

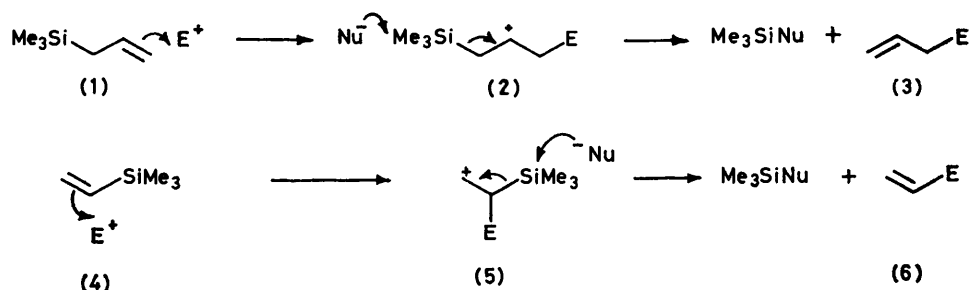
The Mechanism of the Protodesilylation of Allylsilanes and Vinylsilanes †

By Ian Fleming* and Jennifer A. Langley, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The protodesilylation of either 1-dimethyl(phenyl)silyl-3-trimethylsilylpropene (15) or its isomer, 1-trimethylsilyl-3-dimethyl(phenyl)silylpropene (16), gave the same, *ca.* 4 : 1, mixture of allylsilanes, 3-dimethyl(phenyl)silylpropene (18) and 3-trimethylsilylpropene (19), showing that a cationic intermediate (17) is involved in both reactions.

ALLYLSILANES (1) and vinylsilanes (4) almost always react with electrophiles in the sense shown in Scheme 1. It is helpful in understanding the site of electrophilic attack in these compounds to postulate the formation of

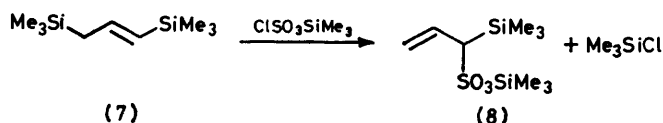
hypervalent intermediate (14), so that the C-S bond-forming step (14, arrows) can be intramolecular. Wetter, Scherer, and Schweitzer³ have recently found in a most elegant experiment that allylsilanes undergo acylation



SCHEME 1

cations (2) and (5) as intermediates. These cations should be formed because each of them is stabilised by overlap of the Si-C bonding orbital with the empty *p* orbital of the cation. Furthermore, the outcome is controlled by the loss of the silyl group (2) \rightarrow (3) and

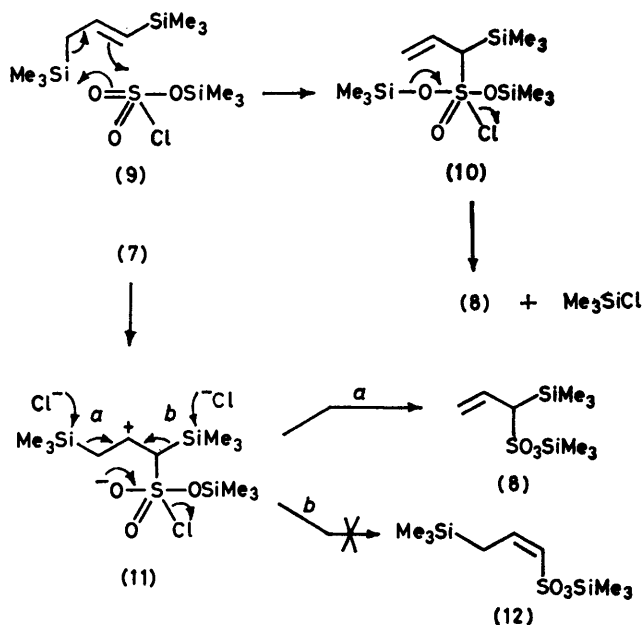
(5) \rightarrow (6). However, although allylsilanes and vinylsilanes behave well in this sense,¹ there is little evidence for free cations as intermediates.



SCHEME 2

(5) \rightarrow (6). However, although allylsilanes and vinylsilanes behave well in this sense,¹ there is little evidence for free cations as intermediates.

