Electrophile Induced Reactions of Medium Ring Vinyl- and 1,2-Epoxy-silanes and Related Compounds

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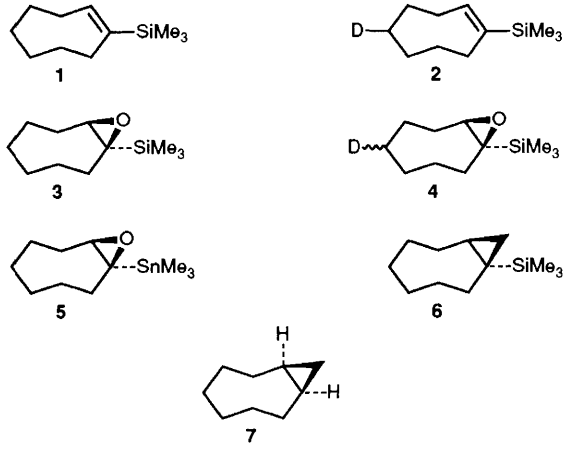
Deuterium labelling studies confirm extensive *trans*-annular participation in acidolysis, acetylation and brominolysis of 1,2-epoxy-1-trimethylsilylcyclooctane and (*E*)-1-trimethylsilylcyclooctene, and require revision of previous mechanistic proposals.

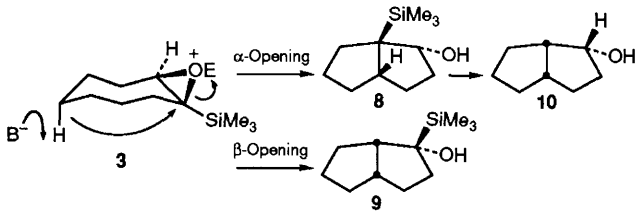
Although the electrophile induced reactions of simple vinyl- and 1,2-epoxy-silanes are qualitatively understood,[1] the cyclooctyl derivatives lead to products consistent with *trans*-annular participation.[2–4] However, the suggested mechanisms[2–4] are strongly inferential and in part, are unconvincing. We are now able to clarify important aspects of these reactions from studies utilising ^{2}H-labelled silanes.

(*E*)-1-Trimethylsilylcyclooctene **1** was readily available[5,6] and the key ^{2}H-labelled analogue **2** was obtained by a sequence commencing with the acetolysis of [1-$^2H_1$]cyclooctyl toluene-*p*-sulfonate.[7,8] This provides cyclooctyl acetate labelled at C-5 (*ca.* 60%) and C-1 (40%), as a result of 1,5-H shifts associated with carbocation formation. Acetate hydrolysis, oxidation (Jones reagent) (which removes ^{2}H from C-1), tosylhydrazone formation and silylation[5] provides **2**. Epoxidation of **1** and **2** with *m*-chloroperbenzoic acid provides epoxysilanes **3** and **4**, respectively with the latter being a 50 : 50 epimeric mixture with deuterium either *cis* or *trans* to the epoxide.†

