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SYNTHESIS OF SOME TRIMETHYLTINNORBORNANOLS

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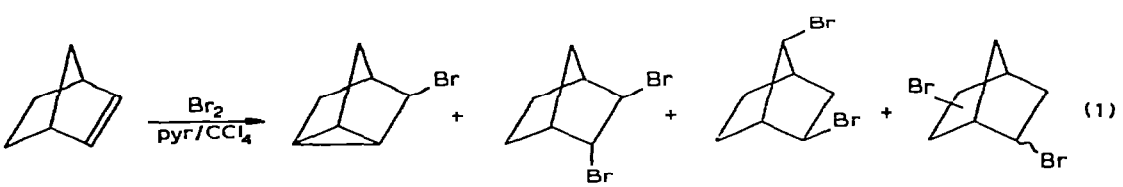
Summary

The stereospecific syntheses of four trimethyltinnorbornanols are reported. These include *syn*-7-trimethyltin-*exo*-2-norbornanol, *anti*-7-trimethyltin-*exo*-2-norbornanol, *syn*-7-trimethyltin-*endo*-2-norbornanol, and *anti*-7-trimethyltin-*endo*-2-norbornanol. The *syn*-trimethyltin group is found to have little steric interference towards *exo* attack at the C-2 and C-3 positions of the norbornyl skeleton in both hydroboration and metal hydride reduction.

In connection with our studies of the stereochemistry of 1,3-elimination reactions of trimethyltin alcohols [1a], various isomeric trimethyltinnorbornyl alcohols have been synthesized. The locked geometry of this system affords all four possible elimination configurations, *U*, *W*, *exo*-sickle, and *endo*-sickle [1b].

Entry into this system was made through *syn*-7-bromonorbornene (II). Bromine was added to norbornene (eqn. 1), following the procedure of Kwart and Kaplan [2].



(I) (1)

From this mixture, 3-bromonortricyclene was separated by vacuum distillation. The remaining mixture was selectively dehydrohalogenated with t-BuOK/t-BuOH at reflux (eqn. 2) with only the amount necessary to react with *trans*-2,3-dibromonorbornane and the minor components (2,5- and 2,6-dibromonorbor-

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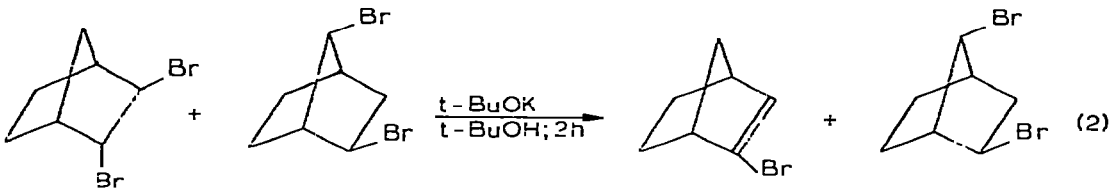
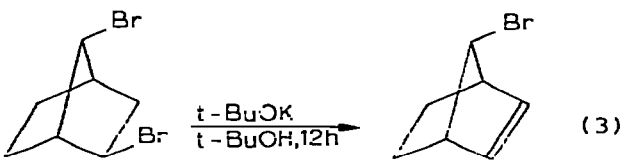
nanes). The reaction was monitored by gas chromatography, and the dehydrohalogenation stopped when the *trans*-2,3-dibromonorbornane had completely reacted. Kwart and Kaplan [2] have also reported the more rapid dehydrobromination of *trans*-2,3-dibromonorbornane. Vacuum distillation yielded pure I, which was then dehydrohalogenated by refluxing with t-BuOK/t-BuOH for 12 h (eqn. 3). The assignment of the minor components is based upon gas

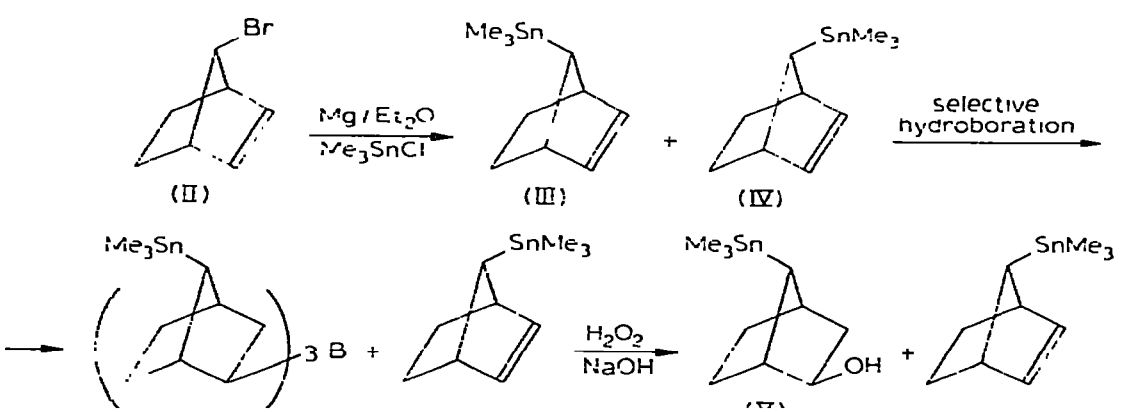




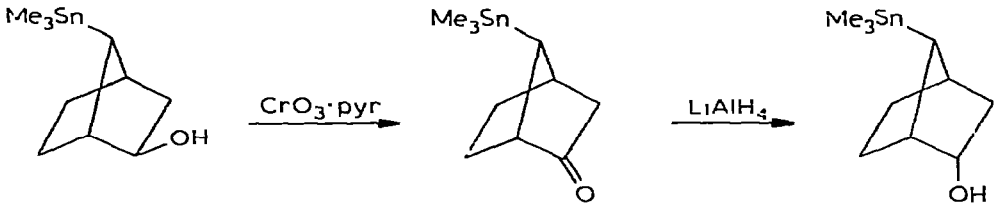
chromatographic data. The retention times are similar to that of the *trans*-2,3-dibromide, and they were assumed to be other isomeric dibromides. These were removed in the selective dehydrohalogenation step. The yield of I was the same as reported by the previous investigators [2], 31%, but the procedure modification eliminates the difficult vacuum distillation separation of the dibromides. Dehydrohalogenation of I gave II in 72% yield.

