Intramolecular radical-chain hydrosilylation catalysed by thiols: cyclisation of alkenyloxysilanes

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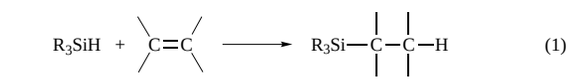
Alkenyloxy(diphenyl)silanes that contain a terminal double bond undergo radical-chain cyclisation at 60–65 °C, in the presence of di-*tert*-butyl hyponitrite as initiator and a thiol as a catalyst. The thiol acts as a polarity-reversal catalyst and promotes the overall abstraction of hydrogen from the Si–H group in the alkenyloxysilane by the cyclic carbon-centred radical, formed by intramolecular addition of the corresponding silyl radical to the C=CH_2 group. Allyloxysilanes give five-membered-ring products *via* 5-*endo*-*trig* cyclisation of the intermediate allyloxysilyl radical. Homoallyloxysilanes give mixtures of five- and six-membered heterocycles, but the intermediate silyl radicals undergo predominantly 6-*endo* cyclisation, in contrast to the corresponding carbon-centred radicals which cyclise preferentially in the 5-*exo* mode. An analogous pentenyloxysilane gives only the seven-membered-ring product *via* a 7-*endo* radical cyclisation. Steric effects play an important part in influencing the final-product stereochemistry when this is determined in the hydrogen-atom transfer reaction between the cyclic adduct radical and the thiol catalyst. Complementary EPR spectroscopic studies of the short-lived intermediate cyclic adduct radicals have been carried out in the absence of thiol and the structures and conformations of these species have been determined. It is emphasised that, for thiol catalysis of the overall cyclisation of alkenyloxysilanes to be successful, it is necessary for the addition of the chain-carrying thiyl radical to the C=CH_2 group to be reversible under the reaction conditions.

Radical-chain addition of simple triorganosilanes to alkenes [eqn. (1)] is inefficient at moderate temperatures and is of little use in synthesis. Although silyl radicals add rapidly to alkenes,[1] the resulting nucleophilic β-silylalkyl radical **1** abstracts hydrogen only slowly from the silane [eqn. (2)].[2]



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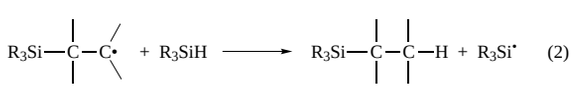

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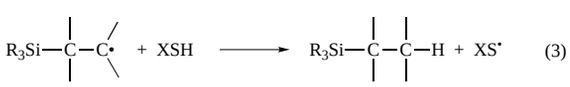
We have reported[3,4] that reaction (2) is subject to polarity-reversal catalysis by thiols, when the direct abstraction of hydrogen from the silane is replaced by the cycle of more rapid reactions (3) and (4), both of which benefit from favourable

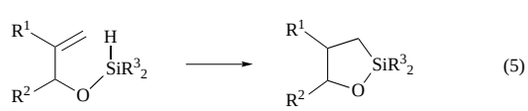


(3)

(4)

polar effects.[5]†,‡ As a consequence, intermolecular thiol-catalysed radical-chain hydrosilylation of alkenes represents a viable synthetic route to organosilanes,[6,8] which complements the well-established transition-metal catalysed pathway.[9]

Cyclisation of allyloxysilanes of the type **2** under the influence of transition-metal catalysts (usually rhodium- or platinum-based) occurs in a 5-*endo* fashion, as shown in eqn. (5).[10,11] Under the same conditions, homoallyloxysilanes (but-



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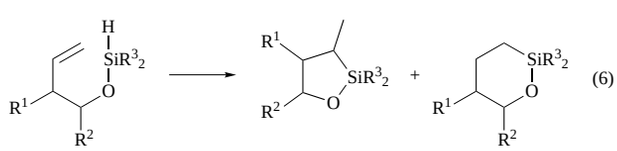


(6)

3 **4** minor product

3-enyloxysilanes) of the type **3** give mainly the product of 5-*exo* cyclisation **4** and this becomes the exclusive cyclisation pathway when the double bond carries one or two terminal substituents.[10,12] Such transition-metal catalysed intramolecular hydrosilylation has been developed into a useful synthetic method by Tamao and co-workers[10,12,13] and by Bosnich and co-workers[11,14] and highly enantioselective cyclisations of alkenyloxysilanes onto prochiral alkene functions have been achieved by using as catalysts rhodium(I) complexes containing homochiral diphosphine ligands. Oxidative cleavage of the Si–C bond by hydrogen peroxide, which occurs with retention of configuration at carbon, provides a route to 1,3-diols of defined stereochemistry.[10–14]

In the present paper we report an investigation of the application of thiol catalysis to promote radical-chain cyclisation of alkenyloxysilanes.

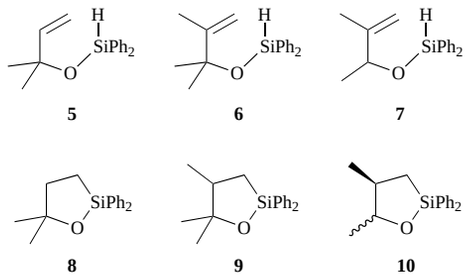
† Reaction (4) is endothermic when X is an alkyl group and thus the activation energy for the reverse process must be less than for the forward reaction. However, the silyl radical is trapped *irreversibly* by addition to the alkene, whilst addition of $XS^{\bullet}$ is generally readily reversible.
‡ Hydrosilylation of alkenes using tris(trimethylsilyl)silane[7] is effective in the absence of thiol, because the Si–H bond is significantly weaker than that in a trialkylsilane.

