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A. Nickon,\* J. J. Frank, D. F. Covey, Y-i Lin

Department of Chemistry, The Johns Hopkins University  
Baltimore, Maryland 21218

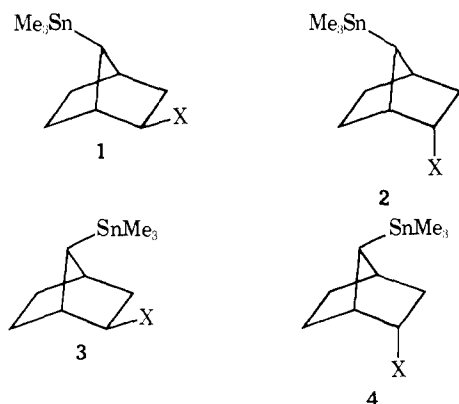
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### Stereospecific Cyclopropane-Ring Formation by 1,3-Deoxymetalation of Trimethyltin-Substituted Norbornyl Mesylates

Sir:

$\gamma$ -Trimethyltin-substituted alcohols and sulfonates have been shown to undergo facile cyclopropane ring-forming reactions.<sup>1</sup> A study of the stereoelectronic effects in the reaction of conformationally rigid 7-(2-mesyloxynorbornyl)trimethyltins has provided some interesting insights into the mechanism of this reaction.

The four epimeric *syn*- and *anti*-7-(2-hydroxynorbor-



a, X = OH  
b, X = OSO<sub>2</sub>CH<sub>3</sub>

Table I. Acetolysis<sup>a</sup> of 7-(2-Mesyloxynorbornyl)trimethyltins

Compound	$k$ , sec <sup>-1</sup> (25.0°) <sup>b</sup>	$k_{rel}$	$k_{exo}/k_{endo}$	$\Delta H^*$ , kcal/mol	$\Delta S^*$ , eu
<b>1b</b>	$(3.37 \pm 0.21) \times 10^{-4}$	5.5	2.6	20.2	-6.7
<b>3b</b>	$(1.18 \pm 0.05) \times 10^{-3}$	19	2960		
<b>5b</b>	$(6.09 \pm 0.28) \times 10^{-5}$	1.0	495	20.5	-8.9
<b>2b</b>	$1.30 \times 10^{-4}$ <sup>c</sup>	(1050)		16.2	-21.9
<b>4b</b>	$3.98 \times 10^{-7}$ <sup>c</sup>	(3.2)		23.5	-8.3
<b>6b</b>	$1.23 \times 10^{-7}$ <sup>c</sup>	(1.0)		25.5	-4.6

<sup>a</sup> Conductometric rates in HOAc (0.5 M H<sub>2</sub>O). <sup>b</sup> Determined by least-squares computer fit. Error values are for the mean of at least three kinetic runs. <sup>c</sup> Extrapolated from higher temperatures by means of the Eyring equation,  $k_{obs}$ , 75°,  $(7.64 \pm 0.34) \times 10^{-3}$ ,  $(1.34 \pm 0.02) \times 10^{-4}$ ,  $(6.80 \pm 0.09) \times 10^{-5}$  sec<sup>-1</sup>, respectively.

nyl)trimethyltins were synthesized from the corresponding 7-norbornenyltrimethyltins.<sup>2</sup>

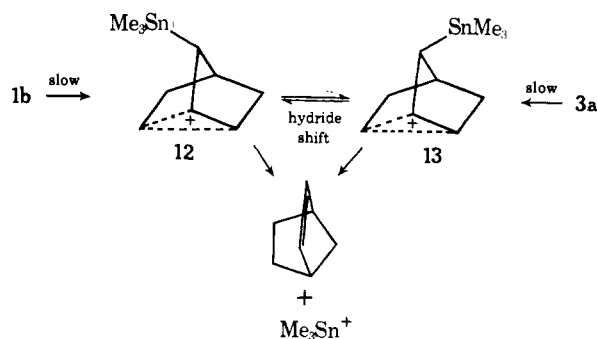
Hydroboration-oxidation of *anti*-7-norbornenyltrimethyltin yields **1a** while **2a** is obtained by chromic oxidation-hydrate reduction of **1a**. Hydroboration-oxidation<sup>3a</sup> of *syn*-7-norbornenyltrimethyltin gives a 55/45 mixture of **3a** and **4a** easily separable by chromatography on silica gel. Stereochemical assignments, discussed in detail elsewhere,<sup>3b</sup> are made on the basis of chemical evidence, nmr spectra, including lanthanide shift reagent studies, and mass spectral fragmentation patterns. Mesylates of the alcohols were prepared in the standard manner<sup>4</sup> and solvolyzed in acetic acid containing 0.5 M water. Rate data for **1b-4b** and the parent *exo*- and *endo*-2-norbornyl mesylates, (**5b**, **6b**, respectively) are given in Table I.

