1,1-Disilyl Alcohols as d[1] Synthons: Harnessing the 1,2-*Brook* Rearrangement

by **Ian Fleming***, **Annabel J. Lawrence**[1]), **Robert D. Richardson**[1]), **David S. Surry**[1]), and **Mark C. West**[2])

Department of Chemistry, Cambridge University, Lensfield Road, Cambridge CB2 1EW, UK

Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

1,1-Disilyl alcohols like **6** give the silyl ethers like **9** on treatment with base and alkyl halides, in a reaction which may be formulated as the alkylation of the *Brook*-rearranged carbanion **8**. The products can be oxidised to give ketones like **10**, showing that this *Brook*-rearranging system supplies a controlled d[1] synthon of the acyl anion class. The alcohols can be prepared from the acid chloride **12** and dimethyl(phenyl)silyllithium, but the intermediate anion **21** need not be worked up; it can be used directly in the alkylation step.

Introduction. – The 1,2-*Brook* rearrangement is usually formulated as an equilibrium between an oxy anion having an α-silyl substituent, such as **1**, and a carbanion having an α-silyloxy substituent, such as **2**, with the former normally in high concentration and the latter in low concentration [1]. Whether or not this is an accurate description of the species present[3]), it often reacts with electrophiles as a carbon nucleophile, and as such it can be classified as a d[1] synthon [3].

For example, if benzaldehyde (PhCHO) is treated with dimethyl(phenyl)silyllithium ($Me_2PhSiLi$) the products are the α-silylbenzyl alcohol **3** and, after workup, the pinacol **4** (*Scheme 1*) [4]. The latter is the product from the reaction of an anion **2** with another molecule of PhCHO, but it is not possible to use this nucleophile with a range of electrophiles. Although homocoupling is relatively easy, as here, it is limited to aromatic aldehydes and ketones [5], because easy *Brook* rearrangement **1** → **2** needs the stabilisation of the carbanion provided by the aromatic ring. We have found, as *Kuwajima* and co-workers have also [6], that it can also be made to give a cross-coupled pinacol **5**, but only when the electrophilic component is a nonenolisable aldehyde [7]. The yield was low, there were several other products, and it was clear that this was not a general or reliable way of gaining access to a reliable d[1] synthon.

The *Brook* rearrangement can be set up in several ways: most commonly when an α-silylcarbinol is treated with base [8], when an aldehyde or ketone is treated with a silyllithium reagent [9], or when an acylsilane is treated with a nucleophile [10]. There are a few reactions in which a *Brook* rearrangement, set up in one of these ways, is the

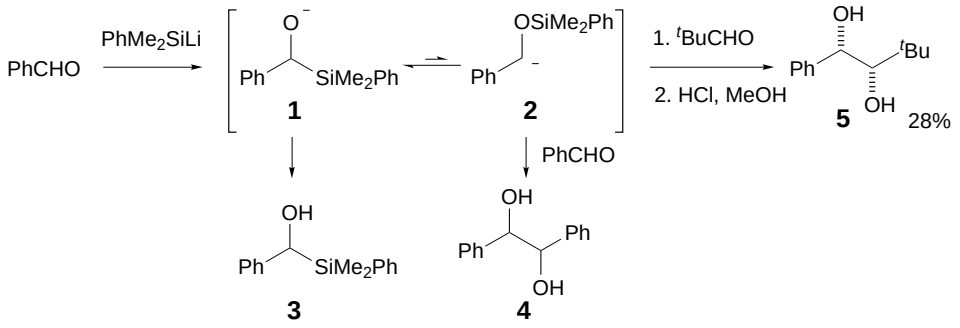
---

[1]) Work carried out in an undergraduate research project, Cambridge, 2001 – 2002.

[2]) Taken from the Ph.D. Thesis of *M. C. W.*, Cambridge University, 2001.

[3]) Calculations of the structure in the gas phase [2] suggest that a pentacoordinate silyl anion is the species present, rather than a mixture of **1** and **2** in equilibrium. If this proves to be the case in solution, the reactions will have to be reformulated somewhat, but, for the purposes of this paper and for simplicity, we continue to use the language of an equilibrating mixture.

Scheme 1



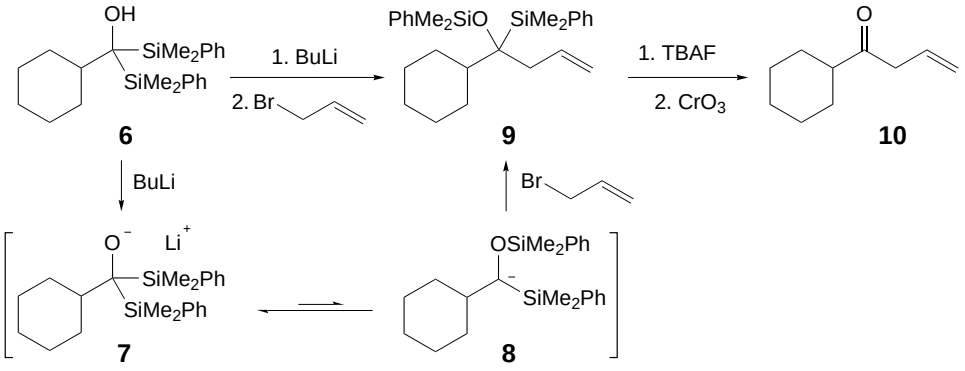
basis of a reliable and versatile synthetic method [11]. *Brook* rearrangements assisted by the presence of a vinyl or ethynyl group, in place of the aryl group in the examples mentioned above, usually give the product of γ-alkylation or protonation, and, hence, the formation of a specific silyl enol ether [6][12]. Similarly, a *Brook* rearrangement induces elimination to give a specific silyl enol ether when there is a nucleofugal group adjacent to the C–O bond [13]. Attack of an enolate on an α,β-unsaturated acylsilane, can lead to five- or seven-membered-ring formation [14], while enolate attack on a saturated acylsilane gives a cyclopropanediol [15]. Only in the last of these reactions is the *Brook* rearrangement being used for its potential as a d^1 synthon, as it is also in a formal sense in those reactions in which it is protonated [16], a reaction of comparatively limited usefulness in synthesis, or silylated in a *retro-Brook* rearrangement [17]. Otherwise, *Brook* rearrangements only turn up as one step in reactions which make excellent seminar problems [18][19], but which are not generally useful.

Reports of the α-alkylation of a *Brook*-rearranging system are few, and all rely upon the anion-stabilising ability of an aromatic ring [20]. We now report that we have tamed the *Brook* rearrangement so that it can be used as a d^1 synthon with alkyl halides: 1,1-disilyl alcohols typified by **6** on treatment with base can be alkylated on the C-atom in the sense **8** → **9** (*Scheme 2*). The second silyl group is evidently good enough at stabilising an anion to allow easy *Brook* rearrangement, even though there is no stabilisation from an aromatic group. The relief of steric compression may also be helping. The product **9** can be hydrolysed and oxidised to give a ketone **10**, revealing the full capacity of the *Brook*-rearranging system as an acyl-anion equivalent.

Results and Discussion. – *The Preparation of 1,1-Disilyl Alcohols.* 1,1-Bis(trimethylsilyl) alcohols such as the alcohol **11** have been prepared by *Kuwajima et al.* by reductive silylation of esters with Na and Me_3SiCl in refluxing THF, followed by acidic hydrolysis to remove the *O*-silyl group [21]. We repeated this synthesis with small a modification.

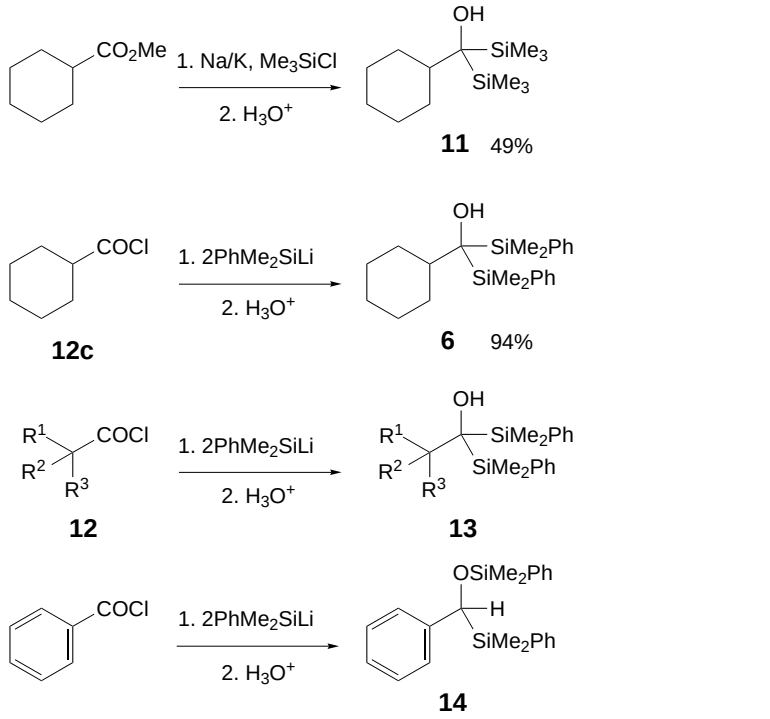
We reported earlier that the Me_2PhSi analogues can be made by treating phenyl esters with an excess of Me_2PhSi in a mixture of THF and toluene [22]. For the present work, we have used a short-cut, which is an improvement over the earlier method. Since we had been making the phenyl esters from the acid chlorides, it is one step shorter to treat the acid chlorides **12** directly with slightly more than 2 equiv. of the silyllithium

Scheme 2



reagent (*Scheme 3*). There was some risk in using this approach, since the product anion such as **7**/**8** might have reacted with the acid chloride. In practice this is not a problem – slow addition of the silyllithium reagent to the acid chloride works just as well as addition of the acid chloride to the silyllithium reagent. Furthermore, the sodium alkoxide, related to **7**/**8** and derived from the alcohol **6** with NaH, did not react

Scheme 3



with 3,5-dinitrobenzoyl chloride, even after 18 h at room temperature. This matches other results we have obtained, showing that many of the standard reagents used to dehydrate alcohols fail completely to react with the 1,1-disilyl alcohol **6**, which is recovered unchanged [23].

We had used phenyl esters earlier, in order to avoid the formation of products in which a Ph group has migrated from the Si- to the C-atom, giving unwanted by-products when alkyl esters had been used. We deduced at that time that the low pK_a of the liberated PhO^- ion makes it less effective in setting off this rearrangement, and Cl^- ion can obviously be expected to be even better in this respect. We have seen no sign of these rearranged products in any of our recent preparations, and we have obtained good yields of the 1,1-disilyl alcohols **13** in almost every case (*Table 1*). Care has to be taken to quench the reaction mixture with acid at low temperature and in the presence of an organic solvent to extract the product rapidly. Less-careful workup is apt to give some of the monosilylated alcohol, the product of a premature *Brook* rearrangement and protonation. This problem is much more severe when Ph_3SiLi is used in place of $Me_2PhSiLi$, when we were unable to prevent the *Brook* rearrangement. Benzoyl chloride also gave directly the product **14** with one *C*-silyl and one *O*-silyl group.