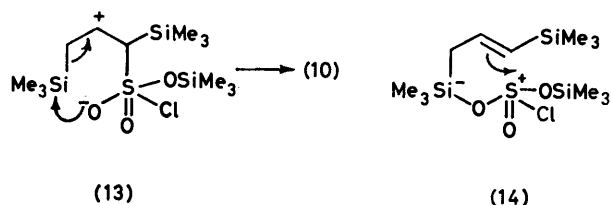
The silane (7) is both an allyl- and a vinyl-silane, yet it reacts with trimethylsilyl chlorosulphonate only as an allylsilane as in Scheme 2.² At one extreme, this could mean that the key step is a concerted reaction in the sense (9) \rightarrow (10). At the other extreme, it could mean that a free cation (11) is an intermediate, but, since it is unsymmetrical, it can choose to lose one of the silyl groups (11) \rightarrow (8) faster than the other (11) \rightarrow (12). Indeed, intramolecular participation by the sulphonyl group in that process (13, arrows) \rightarrow (10) makes it quite likely for that silyl group to be lost, and such participation represents a merging of the extreme mechanisms. Another plausible intermediate mechanism is to have the chlorine or oxygen of the electrophile bonded to the silyl group in a rapidly and reversibly formed



We considered that one electrophile at least might be different. Simple protonation of the silane (7) would give a symmetrical cation, and, if such a cation were an

† There are no reprints of this paper.

intermediate, both silyl groups should be lost to an equal extent. We have now tested this possibility, and find it to be borne out—there is no measurable degree of con-



certedness in the protodesilylation of allylsilanes of this type.

RESULTS AND DISCUSSION

We prepared the allylsilanes (15) and (16) by appropriate modification of the method of Corriu, Masse, and Samate.⁴ Protodesilylation took place with a variety of acids (Table), and in each case the two products (18) and (19) were formed in the same ratio (between 3.5 : 1 and 4.3 : 1, depending upon the nucleophile present) regardless of which allylsilane (15) or (16) was used. This strongly argues that the cation (17) is an intermediate in both cases, and that the trimethylsilyl group is lost about four times faster than the dimethyl(phenyl)silyl group. The only plausible alternative is that the allylsilanes (15) and (16) are rapidly interconverted in acid before protodesilylation occurs. This possibility was ruled out by two experiments. In one, we used a deficiency of acid with each of the allylsilanes (15) and

Clearly the protodesilylation of these allylsilanes involves a true intermediate (17), and the loss of either silyl group is faster than the loss of a proton.

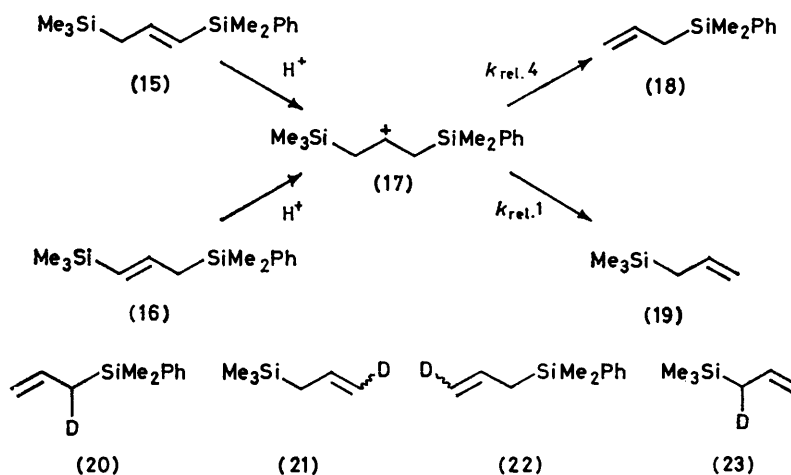
Reactions of the allylsilanes (15) and (16) with acids

Starting material	Acid	t_1^a	Ratio of (18) : (19)
(15)	AcOH	No reaction after 5 days	
(16)	AcOH	No reaction after 5 days	
(15)	$\text{ClCH}_2\text{CO}_2\text{H}$	10.5 h	3.5 ± 0.5^b
(16)	$\text{ClCH}_2\text{CO}_2\text{H}$	10.5 h	3.5 ± 0.5^b
(15)	$\text{Cl}_2\text{CHCO}_2\text{H}$	10 min	3.5 ± 0.5^b
(16)	$\text{Cl}_2\text{CHCO}_2\text{H}$	10 min	3.5 ± 0.5^b
(15)	$\text{CF}_3\text{CO}_2\text{H}$	<1 min	3.7 ^c
(16)	$\text{CF}_3\text{CO}_2\text{H}$	<1 min	3.6 ^c
(15)	25% BF_3 in $\text{CH}_3\text{CO}_2\text{H}$	<1 min	4.3 ^c
(16)	25% BF_3 in $\text{CH}_3\text{CO}_2\text{H}$	<1 min	4.3 ^c

^a Very approximate results for solutions ca. 0.5M in each reagent in CDCl_3 at 26.5 °C. ^b Determined by n.m.r. ^c Determined by g.l.c.