Substitution of the inductively donating Me<sub>3</sub>Sn group ( $\sigma_1 = -0.05$ )<sup>5</sup> gives rise to a modest rate enhancement and an exalted *exo/endo* ratio for the **3b-4b** pair, consistent with data for other 7-substituted norbornyl sulfonates.<sup>6</sup> However, the *anti-endo* isomer, **2b**, solvolyses with a greatly accelerated rate resulting in an *exo/endo* ratio which is the smallest reported value that we are aware of for pairs in which the *exo* isomer is not retarded.<sup>6</sup>

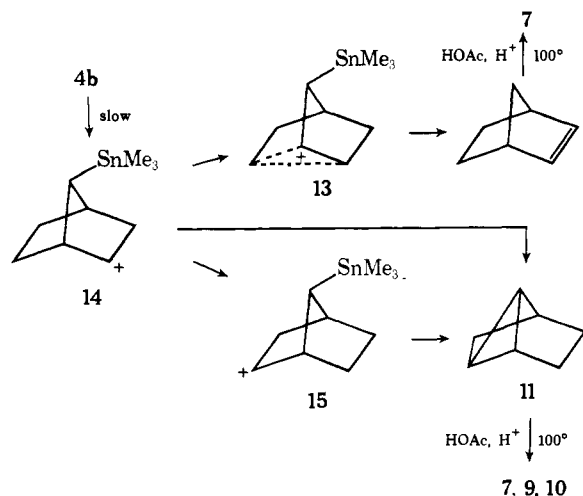
These reactions are unusual in the sense that no products are observed which still retain the Me<sub>3</sub>Sn group. **1b** and **3b** give only norbornene and Me<sub>3</sub>SnOAc at 25°. The *syn-endo* isomer **4b** yields a mixture (100%) composed of 65% *exo*-2-norbornyl acetate (**7**), 3.4% *exo*-2-norbornanol (**8**), 16% *endo*-2-norbornyl acetate (**9**), 16% 7-norbornyl acetate (**10**), and an equivalent of Me<sub>3</sub>SnOAc. For comparison, *exo*-2-norbornyl mesylate (**5b**) gives (25°) 94.5% **7**, 4.2% **8**, and 1.3% nortricyclene, whereas only **7** was observed from the solvolysis of **6b** at 100°. Because of the rate acceleration, it was possible to determine the products from reaction of **2b** at 25°. In addition to 22% **7**, 14% **9**, and 13% **10**, a 50% yield of tricyclo[3.2.0.0.2<sup>7</sup>]heptane (pseudonortricyclene) **11**, was obtained. In buffered (NaOAc) HOAc at 25°, **11** and Me<sub>3</sub>SnOAc are the sole products. The identity of **11** was verified by spectral and chromatographic comparisons with material prepared here and in other laboratories.<sup>7</sup> Control experiments show **11** to be stable in HOAc at 25° but the addition of methanesulfonic acid results in a slow (15 hr) protolytic cleavage to yield nearly equal amounts of the norbornyl acetates, **7**, **9**, and **10**. The 1:1 ratio of **9** and **10** which also occurs in the product distribution for **4b** is suggestive of **11** as an initial product which is subsequently destroyed under the more rigorous conditions (100°, unbuffered). Norbornene and nortricyclene are determined as such at 25° but primarily as **7** in unbuffered systems at 100°.

