The reduction of α-silyloxy ketones using phenyldimethylsilyllithium

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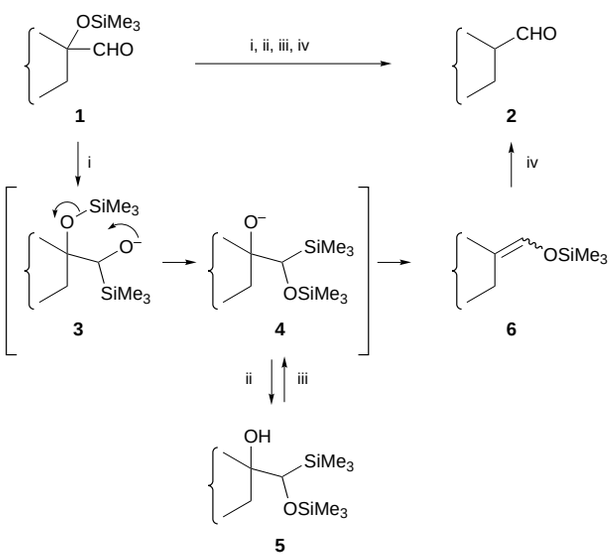
Phenyldimethylsilyllithium reacts with acyloin silyl ethers RCH(OSiMe$_3$)COR 8 to give regiodefined silyl enol ethers RCH=C(OSiMe$_2$Ph)R 9, and hence by hydrolysis ketones RCH$_2$COR 10. The yields can be high but are usually moderate. The mechanism of this reduction is established to involve a Brook rearrangement (Scheme 6) rather than a Peterson elimination (Scheme 1). Although the mechanism appears to be the same in each case, the stereochemistries of the silyl enol ethers 9 are opposite in sense in the aromatic series (R = Ph, Scheme 7) and the aliphatic series (R = cyclohexyl, Scheme 8), with the major aromatic silyl enol ether being the thermodynamically less stable isomer *E*-PhCH=C(OSiMe$_2$Ph)Ph *E*-9aa, and the major aliphatic silyl enol ether being the thermodynamically more stable isomer *Z*-c-C$_6$H$_{11}$CH=C(OSiMe$_2$Ph)-c-C$_6$H$_{11}$ *Z*-9ba. This is a consequence of anomalous anti-Felkin attack in the aromatic series. The reaction with the silyl ether Bu^{t}CH(OSiMe$_3$)COPh 13b is normal in giving *Z*-Bu^{t}CH=C(OSiMe$_2$Ph)Ph *Z*-38 (Scheme 11), but reduction of the silyl ether 8a with lithium aluminium hydride is also anti-Felkin giving with high selectivity the *meso* diol PhCH(OH)CH(OH)Ph 39. The reaction between phenyldimethylsilyllithium and the acyloin silyl ether 8d (R = Bu^t) does not give the ketone Bu^{t}CH$_2$COBu^t, but gives instead the anti-Felkin *meso* diol Bu^{t}CHOHCHOHBu^t 40 also with high selectivity (Scheme 12). Silyllithium and some related reagents react with trifluoromethyl ketones 46 and 48 to give α,α-difluoro silyl enol ethers 47 and 49 (Scheme 14).

Introduction

In their aphidicolin synthesis, Corey *et al.* reduced an α-trimethylsilyloxy aldehyde **1** with trimethylsilyllithium to an aldehyde **2** (Scheme 1).[1] The mechanism that they suggested,



Scheme 1 *Reagents*: i, Me_3SiLi, HMPA; ii, work-up and chromatography; iii, LDA, THF, HMPA; iv, H_3O^+

supported by the isolation of the intermediate **5**, involved the 1,4-oxygen-to-oxygen transfer of the silyl group **3**→**4** followed by the β-silylalkoxide elimination **4**→**6**, often referred to as a Peterson elimination, a name that we find convenient and will use here.

This sequence seemed to us to have been undervalued as a method for reducing α-hydroxycarbonyl compounds, and as a regiocontrolled method for making silyl enol ethers. Having already provided one other example of the reaction taking place in high yield,[2] we undertook a study of its scope and limitations, which we report here. Our principal conclusions are that it is not generally high yielding, and that the mechanism is different from that shown in Scheme 1. In our work we have used the more easily made phenyldimethylsilyllithium rather than trimethylsilyllithium, and have not therefore had to use HMPA as an unavoidable co-solvent which may change the mechanism. It is also possible that the mechanism changes with specific substrates like Corey's aldehyde **1**, and the intermediate **5** would not be on the direct path that our reactions follow.

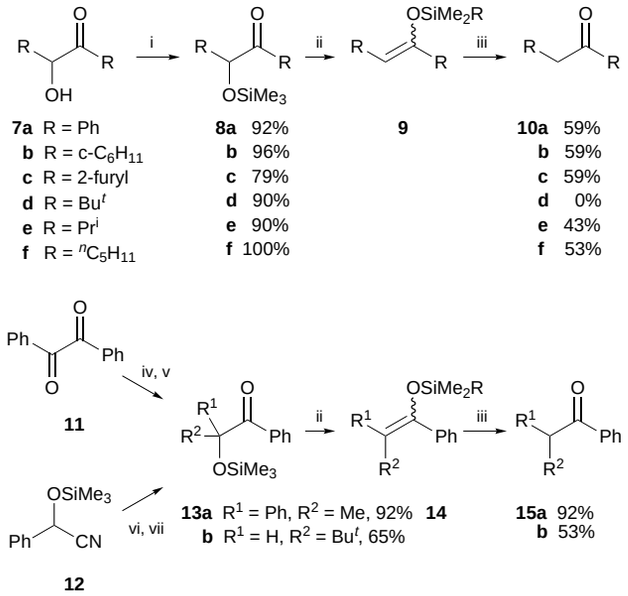
Results and discussion

Our work is divided into four parts: (1) a study of the synthetic usefulness of the reaction, for which we used the trimethylsilyl ethers of acyloins and some of their other derivatives, (2) a study of the mechanism of the reaction, for which we used the acyloin silyl ethers **8a** and **8b**, (3) a study of the stereochemistry of the reaction to explain the remarkable difference in the geometries of the major silyl enol ether products **9** between the aromatic and the aliphatic series, and finally (4) a brief study of a related reaction between the silyllithium reagent and trifluoromethyl ketones **46** and **48**, as a route to α,α-difluoromethyl ketones.

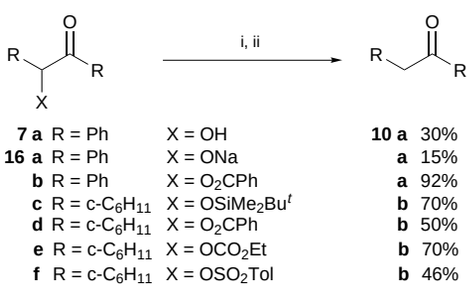
The scope and limitations of the reaction

Our results on the general reaction with a small range of 'symmetrical' acyloin silyl ethers **8** and two 'unsymmetrical' acyloin silyl ethers **13** are summarised in Scheme 2. At this stage, we made no effort to isolate the intermediate silyl enol ethers **9** and **14**, but hydrolysed the crude mixtures and isolated the ketones **10** and **15** directly. Some yields are very acceptable (**15a**; 92%), but the general run of yields was not encouraging. The reason appears to be that the silyllithium reagent attacks the silyl group some of the time, in a reaction shown in the preceding paper to be easy.[3] In consequence, we detected the starting acyloin in the product mixture in all these reactions.

In the hope that varying the leaving group might make the reaction higher yielding, we tried reaction with the acyloin derivatives **16** (Scheme 3). Some of these yields, notably



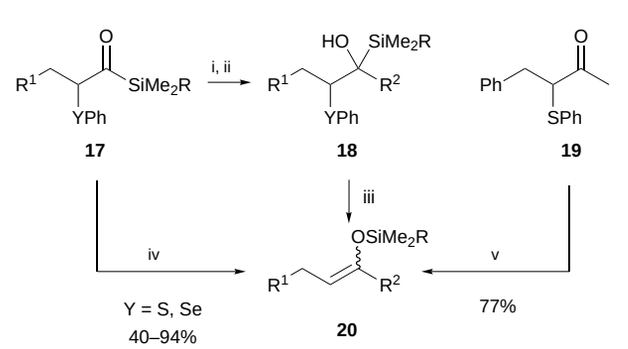
Scheme 2 *Reagents*: i, Me_3SiCl, $(Me_3Si)_2NH$, CH_2Cl_2; ii, $PhMe_2SiLi$, THF; iii, NH_4Cl, H_2O; iv, MeLi; v, NaH, Me_3SiCl; vi, LDA; vii, Bu^tCHO



Scheme 3 *Reagents*: i, $PhMe_2SiLi$, THF; ii, NH_4Cl, H_2O

that from the benzoate **16b** (92%), but regrettably not from all, were better than those from the corresponding reactions with the trimethylsilyl ethers **8** and **13**.

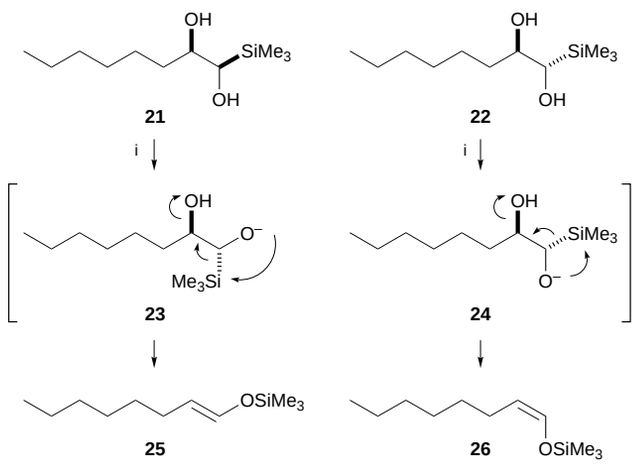
Likewise, Reich *et al*. observed a 77% yield for the generation of a silyl enol ether **20** (R^1 = Ph, R^2 = Me) by a similar reaction of phenyldimethylsilyllithium with the α-phenylthio ketone **19**, but on the whole they obtained higher yields of silyl enol ethers **20** from the reaction of organolithium reagents with the corresponding acyl silanes **17**, either by a one-pot reaction or by isolation of the α-silyl alcohol **18** and a subsequent base-catalysed Brook rearrangement and elimination sequence (Scheme 4).[4]



Scheme 4 *Reagents*: i, R^2M, −78 °C; ii, NH_4OAc–MeOH; iii, base; iv, R^2M, −78→0 °C; v, $PhMe_2SiLi$, THF

The mechanism of the reaction

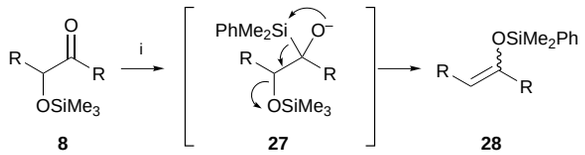
The mechanism in the Corey paper is, of course, entirely reasonable, with each step having good precedent. The attack of a silyllithium reagent on an aldehyde or ketone giving an α-silyl alkoxide is a well used route to a α-silyl alcohols.[5] The to and fro shift of a silyl group in 1,2- and 1,3-diol systems is a common problem in functional group protection,[6] and the Peterson elimination is the thoroughly established *syn* stereospecific second step of the reaction that is properly called Peterson olefination.[7] However, it has also been established by Hudrlik that 1,2-diols with a 1-silyl group **21** and **22** undergo stereospecific 1,2-elimination by a Brook rearrangement followed by, or concerted with, the *anti* expulsion of the β-hydroxy group, summarised as a concerted reaction in **23**→**25** and **24**→**26**, and that this pathway is faster in general than the more direct seeming Peterson reaction in the same substrate (Scheme 5).[8] Similarly Reich showed that his reactions **17**→**20**, with



Scheme 5 *Reagents*: i, KH, Et_2O

better nucleofugal groups, were also stereospecifically *anti*.[4] Although the formation of a pentacovalent intermediate would be unexceptional, it is not clear whether the Brook rearrangement involves a separate carbanion intermediate. It is however known that in the absence of an adjacent leaving group, Brook rearrangement can be consummated by stereospecific protonation, with inversion of configuration when the silyl group is benzylic[9] and with retention of configuration when the substituent α to the silyl group is alkyl.[10] These pathways are equally understandable with or without a carbanion intermediate. We suggest that a pentacovalent siliconate is the only 'carbanion', and that there is unlikely to be another intermediate either in the elimination or in the protonation pathway.

Hudrlik's and Reich's work suggested that the mechanism of the reactions we had been studying might more likely be that shown in Scheme 6, by way of the Brook rearrangement



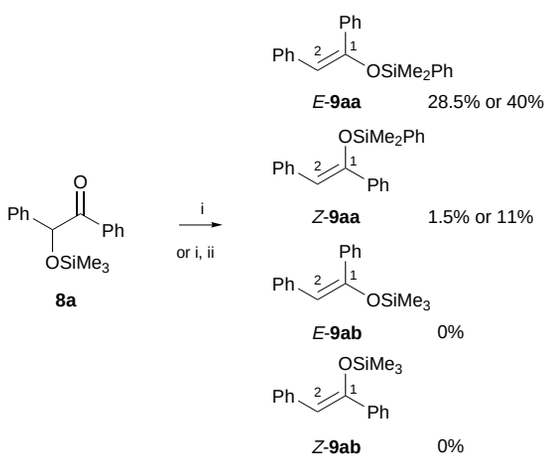
Scheme 6 *Reagents*: i, $PhMe_2SiLi$, THF

coupled with desilylative β-elimination (**27** arrows) which we call the Brook rearrangement route, in contrast to the Peterson route of Scheme 1 as used by Corey, and also by us in our earlier paper.[2]

We tested which mechanism obtains by carrying out the reaction of phenyldimethylsilyllithium on the trimethylsilyl ether **8a**, and this time isolating the intermediate silyl enol ethers (Scheme 7). If the Peterson route were to be followed the products would be trimethylsilyl enol ethers, but if the Brook rearrangement route of Scheme 6 were followed, the products would be phenyldimethylsilyl enol ethers. We found that the

Table 1 NMR chemical shifts for the silyl enol ethers **9aa** and **9ab**. Authentic samples were prepared by reaction of ketone **10a** with LDA and the appropriate silyl chloride.

