Carbon–tin σ-bond participation in solvolysis: a pronounced ε-effect in 5-mesyloxycyclooctyltrimethylstannanes

Bruce H. Riches and William Kitching*

Department of Chemistry, University of Queensland, Brisbane, Australia 4072

***cis*-5-Mesyloxycyclooctyltrimethylstannane solvolyses in 80% ethanol–20% water *ca.* 800 times faster than the *trans*-isomer and affords exclusively bicyclo[3.3.0]octane, consistent with a stereoelectronically regulated 1,5-percaudal interaction (ε-effect) from the C–Sn σ-bond.**

Carbon–silicon and carbon–tin σ-bond participation in carbocation mediated processes is of considerable interest. The best known and exploited phenomenon is the 'β-silyl'[1] or 'β-stannyl'[2] effect **1**,† but influences from more distant locations have been described and significant γ and δ-effects (**2** and **3** respectively) have been identified in open-chain,[3] conformationally controlled[4] and rigid systems.[5] There is no information on the ability of a tin group to transmit an effect formally across five-bonds (ε-effect, **4**), but Lambert has reported that transmission across six-bonds (ζ-effect, **5**) is inconsequential.[6,7]

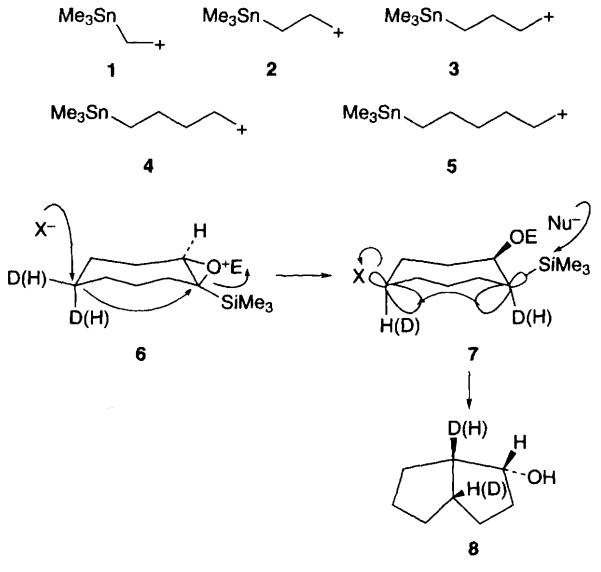
Recently, we proposed[8] that certain electrophile induced reactions of medium-ring 1,2-epoxy-silanes and -stannanes, that cleanly formed bicyclic derivatives **8**, involved 1,5-deoxysilylation of an intermediate **7** formed from the complexed epoxide **6** (Scheme 1). The 1,5-deoxysilylation was envisaged as being carbocationic, formally an ε-effect across five-bonds. We now report kinetic and stereochemical evidence that confirms the operation of a stereoelectronically dependent stabilising effect in the solvolysis of *cis*- but not *trans*-5-mesyloxycyclooctyltrimethylstannanes, and concordant product distributions, thus supporting the process depicted above in **7**.

cis- and *trans*-5-Hydroxycyclooctyltrimethylstannanes **9a** and **10a**,‡ respectively, were synthesised as shown in Scheme 2, and a preliminary low-temperature X-ray crystal structure establishes the anticipated *trans*-stereochemistry of **10**.§

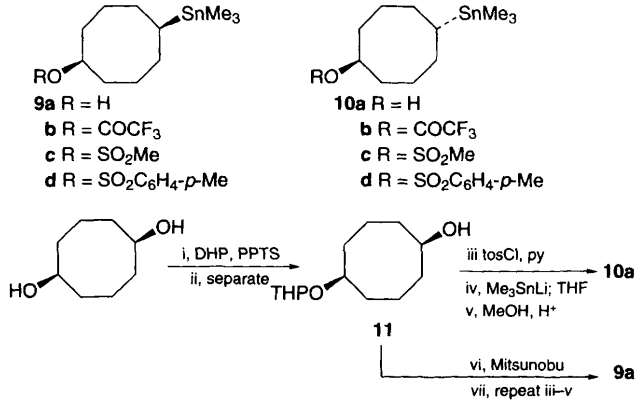
The oily *cis*-isomer **9a**‡ was obtained similarly after Mitsunobu inversion of the monoprotected diol **11**. The stannyl alcohols **9a** and **10a** were converted to their trifluoroacetates, **9b**, **10b**, mesylates **9c**, **10c** and tosylates **9d**, **10d** by standard procedures.‡

The preferred solution conformations of derivatives of **9a** and **10a**, based on NMR coupling constants ($^3J_{HH}$ and $^3J_{SnC}$) are the crown and boat-chair, with the former predominating for the *cis*-isomers (**9b–d**) and the latter for the *trans*-isomers (**10b–d**) shown below for the *cis*- and *trans*-trifluoroacetates, **9b** and **10b** respectively (Fig. 1). The Me_3Sn group appears to be *quasi*-equatorial in both isomeric series.[10]