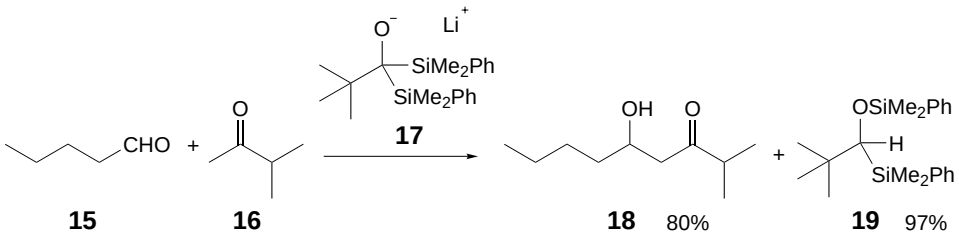
Table 1. *Synthesis of Alcohols* **13** *from* $Me_2PhSiLi$ *and Acid Chloride* **12**

Starting material				Product	Yield [%]
	R^1	R^2	R^3		
12a	Bu	H	H	**13a**	77
12b	C_8H_{17}	H	H	**13b**	29
12c	$-(CH_2)_5-$		H	**13c** (=**6**)	94
12d	$-(CH_2)_4-$		H	**13d**	87
12e	$-(CH_2)_3-$		H	**13e**	72
12f	Me	Me	H	**13f**	87
12g	Me	H	H	**13g**	76
12h	^{i}Pr	Me	H	**13h**	62
12i	Ph	Me	H	**13i**	63

Except in these unsuccessful cases, it appears that the protic acid used in the workup had given *O*-protonation of the oxy anion with kinetic control, and not *C*-protonation, which was the result of thermodynamic control when the oxy anion had been allowed to spend any time in a protic solvent. Extending this observation, we recalled that *Kuwajima et al.* had recommended lithium alkoxides derived from 1,1-bis(trimethylsilyl) alcohols as hindered bases in controlled aldol reactions [21][24]. We imitated one of these, the reaction between methyl isopropyl ketone **16** and pentanal **15**, using the lithium alkoxide **17** derived from pivaloyl chloride (*Scheme 4*). We isolated the aldol product **18** in good yield, comparable to *Kuwajima*'s, but we also looked for, and isolated in even better yield, the product derived from the base. This proved to be the *C*-protonated silyl ether **19**, showing that kinetic protonation of the *Brook*-rearranging system by the *carbon* acid had taken place on the C-atom. This helps to explain the special properties of this type of base that *Kuwajima et al.* had observed. The removal of the proton from the ketone by a carbon base is effectively irreversible, making the

base similar in its properties to LDA: hindered, so that it easily deprotonates only the methyl ketone group, and strong, so that it induces complete deprotonation. *Kuwajima et al.* suggested that this kind of base would have a pK_a value between that of an alkoxide and a metal amide, and, in another context, mentioned the possibility of a *Brook* rearrangement [25], but he did not isolate the product derived from his base. Since it is evidently a carbon base, its pK_a value will indeed be very high.

Scheme 4



There appears to be an emerging pattern with *Brook*-rearranging intermediates like **7**/**8**, in which hard electrophiles, like protic acids, attack the O-atom, and soft electrophiles, like the α-H-atom of a methyl ketone, at the C-atom. This simple perception sets the scene for the alkylations we describe below.

Brook *Rearrangement of 1,1-Disilylalkoxides and Their* C-*Alkylation*. Typically, we treated the disilyl alcohols **11** and **13** with BuLi at 0° in Et_2O, using 2,2-bipyridine to indicate when 1 equiv. had been added, and then added an excess of an alkyl halide. Reaction took place slowly; allyl bromide, for example, and the anion **7**/**8** derived from the alcohol **13c** (=**6**) required a little over 5 h at room temperature to complete the formation of the silyl ether **9**. Accordingly, we usually left the mixtures at room temperature overnight, and invariably obtained the products **20** of *C*-alkylation, sometimes contaminated with the product of *C*-protonation, but with no sign of any *O*-alkylation (*Scheme 5*). This is in contrast to the *O*-methylation seen between an α-silyl alkoxide and dimethyl sulfate [26], a harder alkylating agent than the alkyl halides that we have used. Alkyl halides undergoing S_N2 reactions are, of course, soft electrophiles, and these are the ones that work, ranging from the reactive and usually high-yielding allyl bromide, $PhCH_2Br$ and MeI, to the less-reactive and lower-yielding i-PrI, i-BuI, and 3-(trimethylsilyl)propargyl bromide (*Table 2*). The low yield with i-PrI may have been due to competing elimination; certainly there was no *Brook*-rearranging anion still unchanged at the end of the 18 h in the case of **13c**, for the addition of MeI at this stage gave none of the product of methylation **20cc**. Alkyl halides that failed to give any

Scheme 5

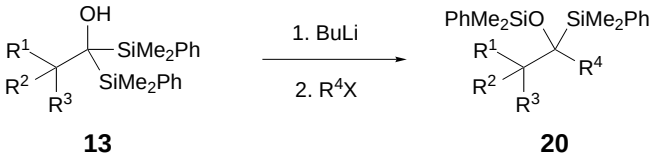


Table 2. *Alkylation of 1,1-Disilylalkoxides with BuLi and Alkyl Halides*

Starting material				Alkyl halide		Product	Yield [%]
	R^1	R^2	R^3	R^4	X		
11				allyl	Br		52 [a])
11				Bn	Br		67 [b])
11				^{i}Pr	I		50[c])
13c (=6)		$-(CH_2)_5-$	H	allyl	Br	**20ca** (=**9**)	98
13c (=6)		$-(CH_2)_5-$	H	Bn	Br	**20cb**	83
13c (=6)		$-(CH_2)_5-$	H	Me	I	**20cc**	82
13c (=6)		$-(CH_2)_5-$	H	Et	I	**20cd**	72
13c (=6)		$-(CH_2)_5-$	H	^{i}Pr	I	**20ce**	48
13c (=6)		$-(CH_2)_5-$	H	^{i}PrCH$_2$	I	**20cf**	43
13c (=6)		$-(CH_2)_5-$	H	$CH_2C{\equiv}CSiMe_3$	I	**20cg**	37
13d		$-(CH_2)_4-$	H	allyl	Br	**20da**	89
13e		$-(CH_2)_3-$	H	allyl	Br	**20ea**	89
13f	Me	Me	H	^{i}Pr	I	**20fe**	61/60

[a]) Product analogous to **20ca** but with Me_3Si groups in place of Me_2PhSi groups. [b]) Product analogous to **20cb** but with Me_3Si groups in place of Me_2PhSi groups. [c]) Product analogous to **20ce** but with Me_3Si groups in place of Me_2PhSi groups.

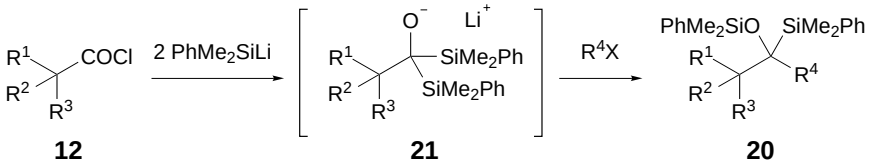
identifiable products other than that of *C*-protonation were ethyl α-bromoacetate, ethyl β-bromopropionate, and (cyclopropyl)methyl bromide.

Alternative bases that can be made to work are NaH and KH, but we find that, although they may be worth trying in some cases, they are usually more troublesome, giving more of the products of protonation unless exceptional care is taken to keep the mixture dry and HO^- ion free. We speculated that the sodium alkoxide might have been a reactive enough base to deprotonate THF, either at C(2), as often occurs with alkyllithium reagents [27], or at C(3), as we had found for a somewhat similarly constituted intermediate in our work on the reaction of silyllithium reagents with tertiary amides [19]. The experiment with 3,5-dinitrobenzoyl chloride and the sodium alkoxide derived from the alcohol **6**, mentioned above, was designed to test this hypothesis, but, in addition to giving no reaction with the alkoxide, it gave no product derived from the THF either – the products were the *C*-protonated silyl ether derived from **8** and 3,5-dinitrobenzoic acid. A similar experiment attempting to trap an elimination product from the THF with (*t*-Bu)Me_2SiCl was equally unsuccessful.

One-Pot Reaction of the Acid Chloride Successively with the Silyllithium Reagent and an Alkyl Halide. Having found that the lithium alkoxide was in general the most straightforward, we considered that it might be more simple not to isolate the disilyl alcohol, but to use directly its lithium alkoxide **21**, which must have been formed in the reaction between the acid chloride **12** and the silyllithium reagent (*Scheme 6*). This idea worked well. In general, it has given us higher yields (*Table 3*), it is easier to carry out, and the workup is straightforward, during which there is no hydrolysis of the silyl ether. The only drawback is that any excess silyllithium reagent consumes the alkyl halide faster than the *Brook*-rearranging nucleophile, and the nonpolar alkyldimethyl(phenyl)silane has to be separated from the hardly more polar silyl ethers **20**.

Oxidation of the Products to give Ketones. We have carried out hydrolysis and oxidation on three of our products, in order to illustrate their potential as d^1 synthons

Scheme 6



12 **21** **20**

Table 3. *Alkylation of 1,1-Disilylalkoxides with Alkyl Halides* in situ

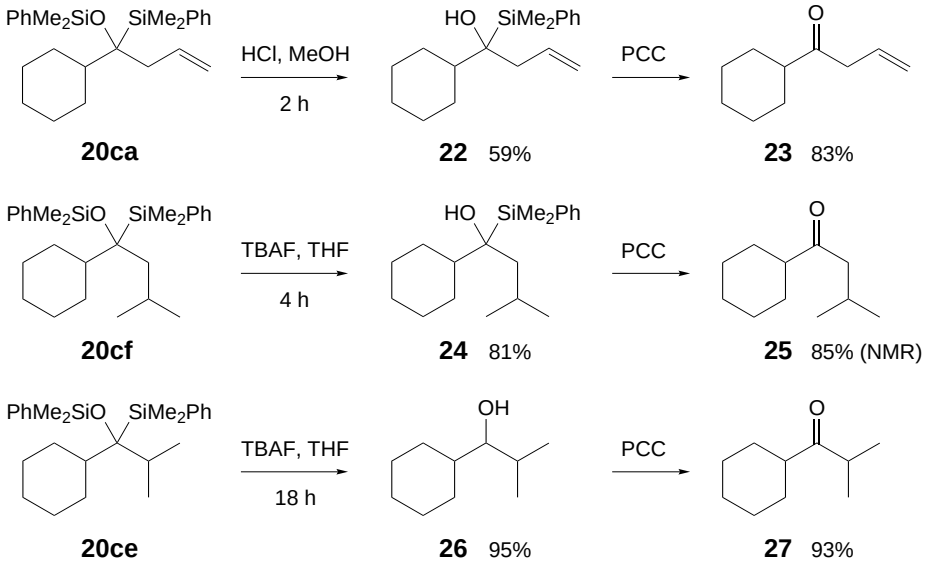
Starting material				Alkyl halide		Product	Yield [%]
	R^1	R^2	R^3	R^4	X		
12a	Bu	H	H	allyl	Br	**20aa**	66
12a	Bu	H	H	^{i}Pr	I	**20ae**	30
12b	C_8H_{17}	H	H	allyl	Br	**20ba**	41
12c	$-(CH_2)_5-$		H	allyl	Br	**20ca** (=**9**)	91/98
12c	$-(CH_2)_5-$		H	^{i}Pr	I	**20ce**	65[a])
12c	$-(CH_2)_5-$		H	^{i}PrCH$_2$	I	**20cf**	45
12f	Me	Me	H	allyl	Br	**20fa**	75
12f	Me	Me	H	Bn	Br	**20fb**	50
12f	Me	Me	H	Me	I	**20fc**	62
12f	Me	Me	H	Br(CH$_2$)$_3$	Br	**20ff**	40[b])
12j	Me	Me	Me	allyl	Br	**20ja**	98
12j	Me	Me	Me	Bn	Br	**20jb**	82

[a]) Together with the silyl ether (30%) from protonation in place of alkylation. [b]) As the alcohol, after hydrolysis of the silyl ether with TsOH in EtOH.

