Allyl Silanes in Organic Synthesis: a New Synthesis of Loganin

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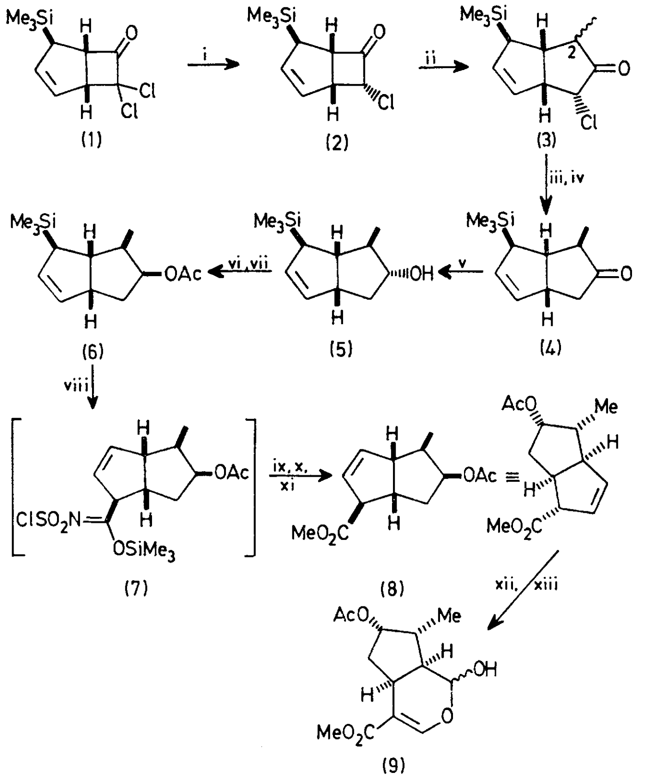
Summary Loganin has been synthesised from the allylsilane (**1**).

Allylsilanes react with electrophiles in the sense shown in Scheme 1 in the preceding communication.[1] We pointed out earlier[2] that the advantage of using allylsilanes rather than other allylmetal compounds in organic synthesis was twofold: allylsilanes are allylically stable (they do not undergo rapid [1,3]sigmatropic shifts) and they are not so reactive that they cannot be carried unscathed through quite a wide range of chemical operations. We now demonstrate how these features can be applied to a total synthesis of loganin.

The ketone (**1**)[1] can easily be monodechlorinated to give the cyclobutanone (**2**) (94%), which reacts with diazoethane to give the cyclopentanone (**3**) as a mixture of stereoisomers at C-2. Removal of the chlorine, column chromatography, and base-catalysed equilibration at C-2 gave the ketone (**4**) (72%), which was reduced stereoselectively to the crystalline alcohol (**5**) (66%). Alternative sequences of the three operations (dechlorination, ring expansion, and equilibration) were less satisfactory. Mesylation of the alcohol (**5**) and displacement of mesylate by acetate ion then gave the key allylsilane (**6**) (80%). Now the allylsilane function, which had successfully survived the earlier operations, was brought into play with an electrophile capable of reacting with olefinic systems: chlorosulphonyl isocyanate reacted cleanly to give a product, the n.m.r. spectrum of which was consistent with the structure (**7**).[3] The best way to hydrolyse this intermediate was found only after much experimentation: treatment successively with sodium nitrite in acetic acid, sodium acetate in water, and diazomethane gave the ester (**8**) (61%). Ozonolysis then gave the racemic aglucone acetate (**9**) (47%) of loganin, identical with a sample obtained by degradation of loganin.† The conversion of this derivative into loganin itself has been reported as part of the earlier syntheses of loganin.[4,5] The overall yield of (**9**) from cyclopentadiene was 5·3%, which compares favourably with the yield in the earlier synthesis[4] (2·7% from cyclopentadiene).



Reagents. i, Zn–AcOH–H_2O; ii, $MeCHN_2$–Et_2O–MeOH; iii, excess Zn–AcOH–H_2O; iv, NaOMe–MeOH; v, $NaBH_4$–MeOH; vi, $MeSO_2Cl$–pyridine; vii, $Et_4N^+AcO^-$–Me_2CO; viii, $ClSO_2NCO$–CCl_4; ix, $NaNO_2$–Ac_2O–AcOH; x, NaOAc–H_2O; xi, CH_2N_2; xii, O_3; xiii, Me_2S.

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[1] B.-W. Au-Yeung and I. Fleming, preceding communication.

[2] M. J. Carter and I. Fleming, *J.C.S. Chem. Comm.*, 1976, 679.

[3] See also G. Deleris, J. Dunogues, and R. Calas, *J. Organometallic Chem.*, 1976, **116**, C45.

[4] G. Büchi, J. A. Carlson, J. E. Powell, and L.-F. Tietze, *J. Amer. Chem. Soc.*, 1973, **95**, 540.

[5] J. J. Partridge, N. K. Chadha, and M. R. Uskokovic, *J. Amer. Chem. Soc.*, 1973, **95**, 532.