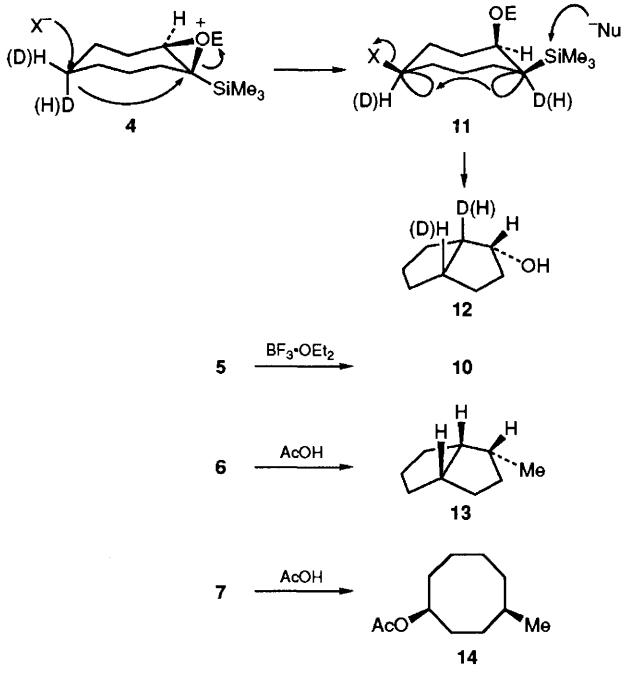
Acidolysis of **3** and **4**: Treatment of **3** with BF_3·OEt_2 has been reported[2] to yield exclusively *endo-cis*-bicyclo[3.3.0]octan-2-ol **10**, and this was considered[2] to arise by deprotonation and *trans*-annular electron-pair shift concerted with epoxide ring opening to yield either **8** (α-opening) or **9** (β-opening). Tertiary silane **8** was favoured and then formed **10** in an unspecified way. This reported[2] proposal is shown in Scheme 1. (Note that *cis*, rather than the *trans*-hydroxysilane **8** suggested[2] and shown in Scheme 1, would result from S_N2 opening of the Lewis acid complexed epoxysilane).



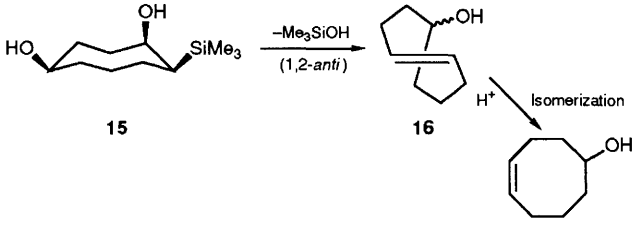
† This is apparent from a duality of ^{2}H-isotope effects on certain of the ^{13}C chemical shifts.



