

Addition of Trimethyltin Hydride and Methylhalotin Hydrides to Norbornadiene

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The additions of trimethyl-, dimethylchloro-, dimethylbromo-, dimethyliodo-, and methylchlorotin hydrides to norbornadiene have been examined. Four isomeric products are formed in each case: norbornenes with the organotin function in the endo-5, exo-5, or syn-7 position, and nortricyclene with this function in the 3 position. The anti-7 isomer is not found and its absence is attributed to steric and torsional effects in the radical from which it would be formed. The endo-5 and syn-7 isomers, products of initial endo attack by the organotin radical, amount to nearly half of the total product. This high value appears not to be attributable in significant degree to coordination between tin atoms and double bonds either during the course of the reaction or in the products.

Free-radical additions to norbornadiene are of considerable interest because their study can reveal information about the existence of nonclassical homoallylic free radicals, about rearrangements, and about factors concerning position and stereochemistry of attack on double bonds by free radicals.¹ The existence of the homoallylic nonclassical free radical **1** (Scheme I) has been rendered highly improbable by work of Cristol, Brindell, and Reeder² on the effect of dilution on the distribution of products obtained in the addition of thiophenols to norbornadiene. More recent results are consistent with this conclusion. All of the products obtained in free-radical additions to norbornadiene can be understood in terms of the series of reactions and intermediates shown in Scheme I. Each of the six radicals can be converted into two epimeric products by atom abstraction from an appropriate donor. Thus, depending on the adding reagent, there could be formed up to four geometrical isomers of each of three structurally isomeric products, and each of the twelve could exist as a *dl* pair. Studies on substituted norbornadienes have been made by Davies^{3a} and by Prilezhaeva^{3b} and their coworkers. Which of the structural isomers are formed depends upon the substrate and addend. The stereochemistry depends upon the configuration and nature of substituents in the 7 position and upon the nature of the attacking free radical: electronic factors seem to dominate over steric factors.

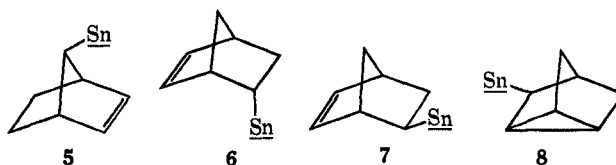
Free-radical reaction of thiols with norbornadiene itself results in formation of the 1,2 adduct and the nortricycyl isomer. Contrary to earlier reports, Van Auken and Rick⁴ have shown that both *exo*- and *endo*-5-thiolacetoxycyclo[2.2.1]hept-2-ene (in the ratio 2:1) are formed upon addition of thiolacetic acid; the only other low-molecular-weight product reported was 3-thiolacetoxynortricyclene.

As an extension of our earlier work on the norbornenyl-nortricycyl free-radical system⁵ and on the addition of trimethyltin hydride to dienes,⁶ we have examined the addition of this hydride and of methylhalotin hydrides to norbornadiene, with particular ref-

erence to the structure and stereochemistry of the products formed. The free-radical chain mechanism for the addition of organotin hydrides to olefins not substituted by strongly electron-attracting groups has been deduced^{7a,b} from evidence provided particularly by Neumann and coworkers,^{7a,c} and the initial attack by the organotin radical has been shown to be reversible.^{7c,8} Thus, kinetic control cannot be assumed to determine product distributions.

Results and Discussion

The reaction of trimethyltin hydride and norbornadiene was carried out by heating the reactants at 60° for several hours or by irradiation through Pyrex. Yields of isolated product amounted to 89–95%. Gas-liquid partition chromatography (glpc) using a column of 1,2,3-tris-2-cyanoethoxypropane on Diatoport P showed three peaks due to norborn-2-en-7-*syn*-yltrimethyltin (**5**) ($\text{Sn} = \text{Me}_3\text{Sn}$), *endo*-norborn-2-en-5-yltrimethyltin (**6**), and a mixture of *exo*-norborn-2-en-5-yltrimethyltin (**7**) and 3-nortricycyltrimethyltin (**8**), in order of increasing retention time. When glpc was carried out using a column of Apiezon L on Chromosorb W, the order of elution was **5**, then **6** plus **7**, and then **8**. Each of the products has been fully characterized by elemental analysis, spectral properties,



and chemical reactions.⁹ Each method of reaction led to the same product mixture, 11% of **5**, 35% of **6**, 43% of **7**, and 11% of **8**, and this distribution was independent of the extent of reaction, indicating no isomerization of the products under the reaction conditions.

Products **5** and **6** must be the result of initial endo attack on the diene by the trimethyltin radical, and some or all of **8** could also be. This amounts to about 50% of the total. None of the epimer of **5**, norborn-2-en-7-*anti*-yltrimethyltin, was observed. This was established by independent synthesis of both isomers

(1) See D. I. Davies and S. J. Cristol in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press, London, England, 1965, pp 155 ff.

(2) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, **80**, 635 (1958).

(3) For recent leading references, see (a) D. I. Davies and M. J. Parrott, *J. Chem. Soc. C*, 659 (1970); (b) E. N. Prilezhaeva, V. A. Asovskaya, G. U. Stepanyanz, D. Mondeshka, and R. J. Shekhtman, *Tetrahedron Lett.*, 4909 (1969).

