1.2 Hz], and J(6n–7s) = 2.4 Hz. When the 1,4-protons are decoupled the C-7 proton appears as a triplet with J = 2.4 Hz (Fig. 2). Similar decoupling experiments were carried out with IIIs*. The results of these analyses are listed in Table 2. The coupling patterns due to the *exo* protons at C-5 and C-6 are so similar in both isomers as to be of no diagnostic value.

Coupling constants between ^{119}Sn and the vinyl protons were in the direction required for the configurational assignment. The value of 6.3 Hz was observed when the tin atom was *anti*, and a value of less then 2 Hz was found when the tin atom was *syn*. The coupling with *anti* presumably arises[15] from interaction between the π-orbital of the double bond and the rear lobe of the orbital through which the tin is bonded to C-7. The analogous coupling between vinyl and *anti*-C-7 protons has been observed[15–19], in several cases to be in the range 0.3–0.9 Hz, but coupling to the *syn*-C-7 protons has not been detected. The larger coupling between *syn*-Sn and C-1,4 protons than between *anti*-Sn and these protons is in the same direction as observed for the corresponding protons in IIIs and IIIx and in other norbornenes[13,14,16–18]. It may be concluded that the NMR data are consistent with the assignments of configurations to IIIs and IIIx.

Further evidence comes from thermal fragmentation behavior of the two

* Copies of the pertinent Parts of the spectra are available on request.

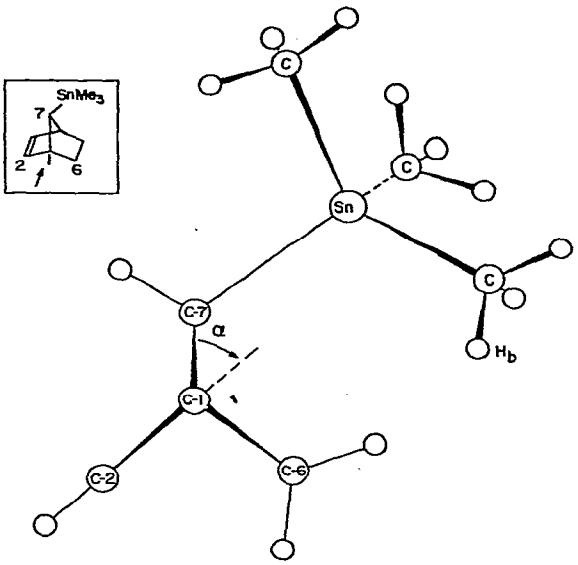


Fig. 3. Projection of Dreiding model of compound IIIa showing how steric strains could be increased on point to the transition state for the retro-Diels–Alder reaction.

isomers in a gas chromatograph. Both undergo clean decomposition to form the same two products, presumably ethylene and cyclopentadienyltrimethyltin; the latter was characterized by identity of GLPC retention time with that of an authentic sample. When a mixture of IIIs and IIIa was injected at a port temperature of 400° 97% of IIIa, but only 5% of IIIs decomposed. That this would be the expected result can be seen by examination of Dreiding models. A projection for IIIa is shown in Fig. 3. As the molecule passes into the transition state, the two major geometric changes will be stretching of C-1 to C-6 and C-4 to C-5 bonds and a decrease of angle α toward 0°. This will result in increased non-bonded interaction between hydrogens like H_b and the *exo* hydrogens on C-5 and C-6, thus raising the energy of the transition state. In IIIs, on the other hand, interaction between the methyl hydrogens on the tin and the vinyl hydrogens would be significantly smaller and it is being relieved in the transition state. The result is more facile decomposition of IIIs.