Results and discussion

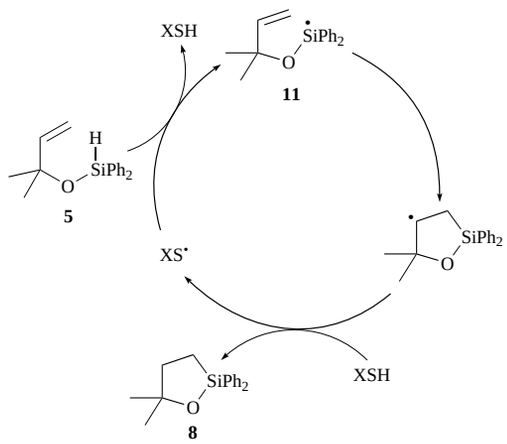
Allyloxysilanes

Diphenyl(2-methylbut-3-en-2-yloxy)silane **5** was recovered unchanged when the silane (*ca.* 0.3 mol dm^{-3}) was heated at 60 or 65 °C in hexane under argon for 3 h, in the presence of 5 mol% di-*tert*-butyl hyponitrite[15] (TBHN) as a thermal source of *tert*-butoxyl radicals [eqn. (7)]. Half the TBHN was present

$$Bu^tON{=}NOBu^t \longrightarrow 2Bu^tO^{\bullet} + N_2 \qquad (7)$$



initially and the remainder was added after 1 h.§ However, when experiment was repeated at 60 °C in the presence of 5 mol% *tert*-dodecanethiol¶ (TDT), added in two equal portions together with the TBHN, the cyclic silane **8** was formed in 95% yield as determined by ^{1}H NMR spectroscopy (isolated yield 88%). In the presence of TDT, but without TBHN, no cyclisation was observed and the allyloxysilane **5** was recovered unchanged. Evidently the silane **5** cyclises by a radical-chain mechanism which involves thiol catalysis, as shown in Scheme 1. The radical **11** undergoes rapid 5-*endo-trig* cyclis-



Scheme 1

ation and similar *endo* cyclisation of allyloxysilyl radicals, generated by a different route, has recently been reported independently by Clive and his co-workers.[16] Thiol-catalysed cyclisations of the allyloxysilanes **6** and **7** were carried out under similar conditions and the results are summarised in Table 1.

1,4-Dioxane was equally suitable as solvent for the TBHN-initiated cyclisation of **5** (entry 2), but neither azoisobutyronitrile (AIBN) nor dilauroyl peroxide (DLP) were satisfactory as initiators (entries 3 and 4), possibly because silyl radicals react rapidly with these compounds by addition to the diazo function (AIBN), to give a chain-terminating hydrazyl radical, or by S_H2 attack at the peroxide linkage (DLP).

With TDT as catalyst, the yield of cyclised product **9** from the allyloxysilane **6** was only moderate (entry 5). It was thought at first that this was the result of slow cyclisation of the intermediate silyl radical, possibly because of a steric interaction between vicinal methyl groups in the transition state. However, EPR studies of this elementary step in isolation (see later) showed that the cyclisation is actually a rapid process (k > *ca.* 10^6 s^{-1} at 60 °C). When alternative thiol catalysts were investigated it was found that triphenylsilanethiol or triisopropylsilanethiol[17] afforded almost quantitative yields of **9** (entries 6 and 7). It is possible that the silanethiyl radicals $R_3SiS^{\bullet}$ abstract hydrogen more rapidly and/or selectively from the Si–H group in the silane **5**,[4] while the alkanethiyl radical derived from TDT may abstract hydrogen competitively from the allylic methyl group to give a chain-terminating allylic radical. Loss of thiol by addition to the C=C group[6] does not seem to be a complicating factor here, because the yield of **9** obtained with TDT as catalyst was not increased significantly by slow addition of the thiol over 3 h using a motor-driven syringe.

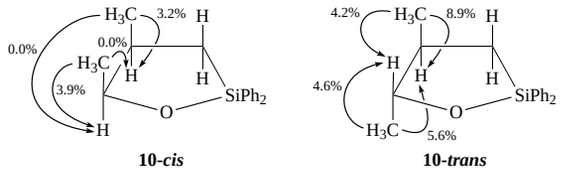
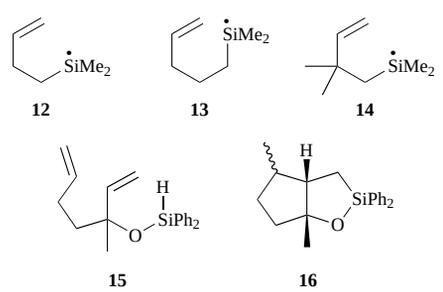


Fig. 1 Nuclear Overhauser enhancements observed in the ^{1}H NMR spectra of the *cis*- and *trans*-isomers of **10**

Similarly, the low yield of cyclised product **10** obtained from the silane **7** with TDT as catalyst is attributed to abstraction of hydrogen by $RS^{\bullet}$ from the allylic C–H groups in **7**, in particular that group adjacent to oxygen,‖ and a greatly improved yield was obtained by using a silanethiol as catalyst (entries 8–10). The *cis*- and *trans*-isomers of **10** were separated by HPLC and identified by NOE studies on the basis of the enhancements shown in Fig. 1; the *cis*:*trans* ratio was 67:33 using Ph_3SiSH and 77:23 using Pr^i_3SiSH. With both thiols, the (presumably) less stable *cis*-product predominates, probably because steric interaction between the thiol and the methyl group β to the radical centre is the most important factor determining the energies of the two diastereoisomeric transition states for hydrogen-atom transfer.**

The preference for *endo-trig* cyclisation of silyl radicals bearing alkenyl side chains has been reported and discussed previously.[18–20] For example, all of the radicals **12**–**14** cyclise in



an *endo* fashion[18,19] to give the thermodynamically more stable product and there appears to be no example of a silyl-radical cyclisation that occurs preferentially in the contra-thermodynamic *exo* mode. The corresponding unsaturated germanium-centred radicals behave similarly.[21] In contrast, cyclisation of the carbon-centred analogues takes place preferentially in an

§ The half-life of TBHN is *ca.* 55 min at 60 °C and *ca.* 29 min at 65 °C.[15a]

¶ This is the isomeric mixture of thiols *tert*-$C_{12}H_{25}SH$ as obtained from the Aldrich Chemical Company.