Treatment of the Grignard reagent from II in diethyl ether with trimethyltin chloride gave a mixture of *anti*-7-trimethyltinnorbornene (III) and *syn*-7-trimethyltinnorbornene (IV), in 2/1 ratio. Separation of these compounds by physical methods proved not to be practical. However, hydroboration, using only the amount of diborane necessary to give the trialkylborane derived from III, occurred selectively with this compound. Peroxide oxidation followed by separation by column chromatography yielded *anti*-7-trimethyltin-*exo*-2-norbornanol (V) and unreacted IV (Scheme 1). Oxidation of V with chromic anhydride—pyridine complex to the norcamphor, followed by $LiAlH_4$ reduction resulted in *anti*-7-trimethyltin-*endo*-2-norbornanol (VI); 63% yield for the two steps (Scheme 2).

SCHEME 1



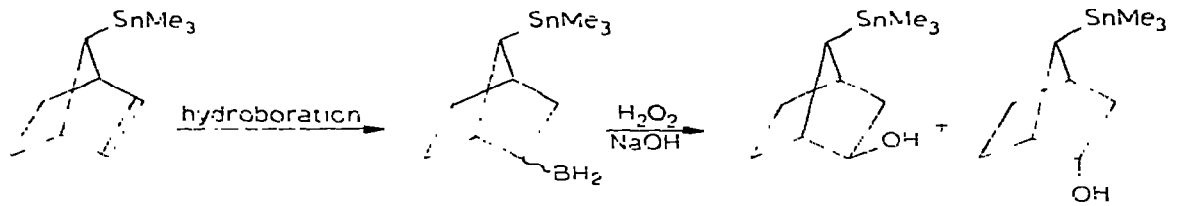
SCHEME 2



(V) (VI)

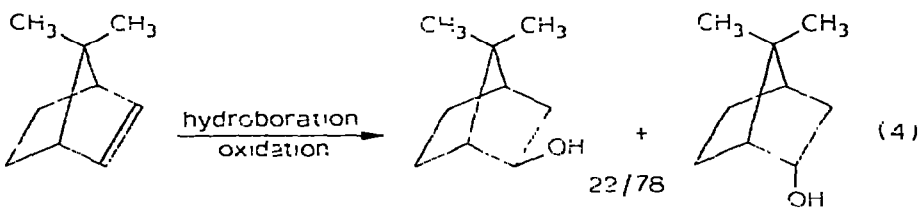
Although the *syn*-norbornene (IV) is unreactive towards hydroboration under competitive reaction conditions, hydroboration is possible with an excess of diborane generated in situ. After peroxide oxidation of the borane formed, a mixture of *syn*-7-trimethyltin-*exo*-2-norbornanol (VII) and *syn*-7-trimethyltin-*endo*-2-norbornanol (VIII) resulted (Scheme 3). Depending upon the exact reaction conditions, the composition of this mixture varied from approximately 60/40 to 50/50 mixtures of VII and VIII.

SCHEME 3

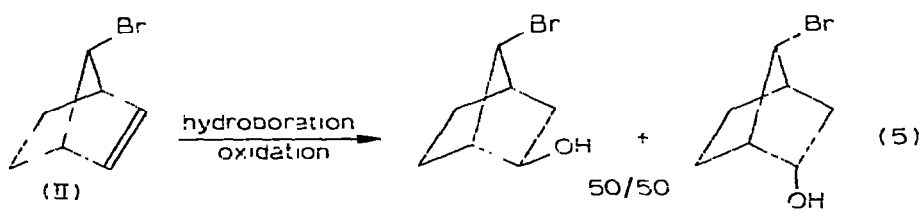


(V) (VII) (VIII)

The high percentage of the *exo* alcohol is somewhat surprising since hydroboration—oxidation of norbornenes hindered by substituents in the *syn*-7 position has been found previously to give a mixture of *exo* and *endo* alcohols with the *endo* isomer generally predominating. Brown and Kawakami [3] reported that a 22/78 mixture of *exo* and *endo* isomeric alcohols was produced from 7,7-dimethylnorbornene (eqn. 4) and similar results for other hindered norbornenes. We have found an *exo*/*endo* ratio of 50/50 following hydroboration—peroxide oxidation of *syn*-7-bromonorbornene (II) (eqn. 5). It is probable



(4)

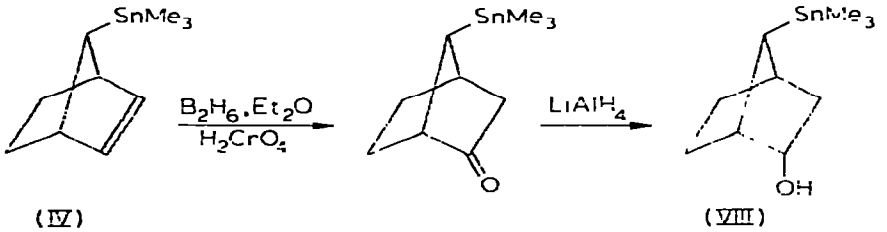


(II) (5)

