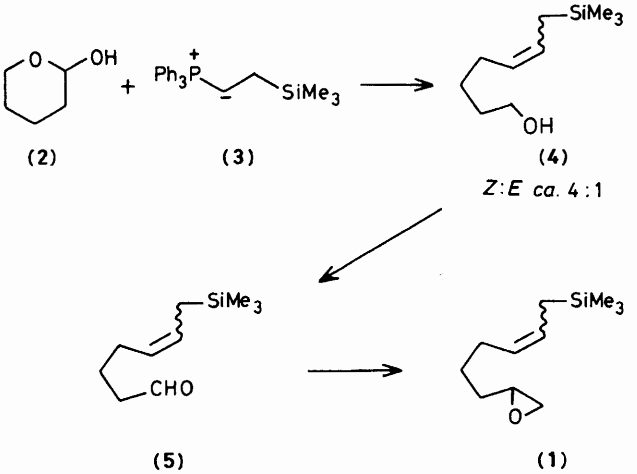
Allylsilane Cyclisations in Organic Synthesis; Formation of a Cyclopentane *via* Cyclisation of an Epoxy-allylsilane

Thuan Siah Tan,[a] Andrew N. Mather,[a] Garry Procter,[a] and Alan H. Davidson[b]

[a] *Department of Chemistry, University College, Cardiff CF1 1XL, U.K.*
[b] *Department of Applied Chemistry, U.W.I.S.T., Cardiff CF1 3NU, U.K.*

The epoxy-allylsilane (**1**) was prepared by two routes and cyclised stereoselectively to give the *cis*-cyclopentane (**9**) on treatment with $TiCl_4$; equilibration of the aldehyde corresponding to (**9**) gave the *trans*-isomer in high yield.

The cyclisation of an allylsilane onto an electrophilic centre[1] is a potentially useful reaction for the construction of cyclic systems. There are few examples of this approach to the synthesis of carbocycles[2] and recently we initiated a project to develop allylsilane cyclisations for use in natural product synthesis. In this communication we describe the results of an investigation into the formation of a cyclopentane by cyclisation of an epoxy-allylsilane.



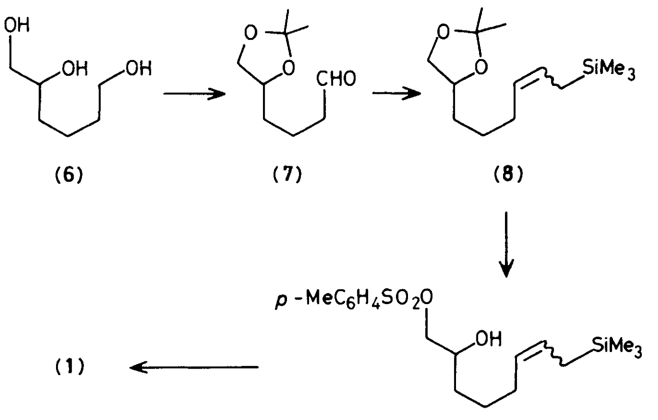
The intermolecular reaction of allylsilanes with simple epoxides is known to take place readily in the presence of $TiCl_4$.[3] The intramolecular version of this reaction is of interest because it would lead to a carbocyclic system with two adjacent 'masked aldehyde' groups. The epoxy-allylsilane (**1**) can be prepared by the two routes described below.

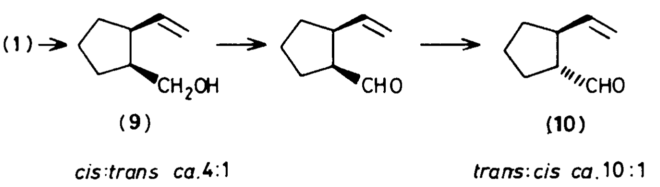
The most direct approach to the preparation of (**1**) uses the reaction of the lactol (**2**)[4] with the phosphorane (**3**)[5] [2.2 equiv., tetrahydrofuran (THF), −78 °C to room temperature, 80%]. Oxidation of the alcohol (**4**) to the aldehyde (**5**) [pyridinium dichromate (PDC),[6] CH_2Cl_2, 71%] followed by reaction with dimethylsulphoxonium methylide[7] [Me_3SOI, NaH, dimethyl sulphoxide (DMSO), 33%] gave the epoxy-allylsilane (**1**).†