‖ Cyclisation of the allyloxysilane **5**, under the conditions specified for entry 1, was completely inhibited in the presence of 10 mol% allyloxytrimethylsilane or allyl butyl ether.

** The *cis*:*trans* product ratio probably does not reflect *quantitatively* the selectivity of hydrogen-atom transfer from the silanethiol, because it is likely that this process is reversible to some extent under the reaction conditions (see later where reversibility is proven for the formation of **26** and **27**, when the relevant secondary C–H group is also activated by an adjacent oxygen atom).

Table 1 Thiol-catalysed cyclisation of allyloxysilanes to give tetrahydro-2-silafurans

Entry	Silane[a]	Solvent	T^b/°C	Thiol[c]	Initiator[c,d]	Product	Yield (%) NMR (isolated)
1	**5**	Hexane	60	TDT	TBHN	**8**	95 (88)
2	**5**	Dioxane	60	TDT	TBHN	**8**	94 (89)
3	**5**	Dioxane	80	TDT	AIBN	**8**	10
4	**5**	Dioxane	80	TDT	DLP	**8**	24
5	**6**	Hexane	60	TDT	TBHN	**9**	47
6	**6**	Dioxane	65	Pr^i_3SiSH	TBHN	**9**	95 (85)
7	**6**	Dioxane	65	Ph_3SiSH	TBHN	**9**	95 (88)
8	**7**	Hexane	65	TDT	TBHN	**10**	25
9	**7**	Dioxane	65	Pr^i_3SiSH	TBHN	**10**	74 (67)
10	**7**	Dioxane	65	Ph_3SiSH	TBHN	**10**	75 (70)

[a] Concentration *ca.* 0.3 mol dm^{-3}. [b] The total reaction time was 3 h. [c] Added in two equal portions; 2.5 mol% initially and a further 2.5 mol% after 1 h. [d] AIBN = azoisobutyronitrile; DLP = dilauroyl peroxide (didodecanoyl peroxide).

Table 2 Thiol-catalysed cyclisation of homoallyloxysilanes at 65 °C in the presence of TBHN initiator[a]

Entry	Silane[b]	Solvent	Thiol[a]	Products (ratio[c])	Total yield (%) NMR (isolated)
1	**17**	Hexane	TDT	**22** + **24** (72:28)	95 (87)
2	**18**	Hexane	TDT	**23** + **25** (82:18)	90
3	**19**	Dioxane	TDT	**26** + **27** (16:84)	75 (68)
4	**19**	Dioxane	MeO_2CCH_2SH	**26** + **27** (14:86)	71 (63)
5	**19**	Dioxane	Pr^i_3SiSH	**26** + **27** (26:74)[d]	90 (83)
6	**19**	Dioxane	Ph_3SiSH	**26** + **27** (42:58)[d]	93 (85)
7	**20**	Hexane	TDT	**28** + **29** (79:21)	51 (46)
8	**20**	Dioxane	MeO_2CCH_2SH	**28** + **29** (69:31)	74 (70)
9	**20**	Dioxane	Pr^i_3SiSH	**28** + **29** (70:30)	95 (90)
10	**20**	Dioxane	Ph_3SiSH	**28** + **29** (72:28)	95 (85)
11	**21**	Dioxane	Pr^i_3SiSH	**33**	90 (82)

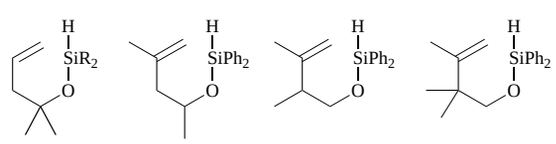
[a] The initiator and the thiol were each added in two equal portions: 2.5 mol% initially and a further 2.5 mol% after 1 h. The total reaction time was 3 h. [b] Concentration was *ca.* 0.3 mol dm^{-3}. [c] Determined by ^{1}H NMR spectroscopy. [d] Control experiments showed that the *trans*-isomer **27** is converted partially to the *cis*-isomer **26** under the reaction conditions (see text).

exo fashion to yield the less stable product radicals, as a result of the interplay of stereoelectronic demands and ring-strain effects.[22,23]

Attempted thiol-catalysed tandem cyclisation of the silane **15** at 60 °C was unsuccessful; the expected bicyclic product **16** could not be identified with certainty (yield ≤5%) and almost all the starting material was recovered unchanged. EPR experiments (see later) show that the silyl radical derived from **15** does indeed undergo rapid sequential cyclisation and the low yield of **16** evidently arises because addition of thiyl radicals to the C=C bonds of **15** is rendered effectively irreversible by rapid 5-*exo* cyclisation of the carbon-centred adduct radicals, resulting in removal of the thiol catalyst from the system. A similar problem appears to account for the failure of the intermolecular thiol-catalysed hydrosilylation of dimethyl diallylmalonate with Et_3SiH, whilst the corresponding reaction of dimethyl allylmalonate gives the silane adduct in good yield.[6] Ready reversibility[24] of the addition of thiyl radicals to C=C groups is clearly of crucial importance for the success of thiol-catalysed inter- or intra-molecular hydrosilylation reactions.