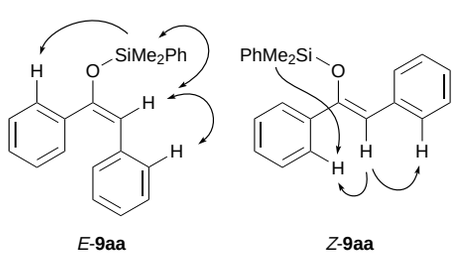
	Authentic trimethylsilyl enol ethers **9ab**		Authentic dimethylphenylsilyl enol ethers **9aa**		Reaction products **8a** + $PhMe_2SiLi$	
	E-**9ab**	*Z*-**9ab**	*E*-**9aa**	*Z*-**9aa**	Major	Minor
Proportion	10	90	10	90	76	24
δ_H(vinyl)	6.18	6.22	6.11	6.16	6.10	6.15
δ_H(SiMe)	0.30	0.14	0.52	0.34	0.51	0.35
δ_C(C-1)	151.68	150.97	151.48	150.90	151.37	≈150
δ_C(C-2)	111.49	110.61	111.97	110.94	111.83	110.82
δ_C(SiMe)	0.47	0.76	−0.94	−0.87	−1.05	−0.95



Scheme 7 *Reagents*: i, $PhMe_2SiLi$, THF; ii, $PhMe_2SiCl$

silyl enol ethers produced were indeed the phenyldimethylsilyl enol ethers *E*-**9aa** and *Z*-**9aa**, in 30% yield and in a ratio of 95 : 5, and not the trimethylsilyl enol ethers **9ab**. The low yield is probably a result of the silyllithium reagent reacting with the silyl enol ether to give the disilane and the lithium enolate, since we find that this reaction does take place when carried out deliberately, as discussed in more detail in the preceding paper.[3] This hypothesis also explains why Reich's yields using alkyl- and aryl-lithium reagents on acylsilanes were higher, because his reagents cleave the silyl enol ethers more slowly than our silyllithium reagent does. In agreement with this hypothesis, we obtained a better yield (51%) of the silyl enol ethers *E*-**9aa** and *Z*-**9aa** by adding phenyldimethylsilyl chloride to the mixture after the reaction was over. The ratio of these silyl enol ethers was now 78 : 22, either because the enolate lost its configurational identity to some extent, or because the *Z*-enolate was desilylated more rapidly than the *E*-enolate. In conclusion, the mechanism is that shown in Scheme 6, by way of the Brook rearrangement.

Proving this simple point was a little more difficult than that bald statement sounds. We prepared authentic samples of the silyl enol ethers **9aa** and **9ab** by treating benzyl phenyl ketone **10a** either with sodium hydride or LDA and either phenyldimethylsilyl chloride or trimethylsilyl chloride. These reactions were selective for the formation of the thermodynamically preferred *Z*-ethers, but we were able to detect and characterise (^{1}H NMR and ^{13}C NMR) the minor *E*-isomers. We proved that these were the thermodynamically preferred isomers by allowing a mixture of the *E*- and *Z*-silyl enol ethers **9aa** to stand in deuteriochloroform for 5 days, after which time the *E*-isomer had completely isomerised to *Z*-**9aa**. This equilibration meant that any ratios of *Z*- and *E*-isomers that we measured were somewhat dependent upon the time between isolating the silyl enol ethers and taking their NMR spectra. This might also contribute to the change in ratio of the silyl enol ethers *E*- and *Z*-**9aa** obtained from the silyl ether **8a** in the direct reaction and in the higher yielding reaction in which the mixture was quenched with phenyldimethylsilyl chloride. We also carried out molecular modelling calculations for the ground state-energies of the trimethylsilyl enol ethers *E*-**9ab** and *Z*-**9ab** using the MM2 force field and Monte Carlo minimisation, which confirmed our expectations, the global minimum energies being 81.2 and 72.3 kJ mol^{-1}, respectively. We proved which isomer was *Z* in the phenyldimethylsilyl case by an NOE difference experiment on a mixture of both isomers. There was a clear enhancement in intensity of the signal from the vinyl proton upon irradiation of the signal from the silyl methyl group, and *vice versa* in only one of the isomers—that to which we assign the structure *E*-**9aa**. We assigned configurations to the corresponding trimethylsilyl enol ethers by analogy, supported by the observation that the major isomers at equilibrium in both series had the signals from the vinyl protons downfield and the signals from the silyl methyl protons upfield of the signals from the minor isomers. The signals in the ^{1}H and ^{13}C NMR spectra of both isomers of the silyl enol ethers **9aa** were identical with the signals from the product of the reaction **8a**→*E*-**9aa** + *Z*-**9aa**, and spiking the product mixture with a mixture of the trimethylsilyl enol ethers *E*-**9ab** and *Z*-**9ab** added four signals to make a total of eight signals from vinyl carbons. The diagnostic peaks in the NMR spectra of each of the four silyl enol ethers are listed in Table 1.



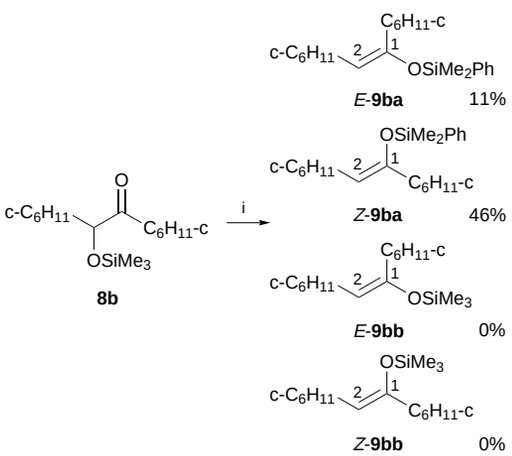
We have therefore shown that this version of Corey's reaction takes the Brook rearrangement pathway, but it is not clear that this will always be the case, since Brook rearrangement is well known to be much easier when there is a phenyl group stabilising the carbanion. We therefore examined the corresponding reaction of the acyloin silyl ether **8b**, with cyclohexyl groups in place of the phenyl groups. As before, we found that the silyl enol ethers produced were the phenyldimethylsilyl enol ethers *E*-**9ba** and *Z*-**9ba**, in 57% yield and in a ratio of 20 : 80, and not the trimethylsilyl enol ethers *E*-**9bb** and *Z*-**9bb** (Scheme 8). Again the products were those expected of the Brook rearrangement pathway and not the Peterson.

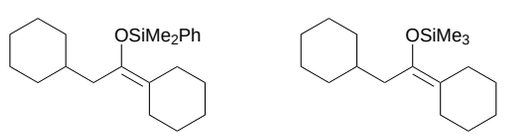
As in the aromatic series, we prepared authentic samples of the silyl enol ethers **9ba** and **9bb** by treating the ketone **10b** with lithium tetramethylpiperidide and either phenyldimethylsilyl chloride or trimethylsilyl chloride. These reactions were not completely selective for the formation of the *E*- and *Z*-silyl enol ethers **9ba** and **9bb**, with a further complication that these compounds were susceptible to equilibration, particularly when

Table 2 NMR chemical shifts for the silyl enol ethers **9ba** and **9bb**

	Authentic trimethylsilyl enol ethers **9bb**		Authentic dimethylphenylsilyl enol ethers **9ba**		Reaction products **8b** + $PhMe_2SiLi$	
	E-**9bb**	*Z*-**9bb**	*E*-**9ba**	*Z*-**9ba**	Major	Minor
Proportion[a]	20	49	6	31	73	18
δ_H(vinyl)	4.34	4.27	4.34	4.27	4.25	4.29
δ_H(SiMe)	0.16	0.18	0.41	0.45	0.43	0.40
δ_C(C-1)	154.55	153.40	154.34	153.37	153.33	154.29
δ_C(C-2)	112.70	112.30	112.68	112.36	112.37	112.70
δ_C(SiMe)	0.57	0.69	−0.75	−0.80	−0.82	−0.74

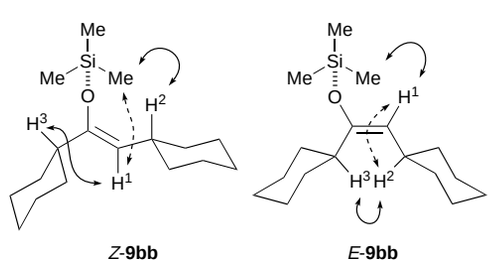
[a] The *E* and *Z* proportions are the percentages of the total silyl enol ether content, the remainder being the regioisomer **29**.





Scheme 8 *Reagents*: i, $PhMe_2SiLi$, THF

they were being distilled, giving the regioisomeric silyl enol ethers **29a** and **29b**, respectively. We again carried out molecular modelling calculations for the trimethylsilyl enol ethers *E*-**9bb** and *Z*-**9bb**, which had global minimum energies of 91.3 and 80.5 kJ mol^{-1}, respectively. We proved which isomer was which in the trimethylsilyl series by 2D COSY and NOESY spectra using a mixture of *E*-**9bb**, *Z*-**9bb** and **29b**. In the isomer



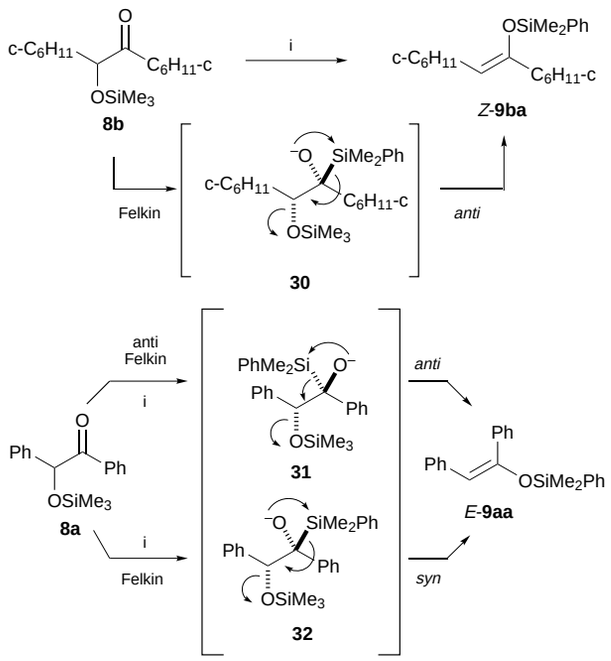
Dashed lines are weak enhancements. The structures drawn are similar to calculated minimum-energy conformations.

to which we assigned the structure *E*-**9bb**, we saw strong cross peaks between the signals from the vinyl protons and the signals from the silyl methyl groups, and between both cyclohexyl methine protons. In the other isomer, we saw a weak cross peak between the signal from the vinyl proton and the signal from the silyl methyl groups, and a definitive cross peak between the signal from the vinyl proton and the methine signal of the *cis* cyclohexyl group. We assigned the stereochemistry to the phenyldimethylsilyl enol ethers by analogy, supported by the observation that the major isomers at equilibrium in each case had the signals from their vinyl protons upfield and their silyl methyl groups downfield. The signals in the ^1H and ^{13}C NMR spectra of both isomers of the silyl enol ethers **9ba** prepared from the ketone **10b** were identical with the signals from the products of the reaction **8b**→*E*-**9ba** + *Z*-**9ba**, and spiking the product mixture with a mixture of the trimethylsilyl enol ethers *E*-**9bb** and *Z*-**9bb** added three signals to make a total of seven signals from vinyl carbons, two of the eight peaks being coincident. The diagnostic peaks in the NMR spectra of each of the four silyl enol ethers are listed in Table 2. Thus the reaction of phenyldimethylsilyllithium with the silyl ether **8b** gave the silyl enol ethers **9ba** in 57% yield with an *E*:*Z* ratio of 20:80.

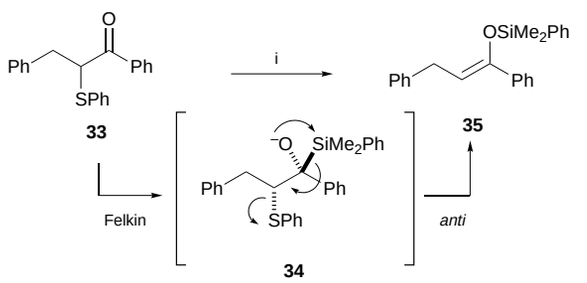
The stereochemistry

It is noteworthy that, whereas the major product in the aliphatic series is the thermodynamically more stable silyl enol ether *Z*-**9ba**, the major product in the aromatic series is the less stable silyl enol ether *E*-**9aa**. The stereochemical outcome in the aliphatic series is what one would expect—attack on the ketone **8b** can be expected to be governed by the Cornforth modification of Cram's rule, or its Felkin–Anh equivalent, hereinafter referred to as Felkin, to give predominantly the intermediate **30**, which will undergo *anti* elimination, following the precedents of Hudrlik and of Reich, to give the silyl enol ether *Z*-**9ba** (Scheme 9). To explain the anomalous result in the aromatic series, however, either the attack on the ketone **8a** had given the anti-Felkin product **31**, which undergoes *anti* elimination, or the Felkin product **32** had given the silyl enol ether *E*-**9aa** by unprecedented *syn* elimination. It is not clear why the ketone **8a** should not obey Felkin's rule—chelation is no more likely in this ketone than in the aliphatic ketone **8b**. Elimination with *syn* stereochemistry, on the other hand, is not unreasonable, because it is, in a sense, the corollary of the inversion of configuration seen in Brook rearrangements followed by protonation when the silyl group is attached to a benzylic position.[9]

However, Reich and his co-workers reported that the α-phenylthio acyl silane **17** (R = Me, R^1 = Ph, Y = S) reacted with both methyllithium and phenyllithium to give largely the silyl enol ethers **20** (R = Me, R^1 = Ph, R^2 = Me or Ph) with the *same* *E*-geometry. We would, if *syn* elimination were taking place in the benzyl series, have expected the reaction with phenyllithium to give the opposite stereochemistry. They also carried out the reaction of phenyldimethylsilyllithium on the methyl ketone **19**, in a reaction which is analogous to our reaction **8b**→*Z*-**9ba**, and obtained the *Z*-silyl enol ether **20** (R = R^1 = Ph, R^2 = Me) presumably by way of a Felkin intermediate and *anti* elimination. The missing experiment in their series was the reaction of the ketone **33** with phenyldimethylsilyllithium, which ought, if *syn* elimination were taking place in the benzyl series, to have given the *E*-isomer of the silyl enol ether **35**, by analogy with our reaction **8a**→*E*-**9aa**. We have therefore carried out this reaction,



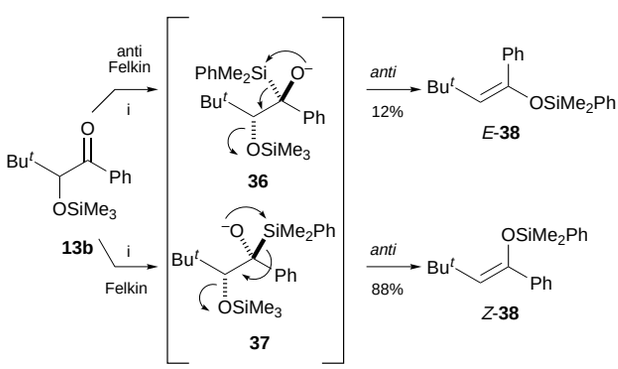
Scheme 9 *Reagents*: i, $PhMe_2SiLi$, THF



Scheme 10 *Reagents*: i, $PhMe_2SiLi$, THF

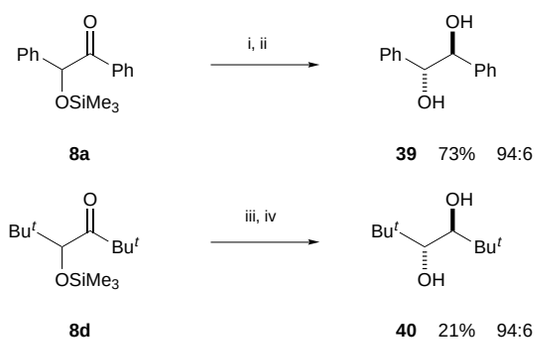
and obtained the silyl enol ether **35** with an $E:Z$ ratio of <1:99 (Scheme 10), the major product corresponding to *anti* elimination from the Felkin intermediate **34**. Hence in all four examples in Reich's series, the stereochemistry appears to be attack on the carbonyl group in the Felkin sense followed by *anti* elimination, regardless of whether the intermediate oxyanion is benzylic as in **34** or not.