Solvolysis in 80% ethanol–20% water, buffered with 2,6-lutidine, was monitored by Creary's ^1H NMR method.[11] The trifluoroacetates **9b** and **10b** experienced simple ester hydrolysis with a narrow rate spread, producing cyclooctanols **9a** and **10a** of retained stereochemistry.[12] However, the mesylates **9c** and **10c** and those from the *cis*- and *trans*-5-methylcyclooctanols were solvolysed, and the kinetic data are summarised in Table 1. The most striking result is the accelerated rate of *cis*-stannyl derivative **9c** (entry 5), relative to the parent mesylate (> 170) or its *trans*-isomer **10c**, (> 850), (entries 1, 4). The *cis*-5-methylmesylate (entry 3) also solvolyses faster (factor of about 6) than its *trans*-relative (entry 2) and this enhancement,



Scheme 1



Scheme 2 DHP = dihydropyran, PPTS = pyridinium toluene-*p*-sulfonate

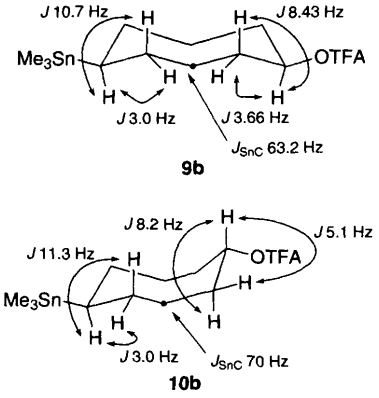


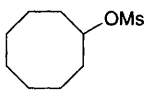
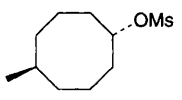
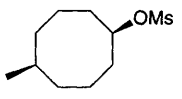
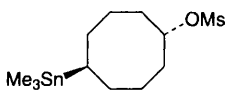
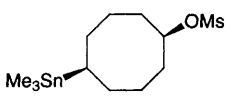
Fig. 1 Coupling constants for **9b** and **10b**

and the product differences, have been associated with enhanced *trans*-annular 1,5-hydride delivery to the developing cation centre.[13] This explanation is not attractive for **9c**, as 1,5-hydride migration would form the unfavourable α-stannyl cation,[1,14] and could not account for the exclusive formation of bicyclo[3.3.0]octane. The products from *trans*-mesylates (entries 2, 4) are analogous,¶ with unrearranged alkene and alcohol (or ether) predominating, although a low level of 1-substituted cyclooctene indicates some 1,5-hydride shift, probably subsequent to cation formation for stereoelectronic reasons.[15]

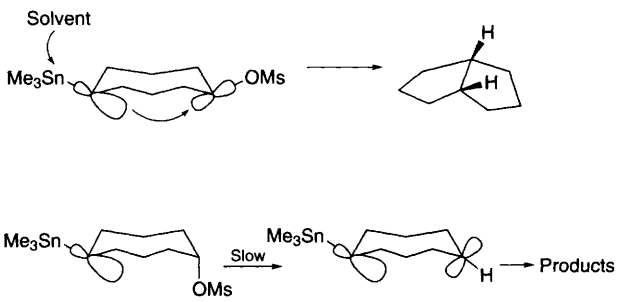
The enhanced rate of **9c**, and exclusive formation of bicyclo[3.3.0]octane is best accounted for by a transannular percaudal interaction ('back-lobe' effect)[3] that is formally an ε-effect, as shown below. The *trans*-isomer (**10c**, entry 4) cannot access a conformation permitting concerted percaudal interaction and ionisation, and its rate is therefore unexceptional. However, with a conformational change in the cation, ring closure competes (*ca.* 15%) with elimination and solvent capture, with the latter two processes giving tin-containing products. The rate and product trends described for the mesylates are reproduced with the tosylates.

Participation of the C–Sn σ-bond in this way may be formally represented as electrophilic substitution at carbon with inversion of configuration, a precedented process in organotin chemistry (Scheme 3).[16] The presently described process is also related to other carbocyclisations[17] effected by formal carbocation substitution at a tin-bearing carbon atom.

Table 1 Rate constants for solvolyses of cyclooctylmesylates in 80% ethanol–20% water at 22 °C[a]

Entry	Substrate	$k_1/10^{-5}$ s^{-1}	Rel. rate
1		10.3	1.00
2		1.7	0.16
3		10.6	1.00
4	 **10c**	2.0	0.2
5	 **9c**	> 1700[b]	> 170

[a] Buffered with 2,6-lutidine and followed by ^{1}H NMR spectroscopy. Proportions of products based on GC–MS analysis of 'spent' solvolysis solutions, comparisons with the behaviour of authentic samples, and high field ^{1}H and ^{13}C NMR spectra of 'spent' solvolysis solutions. [b] Based on estimates of $t_{1/2}$, calculated from the changing intensities, of the reducing and increasing Me_3Sn signals in the 200 MHz ^{1}H NMR spectrum.



Scheme 3

Footnotes

† Structures **1–5** represent the σ-skeletal frameworks only and do not necessarily represent optimised conformational arrangements for transmission of any effect.

‡ All new compounds provided satisfactory spectral (multinuclear NMR and MS) and microanalytical or high resolution MS data.

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¶ Acetolysis of *cis*-5-methylcyclooctyltosylate has been reported[13] to yield predominantly 1-methylcyclooctene (84%) with some 5-methylcyclooctene (10%) and 1-methylcyclooctanol (*ca.* 5%) whereas the *trans*-tosylate provided 8 and 74% of the 1- and 5-methylcyclooctenes respectively, and about 15% of a *cis, trans*-5-methylcyclooctyl acetate mixture. Results are similar, given the differences in solvent nucleophilicity between acetic acid (sodium acetate) and buffered aqueous ethanol.

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