Homoallyloxysilanes

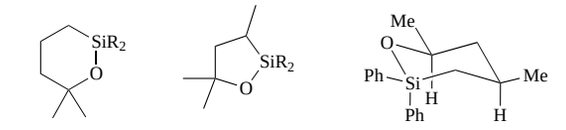
Thiol-catalysed radical-chain cyclisation of the homoallyloxysilanes **17**–**21** was investigated under the conditions used for the allyloxysilanes; mixtures of isomeric products were separated by reversed-phase HPLC and the results are summarised in Table 2.†† Cyclisation of either homoallyloxysilane **17** or **18** (entries 1 and 2) gives mainly the six-membered heterocycle **22** or **23**, respectively, in preference to the five-membered ring products **24** and **25**, which are formed by 5-*exo* cyclisation of the intermediate silyl radicals. Previously, when but-3-enyloxy(dimethyl)silane and di-*tert*-butyl peroxide were heated together at 145 °C, the 2-silatetrahydropyran (presumably also formed *via* 6-*endo* cyclisation of the corresponding silyl radical) was isolated in low yield.[18] In contrast, the non-radical cyclisation of similarly-substituted homoallyloxysilanes catalysed by chloroplatinic acid gives mainly the five-membered heterocycles.[10] Analogous carbon-centred radicals of the hex-5-enyl type show a strong kinetic preference for 5-*exo* ring closure and the different behaviour of the silicon-centred species can be rationalised in terms of the greater length of the Si–O and Si–C bonds, as compared with a C–C bond, and the strongly pyramidal configuration at the silicon radical centre.[19] Cyclisation of the unsaturated silyl radicals occurs preferentially in the 6-*endo* mode to give the more stable product radical. However, this preference for intramolecular addition to the unsubstituted end of the double bond is much smaller than would be observed for an analogous intermolecular addition. Clearly the type of stereoelectronic and ring-strain effects responsible for the preferential 5-*exo* cyclisation of hex-5-enyl radicals,[22,23] though not now predominant, are still operative for the cyclisation of the unsaturated silyl radicals.



17 R = Ph **19** **20** **21**
18 R = Me

As expected, because of the steric and radical-stabilising effects of the methyl group on the double bond, cyclisation of **19**–**21** gives only six-membered heterocycles. In common with the cyclisation of allyloxysilanes, silanethiols are more effective catalysts than alkanethiols. Cyclisation of **19** gives mainly the *trans*-dimethyl product **27** (entries 3–6), while **20** gives pre-

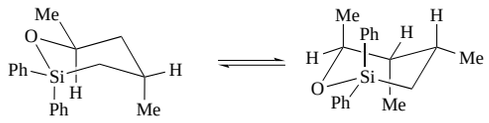
†† The cyclic products **23** and **25** were not isolated and the yields and isomer ratio were determined using ^{1}H NMR spectroscopy.



22 R = Ph
23 R = Me

24 R = Ph
25 R = Me

26



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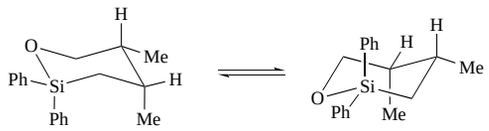
27a **27b**



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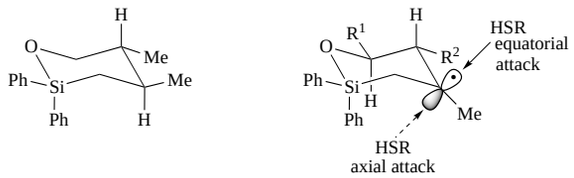
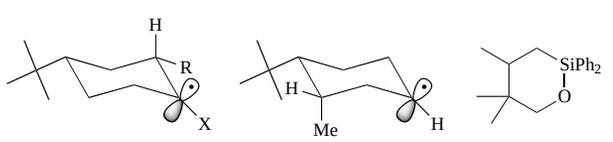
28a **28b**



29 **30**

dominantly the *cis*-product **28** (entries 7–10).‡‡ In both cases, these results imply that hydrogen-atom transfer from the thiol takes place preferentially at the equatorial face of the quasi-planar radical centre in the intermediate 4-oxa-3-silacyclohexyl radical (see structure **30**; R^1 = Me, R^2 = H or R^1 = H, R^2 = Me).[25] The secondary SiOC(Me)–H groups in **26** and **27** should be especially vulnerable to abstraction of hydrogen by electrophilic radicals and the possibility arises that thiol-catalysed radical-chain conversion of the *trans*-isomer **27** to the more stable *cis*-isomer **26** could take place under the reaction conditions. To examine this, the pure *trans*-isomer was heated for a total of 3 h in dioxane at 65 °C in the presence of TBHN and thiol (each 2 × 2.5 mol%) under conditions similar to those used for the cyclisation reactions. With methyl thioglycolate only a trace (*ca.* 2%) of the *cis*-isomer **26** was detected by ^{1}H NMR spectroscopy after reaction, but with triphenylsilanethiol extensive isomerisation took place such that the final ratio **26**:**27** was 79:21. Thus, presumably because silanethiyl radicals are more potent hydrogen-atom abstractors than alkanethiyl radicals,[4] hydrogen transfer from the silanethiol is reversible under the reaction conditions and the isomer ratio **26**:**27** obtained from the cyclisation will not reflect quantitatively the selectivity of hydrogen-atom transfer to **30** from a silanethiol catalyst. However, the less stable *trans*-isomer **27** is still the major product from all the cyclisation reactions.

At 80 °C, hydrogen-atom transfer from $(Me_3Si)_3SiH$ to cyclohexyl radicals of the type **31** [X = $(Me_3Si)_3SiO$, R = H or Me] takes place preferentially at the axial face of the radical centre,[7] as does deuterium-atom transfer from Bu_3SnD to **31** (X = H or Me, R = H).[25,26] Hydroxyl-group transfer (S_H2 reaction at oxygen) from a peroxy acid to **31** (X = H, R = H or Me) takes place with similar stereoselectivity mainly at the axial face.[27] However, corresponding hydroxyl-group transfer to **32** takes place predominantly (75:25) at the equatorial face[27] and the transition state for transfer to the axial face of **32** is evidently destabilised by steric interaction between the reagent and the axial methyl group at C-3.[25,27] The preference for equatorial attack of the thiol on the 4-oxa-3-silacyclohexyl radicals **30** is probably attributable to a similar cause, namely a 1,3-steric interaction between the incoming thiol and the axial phenyl group attached to silicon.