Since the elimination step was always *anti*, we tried to verify whether or not the initial attack on the ketone **8a** was under Felkin control, since anti-Felkin attack followed by *anti* elimination would have led to the observed *E*-silyl enol ether **9aa**. We therefore looked at the stereochemistry of reaction of phenyldimethylsilyllithium with the silyl ether **13b** in which one of the phenyl groups had been replaced by another large group, the *tert*-butyl moiety. We obtained the silyl enol ethers **38** in 53% yield and with an $E:Z$ ratio of 12:88 (Scheme 11).



Scheme 11 *Reagents*: i, $PhMe_2SiLi$, THF

We assigned stereochemistry to this pair of products from the observations that the major isomer was identical with the major (98.5:1.5) product from the silylation of the corresponding ketone, and there was an NOE enhancement in the signal from the *tert*-butyl protons upon irradiation of the signal from the silyl methyl protons only in the major isomer. Thus the stereochemical outcome in this case was the normal pattern of Felkin control followed by *anti* elimination, still leaving the stereochemical result with the ketone **8a** anomalous. Reduction of the silyl ether **8a** using lithium aluminium hydride gave very largely (95:5) the *meso* diol **39**, which is also the anti-Felkin product (Scheme 12). Similarly, in our one failure in Scheme 2, the



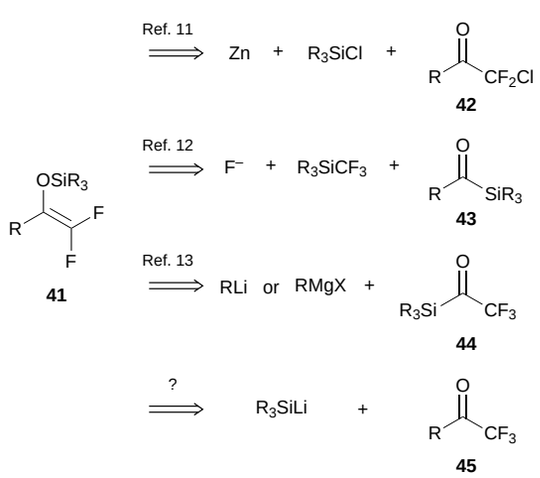
Scheme 12 *Reagents*: i, $LiAlH_4$; ii, Rochelle's salt, MeOH; iii, $PhMe_2SiLi$, THF; iv, NH_4Cl, H_2O

product that we obtained from the reaction of phenyldimethylsilyllithium on the silyl ether **8d** was largely (95:5) the *meso* diol **40**, which is the result from attack in the anti-Felkin sense followed by Brook rearrangement–protonation with retention of configuration. Thus, when *both* groups are phenyl or *tert*-butyl, the Felkin rule breaks down.

In conclusion, acyloin silyl ethers can be reduced to silyl enol ethers using phenyldimethylsilyllithium. The pathway is that shown in Scheme 6, and the yield is less than useful because some of the silyllithium reagent attacks the silyl group, returning the starting acyloin. A further complication is that the product silyl enol ether is also attacked by the silyllithium reagent to give the lithium enolate.

The reaction of the silyllithium reagent with trifluoromethyl ketones

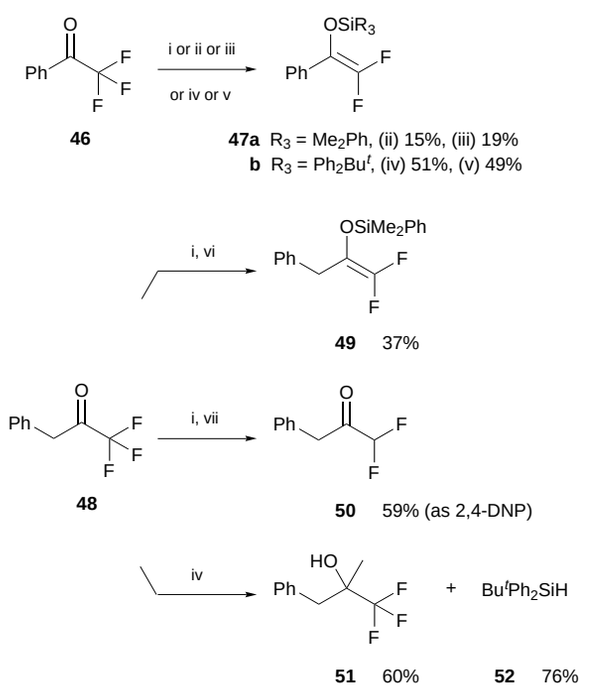
Related to all the work described above is the possibility of making difluorinated silyl enol ethers **41**, by treating trifluoromethyl ketones **45** with the silyllithium reagent. These interesting synthons[11] have been made (Scheme 13) by the other obvious combinations of nucleophile and electrophile: generation of the zinc enolate from the chlorodifluoro ketone **42** in



Scheme 13

the presence of a silyl chloride,[12] reaction of trifluoromethyl and other fluorinated 'anions' with acyl silanes **43**,[13] and reaction of organometallic 'anions' R^- with trifluoromethylacyl silanes **44**.[14] Both the phenyldimethylsilyllithium reagent and trifluoromethyl ketones **45** are easy to make, and should react with ease, since the silyllithium reagent is exceptionally nucleophilic and trifluoromethyl ketones are exceptionally electrophilic ketones. Accordingly, we have investigated the missing possibility.

Phenyldimethylsilyllithium reacted rapidly with (trifluoroacetyl)benzene **46** at −78 °C. The colour was completely discharged by only half an equivalent of the ketone. Presumably the silyl enol ether **47a** was being cleaved by the silyllithium reagent as fast as it was being formed (Scheme 14). We were

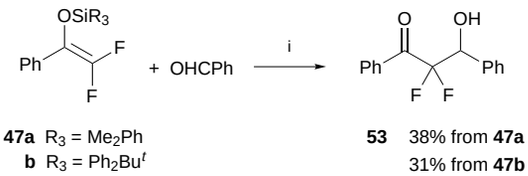


Scheme 14 *Reagents*: i, $PhMe_2SiLi$; ii, $PhMe_2SiMgMe$; iii, $PhMe_2SiLi$, $ZnBr_2$; iv, $Ph_2Bu^tSiMgMe$; v, Ph_2Bu^tSiLi, $ZnBr_2$; vi, $PhMe_2SiCl$; vii, NH_4Cl, H_2O

unable to trap the resultant enolate with silyl halides, acetyl chloride, benzyl bromide or crotonaldehyde. However, we did isolate the silyl enol ether **49** in 37% yield when we treated the superficially more problematic trifluoromethyl ketone **48** with an excess of the silyllithium reagent, and quenched with phenyldimethylsilyl chloride. Working up with a proton source instead, did give the difluoromethyl ketone **50** in up to 59% yield, but we were unable to trap the intermediate enolate in any other way.

A mixed phenyldimethylsilyl(methyl)magnesium reagent did give us the silyl enol ether **47a** from (trifluoroacetyl)benzene, again in low yield (15%), as did a zinc bromide-mediated reaction with the silyllithium reagent (19%). Changing to a more hindered silyl group, in the hope of isolating a more stable silyl enol ether, gave us a better yield—we obtained the silyl enol ether **47b** in 51% yield from a mixed *tert*-butyldiphenylsilyl(methyl)magnesium reagent and in 49% yield from the zinc bromide-mediated reaction with *tert*-butyldiphenylsilyllithium. In contrast, the ketone **48** gave the alcohol **51**, together with the silane **52**, by unprecedented methyl transfer from the mixed reagent.

In conclusion, several experiments, including some not reported here, have shown that silyl enol ethers can be prepared from trifluoromethyl ketones, but the reaction needs more study before it is reliable enough to be used in synthesis. With one reaction, we used the silyl enol ethers **47a** and **47b** to demonstrate some potential for these compounds. They both reacted with benzaldehyde in a Mukaiyama-aldol reaction to give the difluorinated β-hydroxy ketone **53** (Scheme 15).



Scheme 15 *Reagents*: i, $TiCl_4$, CH_2Cl_2

Experimental

Compounds **7a**, **7c** and **11** were available commercially. Light petroleum refers to the fraction bp 40–60 °C. Ether refers to diethyl ether. Standard work-up with a salt (*e.g.* ammonium chloride) refers to the procedure of quenching the reaction mixture with, typically, an equal volume of an aqueous solution of the salt (saturated unless stated otherwise). The mixture was then extracted with a comparable volume of ether (3×), the combined organic fractions were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure.

tert-Butyl(diphenyl)silyllithium

Lithium shot (0.4 g in mineral oil, 55 mmol) was stirred rapidly for 15 min in dry hexane (20 cm^3) under argon. The hexane was removed and the lithium re-suspended in dry THF (30 cm^3). The flask was cooled to 0 °C in an ice-bath and the lithium surface activated by addition of chlorotrimethylsilane (0.01 cm^3, 0.08 mmol). *tert*-Butylchloro(diphenyl)silane (5.0 cm^3, 19.2 mmol) was added and the mixture was stirred rapidly for 7 h at 0 °C to give *tert*-butyl(diphenyl)silyllithium as a red–brown solution. The molarity of the solution was determined by the Gilman double titration method (typically 0.3 mol dm^{-3}).

The acyloins 7

Typically, the ester and an equal volume of dry ether were added dropwise to a stirred suspension of finely divided sodium (2.1 molar equivalents) and trimethylsilyl chloride (2.1 molar equivalents) in dry ether. After 5 min a vigorous reaction started and the ester was added at a rate to maintain reflux; the mixture was refluxed under argon until a white precipitate had replaced the sodium (typically 1–3 d). The mixture was poured into enough water to dissolve the precipitate, acidified with dilute hydrochloric acid (2 mol dm^{-3}) and the organic layer separated. The aqueous layer was washed twice with ether, the organic layers combined and stirred with methanol for 1 h. Evaporation under reduced pressure and further purification gave the acyloin. The following compounds were prepared by this method.

1,2-Dicyclohexyl-2-hydroxyethanone 7b. Isolated as a pale yellow solid [6.44 g, 63% from ethyl cyclohexanecarboxylate (13.07 g)] after distillation, bp 172–182 °C at 22 mmHg; mp 39–42 °C (lit.,[15] mp 44–45 °C); R_f (EtOAc–light petroleum, 5:95) 0.25; ν_{max}(film)/cm^{-1} 3475 (br, OH) and 1702 (C=O); δ_H(250 MHz; $CDCl_3$) 4.1 (1 H, m, C*H*OH), 3.4 (1 H, d, *J* 6.5, OH), 2.5 (1 H, m, COCH) and 1.8–1.0 (21 H, m, C*H*CHOH and 10 × CH_2).

2,2,5,5-Tetramethyl-4-hydroxyhexan-3-one 7d. Isolated as needles [4.11 g, 24% from methyl trimethylacetate (26.55 cm^3)] after distillation (Kugelrohr, 140 °C at 17 mmHg), mp 80–81.5 °C (from toluene at −78 °C) (lit.,[16] mp 80–81 °C, bp 85–87 °C at 20 mmHg); R_f (EtOAc–light petroleum, 20:80) 0.41; ν_{max}(Nujol)/cm^{-1} 3473 (OH) and 1698 (C=O); δ_H(250 MHz; $CDCl_3$) 4.20 (1 H, d, *J* 10.5, C*H*OH), 2.27 (1 H, d, *J* 10.5, CHO*H*), 1.20 (9 H, s, $COCMe_3$) and 1.00 (9 H, s, $CHOHCMe_3$).

2,5-Dimethyl-4-hydroxyhexan-3-one 7e. Isolated as an oil [3.0

g, 41% from methyl isopropanoate (16.2)] after distillation and chromatography (SiO_2, EtOAc–light petroleum, 10:90); bp 72–74 °C at 15 mmHg (lit.,[17] 55–57 °C at 3 mmHg); R_f (EtOAc–light petroleum, 15:85) 0.36; ν_{max}(film)/cm^{-1} 3480 (OH) and 1707 (C=O); δ_H(250 MHz; $CDCl_3$) 4.22 (1 H, d, *J* 2, C*H*OH), 2.82 (1 H, septet, *J* 7, COC*H*Me$_2$), 2.15 (1 H, d, septet, *J* 2 and 7, CHOHC*H*Me$_2$), 1.2–1.0 (9 H, m, 3 × Me) and 0.68 (3 H, d, *J* 7, Me).

7-Hydroxydodecan-6-one 7f. Colourless oil [12.04 g, 60% from methyl hexanoate (29.42 cm^3, 200 mmol)] after distillation, bp 141–146 °C at 17 mmHg (lit.,[17] 105–107 °C at 3 mmHg); R_f (EtOAc–light petroleum, 10:90) 0.25; ν_{max}(film)/cm^{-1} 3480 (br, OH) and 1711 (C=O); δ_H(250 MHz; $CDCl_3$) 4.15 (1 H, m, C*H*OH), 3.50 (1 H, d, *J* 4, OH), 2.44 (1 H, t, *J* 7.5, CH_AH_BCO), 2.42 (1 H, t, *J* 7.5, CH$_A H_B$CO), 1.8–1.2 (12 H, m, 6 × CH_2), 1.60 (2 H, quintet, *J* 7.5, CH_2) and 0.87 (6 H, t, *J* 6.5, 2 × Me).

The silyl ethers 8

Following Cossy and Pale,[18] typically, hexamethyldisilazane (1.3 molar equivalents) and trimethylsilyl chloride (1.3 molar equivalents) were added to a stirred solution of the acyloin **7** (0.1–0.4 mol dm^{-3} solution in dry CH_2Cl_2) under argon at 0 °C. The solution was stirred at room temperature until no starting material was visible by TLC. The mixture was cooled to 0 °C, filtered through a plug of Florosil, evaporated under reduced pressure, the residue taken up in hexane, filtered again and re-evaporated to give the silyl ether. The following silyl ethers were prepared by this method.

1,2-Diphenyl-2-(trimethylsilyloxy)ethanone 8a. Isolated as a pale yellow solid [1.35 g, 92% from benzoin **7a** (1.09 g)], mp 79–80 °C (lit.,[19] 78–79.5 °C); R_f (EtOAc–light petroleum, 50:50) 0.68; ν_{max}(Nujol)/cm^{-1} 1688 (C=O), 1596 (Ph) and 1578 (Ph); δ_H(250 MHz; $CDCl_3$) 8.1–7.9 (2 H, m, PhCO *o*-H), 7.5–7.2 (8 H, m, other Ph), 5.83 (1 H, s, CHOSi) and 0.11 (9 H, s, $SiMe_3$).

1,2-Dicyclohexyl-2-(trimethylsilyloxy)ethanone 8b. Isolated as an oil [2.45 g, 96% from acyloin **7b** (1.92 g)]; R_f (EtOAc–light petroleum, 10:90) 0.64; ν_{max}(film)/cm^{-1} 1706 (C=O) and 1250 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 3.78 (1 H, d, *J* 5.5, CHCOSi), 2.74 (1 H, m, C*H*COCHOSi), 1.8–1.0 (21 H, m, C*H*CHOSi and 10 × CH_2) and 0.07 (9 H, s, $SiMe_3$); δ_C($CDCl_3$ 215.5, 82.9, 45.4, 41.3, 29.6, 29.1, 28.9, 27.9, 26.3, 26.3, 26.0, 25.8, 25.6, 25.5 and 0.2; *m*/*z* (EI) 281 (25%, M − Me), 185 (100, M − c-C_6H_{11}CO), 103 (90, H_2C=OSiMe_3), 95 (100), 83 (50, c-C_6H_{11}) and 73 (95, $SiMe_3$) (Found: M$^+$, 296.2176. $C_{17}H_{32}O_2Si$ requires *M*, 296.2171).