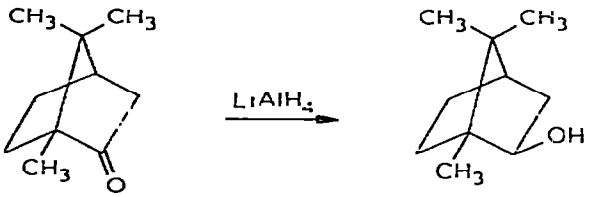
that the longer carbon—tin bond makes the trimethyltin group less effective

in blocking approach to the double bond and models suggest that this is so. When the alkylborane from IV was oxidized by chromic acid in ether, and the resulting norcamphor reduced by $LiAlH_4$, *syn*-7-trimethyltin-*endo*-2-norbornanol (VIII) was isolated (Scheme 4). Again this finding differs markedly from the results in other hindered norbonanones. Both camphor (eqn. 6) and apocamphor are

SCHEME 4



reduced preferentially to the *exo* alcohols while norcamphor gives mostly the *endo* isomer [4]. Similarly, we have found that reduction by both $LiAlH_4$ and $NaBH_4$ of *syn*-7-bromonorcamphor gives predominately the *exo* isomer. A study of the steric effects of the trimethyltin group in hydroboration and epoxidation reactions suggest an effective steric bulk which is similar to Cl- and Br-substituents [5].



Assignment of structure for the various isomers is based on NMR and mass spectral data and chemical evidence. The NMR spectrum of the mixture of III and IV shows two distinct signals in the vinyl region, an apparent triplet at δ 6.15 and a multiplet at 5.95 ppm. The lower-field signal is assigned to the *anti* isomer. The greater complexity of the *syn* vinyl region is due to the long-range splitting of these protons by the bridge proton *anti* to them [6a]. The area of the *anti* vinyl signal is approximately twice that of the *syn*. The typical pattern for the methyl groups on tin is found to be a singlet and associated satellites from ^{117}Sn and ^{119}Sn splitting. The mixture shows two singlets at δ 0 separated by five Hz; the lower field signal is approximately twice the height of the other. Analysis by gas chromatography showed the presence of two components in 2/1 ratio. Upon selective hydroboration, the vinyl signal assigned to III disappeared as well as the larger peak on the gas chromatogram. The change in the position of the trimethyltin protons was too small (2 Hz) to be useful analytically. The ease of hydroboration of III confirms its assignment as the less hindered of the pair. Additionally, carboxylation of 7-norbornenylmagnesium bromide [7] yields *anti*-7-norbornenyl carboxylic acid and *syn*-7-norbornenyl carboxylic acid in 2/1 ratio. The fact that the Grignard reagent carbonation also gives the same ratio of *anti*/*syn* products further supports our assignment of III as the *anti* isomer [8].

Assignment of the *syn* or *anti* configuration in the alcohols is based upon the known configuration of the trimethyltinnorbornenes and the selective hydroboration procedure. The assignment of *exo* and *endo* configuration is based on the C-2 proton signal [6b-f]. Two general conclusions have been reached concerning the C-2 proton NMR spectra of various substituted norbornanes and norbornenes that are useful in assigning configuration. The *endo* proton of the *exo* isomer is shifted upfield (δ 0.3-0.5 ppm) from the *exo* proton of the *endo* epimer. Moreover, there are differences in coupling constants. Since $J(2x—3x) > J(2n—3n)$ and the *exo* proton couples with the bridgehead proton at C-1 while the *endo* proton does not, the *exo* proton of the *endo* isomer exhibits both greater multiplicity and a wider signal than for the epimeric compound. This is further complicated by long range $(2x—6x)$ and $(2n—7a)$ coupling; however, the basic conclusion about greater multiplicity holds. The NMR spectrum for V shows a doublet of doublets at δ 3.68 ppm, and bridgehead protons at δ 2.29 and 2.13 ppm with nearly complete separation into two distinct signals. The *endo* epimer (VI) has a complex multiplet for the C-2 proton at δ 4.02 ppm. The bridgehead protons at δ 2.24 ppm are a distorted triplet, but not split into two signals. The C-2 proton signal of the *syn-exo* isomer (VII), shows a doublet at δ 3.72 ppm and bridgehead protons appear at δ 2.38 and 2.24 ppm, nearly separated into two separate signals. The *endo*

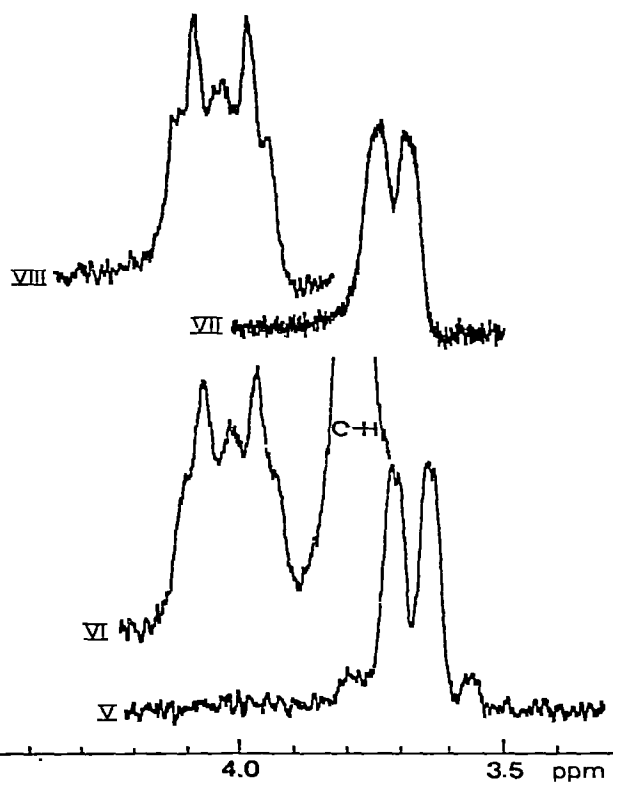


Fig. 1. 100 MHz NMR spectra of the C-2 proton of *anti*-7-trimethyltin-*exo*-2-norbornanol (V), *anti*-7-trimethyltin-*endo*-2-norbornanol (VI); *syn*-7-trimethyltin-*exo*-2-norbornanol (VII) and *syn*-7-trimethyltin-*endo*-2-norbornanol (VIII) in CCl_4 with $CHCl_3$ reference. The hydroxyl proton appears as the upfield signal in VI.

epimer (VIII) has a complex multiplet at δ 4.03 ppm for the C-2 proton and a bridgehead signal at δ 2.25 ppm that is partially split into a doublet. Figure 1 shows the C-2 *exo-endo* areas for compounds V-VIII.

