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Preparation of oxetanes by silicon-directed 4-*exo trig* electrophilic cyclisations of homoallylic alcohols

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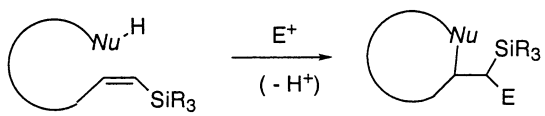
Abstract—The reaction of homoallylic alcohols with bis(*sym*-collidine)bromine(I) hexafluoroantimonate led in good yields to the formation of oxetanes if a silyl group was fixed on the carbon–carbon double bond in terminal position. This reaction was stereospecific when no supplementary substituent was present on the double bond. © 2001 Elsevier Science Ltd. All rights reserved.

We have reported in the preceding paper that oxetanes could be obtained in good yields by electrophile driven 4-*endo* cyclisation of cinnamic alcohols.[1] It was expected that formation of oxetanes by 4-*exo* cyclisations of homoallylic alcohols could be a more easier reaction pathway.[2] In fact, the cyclisations of these alcohols led mainly to the formation of tetrahydrofuran ring system by 5-*endo* processes.[3] However, some results have already been reported concerning the formation of oxetanes by this reaction. In general, mixtures of oxetanes and tetrahydrofurans were obtained,[4] except when the structure of the alcohols did not allow,[5] or disfavoured[6] the 5-*endo* process.

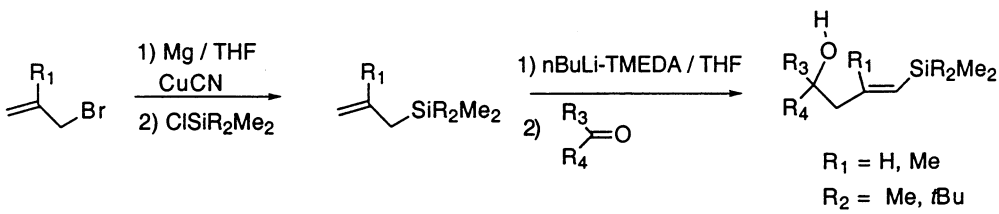
Intramolecular cyclisations of functionalised vinylsilanes are recognised to favour the formation of heterocycles by *exo* processes (Scheme 1). These reactions were used for the formation of cyclic ethers,[7] and amines[7c,8] using Lewis acids or NBS as reagents.

We decided to examine the preparation of oxetanes by this process. There is already one report in the literature concerning such a possibility by reaction of a particular alcohol with NBS.[9] However, attempts of cyclisations using a selenium reagent were unsuccessful.[7c] We thought that bis(collidine)bromine(I) hexafluorophosphate could be an excellent electrophile for these cyclisations. Different alcohols possessing a carbon–carbon double bond of *E*-stereochemistry were prepared, as outlined in Scheme 2, by reaction of the anions derived from allylsilanes with carbonyl compounds.[10]

The starting allylsilanes were either commercially available (allyltrimethylsilane) or prepared by reaction of the corresponding Grignard reagents in THF with the chlorosilane in the presence of a catalytic amount of CuCN (25°C, 24 h). The alcohol **1a** possessing a car-



Scheme 1.



Scheme 2.

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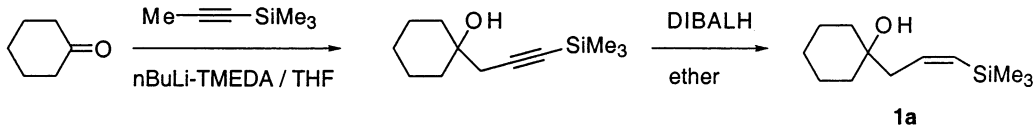
bon–carbon double bond of *Z*-stereochemistry was prepared by DIBALH reduction[11] of the corresponding acetylenic compound[12] (Scheme 3).