(4) T. V. Van Auken and R. A. Rick, *ibid.*, 2709 (1968).

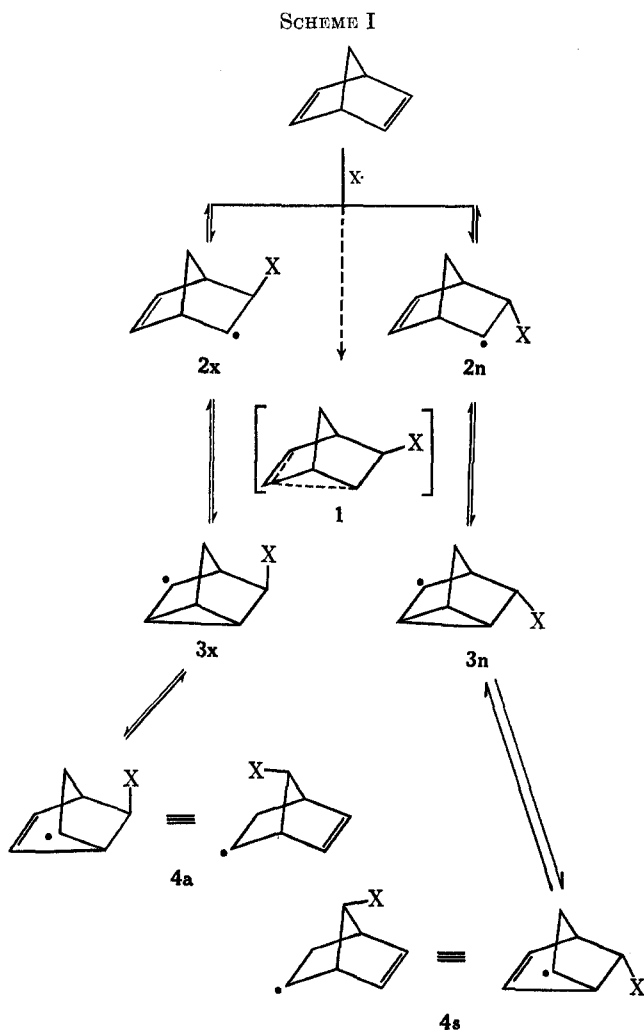
(5) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

(6) R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **89**, 5861 (1967).

(7) (a) W. P. Neumann and R. Sommer, *Justus Liebig's Ann. Chem.*, **675**, 10 (1964); (b) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964); (c) W. P. Neumann, H. J. Albert, and W. Kaiser, *Tetrahedron Lett.*, 2041 (1967).

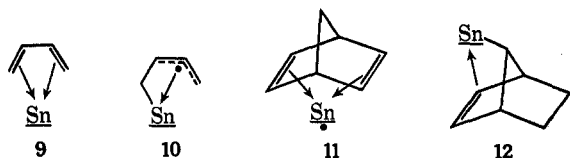
(8) H. G. Kuivila and R. Sommer, *J. Amer. Chem. Soc.*, **89**, 5616 (1961).

(9) H. G. Kuivila, J. D. Kennedy, F. L. Pelczar, and R. Y. Tien, unpublished results.



and demonstration that they have different retention times on the Apiezon L column and that their proton magnetic resonance spectra show differences in both chemical shifts and coupling patterns.

The high incidence of products from endo attack was reminiscent of the high proportion of *cis*-crotyltrimethyltin formed in the addition of trimethyltin hydride to butadiene.⁶ It was suggested that this might be due to formation of coordinated intermediates such as 9 or 10. In the present case the diene could act as a bidentate ligand as in 11. Similarly, the formation



of 5 to the exclusion of its epimer might gain impetus from coordination such as that shown in 12. If this postulate is correct, increasing the Lewis acid character of the tin should result in diversion of more of the reaction toward formation of more 5 and 6 at the expense of 7.

As one test of this postulate, we sought to determine whether proton magnetic resonance studies would provide any evidence for coordination of the type depicted in 11 with the organotin radical replaced by an organotin halide. This might alter the values of the chemical shifts of the protons of the methyl groups on the tin

or the ^{119}Sn - ^1H coupling constants, or both. The methyl proton chemical shifts of the three methyltin chlorides in 2-5% concentration were measured at 35° in carbon tetrachloride, benzene, and norbornadiene and are given in Table I. Included are four values

TABLE I

PROTON CHEMICAL SHIFTS OF METHYL TIN HALIDES^a

Solvent	Me_3SnCl	Me_2SnCl_2	MeSnCl_3
CCl_4	9.34 ^b	8.84 ^b	8.39
C_6H_6	9.78 ^b	9.66 ^b	9.70
C_7H_8	9.51	9.07	8.71

^a In τ units, at 35°; values to ± 0.01 ppm. ^b At 23°, ref 10.

at 23° measured by Okawara and coworkers, but the temperature correction¹⁰ would require our values to be increased by only about 0.03 ppm. The ^{119}Sn - ^1H coupling constants are independent of temperature in this range. [Inclusion of data for tin(IV) chloride was not possible because of its exothermic reaction with norbornadiene.¹¹] The data in Table I show that the proton resonance appears at a higher field in norbornadiene than in carbon tetrachloride and at a still higher field in benzene in which the shift is attributed to the magnetic anisotropy of the aromatic ring.¹⁰ The data of Table II show that the ^{119}Sn - ^1H coupling con-