1,2-Di(2-furyl)-2-(trimethylsilyloxy)ethanone 8c. Isolated as a brown solid [0.875 g, 79% from furoin **7c** (0.814 g)], mp 42–44 °C (lit.,[20] 44–45 °C); R_f (EtOAc–light petroleum, 20:80) 0.33; ν_{max}(Nujol)/cm^{-1} 3015 (vinyl C–H), 1683 (C=O) and 1250 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.59 (1 H, dd, *J* 1 and 0.5, furanoyl H-5), 7.41 (1 H, dd, *J* 4 and 0.5, furanoyl H-3), 7.36 (1 H, dd, *J* 1.5 and 1, furyl H-5), 6.51 (1 H, dd, *J* 3.5 and 1.5, furyl H-3), 6.3 (2 H, m, furyl H-4 and furanoyl H-4), 5.73 (1 H, s, CHOSi) and 0.12 (9 H, s, $SiMe_3$).

2,2,5,5-Tetramethyl-4-(trimethylsilyloxy)hexan-3-one 8d. Isolated as a pale yellow solid [0.96 g, 86% from acyloin **7d** (0.79 g)], mp 35–37 °C (lit.,[21] 37–39 °C); R_f (EtOAc–light petroleum, 20:80) 0.66; ν_{max}(Nujol)/cm^{-1} 1716 (C=O) and 1252 ($SiMe_3$); δ_H(250 MHz; [$^2H_6$]DMSO) 4.36 (1 H, s, CHOSi), 1.13 (9 H, s, COCMe_3) 0.91 (9 H, s, SiOCCMe_3) and 0.13 (9 H, s, $SiMe_3$).

2,5-Dimethyl-4-(trimethylsilyloxy)hexan-3-one 8e. Isolated as an oil [1.34 g, 90% from acyloin **7e** (1.00 g)]; R_f (EtOAc–light petroleum, 50:50) 0.73; ν_{max}(film)/cm^{-1} 1712 (C=O) and 1252 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 3.82 (1 H, d, *J* 5.5, CHOSi), 3.00 (1 H, septet, *J* 7, COC*H*Me$_2$), 1.97 (1 H, m, CHC*H*Me$_2$), 1.05 (6 H, d, *J* 7, COCH*Me*$_2$), 0.87 (3 H, d, *J* 7, CHCH*Me*$_A$Me$_B$), 0.83 (3 H, d, *J* 7, CHCHMe$_A$*Me*$_B$) and 0.08 (9 H, s, $SiMe_3$); δ_C($CDCl_3$) 216.5, 83.1, 35.1, 31.7, 19.2, 19.0, 18.9, 17.4 and −0.1; *m*/*z* (EI) 201 (85%, M − Me), 145 (100, M − Me$_2$CHCO) and 73 (85, $SiMe_3$) (Found: M$^+$ − Me, 201.1311. $C_{11}H_{24}O_2Si$ − Me requires *M*, 201.1311).

7-(Trimethylsilyloxy)dodecan-6-one 8f.[22] Isolated as an oil [5.80 g, 100% from acyloin **7f** (4.27 g)]; R_f (EtOAc–light petroleum, 10:90) 0.54; ν_{max}(film)/cm^{-1} 1716 (C=O) and 1252 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 3.95 (1 H, t, *J* 6.5, CHOSi), 2.48 (2 H, t, *J* 7, CH_2CO), 1.5 (4 H, m, 2 × CH_2), 1.4–1.2 (10 H, m, 5 × CH_2), 0.9–0.8 (6 H, m, 2 × CH_2*Me*), 0.32 (5 H, s, $SiMe_3$) and 0.23 (4 H, s, $SiMe_3$).

2-Phenyl-2-(trimethylsilyloxy)acetonitrile 12

Benzaldehyde (3.6 cm^3, 36 mmol) was added to a stirred suspension of anhydrous zinc(II) iodide (0.33 g, 0.10 mmol) in trimethylsilyl cyanide (5.3 cm^3, 40 mmol) and dry acetonitrile (20 cm^3) under argon. The initial exothermic reaction was cooled in an ice-bath. The mixture was stirred for 1 h at room temperature, diluted with hexane (25 cm^3) and shaken with ice–water (100 cm^3). The aqueous layer was washed with hexane (3 × 40 cm^3), the combined organic extracts washed with cold, saturated sodium bisulfite solution (60 cm^3) and dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the crude product distilled (Kugelrohr, 180 °C at 20 mmHg) (lit.,[23] 64 °C at 0.5 mmHg) to give the silyl ether (6.3 g, 85%) as a pale yellow liquid; R_f (EtOAc–light petroleum, 20:80) 0.56; ν_{max}(film)/cm^{-1} 1602 (Ph); δ_H(270 MHz; $CDCl_3$) 7.5–7.3 (5 H, m, Ph), 5.50 (1 H, s, CHOSi) and 0.24 (9 H, s, $SiMe_3$).

1,2-Diphenyl-2-(trimethylsilyloxy)propan-1-one 13a

Methyllithium (1.4 mol dm^{-3} in ether, 10 cm^3) was added over 25 min to a stirred solution of benzil **11** (2.96 g, 14 mmol) in THF at −78 °C under argon and stirred for 90 min. Standard work-up with ammonium chloride followed by chromatography (SiO_2, EtOAc–light petroleum, 10:90) gave 1,2-diphenyl-2-hydroxypropan-1-one (2.36 g, 75%) as needles [from light petroleum (bp 60–80 °C)], mp 65–67 °C (lit.,[24] 65–66 °C); R_f (EtOAc–light petroleum, 10:90) 0.18; ν_{max}(Nujol)/cm^{-1} 3455 (br, OH), 1677 (C=O), 1597 and 1577 (Ph); δ_H(250 MHz; $CDCl_3$) 7.67 (2 H, dd, *J* 8 and 1.5, PhCO *o*-H), 7.5–7.2 (8 H, m, other Ph), 4.76 (1 H, s, OH) and 1.91 (3 H, s, Me). The acyloin (0.71 g, 3.2 mmol) in dry THF (10 cm^3) was added to a stirred suspension of hexane-washed sodium hydride (60% dispersion in oil, 0.12 g, 3.2 mmol) in dry THF at 0 °C under argon and was stirred for 45 min. Trimethylsilyl chloride (0.52 cm^3, 4.1 mmol) was added, forming a white precipitate, and the mixture stirred for 2 h. The mixture was filtered though a pad of Florisil and the solvent evaporated under reduced pressure. Chromatography (Al_2O_3, EtOAc–light petroleum, 10:90) gave the silyl ether (0.77 g, 81%) as a solid, mp 50–52 °C (lit.,[25] 51–52 °C); R_f (EtOAc–light petroleum, 15:85) 0.73; ν_{max}(Nujol)/cm^{-1} 1679 (C=O), 1597 (Ph), 1580 (Ph) and 1254 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$) 7.91 (2 H, dd, *J* 7.5 and 1.5, PhCO *o*-H), 7.50 (2 H, dd, *J* 7 and 1.5, PhCOSi *o*-H), 7.5–7.2 (6 H, m, other Ph), 1.80 (3 H, s, Me) and 0.07 (9 H, s, $SiMe_3$).

3,3-Dimethyl-1-phenyl-2-(trimethylsilyloxy)butan-1-one 13b

Following Hünig and Wehner,[25] *n*-butyllithium (1.27 mol dm^{-3} in hexane, 8.7 cm^3) was added dropwise to a stirred solution of diisopropylamine (1.6 cm^3, 11 mmol) in dry THF (10 cm^3) under argon at 0 °C. After 20 min, the solution was cooled to −78 °C, silyl ether **12** (2.05 g, 10 mmol) in dry THF (5 cm^3) and trimethylacetaldehyde (1.08 cm^3, 10 mmol) were added, maintaining the temperature below −60 °C. The mixture was allowed to warm over 2 h, precipitating lithium cyanide. When the temperature reached −5 °C, dichloromethane (25 cm^3) and water (5 cm^3) were added. The organic layer was washed with saturated ammonium chloride solution (2 × 30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography (SiO_2, EtOAc–hexane, 2.5:97.5) gave the silyl ether (1.72 g, 65%) as prisms, mp 38–41 °C; R_f (EtOAc–hexane, 5:95)

0.48; ν_{max}(film)/cm^{-1} 1691 (C=O), 1597 (Ph), 1578 (Ph), 1252 ($SiMe_3$), 1110 (Si–O) and 841 ($SiMe_3$); δ_H(270 MHz; $CDCl_3$) 8.05 (2 H, dd, *J* 7.5 and 1, *o*-H), 7.5 (1 H, m, *p*-H), 7.4 (2 H, dt, *J* 1 and 7.5, *m*-H), 4.53 (1 H, s, CHOSi), 0.92 (9 H, s, CMe_3) and 0.05 (9 H, s, $SiMe_3$); δ_C($CDCl_3$) 202.1, 138.0, 132.9, 129.6, 128.4, 83.7, 35.8, 27.0 and 0.0.

Benzoin, sodium salt 16a

Benzoin **7a** (0.50 g, 2.36 mmol) in dry THF (10 cm^3) was added to a stirred suspension of hexane-washed sodium hydride (94 mg of a 60% suspension in oil) in THF (2 cm^3) at 0 °C and used without further purification.

1,2-Diphenyl-2-oxoethyl benzoate 16b

Pyridine (0.45 cm^3, 5.6 mmol), benzoyl chloride (0.65 cm^3, 5.6 mmol), benzoin **7a** (1.00 g, 4.7 mmol) and dry dichloromethane (25 cm^3) were stirred for 90 min at 0 °C and then 90 min at room temperature, under argon. More benzoyl chloride (0.65 cm^3, 5.6 mmol) was added and the mixture stirred for a further 90 min. The solution was washed with hydrochloric acid (3 mol dm^3, 50 cm^3) and saturated sodium hydrogen carbonate solution (2 × 50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude white solid which was recrystallised to give the benzoyl ester (0.658 g, 44%) as needles, mp 121–123 °C (from MeOH) (lit.,[26] 123–124 °C); R_f (EtOAc–light petroleum, 50 : 50) 0.50; ν_{max}(Nujol)/cm^{-1} 1715 (ester C=O), 1695 (ketone C=O), 1598 (Ph) and 1583 (Ph); δ_H(250 MHz; $CDCl_3$) 8.12 (2 H, dd, *J* 8 and 1, $PhCO_2$ *o*-H), 8.00 (2 H, dd, *J* 8 and 1.5, *Ph*COCH *o*-H), 7.6–7.3 (11 H, m, other Ph) and 7.09 (1 H, s, OCHCO).

1,2-Dicyclohexyl-2-(*tert*-butyldimethylsilyloxy)ethanone 16c

tert-Butyldimethylsilyl trifluoromethanesulfonate (1.47 cm^3, 6.4 mmol) was added to a stirred solution of acyloin **7b** (0.96 g, 4.2 mmol) and 2,6-lutidine (1.0 cm^3, 8.4 mmol) in dry dichloromethane (5 cm^3) at 0 °C under argon and stirred for 40 min. Standard work-up with sodium hydrogen carbonate, washing the combined organic extracts with dilute hydrochloric acid (3 mol dm^{-3}, 2 × 20 cm^3) prior to drying, gave a residue which was heated (Kugelrohr, 120 °C at 17 mmHg) to remove a low-boiling impurity. The residual oil was taken up in hexane, filtered, and the solution evaporated under reduced pressure to give the *silyl ether* as an oil (1.27 g, 88%); R_f (EtOAc–light petroleum, 10 : 90) 0.70; ν_{max}(film)/cm^{-1} 1721 (C=O), 1706 (C=O), 1450 and 1252 ($SiMe_2Bu^t$); δ_H(250 MHz; $CDCl_3$) 3.82 (1 H, d, *J* 6, CHOSi), 2.75 (1 H, m, cyclohexyl CHCO), 1.8–1.0 (21 H, m, cyclohexyl H), 0.91 (9 H, s, $SiCMe_3$) and −0.01 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 215.5, 82.9, 45.4, 41.7, 29.7, 29.4, 28.6, 27.8, 26.3, 26.2, 26.2, 26.1, 26.0, 25.8, 25.6, 18.2, −4.4 and −4.9; *m*/*z* (EI) 338 (10%, M$^+$), 323 (55, M − Me), 281 (65, M − Bu^t), 227 (100, M − $C_5H_{11}CO$) and 115 (10, $SiMe_2Bu^t$) (Found: M$^+$, 338.2652. $C_{20}H_{38}O_2Si$ requires *M*, 338.2641).

1,2-Dicyclohexyl-2-oxoethyl benzoate 16d

Pyridine (0.37 cm^3, 4.5 mmol) and benzoyl chloride (0.53 cm^3, 4.5 mmol) were added to a stirred solution of acyloin **7b** (0.85 g, 3.8 mmol) in dry dichloromethane (25 cm^3) under argon at 0 °C and stirred for 3 d. Standard work-up with sodium hydrogen carbonate, washing the combined organic extracts with dilute hydrochloric acid (3 mol dm^{-3}, 3 × 50 cm^3) prior to drying, and chromatography (SiO_2, EtOAc–light petroleum, 8 : 92) gave the *benzoate* (0.66 g, 54%) as needles, mp 73.5–76 °C (from MeOH); R_f (EtOAc–light petroleum, 10 : 90) 0.39; ν_{max}(Nujol)/cm^{-1} 1717 (C=O), 1602 (Ph) and 1584 (Ph); δ_H(400 MHz; $CDCl_3$) 8.07 (2 H, dd, *J* 7.5 and 1.5, *o*-H), 7.57 (1 H, tt, *J* 7.5 and 1.5, *p*-H), 7.45 (2 H, t, *J* 7.5, *m*-H), 5.27 (1 H, d, *J* 4, $PhCO_2CH$), 2.59 (1 H, tt, *J* 11.5 and 3, cyclohexyl-CHCO), 2.0 (2 H, m, cyclohexyl-H), 1.9–1.55 (10 H, m, cyclohexyl-H) and 1.5–1.1 (9 H, m, cyclohexyl-H); δ_C($CDCl_3$) 209.8, 166.1, 133.2, 129.8, 129.7, 128.5, 81.7, 47.5, 39.3, 30.1, 29.3, 27.7, 27.5, 26.3, 26.1, 26.0, 25.9, 25.7 and 25.4; *m*/*z* (EI) 328 (15%, M$^+$), 245.1 (100, M − c-C_6H_{11}), 223 (18, M − COPh), 217.1 (60, M − c-$C_6H_{11}CO$), 206 (25, M − PhCOOH), 105 (100, PhCO), 83 (50, c-C_6H_{11}) and 77 (20, Ph) (Found: M$^+$, 328.2014. $C_{21}H_{28}O_3$ requires *M*, 328.2016).