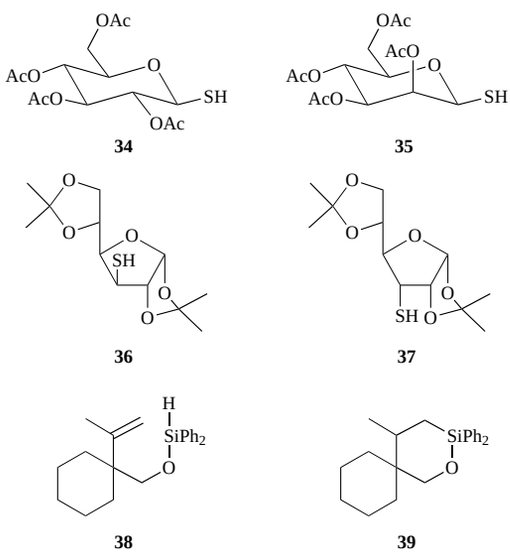


31 **32** **33**

‡‡ The ^{1}H NMR spectra of **27** and **28** are as expected if the two energetically-similar chair conformations **a** and **b** are exchanging rapidly on the NMR timescale at ambient temperature.

Enantioselective hydrogen-atom transfer

Cyclisation of the homoallyloxysilane **21** catalysed by Pr^i_3SiSH gave the racemic product **33** in excellent yield (Table 2, entry 11). The chiral centre in **33** is created in the hydrogen-atom transfer step and this process should become enantioselective if the thiol is optically active.[8] The cyclisation of **21** was repeated using the homochiral thiols **34**–**37** as catalysts, under the conditions specified in Table 2, and the enantiomeric excess (ee) of the product was determined by chiral-stationary-phase HPLC analysis. However, the ee of **33** was small (≤5%) for all four thiol catalysts. Guindon *et al.*[28] have shown that diastereoselectivity in atom-transfer reactions can be enhanced if a geminal pair of substituents β to an acyclic radical centre are replaced by an equivalent ring system (termed the 'cycle effect'),[28] presumably because of conformational restrictions imposed on the transition state, and hence the cyclisation of the homoallyloxysilane **38** was investigated. However, the ee of the product **39** was still small (*ca.* 5%) with the thiols **34**–**37** as catalysts. Assuming that **33** and **39** are configurationally stable under the reaction conditions, the small enantiomeric excesses observed imply that the steric and electronic chirality[29] in the vicinity of the radical centre does not result in sufficient face selectivity in the reaction with the thiol.



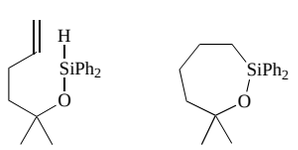
34 **35**

36 **37**

38 **39**

Pent-4-enyloxysilanes

Radical-chain cyclisation of the higher homologue **40** under the usual conditions (65 °C, 3 h, 2 × 2.5 mol% TBHN initiator, 2 × 2.5 mol% thiol) gave excellent yields (≥95%) of the seven-



40 **41**

Table 3 EPR parameters for cyclic radicals **42**–**49** in cyclopropane solvent

Radical	*T*/°C	*g*-Factor	Hyperfine splittings[a]/G
42	−58	2.0027	21.3 ($1H_\alpha$), 34.2 ($2H_\beta$), 1.26 ($6H_\gamma$)
43	−58	2.0027	22.4 ($3H_\beta$), 35.0 ($2H_\beta$), 0.80 ($6H_\gamma$)
44[b]	−58	2.0026	15.2 (1H), 14.6 (1H), 12.1 (1H)
45	−85	2.0027	21.8 ($2H_\alpha$), 20.8 ($1H_\beta$), 1.05 ($3H_\gamma$)
46	−111	2.0027	20.3 ($1H_\alpha$), 30.6 ($1H^2_{\beta ax}$), 4.10 ($1H^2_{\beta eq}$), 18.4 ($1H^1_{\beta ax}$), 5.08 ($1H^1_{\beta eq}$)
46[c]	−83	—	20.4 ($1H_\alpha$), 17.5 (<$2H^2_\beta$>), 11.9 (<$2H^1_\beta$>)
47	−122	2.0028	20.5 ($1H_\alpha$), 31.3 ($1H^2_{\beta ax}$), 3.60 ($1H^2_{\beta eq}$), 18.5 ($1H^1_{\beta ax}$), 5.00 ($1H^1_{\beta eq}$)
47[d]	−53	—	20.6 ($1H_\alpha$), 18.0 (<$2H^2_\beta$>), 12.2 (<$2H^1_\beta$>)
48[c]	−83	2.0026	20.8 ($2H_\alpha$), 14.5 ($1H_\beta$)[e]
49[d]	−53	2.0026	20.5 ($2H_\alpha$), 15.6 ($1H_\beta$), *ca.* 0.6 ($1H_\gamma$)

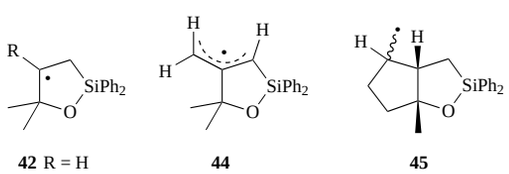
[a] Numbers of nuclei coupling shown in parentheses. [b] Tentative assignment of secondary-product radical detected alongside **43**. [c] Concentration ratio **[46]**:**[48]** = *ca.* 80:20. [d] Concentration ratio **[47]**:**[49]** = *ca.* 90:10. [e] γ-Proton splittings not resolved.

membered heterocycle **41** with either TDT or Ph_3SiSH as catalyst: no six-membered ring isomer was detectable by NMR spectroscopy. The intermediate silyl radical evidently undergoes 7-*endo* cyclisation rapidly and with high regioselectivity.