TABLE II

 ^{119}Sn - ^1H COUPLING CONSTANTS OF METHYL TIN HALIDES^a

Solvent	Me_3SnCl	Me_2SnCl_2	MeSnCl_3
CCl_4	58.2 ^a	68.9 ^a	96.9
C_6H_6	58.9 ^a	69.3 ^a	98.7
C_7H_8	57.5	69.1	98.8

^a Values to ± 0.6 Hz.

stants are substantially the same in the three solvents, whereas specific coordination would result in a considerable difference due to a change in orbital hybridization. The ^{119}Sn - ^1H coupling constant of dimethyltin dichloride, for example, is 47-Hz greater in dimethyl sulfoxide than in carbon tetrachloride.¹⁰ This is attributed to coordination between the sulfoxide oxygen with the tin atom. Because the coupling constant for a given organotin chloride is essentially the same in each of the three solvents, we may conclude that any coordination with norbornadiene is too weak to be manifested in the proton magnetic resonance spectra.

It was of interest to ascertain whether the type of coordination depicted in 12 could be detected in the norborn-2-en-7-*syn*-ylhalodimethyltins prepared by addition of the hydrides to norbornadiene. Such structures would seem to approach an optimum condition in which the interacting groups are held rigidly in close proximity to each other. When the organotin function is in the endo-5 position, the relationship is probably less ideal, and when it is in the exo-5 position interaction cannot occur. The nmr spectra of neat mixtures of the isomers formed in the addition reactions (see below) were examined and the results are shown in Tables III and IV.

(10) G. Matsubayashi, Y. Kawasaki, T. Tanaka, and R. Okawara, *Bull. Chem. Soc. Jap.*, **40**, 1566 (1967).

(11) F. M. Rabel and R. West, *J. Amer. Chem. Soc.*, **84**, 4169 (1962).

TABLE III
CHEMICAL SHIFTS OF TIN-METHYL PROTONS OF
ADDUCTS TO NORBORNADIENE^a

	Exo-5	Nortricyclyl	Endo-5	Syn-7
Me ₃ Sn	9.940	9.952	10.024	10.032
Me ₂ SnCl	9.925	9.442	9.530	9.53 ^b
Me ₂ SnBr	9.323	9.339	9.430	9.43 ^b
Me ₂ SnI	9.198	9.208	9.302	9.30 ^b

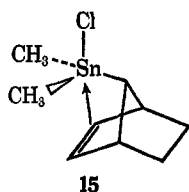
^a In τ units at 37°; relative values accurate to ± 0.003 ppm; absolute values to ± 0.01 ppm. ^b Signals indistinguishable from those due to the *endo*-5 isomer.

TABLE IV
¹¹⁹SN-¹H COUPLING CONSTANTS OF
NORBORNADIENE-ORGANOTIN HYDRIDE ADDUCTS^a

	Exo-5	Nortricyclyl	Endo-5	Syn-7
Me ₃ Sn	49.5	50.65	50.2	51.1
Me ₂ SnCl	53.1	53.65	53.6	55.4
Me ₂ SnBr	52.3	52.8	52.8	54.55
Me ₂ SnI	51.15	51.75	52.0	53.5

^a Values to ± 0.2 Hz.

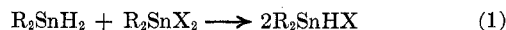
The differences among the chemical shifts of the Sn-methyl protons shown in Table III are small and probably reflect effects due to the position of these protons relative to the double bond. It is noted that the *endo*-5 and *syn*-7 methyl protons are slightly shielded in comparison with those of the *nortricyclyl* and *exo*-5 isomers. Somewhat larger variations result as the halogen is changed. In each isomer a downfield shift of the methyl protons occurs in the order Cl < Br < I. The ¹¹⁹Sn-¹H coupling constants show small, but real, variations. In particular, the values for the *syn*-7 isomer are larger than those for either the *endo*-5 or the *exo*-5 isomer, and the difference is greater for the dimethylhalotin derivatives than for the trimethyltin derivative. If coordination occurs between the double bond and the tin atom as indicated in **12**, the configuration would tend toward that shown in **15**



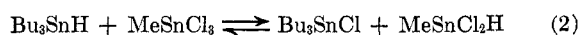
which approaches a trigonal bipyramidal configuration about the tin atom with the chlorine and double bond in the apical positions. In this structure the hybridization of the orbital on the tin atom through which it is attached to the methyl groups would tend from the original *sp*³ toward *sp*². This increase in *s* character would lead to an increase in the coupling constant, as observed.¹² However, the changes in coupling constants are so small that it must be concluded that the interaction in question is very weak, at best.

Another test of the coordination postulate could be made by increasing the Lewis character of the tin atom used in the hydride addition. If it is valid, the result should be an increase in the proportions of adducts **5** and **6** at the expense of **7**. This was done by examining the addition of methylhalotin hydrides to norbornadiene.