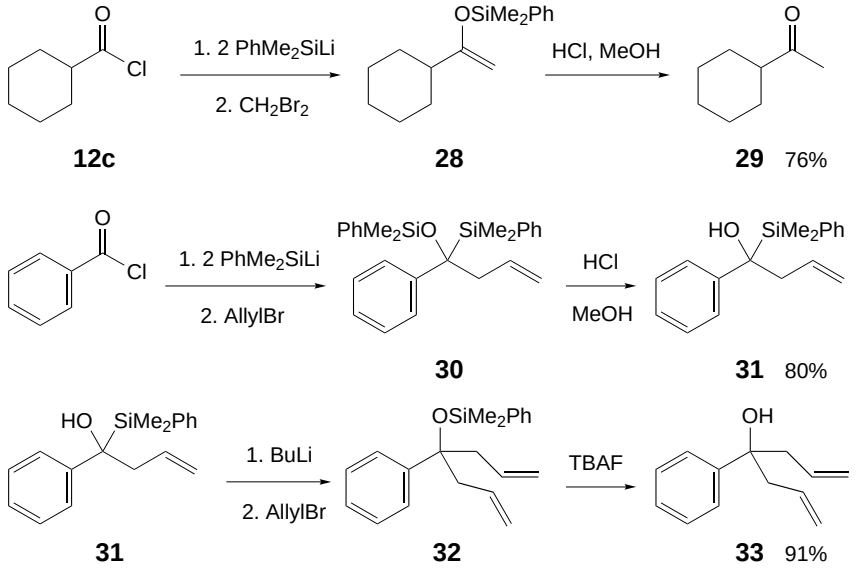
(*Scheme 7*). The silyl ethers, since they are substantially hindered, are slow to hydrolyse in acid, with the conversion **20ca** → **22** almost certainly not as good as it could be, but they cleanly give α-silyl alcohols such as **24** on treatment with tetrabutylammonium fluoride (TBAF) in THF typically for 4 h at room temperature. Longer treatment with TBAF smoothly removes the second silyl group, giving a simple secondary alcohol such as **26**, and it may be that, in preparation for oxidation, there is not much point in trying to remove only the *O*-silyl group. The oxidation may be carried out with several of the reagents normally used for oxidising secondary alcohols to ketones. We have used pyridinium chlorochromate (PCC) in this work, giving the ketones, **23**, **25** and **27** in good yield.

Some Related Observations. Our attempts to use carbon electrophiles other than alkyl halides have been disappointing. There is precedent for aldehydes reacting [6], but they did not give us recognisable products. Epoxides gave no sign of any reaction, but we eschewed the use of hexamethylphosphoric triamide (HMPA), which might well be a necessary cosolvent. We have already commented on the failure of acid chlorides to react. One alkyl halide understandably gave a different outcome (*Scheme 8*) from those described above: CH_2Br_2 reacted with the *Brook*-rearranging system **7**/**8** prepared *in situ* from the acid chloride **12c** to give directly the silyl enol ether **28**, hydrolysis of which gave the methyl ketone **29**, avoiding the use of conventional oxidising agents.

Scheme 7



Scheme 8

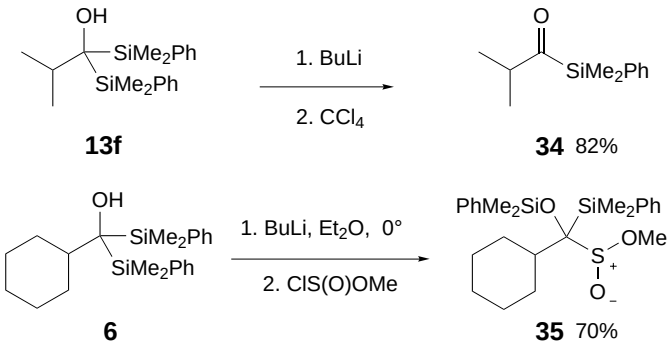


The preparation of the *Brook*-rearranging system directly from the acid chloride allowed us to overcome the premature *Brook* rearrangement–protonation, giving the silyl ether **14** that we had unavoidably suffered when we tried to prepare the disilyl alcohol from PhCOCl. Starting again with PhCOCl, but adding allyl bromide after the silyllithium reagent, gave the silyl ether **30**, hydrolysis of which gave the alcohol **31**. This

alcohol, because of the activating Ph group, could be induced to undergo a second *Brook* rearrangement – alkylation to give the silyl ether **32** and hence the alcohol **33**.

Among heteroatom electrophiles, two are perhaps worth noting (*Scheme 9*). The *Brook*-rearranging system derived from **13f** with BuLi reacted with CCl_4 to give cleanly the acylsilane **34**, in a reaction that resembles *Kuwajima*'s oxidation of a similar system using *tert*-butyl hypochlorite [28]. *Kuwajima* formulated this reaction as *O*-chlorination, followed by elimination of Me_3SiCl. Given that CCl_4 and *tert*-butyl hypochlorite are soft electrophiles, it now seems more likely that it takes place by *Brook* rearrangement and *C*-chlorination, followed by elimination of the silyl chloride. The system **7**/**8** derived from the disilyl alcohol **6** reacted with methane chlorosulfite to give the product of *C*-sulfination **35** apparently as a single diastereoisomer. It was this observation, another fruitless attempt to induce dehydration and/or cationic rearrangement [23], that led us to the present work.

Scheme 9



Conclusions. – Silicon-based solutions to all the d synthons are now in place: d^2 is supplied by the conspicuously useful silyl enol ethers [29], d^4 by silyl dienol ethers [30], d^3 had been achieved by means of the *Brook* rearrangement with a neighbouring vinyl group [6][12], and the present work, together with another recent publication [31] with a different method altogether, fills in the gap for d^1.

Experimental Part

Synthesis of the 1,1-Disilyl Alcohols **13**. Typically, the acid chloride (10 mmol) in toluene (5 ml) was added dropwise over 3 min to $Me_2PhSiLi$ [32] (1 mol dm^{-3} soln. in THF, 22 ml, 22 mmol) and toluene (20 ml) under N_2 at $-78°$ with vigorous stirring. After 0.5–1 h, the soln. was poured into hexane (100 ml) and aq. NH_4Cl soln., the org. layer separated, washed with HCl (3M, 30 ml) and with brine (30 ml), 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 (bulb-to-bulb). The following new compounds were prepared by this method, the alcohols **13b**, **13c** and **13f** being known compounds [22].

1,1-Bis[dimethyl(phenyl)silyl]hexanol (**13a**; 77%). Oil. TLC (hexane/Et_2O, 90:10): R_f 0.43. IR (film): 3556, 2955, 2855, 1465, 1427, 1249, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.60 (4*m*, Ph); 7.43–7.35 (6*m*, Ph); 1.73 (2*dd*, $J = 8.5$, 7.5, CH_2CO); 1.34–1.13 (6*m*, CH_2); 0.87 (3*t*, $J = 7.0$, Me); 0.37 (3*s*, Me_AMe_BSi), 0.31 (6*s*, Me_AMe_BSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.9 (*i*-Ph); 134.6 (*o*-Ph); 129.0 (*p*-Ph); 127.6 (*m*-Ph); 63.6

(CSi_2OH); 37.6 (CH_2CSi_2O); 32.7 (CH_2); 25.0 (CH_2); 22.4 (CH_2); 13.9 (Me); −2.9 (Me_AMe_BSi); −3.3 (Me_AMe_BSi). ESI-MS ($C_{12}H_{34}NaOSi_2$; calc. 393.2046): 393.2046 ($[M+Na]^+$).

Bis[dimethyl(phenyl)silyl](cyclopentyl)methanol (**13d**; 87%) as an oil. TLC (hexane/AcOEt, 90:10): R_f 0.50. IR (film): 3554, 2954, 1427, 1250, 1108. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.58 (4*m*, Ph); 7.38-7.30 (6*m*, Ph); 2.05 (1*tt*, $J=7.5$, 2.0, C*H*CO); 1.56–1.10 (9*m*, OH, 4 CH_2); 0.35 (6*s*, Me_AMe_BSi), 0.19 (6*s*, Me_AMe_BSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.1 (*i*-Ph); 134.7 (*o*-Ph); 128.9 (*p*-Ph); 127.7 (*m*-Ph); 67.5 (CSi_2OH); 48.9 (*C*HCOSi_2); 29.0 (2 CH_2); 24.9 (2 CH_2); −1.3 (Me_AMe_BSi); −1.8 (Me_AMe_BSi). EI-MS: no M^+ observed, 235.1 (40, $[M-SiMe_2Ph]^+$), 135.1 (100, $SiMe_2Ph^+$).

Bis[dimethyl(phenyl)silyl](cyclobutyl)methanol (**13e**; 72%). Oil. TLC (hexane/AcOEt 90:10): R_f 0.46. IR (film): 3547, 2956, 1427, 1251, 1108. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57 (4*m*, Ph); 7.44–7.34 (6*m*, Ph); 2.88 (*tt*, $J=10.0$, 7.5, C*H*CO); 1.85 (2*m*, CH_2); 1.70–1.41 (4*m*, CH_2); 1.30 (br. *s*, OH); 0.25 (6*s*, Me_AMe_BSi); 0.18 (6*s*, Me_AMe_BSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.0 (*i*-Ph); 134.6 (*o*-Ph); 129.0 (*p*-Ph); 127.6 (*m*-Ph); 65.8 (CSi_2OH); 42.6 (*C*HCOSi_2); 25.7 (2 CH_2); 18.6 (CH_2); −2.1 (Me_AMe_BSi); −2.9 (Me_AMe_BSi). ESI-MS ($C_{21}H_{30}NaOSi_2$; calc. 377.1733): 377.1713 ($[M+Na]^+$).

1,1-Bis[dimethyl(phenyl)silyl]propan-1-ol (**13g**; 76%). Oil. TLC (hexane/Et_2O 90:10): R_f 0.43. IR (film): 3556, 2955, 2855, 1465, 1427, 1249, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62 (4*m*, Ph); 7.43–7.37 (6*m*, Ph); 1.83 (2*q*, $J=8.0$, MeCH_2); 0.91 (3*t*, $J=8.0$, *Me*CH_2); 0.39 (6*s*, Me_AMe_BSi); 0.32 (6*s*, Me_AMe_BSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.7 (*i*-Ph); 136.6 (*o*-Ph); 129.0 (*p*-Ph); 128.7 (*m*-Ph); 65.9 (CSi_2OH); 29.8 (CH_2CSi_2O); 10.9 (Me); −2.9 (Me_AMe_BSi); −3.2 (Me_AMe_BSi). ESI-MS ($C_{19}H_{28}NaOSi_2$; calc. 351.1577): 351.1584 ($[M+Na]^+$).

1,1-Bis[dimethyl(phenyl)silyl]-2,3-dimethylbutan-1-ol (**13h**; 62 %). Prepared from 2,3-dimethylbutyryl chloride [33]. Oil. TLC (hexane/Et_2O 97:3): R_f 0.16. IR (film): 3500*w* (OH), 2960, 1427, 1254, 1118. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (4*m*, Ph); 7.41–7.33 (6*m*, Ph); 2.01–1.86 (*m*, Me_2CH); 1.83–1.76 (*m*, i-PrC*H*); 0.88 (3*d*, $J=7.5$, Me); 0.78 (3*d*, $J=7.5$, Me_AMe_BCH); 0.75 (3*d*, $J=7.5$, Me_AMe_BCH); 0.37 (3*s*, MeSi); 0.35 (3*s*, MeSi); 0.31 (3*s*, MeSi), 0.28 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.8 (*i*-Ph); 138.6 (*i*-Ph); 134.2 (*o*-Ph); 133.9 (*o*-Ph); 129.2 (*p*-Ph); 128.9 (*p*-Ph); 127.7 (*m*-Ph); 127.6 (*m*-Ph); 71.0 (CSi_2OH); 36.1 (*C*HCOSi_2); 29.1 (Me_2CH); 22.6 (Me_AMe_BCH); 22.6 (Me_AMe_BCH); 22.0 (i-PrCH*Me*), −0.7 (MeSi); −0.8 (MeSi); −2.9 (MeSi); −3.1 (MeSi). EI-MS: M^+ not observed, 235.1 (40, $[M-SiMe_2Ph]^+$), 135.1 (100 $SiMe_2Ph^+$).

1,1-Bis[dimethyl(phenyl)silyl]-2-phenylpropan-1-ol (**13i**; 63%). Yellow oil. TLC (hexane/Et_2O 97:3): R_f 0.36. IR (film): 3468, 2950, 1580, 1431, 1247, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.64 (2*m*, Ph); 7.48–7.07 (13*m*, Ph); 3.06 (1*q*, $J=7.5$, PhC*H*); 1.30 (*d*, $J=7.5$, Me); 0.48 (3*s*, MeSi); 0.36 (3*s*, MeSi); 0.0 (3*s*, MeSi); −0.11 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 143.1, 139.0, 138.6 (3 i-Ph); 134.9, 134.7, 129.0, 128.9, 128.7, 128.1, 127.5, 127.4, 126.6 (9 Ph); 68.1 (COHSi_2); 46.5 (*C*HPh); 16.6 (Me); −0.6, −1.8, −1.9, −2.6 (4 MeSi). EI-MS ($C_{20}H_{36}OSi_2$; calc. 348.2305): 348.2300 (M^+).

