# The Mechanism of the Protodesilylation of Allylsilanes which are Disubstituted on C-3 †

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3,3-Dialkylallylsilanes react with protons by two delicately balanced mechanisms. The allylsilane (5) reacts directly by protonation on C-3 of the allyl group, followed by loss of the silyl group. On the other hand, the allylsilanes (7) and (10) react, at least in part, by protonation on C-2, followed by hydride shift and loss of the silyl group. The overall result is the same, but the different pathways were revealed by using a deuteron in place of the proton.

ALLYLSILANES with the substitution pattern (1) usually react with electrophiles in the general sense expected of an allylsilane (1)→(4a).[1] Deleris and his co-workers [2] have calculated that the silylmethyl group of (1) polarises the π-bond more than the two methyl groups do, with the result that both the HOMO coefficient and the net charge on C-3 are greater than on C-2. The σ^+ value for a silylmethyl group is approximately twice that of a methyl group,[3] so the polarisation of the π-bond in (1) can be expected, on these empirical grounds too, to be fairly evenly balanced. It is not too disturbing, therefore, that an electrophile appears to attack at the more-substituted end of the double bond faster than at the less-substituted end. However, it is possible that the initial reaction is a rapid and reversible attack of the electrophile (1)⇌(2) at the less-substituted end of the double bond, and only the irreversibility of the step (3a) →(4a) causes the reaction to take this path eventually. It is also possible that the cation (2) is an *intermediate* in the formation of the final product (4a), since rearrangement (2)→(3a) is a plausible step, for which there is some precedent.[4]


(1)   (3a)   (4a)

(2)   (3b)   (4b)

(5)   (6)
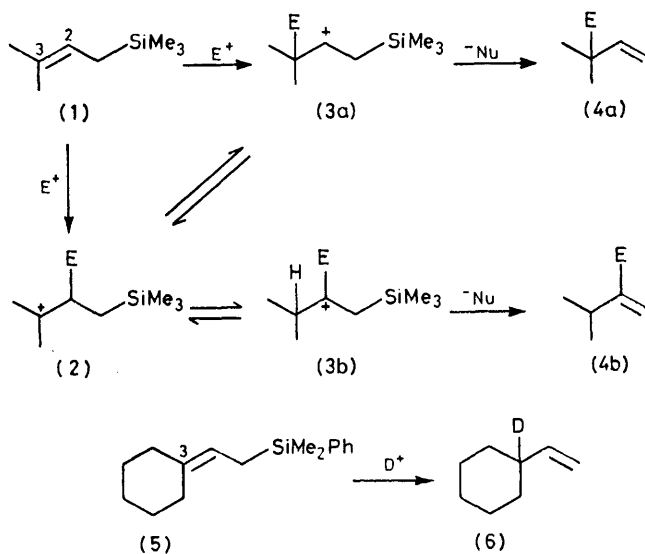
Because of our interest in allylsilane chemistry [1] and in silicon-controlled carbonium-ion rearrangements,[4] we have investigated this type of reaction using the deuteron

† No reprints available.