Ethyl 1,2-dicyclohexyl-2-oxoethyl carbonate 16e

Methyllithium (1.4 mol dm^{-3} in ether, 3.75 cm^3) was added to a stirred solution of acyloin **7b** (1.05 g, 5.0 mmol) in dry THF (5 cm^3) at −78 °C under argon, forming a white precipitate. After 15 min, the mixture was warmed to 0 °C, ethyl chloroformate (0.50 cm^3, 5.3 mmol) was added and the solution stirred for 6 h, and kept overnight. Standard work-up with sodium hydrogen carbonate and chromatography (SiO_2, EtOAc–light petroleum, 8 : 92) gave the *carbonate* (0.92 g, 61%) as needles, mp 59–60 °C (from MeOH); R_f (EtOAc–light petroleum, 8 : 92) 0.31; ν_{max}(Nujol)/cm^{-1} 1746 (C=O) and 1717 (C=O); δ_H(400 MHz; $CDCl_3$), 4.89 (1 H, d, *J* 4, C*H*$COCO_2$Et), 4.20 (1 H, dq, *J* 14.5 and 7, OCH_AH_BMe), 4.17 (1 H, dq, *J* 14.5 and 7, OCH_AH_BMe), 2.5 (1 H, tt, *J* 11 and 3.5, cyclohexoyl-CHCO), 2.0–1.1 (21 H, m, cyclohexyl-H) and 1.30 (3 H, t, *J* 7, OCH_AH_BMe); δ_C($CDCl_3$) 209.7, 154.9, 84.3, 64.4, 47.2, 39.0, 29.7, 29.4, 27.6, 26.9, 26.3, 26.0, 25.9, 25.8, 25.7, 25.3 and 14.2; *m*/*z* (EI) 296 (10%, M$^+$), 214 (100, M − cyclohexene), 241 (M − COC_6H_{11}), 137 (70), 111 (45, COC_6H_{11}), 95 (65) and 83 (C_6H_{11}) (Found: M$^+$, 296.1987. $C_{17}H_{28}O_4Si$ requires *M*, 296.1987).

1,2-Dicyclohexyl-2-(*p*-tolylsulfonyloxy)ethanone 16f

Following Julia and Maumy,[27] toluene-*p*-sulfonyl chloride (0.36 g, 1.9 mmol) was added over 1 h to acyloin **7b** (0.31 g, 1.5 mmol) in dry pyridine (2 cm^3) at 0 °C, the flask stoppered and kept overnight at 4 °C, forming needles. The mixture was poured into cold water (5 cm^3) to give a precipitate, the solid was extracted with ether (4 × 5 cm^3), the organic extracts washed with dilute hydrochloric acid (2 mol dm^{-3}, 4 × 5 cm^3), saturated sodium hydrogen carbonate solution (5 cm^3), water (2 × 5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the *tosylate* (0.48 g, 86%) as needles, mp 102–103.5 °C [from light petroleum (bp 60–80 °C)]; R_f (EtOAc–light petroleum, 10 : 90) 0.31; ν_{max}(Nujol)/cm^{-1} 1714 (C=O), 1599 (Ph), 1369 (OSO_2) and 1176 (OSO_2); δ_H(400 MHz; $CDCl_3$) 7.77 (2 H, d, *J* 8.5, *o*-H), 7.32 (2 H, d, *J* 8.5, *m*-H), 4.65 (1 H, d, *J* 5.5, $CHOSO_2$), 2.55 (1 H, tt, *J* 11 and 3, cyclohexyl-CHCO), 2.43 (3 H, s, *tolyl* Me) and 1.9–0.9 (21 H, m, cyclohexyl-H); δ_C($CDCl_3$) 208.9, 145.0, 133.5, 129.8, 128.0, 87.5, 46.7, 39.6, 29.1, 27.7, 27.4, 25.9, 25.8, 25.7, 25.6, 25.3, and 21.7; *m*/*z* (EI) 378 (15%, M$^+$), 296 (20, M − cyclohexene), 266 (80, M − $C_6H_{11}CHO$), 223 (10, M − SO_2Tol), 139 (30), 123 (40), 111 (80, $C_6H_{11}CO$), 91 (40, C_6H_4Me) and 83 (100, C_6H_{11}) (Found: M$^+$, 378.1864. $C_{21}H_{30}O_4S$ requires *M*, 378.1864).

1,3-Dipheny-2-(phenylthio)propan-1-one 33

Chalcone (2.08 g, 10 mmol) in methanol (10 cm^3) was added with stirring to palladium (5%/C, 0.16 g) suspended in methanol (60 cm^3) under hydrogen at 1 atmosphere. After stirring for 24 h, the hydrogen was replaced with argon, the mixture filtered through Celite and evaporated under reduced pressure to give 1,3-diphenylpropan-1-ol[28] (2.02 g, 95%) as an oil; R_f (EtOAc–light petroleum, 10 : 90) 0.15; ν_{max}(film)/cm^{-1} 3362 (br, OH), 1602 (Ph) and 1585 (Ph; δ_H(250 MHz; $CDCl_3$) 7.4–7.1 (10 H, m, Ph), 4.68 (2 H, dd, *J* 7.5 and 5.5, PhC*H*OH), 2.8–2.6 (2 H, m, $PhCH_2CH_2$), 2.2–1.9 (2 H, m, $PhCH_2CH_2$) and 1.95 (1 H, m, OH). Jones reagent[29] [2.2 cm^3 of a solution prepared from chromium trioxide (26.7 g, 26.7 mmol), concentrated sulfuric acid (23 cm^3) and made up to 100 cm^3 with water] was added dropwise to a stirred solution of the alcohol in acetone (20 cm^3). Standard work-up with water gave 1,3-diphenylpropan-1-one (1.54 g, 89%) as plates, mp 68–69 °C (from MeOH–light petroleum) (lit.,[30] 70–71 °C); R_f (EtOAc–light petroleum, 10 : 90) 0.37; ν_{max}(Nujol)/cm^{-1} 1681 (C=O), 1595 (Ph) and 1580 (Ph); δ_H(200 MHz; $CDCl_3$) 7.97 (2 H, dd, 7 and 1.5, PhCO

o-H), 7.6–7.2 (8 H, m, other Ph), 3.32 (1 H, t, *J* 7.5, $COCH_AH_BCH_CH_D$), 3.30 (1 H, t, *J* 7.5, $COCH_AH_BCH_CH_D$), 3.08 (1 H, t, *J* 7.5, $COCH_AH_BCH_CH_D$) and 3.06 (1 H, t, *J* 7.5, $COCH_AH_BCH_CH_D$). *n*-Butyllithium (1.6 mol dm^{-3} in hexane, 3.6 cm^3) was added dropwise to a stirred solution of diisopropylamine (0.80 cm^3, 5.7 mmol) in dry THF (20 cm^3) under argon at 0 °C, and was stirred for 30 min. The solution was cooled to −78 °C, 1,3-diphenylpropan-1-one (1.09 g, 5.2 mmol) in dry THF (10 cm^3) was added and the solution stirred for a further 90 min at −78 °C. Diphenyl disulfide (1.35 g, 6.2 mmol) in dry THF (15 cm^3) was added over 15 min at 0 °C. The mixture was stirred for 4 h, warming to room temperature. Standard work-up with sodium hydrogen carbonate and chromatography (SiO_2, EtOAc–light petroleum, 7:93) gave the ketone **33** (0.71 g, 39%) as white needles, mp 84–86.5 °C (from MeOH) (lit.,[31] 83–85 °C); R_f (EtOAc–light petroleum, 10:90) 0.32; ν_{max}(Nujol)/cm^{-1} 1668 (C=O), 1594 (Ph) and 1580 (Ph); δ_H(270 MHz; $CDCl_3$) 7.82 (2 H, dd, *J* 7 and 1.5, PhCO *o*-H), 7.50 (1 H, dt, *J* 1.7 and 7, PhCO *p*-H), 7.4–7.1 (12 H, m, other Ph), 4.69 (1 H, dd, *J* 8.5 and 6, $COCHSPh$), 3.41 (1 H, dd, *J* 14 and 8.5, $PhCH_AH_B$) and 3.14 (1 H, dd, *J* 14 and 6, $PhCH_AH_B$).

The silyl enol ethers 9, 35 and 38

1,2-Diphenyl-1-[dimethyl(phenyl)silyloxy]ethene 9aa

Method A. *n*-Butyllithium (1.6 mol dm^{-3} in hexane, 2.5 cm^3) was added dropwise to a stirred solution of diisopropylamine (0.56 cm^3, 4.0 mmol) in dry THF (17 cm^3) under argon at 0 °C. After 20 min, the solution was cooled to −78 °C and 1,2-diphenylethanone **10a** (0.65 g, 3.3 mmol) in dry THF (10 cm^3) was added dropwise. After 1.5 h, dry triethylamine (0.85 cm^3, 6.1 mmol) and dimethyl(phenyl)silyl chloride (0.83 cm^3, 5.0 mmol) were added, the mixture warmed to room temperature and stirred for 30 min and the solution was diluted with light petroleum (100 cm^3). Following standard work-up with sodium hydrogen carbonate, distillation (Kugelrohr, 180 °C at 3 mmHg) failed to purify the product further, giving the *silyl enol ethers* **9aa** (173 mg, 16%) (*Z*-**9aa**:*E*-**9aa**, 88:12), contaminated with the starting ketone (65 mg, 10% recovery) and 1,2-diphenyl-1,1,2,2-tetramethyldisiloxane (76 mg).

Method B. 1,2-Diphenylethanone **10a** (0.42 g, 2.2 mmol) in dry THF (4 cm^3) was added to a stirred suspension of hexane-washed sodium hydride (60% suspension in oil, 0.20 g) in dry THF (6 cm^3) under argon and refluxed for 3 h, before cooling to room temperature. Dry triethylamine (0.46 cm^3, 3.2 mmol) and dimethyl(phenyl)silyl chloride (0.55 cm^3, 3.2 mmol) were added, forming a white precipitate. The mixture was stirred for 15 min and diluted with ether (30 cm^3). Standard work-up with sodium hydrogen carbonate gave crude *silyl enol ether* **9aa** (0.62 g, 85%) (*Z*-**9aa**:*E*-**9aa**, >99:1) as a pale yellow oil, contaminated with 1,2-diphenyl-1,1,2,2-tetramethyldisiloxane (0.25 g).

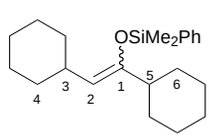
Method C. Dimethyl(phenyl)silyllithium[3] (1.28 mol dm^{-3} in THF, 0.32 cm^3) was added dropwise to a stirred solution of silyl ether **8a** (114 mg, 0.40 mmol) in dry THF (5 cm^3) at −78 °C, under argon and the mixture stirred for 20 min at −78 °C and for 1 h at room temperature. The solution was diluted with hexane (15 cm^3) followed by standard work-up with water. Chromatography (SiO_2, EtOAc–light petroleum, 2:98) of the residue gave the *silyl enol ethers* **9aa** (44 mg, 30%) (*Z*-**9aa**:*E*-**9aa**, 5:95) as a colourless oil.

Method D. Dimethyl(phenyl)silyllithium[3] (0.85 mol dm^{-3} in THF, 2.30 cm^3) was added dropwise to a stirred solution of silyl ether **8a** (454 mg, 1.6 mmol) in dry THF (2 cm^3) at −78 °C, under argon and the mixture stirred for 15 min. Dimethyl-(phenyl)silyl chloride (0.42 cm^3, 2.5 mmol) was added, the mixture warmed to room temperature and stirred for 30 min. Following addition of cold hexane (25 cm^3), standard work-up with ice–water and distillation (Kugelrohr, 180 °C at 3 mmHg) gave the crude *silyl enol ethers* **9aa** (*Z*-**9aa**:*E*-**9aa**, 22:78) as a pale yellow oil, contaminated with starting silyl ether **8a** and 1,2-diphenyl-1,1,2,2-tetramethyldisiloxane. Crude **9aa** was hydrolysed by stirring with dilute hydrochloric acid (3 mol dm^{-3}, 2 cm^3) and methanol (30 cm^3) for 2 h. Evaporation under reduced pressure and chromatography (SiO_2, EtOAc–hexane, 20:80) gave starting silyl ether **8a** (60 mg, 31% recovery) and ketone **10a** (157 mg, 51% from silyl ether **8a**). *Silyl enol ethers* **9aa**: R_f (EtOAc–light petroleum, 2:98) 0.33; ν_{max}(film)/cm^{-1} 1630 (C=C), 1600 (Ph) and 1592 (Ph); δ_H(250 MHz; $CDCl_3$) *Z*-**9aa**: 7.7–7.2 (15 H, m, Ph and SiPh), 6.16 (1 H, s, *vinyl* H) and 0.34 (6 H, s, $SiMe_2$); *E*-**9aa**: 7.7–7.2 (13 H, m, Ph and SiPh), 7.00 (2 H, dd, *J* 7.5 and 1.5, C=CHPh *o*-H), 6.11 (1 H, s, *vinyl* H) and 0.52 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) *Z*-**9aa** (partial): 150.90 (C-1), 139.45 (*ipso* C), 110.82 (C-2) and −0.95 ($SiMe_2$); *E*-**9aa**: 151.4, 137.5, 137.3, 136.7, 133.5, 129.8, 129.1, 128.8, 128.3, 128.1, 128.0, 127.9, 127.7, 125.7 and −0.94 ($SiMe_2$); *m*/*z* (EI) 330 (90%, M^+), 135 (100, $SiMe_2Ph$) (Found: M^+, 330.1438. $C_{22}H_{22}OSi$ requires *M*, 330.1440).

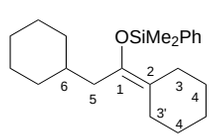
1,2-Diphenyl-1-(trimethylsilyloxy)ethene 9ab

Method A. Following the procedure for the synthesis of **9aa** (Method A), 1,2-diphenylethanone **10a** (0.79 g, 4.0 mmol) in dry THF (10 cm^3) was treated with lithium tetramethylpiperidide [*n*-butyllithium (1.6 mol dm^{-3} in hexane, 2.50 cm^3), 2,2,6,6-tetramethylpiperidine (0.74 cm^3, 4.4 mmol) and dry THF (17 cm^3), 20 min, 0 °C, under argon] for 1 h, and silylated with dry triethylamine (0.85 cm^3, 6.1 mmol) and trimethylsilyl chloride (0.61 cm^3, 4.9 mmol) to give starting ketone **10a** (133 mg, 17% recovery) and the crude silyl enol ethers **9ab** (0.62 g, 58%) (*Z*-**9ab**:*E*-**9ab**, 87:13).

Method B. Following the procedure for the synthesis of **9aa** (Method B), 1,2-diphenylethanone **10a** (0.42 g, 2.2 mmol) was treated with hexane-washed sodium hydride (60% suspension in oil, 0.20 g) in dry THF (10 cm^3) for 3 h, and silylated with dry triethylamine (0.46 cm^3, 3.2 mmol) and trimethylsilyl chloride (0.40 cm^3, 3.2 mmol). Distillation of the residue (Kugelrohr, 160 °C at 3 mmHg) (lit.,[32] 132–136 °C at 1 mmHg) gave the silyl enol ether **9ab** (0.41 g, 70%) (*Z*-**9ab**:*E*-**9ab**, >99:1) as a pale yellow oil, contaminated with starting ketone (15 mg, 4% recovery). **9ab**; ν_{max}(film)/cm^{-1} 1632 (C=C), 1600 (Ph), 1252 ($SiMe_3$) and 846 ($SiMe_3$); δ_H(250 MHz; $CDCl_3$); *Z*-**9ab**: 7.69 (2 H, dd, *J* 1.5 and 7, *o*-H), 7.63 (2 H, dd, *J* 1.5 and 7, other *o*-H), 7.6–7.1 (6 H, m, other Ph), 6.22 (1 H, s, vinyl-H) and 0.14 (9 H, s, $SiMe_3$); *E*-**9ab**: 7.7–7.0 (8 H, m, Ph), 7.10 (2 H, m, C=CHPh *o*-H), 6.18 (1 H, s, vinyl-H) and 0.30 (9 H, s, $SiMe_3$); δ_C($CDCl_3$) *Z*-**9ab** (partial): 150.97 (C-1), 139.7 (*ipso*-C), 110.61 (C-2) and 0.76 ($SiMe_3$); *E*-**9ab** (partial): 151.68 (C-1), 111.49 (C-2), and 0.47 ($SiMe_3$). All other aromatic peaks between 140 and 125 ppm were left unassigned.



