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Cationic rearrangements controlled by the presence of a silyl group

Alain Chénedé [a], Ian Fleming [a,*], Roger Salmon [b], Mark C. West [a]

[a] Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK
[b] Syngenta, Jealott's Hill International Research Centre, Bracknell, Berkshire RG42 6EY, UK

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Abstract

1,1-Disilylcarbinols having two alkyl groups on the adjacent carbon atom react with thionyl chloride in sulfur dioxide to give the product in which one of the alkyl groups has migrated towards the two silyl groups, and one of the silyl groups has been removed from the resultant cation. The reaction is seen in ring-expansion, as in the conversion of cyclohexylbis[dimethyl(phenyl)silyl]carbinol (**7**) into 1-dimethyl(phenyl)silylcycloheptene (**11**), and in open chains, as in the conversion of 1,1-bis[dimethyl(phenyl)silyl]-2-methylpropanol (**26**) into (*E*)- and (*Z*)-2-dimethyl(phenyl)silylbut-2-ene (**27**). Phenyldimethylsilyllithium reacts with pinacolone to give the α-silyl carbinol (**44**), which rearranges in the same way to give 2,3-dimethylbut-2-ene (**46**), effectively achieving a pinacolone-to-pinacol rearrangement.

Keywords: Wagner-Meerwein; Vinylsilane; Allylsilane; 1,1-Disilylcarbinol; α-Silyl carbocation; β-Silyl carbocation

1. Introduction

We described some years ago how a strategically placed silyl group could be used to control the outcome of cationic rearrangements of γ-silyl alcohols in the general sense illustrated as **1**→**2**→**3** in Scheme 1 [1]. In that work, the silyl group caused the substituent R to *move away* from the silyl group **1**→**2** in order to create a cation stabilised by the β-silicon effect. The outcome was also controlled, because the silyl group was the preferred electrofugal group **2**→**3**, determining the site of the double bond. Using this device, we showed that the cationic rearrangements of phosphonyl, phenylthio, hydride, aryl and alkyl groups could be controlled. In this article, we describe how two silyl groups placed on the carbinol carbon can control cationic rearrangements in the general sense **4**→**5**→**6**, in which alkyl or aryl groups R move *towards* the silyl group in order to create a cation **5** stabilised by the β-effect.

Migration of hydride [2] and other groups [3] towards an α-silyl cation or its equivalent has been seen occasionally by others, and we suspected that it was involved in the pathway by which a terminal vinylsilane with only one silyl group was produced as a byproduct when we dehydrated alcohols of the type 4 in which one or both of the R groups was a hydrogen atom [4]. A carbene pathway has been suggested for the purely thermal reaction of this type [5], but in our work we usually used thionyl chloride in pyridine, at room temperature or below, which makes that pathway unlikely. The present work was undertaken to see if we could make rearrangement the major pathway when both R groups were alkyl.

2. Results and discussion

We studied most carefully the reaction of the disilyl alcohol **7**, prepared from cyclohexylcarbonyl chloride

* Corresponding author. Tel.: +44-1223-33-6372; fax: +44-1223-33-6362.
E-mail address: if10000@cam.ac.uk (I. Fleming).

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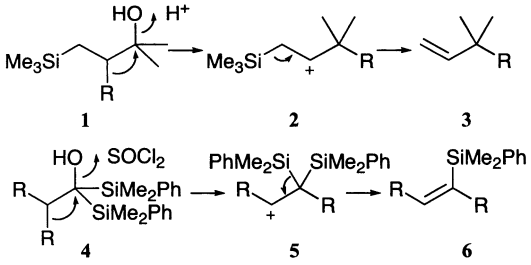


Scheme 1.

with an excess of phenyldimethylsilyllithium [6]. We tried a wide range of the reagents commonly used for the dehydration of alcohols, but a surprising number of them, including such obvious candidates as methanesulfonyl chloride, Burgess's reagent and Martin's sulfurane, had no effect, and the alcohol **7** was recovered unchanged under all conditions mild enough to isolate any recognisable products. The most promising exceptions were thionyl chloride, thionyl diimidazole, and phosphorus oxychloride. These reagents can be expected to encourage the formation of the cation **8**, which may or may not be a discrete intermediate, and hence the formation of either of the rearranged cations **9** from ring-expansion or **10** from hydride shift. The chloride ion released from the thionyl chloride can be expected to remove selectively the silyl group from these cations, leading to such products as **11** and **13**, and the nitrogen-based counterion released from thionyl diimidazole can be expected to remove selectively a proton, leading to such alkenes as **12** and **14**. Another possible product would follow from the loss of the ring proton in the cation **8** (or the exocyclic proton in the cation **10**), leading to an exocyclic alkene with two silyl groups attached. Although we saw each of the alkenes **11**–**14**, we found none of the exocyclic alkene with two silyl groups. There cannot have been much of it present, but we cannot be completely sure that it was absent, since it would not have any distinctive protons with which to characterise it in the ^{1}H-NMR spectra of the mixtures we obtained, and we were unable to make an authentic sample to make identification easier.

We record in Table 1 the yields of the products under the various conditions that we tried for these three reagents. The major products in almost every case were the skeletally rearranged vinylsilane **11** and the product of hydride shift, the exocyclic vinylsilane **13**. The ratio of skeletally rearranged to unrearranged product was affected by solvent polarity, with skeletal rearrangement encouraged in the more polar solvents, as shown by entries 1–7. To our surprise, the expectation that the absence of a halide counterion would lead to more proton loss was not fulfilled: the products in entry 8 are the same as those in entry 4, and in much the same ratio. The deliberate addition of halide ion to the imidazole-containing reaction in entry 9 merely changed the ratio in favour of the exocyclic vinylsilane **13**. Phosphorus oxychloride in pyridine (entry 11) needed a much higher temperature to induce elimination, and the surprising product, in low yield, but which we saw otherwise only in even smaller amounts, was the allyldisilane **14**.