as an electrophile. We find that the allylsilane (5) reacts with deuteriated trifluoroacetic acid to give the vinylcyclohexane (6). Within the limits of n.m.r. integration, only the methine signal was reduced in intensity, and there was no sign in the low-voltage mass spectrum of any polydeuteriation. This reaction evidently takes the simple course corresponding to the path (1)→(3a)→(4a), just as Deleris and his co-workers had predicted. However, simply by changing the ring size, we can upset this picture. The allylsilane (7) reacted with deuteriated trifluoroacetic acid to give a mixture of the vinylcyclopentanes (8) and (9), in nearly equal amounts. Integration of the internal vinyl signal and of the methine signal in the 400 MHz spectrum gave a ratio of 52 : 48; the mass spectrum again showed the presence of only one deuterium atom. Evidently the reaction has not taken the simple course corresponding to (1)→(3a)→ (4a), nor is the step corresponding to (1)⇌(2) simply a reversible side-reaction. There are three possibilities. (i) The deuteron has attacked initially at C-2, and rearrangement has taken place in the sense (2)→(3a) + (3b) →(4a) + (4b), with a negligible isotope effect. The kinetic isotope effect k_H/k_D in rearrangements is usually in the range 1.5—3,[5] so this possibility seems unlikely to be the whole story. (ii) The deuteron has attacked competitively at C-2 and C-3, and there has then been rapid equilibration in the sense (3a)→(2)→(3b). The near equality in the amounts of (8) and (9) is consistent with this possibility. (iii) The reaction has taken the indirect course in the sense (1)→(2)→(3a) + (3b)→(4a) + (4b), and there is either incomplete equilibration in the sense (3a)⇌(2)⇌(3b) or some of the reaction takes the direct course in the sense (1)→(3a)→(4a) in competition with the indirect course. Acylation of the allylsilane (7) gave the anomalous product (10). This type of reaction is not unprecedented for allylsilanes,[6] and supports the idea that some at least of the initial attack takes place at C-2 of the allylsilane (7). It seems reasonable that the change of ring-size should encourage the attack by the electrophiles at the less-substituted end of the double bond: cyclopentyl cations are usually formed faster than the corresponding cyclohexyl cations.[7]
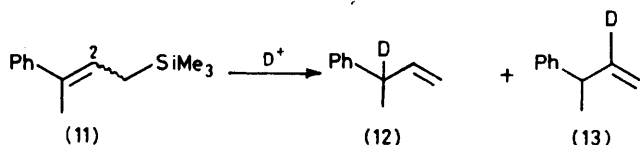
Finally, deuteriodesilylation of the allylsilane (11) gave the 1-methylallylbenzenes (12) and (13). This time, a fairly accurate estimate of the proportion of each was possible using the ^2H n.m.r. spectrum, where signals

of the deuterium in (12) and (13) were in the ratio 40 : 60. In this case, the ratio shows that at least some of the reaction has taken the course corresponding to (1)→(2)→ (3b)→(4) and that equilibration in the sense (3a)⇌(2)⇌ (3b), if it is taking place at all, is incomplete. In this
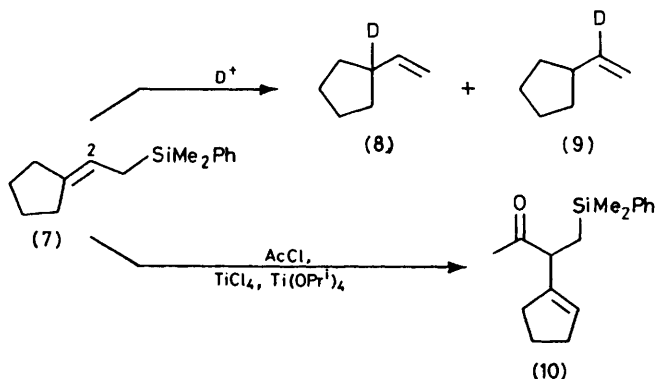
case, there was a small amount (<20%) of $^2H_2$ product, but the ^2H n.m.r. spectrum showed that the extra deuterium was largely in the methyl group.

The allylsilane (10) was prepared by the method of Seyferth and his co-workers,[8] using the appropriate Wittig reaction on acetophenone. Although this method gave good yields with cyclohexanone,[8,9] it was very poor with cyclopentanone.[9,10] The allylsilane (7) was therefore made by the new route, which we have reported elsewhere, using our phenyldimethylsilylcuprate reagent

and the appropriate allylic acetate.[11] The allylsilane (5) was made by a similar method. We used it, rather than its known [8,9] trimethylsilyl analogue, in order to ensure that the pattern of deuterium incorporation had nothing to do with the presence of a phenyl group in (7).