Sawyer and Kuivila¹³ showed that dialkylhalotin hydrides can be easily prepared by mixing dialkyltin dihydride and dialkyltin dihalide (eq 1), and Neumann



and Pedain¹⁴ showed that they add readily to unsaturated hydrocarbons. Dimethylchlorotin hydride and norbornadiene reacted readily to provide a 94% yield of the isomeric adducts. The bromide and iodide were more reactive than the chlorohydride. The corresponding fluoro compound could not be prepared, presumably because of the extremely low solubility of dimethyltin difluoride. Methylchlorotin hydride did not give good yields of adduct by the same procedure. This was undoubtedly due to complications in the addition reaction rather than in the exchange reaction of eq 2, for treatment of the reaction product



mixture with methylmagnesium bromide gave about 90% of tributylmethyltin and only about 25% of the methylated hydride adducts.

Results obtained in the addition of these organohalotin hydrides and of trimethyltin hydride to norbornadiene are gathered in Table V. Clearly the product distribution is not affected profoundly by the replacement of methyl on the organotin hydride by halogen. However, the proportion of *endo*-5 isomer plus *syn*-7 isomer increases as methyls of trimethyltin hydride are replaced by one and two chlorines from 46 to 51 and 55%, respectively. As methyl is replaced by chlorine, bromine, and iodine, the proportion goes from 46 to 51 to 49 to 46%, respectively. Thus, there appears to be a small, but real, effect of increased electronegativity of the tin atom in increasing the proportion or products resulting from initial *endo* attack by the organotin radical. This is then counterbalanced by the steric effect as the size of the halogen atom is increased from chlorine to bromine to iodine.

The proportion of the *syn*-7 isomer shows no discernible trend as the nature of the hydride used is changed. As the dimethylhalotin hydrides produce less of this isomer than does trimethyltin hydride, involvement of the type of coordination depicted in **12** can be eliminated as the primary driving force for the formation of this isomer.

The absence of any *anti*-7 isomer in the product mixture is striking and requires explanation. Certainly initial *exo* attack by the trimethyltin radical, a primary requisite, is met as evidenced by the large amount of *exo*-5 adduct formed. Thus, radical **4a** is either not formed or does not go on to product by abstracting hydrogen from organotin hydride. The latter possibility appears to be the more likely one. There is good evidence that *exo* attack on radicals such as **4a** and **4s** is more facile than *endo* attack.¹⁵ This is so because the hydrogen on the radical carbon (C-6) must pass through a conformation in which it is eclipsed with the hydrogen on the bridgehead carbon (C-1) if the attack is *endo* but not if the attack is *exo* (Scheme II). The nearer these hydrogens are to

(13) A. K. Sawyer and H. G. Kuivila, *Chem. Ind. (London)*, 260 (1961).

(14) W. P. Neumann and J. Pedain, *Tetrahedron Lett.*, 2461 (1964).

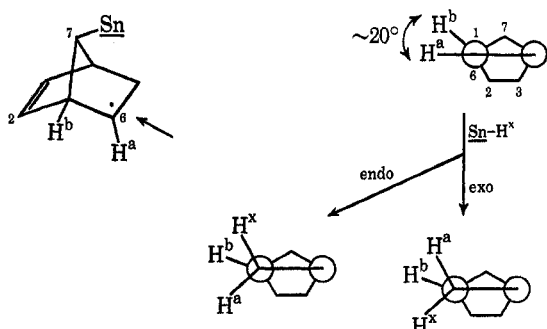
(15) For a recent review, see P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Hegelson, *Accounts Chem. Res.*, **3**, 177 (1970).

(12) J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

TABLE V
 YIELDS AND PRODUCT DISTRIBUTIONS IN THE ADDITION OF THE METHYLTIN HYDRIDES TO NORBORNADIENE

Hydride	Yield, %	Product distribution, %			
		Exo-5	Endo-5	Tricyclo	Syn-7
Me ₃ Sn	95	43 ± 1	35 ± 1	11 ± 1	11 ± 1
Me ₂ SnCl	94	41 ± 1.5	42.5 ± 1.5	8.0 ± 0.5	8.4 ± 0.5
Me ₂ SnBr	91	43 ± 1.5	38 ± 1.5	8.0 ± 0.5	10.8 ± 0.5
Me ₂ SnI	80 ^a	46 ± 1.5	42 ± 1.5	8.2 ± 0.5	3.8 ± 0.5
	81 ^b	48.5 ± 1.5	36.5 ± 1.5	7.5 ± 0.5	7.7 ± 0.5
MeSnCl ₂	24 ^c	32.5 ± 2.0	43.5 ± 2.0	12.7 ± 0.5	11.5 ± 1.0

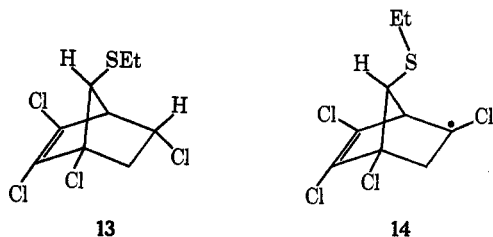
^a Norbornadiene added to iodohydride. ^b Reverse order of addition. ^c Yield of methylated product. Dichloride adduct not isolated.