Because all the reactions in entries 1–10 gave mixtures of at least two products, we were inclined at this stage to think that the reaction had very limited potential in organic synthesis. Furthermore, the total yield was rarely outside the 40–60% range, and we were unable to find the lost mass, indicating perhaps that both silyl groups had been removed to some extent. The breakthrough came when we discovered that *reactions carried out in sulfur dioxide as the solvent* (entries 12–14), although still not giving a high yield, *were cleanly in*

Table 1
Yields of alkenes **11**–**14** from the 1,1-dislylcarbinol 7 (Scheme 2)

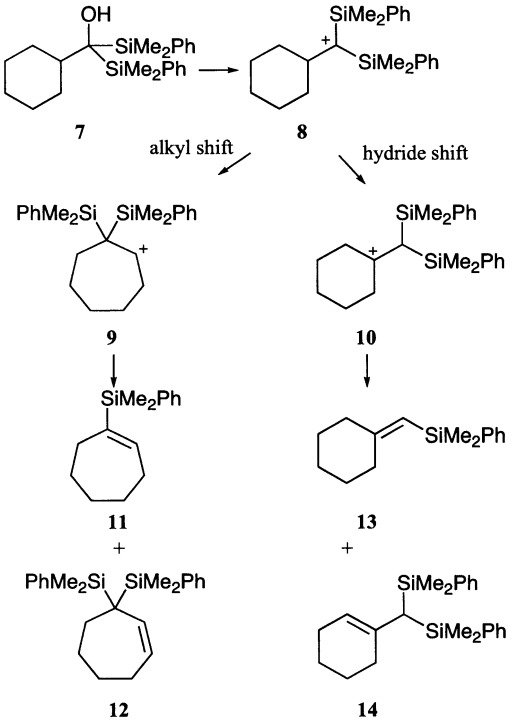
Entry	Reagents and conditions	**11** Yield (%)	**12** Yield (%)	**13** Yield (%)	**14** Yield (%)
1	$SOCl_2$, Py, MeCN, r.t.	33	-	5	-
2	$SOCl_2$, Py, CH_2Cl_2, r.t.	32	-	18	-
3	$SOCl_2$, $CDCl_3$, r.t.	37	-	13	-
4	$SOCl_2$, Py, THF, r.t.	15	-	25	-
5	$SOCl_2$, Py, Et_2O, r.t.	9	-	37	-
6	$SOCl_2$, Py, toluene, r.t.	8	-	30	-
7	$SOCl_2$, Py, CCl_4, r.t.	8	-	52	-
8	$SOIm_2$, THF, r.t.	21	-	38	-
9	$SOIm_2$, LiCl, THF, r.t.	17	-	50	-
10	$SOIm_2$, Et_2O, r.t.	10	5	31	-
11	$POCl_3$, Py, 110 °C	-	-	-	20
12	$POCl_3$, Py, SO_2, 10 °C	50	-	-	-
13	$SOCl_2$, Py, SO_2, 10 °C	70	-	-	-
14	$SOIm_2$, Py, SO_2, 10 °C	68	-	-	-

Determined by integration of characteristic signals in the ^{1}H-NMR spectra using an internal standard (CH_2I_2) added in weighed amounts to the crude product. Yields of 1% or less are entered as a hyphen.

favour of the more interesting product, the skeletally rearranged vinylsilane **11**.

We also carried out a reaction on the bistrimethylsilyl analogue of the disilylcarbinol **7** using thionyl chloride and pyridine in sulfur dioxide, and obtained a 65% yield of 1-trimethylsilylcycloheptene, analogous to the vinylsilane **11**. Using other substrates, we found mixtures of products in most solvents, similar to the results in entries 1–10 in Table 1, but predominantly one in sulfur dioxide, similar to the results in entries 12–14. Selections [7] of our results for candidates for ring-expansion are shown in Scheme 3, and for candidates for open-chain rearrangements in Scheme 4. Although not all of our results are illustrated, we saw the same trends in both sets as we had seen in the reactions in Scheme 2: hydride shift was the major pathway in the less polar solvents, alkyl shift was the major pathway in the more polar solvents, and almost the only pathway in sulfur dioxide.

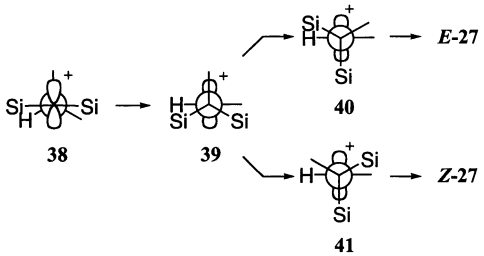
In Scheme 3, the cyclobutyldisilylcarbinol **20** was anomalous in giving in sulfur dioxide some of the product **22** of hydride shift, although the product of ring-expansion **21** was still the major product. Consistent with this result, the same reaction in dichloromethane gave a higher proportion than usual of the product of hydride shift **22**. The case of hydride shift in this case may be a consequence of the unusual stability of cyclobutyl cations. In contrast, the corresponding cyclopropyldisilylcarbinol **23** gave no product from hydride shift in any solvent, presumably because a cyclopropylmethyl cation is intrinsically much better stabilised than a cyclopropyl cation. The only problem, in this otherwise clean ring-expansion, was the formation of a little of the butadiene **25**, which might be the result of electrocyclic ring-opening of the major product, the cyclobutene **24**, or it might be a product from the homoallyl isomer of the cyclopropylmethyl cation.