EXPERIMENTAL

The Deuteriodesilylations.—The allylsilanes (5) and (7) (0.30 mmol) and trifluoro[^2H]acetic acid (^2H-TFA) (0.30 mmol) were kept in carbon tetrachloride (0.5 ml) at room temperature for 20 h (5) and 2.5 h (7). An aqueous work-up and distillation gave the alkenes, which were identified by ^1H n.m.r. and mass spectrometry. The reactions appear to be essentially quantitative, but the products are too volatile for an accurate yield. The allylsilane (11) (1 mmol) and ^2H-TFA were kept in carbon tetrachloride containing boron trifluoride–diethyl ether (1 mmol) at room temperature for 2 min. Aqueous work-up and column chromatography (SiO$_2$, light petroleum) gave the alkenes (12) and (13) (75%), the n.m.r. spectrum for which was identical with that reported [12] except for the effect of the deuterium. Integration of the ^1H n.m.r. spectrum confirmed that the ratio of (12) : (13) was 40 : 60 (Found M^+, 133.1017, $C_{10}H_{11}D$ requires M,

133.1017), m/z 134 (8%, $^2H_2$-M^+), 133 (35, $^2H_1$-M^+), and 132 (42, $^2H_2$-M — ^2H or $^2H_1$-M — H).

3-Cyclopent-1-enyl-4-dimethyl(phenyl)silylbutan-2-one (10). —The allylsilane (7)[11] (0.46 g, 2 mmol) in dichloromethane (30 ml) was added to a mixture of titanium tetrachloride (0.8 mmol) and titanium tetraisopropoxide (1.6 mmol) and acetyl chloride (2 mmol) under nitrogen at −78 °C. After 4 h at this temperature, an aqueous work-up and preparative t.l.c. gave the *ketone* (10) (0.38 g, 65%) as an oil (Found: C, 75.3; H, 8.9. $C_{17}H_{24}OSi$ requires C, 75.2; H, 8.8%), $\nu_{max.}$ (film) 1 715 (CO), 1643 (C=C), and 1 250 cm^{-1} (SiMe); δ(CCl$_4$) 7.1—7.6 (5 H, m, Ph), 5.50 (1 H, m, =CH), 3.35 (1 H, t, J 7 Hz, CHCH$_2$), 1.5—2.65 (9 H, m, overlaid by a singlet at 2.00, CH$_2$'s and COMe), 1.45 (1 H, dd, J 16 and 7 Hz, CH$_A$H$_B$), 1.05 (1 H, dd, J 16 and 7 Hz, CH$_A$H$_B$), and 0.40 (6 H, s, SiMe$_2$) (Found: M^+, 272.1577. $C_{17}H_{24}OSi$ requires M, 272.1597).

2-Phenyl-4-trimethylsilylbut-2-ene (11).—Acetophenone (1.20 g, 10 mmol) was treated with the ylide following the method of Seyferth *et al.*[8] as modified by Paterson.[9] The *allylsilane* was purified by column chromatography (SiO$_2$, light petroleum) to give a mixture of stereoisomers (0.92 g, 45%), $\nu_{max.}$ (film) 1 638 (C=C), 1 603 (Ar), and 1 250 cm^{-1} (SiMe); δ(CCl$_4$) 7.12 (5 H, m, Ph), 5.74 (1 H, t, J 8 Hz, =CH of E-isomer), 5.36 (1 H, t, J 8.5 Hz, =CH of Z-isomer), 1.88 (3 H, s, Me), 1.53 (2 H, d, J 8 Hz, CH$_2$ of E-isomer), 1.30 (2 H, d, J 8.5 Hz, CH$_2$ of Z-isomer), −0.07 (9 H, s, SiMe$_3$ of E-isomer), and −0.20 (9 H, s, SiMe$_3$ of Z-isomer) (Found: M^+, 204.1323. $C_{13}H_{20}Si$ requires M, 204.1312), m/z 204 (5%, M^+), 189 (1, M — Me), and 73 (100, SiMe$_3$).

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