9ba



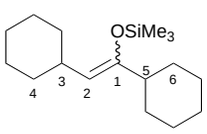
29a

1,2-Dicyclohexyl-1-[dimethyl(phenyl)silyloxy]ethene 9ba

Method A. Following the procedure for the synthesis of **9aa** (Method A), 1,2-dicyclohexylethanone **10b** (0.41 g, 2.0 mmol) in dry THF (5 cm^3) was treated with lithium tetramethylpiperidide [*n*-butyllithium (1.6 mol dm^{-3} in hexane, 1.38 cm^3), 2,2,6,6-tetramethylpiperidine (0.37 cm^3, 2.2 mmol) and dry THF (8 cm^3), 30 min, 0 °C under argon] for 3 h at −78 °C, and was silylated with dry triethylamine (0.42 cm^3, 3.0 mmol) and dimethyl(phenyl)silyl chloride (0.40 cm^3, 2.4 mmol). Distillation (Kugelrohr, 170–200 °C at 16 mmHg) gave the *silyl enol ethers* **9ba** and regioisomer 2-*cyclohexyl*-1-*cyclohexylidene*-1-[*dimethyl*(*phenyl*)*silyloxy*]*ethane* **29a** (67 mg, 10%) (*Z*-**9ba**:*E*-**9ba**:**29a**, 31:6:63) as an oil.

Method B. Following the procedure for the synthesis of **9aa** (Method C), silyl ether **8b** (238 mg, 0.80 mmol) in dry THF

(1 cm^3) was treated at −78 °C with dimethyl(phenyl)silyllithium[3] (1.25 mol dm^{-3} in THF, 0.77 cm^3) for 5 h. Standard work-up with water gave the crude *silyl enol ethers* **9ba** and **29a** (*Z*-**9ba**:*E*-**9ba**:**29a**, 73:18:9). Distillation (Kugelrohr, 160 °C at 14 mmHg) gave the *silyl enol ethers* **9ba** and **29a** (153 mg, 56%) (*Z*-**9ba**:*E*-**9ba**:**29a**, 45:5:60) as an oil; ν_{max}(film)/cm^{-1} 1661 (C=C), 1250 ($SiMe_2$), 1118 (SiPh) and 841 ($SiMe_2$); δ_H(400 MHz; $CDCl_3$) *Z*-**9ba**: 7.6 (2 H, m, *m*-H), 7.4 (3 H, m, *o*- and *p*-H), 4.27 (1 H, d, *J* 9.5, H-2), 2.4–0.8 (22 H, m, cyclohexyl CH and CH_2) and 0.45 (6 H, s, $SiMe_2$); *E*-**9ba**: 7.6 (2 H, m, *m*-H), 7.4 (3 H, m, *o*- and *p*-H), 4.34 (1 H, d, *J* 9.5, H-2), 2.4–0.8 (22 H, m, cyclohexyl-CH and CH_2) and 0.41 (6 H, s, $SiMe_2$); **29a** 7.6 (2 H, m, *m*-H), 7.4 (3 H, m, *o*- and *p*-H), 2.18 (2 H, t, *J* 6, H-3), 2.03 (2 H, t, *J* 6, H-3′), 1.87 (2 H, d, *J* 7, H-5), 1.9–0.8 (12 H, m, cyclohexyl-CH_2), 1.49 (1 H, m, H-6), 1.45 (4 H, m, H-4) and 0.43 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) *Z*-**9ba** (partial): 153.37 (C-1), 138.42 (*ipso*-C), 133.35 (*o*-C), 129.53 (*p*-C), 127.72 (*M*-C), 112.36 (C-2), 44.32 (C-3 or C-5), 34.43 (C-5 or C-3) and −0.80 ($SiMe_2$); *E*-**9ba** (partial): 154.34 (C-1), 138.42 (*ipso*-C), 133.51 (*o*-C), 129.39 (*p*-C), 127.62 (*m*-C), 112.68 (C-2), 39.65 (C-3 or C-5), 35.81 (C-5 or C-3) and −0.75 ($SiMe_2$); **29a** (partial): 140.39 (C-1), 138.47 (*ipso*-C), 133.41 (*o*-C), 129.53 (*p*-C), 127.75 (*m*-C), 119.37 (C-2), 39.16 (C-5), 35.74 (C-6) and −0.96 ($SiMe_2$). All other cyclohexyl carbon signals between 35 and 21 ppm were left unassigned; *m*/*z* (EI) 342 (15%, M^+), 135 (30, $SiMe_2Ph$), 97 (50, $CH_2C_6H_{11}$ from **29a**) and 83 (65, C_6H_{11}) (Found: M^+, 342.2377. $C_{22}H_{34}OSi$ requires *M*, 342.2379).



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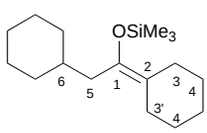

29b

1,2-Dicyclohexyl-1-(trimethylsilyloxy)ethene 9bb

Following the procedure for the synthesis of **9aa** (Method A), 1,2-dicyclohexylethanone **10b** (0.41 g, 2.0 mmol) in dry THF (5 cm^3) was treated with lithium tetramethylpiperidide [*n*-butyllithium (1.6 mol dm^{-3} in hexane, 1.38 cm^3), 2,2,6,6-tetramethylpiperidine (0.37 cm^3, 2.2 mmol) and dry THF (8 cm^3), 30 min, 0 °C, under argon] for 2.5 h at −78 °C and was silylated with dry triethylamine (0.42 cm^3, 3.0 mmol) and trimethylsilyl chloride (0.30 cm^3, 2.4 mmol). Distillation (Kugelrohr, 170 °C at 14 mmHg) gave the *silyl enol ethers* **9bb** and the regioisomer 2-*cyclohexyl*-1-*cyclohexylidene*-1-(*trimethylsilyloxy*)*ethane* **29b** (215 mg, 38%) (*Z*-**9bb**:*E*-**9bb**:**29b**, 49:21:30) as an oil, contaminated with starting ketone (53 mg, 13% recovery); ν_{max}(film)/cm^{-1} 1661 (C=C), 1250 ($SiMe_3$) and 841 ($SiMe_3$); δ_H(500 MHz; $CDCl_3$) *Z*-**9bb**: 4.28 (1 H, d, *J* 9, H-2), 2.24 (1 H, m, H-3), 1.9–0.8 (12 H, m, 6 × cyclohexyl-CH_2), 1.85 (1 H, or 2 H, m, H-5 or equatorial H-6), 1.73 (2 H, or 1 H, m, equatorial H-6 or H-5), 1.59 (2 H, m, equatorial H-4), 1.10 (2 H, m, axial H-6), 0.98 (2 H, m, axial H-4) and 0.18 (9 H, s, $SiMe_3$); *E*-**9bb**: 4.35 (1 H, d, *J* 9.5, H-2), 2.28 (1 H, m, H-5), 2.04 (1 H, m, H-3), 1.9–0.8 (16 H, m, 6 × cyclohexyl CH_2), 1.62 (2 H, m, equatorial H-4), 1.05 (2 H, m, axial H-4) and 0.16 (9 H, $SiMe_3$); **29b** 2.15 (2 H, t, *J* 6, H-3), 2.06 (2 H, t, *J* 6, H-3′), 1.97 (2 H, d, *J* 7, H-5), 1.9–0.8 (12 H, m, cyclohexyl-CH_2), 1.49 (1 H, m, H-6), 1.45 (4 H, m, H-4) and 0.16 (9 H, s, $SiMe_3$); δ_C($CDCl_3$) *Z*-**9bb** (partial): 153.40 (C-1), 112.30 (C-2), 44.35 (C-3 or C-5), 34.47 (C-5 or C-3) and 0.69 ($SiMe_3$); *E*-**9bb** (partial): 154.55 (C-1), 112.40 (C-2), 39.56 (C-3 or C-5), 35.81 (C-5 or C-3) and 0.57 ($SiMe_3$); **29b** (partial): 140.37 (C-1), 119.20 (C-2), 39.47 (C-5), 35.81 (C-6) and 0.62 ($SiMe_3$). All cyclohexyl peaks between 139 and 126 ppm were left unassigned; *m*/*z* (EI) 280 (75%, M^+), 237 (55), 197 (55, M − C_6H_{11}), 183.1 (35, M − $CH_2C_6H_{11}$), 143 (50) and 73 (100, $SiMe_3$) (Found: M^+, 280.2226. $C_{17}H_{32}OSi$ requires *M*, 280.2222).

1,3-Diphenyl-1-[dimethyl(phenyl)silyloxy]prop-1-ene 35

Dimethyl(phenyl)silyllithium[3] (1.2 mol dm^{-3} in THF, 0.35 cm^3) was added dropwise to a stirred solution of ketone **33** (101 mg, 0.32 mmol) in dry THF (5 cm^3) at −78 °C, under argon, the mixture stirred for 20 min, warmed to room temperature and stirred for 1 h. The mixture was quenched with water (10 cm^3), extracted with hexane (10 cm^3), washed with aqueous sodium hydroxide (5% w/v, 2 × 10 cm^3), brine (20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography (SiO_2, EtOAc–light petroleum, 2:98) gave the *silyl enol ether* **35** (63 mg, 57%) (*Z*-**35**:*E*-**35**, >99:1) as an oil; R_f (ether–light petroleum, 2:98) 0.31; ν_{max}(film)/cm^{-1} 1645 (C=C), 1599 (Ph), 1581 (Ph); δ_H(400 MHz; $CDCl_3$) *Z*-**35**: 7.65 (2 H, dd, *J* 1.5 and 7.5, Ph *o*-H), 7.50 (2 H, dd, *J* 1.5 and 7.5, other Ph *o*-H), 7.5–7.2 (11 H, m, Ph), 5.39 (1 H, t, *J* 7, *vinyl* H), 3.46 (2 H, d, *J* 7, CH_2) and 0.44 (6 H, $SiMe_2$); δ_C($CDCl_3$) 149.69, 141.43, 138.88, 137.25, 133.50, 129.86, 128.43, 128.36, 128.05, 127.85, 127.69, 125.83, 125.80, 110.27, 32.41 and −0.82; *m*/*z* (EI) 344 (5%, M^+), 253 (5, M − CH_2Ph), and 135 (100, $SiMe_2Ph$) (Found: M^+, 344.1597. $C_{23}H_{24}OSi$ requires *M*, 334.1596).

3,3-Dimethyl-1-phenyl-1-[dimethyl(phenyl)silyloxy]but-1-ene 38

Method A. 3,3-Dimethyl-1-phenylbutan-1-one **15b** (1.00 g, 5.7 mmol) in dry THF (3 cm^3) was added dropwise to a stirred suspension of hexane-washed sodium hydride (60% suspension in oil, 0.50 g, 12.5 mmol) under argon at room temperature and stirred for 4.5 h. Dry triethylamine (1.2 cm^3, 8.6 mmol) and dimethyl(phenyl)silyl chloride (1.5 cm^3, 9.0 mmol) were added, forming a white precipitate, the mixture stirred for 30 min, diluted with hexane (30 cm^3), washed with saturated sodium hydrogen carbonate solution (2 × 40 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Kugelrohr distillation (bath temperature 160 °C at 15 mmHg) gave the *silyl enol ether* **38** (0.75 g, 42%) (*Z*-**38**:*E*-**38**, >99:1) as an oil, contaminated with disiloxane (0.25 g).

Method B. Following the procedure for the synthesis of **9aa** (Method A), silyl ether **13b** (0.44 g, 1.67 mmol) in dry THF (5 cm^3) was treated with dimethyl(phenyl)silyllithium[3] (1.0 mol dm^{-3} in THF, 2.0 cm^3) for 4.5 h at −78 °C and distilled (Kugelrohr, 120 °C at 0.5 mmHg) to give the *silyl enol ether* **38** (*Z*-**38**:*E*-**38**, 88:12); ν_{max}(film)/cm^{-1} 1645 (C=C), 1600 (Ph), 1253 ($SiMe_2$), 1119 (SiPh) and 832 ($SiMe_2$); δ_H(250 MHz; $CDCl_3$) *Z*-**38**: 7.45 (2 H, dd, *J* 7.5 and 1.5, *o*-H), 7.4–7.1 (8 H, m, other Ph), 4.80 (1 H, s, vinyl-H), 1.14 (9 H, s, CMe_3) and 0.31 (6 H, s, $SiMe_2$); *E*-**38**: 7.5–7.0 (10 H, m, Ph), 5.15 (1 H, s, vinyl-H) and 0.31 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) *Z*-**38**: 148.63, 140.82, 137.60, 133.49, 129.51, 127.67, 127.57, 127.30, 127.15, 121.47, 31.67, 30.65 and −0.53; *E*-**38** (partial): 148.04, 137.77, 128.42, 122.96, 31.76 and −0.92; *m*/*z* (EI) 310 (20%, M^+), 295 (70, M − Me), 135 (70, $SiMe_2Ph$) and 69 (100) (Found: M^+, 310.1757. $C_{20}H_{26}OSi$ requires *M*, 310.1753).

Silyl enol ether **38** was hydrolysed by stirring in methanol (10 cm^3) and dilute hydrochloric acid (3 mol dm^{-3}, 2 drops) for 48 h, the solvent evaporated under reduced pressure and the residue chromatographed (SiO_2, EtOAc–light petroleum, 5:95) to give ketone **15b** (155 mg, 53% from silyl ether **13b**) as an oil.

The reaction between dimethyl(phenyl)silyllithium and carbonyl compounds 7, 8, 13 and 16

Typically, dimethyl(phenyl)silyllithium[3] (1–2 molar equivalents in THF) was added to the carbonyl compound (0.1–1 mol dm^{-3}) in dry THF under argon at −78 °C. The mixture was stirred for 1–24 h (the colour of the silyl lithium reagent often discharging by this time), followed by standard work-up with ammonium chloride. The residue was stirred overnight in methanol and hydrochloric acid (3 mol dm^{-3}) to hydrolyse the silyl ethers **8** to their corresponding acyloins **7**. The solvent was re-evaporated under reduced pressure and the residue chromatographed (SiO_2, EtOAc–light petroleum, 10:90) to give the products. The following compounds were treated in this way.

Reaction with benzoin 7a. Dimethyl(phenyl)silyllithium (0.90 mol dm^{-3} in THF, 1.36 cm^3) and benzoin **7a** (108 mg, 0.51 mmol) in THF (0.5 cm^3) gave after 6 h at −78 °C, 15 h at room temperature and chromatography (SiO_2, CH_2Cl_2–light petroleum, 50:50), ketone **10a** (30 mg, 30%).

Reaction with silyl ether 8a. Dimethyl(phenyl)silyllithium (1.04 mol dm^{-3} in THF, 0.65 cm^3) and silyl ether **8a** (0.16 g, 0.57 mmol) in THF (0.5 cm^3) gave, after 1.5 h at −78 °C and chromatography (SiO_2, EtOAc–light petroleum, 10:90), ketone **10a** (66 mg, 59%).