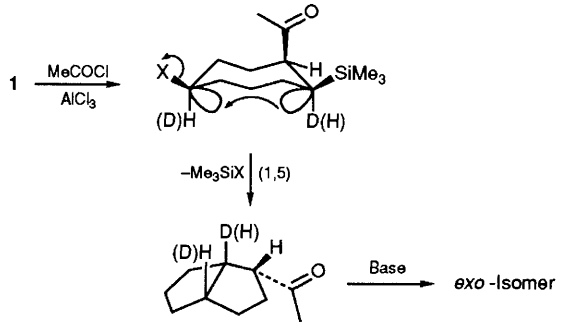
Scheme 1



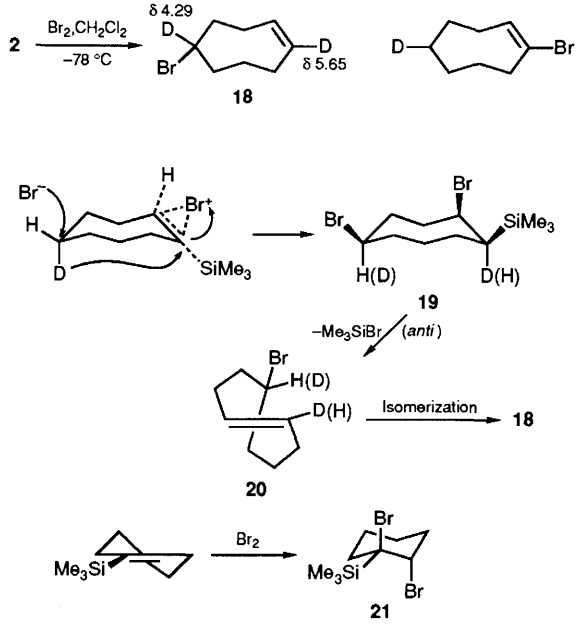
Scheme 2



Scheme 3



Scheme 4



Scheme 5

Repetition of this reaction using **4** led to the bicyclic alcohol **12**[2,9] as the exclusive product, and detailed ^{13}C, ^{1}H and ^{2}H NMR studies on it established that the ^{2}H label was equally distributed between C-1 and C-5 in **12**. This followed from the ^{2}H isotope effects[8] on the C-1 and C-5 chemical shifts (47.2 and 42.3, ppm respectively), and the close equiintense ^{2}H NMR signals at δ 2.3, established by correlated spectra to correspond to the H-1 and H-5 chemical shifts.[10] The proposed mechanism,[2] summarised in Scheme 1, is therefore unimportant, as no *trans*-annular hydride shift was invoked. We suggest that 1,5-hydride (or deuteride) shift is concerted with α-opening[11] of the complexed epoxide, with inversion at both centres, to yield the all-*cis* silane**11**. The stereoelectronic features of dual inversion permits migration of only one-half of the ^{2}H-label. Silane **11** now experiences 1,5-deoxysilylation, again with dual inversion to provide bicyclic alcohol **12** with the correct relative stereochemistry and ^{2}H-distribution.[12]

Epoxystannane **5** also yields **10**, whereas cyclopropylsilane **6**[13,14] leads predominantly to *endo*-methyl derivative **13**, presumably by an analogous mechanism. The acetolysis[15] of *cis*-bicyclo[6.1.0]nonane **7**,[15] and various [$^{2}H_1$]-derivatives,[16] proceeds with 1,5-hydride shifts to provide largely *cis*-4-methylcyclooctyl acetate **14**, consistent with the proposals in Scheme 2. Exposure of **3** to aqueous dioxane–H_2SO_4 also leads to alcohol **10** (80%) together with a mixture of cyclooctenols (*ca.* 20%),[2] which are (*Z*)-cyclooctenols[8] and not derivatives of (*E*)-cyclooctene as originally claimed.[2] The well-precedented *anti*-elimination[1] of Me_3SiOH from an all-*cis* intermediate such as **15** would generate (*E*)-cyclooctene-5-ol **16** which could isomerize under the acidic conditions,[17] to which, however, bicyclic alcohol **10** is stable.

Acylation of **1** and **2**: Treatment of **2** with MeCOCl under Friedel–Craft conditions[3] provides a single ketone, which epimerized on extended exposure to base. ^{13}C, ^{1}H and ^{2}H NMR studies[10] established the kinetic formation of *endo*-ketone **17**, in which the ^{2}H label was equally distributed between the C-1 and C-5 positions. A 1,5-H (or D) shift to the carbon bearing silicon[11] and 1,5-desilylative ring closure with inversion are key elements of Scheme 4. The previously suggested[3] mechanism involving deprotonation and *trans*-annular electron-pair shift is thus unimportant.

Brominolysis of **1** and **2**: Treatment of **1** and **2** with bromine at −78 °C yielded no bicyclic product, but ^{13}C and ^{2}H NMR spectra established the presence of (*Z*)-5-bromocyclooctene **18** with approximately equal distribution of deuterium between C-1 and C-5. This requires *trans*-annular hydride (or deuteride) migration as previously inferred,[4] possibly resulting in formation of all-*cis*-silane **19**. The route from **19** to 5-bromocyclooctene **18** is unclear, but (unprecedented) *cis* elimination of Me_3SiBr has been suggested. [4] Alternatively,

anti-elimination would provide (*E*)-5-bromocyclooctene **20** which may suffer facile $E \rightarrow Z$ ring isomerisation in the presence of the potent electrophiles, Me_3SiBr and Br_2. In the cyclohexyl- and cycloheptyl-silane systems, the dibromo adducts (*e.g.* **21**) resulting from bromine addition to the vinyl silanes are quite stable and facile *cis*-loss of Me_3SiBr is not observed.[11] We are unsure why 1,5-loss of Me_3SiBr does not compete in the case of **19**, to provide bicyclic bromide product.

The central feature of the acid- and acyl-desilylation reactions is proposed to be a facile and stereospecific 1,5-desilylative (or destannylative) ring closure. Solvolytic studies with appropriate *cis*- and *trans*-trimethylsilyl- and -stannylcyclooctanol and -cyclononanol derivatives are being conducted to define this novel process.

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