EPR studies

EPR spectra were recorded during continuous UV irradiation of cyclopropane solutions containing di-*tert*-butyl peroxide (DTBP) (*ca.* 20% v/v) and an alkenyloxysilane (*ca.* 15% v/v), while the sample was in the microwave cavity of the spectrometer, as described previously.[30] Photolysis of the DTBP yields *tert*-butoxyl radicals which go on to abstract hydrogen rapidly from the silane to give ultimately the radicals detected in steady-state concentration by EPR spectroscopy: experiments were usually carried out at in the temperature range −40 to −110 °C. Hydrogen-atom abstraction by *tert*-butoxyl radicals would be expected to be more exothermic and less selective than the corresponding reactions of thiyl radicals. When the alkenyloxysilane contains C–H groups attached to oxygen, especially when these are also allylic, hydrogen-atom abstraction by $Bu^tO^\bullet$ appeared to take place from these groups as well as from the Si–H group, resulting in complex EPR spectra that proved difficult to interpret.

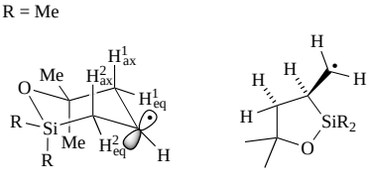
The alkenyloxysilanes **5** and **6** afforded EPR spectra of the radical products of 5-*endo* cyclisation **42** and **43**, respectively;



42 R = H
43 R = Me

44

45



46 R = Ph
47 R = Me

48 R = Ph
49 R = Me

the spectrum of the former is shown in Fig. 2(*a*) and the spectroscopic parameters for all the radicals are collected in Table 3. The central components of the β-proton triplet for **42** are relatively broad as a result of unresolved second-order splittings, an effect reproduced in the computer-simulated spectrum [Fig. 2(*b*)]; second-order splittings were resolved in the spectrum of **43**. The proton hyperfine coupling constants are in accord with the assignments and no spectra attributable to the uncyclised silyl radicals could be detected, although these spectra would be complex and therefore difficult to observe. However, the detection of strong spectra from the cyclised radicals implies that the rate constants for cyclisation are $\geqslant 10^3$ s^{-1} at *ca.* −100 °C.[31] If a reasonable Arrhenius *A*-factor of $10^{10.4}$ s^{-1} (that for cyclisation

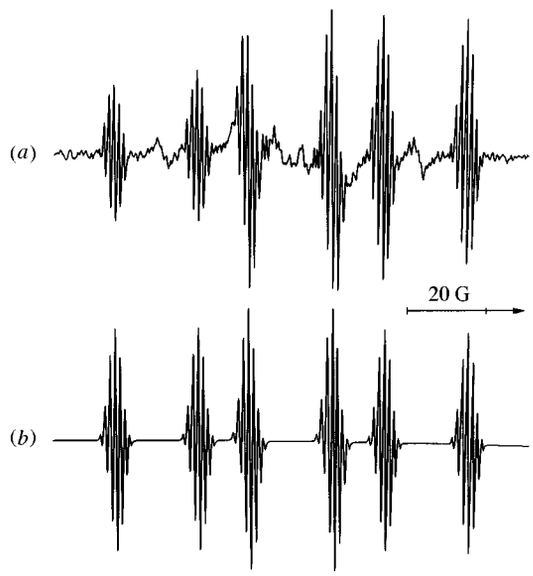


Fig. 2 (*a*) EPR spectrum of the radical **42** in cyclopropane at −58 °C. (*b*) Computer simulation of the spectrum based on the parameters given in Table 3 and including second-order effects.

of the hex-5-enyl radical[32]) is assumed, the rate constant extrapolated to 60 °C would be $\geqslant 10^6$ s^{-1}. The spectrum of a secondary-product radical, which increases in intensity with the duration of UV irradiation, was apparent alongside the spectrum of **43** and is tentatively ascribed to the allylic radical **44**.

The EPR spectrum obtained from the silane **15** is as expected for the tandem-cyclisation product **45**; a *cis* ring junction is assumed. Although the isomeric composition of **45** could not be determined, the $\dot{C}H_2$ group is expected[23] to be mainly *cis* to the silicon-containing ring.

From the homoallyloxysilanes **17** and **18**, the products of both 6-*endo* cyclisation (**46** and **47**, respectively) and of 5-*exo* cyclisation (**48** and **49**, respectively) were detected (see Fig. 3).§§ For both silanes, the 6-*endo* product predominated and the steady-state concentration ratios **[46]**:**[48]** and **[47]**:**[49]** were *ca.* 80:20 (at −83 °C) and 90:10 (at −53 °C) respectively. These ratios parallel those of the final-product silanes at +65 °C (see above) and their magnitudes are as expected if the regioselectivity of ring closure is determined principally by a difference in the activation energies of the competing processes.[20] In the chair conformations of **46** and **47** the pairs of axial and equatorial protons H^1 and H^2 are instantaneously nonequivalent, but are evidently exchanging on the EPR timescale, as a result of chair–chair inversion of the ring, giving rise to pronounced selective line broadening. Only the eight lines

§§ The EPR spectra of **42**, **43** and **45**–**49** are not centrosymmetric (see Figs. 2 and 3) and show emission/enhanced absorption (E/A) chemically-induced dynamic electron polarisation (CIDEP) effects.[33]

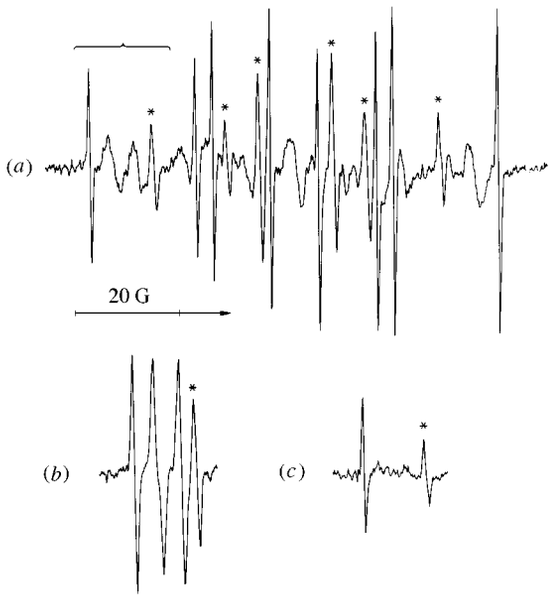


Fig. 3 (*a*) EPR spectra of the radicals **46** and **48**, formed by cyclisation of the silyl radical derived from **17**, in cyclopropane at −85 °C; the lines from **48** are indicated with asterisks. The spectrum of **46** shows pronounced selective line-broadening and both spectra exhibit E/A polarisation (see text), the effects of which are reduced to some extent as a result of sample depletion during the scan. The bracketed low-field wing region of (*a*) is shown recorded at −113 °C in (*b*) and at −69 °C in (*c*).

