Facile β-trimethylstannyl promoted 1,5-hydride shifts in cyclooctyl and cyclodecyl systems

Matthew P. Glenn, Kerry G. Penman and William Kitching*

Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia.
E-mail: kitching@chemistry.uq.edu.au

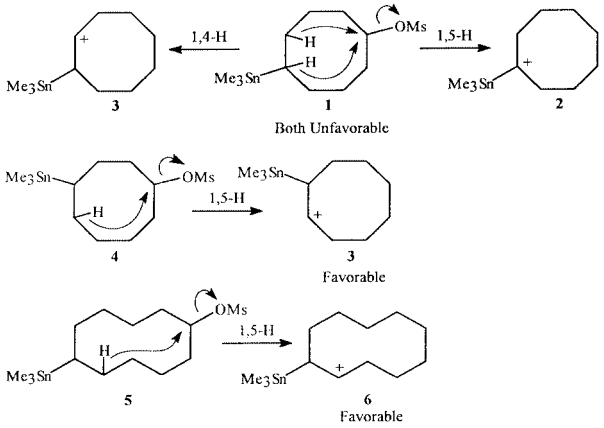
Received (in Cambridge, UK) 30th November 1999, Accepted 19th January 2000

Deuterium labelling and ^{2}H NMR mapping demonstrate that cyclooctyl and cyclodecyl mesylates in aqueous EtOH exhibit greatly enhanced or exclusive levels of 1,5-hydride shift, provided a Me_3Sn group is β to the migrating hydrogen, and after tin group loss from the formal β-stannyl cation, results in regiospecific, transannular alkene formation.

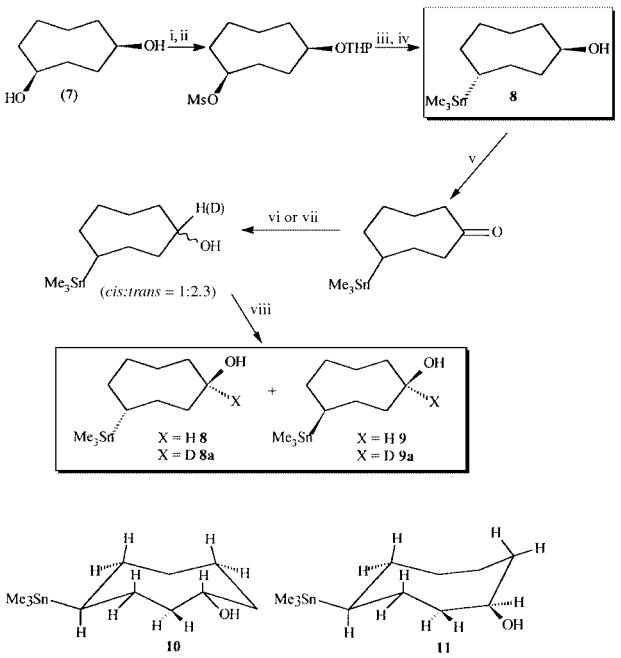
Recently we have described how suitably located Group 14 centred substituents (*e.g.* Me_3Si, Me_3Sn) may regulate transformations of medium-ring epoxides and mesylates.[1] Although 1,5-H shift occurs to the extent of *ca.* 50% in solvolysis of cyclooctyl mesylate,[1,2] this phenomenon is essentially completely suppressed in *cis*- and *trans*-5-mesyloxycyclooctyltrimethylstannanes **1** and is attributable to the relatively unfavourable nature of the α-stannyl cation **2**.[1] Nor do 1,4-hydride shifts compete in these systems, despite the generation of a formal β-stannyl cation intermediate **3**. Other pathways intervene.[1] However, there would be justifiable anticipation that in the 4-mesyloxycyclooctyl- and 6-mesyloxycyclodecyltrimethylstannanes **4** and **5** transannular hydride migration would be especially facile if the 'β-stannyl effect'[3] can operate to stabilise intermediates resembling **3** and **6**, as stable ion data[4] require that cyclooctyl and cyclodecyl cations possess the 1,5-μ-hydrido bridged stuctures (Scheme 1). This proposition is now verified. *cis*-Cyclooctane-1,4-diol **7**[5] was processed as shown below (Scheme 2) to provide *trans*- and *cis*-4-hydroxycyclooctyltrimethylstannanes **8** and **9**, respectively, and the corresponding 4-$^2H_1$-isotopomers **8a** and **9a**.[6]

All stereochemically validated cases of stannyl anion displacement of sulfonate ester groups proceed with inversion of configuration at carbon,[1,7] and on this basis, *cis*-diol **7** provides *trans*-stannyl alcohol **8**. The similar patterns of ^{13}C chemical shifts, through-bond ^{119}Sn–^{13}C coupling constants (especially $^3J_{Sn-C}$)[8] and certain ^{1}H chemical shifts for **8** and **9** indicate that the *chair–chair* (**10**) and *boat–chair* (**11**) conformations are important for the *trans* (**8**) and *cis* stannanes (**9**), respectively.