The situation is quite different with the 5-trimethylstannylnorbornenes In and Ix, respectively. When equal amounts were introduced into the gas chromatograph at a temperature of 400°, for example, only two products, presumably trimethylvinyltin and cyclopentadiene, confirmed by coinjection, were formed in each case. In this particular experiment, confirmed by similar ones, area ratios indicated about 63% decomposition of the *exo* isomer Ix and 31% decomposition of the *endo* isomer In. These results indicate a small steric effect in Ix which is relieved in the transition state, as can be seen by examination of an appropriate model.

The compounds described were characterized because four of them were products of the addition of trimethyltin hydride to norbornadiene. We have also carried out electron impact fragmentation study of these compounds and others which might provide pertinent comparisons. The characterizations of these follow for they have not been reported previously.

Norborna-2,5-dien-7-yltrimethyltin was prepared by the method represented by Eqn. 3 in 10% yield. NMR spectral data are given in the Experimental. Due to its modest stability an elemental analysis was not obtained, but the mass spectrum is in full accord with the expected elemental composition[3].

Allyltrimethyltin and *cis*- and *trans*-crotyltrimethyltins were also examined in the electron impact study and reference to their preparations and properties made.

The *syn*- and *anti*-7-trimethylsilylnorborn-2-enes Vs and Va, respectively were prepared by the method represented by Eqn. 3. Configurational assignments were made on the basis of NMR spectra which were similar to those of IIIs and IIIa, and which are listed in the Experimental.

EXPERIMENTAL

Norbornadiene (Shell Chemical) and trimethyltin chloride* were distilled before use. Norbornene (Aldrich Chemical) and trimethylchlorosilane (Anderson) were used as obtained. Tetrahydrofuran was dried by distillation from lithium aluminum hydride and then stored over sodium.

NMR spectra were obtained with Varian A60A and HA100 spectrometers.

Infrared spectra were recorded on a Perkin–Elmer 337 or a Beckman IR-8 spectrophotometer. Mass spectra of most of the compounds reported were obtained with an AEI MS 9 spectrometer and are recorded elsewhere[3].

Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee or by Instranal Laboratory, Inc., Rensselaer, N.Y.

All operations involving trimethyltin hydride or trimethyltin sodium were carried out under nitrogen or argon.

exo- and endo-Norborn-2-en-5-yltrimethyltin. Reaction of trimethyltin hydride with norbornadiene[2] yielded a mixture of four isomeric adducts. GLPC on an Apiezon L on Chromosorb W column yielded three peaks. The first was *syn*-norborn-2-en-7-yltrimethyltin (11%), identical with that whose preparation is described below; the second was a mixture of *endo*- and *exo*-norborn-2-en-5-yltrimethyltin; the third was 3-nortricyclyltrimethyltin, identical with that whose preparation is described below. Resolution of the mixture obtained in the middle cut was achieved by use of a 1,2,3-tris(2-cyanoethoxy)propane on Diatoport P column.

An authentic sample, prepared by an alternative route** was found to be identical.

3-Nortricyclyltrimethyltin. The sample collected in the experiment was shown to have identical IR and NMR spectra with a sample prepared by an alternative method**. (Found: C, 46.92; H, 7.00. $C_{10}H_{20}Sn$ calcd.: C, 46.74; H, 7.01%.)

Exo-Norborn-2-en-5-yltrimethyltin. In a Pyrex tube were placed 4.25 g (0.025 mol) of trimethyltin hydride and 2.25 g (0.025 mol) of norbornene. The mixture was photolyzed at 25° for 33 h using a 100 watt Hanovia lamp. It was then distilled; b.p. 40–42°/0.01 mm, yield 4.9 g (76%). GLPC (1,2,3-tris(2-cyanoethoxy)propane on Diatoport P $\frac{1}{4}$ in. by 15 ft.) showed the presence of one product. IR neat 3065 (no band

* We thank M&T Chemicals for a gift of this material provided through the courtesy of Mr. Bernard Kushlevsky.