EXPERIMENTAL

3-Dimethyl(phenyl)silylpropene (18) and *3-Trimethylsilylpropene* (19).—These compounds were prepared by the methods of Topchiev and his co-workers,⁵ and of Sommer, Tyler, and Whitmore,⁶ respectively, in 62.5% and 31% yields. Compound (18): $\delta(\text{CDCl}_3)$ 7.75—7.35 (5 H, m, Ph), 5.83 (1 H, ddt, J 8, ca. 9, and ca. 15 Hz, $\text{CH}_2\text{CH}=\text{C}$), 5.01 (1 H, dd, J ca. 2 and ca. 15 Hz, *trans*- $\text{CH}=\text{CH}_\text{A}\text{H}_\text{B}$), 4.95 (1 H, dd, J ca. 2 and ca. 9 Hz, *cis*- $\text{CH}=\text{CH}_\text{A}\text{H}_\text{B}$), 1.85 (2 H, d, J 8 Hz, $\text{CH}_2\text{CH}=\text{C}$), and 0.37 (6 H, s, SiMe_2). (19): $\delta(\text{CDCl}_3)$ 5.74



(16). In both cases, we recovered the allylsilanes unchanged. In the other, we used deuterated trifluoroacetic acid and examined the products by ^1H n.m.r., from which we deduced that the allylsilane (15) gave the monodeuteriated silanes (20) and (21), and the allylsilane (16) gave the monodeuteriated silanes (22) and (23). Finally, from a competition experiment, we find that the two allylsilanes (15) and (16) react at very similar rates, with, if anything, (16) reacting slightly faster (about 10%).

(1 H), 4.88 (1 H), 4.80 (1 H), 1.50 (2 H), and 0.0 (9 H, SiMe_3), with identical coupling constants to those of the corresponding hydrogens in (18).

1-Dimethyl(phenyl)silyl-3-trimethylsilylpropene (15).—3-Dimethyl(phenyl)silylpropene (18) (3.32 g, 20 mmol) was added dropwise to a stirred mixture of tetramethylethylenediamine (TMEDA) (3.5 ml, 23 mmol) and *n*-butyllithium (15 ml of a 1.5M solution in hexane, 22.5 mmol) under nitrogen at -5°C , and the mixture kept at -5°C for 3.25 h. Chlorotrimethylsilane (2.54 ml, 20 mmol) was added dropwise and the mixture kept at -5°C for 1 h, and then

poured into aqueous hydrochloric acid (20 ml, 1M) and extracted with hexane. The extract was washed with hydrochloric acid (20 ml) and water (20 ml), dried (MgSO₄), and evaporated *in vacuo*. The residue was distilled to give the silane (15) (3 g, 67%), b.p. 66–68 °C at 0.1 mmHg (Found: C, 67.8; H, 9.5. C₁₄H₂₄Si₂ requires C, 67.6; H, 9.75%), *R_F*[light petroleum (b.p. 60–80 °C)] 0.45; δ(CDCl₃) 7.6–7.24 (5 H, m, Ph), 6.15 (1 H, dt, *J* 18 and 8 Hz, CH₂CH=CH), 5.79 (1 H, dt, *J* 18 and 1 Hz, CH₂CH=CH), 1.70 (2 H, dd, *J* 8 and 1 Hz, CH₂), 0.33 (6 H, s, SiMe₂Ph), and 0.03 (9 H, s, SiMe₃); ν_{max} (film) 1 615 (Ph) and 1 258 cm⁻¹ (SiMe).

3-Dimethyl(phenyl)silyl-1-trimethylsilylpropene (16).—3-Trimethylsilylpropene (19) (3.6 g, 31.8 mmol) was metalated with butyl-lithium as described above, and treated with a 1 : 2 mixture of bromo- and chloro-dimethyl(phenyl)silane⁷ (4.77 g, 32 mmol). Work-up and distillation gave the silane (16) (5.44 g, 69%), b.p. 76–80 °C at 0.4 mmHg (Found: C, 67.4; H, 9.7. C₁₄H₂₄Si₂ requires C, 67.6; H, 9.75%), *R_F*[light petroleum (b.p. 60–80 °C)] 0.45; δ(CDCl₃) 7.58–7.28 (5 H, m, Ph), 6.04 (1 H, dt, *J* 18 and 7.5 Hz, CH₂CH=CH), 5.45 (1 H, d, *J* 18 Hz, CH₂CH=CH), 1.88 (2 H, dd, *J* 7.5 and 1 Hz, CH₂), 0.3 (6 H, s, SiMe₂), and 0.05 (9 H, s, SiMe₃); ν_{max} (film) 1 605 (Ph) and 1 250 cm⁻¹ (SiMe).

