Allyl Silanes in Organic Synthesis: Some Reactions of 3-Trimethylsilylcyclohex-4-ene-1,2-dicarboxylic Acid and its Derivatives

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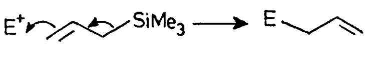
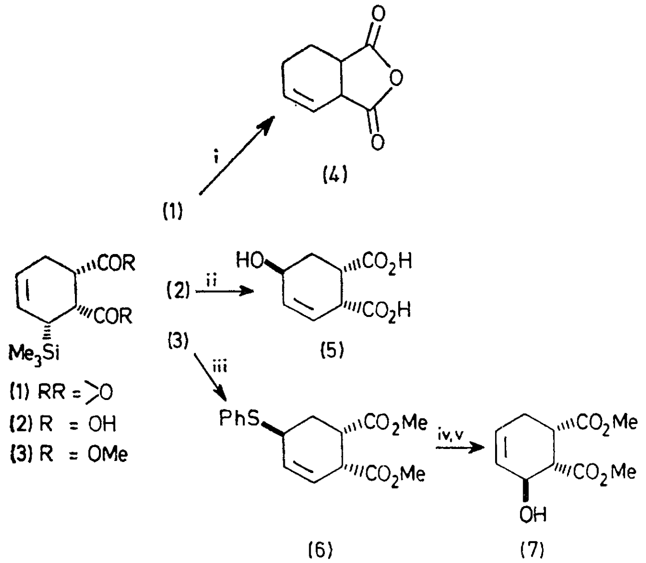
Summary The allyl silanes (**1**), (**2**), and (**3**) react with acid, peracetic acid, and phenylsulphenyl tetrafluoroborate, respectively, to give electrophilic substitution products with loss of the trimethylsilyl group and a shift of the double bond.

ALLYL silanes are versatile functional groups with considerable potential for organic synthesis. Thus, Calas and Dunogues and their co-workers,[1] and Sakurai and his co-workers[2] have shown that allyl silanes react with carbon electrophiles in the sense shown in Scheme 1. We demonstrate here the wider versatility of allyl silanes with some reactions of the allyl silane (**1**) and its simple derivatives (**2**) and (**3**) with other electrophiles. The compounds (**1**), (**2**), and (**3**) are readily available from the Diels–Alder reaction[3] of maleic anhydride with 1-trimethylsilylbutadiene (**8**) (74%) (the stereochemistry shown is assumed from the *endo* rule).



SCHEME 1

Protodesilylation of (**1**) gave the anhydride (**4**) in 76% yield. Clearly, the ability to move the double bond of a Diels–Alder adduct in this way has wide implications in the design of organic syntheses. Treatment of the dicarboxylic acid (**2**) with unbuffered peracetic acid gave the allyl alcohol (**5**) in 66% yield, presumably by way of an intermediate epoxide. (Hudrlik[4] has recently shown that some allyl silane epoxides, apparently, do not undergo the reaction we have observed. His reactions were carried out under basic conditions, and it may therefore be significant that our reaction only worked well under acidic conditions.) Phenylsulphenyl tetrafluoroborate[5]† in nitromethane reacted with the diester (**3**) to give the allyl sulphide (**6**) in 80% yield, probably accompanied by its *cis* isomer (10%), which we did not isolate. The allyl sulphide (**6**) could be converted into the allyl alcohol (**7**) (50%) using Evans' procedure.[6] These reactions demonstrate how easily allyl alcohols and allyl sulphides, themselves versatile intermediates in organic synthesis, can be made from allyl silanes.

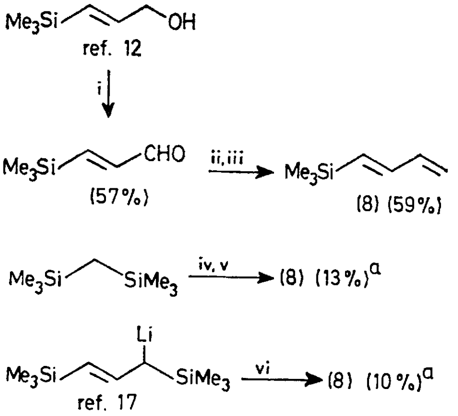


Reagents: i, p-$MeC_6H_4SO_3H$–C_6H_6 (reflux); ii, $MeCO_3H$–Et_2O (room temperature); iii, $PhSBF_4$–$MeNO_2$ (0° C); iv, $NaIO_4$–$MeOH$–H_2O; v, $(MeO)_3P$–$MeOH$.

Our reactions and the reactions with carbon electrophiles cited earlier show that allyl silanes do, as has long been suggested,[7] react with electrophiles to give substitution with allylic rearrangement in the sense shown in Scheme 1.

This type of electrophilic substitution is normal for allyl metal compounds;[8] the advantages of using allyl silanes rather than other allyl metal compounds are, firstly, that allyl silanes are compatible with many functional groups and many reaction conditions, and, secondly, that the [1,3]-allylic rearrangement is slow with allyl silanes at ordinary reaction temperatures.[9] There is therefore little risk that an allyl silane, once made, will isomerise by a [1,3]-sigmatropic rearrangement, a common reaction with metallic elements like lithium and magnesium.[10]

The 1-trimethylsilylbutadiene (**8**) used in this work was made by several new routes (Scheme 2). Previously, it has been made by hydrosilation of vinyl acetylene.[11] The new routes are designed to be adaptable to the synthesis of substituted analogues.



SCHEME 2. i, MnO_2; ii, Me_3SiCH_2MgCl (ref. 13); iii, p-MeC_6H_4-SO_3H–Et_2O (ref. 14); iv, $BuLi$–$Me_2NCH_2CH_2NMe_2$–Et_2O (ref. 15); v, $CH_2{=}CHCHO$ (ref. 16); vi, HCHO (ref. 16).

[a] Much better yields were obtained when other aldehydes were used.

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