A second route was developed which would allow the preparation of epoxy-allylsilanes from readily available optically active starting materials. Racemic triol (**6**) (Sigma Chemical Co.) was converted into the acetonide (Me_2CO,

---

† The yields quoted in this communication refer to pure, isolated material, homogeneous by t.l.c. and 360 MHz ^1H n.m.r. spectroscopy. All new compounds gave satisfactory elemental analyses.





p-$MeC_6H_4SO_2OH$, room temperature, 92%) and oxidised to the aldehyde (**7**) (PDC, CH_2Cl_2, 88%). Treatment of this aldehyde with phosphorane (**3**) (1.1 equiv., THF, −78 °C to room temperature, 64%) gave the allylsilane (**8**). Deprotection (dil. HCl, $CHCl_3$–MeOH, 73%), selective tosylation of the primary hydroxy group (p-$MeC_6H_4SO_2Cl$, CH_2Cl_2, pyridine, 83%), followed by reaction with base (NaOMe, MeOH–$CHCl_3$, 78%) gave the epoxide (**1**).

These two approaches demonstrate that epoxy-allylsilanes such as (**1**) can be prepared easily, and in principle both routes could use carbohydrate-derived starting materials for the preparation of optically pure precursors.

Cyclisation of the epoxy-allylsilane (**1**) was achieved by treatment with $TiCl_4$ ($TiCl_4$, CH_2Cl_2, −95 °C, 55%). The product of this reaction was mainly the *cis*-isomer (*cis* : *trans* *ca.* 4 : 1) as shown by conversion into the aldehydes (PDC, CH_2Cl_2, 61%) and integration of the aldehyde peaks in the 360 MHz ^1H n.m.r. spectrum.‡ Base catalysed equilibration of this mixture (NaOMe, MeOH, 90%) produced mainly the *trans*-isomer (**10**) (*trans* : *cis* *ca.* 10 : 1).

The results described in this communication show that it is possible to prepare functionalised cyclopentanes, with considerable stereoselectivity, using an epoxy-allylsilane cyclisation.§ It is of particular interest that the product from the cyclisation of (**1**) is mainly the *cis*-isomer, since there are few cyclisations which produce cyclopentanes with this stereochemistry.

We thank the S.E.R.C. for a Postgraduate Research Assistantship (A. N. M.).

Received, 8th February 1984; Com. 172

References

1 T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; E. W. Colvin, 'Silicon in Organic Synthesis,' Butterworths, 1981, Ch. 9.
2 I. Fleming, A. Pearce, and R. L. Snowden, *J. Chem. Soc., Chem. Commun.*, 1976, 182; L. R. Hughes, R. Schmid, and W. S. Johnson, *Bioorg. Chem.*, 1979, **8**, 513.
3 I. Fleming and I. Patterson, *Synthesis*, 1979, 446.
4 L. E. Schniepp and H. H. Geller, *J. Am. Chem. Soc.*, 1946, **68**, 1646.
5 D. Seyferth, K. R. Wursthorn, and R. E. Mammarella, *J. Org. Chem.*, 1977, **42**, 3104; see also refs. 1 and 3.
6 E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, 399.
7 E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353.
8 I. Cutting and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 1983, 1435.

---

‡ The aldehyde proton of the *cis*-isomer absorbs at δ 9.68, and the *trans*- at δ 9.63.

§ The cyclisation of epoxy-allylsilanes is evidently dependent on the structure of the substrate. A recent attempt to cyclise epoxy-allylsilanes resulted in rearrangement rather than cyclisation, see ref. 8.