The NMR spectrum of V was further analyzed by use of the lanthanide shift reagent [9a], tris(dipivalomethanato)europium(III). The spectrum with 30 mol % $Eu(DPM)_3$ is shown in Fig. 2 along with the spectrum of V alone. Benzene was used as the internal standard. The C-2 *endo* proton is the most down-field signal and appears as a broad doublet from splitting by the C-3 *endo* proton, $J(2n-3n)$ 6 Hz. The *exo* proton on C-3 is a broad doublet from splitting by the C-3 *endo* proton, $J(3x-3n)$ 14 Hz, and appears to have further splitting from the C-4 proton, $J(3x-4)$ 3 Hz, that is only partially resolved.

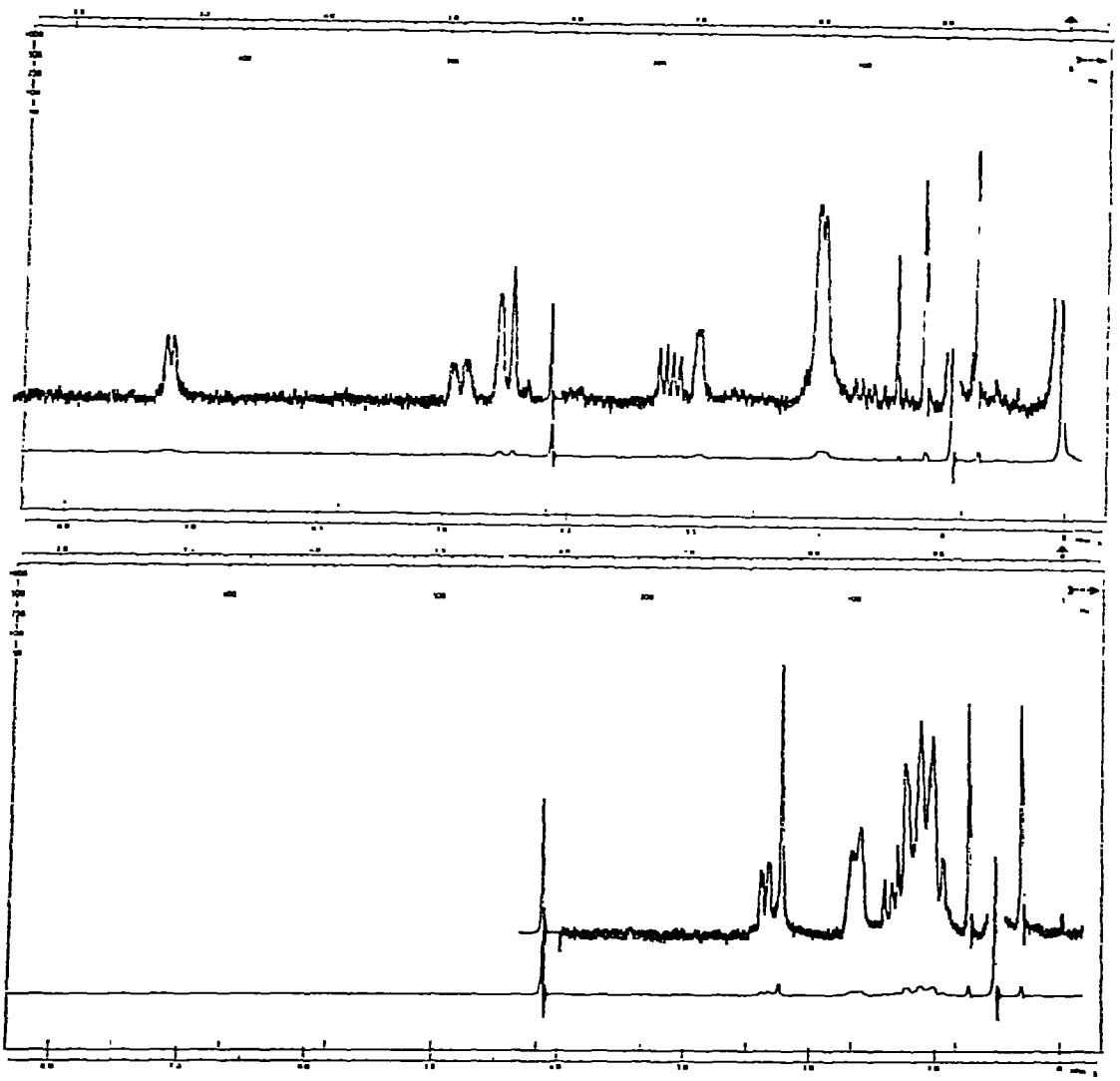


Fig. 2. Top, 60 MHz NMR spectrum of V with 30 mol % $Eu(DPM)_3$ in CCl_4 with internal benzene. Sweep width kHz. Bottom, NMR spectrum of V alone. Both spectra are offset to show DPM protons and Sn satellites.