** Via the reaction of 3-bromonortricyclene with trimethyltinlithium by J. L. Considine (to be published).

near 1600 cm^{-1}); n_D^{25} 1.5167. (Found: C, 46.15; H, 7.60, Sn, 46.20. $C_{10}H_{20}Sn$ calcd.: C, 46.39; H, 7.73; Sn, 45.88%.)

Norborn-2-en-2-yltrimethyltin. Norborn-2-en-2-yl bromide was prepared by the method of LeBel[19]. Lithium sand (1.5 g) and 25 ml of dry tetrahydrofuran were added to a flask equipped with a magnetic stirrer and an addition funnel. The reaction flask was chilled to 0°, flushed with argon, and 7.5 g (0.046 mol) of bromide was added dropwise with rapid stirring. The stirring was continued for 2 h at 0°. Trimethyltin chloride (9 g, 0.047 mol) in 15 ml of THF was added dropwise over a 15 min period and stirring was continued for one hour at 0°. The reaction mixture was poured into a mixture of saturated ammonium chloride, ice and 200 ml of ether. The ether layer was separated, extracted successively with 50 ml of water and 50 ml of saturated sodium chloride solution, and dried ($MgSO_4$). The ether was removed at atmospheric pressure and the tetrahydrofuran at 100 mm. Further distillation yielded 4.5 g (38%) of the anticipated product, b.p. 48–50° (0.1 mm); IR_{max} (film) 3030, 1545 and 1250 cm^{-1}.

endo-Norborn-2-yltrimethyltin. Following a general procedure for diimide reductions[20] 3 g (0.012 mol) of norborn-2-en-2-yltrimethyltin, 4.8 ml of 95% hydrazine, 35 ml of anhydrous ethanol and 1 ml of a 1% solution of $CuSO_4 \cdot 5H_2O$ were mixed and treated at 0° in an argon atmosphere with 2.4 ml of 30% hydrogen peroxide over 15 min. Work-up yielded 2.2 g (74%) of product; b.p. 46–48°/0.1 mm; GLPC indicated greater than 99% purity; IR indicated no olefinic bands at 3030 and 1545 cm^{-1}. (Found: C, 46.18; H, 7.62; Sn, 46.25. $C_{10}H_{20}Sn$ calcd.: C, 46.39; H, 7.73; Sn, 45.88%.)

syn- and anti-Norborn-2-en-7-yltrimethyltins (III)

Method A. Anhydrous magnesium bromide was prepared by adding a solution of 2.35 g (12.5 mmol) of ethylene dibromide in 15 ml of tetrahydrofuran to 0.30 g (12.5 mmol) of magnesium in 15 ml of tetrahydrofuran. To this solution was added 1.52 g (10.0 mmol) of *syn*-7-bromonorbornene. An 0.44 *M* solution of sodium naphthalene in tetrahydrofuran was added dropwise. Instant decolorization occurred giving an orange-yellow suspension until about 60 ml had been added, whence a green color persisted. Trimethyltin chloride (2.0 g, 10.0 mmol) in 20 ml of tetrahydrofuran was added and the mixture was stirred for 30 min. It first turned to a pale blue and then to light gray. Solvent was removed under reduced pressure below room temperature and the residue was poured onto 40 ml of water containing 0.1 ml concentrated sulfuric acid. The mixture was shaken and extracted twice with 30-ml portions of ether. The extracts were combined, dried ($MgSO_4$) and concentrated. GLPC using a 320″ × 3/4″ column packed with 15% Apiezon L on Chromosorb provided 0.50 g (19%) of product containing 33% of the *syn* isomer IIIs, which eluted first, and 67% of the *anti* isomer IIIa; IR_{max}^{neat} *syn*: 3060 and 1565 cm^{-1}; *anti*: 3130 and 1565 cm^{-1}; n_D^{25} *syn*, 1.5083; n_D^{25} *anti*, 1.5105. (Found: *syn*: C, 46.81; H, 7.08; Sn, 46.30; *anti*: C, 45.86; H, 7.07; Sn, 46.31. $C_{10}H_{18}Sn$ calcd.: C, 46.74; H, 7.01; Sn, 46.24%.)