Brook *Rearrangement-Alkylation Reactions with 1,1-Disilyl Alcohols.* Typically, BuLi (1M in hexane, 1 ml, 1 mmol) was added to the alcohol (1 mmol) and 2,2′-bipyridine (1 mg) in Et_2O (5 ml). After 5 min, the alkyl halide (2 mmol) was added. After 12 h, the mixture was diluted with hexane (20 ml) and passed through a silica pad to remove inorganics. The eluant was evaporated under reduced pressure and, if necessary, purified further by column chromatography (SiO_2, Et_2O/hexane). The following compounds were prepared by this method.

4-Cyclohexyl-(Trimethylsilyl)-4-(trimethylsilyloxy)but-1-ene (52%). Oil. TLC (hexane): R_f 0.66. IR (film): 3077 (C=CH), 2931, 2852, 1638, 1450, 1248, 1077. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.73 (*ddt*, $J=17.5$, 11.0, 7.0, C*H*=CH_2); 5.11–4.99 (2*m*, CH=CH_2); 2.53 (*dd*, $J=14.0$, 7.0, CH_AH_BC=C); 2.41 (*dd*, $J=14.0$, 7.0, CH_AH_BC=C); 1.34–1.00 (6*m*); 0.93–0.76 (4*m*); 0.10 (9*s*, Me_3Si); 0.05 (9*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 135.0 (C=*C*H$_2$); 117.0 (*C*=CH_2); 78.1 (CO); 44.2 (*C*H$_2$C=C); 41.3 (*C*HCO); 30.0 (CH_2); 29.4 (CH_2); 27.0 (CH_2); 26.7 (CH_2); 26.4 (CH_2); 3.2 (Me_3Si); −0.6 (Me_3Si). EI-MS ($[C_{16}H_{34}OSi_2-Me]^+$; calc. 283.1913): 283.1928 ($[M-Me]^+$), no M^+ observed.

1-Cyclohexyl-2-phenyl-1-(trimethylsilyl)-1-(trimethylsilyloxy)ethane (67%). Oil. TLC (hexane): R_f 0.34. IR (film): 2918, 1451, 1253, 1248 (C–O). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.26–7.15 (5*m*, Ph); 2.94 (*d*, $J=8.0$, CH_AH_BPh); 2.86 (*d*, $J=8.0$, CH_AH_BPh); 1.93–1.62 (5*m*, CH, CH_2); 1.31–1.10 (6*m*, CH_2); 0.13 (9*s*, Me_3Si); −0.13 (9*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.0 (*i*-Ph); 131.1 (*o*-Ph); 127.6 (*m*-Ph); 125.9 (*p*-Ph); 79.2 (CO); 45.3 (Ph*C*H$_2$); 41.1 (*C*HCO); 28.9 (CH_2); 28.7 (CH_2); 26.9 (CH_2); 26.8 (CH_2); 3.3 (Me_3Si); −0.5 (Me_3Si). EI-MS ($C_{20}H_{36}OSi_2$; calc. 348.2305): 348.2300 (M^+).

1-Cyclohexyl-2-methyl-1-(trimethylsilyl)-1-(trimethylsilyloxy)propane (50%). Oil. TLC (hexane): R_f 0.38. IR (film): 2903, 1258, 1076 (SiOC). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.02 (*sept.*, $J=6.5$, Me_2CH); 1.86–1.58 (6*m*, CH_{ax}); 1.30–1.12 (5*m*, CH_{eq}); 0.11 (9*s*, Me_3Si); 0.09 (9*s*, Me_3Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 82.0 (C–O); 46.7

(CH ring); 34.7 (Me_2CH); 29.5 (CH_2); 29.0 (CH_2); 27.2 (CH_2); 26.9 (CH_2); 26.4 (CH_2); 2.6 (Me_3Si); 1.0 (Me_3Si). ESI-MS: no M^+ observed.

4-Cyclohexyl-4-[dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]but-1-ene (**20ca** = **9**; 98%). Oil. TLC (hexane): R_f 0.47. IR (film): 2900, 1635, 1448, 1248, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63–7.55 (4*m*, Ph); 7.40–7.29 (6*m*, Ph); 5.80 (*ddt*, *J* = 17.5, 10.5, 7.0, C*H*=CH_2); 5.06–4.98 (2*m*, CH=CH_2); 2.57 (*dd*, *J* = 14.5, 7.0, CH_AH$_B$C=C); 2.51 (*dd*, *J* = 14.5, 7.0, CH_AH_BC=C); 1.84 (*m*, CHCO); 1.76–1.50 (5*m*, CH_{eq}); 1.76–1.50 (5*m*, CH_{ax}); 0.45 (3*s*, MeSi); 0.44 (3*s*, MeSi); 0.41 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.4 (*i*-Ph); 138.6 (*i*-Ph); 134.6 (*C*=CH_2); 134.4 (*o*-Ph); 133.4 (*o*-Ph); 128.6 (*p*-Ph); 128.3 (*p*-Ph); 127.4 (*m*-Ph); 127.2 (*m*-Ph); 117.2 (C=*C*H_2); 78.7 (CO); 43.3 (*C*H_2C=C); 41.1 (*C*HCO); 28.9 (CH_2); 27.7 (CH_2); 26.5 (CH_2); 26.5 (CH_2); 26.3 (CH_2); 1.8 (MeSi); 1.6 (MeSi); −2.1 (MeSi). ESI-MS ($C_{26}H_{38}NaOSi_2$; calc. 445.2359): 445.2348 ([M + Na]$^+$).

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]-2-phenylethane (**20cb**; 83%). Oil. TLC (hexane/Et_2O, 96:4): R_f 0.56. IR (film): 2887, 1594, 1450, 1247, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.58–7.46 (4*m*, Ph); 7.40–7.28 (6*m*, Ph); 7.24–7.17 (3*m*, Ph); 7.11 (2*m*, Ph); 3.12 (*d*, *J* = 14.5, PhCH_AH$_B$); 3.07 (*d*, *J* = 14.5, PhCH$_A$$H_B$); 1.98 (*m*, CHCO); 1.85–1.62 (5*m*, CH_{ax}); 1.21–1.04 (5*m*, CH_{eq}); 0.36 (3*s*, MeSi); 0.33 (3*s*, MeSi); 0.24 (3*s*, MeSi); 0.19 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 141.0, 139.0, 137.9 (3 i-Ph); 134.9, 133.4, 131.1 (3 *o*-Ph); 128.4, 128.3 (2 *p*-Ph); 127.7, 127.4, 127.3 (3 *m*-Ph); 126.2 (*p*-Ph); 81.2 (CO); 45.0 (Ph*C*H_2); 41.6 (*C*HCO); 29.9 (CH_2); 29.3 (CH_2); 26.7 (CH_2); 26.6 (CH_2); 25.5 (CH_2); 2.1 (MeSi); 1.5 (MeSi); −1.3 (MeSi); −2.4 (MeSi). EI-MS: no M^+ observed.

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]ethane (**20cc**; 82%). Oil. TLC (hexane): R_f 0.34. IR (film): 2937, 1425, 1250, 1109. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.65–7.58 (4*m*, Ph); 7.45–7.34 (6*m*, Ph); 1.95–0.91 (14*m*, Me, CH_{ax}, CH_{eq}); 0.30 (6*s*, MeSi); 0.22 (3*s*, MeSi); 0.21 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.6 (*i*-Ph); 138.9 (*i*-Ph); 134.7 (*o*-Ph); 133.3 (*o*-Ph); 129.2 (*p*-Ph); 128.9 (*p*-Ph); 127.6 (*m*-Ph); 127.5 (*m*-Ph); 79.8 (CO); 50.3 (CO*Me*); 31.4 (CH_2); 29.6 (CH_2); 26.7 (CH_2); 26.6 (CH_2); 26.4 (CH_2); 2.1 (MeSi); 0.9 (MeSi); −2.9 (MeSi); −3.0 (MeSi). EI-MS: no M^+ peak observed, 135.1 (100, $SiMe_2Ph^+$).

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]propane (**20cd**; 72%). Oil. TLC (hexane): R_f 0.40. IR (film): 2876, 1427, 1253, 1111. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.82–7.77 (4*m*, Ph); 7.56–7.48 (6*m*, Ph); 1.95 (2*q*, *J* = 7.0, MeCH_2); 1.91–0.86 (14*m*, Me, CH_{ax}, CH_{eq}); 0.36 (3*s*, MeSi); 0.34 (3*s*, MeSi); 0.19 (3*s*, MeSi); 0.18 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.6 (*i*-Ph); 138.9 (*i*-Ph); 134.6 (*o*-Ph); 134.3 (*o*-Ph); 129.1 (*p*-Ph); 128.9 (*p*-Ph); 127.7 (*m*-Ph); 127.5 (*m*-Ph); 80.2 (CO); 45.6 (CO*C*H_2) 32.5 (CH_2); 29.6 (CH_2); 26.4 (CH_2); 26.4 (CH_2); 26.3 (CH_2); 19.6 (Me); −0.7 (MeSi); −0.8 (MeSi); −3.2 (MeSi); −3.3 (MeSi). EI-MS ($C_{25}H_{38}OSi_2$; calc. 410.2461): 410.2445 (M^+).

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]-2-methylpropane (**20ce**; 48%). Oil. TLC (Et_2O/hexane 1:99) 0.58. IR (neat): 3049 (CH), 1487 (Ph), 1253 (MeSi), 1117 (PhSi). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.58 (4*m*, *o*-Ph); 7.35 (6*m*, *m*- and *p*-Ph); 2.00 (*sept.*, *J* = 7, Me_2CH); 1.86 (*m*, CH); 1.72–1.48 (5*m*, c-Hex); 1.13–0.83 (5*m*, c-Hex); 0.92 (3*d*, *J* = 7, Me_AMe$_B$CH); 0.89 (3*d*, *J* = 7, Me$_A$$Me_B$CH); 0.44 (3*s*, Me_AMe$_B$Si); 0.43 (3*s*, Me$_A$$Me_B$Si); 0.42 (3*s*, Me_AMe$_B$Si); 0.41 (3*s*, Me$_A$$Me_B$Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.9 (+, Ph *C*Si); 140.5 (+, Ph *C*Si); 135.0 (−, arom. *C*H); 133.3 (−, arom. *C*H); 128.9 (−, arom. *C*H); 128.4 (−, arom. *C*H); 127.5 (−, arom. *C*H); 127.2 (−, arom. *C*H); 84.8 (+, CO); 47.2 (−, CH); 35.3 (−, CH); 30.1 (+, CH_2); 28.4 (+, CH_2); 27.3 (+, CH_2); 26.9 (+, CH_2); 26.6 (+, CH_2); 20.6 (−, Me); 18.9 (−, Me); 1.7 (−, MeSi); 1.6 (−, MeSi); 0.4 (−, MeSi); 0.3 (−, MeSi). ESI(Na$^+$)-MS ($C_{26}H_{40}OSi_2Na$; calc. 447.2516): 447.2508 ([M + Na]$^+$).

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]-3-methylbutane (**20cf**; 43%). Oil. TLC (Et_2O/hexane, 1:99) 0.40. IR (film): 2914 (*s*, CH), 2852*s* (CH), 1453*m* (Ph), 1264*w* (MeSi), 1115*s* (PhSi). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.57–7.48 (4*m*, Ph); 7.36–7.23 (6*m*, Ph); 1.79–1.47 (9*m*, CH_{eq}, CH, CH_2C*H*Me$_2$); 1.18–0.91 (5*m*, CH_{ax}); 0.78 (6*d*, *J* = 6, Me_2CH); 0.39 (6*s*, Me$_2$Si); 0.34 (3*s*, Me_AMe$_B$Si); 0.33 (3*s*, Me$_A$$Me_B$Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.8 (*i*-Ph); 139.4 (*i*-Ph); 134.8 (*o*-Ph); 133.5 (*o*-Ph); 128.9 (*p*-Ph); 128.5 (*p*-Ph); 127.5 (*m*-Ph); 127.3 (*m*-Ph); 81.2 (CO) 45.4 (*C*HCOSi); 44.7 (*C*H_2COSi); 29.8 (CH_2); 28.3 (CH_2); 26.8 (CH_2); 26.7 (CH_2); 26.5 (CH_2); 25.2 (Me_2CH); 24.8 (Me_AMe$_B$CH); 24.5 (Me$_A$$Me_B$CH); 2.12 (MeSi); 2.08 (MeSi); −1.3 (MeSi); −1.6 (MeSi). ESI-MS ($C_{27}H_{42}NaOSi_2$; calc. 461.2672): 461.2672, ([M + Na]$^+$).