for which $m_I(H^1_{ax}) = m_I(H^1_{eq})$ and $m_I(H^2_{ax}) = m_I(H^2_{eq})$ remain sharp at all temperatures and the other lines are so broadened as to be barely detectable above −75 °C [see Fig. 3(*c*)]; the fast-exchange spectra were not observed because the radicals could not be detected at sufficiently high temperatures. Below −100 °C, the splittings from the individual axial and equatorial β-protons could be measured [see Fig. 3(*b*) and Table 3]. Although a detailed lineshape analysis[30c] was not carried out, computer simulation of the spectrum of **46** obtained at −85 °C indicated that the rate constant for chair–chair interconversion is *ca.* 4×10^7 s^{-1} at this temperature, about 3–4 times larger than the corresponding rate constant for inversion of the cyclohexyl radical.[30c] The assignments of the β-proton splittings are supported by semi-empirical UHF molecular orbital calculations at the AM1 level,[34] which predict hyperfine splittings[35] of −21.85 (H_α), 25.50 (H^1_{ax}), 3.04 (H^1_{eq}), 43.28 (H^2_{ax}) and 2.45 (H^2_{eq}) for **47**.¶¶ The magnitude of the β-proton hyperfine splitting for a fragment of the type $H_\beta C_\beta \dot{C}_\alpha$ in an alkyl radical is given by the Heller–McConnell eqn. (10),[36,37] in which θ is the

$$a(H_\beta) = (A + B\cos^2\theta)\rho^\pi_{C\alpha} \qquad (10)$$

dihedral angle between the β-C–H bond and the axis of the C_α-$2p_\pi$ orbital, $\rho^\pi_{C\alpha}$ is the unpaired-electron population in this orbital and A and B are constants, the former of which is small and often neglected. The smaller value of $a(<2H^1>)$ compared to $a(<2H^2>)$ arises because of conformational differences such that ($\cos^2\theta_{1ax} + \cos^2\theta_{1eq}$) is less than ($\cos^2\theta_{2ax} + \cos^2\theta_{2eq}$) and because the value of B appropriate for the $C_\beta H_2Si$ group is larger than that for the $C_\beta H_2C$ group, as a consequence of the lower electronegativity of silicon compared with carbon.[38]

The pent-4-enyloxysilane **40** afforded an EPR spectrum that was generally consistent with that expected for the product of 7-*endo* ring closure of the intermediate silyl radical but, as anticipated, the spectrum was very complex (and therefore weak) and definitive analysis was not possible.

Conclusion

Intramolecular radical-chain hydrosilylation catalysed by thiols provides a potentially useful alternative to transition-metal catalysis for the cyclisation of alkenyloxysilanes. The thiol-catalysed radical process, like its intermolecular analogue[6] and the related thiol-catalysed hydroacylation reactions,[39] has two significant limitations; (i) addition of the thiyl radical to C=C groups must be readily reversible under the reaction conditions and, (ii) the presence of C–H bonds in the substrate which are appreciably weaker than the S–H bond can cause inhibition of the chain process.

Experimental

NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for ^{1}H). The solvent was $CDCl_3$ and chemical shifts are reported relative to Me_4Si; J values are quoted in Hz. Mass spectra were obtained with VG 7070H or VG ZAB-2F instruments using electron impact ionisation. Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F_{254} aluminium-backed precoated plates, respectively. HPLC was carried out on Kromasil C18 (10 μm particle size) for reversed-phase work, Nucleosil (5 μm particle size) for normal-phase work and Chiralcel-OD for the determination of enantiomeric excesses. All manipulations and reactions of air-sensitive compounds were carried out under an atmosphere of dry argon or nitrogen and all extracts were dried over anhydrous $MgSO_4$. Petroleum refers to the fraction of bp 40–60 °C.

Materials

TBHN was prepared by the reaction of sodium hyponitrite with *tert*-butyl bromide in diethyl ether, in the presence of zinc chloride, using the method described by Mendenhall and co-workers.[15b–d]

Triisopropylsilanethiol,[17] the thiols **35**,[40] **36**[41] and **37**[41] were prepared by published methods; other thiols were obtained commercially (Aldrich or Lancaster) and were used without further purification, as was chlorodimethylsilane (Aldrich).

Chlorodiphenylsilane was prepared by a slightly-modified published procedure.[42] A solution of diphenylsilane (24.3 g, 0.13 mol) and chlorotriphenylmethane (36.2 g, 0.13 mol) in dry benzene (120 cm^3) was heated under reflux for 48 h. Most of the benzene was removed by rotary evaporation and the white solid (triphenylmethane) precipitated was removed by filtration. The filtrate was distilled under reduced pressure to give a colourless oil (26.1 g, 92%); bp 90–92 °C/0.5 Torr (lit.,[42] bp 99–101 °C/1 Torr); δ_H 5.74 (1H, s, SiH), 7.34–7.73 (10H, m, Ph).

Preparation of alcohols

2-Methylbut-3-en-2-ol (Aldrich) and 2,3-dimethylbut-3-en-2-ol (Wiley Organics) were obtained commercially and were used without further purification.