That both *exo* isomers, **1b** and **3b**, produce only norbornene with a small rate acceleration relative to the unsubstituted norbornyl mesylate supports a scheme in which solvol-

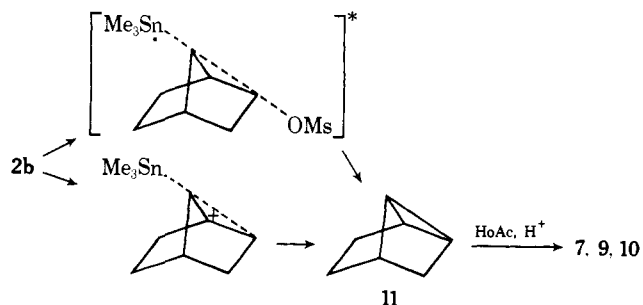
ysis occurs to yield a 7-Me<sub>3</sub>Sn-substituted-2-norbornyl cation which undergoes a rapid 1,2-deoxystannylation reac-



tion.<sup>8</sup> Similarly **4b** gives rise to an acetate mixture derived from norbornene and pseudonortricyclene. Absence of a significant rate effect argues that the Me<sub>3</sub>Sn group is not involved in the rate determining step, the products resulting from subsequent competitive 1,2- and 1,3-deoxystannylation reactions. 1,3-Elimination from the endo cation, **14**, can occur with retention at the carbon-tin bond or, maintaining a preference for the *W* configuration, *vide infra*, from **15** concerted with or following a 6,2-hydride shift.



The 1000-fold rate acceleration shown by **2b** and the exclusive formation of **11** indicates a strong preference for double inversion, limiting structures for possible intermediates and transition states to those differing little from the *W* configuration.<sup>9</sup> This percaudal interaction may provide homoconjugative stabilization<sup>10-13</sup> if carbocationic intermediates are involved or may represent the bond making interaction in the transition state for a concerted 1,3-elimination.<sup>14</sup>



Further work on the question of concerted 1,3-eliminations and/or metal stabilized cations in these 1,3-deoxymetalation reactions is continuing.

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Dennis D. Davis,\* Harry T. Johnson

Department of Chemistry, New Mexico State University  
Las Cruces, New Mexico 88003

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## Mechanism of Reductive Elimination. I. Dinuclear Elimination of Hydrogen from *cis*-Dihydridotetracarbonylosmium

Sir:

Attention has recently been called<sup>1</sup> to the possible importance of dinuclear elimination as a reaction mode in organo transition metal chemistry. We wish to report evidence for, and details of the mechanism of, the dinuclear elimination of hydrogen from the *cis* dihydride H<sub>2</sub>Os(CO)<sub>4</sub>.<sup>2</sup>

Our attention was drawn to this compound by the high stability of both it and Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> in comparison with Os(CO)<sub>4</sub>(H)CH<sub>3</sub>.<sup>3,4</sup> (The dihydride begins to decompose rapidly only at 125°, the dimethyl compound decomposes slowly even at 165°, while Os(CO)<sub>4</sub>(H)CH<sub>3</sub> decomposes rapidly at 40°.) Clearly all three compounds cannot decompose by the same mechanism. Dinuclear elimination seemed likely to be occurring in one or more cases. We selected the simplest member of the series, the dihydride, for initial examination.

Under all conditions investigated the primary product of the thermal decomposition of H<sub>2</sub>Os(CO)<sub>4</sub> was H<sub>2</sub>Os<sub>2</sub>(CO)<sub>8</sub>, originally synthesized by Moss and Graham and believed to have two terminal hydrides *cis* to an Os-Os bond.<sup>5</sup> Other products, Os<sub>3</sub>(CO)<sub>12</sub>, H<sub>4</sub>Os<sub>4</sub>(CO)<sub>12</sub>,<sup>6-8</sup> and other polynuclear hydridocarbonyls, appear subsequently. The observation that they are produced upon heating H<sub>2</sub>Os<sub>2</sub>(CO)<sub>8</sub> confirms that they are indeed secondary products.<sup>9</sup>

Of course the dimeric nature of the primary product does