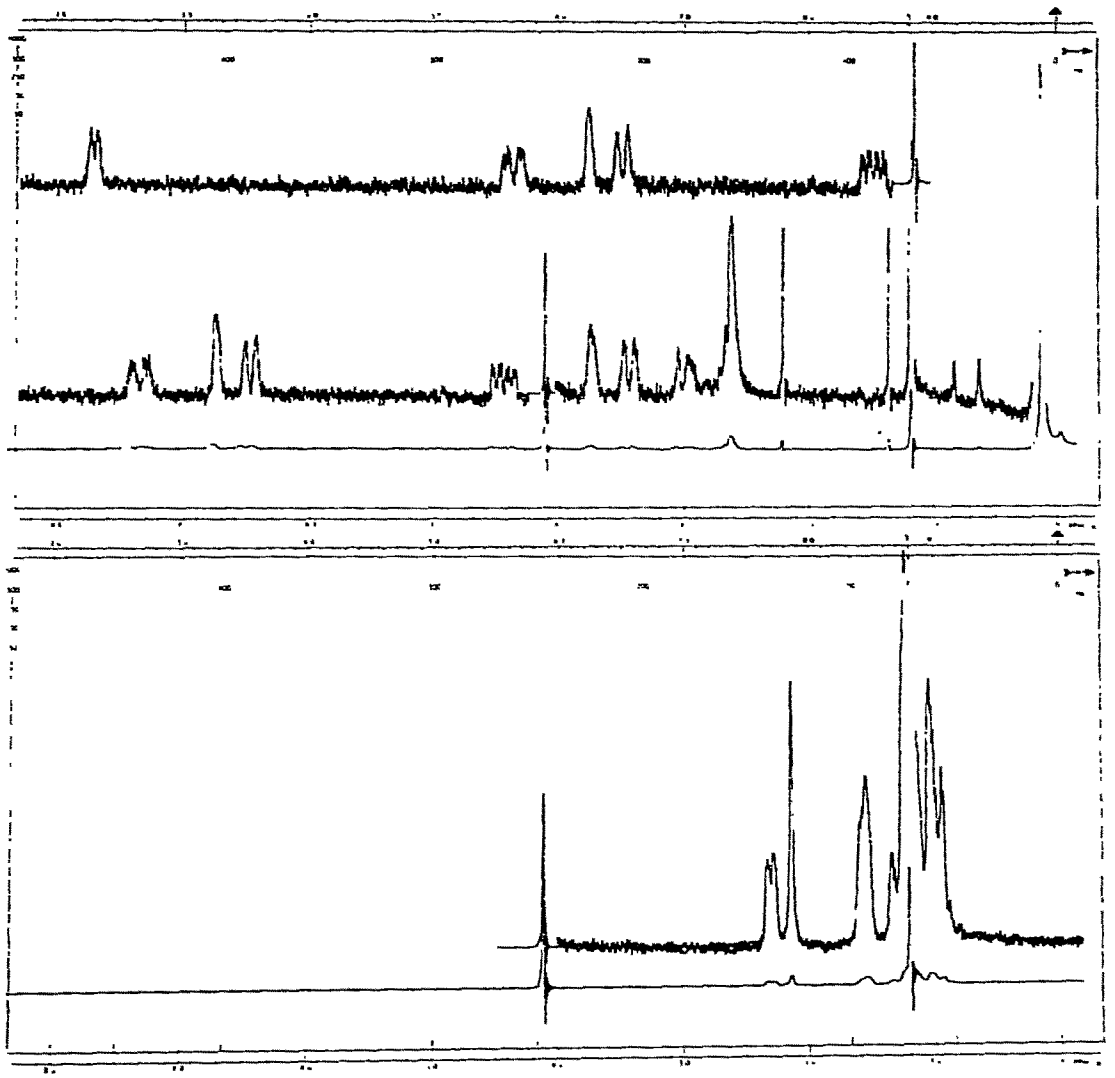


Fig. 3. Top, 60 MHz spectrum of *exo*-norbornanol with 40 mol % $Eu(DPM)_3$ in CCl_4 with internal benzene and cyclohexane. Sweep width 1 kHz. Top trace is offset to include the 2-*endo* proton. Bottom, NMR spectrum of *exo*-norbornanol alone. Both spectra are offset to show DPM protons.

The C-3 *endo* proton is a doublet of doublets from the two splittings above. This is in contrast to the C-3 *endo* proton in *exo*-norbornanol (Fig. 3), which has another long-range splitting by the C-7 *anti* proton with $J(3n—7a)$ 2 Hz. The C-7 *syn* proton of V is a singlet since there is no C-7 *anti* proton to split the signal. In contrast, the C-7 *syn* and *anti* protons in *exo*-norbornanol split one another strongly, $J(7s—7a)$ 10 Hz. The assignment of the signal for C-7 *syn* and C-1 protons is based on the rate at which the two signals are shifted by increasing $Eu(DPM)_3$ concentration. The rate of shift is a function of distance from the proton to the lanthanide coordinated with the oxygen of the alcohol [9b]. Models suggest the C-7 *syn* proton should be closer than the C-1 proton. The other bridgehead proton, C-4, has a much slower rate of shifting due to the

TABLE 1

IMPORTANT PEAKS IN THE MASS SPECTRA OF 7-Me_3Sn-NORBORNANOLS [a]