Reactions of (15) and (16) with Acid.—Typically, the acid (0.25 mmol) in deuteriochloroform (0.5 ml) was added to the silane (15) or (16) (0.25 mmol) in an n.m.r. tube, the mixture shaken, and examined periodically by ¹H n.m.r. When reaction was complete (Table), the solution showed all the signals of the n.m.r. spectra of the two allylsilanes (18) and (19) in a ratio, determined from the methylene group doublets at 1.85 (18) and 1.5 (19) of *ca.* 4 : 1. G.l.c. analyses (Table) were the averages of three injections, and are corrected for response factors. The column was 15% silicon grease, 1/8 in × 12 ft, with the temperature programmed to rise after 5 min at 60 °C by 20 °C min⁻¹ to a maximum of 200 °C, with nitrogen as the carrier gas. Retention times were (18), 12.65 min and (19), 3.33 min.

Reaction of (15) and (16) with Deuteriated Acid.—A solution of (15) (1.0 g, 4 mmol) in deuteriochloroform (2 ml) was added to deuteriated trifluoroacetic acid (0.46 g, 4 mmol). The mixture was stirred at room temperature for 5 min, washed with sodium carbonate solution (2N), and water, dried (MgSO₄), and distilled to give the deuteriated allylsilane (21) and deuteriochloroform in one fraction (b.p. 65–67 °C) and the deuteriated allylsilane (20) (b.p. 45–47 °C at 0.05 mmHg) in another. The ¹H n.m.r. spectrum of (20) showed the doublet at δ 1.85 halved in intensity and that of (21) showed the multiplet at δ 4.7–4.9 halved in intensity, and appropriate changes elsewhere in the spectra. In a

closely similar reaction, (16) (1 g, 4 mmol) gave the deuteriated allylsilane (23) and deuteriochloroform (b.p. 65–67 °C) and the deuteriated allylsilane (22) (b.p. 55–56 °C at 0.1 mmHg). The ¹H n.m.r. spectrum of (22) showed the multiplet at δ 4.85–5.05 halved in intensity and that of (23) showed the doublet at δ 1.5 halved in intensity, and appropriate changes elsewhere in the spectra.

Reaction of (15) and (16) with a Deficiency of Trifluoroacetic Acid.—A solution of (15) (302 mg, 1.2 mmol) in deuteriochloroform (1.5 ml) was added to trifluoroacetic acid (62 mg, 0.54 mmol). The mixture was stirred at room temperature for 5 min, washed with sodium carbonate solution (2N), dried (MgSO₄), and evaporated *in vacuo*. The residue was purified by t.l.c. eluting with light petroleum (b.p. 60–80 °C). The band with *R_F* 0.45 (SiO₂) was a mixture of (15) and (18) (n.m.r.) with no sign of the doublet at δ 1.88 characteristic of (16). A closely similar reaction with (16) (296 mg, 1.2 mmol) gave a mixture containing (16) and (18) (n.m.r.) with no sign of the doublet at δ 1.70 characteristic of (15).

Reaction of a Mixture of (15) and (16) with Trifluoroacetic Acid.—A solution of (15) (400 mg, 1.6 mmol) and (16) (400 mg, 1.6 mmol) in deuteriochloroform (2 ml) was added to trifluoroacetic acid (177 mg, 1.55 mmol). The mixture was stirred at room temperature for 5 min, and then subjected to preparative g.l.c. using a 30% Carbowax 20M on 60–80 Chromosorb column, 3/8 in × 20 ft, at 190 °C, using hydrogen as the carrier gas. The unreacted starting materials (retention time, 7.6 min) were collected together and examined by n.m.r. The integrations for the peaks at δ 6.15(15) and 6.04(16), at δ 5.79(15) and 5.45(16), and at δ 1.70(15) and 1.88(16) averaged at 1.1 : 1.

We thank the S.R.C. for a maintenance award (to J. A. L.).

[0/1477 Received, 29th September, 1980]

REFERENCES

- 1 T. H. Chan and I. Fleming, *Synthesis*, 1979, 761.
- 2 M. Grignon-Dubois, J.-P. Pillot, J. Dunoguès, N. Duffaut, R. Calas, and B. Henner, *J. Organomet. Chem.*, 1977, **124**, 135.
- 3 H. Wetter, P. Scherer, and W. B. Schweizer, *Helv. Chim. Acta*, 1979, **62**, 1985.
- 4 R. J. P. Corriu, J. Masse, and D. Samate, *J. Organomet. Chem.*, 1975, **93**, 71.
- 5 A. V. Topchiev, N. S. Nametkin, T. I. Chernyshev, and S. G. Durgar'yan, *Dokl. Akad. Nauk, SSSR*, 1956, **110**, 97 (*Chem. Abstr.*, 1957, **51**, 4979).
- 6 L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *J. Am. Chem. Soc.*, 1948, **70**, 2872.
- 7 K. Andrainov and N. V. Delazari, *Dokl. Akad. Nauk, SSSR*, 1958, **122**, 393 (*Chem. Abstr.*, 1959, **53**, 2133).