 SCHEME II
 HYDROGEN TRANSFER TO C-6 OF NORBORNENYL RADICAL^a


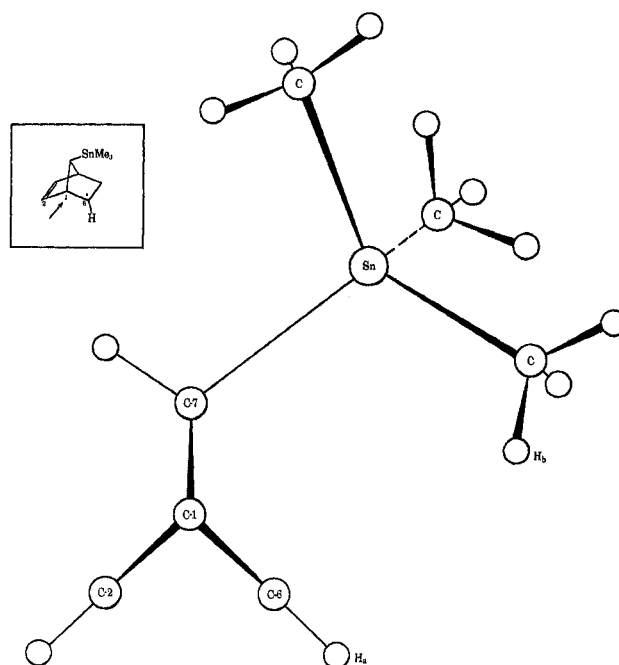
^a In endo attack the dihedral angle of ca. 20° must pass through zero, whereas for exo attack it increases from 20°.

this eclipsed conformation in the transition state the greater is this torsional strain, which can amount to about 1 kcal.¹⁶ A projection of a Dreiding model of **4a** is shown in Chart I. It is evident that the trimethyltin group forms a canopy over C-6 (as well as C-5) such that exo attack at C-6 is impossible. The model indicates that the closest point of approach of H_a and H_b to each other is less than 2 Å; the sum of the van der Waals radii is 2.4 Å! Furthermore, these nonbonded interactions are greater than those between the trimethyltin hydrogens and the nearest C-7 hydrogen in **2x**. Thus, the equilibrium **2x** ⇌ **3x** ⇌ **4a**, is shifted to the left. If the trimethyltin group is placed anti to C-6, forming **4s**, exo attack on the radical is not hindered. Also, nonbonded interactions involving the trimethyltin hydrogens are negligible in both **2n** and **4s** and should have little effect on the **2n** ⇌ **3n** ⇌ **4s** equilibrium. It may be concluded that the steric bulk of the trimethyltin group prevents the formation of the anti-7 isomer by virtue of the steric strain it introduces into the precursor radical and by steric blocking of hydrogen transfer from the exo side to C-6 of that radical.

Rearranged adducts of the anti-7 configuration have been obtained in other additions to norbornadienes. For example, 1,2,3,4-tetrachloronorbornadiene gives the exo and endo 1,2 adducts along with **13**, whose radical



(16) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967).

 CHART I
 END VIEW OF THE INTERMEDIATE
 NORBORN-2-EN-6-YL RADICAL^a


^a The radical shows the "canopy" effect of the trimethyltin group. Bond angles are not precise.

precursor must be **14**.¹⁷ However, in this case the ethyl group can be rotated into conformations such as that shown, thus minimizing the steric obstruction to hydrogen atom transfer from the exo side.

Experimental Section

General.—Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer. Spectra were run on neat samples with tetramethylsilane as internal standard. Chemical shifts are recorded in τ values. Analyses were performed by Galbraith Laboratories. All operations involving organotin hydrides were conducted under nitrogen or argon.

Materials.—Dimethyltin dichloride, dimethyltin diiodide, dimethyltin difluoride, dimethyltin dibromide, and methyltin trichloride, bp 172–175°, mp 45°, were prepared and purified by standard procedures.

Trimethyltin hydride was prepared as previously described.⁶ Tributyltin hydride was obtained by the reaction of tributyltin oxide with polymethylhydrosiloxane.¹⁸ Dimethyltin dihydride, bp 36°, was made by an exchange reaction between tributyltin hydride and dimethyltin dichloride. Tri-*n*-butyltin hydride (33 g, 113 mmol) was added to 10 g (45 mmol) of dimethyltin dichloride in a flask equipped with a magnetic stirrer and a glass

(17) D. I. Davies and P. J. Rowley, *J. Chem. Soc. C*, 2249 (1967).

(18) K. Hayashi, J. Iyoda, and I. Shiihara, *J. Organometal. Chem.*, **10**, 81 (1967).

connection to a receiving vessel cooled to -70° . Pressure in the system was reduced slowly (compatible with the smooth evolution of the volatile dihydride) to 20 mm. The reaction vessel was then heated to ca. 60° for 15 min. The collected liquid was redistilled at atmospheric pressure, yielding dimethyltin dihydride, bp $36-37^{\circ}$ (6.0 g, 88%). All processes were carried out under nitrogen. Norbornadiene was redistilled and stored in a refrigerator.

Addition of Trimethyltin Hydride to Norbornadiene. A.—To 46 g (0.5 mol) of freshly distilled bicycloheptadiene heated to 60° in an argon atmosphere was added 83 g (0.50 mol) of trimethyltin hydride over 1 hr. Heating was continued for an additional 3 hr. Distillation afforded a product (115 g, 95%), bp 40° (0.1 mm). Gas-liquid chromatography on a 15 ft \times 0.25 in. column of 1,2,3-tris-2-cyanoethoxypropane on 60–80 mesh Diatoport showed three peaks with relative areas 11% (compound 5), 36% (compound 6), and 53% (compounds 7 and 8). Glpc on an Apiezon L column changed the order of elution to 5, then 6 plus 7, and then 8.