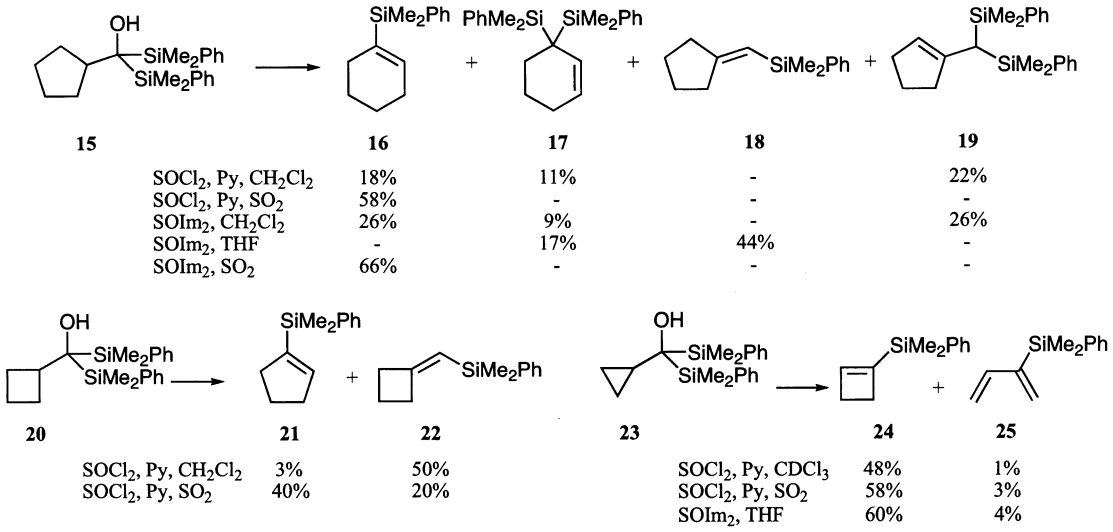


Scheme 2.

In the open-chain substrates in Scheme 4, it is perhaps noteworthy that the phenyl group migrates rather than the methyl in the alcohol **34**, as usual for cationic rearrangements, but the methyl group migrates rather than the isopropyl in the alcohol **31**, which is not the usual pattern. It seems likely that the migration of the larger group towards the relatively hindered cationic centre carrying two silyl groups may be inhibited.

Some of the products in Scheme 4 can be *E*- or *Z*-isomers, and in each case the major product was the *E*-isomer. The loss of the silyl group is almost certainly irreversible, and the products are unlikely to be able to equilibrate under these reaction conditions, suggesting that the *E*:*Z* ratio is kinetically controlled. On the whole, the proportion of *E*-isomer was greater in those reactions carried out in the less polar solvents, indicating that the first-formed conformations of the rearranged cations may not reflect the relative energies of the transition structures. If an α-silyl cation is formed in the first step from the alcohol **26**, it will have a conformation **38**, from which a methyl group can migrate suprafacially in the usual way to give a cation **39**. Although it is probably not a discrete intermediate, it is a useful simplification to think of it as such. This cation can change its conformation to increase the β-silicon effect by rotation about the central bond, clockwise to give the cation **40** or anticlockwise to give the cation **41**. The former is the lower-energy pathway, since the left hand silyl group has to eclipse briefly only the hydrogen atom, whereas in the latter the right hand silyl group has to eclipse briefly the methyl group. The cation **40** has the conformation suitable for giving the vinylsilane *E*-**27**. In sulfur dioxide, the cations can be expected to live longer, and so the ratio of the isomeric cations **40** and **41** can change more nearly to reflect their thermodynamic energies. In this way the proportion of the kinetically less-favoured cation **41** may build up, and hence account for the formation of mote of the vinylsilane *Z*-**27** in this and other polar solvents. It is

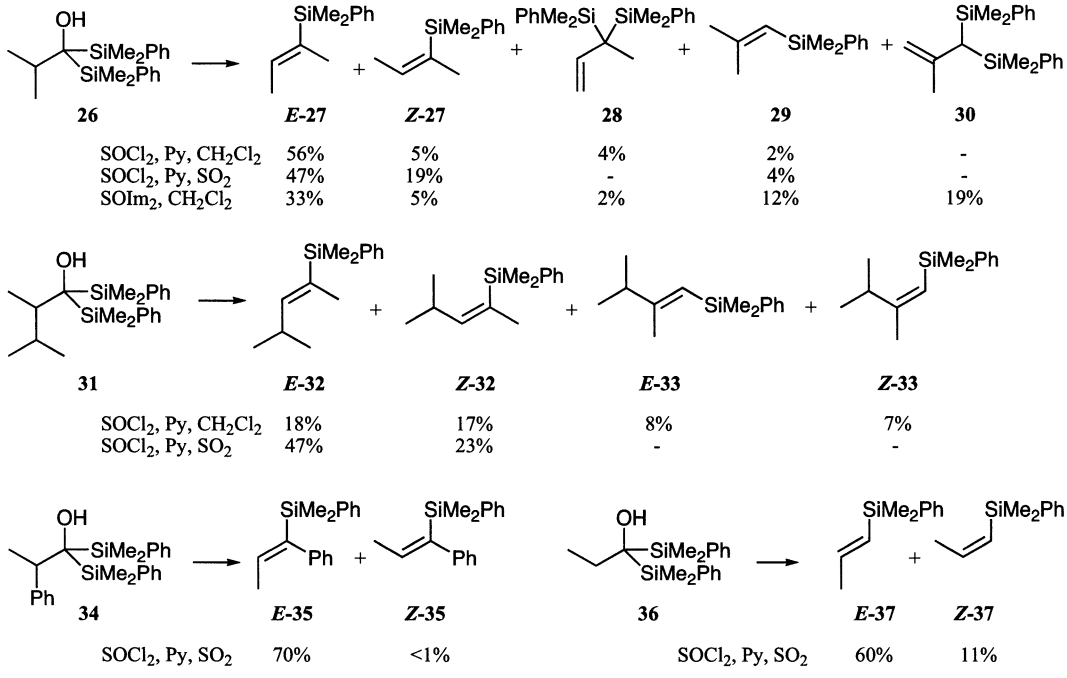




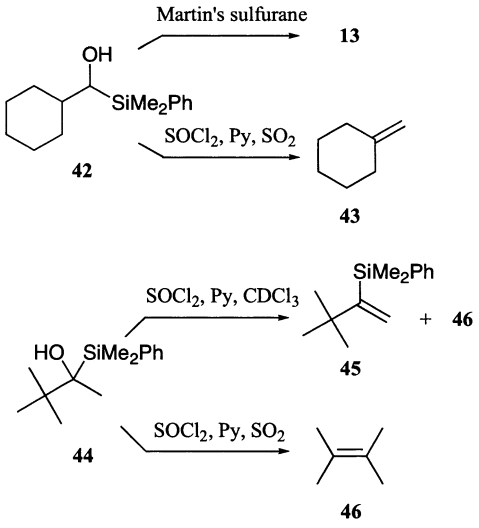
Scheme 3.

part of this argument that a silyl group, with its long C–Si bond, is not as big a steric encumbrance as its actual size might lead one to think, making it less obvious which of the two cations **40** or **41** is the lower in energy.