The behaviour of the mesylates from **8**, **8a**, **9** and **9a** in 75% EtOH–H_2O, buffered with 2,6-lutidine, was examined and the product profiles and ^{2}H location were determined by a combination of ^{1}H, ^{2}H and ^{13}C NMR spectroscopy of (total) product solutions, combined GC-MS analyses and comparisons with the spectra of authentic compounds. This data is summarised in Scheme 3.

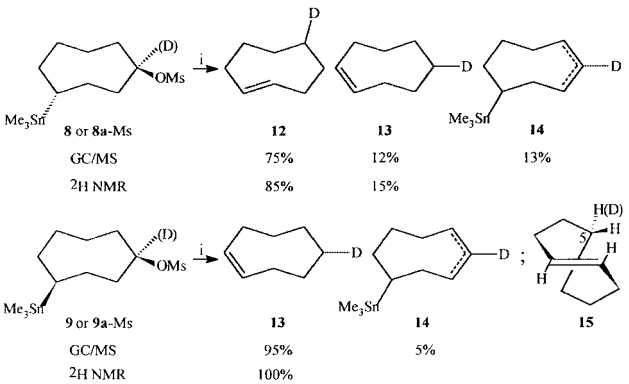


Scheme 1



Scheme 2 *Reagents and conditions*: i, dihydropyran, TsOH, CH_2Cl_2, 52%; ii, MsCl, Et_3N, CH_2Cl_2, 93%; iii, Me_3SnLi, THF, 84%; iv, TsOH, MeOH, 89%; v, tetrapropylammonium perruthenate, NMO, CH_2Cl_2, 77%; vi, $LiAlH_4$, Et_2O, 91%; vii, $LiAlD_4$, Et_2O, 93%; viii, HPLC.

trans-Mesylates from **8** or **8a** afforded very predominantly (*E*)-cyclooctene **12**, whereas *cis*-mesylates provided almost exclusively (*Z*)-cyclooctene **13** and very little Me_3Sn-containing products **14**. The ^{2}H NMR spectra of the cyclooctenes **12** and **13** from the labelled mesylates (from **8a** and **9a**) each

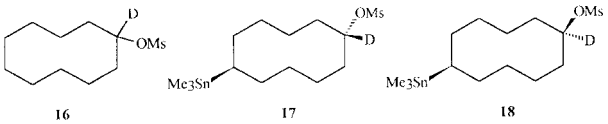


Scheme 3 *Reagents and conditions*: i, 75% EtOH–H_2O, 2,6-lutidine, 300 K.

consisted of a single, sharp high-field resonance at δ 1.42 for labelled (*Z*)-cyclooctene **13** and at δ 1.72 for (*E*)-cyclooctene **12**, confirming exclusive location of the label on a methylene carbon. Because we had already assigned the ^{13}C NMR spectra of a number of specifically ^{2}H-labelled (*Z*)- and (*E*)-cyclooctenes,[9] we were able to establish from the ^{13}C NMR spectra of the product that only 5-$^{2}H_1$-(*Z*)-cyclooctene **13** formed from **9a** and (as a minor product) from **8a** and only *one* diastereomer of **12** from labelled *trans*-mesylate **8a**.

Hence the H-shift was *complete* and *regiospecific* in a *1,5-sense*, and *diastereospecific* in the formation of **12**, which incorporates two stereogenic features. Furthermore, there is a substantial difference in the chemical shifts of the 'inside' and 'outside' protons on C-5 in the rigid (*E*)-cyclooctene systems[10] (see **15**) (δ 0.82 and 1.41;[11] δ 0.7 and 1.7[12]) that reflects the influence of the double bond. Deuterium is located only at an 'outside' position in **12** (δ 1.7) and this specificity appears to require that there is a nexus, perhaps weak, between ionisation and the 1,5-hydride shift. Consideration of the likely conformations **10** and **11** for the stannanes and likely distortions as ionisation proceeds, indicates a favourable pseudo-antiperiplanar disposition of the migrating C–H bond and β-Sn–C bond is accessible and meets the proximity and trajectory requirements of the migration.

β-Trimethylstannyl enhanced 1,5-H shifts have also been observed in similar reactions of the ^{2}H-labelled *trans*- and *cis*-6-mesyloxycyclodecyltrimethylstannanes **17** and **18**, which were acquired from *trans*-cyclodecane-1,6-diol[13,14] in the way summarised in Scheme 2 for the 1,4-cyclooctyl system.