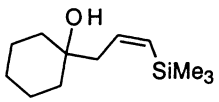
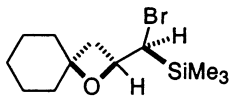
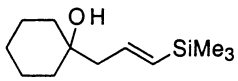
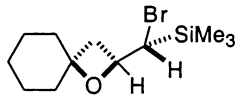
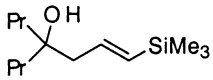
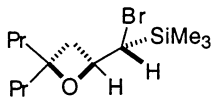
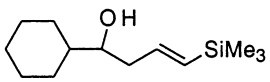
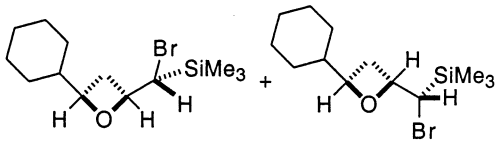
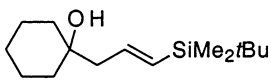
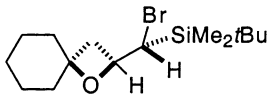
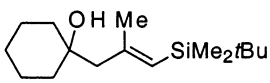
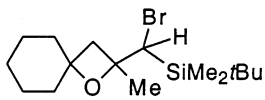
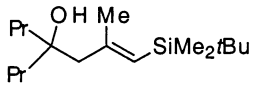
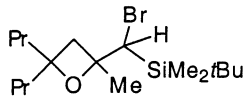
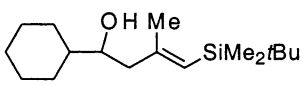
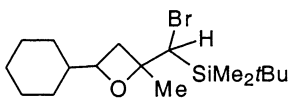
In a preliminary study, we found that reaction of vinylsilanes with bis(collidine)bromine(I) nitrate or hexafluorophosphate led to oxetanes in modest to low yields. Numerous unidentified products were generally formed. However, clean reactions were observed using bis(collidine)bromine(I) hexafluoroantimonate.[13] Best yields were obtained when the reactions were conducted in methylene chloride at reflux.[14] Our results are reported in Table 1. The structures of the products **2** were established from their spectral data.[15] In the case of tertiary alcohols unsubstituted on the carbon–carbon double bond only one diastereoisomer was isolated (entries a–c, e). Their stereochemistries were deduced from their NMR spectra supposing the anti addition of the alcohol function and the bromonium on the CC double bonds. This means that vinylsilane **1a** of *Z* stereochemistry led to the oxetane **2a**, while the vinyl silane **1b** of *E* stereochemistry led to the oxetane **2b**



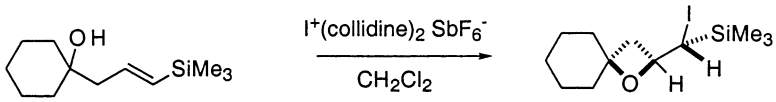
1a

Scheme 3.

Table 1. Reaction of vinylsilanes with biscollidinebromine(I) hexafluoroantimonate

Entry	Vinylsilane **1**	Oxetane(s) **2** (Yield, %)
a		 (80)
b		 (60)[a] (89)
c		 (90)
d		 (32) *cis* (18) *trans*
e		 (57)
f		 (75) 80-20[b]
g		 (60) 80-20[b]
h		 (44)[c] (76) 90-10[b]

[a] Reaction with $Br^{+}(collidine)_2\ PF_6^{-}$. [b] ratio of diastereomers. [c] Reaction carried out at rt.



1b 3

Scheme 4.

diastereoisomer of **2a**. When a methyl group was fixed on the carbon–carbon double bond a mixture of two diastereoisomers was obtained (entries f, g) whose stereochemistries were not determined. However, we can conclude from these results, that the formation of oxetanes occurred by intervention of a bromonium (vinylsilanes **1a–e**), or a carbocation (vinylsilanes **1f–h**) depending of the substitution of the carbon–carbon double bond. With the secondary alcohol **1d**, we could expect that the cyclisation was also diastereospecific. In fact we obtained a mixture of two isomers, due to the low facial diastereoselection induced by the cyclohexyl group. The stereochemistry of these two diastereomers was determined by a NOESY experiment. In the case of alcohol **1h**, we isolated only two diastereoisomers, instead of the four possible, whose stereochemistries were not established.

We examined also the reactivity of bis(collidine)iodine(I) hexafluoroantimonate with the vinylsilane **1b**. We obtained the oxetane **3** in 35% yield (Scheme 4). This reagent appears thus less interesting that the bromo reagent for the preparation of oxetanes.

In conclusion, we report that formation of oxetanes by 4-*exo* electrophilic cyclisation of homoallylic alcohols using bis(collidine)bromine hexafluoroantimonate is an efficient process, if a silicon atom is fixed in terminal position on the carbon–carbon double bond. These cyclisations are diastereospecific when the carbon of the double bond in β of the silicon atom is non substituted.