1-Cyclohexyl-1-dimethyl(phenyl)silyl-1-[dimethyl(phenyl)silyloxy]-4-trimethylsilyl-3-butyne (**20cg**; 37%). Oil. TLC (Et_2O/hexane, 1:99) 0.21. IR (film): 2928*s* (CH), 2852*s* (CH), 2172*s* (C≡C), 1427*m* (Ph), 1249*s* (Me_3Si), 1115*s* (PhSi), 1054*s* (O−Si), 840*s* (Me_3Si). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.59–7.50 (4*m*, Ph); 7.37–7.26 (6*m*, Ph); 2.51 (*d*, *J* = 17, CH_AH$_B$C≡C); 2.44 (*d*, *J* = 17, CH_AH_BC≡C); 1.90–1.56 (6*m*, CH_{eq}, CH); 1.16–0.93 (5*m*, CH_{ax}); 0.403 (3*s*, Me_AMe$_B$Si); 0.397 (3*s*, Me$_A$$Me_B$Si); 0.377 (3*s*, Me_AMe$_B$Si); 0.371 (3*s*, Me$_A$$Me_B$Si); 0.14 (9*s*, Me_3Si). ^{13}C-NMR (125 MHz, $CDCl_3$): 140.4 (*i*-Ph); 138.2 (*i*-Ph); 134.8 (*o*-Ph); 133.3 (*o*-Ph); 129.0

(*p*-Ph); 128.8 (*p*-Ph); 127.5 (*m*-Ph); 127.3 (*m*-Ph); 104.7 ($CH_2C{\equiv}CSi$); 88.6 ($C{\equiv}CSi$); 77.5 (CO) 46.6 (*C*HCOSi); 29.1 (CH_2); 29.0 (CH_2); 28.7 (CH_2); 27.0 (CH_2); 26.9 (CH_2); 26.6 (CH_2); 1.9 (MeSi); 1.4 (MeSi); −0.1 (Me_3Si); −2.1 (MeSi); −2.2 (MeSi). ESI-MS ($C_{29}H_{44}NaOSi_3$; calc. 515.2598): 515.2598, ($[M+Na]^+$).

4-Cyclopentyl-4-[dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]but-1-ene (**20da**; 89%). Oil. TLC (hexane): R_f 0.42. IR (film): 2946, 1631, 1427, 1251, 1109. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57 (2*m*, Ph); 7.51 (2*m*, Ph); 7.37–7.30 (4*m*, Ph); 7.26 (2*m*, Ph); 5.71 (*ddt*, *J* = 17.0, 10.5, 7.0, C*H*=CH_2); 5.04–4.96 (2*m*, CH=CH_2); 2.52 (*ddt*, *J* = 13.5, 7.0, 1.5, C$H_A$$H_B$C=C); 2.45 (*ddt*, *J* = 13.5, 7.0, 1.5, C$H_A$$H_B$C=C); 2.06 (*m*, CHCO); 1.60–1.26 (8*m*, 4 CH_2); 0.40 (3*s*, MeSi); 0.39 (3*s*, MeSi); 0.33 (3*s*, MeSi); 0.33 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.6 (*i*-Ph); 138.4 (*i*-Ph); 135.0 (*o*-Ph); 134.8 (*C*=CH_2); 133.4 (*o*-Ph); 129.0 (*p*-Ph); 128.6 (*p*-Ph); 127.6 (*m*-Ph); 127.2 (*m*-Ph); 117.3 (C=*C*H_2); 76.8 (CO); 46.6 (*C*H_2C=C); 44.1 (*C*HCO); 28.0 (CH_2); 25.8 (CH_2); 25.7 (CH_2); 24.9 (CH_2); 2.2 (MeSi); 2.0 (MeSi); −2.3 (MeSi); −2.5 (MeSi). ESI-MS ($C_{25}H_{36}NaOSi_2$; calc. 431.2202): 431.2189 ($[M+Na]^+$).

4-Cyclobutyl-4-[dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]but-1-ene (**20ea**; 89%). Oil. TLC (pentane): R_f 0.42. IR (film): 2946, 1631, 1427, 1251, 1109. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.63 (2*m*, Ph); 7.50 (2*m*, Ph); 7.40–7.26 (6*m*, Ph); 5.64 (*ddt*, *J* = 17.0, 10.0, 7.5, C*H*=CH_2); 5.00 (*d*, *J* = 17.0, CH=C$H_{(Z)}$$H_{(E)}$); 4.94 (*d*, *J* = 10.0, CH=C$H_{(Z)}$$H_{(E)}$); 2.62 (*m*, CHCO); 2.46 (*dd*, *J* = 13.5, 7.5, C$H_A$$H_B$C=C); 2.30 (*dd*, *J* = 13.5, 7.5, C$H_A$$H_B$C=C); 2.09 (*m*, CH); 1.87 (*m*, CH); 1.76–1.61 (3*m*, 3 CH); 0.43 (3*s*, MeSi); 0.39 (3*s*, MeSi); 0.30 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.6 (*i*-Ph); 138.0 (*i*-Ph); 134.9 (*o*-Ph); 134.8 (*C*=CH_2); 133.4 (*o*-Ph); 129.1 (*p*-Ph); 128.8 (*p*-Ph); 127.6 (*m*-Ph); 127.3 (*m*-Ph); 117.0 (C=*C*H_2); 76.1 (CO); 42.3 (*C*H_2C=C); 42.3 (*C*HCO); 24.4 (CH_2); 22.5 (CH_2); 17.6 (CH_2); 2.1 (MeSi); 1.9 (MeSi); −2.8 (MeSi); −3.5 (MeSi). ESI-MS ($C_{24}H_{34}NaOSi_2$; calc. 417.2046): 417.2043 ($[M+Na]^+$).

2,4-Dimethyl-3-[dimethyl(phenyl)silyl]-3-[dimethyl(phenyl)silyloxy]pentane (**20fe**; 61%). Oil. TLC (hexane): R_f 0.31. IR (film): 2938, 1427, 1250, 1117. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.66–7.55 (4*m*, Ph); 7.43–7.37 (6*m*, Ph); 2.01 (2*sept.*, *J* = 7.0, Me_2C*H*); 0.90 (6*d*, *J* = 7.0, *Me*$_A$Me$_B$CH); 0.89 (6*d*, *J* = 7.0, Me$_A$*Me*$_B$CH); 0.43 (3*s*, *Me*$_A$Me$_B$Si); 0.41 (3*s*, Me$_A$*Me*$_B$Si); 0.39 (3*s*, *Me*$_A$Me$_B$Si); 0.38 (3*s*, Me$_A$*Me*$_B$Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.7 (*i*-Ph); 133.4 (*i*-Ph); 133.0 (*o*-Ph); 129.2 (*o*-Ph); 129.0 (*p*-Ph); 128.5 (*p*-Ph); 127.7 (*m*-Ph); 127.2 (*m*-Ph); 84.4 (CO); 35.7 (Me_2*C*H); 20.2 (*Me*$_A$Me$_B$CH); 18.9 (Me$_A$*Me*$_B$CH); 1.3 (Me_2Si); 0.6 (Me_2Si). EI-MS: no M^+ observed.

1-[Dimethyl(phenyl)silyl]-2-methylpropan-1-one (**34**) [22] (82%), from the disilyl alcohol **13f** and CCl_4. Oil. TLC (Et_2O/hexane 10:90): R_f 0.48. IR (neat): 3095 (CH), 1639 (C=O), 1249 (CSi), 1117 (PhSi). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (2*m*, Ph); 7.37 (3*m*, Ph); 2.89 (*sept.*, *J* = 7, Me_2C*H*); 0.90 (6*d*, *Me*$_2$CH); 0.49 (6*s*, Me_2Si).

The Aldol Reaction: 5-Hydroxy-2-methylnonan-3-one (**18**) *and 2,2-Dimethyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]propane* (**19**). BuLi (1 mmol) was added to a soln. of the silyl alcohol (1 mmol) in THF (5 ml). After 5 min, the mixture was cooled to −40°. Pentanal (**15**; 0.12 ml, 1 mmol) and isopropyl methyl ketone (**16**; 0.11 ml, 1 mmol) were added. After 2 h, the mixture was diluted with hexane, and the org. fraction was washed with brine (20 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The ^{1}H-NMR spectrum contained resonances corresponding to **18** (80%, NMR) and the **19** (98%; NMR). Chromatography gave the pure compounds as oils.

Data of **18**: IR (film): 1710. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.08 (*m*, CHO); 2.53 (*sept.*, *J* = 7, Me_2C*H*); 2.49 (2*d*, *J* = 6.5, $COCH_2$); 1.45–1.18 (10*m*, CH_2); 1.10 (3*t*, Me); 1.07 (6*d*, *J* = 7, *Me*$_2$CH).

Data of **19**: TLC (hexane): R_f 0.27. IR (film): 3050, 2954, 1428, 1249, 1116. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55–7.51 (4*m*, Ph); 7.42–7.30 (6*m*, Ph); 3.47 (*s*, CHCO); 0.86 (9*s*, Me_3C); 0.38 (3*s*, MeSi); 0.36 (3*s*, MeSi); 0.31 (3*s*, MeSi); 0.23 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.7 (*i*-Ph); 139.2 (*i*-Ph); 134.2 (*o*-Ph); 133.6 (*o*-Ph); 129.0 (*p*-Ph); 128.7 (*p*-Ph); 127.6 (*m*-Ph); 127.5 (*m*-Ph); 78.0 (CO); 36.5 (Me_3*C*CO); 28.3 (Me_3C); −0.4 (MeSi); −0.8 (MeSi); −1.2 (MeSi); −2.6 (MeSi). EI-MS: no M^+ peak observed.

One-Pot Brook *Rearrangement–Alkylation Reactions Starting from Acid Chlorides.* Typically, the acid chloride (3.8 mmol) was added to a stirred soln. of Me_2PhSiLi (1M in THF, 9.1 ml, 9.1 mmol) and toluene (9 ml) under N_2 at −78°. After 1 h, alkyl halide (17 mmol) was added and the soln. was allowed to warm to r.t. After 3–18 h, the soln. was poured onto hexane (50 ml), separated, and the org. layer washed with brine (20 ml). The org. solvent was evaporated off under reduced pressure, and the residue was chromatographed (SiO_2; hexane) to give the silyl ether. The following compounds were prepared by this method.

4-[Dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]non-1-ene (**20aa**; 66%). Oil. TLC (light petroleum (b.p. 40–60°)/Et_2O 99.9:0.1): R_f 0.19. IR (film): 2958, 1648, 1249, 1112. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.59–7.57 (4*m*, Ph); 7.41–7.33 (6*m*, Ph); 5.79 (*ddt*, *J* = 17.9, 9.4, 7.1, C*H*=CH_2); 5.01 (2*m*, CH=CH_2); 2.45 (*dd*, *J* = 13.9, 7.2, C$H_A$$H_B$C=C); 2.41 (*dd*, *J* = 13.9, 7.2, CH$_A$$H_B$C=C); 1.66–1.55 (2*m*, CH_2C(OSi)Si); 1.31–1.13 (8*m*, CH_2); 0.86 (3*t*, *J* = 7.0, Me); 0.38 (6*s*, MeSi); 0.37 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.7 (*i*-Ph); 138.2 (*i*-Ph); 135.2

(*C*H=CH_2); 135.0 (*o*-Ph); 133.5 (*o*-Ph); 129.0 (*p*-Ph); 128.9 (*p*-Ph); 127.7 (*m*-Ph); 127.5 (*m*-Ph); 117.3 (CH=*C*H_2); 75.5 (C(OSi)Si); 44.0 (*C*H_2C=C); 39.4 (CH_2); 32.7 (CH_2); 24.5 (CH_2); 22.7 (CH_2); 14.2 (Me); 2.2 (2 MeSi); −3.1 (*Me*$_A$Me$_B$Si); −3.4 (Me$_A$*Me*$_B$Si). ESI-MS ($C_{25}H_{38}NaOSi_2$; calc. 433.2359): 433.2461.