16 **17** **18**

For 1-$^{2}H_1$-cyclodecylmesylate **16** the major products (~90%) were the (*E*) and (*Z*) cyclodecenes with about 67% of the ^{2}H label on the double bond (δ 5.3–5.4) representing unrearranged products, with *ca.* 20% corresponding to rearranged transannular product (δ 1.26).[15,16] However, the *trans*-stannane **17** also provided largely cyclodecenes (~80%) but now the majority of the label (~75%) is located transannularly (δ 1.26), confirming considerably enhanced 1,5-H migration. [Small amounts of both *cis* and *trans* decalins also form (δ 1.55 and 0.76, corresponding to bridgehead absorption)]. The labelled *cis*-mesylate **18** also provides cyclodecenes that are substantially rearranged (δ 1.33, 65–70%), in addition to *cis*-decalin (~20%, δ 1.54) which may result from 'back-lobe' bond formation, as proposed for the exclusive formation of *cis*-bicyclo[3.3.0]octane from *cis*-5-mesyloxycyclooctyltrimethylstannane.[1]

For a variety of alkyl and stannyl substituted cyclooctyl sulfonate esters, and for the stannyl substituted cyclodecylmesylates, relative to the parent system,[17] there is a narrow rate spread within each system, despite substantial variations in the levels of associated transannular hydride shift.[1,18] This fact, along with values for α-secondary ^{2}H-isotope effects,[19] implies that hydride shift lags behind primary ionisation. The present results confirm that 1,5- and not 1,6-H shifts are generally operative in cyclooctyl and cyclodecyl systems and are strongly promoted by a β-Me_3Sn group. These results and those from cyclononyl systems will be discussed in full at a later date, but demonstrate that Me_3Sn-driven transannular functionalization is facile and regiospecific.

The authors are grateful to the Australian Research Council for financial support.

Notes and references

1 B. H. Riches and W. Kitching, *Chem. Commun.*, 1996, 1907; A. P. Wells, B. H. Riches and W. Kitching, *J. Chem. Soc., Chem. Commun.*, 1992, 1575.
2 R. Heck and V. Prelog, *Helv. Chim. Acta*, 1955, **38**, 1541; A. P. Wells and W. Kitching, *J. Org. Chem.*, 1992, **57**, 2517.
3 See for example, J. B. Lamberg, G.-T. Wang and D. H. Teramura, *J. Org. Chem.*, 1988, **53**, 5422.
4 R. P. Kirchen, T. S. Sorensen, K. Wagstaff and A. M. Walker, *Tetrahedron*, 1986, **42**, 1063 and references therein; M. Saunders and H. A. Jiménex-Vasquez, *Chem. Rev.*, 1991, **91**, 375; V. Galasso, *Int. J. Quantum Chem.*, 1998, **20**, 119.
5 A. C. Cope, J. M. Grisar and P. E. Petersen, *J. Am. Chem. Soc.*, 1959, **81**, 1640.
6 All new compounds exhibited concordant ^{1}H and ^{13}C NMR spectra and high resolution mass spectral (accurate mass) data.
7 W. Kitching, H. A. Olszowy and K. J. Harvey, *J. Org. Chem.*, 1982, **47**, 1893 and references therein. This is not the case for bromide or iodide systems, in which e-transfer and exchange processes compete.
8 D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C. Lee, R. J. Mynott, J. L. Considine, H. Kuivila and R. H. Sarma, *J. Am. Chem. Soc.*, 1974, **96**, 1640.
9 K. G. Penman, W. Kitching and A. P. Wells, *J. Chem. Soc., Perkin Trans. 1*, 1991, 721; G. Read and J. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2287; K. G. Penman and W. Kitching, unpublished results.
10 K. T. Burgoine, S. G. Davies, M. J. Peagram and G. H. Whitham, *J. Chem. Soc.*, 1974, 2629 and papers in this series.
11 I. Sauers, L. A. Grezzo, S. W. Staley and J. H. Moore, *J. Am. Chem. Soc.*, 1976, **98**, 4218; K. J. Shea and J.-S. Kim, *J. Am. Chem. Soc.*, 1992, **114**, 3044.
12 K. G. Penman and W. Kitching, unpublished results.
13 O. Ermer and J. D. Dunitz, *Isr. J. Chem.*, 1989, **29**, 137; O. Ermer, J. D. Dunitz and I. Bernal, *Acta Crystallogr.*, 1973, **1329**, 2278.
14 Large prisms of the *trans*-diol (we thank Dr P. Bernhardt for an X-ray structural analysis) were processed to a single stannane isomer (see Scheme 1) concluded to be the *cis* on the basis of argument presented in the text.
15 These figures agree well with the original data based on degradative studies of the ^{14}C and ^{2}H labelled cyclodecene products.
16 V. Prelog and J. G. Traynham, in *Molecular Rearrangements*, ed. P. de Mayo, Interscience, New York, 1963, vol. 1, p. 593; A. C. Cope, M. M. Martin and M. A. McKervey, *Quart. Rev. Chem. Soc.*, 1966, **20**, 119.
17 A. C. Cope and D. M. Gale, *J. Am. Chem. Soc.*, 1963, **85**, 3743; N. L. Allinger and W. Szknybal, *Tetrahedron*, 1968, **24**, 4699; A. C. Cope and R. B. Kinnel, *J. Am. Chem. Soc.*, 1966, **88**, 752; H.-J. Schneider and D. Heiske, *J. Am. Chem. Soc.*, 1981, **103**, 3501.
18 We are unaware of solvolytic data for any other stereochemically defined, substituted cyclodecylsulfonate esters.
19 W. Parker and C. I. F. Watt, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1647; M. P. Glenn and W. Kitching, unpublished results.

Communication a909463f