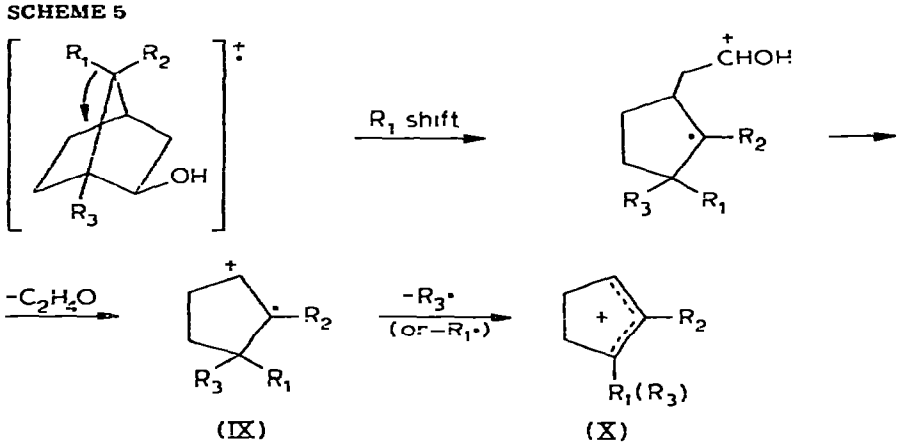
m/e [b]	Relative intensities			
	VI	VI	VII	VIII
276 [c]	2	1	None	8
261	17	13	29	47
247				2
245		1		1
243		1	4	5
232	15	12	Trace	7
230				4
215			1	4
209	4	3		3
185	6	6	2	4
183				10
167			100	
165	81	64	33	100
152			2	
151	9	9	3	70
150	6	6	5	16
137			13	
135	25	21	19	50
121	4	6	3	8
120	5	6	4	10
67	100	100	19	68
66	26	47	31	77

[a] Compounds were injected into liquid inlet in CH_2Cl_2 solution; chamber ionization potential was 75 V. [b] All tin-containing ions are based on ^{120}Sn; only *m/e* 67 and 66 do not contain tin. [c] Parent.

greater distance from the europium. The protons on C-5 and C-6 have not been shifted away from one another enough to be analyzed.

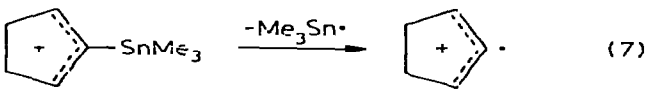
The mass spectral data further strengthen the *anti* and *syn* structural assignments and the assignment of *syn-exo* configuration to VII. (Table 1). Major differences can be seen between the *anti* and *syn* pairs in the tin containing fragments and the non-tin containing fragments, *m/e* 66 and 67. Dimmel and Wolinsky [10] have examined a number of methyl substituted *exo*- and *endo*-2-norbornanols. They found a strong tendency for the alcohols to fragment to give a cyclopentenyl ion (X). They proposed Scheme 5 by which X could arise.

SCHEME 5



(IX) (X)

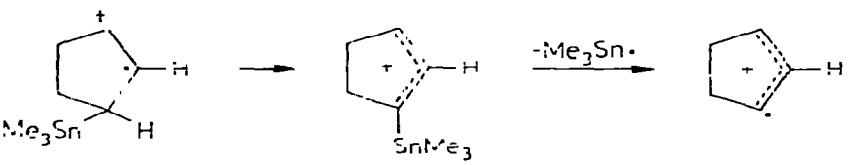
The ion of 7-trimethyltin-2-norbornanols (IX) would have *m/e* of 232, and this peak is found for all four compounds although it is very weak for VII. For the *anti*-Me_3Sn isomers, R_1 is Me_3Sn and R_2 and R_3 are H, and loss of R_1 ($Me_3Sn^{\cdot}$) should be particularly favorable. This would result in a *m/e* peak of 67 for ion X; both V and VI exhibit a base peak of 67. For the *syn*-Me_3Sn isomers, where R_2 is Me_3Sn and R_1 and R_3 are H, loss of $H^{\cdot}$ would result in a *m/e* of 231 for ion X. Only a trace of this *m/e* can be found for VII and none for VIII. Both VII and VIII have strong peaks at *m/e* of 67 which can arise by loss of R_2 ($Me_3Sn^{\cdot}$) from IX. However, *m/e* of 66 is stronger for both isomers and probably occurs by loss of $Me_3Sn^{\cdot}$ from Xa (eqn. 7).



(7)

(Xa) *m/e* 231 (XI) *m/e* 66

The fairly strong *m/e* peak at 66 for V and VI could arise by loss of R_1 ($H^{\cdot}$) from IX followed by loss of $Me_3Sn^{\cdot}$ from Xb.



(8)

(Xb) *m/e* 231 (XII) *m/e* 66

Tin-containing fragments in the mass spectra are easily identified by the characteristic isotopic abundance pattern of tin. The parent ion is found for all the alcohols except VII though the relative abundance is low. The fragmentation of VII appears to occur so readily that no parent ion is found even at an ionization potential of 12V. All four compounds have a peak at *m/e* of 261 which corresponds to loss of a methyl group from the parent compound; the peak appears to be more important for the *syn* isomers. The loss of further methyl groups from 261 does not appear to be important in the mass spectra of the norbornyltin alcohols. There are also peaks at *m/e* 165, 150, 135, and 120 which correspond to Me_3Sn^+, Me_2Sn^+, $MeSn^+$ and Sn^+. The peaks at 121 and 151 are from rearrangement processes that result in SnH^+ and Me_2SnH^+ respectively. The loss of water from the parent molecule does not occur for any of the isomers. The two *syn* isomers have peaks at *m/e* 243 which corresponds to loss of water from fragment *m/e* 261 (parent minus a methyl group). Additionally, the *syn-exo* isomer, VII, shows a metastable ion peak at approximately 226.5, which can be calculated to arise from the transition 261 to 243. The *syn-exo* isomer alone has a very strong peak at 167, Me_2SnOH^+, which apparently arises from OH abstraction by the Me_2Sn^+ group in fragmentation from the *m/e* 261 ion (parent minus methyl). Similarly, *m/e* peaks for $MeSnOH^+$, 152, and $SnOH^+$, 137, are present. The *syn-exo* isomer is the only one with geometry where the OH is close to tin and can readily be abstracted by the leaving tin group.