We also investigated briefly the possibility that one silyl group might still encourage migration towards it (Scheme 5). The α-silylcarbinol **42**, derived from the reaction of cyclohexanecarboxaldehyde and phenyldimethylsilyllithium, underwent simple dehydration with Martin's sulfurane to give the vinylsilane **13**, but with thionyl chloride in sulfur dioxide the major product, too volatile to measure the yield, appeared to be the product of hydride shift, the exocyclic alkene **43**. Had ring-expansion and silyl loss taken place the product would have been cycloheptene, but there were no signals in the ^{1}H-NMR spectrum of the crude product to indicate that this had been formed. More interesting was the α-silylcarbinol **44** derived from pinacolone in 69% yield. It



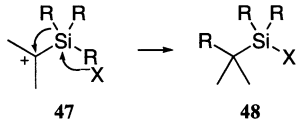
Scheme 4.



Scheme 5.

underwent simple dehydration to give the vinylsilane **45** with most reagents, but underwent relatively clean rearrangement with thionyl chloride in sulfur dioxide to give 2,3-dimethylbut-2-ene **46** in 23% yield when isolated as its dibromide. Since this alkene can be dihydroxylated to give pinacol [8], this reaction provides a pathway for a pinacolone-to-pinacol transformation, but more work is needed to raise the yield before it can be said to compete with the standard retro-pinacol rearrangement of pinacolyl alcohols to tetraalkylethylenes [9].

An alternative reaction of the general type **47**→**48**, in which a substituent migrates from the silyl group to the neighbouring electrophilic carbon, is a much better known pathway, but was not detectable in any of the work described here. This type of rearrangement is more often than not either a unimolecular, diotropic, and often gas-phase reaction [10], or one promoted by a nucleophilic 'push' from a fluoride ion [11], an alkoxide ion [12,13] or a powerful nucleophile already coordinated to the silyl group [14]. It is relatively rarely seen when it is initiated by electrophilic 'pull' from a well-developed carbocation [15], as in the work described here. With respect to the extent to which a cation α to a silyl group is stabilised, the consensus appears, both computationally [16] and experimentally [17], to be that a trialkylsilyl group is effectively more stabilising than a hydrogen atom, but less stabilising than a methyl group. Part of the apparent 'stabilisation,' in solvolysis studies at least, may be steric destabilisation of the starting materials [18], but, in any case, the effect is much less than β-stabilisation by a silyl group [19]. It seems likely from this evidence that the cation **8** is an intermediate.



3. Experimental

3.1. General

Infrared spectra were recorded on a Perkin–Elmer FT-IR 1600 spectrometer, using sodium chloride plates. NMR spectra were recorded on a Bruker Avance DPX 250 or a Bruker Ultrashield 400. Chemical shifts were measured relative to chloroform (^{1}H δ 7.25, ^{13}C δ 77.0). ^{13}C-NMR spectra taken using the APT protocol are labelled + for quaternary and methylene carbons, and − for methane and methyl carbons. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography was performed using plates coated with Kieselgel 60 PF_{254}. Ether and THF were distilled from lithium aluminium hydride immediately before use. Toluene, hexane, dichloromethane and acetonitrile were distilled from calcium hydride.

3.2. Synthesis of the 1,1-disilyl alcohols

Typically, the acid chloride (10 mmol) in toluene (5 cm^3) was added dropwise over 3 min to dimethyl(phenyl)silyllithium [20] (1 mol dm^{-3} solution in THF, 22 cm^3, 22 mmol) and toluene (20 cm^3) under nitrogen with vigorous stirring and cooling in a dry-ice acetone bath. After 0.5–1 h, the solution was poured into hexane (100 cm^3) and aqueous ammonium chloride solution, the organic layer separated, washed with hydrochloric acid (3 mol dm^{-3}, 30 cm^3) and with brine (30 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane–Et_2O) to give the 1,1-disilyl alcohols. In some cases the product was distilled (kugelrohr). The synthesis by this method and the characterisation of the alcohols **7** (94%), **15** (87%), **20** (72%), **26** (87%), **31** (62%), **34** (63%) and **36** (76%) have been described earlier [6,13].

The TMS analogue of structure **11** was prepared by the method of Kuwajima [21]. The major product of its rearrangement, 1-trimethylsilylcycloheptene, is also known [22].