Method B. A solution of 2.0 g (10.0 mmol) of trimethyltin chloride and 1.52 g (10.0 mmol) of *syn*-7-bromonorborn-2-ene in 35 ml of tetrahydrofuran was titrated with 0.44 *M* sodium naphthalene in tetrahydrofuran until the green color of the sodium naphthalene persisted (ca. 70 ml). Work-up as above gave 0.80 g (31%) of a mixture comparising 45% of the *syn* and 55% of the *anti* isomer.

Method C. A solution of 10.7 g (61.8 mmol) of *syn*-7-bromonorborn-2-ene and 14.4 g (68 mmol) of trimethyltin chloride in 25 ml of tetrahydrofuran was added drop-

wise to a suspension of 1.7 g (245 mmol) of lithium in 15 ml tetrahydrofuran maintained at 60–65°. After stirring for 2 h work-up yielded 4.9 g (40%) of a mixture comprising 31% the *syn* and 69% of the *anti* isomer.

Norborna-2,5-dien-7-yltrimethyltin (IV)

Method A. When method A described above for the preparation of the norborn-2-en-7-yltrimethyltins was carried out using 7-chloronorbornadiene only about 1% of material presumed to be the desired product IV was obtained. IR_{max}^{neat}: 3060, 1300 cm^{-1}; NMR: δ 0.05 ppm (Me_3Sn), 2.38, broad singlet (H-7), 3.35, broad singlet (H-1,4); 6.92, 6.78, triplets with unresolved fine structure (H-2,3,5,6). The mass spectrum[4] showed *m/e* for the molecular ion containing ^{120}Sn at the calculated value of 245 for $C_{10}H_7Sn$.

Method B. To a solution of 2.20 g (11.1 mmoles) of trimethyltin chloride and 1.26 g (10.0 mmoles) of 7-chloronorbornadiene in 35 ml of THF was added dropwise 0.44 *M* sodium naphthalene until the green color persisted (ca. 55 ml). Air was bubbled through the solution until the color was discharged. Volatile components were removed under reduced pressure. The amber residue was shaken with 50 ml of saturated aqueous ammonium chloride solution and extracted thrice with 30-ml portions of ether. The extracts were combined, dried (Na_2SO_4), and concentrated. GLPC was used to collect the product (0.255 g; 10%).

syn- and anti-norborn-2-en-7-yltrimethylsilanes. These compounds were prepared by Method B described above for the corresponding tin analogs from *syn*-7-bromonorbornene and trimethylsilyl chloride. Pure samples were obtained by preparative GLPC on an Apiezon L column, the *syn* isomer eluting first. *Anal.* $C_{10}H_{18}Si$ calcd.: C, 72.3; H, 10.8. Found: *syn*: C, 72.36; H, 11.10; *anti*: 72.16; H, 10.79. NMR: *syn*: −0.11 ppm (Me_3Si); δ 0.71, triplet, *J* 1.4 Hz (H-7); δ 0.8–2.0 (H-5,6), multiplet; 2.90 (H-1,4), multiplet; 5.85 (H-2,3), triplet, *J* 1.9 Hz. *anti*: δ −0.03 (Me_3Si); 0.86 (H-7), multiplet; 0.8–2.0 (H-5,6), multiplet; 2.89 (H-1,4), multiplet; 6.10 (H-2,3), triplet, *J* 1.7 Hz.

Allyltrimethyltin was prepared by the method of Jones and collaborators[21].

cis- and *trans-Crotyltrimethyltins* were prepared by the method of Verdone[22].

ACKNOWLEDGEMENTS

We thank R. Lane and S. Ulrich for obtaining the 100 MHz spectra, and the National Science Foundation for financial support. We also thank Ms. Irene J. Tyminski for carrying out helpful experiments.

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