Anal. Calcd for $C_{10}H_{18}Sn$: C, 46.75; H, 7.01; Sn, 46.24. Found for mixture: 46.47; H, 6.95; Sn, 46.50. Found for 5: C, 46.51; H, 6.94; Sn, 46.47. Found for 6: C, 46.55; H, 6.96; Sn, 46.50; Found for 7 plus 8: C, 46.58; H, 6.97; Sn, 46.43.

B.—A mixture of 5 g (52 mmol) of norbornadiene and 8.3 g (50 mmol) of trimethyltin hydride at 0° was irradiated in a Pyrex tube with a mercury vapor lamp for 6 hr. Distillation yielded 11.3 g (89%) of product with composition identical with that obtained in the thermal reaction as shown by glpc.¹⁹

Reaction of Dimethylchlorotin Hydride with Norbornadiene.—Dimethyltin dihydride (6.0 g, 40 mmol) was added to dimethyltin dichloride (8.3 g, 38 mmol) at -70° . A clear homogenous colorless liquid was produced on warming to room temperature and shaking. This was cooled to -70° and norbornadiene (9.0 ml, 108 mmol) was added; this was warmed to room temperature; shaking gave a clear colorless liquid. After 1 min, the evolution of heat was noted. The vessel was cooled from time to time in a bath at 0° . When the spontaneous reaction had ceased, the product was heated at 60° for 30 min and then distilled, yielding a mixture of dimethylnorbornenyltin chloride isomers, bp $68-70^{\circ}$ (0.10 mm) (15.2 g, 94%), as a clear colorless liquid. *Anal.* Calcd for $C_9H_{16}ClSn$: C, 39.0; H, 5.4; Cl, 12.8. Found: C, 39.2; H, 5.4; Cl, 12.8.

Reaction of Dimethylbromotin Hydride with Norbornadiene.—Dimethyltin dihydride (4.2 g, 27.8 mmol) was added to dimethyltin dibromide (8.6 g, 27.8 mmol) at -70° . A homogenous clear colorless liquid was produced on warming to room temperature and shaking (mp $>0^{\circ}$). This was cooled to -70° , and norbornadiene (6.0 ml, 72 mmol) was added. On warming, a vigorous exothermal reaction commenced before complete dissolution of the bromotin hydride had occurred; this was moderated by plunging the vessel into a bath at -70° . The mixture was again allowed to warm and was further moderated by cooling in a bath at 0° . When the spontaneous reaction had ceased, the product was heated at 65° for 40 min and then distilled, yielding a mixture of dimethylnorbornenyltin bromide isomers, bp $75-76^{\circ}$ (0.30 mm) (16.3 g, 91%), as a clear colorless liquid.

Anal. Calcd for $C_9H_{16}BrSn$: C, 33.6; H, 4.66; Br, 24.8. Found: C, 33.7; H, 4.66; Br, 24.82.

Reaction of Dimethyliodotin Hydride with Norbornadiene. A.—Dimethyltin dihydride (4.3 g, 28.5 mmol) was added to dimethyltin diiodide (11.5 g, 28.6 mmol) at -70° . The mixture was warmed to room temperature and shaken, yielding a clear colorless liquid (mp 0°). To this was added slowly, with shaking and cooling in a bath at 0° , norbornadiene (7.0 ml, 68.5 mmol). The reaction was very exothermic, and slight effervescence occurred. The product was heated for 60 min at 65° , yielding a colorless liquid containing a small amount of white solid. Distillation under reduced pressure gave a forerun of dimethyltin diiodide and one main fraction, bp $78-80^{\circ}$ (0.30 mm), a mixture of dimethylnorbornenyltin iodide isomers (16.9 g, 80%). A dark gray residue remained in the distillation flask.

B.—Dimethyltin dihydride (5.6 g, 37.1 mmol) and benzene (25 ml) were added to dimethyltin diiodide (14.9 g, 37.0 mmol) at -70° . The mixture was allowed to warm with shaking. As soon as a homogenous solution was formed (estimated temperature $6-10^{\circ}$), it was added to a cold solution of benzene (20 ml)

and norbornadiene (8.0 ml, 79.0 mmol). No immediate reaction occurred. On warming of the mixture, the rate of temperature increase increased with temperature; this was maintained at $28-32^{\circ}$ by cooling in a bath at 0° . When the spontaneous reaction had ceased (10 min), the solution was refluxed for 20 min leaving a clear colorless solution. Removal of the benzene and distillation as above gave a mixture of the dimethylnorbornenyltin iodide isomers, bp $76-78^{\circ}$ (0.18 mm), together with a small amount of dimethyltin diiodide. The yield was 22.1 g (81%). An off-white residue remained in the flask.

Anal. Calcd for $C_9H_{16}ISn$: C, 29.4; H, 4.1; I, 34.4. Found for sample C: 29.1; H, 3.95; I, 34.2.