3.3. 3,3-Dimethyl-2-dimethyl(phenyl)silylbutan-2-ol (*44*)

Pinacolone (2.8 g, 20 mmol) was added at −78 °C to dimethyl(phenyl)silyllithium(1.08 mol dm^{-3} in THF, 25

cm^3, 27 mmol) and toluene 20 cm^3 via syringe, and the mixture kept at −78 °C for 1 h. The mixture was added to hydrochloric acid (3 mol dm^{-3}, 20 cm^3). Hexane (250 cm^3) was added to the mixture, the organic layer was separated and washed with brine (30 cm^3) and dried ($MgSO_4$). The solvents were removed under reduced pressure and the residue chromatographed (SiO_2, hexane–Et_2O, 25:1) giving the *alcohol* as an oil (326 mg, 69%); R_f (hexane–Et_2O, 94:6) 0.22; ν_{max} (film) cm^{-1} 3330 (OH), 2953 (C–H), 1427 (Ph), 1248 (br, OH and SiMe) and 1110 (SiPh); δ_H (400 MHz; $CDCl_3$) 7.64 (2H, m, Ph), 7.37–7.35 (3H, m, Ph), 1.34 (1H, br s, OH), 1.21 (3H, s, Me), 0.89 (9H, s, Bu^t), 0.47 (3H, s, $SiMe_AMe_B$) and 0.46 (3H, s, $SiMe_AMe_B$; δ_C(100 MHz; $CDCl_3$) 139.1 (*i*-Ph), 134.5 (*o*-Ph), 128.8 (*p*-Ph), 127.6 (*m*-Ph), 72.5 (CO), 38.5 (CMe_3), 26.4 (CMe_3), 21.8 (Me), −1.7 (SiMe) and −2.1 (SiMe); *m/z* (EI) 236 (1%, [M^1]), 235 (5, [M–H]) and 221 (6, [M–Me]); (ESI) (Found: [M+Na^1], 259.1490. $C_{14}H_{24}OSi$ requires [M+Na], 259.1494). The known alcohol **42** (86%) was prepared similarly [23].

3.4. General procedures for the rearrangement reactions

Many procedures were tried, but the following were the most informative and are representative. For assessing the yields, a measured quantity of diiodomethane was added to a known weight of the crude product, and the ^{1}H-NMR spectrum taken before any chromatography. For the isolation of the various products, the residue was chromatographed (SiO_2, hexane or pentane).

3.4.1. Method A

Thionyl chloride (0.15 cm^3, 4 mmol) was added to a stirred solution of the silylalcohol (1 mmol) and pyridine (2 mmol) in dichloromethane (3 cm^3) at 0 °C under nitrogen and then allowed to warm to room temperature (r.t.). After 1 h, the brown solution was diluted with ether (15 cm^3), washed with hydrochloric acid (3 mol dm^{-3}, 2 × 10 cm^3) and with brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure.

3.4.2. Method B

Thionyl chloride (0.15 cm^3, 4 mmol) was added to a stirred slurry of imidazole (0.544 g, 8 mmol) in THF (6 cm^3) at 0 °C under nitrogen and after 10 min the supernatant filtered into a solution of the silylalcohol (1 mmol) in THF (1 cm^3) at 0 °C. After 2 h the solution was diluted with hexane (100 cm^3) and washed with hydrochloric acid (3 mol dm^{-3}, 30 cm^3) and with brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure.

3.4.3. Method C

Thionyl chloride (0.15 cm^3, 4 mmol) was added to a stirred solution of the silylalcohol (1 mmol) and pyridine (2 mmol) in sulfur dioxide (3 cm^3 distilled from P_2O_5 into the flask containing the alcohol) at −10 °C under nitrogen, and then allowed to warm to r.t. After 1 h, the brown residue was either: (a) diluted with water (5 cm^3), extracted with pentane (2 × 20 cm^3), the extract washed with hydrochloric acid (3 mol dm^{-3}, 2 × 10 cm^3) and with brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure, or (b) diluted with pentane (5 cm^3) and stirred for 2 min then passed through a silica pad (ca. 4 cm^3) and eluted with pentane (20 cm^3); the solvent was then evaporated off under reduced pressure.

The following compounds were isolated by one or more of these methods, or by minor variations of them.

3.4.4. 1-Dimethyl(phenyl)silylcycloheptene (*11*)

R_f-(hexane) 0.50; ν_{max}(film) cm^{-1} 2919 (C–H), 1616 (C=C), 1446 (Ph), 1427 (Ph), 1246 (Si–Me) and 1112 (SiPh); δ_H(400 MHz; $CDCl_3$) 7.57 (2H, m, Ph), 7.41–7.35 (3H, m, Ph), 6.33 (1H, t, *J* 6.0, CSi=CH), 2.22 (2H, m, allylic CH_2), 2.18 (2H, m, allylic CH_2), 1.80 (2H, m, CH_2), 1.51 (2H, m, CH_2), 1.42 (2H, m, CH_2) and 0.36 (6H, s, $SiMe_2$); δ_C(100 MHz; $CDC1_3$) 143.8− (C=CH), 143.5+ (Si*C*=CH), 138.9+ (*i*-Ph), 134.0− (*o*-Ph), 128.7− (*p*-Ph), 127.6− (*m*-Ph), 33.0+ (CH_2), 30.7+ (CH_2). 27.4+ (CH_2), 26.8+ (CH_2) and −3.4− ($SiMe_2$); *m/z* (EI) 230.1 (58%, [M]), 215.1 (47%, [M–Me]) and 135.1 (100%, $SiMe_2Ph$) (Found: [M^4], 230.1491, $C_{15}H_{22}Si$ requires 230.1491). An alternative synthesis to confirm this structure was carried out in 96% yield using dimethyl(phenyl)silyllithium and cycloheptanone, followed by dehydration using Method A. The products were identical (^{1}H-NMR, TLC).

3.4.5. 3,3-Bis[dimethyl(phenyl)silyl]cycloheptene (*12*)

δ_H(400 MHz; $CDCl_3$) 5.81 (1H, d, *J* 12.9, Si_2CCH=CH), 5.68 (1H, dt, *J* 12.9 and 5.1, Si_2CCH–C*H*), 0.25 (3H, s, $SiMe_AMe_B$) and 0.15 (3H, s, $SiMe_AMe_B$).