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13. This reagent was prepared in two steps (70% overall yield) by reaction of silver hexafluoroantimonate with collidine in water, followed by reaction of the silver salt with bromine as reported for the preparation of the hexafluorophosphate salt. See: Homsi, F.; Robin, S.; Rousseau, G. *Org. Synth.* **2000**, *77*, 206–211.
14. **Representative procedure**: To a solution of alcohol (2 mmol) in methylene chloride (10 mL) heated at reflux was added over 6 h a methylene chloride solution (40 mL) of bis(collidine)bromine(I) hexafluoroantimonate (5 mmol). After complexion of the addition and cooling, the solvent was removed under vacuum and the residue purified by liquid chromatography over silica gel (hexanes–ether).
15. **Selected data**: *Oxetane **2a**:* ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.72 (q, $J=8$ Hz, 1H), 3.38 (d, $J=10$ Hz, 1H), 2.35 (dd, $J=6$ and 11 Hz, 1H), 2.08 (dd, $J=6$ and 11 Hz, 1H), 2.00–1.20 (m, 10H). *Oxetane **2b***: ^{1}H NMR 4.75 (q, $J=7$ Hz, 1H), 3.45 (d, $J=7$ Hz, 1H), 2.42–2.20 (m, 2H), 2.00–1.00 (m, 10H). ^{13}C NMR 81.7, 74.7, 47.5, 39.1, 38.2, 37.9, 25.1, 22.8, 22.2, –2.3. *Oxetane **2c***: ^{1}H NMR 4.65 (q, $J=7$ Hz, 1H), 3.40 (d, $J=8$ Hz, 1H), 2.45–2.20 (m, 2H), 1.80–1.10 (m, 8H), 1.05–0.80 (m, 6H), 0.15 (s, 9H). ^{13}C NMR 83.7, 76.4, 47.1, 42.3, 41.0, 37.5, 29.7, 16.6, 16.4, 14.5, –2.3. *Oxetane **2d** (major diastereomer)*: ^{1}H NMR 4.75 (d, $J=7$ Hz, 1H), 4.26 (q, $J=7$ Hz, 1H), 3.35 (d, $J=8$ Hz, 1H), 2.75–2.55 (m, 1H), 2.35–2.15 (m, 1H), 2.00–1.05 (m, 11H), 0.15 (s, 9H). ^{13}C NMR 81.3, 77.3, 46.8, 44.5, 32.4, 27.7, 26.4, 26.0, 25.5, 25.3, –2.3. *Oxetane **2d** (minor diastereomer)*: ^{1}H NMR 4.83–4.72 (m, 1H), 4.32 (q, $J=7$ Hz, 1H), 3.55 (d, $J=5$ Hz, 1H), 2.70–2.55 (m, 1H), 2.45–2.28 (m, 1H), 1.80–1.05 (m, 11H), 0.15 (s, 9H). *Oxetane **2e**:* ^{1}H NMR 4.78 (q, $J=8$ Hz, 1H), 3.62 (d, $J=8$ Hz, 1H), 2.40–2.15 (m, 2H), 2.00–1.10 (m, 10H), 0.95 (s, 9H), 0.15 (s, 3H), 0.05 (s, 3H). ^{13}C NMR 81.4, 74.7, 46.0, 38.6, 38.2, 37.5, 27.0, 25.2, 22.9, 22.3, 17.3, –5.4, –6.5. *Oxetane **2f** (major diastereomer):* ^{1}H NMR 3.81 (s, 1H), 2.25 (d, $J=9$ Hz, 1H), 2.08 (d, $J=9$ Hz,

1H), 1.55 (s, 3H), 1.50–1.10 (m, 10H), 1.00 (s, 9H), 0.25 (s, 3H), 0.05 (s, 3H). *Minor diastereomer:* ^{1}H NMR 3.60 (s, 1H), 2.35 (d, $J=9$ Hz, 1H), 2.15 (d, $J=9$ Hz, 1H), 1.54 (s, 3H), 1.50–1.10 (m, 10H), 1.00 (s, 9H), 0.20 (s, 6H). *Oxetane* ***2g*** *(major diastereomer)*: ^{1}H NMR 3.89 (s, 1H), 2.20 (q, 2H, AB system), 1.50 (s, 3H), 1.50–1.10 (m, 10H), 0.97 (s, 9H), 0.20 (s, 3H), 0.03 (s, 3H). *Minor diastereomer:* ^{1}H NMR 3.65 (s, 1H), 2.25 (q, 2H, AB system), 1.55 (s, 3H), 1.50–1.10 (m, 10H), 1.05 (s, 3H), 0.97 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H). *Oxetane* ***3***: ^{1}H NMR 4.42 (q, $J=7$ Hz, 1H), 3.35 (d, $J=9$ Hz, 1H), 2.40 (dd, $J=8$ and 10 Hz, AB system (part A), 2.08 (dd, $J=8$ and 10 Hz, AB system (part B)), 1.90–1.50 (m, 10H), 0.10 (s, 9H).