Attempted Reaction between Dimethyltin Difluoride, Dimethyltin Dihydride, and Norbornadiene.—Dimethyltin dihydride (5.3 g, 35.1 mmol) was added to dimethyltin difluoride (6.5 g, 34.9 mmol) and stirred, and norbornadiene (12 ml, 118 mmol) added. The suspension was stirred for 12 hr at room temperature and then for 12 hr at $60-70^{\circ}$; at this stage the infrared spectrum showed ν_{max} 1820 cm^{-1} (ν_{SnH}). The product was distilled at 100° (bath) yielding no dimethyltin dihydride, excess norbornadiene [bp $70-75^{\circ}$ (ca. 400 mm)], and no further products, even after 1 hr at 0.10 mm. Tetrahydrofuran (20 ml) was added to the residual suspension, and a solution of methyl Grignard reagent, from methyl iodide (11.5 g, 81 mmol) and magnesium (1.8 g, 75 mg-atoms) in ether (35 ml), was slowly added dropwise with stirring. After refluxing for 6 hr the mixture hydrolyzed. Distillation gave no tetramethyltin and no products of the volatility expected for trimethylnorbornenyltin or dimethylnorbornenyltin or dimethylnorbornenyltin hydride. Only one product fraction, identified as a mixture of dimethylbis(norbornenyl)tin isomers, bp $87-89^{\circ}$ (0.15 mm), was obtained (8.4 g, 72%).

Anal. Calcd for $C_{16}H_{24}Sn$: C, 57.4; H, 7.17. Found: C, 57.2; H, 7.24.

Reaction between Tributyltin Hydride, Methyltin Dichloride, and Norbornadiene.—A freshly prepared mixture of tributyltin hydride (10.90 g, 37.4 mmol) and norbornadiene (3.50 g, 38.1 mmol) was added, dropwise with stirring, to a solution of methyltin trichloride (9.0 g, 37.5 mmol) in ether (30 ml). A very exothermic reaction occurred. The vessel was cooled in a bath at 20° and the addition performed at such a rate as to maintain a gentle rate of reflux. After completion of the addition, the resulting white suspension was refluxed for 30 min. Ether (20 ml) was added and to the still refluxing suspension was added a solution of methyl Grignard reagent from methyl iodide (19 g, 134 mmol) and magnesium (3.0 g, 125 mg-atoms) in ether (35 ml) slowly with stirring. Refluxing was continued for 40 min. Work-up and distillation under reduced pressure gave a mixture of trimethylnorbornenyltin isomers, bp $42-46^{\circ}$ (0.6 mm) (2.3 g, 24%), and tributylmethyltin, bp $73-74^{\circ}$ (0.6 mm) (10.2 g, 89%). The product ratio of the trimethylnorbornenyltin mixture was determined as described below.

Determination of the Product Ratios Resulting from the Addition of Dimethylhalotin Hydrides and Methylchlorotin Hydride to Norbornadiene.—Attempted glpc analysis of dimethylnorbornenyltin halide isomer mixtures on UCW 98, Apiezon L, and diethylene glycol succinate columns resulted in only qualitative separation. The proton magnetic resonance spectra, however, exhibited sufficient resolution for the \underline{Sn} methyl protons so that, for all the dimethylnorbornenyltin halides, the ratio (exo-5 + tricyclo):(endo-5 + syn-7) could be determined with a maximum error estimated at $\pm 1.5\%$. The smaller separation between the \underline{Sn} methyl proton resonances of the trimethylnorbornenyltin isomers resulted in a slightly greater uncertainty ($\pm 2\%$) in the measurement of the same ratio for the methylated isomers of the methyltin dihalide dihalide adducts. The amounts of tricyclo- and syn-7 isomers present in the dimethylnorbornenyltin halide mixtures were estimated by exhaustive methylation followed by glpc analysis of the resulting trimethylnorbornenyltin isomer mixture. A 6 ft \times $\frac{1}{8}$ in. 10% Apiezon L column gave sufficient resolution for the ratio of syn-7:(exo-5 + endo-5):tricyclo isomers to be determined with a maximum error estimated at $\pm 0.5\%$; optimum results were obtained using Helium carrier gas, 30 lb/in.² inlet pressure, isothermal 140° , and a sample of 0.1 μ l. From these pmr and glpc results the product ratios given in Table I were calculated.

That the results thus obtained reflect the isomer ratios of the original hydride addition is supported by the following. (a) Nmr monitoring of the reactions at all stages from just after the initial addition of the hydride to the distillation of the methylated

(19) Details on structural proofs, properties, and alternate syntheses will be submitted.

TABLE VI
SUMMARY OF REACTANT RATIOS AND YIELDS FOR THE METHYLATIONS OF DIMETHYLNORBORNENYL TIN HALIDES BY GRIGNARD REAGENT. THE PRODUCT IS TRIMETHYLNORBORNENYL TIN. WEIGHTS ARE IN GRAMS

X in C ₉ H ₁₆ SnX	Halide		Magnesium		Methyl iodide		Product	
	Wt (g)	mmoles	Wt (g)	mg-atoms	Wt (g)	mmoles	Wt (g)	% yield
Cl	9.8	36	1.00	41.1	6.0	42.3	7.7	86 ^a
Br	9.0	28	0.75	30.6	5.0	35.2	6.3	88
I	10.0	27	0.75	30.6	5.0	35.2	6.1	88 (A)
							6.3	91 (B)

^a Some product lost due to sudden foaming during vacuum distillation; maximum pure yield must be a few per cent greater than this.

product showed that the ratio of (exo-5 + tricyclo):(endo-5 + syn-7) was constant. (b) The first and last cuts of a distillation of a dimethylnorbornenyln tin halide mixture showed a similarly constant ratio. (c) An excess of Grignard reagent was used for each methylation, and completeness of methylation was verified by glpc analysis. Furthermore, all methylation yields were excellent. (d) The first and last cuts of a distillation of a trimethylnorbornenyln tin mixture showed identical isomer ratios. (e) Treatment of a sample of a dimethylnorbornenyln tin bromide isomer mixture with a deficiency of a methyl Grignard reagent showed no preferential reaction of the isomers under the conditions used for the complete methylation.