Reaction with silyl ether 8b. Dimethyl(phenyl)silyllithium (0.85 mol dm^{-3} in THF, 0.61 cm^3) and silyl ether **8b** (128 mg, 0.43 mmol) in THF (2 cm^3) gave, after 8 h at −78 °C and chromatography (SiO_2, EtOAc–light petroleum, 4:96), ketone **10b** (47 mg, 59%).

Reaction with silyl ether 8c. Dimethyl(phenyl)silyllithium (0.67 mol dm^{-3} in THF, 1.04 cm^3) and silyl ether **8c** (154 mg, 0.58 mmol) in THF (1.5 cm^3) gave, after 8 h in the dark (warming to room temperature) and chromatography (SiO_2, EtOAc–light petroleum, 20:80), ketone **10c** (60 mg, 59%) and 1,2-di-(2-furyl)ethanedione (14 mg, 12%).

Reaction with silyl ether 8d. Dimethyl(phenyl)silyllithium (0.9 mol dm^{-3} in THF, 2.40 cm^3) and silyl ether **8d** (174 mg, 0.71 mmol) in dry toluene–THF (1.5 cm^3, 50:50) gave, after 1.5 h at −78 °C, 20 h at room temperature and chromatography (SiO_2, EtOAc–light petroleum, 5:95), a compound {43 mg, tentatively assigned as 4-[dimethyl(phenyl)silyloxy]-2,2,5,5-tetramethylhexan-3-ol}; R_f (EtOAc–light petroleum, 20:80) 0.38. The compound decomposed on standing for several days, the residual oil being a 35:65 mixture of 1,2-diphenyl-1,1,2,2-tetramethyldisiloxane, identical to an authentic sample, and diol **40** (25 mg, 21%) (*meso*:*dl*, 96.5:3.5).

Reaction with silyl ether 8e. Dimethyl(phenyl)silyllithium (0.85 mol dm^{-3} in THF, 7.0 cm^3) and silyl ether **8e** (497 mg, 2.3 mmol) in THF (5 cm^3) gave, after 20 h (warming to 10 °C), ketone **10e** (43% by gas chromatography).

Reaction with silyl ether 8f. Dimethyl(phenyl)silyllithium (1.20 mol dm^{-3} in THF, 0.84 cm^3) and silyl ether **8f** (229 mg, 0.84 mmol) in THF (2 cm^3) gave, after 20 h (warming to 10 °C) and chromatography (SiO_2, EtOAc–light petroleum, 3:97), ketone **10f** (77 mg, 53%) and 6-[*dimethyl*(*phenyl*)*silyl*]*dodecan*-6-*ol* (6 mg, 6%).

Reaction with silyl ether 13a. Dimethyl(phenyl)silyllithium (1.14 mol dm^{-3} in THF, 1.8 cm^3) and silyl ether **13a** (205 mg, 0.69 mmol) in THF (1 cm^3) gave, after 1.5 h at −78 °C, 5 h at 0 °C and chromatography (SiO_2, EtOAc–light petroleum, 5:95), ketone **15a** (119 mg, 83%).

Reaction with sodium salt 16a. Dimethyl(phenyl)silyllithium (0.71 mol dm^{-3} in THF, 4.0 cm^3) and crude salt **16a** in THF (10 cm^3) gave after 20 h (warming to room temperature) and chromatography (SiO_2 plate, run in 5 × CH_2Cl_2–light petroleum, 50:50), ketone **10a** (69 mg, 15%) and benzil **11** (75 mg, 15%).

Reaction with benzoate ester 16b. Dimethyl(phenyl)silyllithium (1.08 mol dm^{-3} in THF, 1.64 cm^3) and ester **16b** (187 mg, 0.59 mmol) in THF (1 cm^3) gave, after 2 h at −78 °C, 6 h at 0 °C and chromatography (SiO_2, EtOAc–light petroleum, 15:85), ketone **10a** (106 mg, 92%).

Reaction with silyl ether 16c. Dimethyl(phenyl)silyllithium (0.90 mol dm^{-3} in THF, 0.81 cm^3) and silyl ether **16c** (207 mg, 0.61 mmol) in THF (1 cm^3) gave, after 4 h at −78 °C and chromatography (SiO_2, EtOAc–light petroleum, 4:96), ketone **10b** (89 mg, 70%).

Reaction with benzoate ester 16d. Dimethyl(phenyl)silyllithium (1.4 mol dm^{-3} in THF, 1.16 cm^3) and benzoate ester **16d** (178 mg, 0.54 mmol) in dry THF (1 cm^3) gave, after 2 h at −78 °C, 3 h at 0 °C and chromatography (SiO_2, EtOAc–light petroleum, 5:95), ketone **10b** (56 mg, 50%).

Reaction with carbonate 16e. Dimethyl(phenyl)silyllithium (1.3 mol dm^{-3} in THF, 1.40 cm^3) and carbonate **16e** (181 mg, 0.61 mmol) in THF (1 cm^3) gave, after 1.5 h at −78 °C, 2 h at 0 °C and chromatography (SiO_2, EtOAc–light petroleum, 5:95), ketone **10b** (88 mg, 70%).

Reaction with tosylate 16f. Dimethyl(phenyl)silyllithium (0.6 mol dm^{-3} in THF, 0.25 cm^3) and tosylate **16f** (55 mg, 0.145 mmol) in THF (0.25 cm^3) gave, after 12 h (warming to room temperature) and chromatography (SiO_2, EtOAc–light petroleum, 5:95), ketone **10b** (14 mg, 46%).

The following compounds were prepared by these methods.

1,2-Diphenylethanone 10a. Isolated as a solid, mp 52–54 °C (lit.,[33] 56–57 °C); R_f (CH_2Cl_2–light petroleum, 50:50) 0.31; ν_{max}(Nujol)/cm^{-1} 1685 (C=O); δ_H(250 MHz; $CDCl_3$) 8.0 (2 H, dd, *J* 7 and 1.5, PhCO *o*-H), 7.7–7.2 (8 H, m, other Ph) and 4.28 (2 H, s, CH_2).

1,2-Dicyclohexylethanone 10b. Isolated as an oil;[34] R_f (EtOAc–light petroleum, 4:96) 0.30; ν_{max}(film)/cm^{-1} 1707 (C=O); δ_H(250 MHz; $CDCl_3$) 2.27 1 H, cyclohexyl COCH), 2.27 (2 H, d, *J* 7, $COCH_2$), 1.9–1.5 (11 H, m, cyclohexyl H) and 1.0–0.8 (2 H, m, cyclohexyl H); δ_C($CDCl_3$) 213.7, 51.1, 48.3, 33.6, 33.3, 28.3, 26.2, 26.0, 25.8, 25.6.

1,2-Di-(2-furyl)ethanone 10c. Isolated as an oil (lit.,[35] mp 20–23 °C); R_f (EtOAc–light petroleum, 20:80) 0.25; ν_{max}(film)/cm^{-1} 3131 (vinyl-C–H), 1677 (C=O) 1592 (C=C) and 1569 (C=C); δ_H(250 MHz; $CDCl_3$) 7.60 (1 H, m, furoyl-H-5), 7.33 (1 H, m, furyl-H-5), 7.25 (1 H, d, *J* 3.5, furoyl-H-3), 6.54 (1 H, dd, *J* 3.5 and 1.5, furoyl-H-4), 6.33 (1 H, dd, *J* 3.5 and 1.5, furyl-H-4), 6.25 (1 H, d, *J* 3.5, furyl-H-3) and 4.14 (2 H, s, CH_2).

2,5-Dimethylhexan-3-one 10e.[36] Isolated as an oil; R_f (EtOAc–light petroleum, 10:90) 0.49; ν_{max}(film)/cm^{-1} 1709 (C=O); δ_H(250 MHz; $CDCl_3$) 2.55 (1 H, septet, *J* 7.5, COC*H*Me_2), 2.31 (2 H, d, *J* 7.5, COCH_2CHMe_2), 2.15 (1 H, nonet, *J* 7.5, $COCH_2$-C*H*Me_2), 1.06 (6 H, d, *J* 7.5, COCH*Me*$_2$) and 0.89 (6 H, d, *J* 7.5, $COCH_2$CH*Me*$_2$).

Dodecan-6-one 10f.[22] Isolated as an oil; R_f (EtOAc–light petroleum, 2:98) 0.23; ν_{max}(film)/cm^{-1} 1715 (C=O); δ_H(250 MHz; $CDCl_3$) 2.36 (4 H, t, *J* 7.5, 2 × $COCH_2$), 1.57 (4 H, 2 × $COCH_2CH_2$), 1.4–1.2 (10 H, m, CH_2), 0.90 (3 H, t, *J* 7.5, Me) and 0.88 (3 H, t, *J* 7.5, Me).

Benzil 11. Isolated as yellow needles, mp 88–94 °C (lit.,[37] 92–94 °C); R_f (CH_2Cl_2–light petroleum, 50:50) 0.57; ν_{max}(Nujol)/cm^{-1} 1659 (C=O), 1593 (Ph) and 1578 (Ph); δ_H(250 MHz; $CDCl_3$) 7.95 (4 H, dd, *J* 8 and 1, *o*-H), 7.65 (2 H, tt, *J* 8 and 1, *p*-H) and 7.53 (4 H, t, *J* 8, *m*-H).

1,2-Diphenylpropan-1-one 15a. Isolated as needles, mp 46–48 °C (from hexane) (lit.,[38] 53–54 °C); R_f (ether–light petroleum, 12:88) 0.33; ν_{max}(film)/cm^{-1} 1682 (C=O), 1597 (Ph) and 1582 (Ph); δ_H(250 MHz; $CDCl_3$) 7.97 (2 H, dd, *J* 7.5 and 1, PhCO *o*-H), 7.5–7.1 (8 H, m, other Ph), 4.70 (1 H, q, *J* 7.5, C*H*Me) and 1.55 (3 H, d, *J* 7.5, CH*Me*).

2,2,5,5-Tetramethylhexane-3,4-diol 40.[39] Isolated as an oil; R_f (EtOAc–light petroleum, 20:80) 0.08; ν_{max}(film)/cm^{-1} 3411 (br, OH); δ_H(400 MHz; $CDCl_3$) *meso*: 3.24 (2 H, s, C*H*OH), 1.40 (2 H, br s, CHO*H*) and 1.00 (18 H, s, CMe_3); (±) (partial): 3.31 (2 H, s C*H*OH) and 0.90 (18 H, s, CMe_3); δ_C($CDCl_3$) *meso*: 80.4, 35.6 and 26.5; (±) (partial): 74.9 and 25.8; *m*/*z* (EI) 156 (0.5%, M − H_2O), 117 (5, M − C_4H_9), 99 (15, M − H_2O − C_4H_9), 87 (25, C_4H_9CHOH), 57 (100, C_4H_9) and 41 (50, C_3H_5).

1,2-Di(2-furyl)ethanedione. Isolated as yellow needles, mp 159–163 °C (from EtOAc–hexane) (lit.,[40] 164–165 °C); R_f (EtOAc–light petroleum, 20:80) 0.18; ν_{max}(Nujol)/cm^{-1} 3148 (furyl-C–H) and 1643 (C=O); δ_H(250 MHz; $CDCl_3$) 7.77 (2 H, s, *J* 1.5, H-5), 7.64 (2 H, d, *J* 3.5, H-3) and 6.63 (2 H, dd, *J* 3.5 and 1.5, H-4); δ_C($CDCl_3$) 176.9, 149.4, 149.3, 124.7 and 113.1.

6-[Dimethyl(phenyl)silyl]dodecan-6-ol. Isolated as an oil; R_f (EtOAc–light petroleum, 4:96) 0.13; ν_{max}(film)/cm^{-1} 3462 (br, OH), 1248 ($SiMe_2$), 1112 (Si–Ph) and 831 ($SiMe_2$); δ_H(400 MHz; $CDCl_3$) 7.6 (2 H, m, *m*-H), 7.3 (3 H, m, *o*- and *p*-H), 1.6 (4 H, m, 2 × CH_2CHOH), 1.4–1.2 (15 H, m, 7 × CH_2 and OH), 0.88 (3 H, t, *J* 6.5, CH_2Me), 0.87 (3 H, t, *J* 6.5, CH_2Me) and 0.37

(6 H, s, $SiMe_2$); δ_C($CDCl_3$) 137.3, 134.6, 129.1, 127.7, 69.1, 37.3, 37.2, 32.6, 31.8, 30.1, 23.2, 22.9, 22.6, 22.6, 14.1, 14.0 and −4.3; *m/z* (EI) 320 (23%, M^+), 319 (55, M − H), 305 (65, M − Me), 249 (70, M − C_5H_{11}), 235 (70, M − C_6H_{13}) and 185 (65, M − $SiMe_2Ph$) (Found: M^+, 320.2535. $C_{20}H_{36}OSi$ requires *M*, 320.2535).

1,2-Diphenylethane-1,2-diol 39

Silyl ether **8a** (208 mg, 0.73 mmol) in dry ether (10 cm^3) was stirred with a suspension of lithium aluminium hydride (28 mg, 0.74 mmol) in dry ether (40 cm^3) under argon at −78 °C for 6 h. The reaction was quenched at −78 °C with methanol (10 cm^3) and warmed to room temperature. Standard work-up with potassium sodium tartrate and chromatography (SiO_2, EtOAc–light petroleum, 20:80) gave the diol (114 mg, 73%) [*meso*:(±) 94:6], as needles, mp 128–133 °C (lit., *meso*[41] 128–130 °C; (±)[42] 148–149 °C); R_f (EtOAc–light petroleum, 20:80) 0.12; ν_{max}(Nujol)/cm^{-1} 3366 (br, OH) and 3314 (br, OH); δ_H(250 MHz; $CDCl_3$) *meso*: 7.4–7.1 (10 H, m, Ph), 4.82 (2 H, s, C*H*OH) and 2.23 (2 H, br s, CHO*H*); (±): 7.4–7.1 (10 H, m, Ph), 4.70 (2 H, s, C*H*OH) and 2.86 (2 H, br s, CHO*H*).

Standard work-up procedure for fluoro compounds 47–53

Unless stated otherwise, the reaction mixture was diluted with hexane (20 cm^3), quenched with saturated potassium sodium tartrate solution (20 cm^3), the aqueous layer extracted with hexane–ether (1:1, 3 × 20 cm^3), the combined organic extracts washed with saturated potassium sodium tartrate solution (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure.

1,1-Difluoro-2-phenyl-2-[dimethyl(phenyl)silyloxy]ethene 47a

Method A. Zinc bromide (4.5 g, 20 mmol) was dried under vacuum (110 °C, 0.1 mmHg overnight, then 200 °C, 4 h), allowed to cool and was suspended in dry THF–ether (75 cm^3, 1:4) under argon. (Trifluoroacetyl)benzene **46** (0.25 cm^3, 1.78 mmol) was added, the solution cooled to −78 °C and stirred for 15 min. Dimethyl(phenyl)silyllithium[3] (1.1 mol dm^{-3} in THF, 6.6 cm^3) was added dropwise over 10 min, the mixture stirred for 20 min, warmed to 0 °C and stirred a further 1 h. Water (40 cm^3) was added followed by standard work-up. Distillation (Kugelrohr, 110 °C increasing to 150 °C at 1.5 mmHg) gave the crude *silyl enol ether* as an oil, contaminated with 1,2-diphenyl-1,1,2,2-tetramethyldisilane (140 mg), identical to an authentic sample. Yield of **47a** by estimation of the ^1H NMR spectrum; 19%.