3.4.6. Dimethyl(phenyl)silylmethylenecyclohexane (*13*)

R_f (hexane) 0.44; ν_{max}(film) cm^{-1} 2918 (C–H), 1451 (Ph), 1253 (Si–Me); δ_H(400 MHz; $CDCl_3$) 7.58 (2H, m, Ph), 7.42–7.37 (3H, m, Ph), 5.30 (1H, s, C=CHSi) 2.03 (2H, br s, allylic CH_2), 1.85 (2H, br s, allylic CH_2), 1.71 (2H, br s, CH_2), 1.62–1.55 (4H, m, CH_2) and 0.36 (s, $SiMe_2$); δ_C(100 MHz; $CDC1_3$) 140.4 (*C*=CSi), 134.7 (*i*-Ph), 133.6 (*o*-Ph), 128.8 (*p*-Ph), 127.6 (*m*-Ph), 119.8 (C–*C*HSi), 31.2 (CH_2), 27.4 (CH_2), 26.3 (CH_2), 23.3 (CH_2), 21.7 (CH_2) and −2.6 ($SiMe_2$.). An alternative synthesis to confirm the structure of this known compound [24] was carried out in 51% yield by dehydration of the alcohol **42** using Martin's sulfurane [25]. The products were identical (^{1}H-NMR, TLC).

*3.4.7. Cyclohexenylbis[dimethyl(phenyl)silyl]methane (**14**)*

R_f (hexane) 0.35; ν_{max}(film) cm^{-1} 2900 (C–H), 1635 (C=C), 1448 (Ph), 1248 (Si–Me) and 1110 (SiPh); δ_H(400 MHz; $CDCl_3$) 7.45 (4H, m, Ph), 7.32–7.27 (6H, m, Ph), 5.23 (1H, m, C*H*=C), 1.97 (2H, m, allylic CH_2), 1.47 (2H, m, allylic CH_2), 1.35–1.30 (4H, m, CH_2), 0.98 (1H, s, $CHSi_2$), 0.24 (6H, s, Si*Me*$_A$Me$_B$) and 0.22 (6H, s, SiMe$_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 140.0 (*i*-Ph), 136.1 (*C*=CH), 133.8 (*o*-Ph), 128.7 (*p*-Ph), 127.3 (*m*-Ph), 120.3 (C=*C*H), 33.8 (CH_2), 27.7 ($CHSi_2$), 25.5 (CH_2), 23.0 (CH_2), 22.0 (CH_2) and −1.7 (Si*Me*$_A$*Me*$_B$); *m/z* (EI) (Found: [M^+], 364.2040, $C_{23}H_{32}Si_2$ requires 364.2043).

*3.4.8. 1-Dimethyl(phenyl)silylcyclohexene (**16**)*

R_f (hexane) 0.46; ν_{max}(film) cm^{-1} 2920 (C–H), 2849 (C–H), 1618 (C=C), 1429 (SiPh), 1243 (Si–Me) and 1111 (SiPh); δ_H(400 MHz; $CDCl_3$) 7.54 (2H, m, Ph), 7.40–7.36 (3H, m, Ph), 6.17 (1H, m, C=CH), 2.11 (2H, m, allylic CH_2), 2.07 (2H, m, allylic CH_2), 1.70–1.62 (4H, m, CH_2) and 0.37 (6H, s, $SiMe_2$); δ_C(100 MHz; $CDCl_3$) 138.8 (*C*=CH), 137.9 (C=*C*H), 136.7 (*i*-Ph), 133.9 (*o*-Ph), 128.7 (*p*-Ph), 127.6 (*m*-Ph), 26.8 (CH_2), 26.8 (CH_2), 22.9 (CH_2), 22.4 (CH_2) and −3.6 ($SiMe_2$). An alternative synthesis to confirm the structure of this known compound [26] was carried out in 92% yield using dimethyl(phenyl)silyllithium and cyclohexanone, followed by dehydration using Method A. The products were identical (^{1}H-NMR, TLC).

*3.4.9. 3,3-Bis[dimethyl(phenyl)silyl]cyclohexene (**17**)*

δ_H(400 MHz; $CDCl_3$) 5.91 (1H, dd, *J* 10.0 and 2.5, Si_2CCH=CH), 5.78 (1H, dt, *J* 10.0 and 4.8, Si_2CCH=C*H*),1.8 2H, m, CH=CHCH_2), 0.31 (6H, s, SiA*Me*$_A$-Me$_B$) and 0.21 (6H, s, SiMe$_A$*Me*$_n$) with COSY connections between the signals at δ5.91 and δ5.78, and of both of these with the signal at δ1.8.

*3.4.10. Dimethyl(phenyl)silylmethylenecyclopentane (**18**) [24]*

R_f (hexane) 0.55; ν_{max}(film) cm^{-1} 2900 (C–H), 1635 (C=C), 1448 (Ph), 1248 (Si–Me) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.52 (2H, m, Ph), 7.39–7.32 (3H, m, Ph), 6.07 (1H, septet, *J* 2.0, C*H*=C), 2.12–1.96 (4H, m, allylic CH_2), 1.66–1.52 (4H, m, CH_2) and 0.31 (6H, s, $SiMe_2$); δ_C(100 MH_2; $CDCl_3$) 138.9+ (*C*=CH), 137.9− (C=*C*H), 136.7+ (*i*-Ph), 134.0− (*o*-Ph), 128.7− (*p*-Ph), 127.7− (*m*-Ph), 26.9+ (CH_2), 26.8+ (CH_2), 22.9+ (CH_2), 22.4+ (CH_2), and −3.6− ($SiMe_2$); *m/z* (E1) (Found: [M^+], 216.1336, $C_{14}H_{20}Si$ requires 216.1334).