2-Methyl-3-[dimethyl(phenyl)silyl]-3-[dimethyl(phenyl)silyloxy]octane (**20ae**; 30%). Oil. TLC (light petroleum (b.p. 40–60°)/Et_2O, 99.9:0.1): R_f 0.23. IR (film): 2951, 1426, 1247, 1107 (PhSi). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.69–7.61 (4*m*, Ph); 7.49–7.38 (6*m*, Ph); 1.99 (*sept.*, *J* = 6.8, Me$_2$C*H*); 1.76 (*td*, *J* = 13.7, 5.2, C*H*$_A$CH$_B$C(OSi)Si); 1.70 (*td*, *J* = 13.7, 4.7, CH$_A$C*H*$_B$C(OSi)Si); 1.38-1.15 (6*m*, CH_2); 1.00 (3*d*, *J* = 6.8, *Me*$_A$Me$_B$CH); 0.94 (3*t*, *J* = 7.2, *Me*CH_2); 0.92 (3*d*, *J* = 6.8, Me$_A$*Me*$_B$CH); 0.50 (3*s*, MeSi); 0.48 (3*s*, MeSi); 0.44 (3*s*, MeSi); 0.43 (MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.9 (*i*-Ph); 139.9 (*i*-Ph); 134.8 (*o*-Ph); 133.5 (*o*-Ph); 129.0 (*p*-Ph); 128.7 (*p*-Ph); 127.6 (*m*-Ph); 127.4 (*m*-Ph); 79.7 (*C*(OSi)Si); 37.7 (*C*H_2C(OSi)Si); 34.1 (Me$_2$*C*H); 32.7 (CH_2); 24.2 (CH_2); 22.6 (CH_2); 19.5 (*Me*$_A$Me$_B$CH); 17.7 (Me$_A$*Me*$_B$CH); 14.2 (*Me*CH_2); 2.3 (MeSi); 2.0 (MeSi); −1.5 (MeSi); −1.81 (MeSi). ESI-MS ($C_{29}H_{48}OSi_2$; calc. 435.2517): 435.2515 ([*M* + Na]$^+$).

4-[Dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]tridec-1-ene (**20ba**; 41%). Oil. TLC (light petroleum (b.p. 40–60°)): R_f 0.25. IR (film): 2919, 1615, 1115. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.57–7.54 (4*m*, Ph); 7.37–7.26 (6*m*, Ph); 5.77 (*ddt*, *J* = 17.8, 9.4, 7.2, C*H*=CH_2); 4.99 (2*m*, CH=C*H*$_2$); 2.44 (*dd*, *J* = 14.0, 7.2, C*H*$_A$H$_B$C=C); 2.39 (*dd*, *J* = 14.0, 7.2, CH$_A$*H*$_B$C=C); 1.66–1.55 (2*m*, CH_2C(OSi)Si); 1.32–1.14 (14*m*, CH_2); 0.92 (3*t*, *J* = 6.8, Me); 0.363 (6*s*, MeSi); 0.357 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.7 (*i*-Ph); 138.1 (*i*-Ph); 135.1 (*C*H=CH_2); 134.8 (*o*-Ph); 133.4 (*o*-Ph); 129.0 (*p*-Ph); 128.8 (*p*-Ph); 127.6 (*m*-Ph); 127.4 (*m*-Ph); 117.2 (CH=*C*H_2); 75.4 (C(OSi)Si); 43.9 (*C*H_2C=C); 39.3 (CH_2); 31.9 (CH_2); 30.3 (CH_2); 29.52 (CH_2); 29.47 (CH_2); 29.3 (CH_2); 24.6 (CH_2); 22.7 (CH_2); 14.1 (Me); 2.0 (2 MeSi); −3.3 (*Me*$_A$Me$_B$Si); −3.5 (Me$_A$*Me*$_B$Si). ESI-MS ($C_{29}H_{46}ONaSi_2$; calc. 489.3087): 489.3107 ([*M* + Na]$^+$).

4-Cyclohexyl-4-[dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]but-1-ene (**20ca**; 98%). Identical (TLC, ^{1}H-NMR) to the sample prepared earlier.

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]-2-methylpropane (**20ce**; 65%). Identical (TLC, ^{1}H-NMR) to the sample prepared earlier.

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-1-[dimethyl(phenyl)silyloxy]-3-methylbutane (**20cf**; 45%). Identical (TLC, ^{1}H-NMR) to the sample prepared earlier.

4-[Dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]-5-methylhex-1-ene (**20fa**; 75%). Oil. TLC (hexane/Et_2O 99:1): R_f 0.30. IR (film): 2959, 1637, 1427, 1252, 1115. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.67–7.58 (4*m*, Ph); 7.43–7.31 (6*m*, Ph); 5.85 (*ddt*, *J* = 17.5, 9.5, 7.0, C*H*=CH_2); 5.12–5.05 (2*m*, CH=C*H*$_2$); 2.58 (2*dd*, *J* = 7.0, 1.0, CH_2C=C); 1.98 (*sept.*, *J* = 7.0, Me$_2$C*H*); 0.96 (3*d*, *J* = 7.0, *Me*$_A$Me$_B$CH); 0.93 (3*d*, *J* = 7.0, Me$_A$*Me*$_B$CH); 0.47 (3*s*, MeSi); 0.46 (3*s*, MeSi); 0.44 (6*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.7 (*i*-Ph); 138.9 (*i*-Ph); 135.0 (*C*=CH_2); 134.7 (*o*-Ph); 133.4 (*o*-Ph); 129.0 (*p*-Ph); 128.7 (*p*-Ph); 127.6 (*m*-Ph); 127.4 (*m*-Ph); 117.6 (C=*C*H_2); 79.0 (CO); 42.0 (*C*H_2C=C); 31.6 (Me$_2$*C*H); 19.3 (*Me*$_A$Me$_B$CH); 17.9 (Me$_A$*Me*$_B$CH); 2.2 (MeSi); 2.0 (MeSi); −1.8 (MeSi). EI-MS: no M^+ peak observed, 247.2 (40, [*M* − SiMe$_2$Ph]$^+$),135.1 (100, SiMe$_2$Ph$^+$).

2-[Dimethyl(phenyl)silyl]-2-[dimethyl(phenyl)silyloxy]-3-methyl-1-phenylbutane (**20fb**; 50%). Oil. TLC (hexane): R_f 0.23. IR (film): 2935, 1602, 1589, 1426, 1250, 1114. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.55 (2*m*, Ph); 7.46 (2*m*, Ph); 7.41–7.12 (11*m*, Ph); 3.09 (2 br. *s*, C*H*$_A$*H*$_B$Ph); 2.09 (1*sept.*, *J* = 6.5, Me$_2$C*H*); 1.02 (3*d*, *J* = 6.5, *Me*$_A$Me$_B$CH); 0.96 (3*d*, *J* = 6.5, Me$_A$*Me*$_B$CH); 0.36 (3*s*, MeSi); 0.32 (6*s*, MeSi), 0.20 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.9 (*i*-PhSi); 139.0 (*i*-PhSi); 137.7 (*i*-Ph); 134.9 (*o*-PhSi); 133.5 (*o*-PhSi); 131.5 (*o*-Ph); 128.9 (*p*-PhSi); 128.6 (*p*-PhSi); 127.8, 127.5, 127.3 (3 *m*-Ph); 126.3 (*p*-Ph); 81.2 (CO); 42.0 (Ph*C*H_2); 33.9 (*C*HCO); 20.0 (*Me*$_A$Me$_B$CH); 19.2 (Me$_A$*Me*$_B$CH); 2.2 (MeSi); 1.7 (MeSi); −1.5 (MeSi); −2.0 (MeSi). EI-MS: no M^+ peak observed, 297.2 (41, [M^+ − SiMe$_2$Ph]$^+$), 135.1 (100, SiMe$_2$Ph$^+$).

2-[Dimethyl(phenyl)silyl]-2-[dimethyl(phenyl)silyloxy]-3-methylbutane (**20fc**; 62%). Oil. TLC (hexane-Et_2O, 99:1): R_f 0.37. IR (film): 2909, 1427, 1250, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.72–7.63 (4*m*, Ph); 7.48–7.37 (6*m*, Ph); 1.91 (1*sept.*, *J* = 7.0, Me$_2$C*H*); 1.42 (3*s*, COSi*Me*); 0.96 (3*d*, *J* = 7.0, *Me*$_A$Me$_B$CH); 0.91 (3*d*, *J* = 7.0, Me$_A$*Me*$_B$CH); 0.48 (3*s*, MeSi); 0.47 (6*s*, MeSi); 0.42 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.6 (*i*-Ph); 138.9 (*i*-Ph); 134.6 (*o*-Ph); 133.3 (*o*-Ph); 128.9 (*p*-Ph); 128.7 (*p*-Ph); 127.5 (*m*-Ph); 127.5 (*m*-Ph); 78.5 (CO); 32.3 (Me$_2$*C*H); 21.6 (CO*Me*); 19.3 (*Me*$_A$Me$_B$CH); 17.9 (Me$_A$*Me*$_B$CH); 2.1 (MeSi); 1.8 (MeSi); −1.9 (MeSi); −2.1 (MeSi). EI-MS ($C_{12}H_{32}OSi_2$; calc. 356.1992): 356.2004 (M^+).

6-Bromo-3-[dimethyl(phenyl)silyl]-3-[dimethyl(phenyl)silyloxy]-2-methylhexane (**20ff**). With a 5-fold excess of 1,3-dibromopropane, followed by ethanolysis (40%), together with some silyl ether. TLC (hexane/Et_2O 90:10): R_f 0.54. IR (film): 3600, 2957, 1427, 1254, 1118, 1051. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.65 (2*m*, Ph); 7.40–7.33 (3*m*, Ph); 3.81 (1*m*, C*H*$_A$H$_B$Br); 3.47 (*m*, CH$_A$*H*$_B$Br); 1.98–1.72 (4*m*, 2 CH_2); 1.58 (*m*, Me$_2$C*H*); 0.85 (3*d*, *J* = 7.0, *Me*$_A$Me$_B$CH); 0.85 (3*d*, *J* = 7.0, Me$_A$*Me*$_B$CH); 0.41 (3*s*, *Me*$_A$Me$_B$Si), 0.40 (3*s*, Me$_A$*Me*$_B$Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.5 (*i*-Ph); 134.5 (*o*-Ph); 128.7 (*p*-Ph); 127.4 (*m*-Ph); 82.4 (CO); 68.7 (*C*H_2Br); 35.5

(*C*HCO); 29.0 (CH_2); 27.3 (CH_2); 19.0 (Me_AMe$_B$CH); 17.8 (Me$_A$$Me_B$CH); −3.2 (MeSi); −3.4 (MeSi). EI-MS: no M^+ peak observed.

4-[Dimethyl(phenyl)silyl]-4-[dimethyl(phenyl)silyloxy]-5,5-dimethylhexene (**20ja**; 98%). Oil. TLC (hexane): R_f 0.38. IR (film): 2956, 1427, 1254, 1115, 1050. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62 (2*m*, Ph); 7.55 (2*m*, Ph); 7.41-7.24 (6*m*, Ph); 6.01 (*ddt*, *J* = 17.5, 10.5, 7.0, CH_2CH=CH_2); 5.08 (br. *d*, *J* = 17.5, CH=CH$_E$$H_{(Z)}$); 5.01 (br. *d*, *J* = 10.5, CH=C$H_{(E)}$H$_Z$); 2.70 (2*d*, *J* = 7.0, C$H_A$$H_B$C=C); 0.86 (9*s*, Me_3C); 0.43 (3*s*, MeSi); 0.40 (9*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.4 (*i*-Ph); 140.0 (*i*-Ph); 136.8 (*C*=CH_2); 135.1 (*o*-Ph); 133.5 (*o*-Ph); 129.0 (*p*-Ph); 128.6 (*p*-Ph); 127.6 (*m*-Ph); 127.4 (*m*-Ph); 116.2 (C=*C*H$_2$); 82.8 (CO); 43.3 (*C*H$_2$C=C); 40.3 (Me_3*C*CO); 27.9 (*Me*$_3$C); 2.4 (MeSi); 1.9 (MeSi); 0.2 (MeSi); −0.3 (MeSi). EI-MS: no M^+ observed.