Experimental

Reactions involving organotin compounds were carried out in an atmosphere of dry nitrogen using three-necked flasks equipped with reflux condenser, self-equalizing funnel, magnetic stirrer and a nitrogen inlet system with a mercury bubbler. No attempts were made to determine optimal conditions for the preparation of the organotin compounds.

Melting points were taken with a Mel-Temp capillary melting point apparatus and are uncorrected.

Infrared spectra were recorded using the Perkin—Elmer 621 spectrophotometer. NMR spectra were obtained with NMR spectrometers from Varian Associates (model A-60A) and JEOL (model PS 100). Spectra of organotin compounds were run using chloroform as an internal standard in 10-20% solutions in carbon tetrachloride. Chemical shifts are reported in parts per million downfield from TMS with the chloroform signal set at 7.25 ppm. Spectra of non-tin compounds were made with TMS as the internal standard. Mass spectra were recorded on Hitachi RMU-6E at ionizing voltages of 75 and 12 V.

The gas chromatographic analyses were performed on an F and M Model 700 equipped with thermal conductivity detectors with rhenium—tungsten filaments. The following instrumental conditions were employed: injection port temperature 210°, cell bath temperature 240°, helium flow rate 30 ml/min for 1/8-inch columns and 60 ml/min for 1/4-inch columns.

Norbornene was purchased from Aldrich Chemical Co. and from Columbia Organic Chemicals Co.; norbornadiene was also purchased from Aldrich. Both materials were used without further purification. Trimethyltin chloride was obtained from Carlisle Chemical Company and M and T Chemicals Inc. and was used without further purification. The gift of this reagent by M and T is acknowledged. All other reagents used were purchased from commercial sources and used without further purification.

Ether used as solvent for preparation of Grignard reagents and for metal hydride reductions was distilled from P_2O_5. Diglyme used in hydroboration reactions was distilled from $LiAlH_4$. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. Other solvents were generally redistilled prior to use.

exo, syn-2,7-Dibromonorbornane (I)

Bromine (249.7 g, 1.5 mol) was added to 141 g (1.5 mol) of norbornene and 118.7 g (1.5 mol) of pyridine in 800 ml of carbon tetrachloride [2]. Vacuum distillation of the crude product gave 45.85 g (0.26 mol, 17% yield) of 3-bromonortricyclene. The crude dibromonorbornane fraction, 231 g (0.912 mol) was added to a solution of potassium tert-butoxide (0.3 mol) in 400 ml of tert-butanol and refluxed for 2 h [11]. Water was added and the material extracted three times with ether. The combined ether layers were washed with cold water and dried. Vacuum distillation of the residue left after solvent removal gave 42.4 g (0.25 mol), b.p. 62-68°/16 mm, that was mostly 2-bromonorbornene. Pure I, 166.6 g (0.46 mol) was obtained by distillation at lower pressure, b.p. 110-112°/0.7 mm. (Lit. [2] 70-74°/0.25-0.30 mm.)

syn-7-Bromonorbornene (II)

This compound was prepared from I in the manner of Kwart and Kaplan [2].

7-Trimethyltinnorbornenes (III and IV)

A Grignard reagent was prepared in 250 ml of diethyl ether from 34.61g (0.2 mol) of II and 6.08 g (0.25 g-atom) of magnesium using a small amount of 1,2-dibromoethane to initiate reaction. The ether solution was filtered through glass wool to remove unreacted magnesium. Trimethyltin chloride (13.93 g, 0.10 mol) in 50 ml of ether was added dropwise over 30 min to the stirred Grignard solution. The reaction mixture then was heated at reflux for 4 h and subsequently was poured into cold ammonium chloride solution. The ether layer was separated and dried over $MgSO_4$, cooled (ice-bath) and saturated with dry ammonia to precipitate unreacted trimethyltin chloride. Removal of solvent and vacuum distillation gave 20.69 g (80%) of mixed III and IV: b.p. 74-91°/ 27 mm; IR (CCl_4) 1560 cm^{-1} (double bond in norbornyl skeleton); NMR (CCl_4): δ 6.15 (triplet, *anti* vinyl), 5.95 (multiplet, *syn* vinyl), 3.05 (broad singlet, bridgehead), 1.8-0.8 (complex multiplet, *exo,endo* and bridge protons), 0.0 ppm (two singlets separated by 5 Hz, trimethyltin). Analysis of the distillate by GLC (6 ft. × 1/8 inch 5% W-98 on Chromosorb P column at 140°) showed the presence of two compounds in 2/1 ratio. A pot residue of coupling product from the Grignard preparation remained.

anti-7-Trimethyltin-exo-2-norbornanol (V)

Mixed III and IV (8.22 g, 0.032 mol) were placed with 0.22 g (0.0057 mol) of $NaBH_4$ in 35 ml of diglyme. $BF_3 \cdot Et_2O$ (1.42 g, 0.010 mol) was added dropwise, and the solution stirred for 1 h. After excess hydride was destroyed by careful addition of water, 4 ml of 6 *N* NaOH was added followed by dropwise addition of 4.1 ml (0.036 mol) of 30% H_2O_2. After initial spontaneous heating, the two-phase system was stirred at ambient temperature for 3 h. The reaction mixture was extracted with ether, washed with ice water, dried over K_2CO_3. Removal of solvent gave 9 g of crude material. This was placed on a silica column and eluted with 30-60° petroleum ether to give pure IV. Elution with mixed petroleum ether/CH_2Cl_2 and later CH_2Cl_2 alone gave a white solid, V, 3.59 g (62%): m.p. 61.5-63°; IR 3620 (OH) and 1075 cm^{-1} (C—O); NMR (CCl_4) δ 3.68 (doublet of doublets, *endo*-C-2 proton), 2.29 and 2.13 (multiplets, bridgehead), 1.9-0.7 (complex multiplet, *exo,endo*, and bridge protons), 0.0 ppm (singlet, trimethyltin). Analysis by GLC (W-89 at 170°) showed only one compound. The mass spectrum is given in Table 1. (Found: C, 43.98; H, 7.46. $C_{10}H_{20}OSn$ calcd.: C, 43.68; H, 7.33%.)