*3.4.11. Cyclopentenylbisdimethyl(phenyl)silylmethane (**19**)*

R_f (hexane) 0.50; ν_{max}(film) cm^{-1} 2900 (C–H), 1635 (C=C), 1448 (Ph), 1248 (Si–Me) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.55 (4H, m, Ph), 7.42–7.32 (6H, m, Ph), 5.27 (1H, s, C*H*=C), 2.38 (2H, m, allylic CH_2), 1.95 (2H, m, allylic CH_2), 1.67 (2H, septet, *J* 7.5, CH_2), 1.35 (1H, s, $CHSi_2$), 0.33 (6H, s, SiA*Me*$_A$Me$_B$) and 0.31 (6H, s, SiMe$_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 142.7+ (*C*=CH), 140.1+ (*i*-Ph), 133.9− (*o*-Ph), 128.6− (*p*-Ph), 127.6− (*m*-Ph), 122.2− (C=*C*H), 40.6+ (CH_2), 33.4+ (CH_2), 23.6+ (CH_2), 22.3− ($CHSi_2$), −2.9− (Si*Me*$_A$Me$_B$) and −3.0− (SiMe$_A$-*Me*$_B$); *m/z* (EI) (Found0: [M^+], 350.1900, $C_{22}H_{30}Si_2$ requires 350.1886).

*3.4.12. 1-Dimethyl(phenyl)silylcyclopentene (**21**) [26]*

R_f (hexane) 0.40; ν_{max}(film) cm^{-1} 2910 (C–H), 1610 (C=C), 1431 (SiPh), 1250 (Si–Me) and 1110 (SiPh); δ_H(400 MHz; $CDC1_3$) 7.56 (2H, m, Ph), 7.38–7.35 (3H, m, Ph), 5.35 (1H, sept, *J* 2.5, C=CH), 2.81 (2H, m, allylic CH_2), 2.68 (2H, m, allylic CH_2), 1.95 (2H, qn, *J* 6.5, CH_2) and 0.35 (6H, s, $SiMe_2$); δ_C(100 MHz; $CDCl_3$) 139.9 (*C*=CH), 138.8 (*i*-Ph), 133.8 (*o*-Ph), 128.9 (*p*-Ph), 127.7 (*m*-Ph), 116.7 (C=*C*H), 35.6 (allylic CH_2), 33.6 (allylic CH_2), 16.4 (CH_2) and −1.6 ($SiMe_2$).

*3.4.13. Dimethyl(phenyl)silylmethylenecychbutane (**22**) [24]*

R_f (hexane) 0.47; ν_{max}(film) cm^{-1} 2953 (C–H), 2840 (C–H), 1649 (w, C=C), 1589 (Ph), 1448 (SiPh), 1250 (Si–Me) and 1110 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.52 (2H, m, Ph), 7.39–7.33 (3H, m, Ph), 6.08 (1H, s, C*H*=C), 2.45–2.35 (4H, m, allylic CH_2), 1.84 (2H, quintet, *J* 7.5, CH_2) and 0.36 (6H, s, $SiMe_2$); δ_C(100 MHz; $CDCl_3$) 142.6 (C=*C*H), 142.4 (*C*=CH), 138.8 (*i*-Ph), 133.7 (*o*-Ph), 128.8 (*p*-Ph), 127.7 (*m*-Ph), 36.0 (allylic CH_2), 35.0 (allylic CH_2), 24.1 (CH_2) and −3.0 ($SiMe_2$).

*3.4.14. 1-Dimethyl(phenyl)silylcyclobutene (**24**)*

R_f (hexane) 0.5; ν_{max}(film) cm^{-1} 2918 (C–H), 1607w (C=C), 1428 (Ph), 1249 (Si=Me) and 1111 (SiPh); δ_H(400 MHz; $CDCl_3$) 7.52 (2H, m, Ph), 7.36–7.32 (3H, m, Ph), 6.56 (1H, t, *J* 1.0, C=CH), 2.69 (2H, ddd, *J* 3.5, 3.1 and 1.0, CH_2CH–) and 2.57 (2H, dd, *J* 3.5 and 3.0, CH_2CSi–); δ_C(100 MHz; $CDCl_3$) 153.5+ (*C*Si=CH), 149.8− (C=*C*H), 138.2+ (*i*-Ph), 129.2− (*m*-Ph), 127.9− (*o*-Ph), 127.7− (*p*-Ph), 32.4+ (CH_2) and 32.2+ (CH_2); *m/z* (EI) (Found: [M^+], 188.1012, $C_{12}H_{16}Si$ requires 188.1021).

*3.4.15. 2-Dimethyl(phenyl)silylbuta-l,3-diene (**25**)*

This known [27] diene was only present in small amounts. It could not be completely separated, but was identified in the mixture from HMBC and MQC correlations: δ_H(400 MHz; $CDCl_3$) 7.53 (2H, m, Ph),

7.35–7.32 (3H, m, Ph), 6.46 (1H, dd, J 17.5 and 11.0, CH=CH_2), 5.88 (1H, d, J 3.0, CSi=C$H_A$$H_B$), 5.50 (1H, d, J 3.0, CSi=C$H_A$$H_B$), 5.10 (1H, d, J 17.5, CH=C$H_E$$H_Z$), 4.99 (1H, d, J 11.0, CH=C$H_E$$H_Z$) and 0.32 (6H, s, $SiMe_2$); δ_C (100 MHz; $CDCl_3$) 149.8 (CH=CH_2), 130.4 (CSi=CH_2), 116.7 (CH=CH_2) and 0.8 ($SiMe_2$).

3.4.16. E-2-Dimethyl(phenyl)silylbut-2-ene (E-27) [28,29]

δ_H(400 MHz; $CDCl_3$) 7.69 (2H, m, Ph), 7.47–7.43 (3H, m, Ph), 6.04 (1H, qq, J 6.5 and 1.5, C=CH), 1.83 (1H, d, J 6.5, CH_3CH–C), 1.80 (1H, s, CH=CCH_3) and 0.35 (6H, s, $SiMe_2$); nOe 6.04–7.68, 7.45, 1.83 and 0.35, no effect to 1.80.

3.4.17. Z-2-Dimethyl(phenyl)silylbut-2-ene (Z-27) [29]

δ_H(400 MHz; $CDCl_3$) 7.62 (2H, m, Ph), 7.46–7.43 (3H, m, Ph), 6.33 (1H, qq, J 7.0 and 1.5, C=CH), 1.94 (3H, dq, J 1.5 and 1.5, CH=CCH_3), 1.73 (3H, dq, J 7.0 and 1.5, CH_3CH=C) and 0.54 (6H, s, $SiMe_2$); nOe 6.33–1.94 and 1.73, no effect to 7.62, 7.45 or 0.54.