2-[Dimethyl(phenyl)silyl]-2-[dimethyl(phenyl)silyloxy]-3,3-dimethyl-1-phenylbutane (**20jb**; 82%). Oil. TLC (hexane): R_f 0.27. IR (film): 3068, 2956, 1427, 1257, 1114. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.70 (2*m*, Ph); 7.62 (2*m*, Ph); 7.46–7.19 (11*m*, Ph); 3.32 (*d*, *J* = 14.0, PhC$H_A$$H_B$); 3.26 (*d*, *J* = 14.0, PhCH$_A$$H_B$); 0.84 (9*s*, Me_3C); 0.60 (3*s*, MeSi); 0.59 (3*s*, MeSi); 0.39 (3*s*, MeSi); 0.34 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 140.5 (*i*-PhSi); 140.4 (*i*-PhSi); 139.4 (*i*-Ph); 135.1 (*o*-PhSi); 133.7 (*o*-PhSi); 131.3 (*o*-Ph); 129.2 (*p*-PhSi); 128.5 (*p*-PhSi); 127.7, 127.6, 127.3 (3 *m*-Ph); 126.1 (*p*-Ph); 85.8 (CO); 43.8 (Ph*C*H$_2$); 40.6 (Me_3*C*CO); 28.5 (*Me*$_3$C); 2.6 (MeSi); 2.4 (MeSi); 0.4 (MeSi); 0.4 (MeSi). EI-MS: no M^+ peak observed, 312.0 (50, $[M + H - SiMe_2Ph]^+$), 135.1 (100, $SiMe_2Ph^+$).

[(1-Cyclohexyl(ethenyl)oxy]dimethyl(phenyl)silane (**28**). Prepared from the acid chloride **12c** and CH_2Br_2 after transferring the silyllithium reagent from THF into Et_2O and with pentane in place of toluene as the solvent. The silyl enol ether was characterised after desilylation as *1-cyclohexylethan-1-one* (**29**).

3-[Dimethyl(phenyl)silyl]-3-[dimethyl(phenyl)silyloxy]-4-phenylbut-1-ene (**30**; 86%). Prepared from PhCOCl and characterised after desilylation as *1-phenyl-1-[dimethyl(phenyl)silyl]but-3-en-ol* (**31**).

4-[Dimethyl(phenyl)silyloxy]-4-phenylhepta-1,6-diene (**32**). Prepared from PhCOCl and characterised after desilylation as *hepta-1,6-dien-4-ol* (**33**).

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]but-3-en-1-ol (**22**). HCl (10M, 0.5 ml, 5 mmol) and **20ca** (0.57 g, 1.0 mmol) were stirred in MeOH (5 ml) for 2 h, which was probably not optimal. Most of the solvent was removed under reduced pressure, the residue was poured into H_2O and extracted with Et_2O (3 × 20 ml). The extract was washed with brine (20 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. The residue was chromatographed (SiO_2; hexane/Et_2O 9:1) to give **22** (59%) as an oil. TLC (light petroleum (b.p. 40–60°)/Et_2O 9:1): R_f 0.19. IR (film): 3564 (br., OH), 2934 (CH), 1634 (C=C), 1427 (Ph), 1248 (Si–Me), 1115 (SiPh). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.59 (2*m*, *o*-Ph); 7.40–7.29 (3*m*, *m*- and *p*-Ph); 5.80 (*ddt*, *J* = 17.5, 10.0, 7.6, C*H*=CH_2); 5.10–5.01 (2*m*, CH=CH_2); 2.39 (*dd*, *J* = 14.0, 7.0, CH_ACH$_B$C=C); 2.33 (*dd*, *J* = 14.0, 7.0, CH$_A$CH_BC=C); 1.77–1.46 (6*m*, CHC(OSi)Si, 5 CH_{eq}); 1.18–0.95 (5*m*, CH_{ax}); 0.40 (6*s*, Me_2Si). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.1 (*i*-Ph); 134.7 (*o*-Ph); 134.3 (*C*H=CH_2); 128.9 (*p*-Ph); 127.6 (*m*-Ph); 118.4 (C=*C*H$_2$); 71.2 (CO); 46.2 (*C*HCO); 39.9 (*C*H$_2$C=C); 28.6 (CH_2); 27.7 (CH_2); 26.9 (CH_2); 26.9 (CH_2); 26.7 (CH_2); −2.1 (Me_2Si). ESI-MS ($C_{18}H_{28}NaOSi$; calc. 311.1807): 311.1800 ($[M + Na]^+$).

1-Cyclohexylbut-3-en-1-one (**23**). The alcohol **22** (0.10 g, 0.3 mmol) in CH_2Cl_2 (0.5 ml) was stirred with PCC (0.12 g, 0.6 mmol) in CH_2Cl_2 (1 ml) for 18 h. The mixture was passed through a silica pad, and the solvent was removed under reduced pressure. The residue was chromatographed (SiO_2; CH_2Cl_2/pentane 3:7) to give **23** (83%). TLC (light petroleum (b.p. 30–40°)/CH_2Cl_2 4:6): R_f 0.25. IR (film): 2939, 1708, 1639. ^{1}H-NMR (400 MHz; $CDCl_3$): 5.89 (*ddt*, *J* = 17.1, 10.2, 6.9, C*H*=CH_2); 5.12 (*dq*, *J* = 10.2, 1.4, CH=CH$_2$C$H_{(E)}$); 5.08 (*dq*, *J* = 17.1, 1.4, CH=C$H_{(Z)}$CH$_E$); 3.18 (2*dt*, *J* = 6.9, 1.3, CH_2CH=CH_2); 2.36 (*tt*, *J* = 10.7, 3.0 CHCO); 1.82–1.65 (5*m*, CH_{eq}); 1.33–1.15 (5*m*, CH_{ax}). ^{13}C-NMR (100 MHz, $CDCl_3$): 211.6 (C=O); 131.0 (*C*H=CH_2); 118.3 (CH=*C*H$_2$); 50.4 (*C*HCO); 45.5 (*C*H$_2$CO); 28.4 (2 CH_2); 25.8 (2 CH_2); 25.6 (2 CH_2).

1-Cyclohexyl-1-[dimethyl(phenyl)silyl]-3-methylbutan-1-ol (**24**). The silyl ether **20cf** (0.336 g, 0.77 mmol) was stirred with TBAF (1M in THF, 2.3 ml, 2.3 mmol) at r.t. for 4 h. The mixture was diluted with distilled H_2O and CH_2Cl_2, and the org. phase was passed through a silica pad, and washed with Et_2O. The solvent was evaporated under reduced pressure to give the crude product as a colourless oil (0.189 g, 0.62 mmol, 81%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.62–7.57 (2*m*, Ph); 7.41–7.36 (3*m,* Ph); 1.82–1.60 (10*m*, CH_{eq}, CH, CH_AH_B, Me_2C*H*, OH); 1.21-1.00 (5*m,* CH_{ax}); 0.93 (3*d*, *J* = 7, *Me*$_A$Me$_B$CH); 0.89 (3*d*, *J* = 7, Me$_A$*Me*$_B$CH); 0.30 (6*s,* Me_2Si).

1-Cyclohexyl-3-methylbutan-1-one (**25**). The alcohol **24** (0.189 g, 0.62 mmol) was stirred in CH_2Cl_2 (5 ml) with PCC (0.530 g, 2.5 mmol) for 18 h at r.t. The mixture was passed through a silica pad, and washed with CH_2Cl_2. The solvent was evaporated under reduced pressure to give **25** [34] as a colourless oil (0.087 g, 83%). TLC (light petroleum (b.p. 30–40°)): R_f 0.57 (staining with 2,4-dinitrophenylhydrazine). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.28 (3*m,* CHCO, CH_2CO); 2.12 (*nonet.*, *J* = 7, Me_2C*H*); 1.82–1.59 (5*m,* CH_{eq},); 1.18–0.91 (5*m,* CH_{ax});

0.87 (6*d*, $J = 7$, Me_2CH). ^{13}C-NMR (400 MHz, $CDCl_3$): 213.2 (CO); 50.7 (*C*HCO); 49.3 (CH_2CO); 28.0 (CH_2); 25.5 (CH_2); 25.3 (CH_2); 22.3 (Me_2CH); 21.95 (Me_2C). EI-MS ($C_{11}H_{20}O$; calc. 168.1514): 168.1520, (M^+).

1-Cyclohexyl-2-methylpropanol (**26**). The silyl ether **20ce** (2.5 g, 6 mmol) in THF (1 ml) was stirred with TBAF (4.0 g, 15 mmol) in THF (20 ml) at r.t. for 18 h. The THF was evaporated off, distilled H_2O (20 ml) was added to the residue, which was extracted with CH_2Cl_2 (5×20 ml). The combined org. layers were washed with brine (20 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give the crude **26** (2.5 g). Part of the residue (0.5 g) was purified by flash column chromatography to give **26** [**35**] (0.172 g, 95%). The crude mixture was used directly in the oxidation below. TLC (Et_2O/hexane 10:90): R_f 0.24. IR ($CHCl_3$): 3456 (OH), 2926 (CH). ^{1}H-NMR (400 MHz, $CDCl_3$): 4.01 (*t*, $J = 5$, C*H*OH); 1.75 (*sept.*, *d*, $J = 7, 5$, Me_2CH); 1.84 (*m*, CH); 1.81–1.52 (5*m*, c-Hex); 1.42–0.91 (5*m*, c-Hex); 0.90 (3*d*, $J = 7$, Me_AMe_BCH); 0.88 (3*d*, $J = 7$, Me_AMe_BCH).

1-Cyclohexyl-2-methylpropan-1-one (**27**). The crude alcohol **20ce** (2.4 mmol) in CH_2Cl_2 was stirred with PCC (10 mmol) for 18 h at r.t. The mixture was diluted with pentane (20 ml), passed through a silica pad, washed with CH_2Cl_2 (20 ml), and the solvent was carefully evaporated under reduced pressure. The residue was purified by flash column chromatography (CH_2Cl_2/light petroleum (b.p. 30–40°) 30:70) to yield **27** (2.1 mmol, 88% over two steps from **20ce**). TLC (Et_2O/hexane 20:80): R_f 0.40. IR (neat): 2930 (C–H), 1706 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.74 (*sept.*, $J = 7$, Me_2CH); 2.49 (*tt*, $J = 11, 3$, CH); 1.77 (4*m*, c-Hex); 1.67 (*m*, c-Hex); 1.42-1.13 (5*m*, c-Hex); 1.05 (6*d*, $J = 7$, Me_2CH).

1-Cyclohexyl ethan-1-one (**29**). HCl (10M, 0.5 ml, 5 mmol) and crude **28** (1.0 mmol) were stirred in MeOH (10 ml) at r.t. for 18 h. Distilled H_2O (30 ml) was added to the mixture, which was extracted with CH_2Cl_2 (3×20 ml). The combined org. layers were washed with brine (10 ml), dried ($MgSO_4$), and the solvent was carefully removed under reduced pressure to give **29** [36] as a yellow liquid (76% from cyclohexanecarbonyl chloride). TLC (Et_2O/hexane 10:90): R_f 0.30. IR (neat): 1711 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.31 (*tt*, $J = 11, 3$); 2.11 (3*s*, Me); 1.89–1.49 (5*m*, c-Hex); 1.35-0.81 (5*m*, c-Hex).