anti-7-Trimethyltin-endo-2-norbornanol (VI)

A chromic anhydride/pyridine complex was prepared by dissolving 1.2 g (0.012 mol) of chromium trioxide in 1 ml of water and adding this solution to 15 ml of cold pyridine. The complex was added dropwise to 1.59 g (0.0058 mol) of V in 5 ml of pyridine and stirred at room temperature for 16 h. The reaction mixture was acidified with dilute HCl and extracted with ether. The ether layer was dried over $MgSO_4$ and then added to 0.38 g (0.01 mol) of

$LiAlH_4$ in 200 ml of ether. After stirring overnight, excess hydride was destroyed with $Na_2SO_4 \cdot 10H_2O$. Water was added, and the ether layer was separated and dried over K_2CO_3. Removal of solvent gave VI, 1.0 g (63%): m.p. 58-60°; IR (CCl_4) 3625 (OH) and 1080 and 1020 cm^{-1} (C—O); NMR (CCl_4): δ 4.02 (broad multiplet, *exo*-C-2 proton), 2.24 (distorted triplet, bridgehead), 2.1-0.7 (*exo*,*endo* and bridge protons), and 0.0 ppm (singlet, trimethyltin). The mass spectrum is given in Table 1. (Found: C, 43.95; H, 7.30. $C_{10}H_{20}OSn$ calcd.: C, 43.68; H, 7.33%.)

syn-7-Trimethyltin-exo-2-norbornanol (VII) and syn-7-trimethyltin-endo-2-norbornanol (VIII)

Sodium borohydride (0.38 g, 0.01 mol) and 2.67 g (0.010 mol) of IV were taken up in 15 ml of diglyme and 2.84 g (0.020 mol) of $BF_3 \cdot Et_2O$ was added dropwise. The resulting solution was stirred at room temperature for 21 h, during which time some white precipitate formed. The excess hydride was destroyed with water and 3.5 ml of 6 *N* NaOH was added, followed by dropwise addition of 2.3 ml (0.02 mol) of 30% H_2O_2. After initial spontaneous heating had ceased, the mixture was stirred for 3 h. Ether extraction, ice-water washing, drying, and solvent removal yielded a residue that showed approximately equal amounts of VII and VIII by GLC (W-98 at 180°). Chromatography on silica using petroleum ether, mixed petroleum ether/CH_2Cl_2, and CH_2Cl_2 gave 1.83 g (64%) of VII and VIII in various fractions. Earlier CH_2Cl_2 fractions gave 0.59 g of VII: m.p. 55-57.5°; IR (CCl_4) 3620 (OH), and 1085 cm^{-1} (C—O); NMR (CCl_4): δ 3.72 (doublet), *endo* C-2 proton), 2.38 and 2.24 (distorted singlets, bridgehead), 1.6-0.7 (complex multiplet, *exo*,*endo* and bridge protons), and 0.0 ppm (singlet, trimethyltin). The mass spectrum is given in Table 1. (Found: C, 43.93; H, 7.08. $C_{10}H_{20}Sn$ calcd.: C, 43.68; H, 7.33%.)

Concentration of later CH_2Cl_2 fractions gave 0.84 g of VIII: m.p. 61.5-63°; IR (CCl_4) 3625 (OH), and 1080 and 1020 cm^{-1} (C—O); NMR (CCl_4): δ 4.03 (multiplet, *exo* C-2 proton), 2.25 (singlet, partially split into a doublet, bridgehead), 2.0-0.5 (complex multiplet, *exo*,*endo*, and bridge protons), and 0.0 ppm (singlet, trimethyltin). The mass spectrum is given in Table 1. (Found: C, 43.77; H, 7.51. $C_{10}H_{20}OSn$ calcd.: C, 43.68; H, 7.33%.)

syn-7-Trimethyltin-*endo*-2-norbornanol, VIII, could also be prepared by hydroboration-chromic oxidation. Sodium borohydride (0.57g, 0.015 mol) was stirred in 20 ml of ether with 0.1 g (0.0007 mol) of $ZnCl_2$ for 1.5 h. To this suspension was added 2.5 g (0.01 mol) of IV in 10 ml of ether. $BF_3 \cdot Et_2O$ (2.84 g, 0.020 mol) was taken up in 10 ml of ether and added dropwise to the olefin/$NaBH_4$ solution during 1 h. The reaction mixture was stirred at room temperature for 1 h more and excess hydride was destroyed by addition of water. A solution of 3.47 g (0.015 mol) of $Na_2Cr_2O_7 \cdot 2H_2O$ in 4 ml of sulfuric acid and 18 ml of water was added dropwise to the borane solution. After the initial spontaneous reflux had ceased, the reaction mixture was heated at reflux for 2 h. The ether was separated, the aqueous layer extracted once, the combined ether layers washed with water until neutral, and dried over $MgSO_4$. The solvent was removed and the carbonyl stretching frequency was measured at 1747 cm^{-1}. The residue was taken up in 20 ml of ether, added dropwise to 1.14 g (0.03 mol) of $LiAlH_4$ in 100 ml of ether, and stirred at ambient temper-

ature for 1.5 h. The excess hydride was destroyed with $Na_2SO_4 \cdot 10H_2O$. The ether layer was separated, the aqueous layer extracted once with ether, and the ether layers dried over K_2CO_3. Removal of solvent left a waxy solid, 0.46 g (17%). This was found by GLC (W-98 at 170°) and NMR to be VIII contaminated with some VII. Chromatography on silica as described previously gave pure VIII.

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