3.4.18. 3,3-Bisdimethyl(phenyl)silylbutene (28)

δ_H(400 MHz; $CDCl_3$) 6.41 (1H, dd, J 17.0 and 10.5, CH_2=CH), 5.16 (1H, dd, J 10.5 and 1.5, C$H_E$$H_Z$=CH), 4.76 (1H, dd, J 17.0 and 1.5, C$H_E$$H_Z$=CH), 1.32 (3H, s, CH_3), 0.32 (6H, s, Si$Me_A$$Me_B$) and 0.28 (6H, s, $SiMe_A$$Me_B$).

3.4.19. 1-Dimethyl(phenyl)silyl-2-methylpropene (29)

δ_H(400 MHz; $CDCl_3$) 5.56 (1H, br s, C=CHSi), 2.07 (3H, d, J 1.0, Me), 1.91 (3H, br s, Me) and 0.53 (6H, s, $SiMe_2$).

3.4.20. 3,3-Bisdimethyl(phenyl)silyl-2-methylpropene (30)

δ_H(400 MHz; $CDCl_3$) 4.89 (1H, m, CH_2=C), 4.69 (1H, m, CH_2=C, 1.65 (3H, br s, CH_3), 1.45 (1H, s, $CHSi_2$), 0.44 (6H, s, Si$Me_A$$Me_B$) and 0.42 (6H, s, $SiMe_A$$Me_B$).

3.4.21. E-4-Methyl-2-dimethyl(phenyl)silylpent-2-ene (E-32)

δ_H(400 MHz; $CDCl_3$) 5.86 (1H, dq, J 10.5 and 1.5, C=CH), 2.34 (1H, d septet, J 10.5 and 6.5, C$H$$Me_2$), 1.77 (3H, d, J 6.5, C=CCH_3), 0.80 (6H, d, J 6.5, CMe_2) and 0.37 (3H, s, $SiMe_2$), with configuration assigned by comparison with the chemical shift values for 2-dimethyl(phenyl)silylbut-2-ene, (E-27).

3.4.22. Z-4-Methyl-2-dimethyl(phenyl)silylpent-2-ene (Z-32)

δ_H(400 MHz; $CDCl_3$) 5.63 (1H, dq, J 9.0 and 1.5, C=CH), 2.71 (1H, d septet, J 9.0 and 7.0, C$H$$Me_2$), 1.65 (3H, d, J 1,5, C=CCH_3), 0.80 (6H, d, J 7.0, CMe_2) and 0.37 (3H, s, $SiMe_2$).

3.4.23. E-1-Dimethyl(phenyl)silyl-1-phenyl-propene (E-35)

δ_H(400 MHz; $CDCl_3$) 7.62 (2H, m, Ph), 7.40–7.30 (8H, m, Ph), 6.37 (1H, q, J 7.0, C=CH), 1.78 (3H, d, J 7.0, Me) and 0.36 (6H, s, $SiMe_2$).

3.4.24. Z-1-[Dimethyl(phenyl)silyl]-1-phenyl-propene (Z-35)

δ_H(400 MHz; $CDCl_3$) 7.52 (2H, m, Ph), 7.35–7.25 (8H, m, Ph), 6.14 (1H, q, J 7.0, C=CH), 1.59 (3H, d, J 7.0, Me) and 0.43 (6H, s, $SiMe_2$).

3.4.25. E-1-Dimethyl(phenyl)silylpropene (E-37) [30]

δ_H(400 MHz; $CDCl_3$) 7.52 (2H, m, Ph), 7.35–7.33 (3H, m, Ph), 6.12 (1H, dq, 18.5 and 6.0, CH=CHMe), 5.78 (1H, dq, 18.5 and 1.5, CH=CHMe), 1.84 (3H, dd, 6.0 and 1.5, allylic Me) and 0.30 (6H, s, $SiMe_2$).

3.4.26. Z-1-Dimethyl(phenyl)silylpropene (Z-37) [30]

δ_H(400 MHz; $CDCl_3$) 7.57 (2H, m, Ph), 7.39–7.31 (3H, m, Ph), 6.54 (1H, dq, 14.0 and 7.0, CH=CHMe), 5.67 (1H, dq, 14.0 and 1.5, CH=CHMe), 1.84 (3H, dd, 7.0 and 1.5, allylic Me) and 0.39 (6H, s, $SiMe_2$).

3.4.27. Methylenecyclohexane (43) [31]

R_f (pentane) 0.80; δ_H(400 MHz; $CDCl_3$) 4.62 (2H, s, C=CH_2), 2.15 (4H, m, allylic CH_2), 1.59–1.55 (6H, m, $3 \times CH_2$); COSY correlations 4.62–2.15, 2.15–1.55; identical (^{1}H-NMR) with an authentic sample.

3.5. 2,3-Dibromo-2,3-dimethylbutane

The alcohol **44** (0.55 g, 2.3 mmol) was dehydrated using Method C. The residue was diluted with heptane (30 cm^3), washed with hydrochloric acid (3 mol dm^{-3}, 20 cm^3) and saturated sodium hydrogencarbonate solution (20 cm^3), and dried ($MgSO_4$). The mixture was carefully concentrated using a fractionating column, and the residue cooled to 0 °C. Bromine (0.5 cm^3, 10 mmol) was added. After 5 min the solution was washed with saturated sodium thiosulfate solution (5×50 cm^3) and brine (20 cm^3), dried ($MgSO_4$), and solvent removed under reduced pressure to give the dibromide (0.15 g, 23%) as needles m.p. 175–177 °C (from hexane) (Ref. [32] 177 °C, mixed m.p. 176–177 °C).

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