1-[Dimethyl(phenyl)silyl]-1-phenylbut-3-en-1-ol (**31**). HCl (10M, 0.5 ml, 5 mmol) and **30** were stirred in MeOH at r.t. for 3 h, and MeOH was removed at reduced pressure. The residue was dissolved in CH_2Cl_2 (20 ml), washed with distilled H_2O (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash column chromatography (Et_2O/hexane 5:95) to yield **31** (80% over two steps from PhCOCl) as an oil. TLC (Et_2O/hexane 10:90) R_f 0.28. IR (neat): 3555 (OH), 2926 (CH), 1638 (C=C), 1493 (Ph), 1255 (MeSi), 1116 (PhSi). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.39 (3*m*, *m*- and *p*-Ph); 7.32 (2*m*, *o*-Ph); 7.22 (2*m*, *m*-Ph); 7.12 (3*m*, *o*- and *p*-Ph); 5.43 (*dddd*, $J = 17, 11, 8, 5$, C*H*=CH_2); 5.09 (2*m*, =CH_2); 2.98 (2*ddt*, $J = 14, 5, 1$, =CHCH_AH_B); 2.51 (2*dd*, $J = 14, 8$, =CHCH_AH_B); 1.86 (br. *s*, O*H*); 0.30 (3*s*, Me_AMe_BSi); 0.24 (3*s*, Me_AMe_BSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 146.6 (+, Ph); 137.4 (+, CSi); 136.5 (–, Ph); 134.2 (–, Ph); 131.0 (–, Ph); 129.4 (–, Ph); 129.2 (–, Ph); 129.1 (–, Ph); 126.9 (–, *C*H=CH_2); 121.7 (+, CH=*C*H_2); 72.4 (+, CO); 43.1 (+, CH_2); –3.8 (–, MeSi); –4.4 (–, MeSi). ESI(Na^+)-MS: no M^+ observed.

4-Phenylhepta-1,6-dien-4-ol (**33**). The silyl ether **32** (0.5 mmol) was stirred with TBAF in THF (1.5 ml, 1.0M) at r.t. for 3 h, diluted with CH_2Cl_2 (10 ml), washed with distilled H_2O (10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash column chromatography (Et_2O/hexane 10:90) to give **33** [37] (91% over 2 steps) as an oil. TLC (Et_2O/hexane 50:50): R_f 0.30. IR (neat): 3511 (OH), 3069 (CH), 1634 (C=C), 1469 (Ph), 1246 (MeSi), 1114 (PhSi). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.42–7.15 (5*m*, Ph); 5.61 (2*dddd*, $J = 14, 10, 8, 6$, C*H*=CH_2); 5.11 (4*m*, CH=C*H*$_2$); 2.70 (2*ddt*, $J = 14, 6, 1$, =CHCH_AH_B); 2.53 (2*dd*, $J = 14, 8$, =CHCH_AH_B); 2.19 (br., OH).

Methyl (Cyclohexyl)[dimethyl(phenyl)silyl][dimethyl(phenyl)silyloxy]methanesulfite (**35**; 70%). Oil. Prepared by the same method as for the reactions with alkyl halides, except that the electrophile was methane chlorosulfite. TLC (hexane/Et_2O, 96:4): R_f 0.06. IR (film): 2932, 2854, 1427, 1254, 1189, 1109. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.67–7.62 (4*m*, Ph); 7.40–7.33 (6*m*, Ph); 3.75 (3*s*, MeO); 2.19–2.07 (2*m*, CH_{ax}); 1.97–1.92 (*m*, $CH_{ax}CO$); 1.75–1.57 (3*m*, CH_{ax}); 1.25–1.10 (3*m*, CH_{eq}); 1.05–0.92 (2*m*, CH_{eq}); 0.55 (3*s*, MeSi); 0.50 (3*s*, MeSi); 0.37 (3*s*, MeSi), 0.33 (3*s*, MeSi). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.9 (*i*-Ph); 137.8 (*i*- Ph); 135.4 (*o*-Ph); 135.3 (*o*-Ph); 129.5 (*p*-Ph); 129.5 (*p*-Ph); 127.5 (*m*-Ph); 127.5 (*m*-Ph); 89.7 (CO); 47.8 (MeO); 45.9 (*C*HCO); 31.5 (CH_2); 31.1 (CH_2); 26.7 (CH_2); 26.7 (CH_2); 26.5 (CH_2); 0.5 (MeSi); 0.4 (MeSi); –0.5, –0.6 (MeSi). EI-MS ($C_{24}H_{36}O_3SSi_2$; calc. 460.1924): 460.1945 (M^+), 460.2 (11, M^+), 381.2 (20, [$M - SO_2Me$]$^+$), 135.1 (100, $SiMe_2Ph^+$).

REFERENCES

[1] A. G. Brook, *Acc. Chem. Res.* **1974**, *7*, 77.
[2] P. Antoniotti, G. Tonachini, *J. Org. Chem.* **1993**, *58*, 3622; P. Antoniotti, C. Canepa, G. Tonachini, *J. Org. Chem.* **1994**, *59*, 3952.
[3] D. Seebach, *Angew. Chem.*, *Int. Ed.* **1979**, *18*, 239.
[4] D. Wittenberg, T. C. Wu, H. Gilman, *J. Org. Chem.* **1959**, *24*, 1349; T. Hiyama, M. Obayashi, I. Mori, H. Nozaki, *J. Org. Chem.* **1983**, *48*, 912.
[5] A. G. Brook, N. V. Schwartz, *J. Am. Chem. Soc.* **1960**, *82*, 2435; A. Degl'Innocenti, S. Pike, D. R. M. Walton, G. Seconi, A. Ricci, M. Fiorenza, *J. Chem. Soc.*, *Chem. Commun.* **1980**, 1201; D. Schinzer, C. H. Heathcock, *Tetrahedron Lett.* **1981**, 1881; P. C. B. Page, S. Rosenthal, *J. Chem. Res. (S)* **1990**, 302.
[6] M. Kato, A. Mori, H. Oshino, J. Enda, K. Kobayashi, I. Kuwajima, *J. Am. Chem. Soc.* **1984**, *106*, 1773.
[7] R. S. Roberts, Ph.D. Thesis, Cambridge University, 1997, pp. 180, 181.
[8] J. M. Aizpurua, C. Palomo, in 'Science of Synthesis, Vol. 4, Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds', Ed. I. Fleming, Thieme, Stuttgart, 2001, Chapt. 4.4.25.
[9] R. D. Singer, in 'Science of Synthesis, Vol. 4, Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds', Ed. I. Fleming, Thieme, Stuttgart, 2001, Chapt. 4.4.11.
[10] P. C. B. Page and M. J. McKenzie, in 'Science of Synthesis, Vol. 4, Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds', Ed. I. Fleming, Thieme, Stuttgart, 2001, Chapt. 4.4.28.
[11] W. H. Moser, *Tetrahedron* **2001**, *57*, 2065.
[12] M. Kato, I. Kuwajima, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 827; H. J. Reich, E. K. Eisenhart, R. E. Olson, M. J. Kelly, *J. Am. Chem. Soc.* **1986**, *108*, 7791; M. Koreeda, S. Koo, *Tetrahedron Lett.* **1990**, *31*, 831; E. J. Corey, S. Lin, G. Luo, *Tetrahedron Lett.* **1997**, *38*, 5771; E. J. Corey, G. Luo, L. S. Lin, *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1126.
[13] E. Vedejs, M. J. Arnost, J. M. Eustache, G. A. Krafft, *J. Org. Chem*. **1982**, *47*, 4384; P. F. Hudrlik, A. M. Hudrlik, A. K. Kulkarni, *J. Am. Chem. Soc.* **1985**, *107*, 4260; H. J. Reich, R. C. Holtan, C. Bolm, *J. Am. Chem. Soc.* **1990**, *112*, 5609; T. Nakajima, M. Segi, F. Sugimoto, R. Hioki, S. Yokota, Y. Miyashita, *Tetrahedron* **1993**, *49*, 8343; F. Jin, Y. Xu, W. Huang, *J. Chem. Soc., Perkin Trans. 1* **1993**, 795; T. Brigaud, P. Doussot, C. Portella, *J. Chem. Soc., Chem. Commun.* **1994**, 2117; O. Lefebvre, T. Brigaud, C. Portella, *Tetrahedron* **1998**, *54*, 5939; O. Lefebvre, T. Brigaud, C. Portella, *Tetrahedron* **1999**, *55*, 7233; I. Fleming, R. S. Roberts, S. C. Smith, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1215.
[14] K. Takeda, M. Fujisawa, T. Makino, E. Yoshii, *J. Am. Chem. Soc.* **1993**, *115*, 9351; K. Takeda, T. Tanaka, *Synlett* **1999**, 705.
[15] K. Takeda, J. Nakatani, H. Nakamura, K. Sako, E. Yoshii, K. Yamaguchi, *Synlett* **1993**, 841.
[16] M. R. Burns, J. K. Coward, *J. Org. Chem.* **1993**, *58*, 528.
[17] R. E. Ireland, M. D. Varney, *J. Am. Chem. Soc.* **1984**, *106*, 3668; R. J. Linderman, A. Ghannam, *J. Am. Chem. Soc.* **1990**, *112*, 2392.
[18] G. J. D. Peddle, *J. Organomet. Chem.* **1967**, *10*, 377; Y. Ito, T. Mastsuura, S. Nishimura, M. Ishikawa, *Tetrahedron Lett.* **1986**, *27*, 3261; P. Jutzi, F.-W. Schröder, *J. Organomet. Chem.* **1970**, *24*, C43; I. Fleming, M. Solay, F. Stolwijk, *J. Organomet. Chem.* **1996**, *521*, 121; I. Fleming, U. Ghosh, S. R. Mack, B. P. Clark, *Chem. Commun*. **1998**, 711; M. A. Tius, H. Hu, *Tetrahedron Lett.* **1998**, *39*, 5937; R. E. Maleczka Jr., F. Geng, *Org. Lett.* **1999**, *1*, 1111.
[19] I. Fleming, S. R. Mack, B. P. Clark, *Chem. Commun*. **1998**, 713, 715.
[20] N. V. Schwartz, A. G. Brook, *J. Am. Chem. Soc.* **1960**, *82*, 2439.
[21] I. Kuwajima, N. Minami, T. Abe, T. Sato, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2391; R. Calas, J. Dunoguès, *J. Organomet. Chem. Library* **1976**, *2*, 277.
[22] I. Fleming, U. Ghosh, *J. Chem. Soc., Perkin Trans. 1* **1994**, 257.
[23] M. C. West, Ph.D. Thesis, Cambridge, 2001, and paper in preparation.
[24] I. Kuwajima, T. Sato, M. Arai, N. Minami, *Tetrahedron Lett.* **1976**, 1817; I. Kuwajima, N. Minami, T. Sato, *Tetrahedron Lett.* **1976**, 2253.
[25] I. Kuwajima, M. Arai, T. Sato, *J. Am. Chem. Soc.* **1977**, *99*, 4181.
[26] A. Murai, A. Abiko, N. Shimada, T. Masamune, *Tetrahedron Lett.* **1984**, *25*, 4951.
[27] R. B. Bates, L. M. Kroposki, D. E. Potter, *J. Org. Chem.* **1972**, *37*, 560.
[28] I. Kuwajima, T. Abe, N. Minami, *Chem. Lett.* **1976**, 993.
[29] S. Kobayashi, in 'Science of Synthesis, Vol. 4, Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds', Ed. I. Fleming, Thieme, Stuttgart, 2001, Chapt. 4.4.16.

[30] I. Fleming, T. V. Lee, *Tetrahedron Lett.* **1981**, *22*, 705; I. Fleming, J. Iqbal, *Tetrahedron Lett.* **1983**, *24*, 2913.
[31] A. Inoue, J. Kondo, H. Shinokubo, K. Oshima, *Chem. Commun.* **2002**, 114.
[32] I. Fleming, in 'Organocopper Reagents: A Practical Approach', Ed. R. J. K. Taylor, OUP, Oxford, 1994, Chapt. 12, p. 257.
[33] J. K. Stille, F. Huang, M. T. Regan, *J. Am. Chem. Soc.* **1974**, *96*, 1518.
[34] H. C. Brown, M. W. Rathke, *J. Am. Chem. Soc.* **1967**, *89*, 4528.
[35] W. Kirmse, W. Gruber, *Chem. Ber.* **1971**, *104*, 1789.
[36] 'Dictionary of Organic Compounds', Chapman & Hall, London, 6th edn., 1996, Vol. 1, p. 25.
[37] B. Hamann-Gaudinet, J.-L. Namy, H. B. Kagan, *J. Organomet. Chem.* **1998**, *567*, 39.

Received May 15, 2002