Method B. Methylmagnesium bromide (3.0 mol dm^{-3} in ether, 0.6 cm^3) was added to dimethyl(phenyl)silyllithium[3] (0.51 mol dm^{-3} in THF, 3.5 cm^3) at 0 °C under argon, and was stirred for 20 min. The silyl(methyl)magnesium reagent was then added dropwise over 10 min to (trifluoroacetyl)benzene **46** (0.25 mmol, 1.78 mmol) in dry ether (12 cm^3) at −78 °C. After stirring for 30 min, the solution was warmed to 0 °C and stirred a further 90 min. Standard work-up and rapid chromatography through a short column (SiO_2, EtOAc–light petroleum, 1:99) gave the crude *silyl enol ether*, as an oil contaminated with (difluoroacetyl)benzene.[43] Yields by estimation of the ^1H NMR spectrum; **47a** (15%) and (difluoroacetyl)benzene (15%). **47a**; R_f (ether–light petroleum, 2:98) 0.44; ν_{max}(film)/cm^{-1} 1722 (C=C), 1598 (Ph), 1256 ($SiMe_2$), 1119 (SiPh) and 832 ($SiMe_2$); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph) and 0.33 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) (partial) 154.9 (t, $^1J_{CF}$ 175, CF_2), 139.9, 136.4, 133.6, 133.2, 126.3 (dd, $^2J_{CF}$ 27.5 and 16, *C*=CF_2) and 1.0; *m/z* (+FAB) 290 (55%, M^+), 271 (55, M − F), 209 (100) and 193 (100) (Found: M^+, 290.0935. $C_{16}H_{16}F_2OSi$ requires *M*, 290.0938). (Difluoroacetyl)benzene; R_f (hexane) 0.05; ν_{max}(film)/cm^{-1} 1696 (C=O) and 1598 (Ph); δ_H(250 MHz; $CDCl_3$) 8.15 (2 H, dd, *J* 7.5 and 1, *o*-H), 7.8–7.3 (3 H, other Ph) and 6.32 (1 H, t, $^2J_{HF}$ 53.5, CHF_2).

1,1-Difluoro-2-phenyl-2-(*tert*-butyldiphenylsilyloxy)ethene 47b

Method A. Following the procedure for the synthesis of silyl enol ether **47a** (Method A), trifluoromethyl ketone **46** (0.25 cm^3, 1.78 mmol) was treated with dry zinc bromide (1.2 g, 5.3 mmol) and *tert*-butyldiphenylsilyllithium (0.51 mol dm^{-3} in THF, 3.53 cm^3) in dry THF–ether (1:2, 24 cm^3) for 20 min at −78 °C and 90 min at 0 °C. Standard work-up and chromatography (SiO_2, EtOAc–light petroleum, 1:99) gave the *silyl enol ether* **47b** (346 mg, 49%) as an oil.

Method B. Following the procedure for the synthesis of silyl enol ether **47a** (Method B), trifluoromethyl ketone **46** (0.25 mmol, 1.78 mmol) in dry ether (15 cm^3) was treated with the reagent formed from methylmagnesium bromide (3.0 mol dm^{-3} in ether, 0.6 cm^3) and *tert*-butyldiphenylsilyllithium (0.28 mol dm^{-3} in THF, 6.4 cm^3) for 20 min at −78 °C and for 50 min at 0 °C. Standard work-up and chromatography (SiO_2, EtOAc–light petroleum, 1:99) gave the *silyl enol ether* **47b** (357 mg, 51%) as an oil; R_f (ether–light petroleum, 2:98) 0.38; ν_{max}(film)/cm^{-1} 3072 (C–H), 3050 (C–H), 1732 (C=C), 1590 (Ph) and 1114 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.8–7.7 (6 H, m, 6 × *o*-H), 7.5–7.2 (9 H, m, other H) and 1.17 (9 H, s, CMe_3); δ_C($CDCl_3$) 154.0 (dd, $^1J_{CF}$ 284 and 289, CF_2), 137.6, 135.6, 135.6, 132.5 (dd, $^3J_{CF}$ 6 and 4, *Ph*C=CF_2 *ipso*-C), 130.0, 128.1, 127.6, 127.6, 127.0 (dd, $^2J_{CF}$ 5.5 and 3, *C*=CF_2), 26.8 and 19.8; *m/z* (EI) 394 (5%, M^+), 353 (40, M − C_3H_5), 337 (95, M − Bu′), 303 (95, M − $PhCH_2$), 259 (60), 231 (35) and 201 (100) (Found: M^+, 394.1566. $C_{24}H_{24}F_2OSi$ requires *M*, 394.1564).

1,1-Difluoro-3-phenyl-2-[dimethyl(phenyl)silyloxy]prop-1-ene 49

1,1,1-Trifluoro-3-phenylpropan-2-one **48** (0.10 cm^3, 0.65 mmol) was added to a stirred solution of dimethyl(phenyl)silyllithium[3] (0.13 mol dm^{-3} in THF, 10.8 cm^3) under argon at −78 °C and stirred for 15 min. Chlorodimethyl(phenyl)silane (0.14 cm^3, 0.85 mmol) was added and the mixture warmed to room temperature over 20 min. Standard work-up and rapid chromatography through a short column (SiO_2, EtOAc–light petroleum, 1.5:98.5) gave the crude *silyl enol ether* **49** contaminated with 1,1,2,2-tetramethyl-1,2-diphenyldisilane, identical to an authentic sample. Distillation (Kugelrohr, 180 °C at 28 mmHg) failed to purify the product further. Yield of **49** (from ^1H NMR spectrum) 37%; R_f (ether–light petroleum, 2:98) 0.46; ν_{max}($CDCl_3$)/cm^{-1} 1763 (C=C), 1602 (Ph), 1592 (Ph) and 1255 ($SiMe_2$); δ_H(250 MHz; $CDCl_3$) 7.6–7.2 (8 H, m, Ph), 7.16 (2 H, dd, *J* 7.5 and 2, *Ph*CH_2 *o*-H), 3.32 (2 H, dd, $^4J_{HF}$ 4 and 2, PhC*H*$_2$) and 0.33 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 153.6 (dd, $^1J_{CF}$ 282 and 276, CF_2), 137.0 (t, $^4J_{CF}$ 2, $PhCH_2$ *ipso*-C), 136.5, 133.2, 129.8, 128.9, 128.3, 127.7, 126.6, 112.9 (dd, $^2J_{CF}$ 42 and 15, *C*=CF_2), 35.0 (t, $^3J_{CF}$ 1, Ph_CH_2), −1.6 and −1.7; *m/z* (EI) 304 (20%, M^+), 135 (100, $SiMe_2Ph$), 91 (35, $PhCH_2$), 87 (45) and 74 (80) (Found: M^+, 304.1078. $C_{17}H_{18}F_2OSi$ requires *M*, 304.1095).

1,1-Difluoro-3-phenylpropan-2-one 50[44]

Dimethyl(phenyl)silyllithium[3] (1.28 mol dm^{-3} in THF, 2.60 cm^3) was added dropwise over 5 min to a stirred solution of trifluoromethyl ketone **48** (0.25 cm^3, 1.64 mmol) in dry ether (40 cm^3) at −100 °C, under argon. The mixture was stirred for 30 min, warming to −40 °C. Excess methyl iodide (0.8 cm^3) was added (ineffectually) and the mixture was allowed to warm to room temperature. A solution of 2,4-dinitrophenylhydrazine (0.26 g, 1.3 mmol) and concentrated sulfuric acid (0.33 cm^3) in methanol (10 cm^3) was added, the mixture heated to boiling, allowed to cool and water (30 cm^3) added. The precipitate was filtered off, the mother liquor extracted with ether (3 × 40 cm^3) and the precipitate and the organic extracts combined and evaporated under reduced pressure. Chromatography (SiO_2, EtOAc–light petroleum, 10:90) gave 1,1-*difluoro*-3-*phenylpentan*-2-*one* (2,4-*dinitrophenyl*)*hydrazone* (330 mg, 59%) as an orange solid, mp 107–108 °C (from MeOH); R_f (ether–light petroleum, 20:80) 0.40; ν_{max}(Nujol)/cm^{-1} 3290 (N–H), 1632 (C=N), 1597 (Ph), 1549 (NO_2), 1339 (NO_2) and 1314 (NO_2); δ_H(250 MHz; $CDCl_3$) 11.02 (1 H, br s, NH), 9.04 (1 H, d, *J* 2.5, NH*Ar* H-3),

8.34 (1 H, dd, *J* 9.5 and 2.5, NH*Ar* H-5), 7.97 (1 H, d, *J* 9.5, NH*Ar* H-6), 7.4–7.3 (5 H, other Ph), 6.35 (1 H, t, $^2J_{HF}$ 55, CHF_2) and 3.98 (2 H, s, PhCH_2); δ_C($CDCl_3$) 171.1, 147.7, 144.1, 139.6, 132.0, 130.0, 129.4, 128.6, 127.9, 122.9, 116.9, 114.5 (t, $^1J_{CF}$ 239, CHF_2) and 60.4; *m*/*z* (EI) 350 (95%, M^+), 315 (80), 269 (30), 143 (55), 117 ($PhCH_2CN$) and 91 (100 $PhCH_2$) (Found: M^+, 350.0825. $C_{15}H_{12}F_2N_4O_4$ requires *M*, 350.0826).

1,1-Difluoro-3-phenylpentan-2-one (2,4-dinitrophenyl)hydrazone (0.41 g, 1.17 mmol), titanium trichloride (1.8 mol dm^{-3} in water, 10 cm^3) and dry 1,2-dimethoxyethane (60 cm^3) were refluxed under argon for 15 min, until no starting material was visible by TLC. The mixture was cooled to room temperature and water (50 cm^3) was added. The aqueous layer was extracted with ether (3 × 60 cm^3), the combined organic extracts washed with brine (100 cm^3) and dried ($MgSO_4$). The solvents were distilled using a Vigreux column (oil-bath temperature 110 °C). Chromatography of the residue (SiO_2, light petroleum then EtOAc–light petroleum, 20:80) gave the ketone **50** (90 mg, 45%) as an oil; R_f (ether–light petroleum, 15:85) 0.29; ν_{max}($CDCl_3$)/cm^{-1} 1749 (C=O) and 1603 (Ph); δ_H(250 MHz; $CDCl_3$) 7.4–7.1 (5 H, m, Ph), 5.78 (1 H, t, $^2J_{HF}$ 54, CHF_2) and 3.98 (2 H, s, PhCH_2); δ_C($CDCl_3$) 196.8 (t, $^2J_{CF}$ 26.5, *C*OCHF_2), 131.3, 129.7, 128.9, 127.6, 109.8 (t, $^1J_{CF}$ 253, CHF_2) and 43.0.

1,1,1-Trifluoro-2-methyl-3-phenylpropan-2-ol 51[45]

Following the procedure for the synthesis of silyl enol ether **47a** (Method B), trifluoromethyl ketone **48** (0.25 mmol, 1.64 mmol) in dry ether (15 cm^3) was treated with the reagent formed from methylmagnesium bromide (3.0 mol dm^{-3} in ether, 0.55 cm^3) and *tert*-butyldiphenylsilyllithium (0.26 mol dm^{-3} in THF, 6.3 cm^3) for 20 min at −78 °C and 50 min at 0 °C. Standard work-up and chromatography (SiO_2, EtOAc–light petroleum, 1:99) gave alcohol **51** (0.20 g, 61%); R_f (EtOAc–light petroleum, 20:80) 0.33; ν_{max}(film)/cm^{-1} 3464 (br OH) and 1606 (Ph); δ_H(250 MHz; $CDCl_3$) 7.4–7.2 (5 H, m, Ph), 3.10 (1 H, d, *J* 14, PhCH_AH_B), 2.84 (1 H, d, *J* 14, PhCH_AH_B), 1.98 (1 H, s, OH) and 1.28 (3 H, s, Me); δ_C($CDCl_3$) 134.4, 130.8, 128.4, 127.2, 73.7 (q, *J* 28, CF_3), 40.8 and 20.5; *m*/*z* (EI) 204 (25%, M^+) and 91 (100, $PhCH_2$) (Found: M^+, 204.0766. $C_{10}H_{11}F_3O$ requires *M*, 204.0762).

Chromatography also gave *tert*-butyl(diphenyl)silane **52** (0.30 g, 76%) as an oil; R_f (ether–light petroleum, 2:98) 0.55; ν_{max}($CDCl_3$)/cm^{-1} 2113 (Si–H), 1588 (Ph) and 1111 (SiPh); δ_H(250 MHz; $CDCl_3$) 7.87 (4 H, dd, *J* 5.5 and 2, *o*-H), 7.54 (6 H, m, *m*- and *p*-H), 4.88 (1 H, s, SiH) and 1.28 (9 H, s, CMe_3); δ_C($CDCl_3$) 135.9, 134.2, 129.6, 128.0, 27.8 and 18.0.

2,2-Difluoro-3-hydroxy-1,3-diphenylpropan-1-one 53[46]

Method A. Silyl enol ether **47a** was prepared following the procedure detailed in Method B, and was worked up prior to chromatography. The crude silyl enol ether in dry dichloromethane (20 cm^3) was added to a stirred solution of benzaldehyde (0.87 cm^3, 8.6 mmol) in dry dichloromethane at −78 °C. Titanium tetrachloride (1.0 mol dm^{-3} in dichloromethane, 10.7 cm^3) was added, the solution stirred for 15 min, warmed to −15 °C and stirred overnight, warming to room temperature and forming a brown precipitate. Water (100 cm^3) and saturated potassium sodium tartrate solution (100 cm^3) were added, the aqueous layer extracted with EtOAc (3 × 100 cm^3), the combined organic extracts washed with brine (150 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography (SiO_2, EtOAc–light petroleum, 12:88) gave the aldol **53** (0.715 g, 38%), inseparable from dimethyl(phenyl)silanol (0.30 g), identical to an authentic sample.

Method B. Titanium tetrachloride (1.32 cm^3 of a 1.0 mol dm^{-3} solution in CH_2Cl_2, 1.32 mmol) was added to a solution of pure silyl enol ether **47b** (346 mg, 0.88 mmol) and benzaldehyde (0.11 cm^3, 1.06 mmol) in dichloromethane (10 cm^3) at −78 °C, and the mixture was stirred overnight, warming to room temperature. Saturated potassium sodium tartrate solution (15 cm^3) was added, the aqueous layer extracted with ether (4 × 15 cm^3), the combined organic extracts washed with brine (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Chromatography (SiO_2, EtOAc–light petroleum, 12:88) gave the aldol **53** (72 mg, 31%); R_f (EtOAc–light petroleum, 20:80) 0.30; ν_{max}(film)/cm^{-1} 3364 (OH), 1702 (C=O), 1597 (Ph), and 1579 (Ph); δ_H(250 MHz; $CDCl_3$) 8.05 (2 H, dd, *J* 8.5 and 1, PhCO *o*-H), 7.7–7.3 (8 H, m, other Ph), 5.39 (1 H, ddd, $^3J_{HH}$ 4.5, $^2J_{HF}$ 18.5 and 4.5, C*H*OH) and 3.04 (1 H, d, *J* 4, OH).

Acknowledgements

We thank the EPSRC and Zeneca Argrochemicals for a CASE award (R. S. R.).

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Paper 7/09114A
Received 22*nd December* 1997
Accepted 5*th February* 1998