Methylation of Dimethylnorbornenyln Tin Halides.—The procedure for each of the halides was identical. That for the bromide is described here; the other reactions are summarized in Table VI. Methyl iodide (5.0 g, 35.2 mmol) in ether (20 ml) was added to magnesium (0.75 g, 30.6 mg-atoms); the mixture was refluxed briefly to allow complete dissolution of the metal. A sample of the dimethylnorbornenyln tin bromide mixture (9.00 g, 28.0 mmol) in ether (20 ml) was added dropwise with stirring to the refluxing solution. A mildly exothermic reaction occurred. The solution was refluxed further for 40 min, cooled, and poured onto a mixture of sulfuric acid (1.5 ml) and crushed ice (50 g). The ethereal layer was separated, washed with 10% aqueous sulfuric acid (two 10-ml portions) and water (two 15-ml portions), dried over calcium chloride, and distilled, yielding ether and a methylation product, bp 42–48° (0.6 mm), as a clear colorless liquid (6.3 g, 88%).

Reaction of Dimethylnorbornenyln Tin Bromide with Deficiency of Methyl Grignard.—Magnesium (0.397 g, 16.5 mg-atoms) in ether (5 ml) was dissolved in methyl iodide (2.7 g, 19.0 mmol) in ether-

al solution (15 ml), using the normal Grignard technique, and then added dropwise with stirring to a gently refluxing solution of dimethylnorbornenyln tin bromide (10.1 g, 31.4 mmol). Refluxing was continued for 30 min; the mixture was cooled and shaken with 2% aqueous hydrobromic acid (100 ml). The aqueous layer was extracted with ether (two 25-ml portions). The combined ethereal extracts were washed with water (two 25-ml portions), dried over calcium chloride, and distilled, yielding ether, trimethylnorbornenyln tin, bp 38–40° (0.5 mm) (3.2 g, 40%), and dimethylnorbornenyln tin bromide, bp 77–79° (0.5 mm) (4.5 g, 44%). Nmr analysis of the original and final bromide mixtures and of the trimethyl tin mixture showed that in each case the ratio (exo-5 + tricyclo):(endo-5 + syn-7) fell within the limits 51 ± 2.0:49 ± 2.0.

Registry No.—Trimethyl tin hydride, 1631-73-8; norbornadiene, 121-46-0; dimethylchlorotin hydride, 16561-41-4; dimethylbromotin hydride, 16561-23-2; dimethyliodotin hydride, 16561-40-3.

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Halogenation with Copper(II) Halides. The Synthesis of Chloroiodoalkanes

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Vicinal chloroiodoalkanes have been synthesized by a simple, single-step reaction of olefins with copper(II) chloride and iodine or an iodine donor. The reaction is capable of application to substituted and unsubstituted olefins. Conjugated diolefins yield dichlorides *via* halide exchange reactions with initially formed chloroiodides.

The addition of halogens and of halogen derivatives to olefinic unsaturation has been the topic of substantial synthetic and mechanistic investigation.¹ While the interhalogen compounds, iodine and bromine monochloride, have been included in these studies as diagnostic tools for reaction mechanism, these reagents have been largely unexploited for synthetic purposes. The lack of simple and efficient syntheses for chloroiodoalkanes is particularly curious in view of the desirable agricultural² and chemical properties³ exhibited by these organic halides.

(1) H. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Wiley, New York, N. Y., 1964, pp 1563-1579.

(2) (a) H. Johnston, U. S. Patent 2,808,444 (1957); (b) G. O. Turner, U. S. Patent 2,875,118 (1959).

(3) For example, the energy difference between the carbon-chlorine and the carbon-iodine bonds in 1-chloro-2-iodoethane permits its selective pyrolysis to vinyl chloride and iodine.⁴

Chloroiodoalkanes have not generally been prepared by the addition of preformed iodine monochloride to olefins. This is due to two factors: one is the necessity of preparing the reagent from the elemental halogens;⁵ the other is the dissociable nature of the compound which frequently leads to high yields of unstable diiodides along with small amounts of desired product.⁶⁻⁸ Attempts to generate chloroiodoalkanes through the addition of hydrogen iodide to olefinic chlorides have also been only partially successful owing

(4) (a) E. T. Butler, E. Mandel, and M. Polanyi, *Trans. Faraday Soc.*, **41**, 298 (1945); (b) D. M. Fenton, U. S. Patent 3,206,517 (1965).

(5) L. F. Fieser and M. F. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 502.

(6) M. Simpson, *Justus Liebig's Ann. Chem.*, **125**, 101 (1863); **127**, 372 (1863).

(7) V. Voorhees and G. S. Skinner, *J. Amer. Chem. Soc.*, **47**, 1124 (1925).

(8) A. W. Francis, *ibid.*, **47**, 2340 (1925).