2-Methylpent-4-en-2-ol[43a] was prepared from allylmagnesium bromide and acetone, following a published general procedure;[44] bp 26–31 °C/17 Torr (lit.,[43a] bp 115 °C/760 Torr). δ_H 1.22 (6H, s, 2Me), 2.10 (1H, br s, OH), 2.20 (2H, d, J 8.4, 3-H), 4.90 (1H, br s, 5-H), 5.17 (1H, br s, 5-H), 5.85 (1H, m, 4-H). 2-Methylhex-5-en-2-ol[43b] was prepared in a similar way from methylmagnesium iodide and hex-5-en-2-one; bp 52–54 °C/12 Torr (lit.,[43b] bp 58–59 °C/17 Torr); δ_H 1.21 (6H, s,

¶¶ A chair conformation is predicted for **47** ($\Delta H^o_f = -380.8$ kJ mol^{-1}) in which the geometry at the radical centre is almost exactly planar: the calculated dihedral angles between the β-C–H bonds and the axis of the C_α-$2p_\pi$ orbital (taken to be perpendicular to the $C_\beta C_\alpha C_\beta$ plane) are 37.8° (H^1_{ax}), 80.3° (H^1_{eq}), 27.0° (H^2_{ax}) and 89.0° (H^2_{eq}). If H_α is constrained to be 15° out of the $C_\beta C_\alpha C_\beta$ plane in the axial direction, the otherwise-optimised structure is less stable by only 2.9 kJ mol^{-1} and the predicted coupling constants become −20.7 (H_α), 17.67 (H^1_{ax}), 4.38 (H^1_{eq}), 35.53 (H^2_{ax}) and 3.16 (H^2_{eq}), closer to the experimental values.

2Me), 1.56 (2H, m, 3-H), 1.70 (1H, br s, OH), 2.12 (2H, m, 4-H), 5.00 (2H, m, 6-H), 5.84 (1H, m, 5-H).

The following alcohols were prepared by methods described in the literature.

3-Methylbut-3-en-2-ol:[45] bp 115–117 °C (lit.,[45] bp 113–114 °C); δ_H 1.28 (3H, d, *J* 6.5, 1-H), 1.58 (1H, s, OH), 1.75 (3H, br s, 3-Me), 4.25 (1H, q, *J* 6.5, 2-H), 4.80 (1H, m, 4-H), 4.96 (1H, m, 4-H).

4-Methylpent-4-en-2-ol:[44] bp 126–129 °C; δ_H 1.21 (3H, d, *J* 6.1, 1-H), 1.74 (1H, s, OH), 1.76 (3H, br s, 4-Me), 2.15 (2H, m, CH_2), 3.94 (1H, m, 2-H), 4.80 (1H, m, 5-H), 4.88 (1H, m, 5-H).

2,3-Dimethylbut-3-en-1-ol:[46] bp 130–133 °C (lit.,[46] bp 132–133 °C); δ_H 1.02 (3H, d, *J* 7.0, 2-Me), 1.50 (1H, s, OH), 1.72 (3H, s, 3-Me), 2.38 (1H, m, 2-H), 3.50 (2H, d, *J* 6.9, CH_2), 4.81 (1H, m, 4-H), 4.88 (1H, m, 4-H).

2,2,3-Trimethylbut-3-ene-1-ol[47] was prepared as described in the literature, except that the required 2,2,3-trimethylbutane-1,3-diol was obtained by treatment of 4-hydroxy-3,3-dimethylbutan-2-one[48] with methylmagnesium iodide; bp 93–95 °C/100 Torr (lit.,[47] bp 65–67 °C/35 Torr); δ_H 1.06 (6H, s, 2-Me), 1.48 (1H, br s, OH), 1.74 (3H, br s, 3-Me), 3.39 (2H, br s, CH_2), 4.83 (1H, br s, 4-H), 4.93 (1H, br s, 4-H); δ_C 19.5, 23.8, 41.2, 69.7, 111.9, 149.5.

1-(Hydroxymethyl)-1-isopropenylcyclohexane was prepared by a procedure similar to that used for 2,2,3-trimethylbut-3-en-1-ol, starting from cyclohexyl methyl ketone; bp 104 °C/8 Torr; δ_H 1.29–1.79 (10H, m, 5 × CH_2), 1.72 (3H, br s, Me), 3.31 (2H, d, *J* 6.4, CH_2), 4.90 (1H, br s, 4-H), 5.15 (1H, br s, 4-H); δ_C 19.5, 22.1, 26.5, 31.7, 45.1, 68.0, 114.8, 133.1; *m*/*z* 154 (M^+, 1%), 123 (41), 81 (100) (Found: C, 77.6; H, 11.8. $C_{10}H_{18}O$ requires C, 77.9; H, 11.8%).

3-Methylhepta-1,6-dien-3-ol was prepared from vinylmagnesium bromide and hex-5-en-2-one following a general procedure,[44] as a colourless oil; bp 69–71 °C/26 Torr; δ_H 1.27 (3H, s, Me), 1.57 (1H, s, OH), 1.62 (2H, m, 4-H), 2.09 (2H, m, 5-H), 4.95 (2H, m, 7-H), 5.04 (1H, dd, *J* 10.7 and 1.3, 1-H), 5.19 (1H, dd, *J* 17.3 and 1.3, 1-H), 5.81 (1H, m, 6-H), 5.88 (1H, dd, *J* 17.3 and 10.7, 2-H); δ_C 27.9, 28.4, 41.1, 73.2, 111.8, 114.5, 138.8, 144.9; *m*/*z* 126 (M^+, 2%), 71 (100), 55 (28) (Found: C, 76.4; H, 11.5. $C_8H_{14}O$ requires C, 76.1; H, 11.2%).

Preparation of alkenyloxysilanes

A solution of the alcohol (20 mmol), triethylamine (3.1 cm^3, 22 mmol) and 4-(dimethylamino)pyridine (0.09 g, *ca.* 4 mol%) in dry diethyl ether (50 cm^3) was cooled in an ice–water bath and stirred mechanically during dropwise addition of chlorodiphenylsilane or chlorodimethylsilane (20 mmol). Voluminous amounts of triethylamine hydrochloride were precipitated. The mixture was stirred for 0.5 h after the addition was complete, the cooling bath was removed, and stirring was continued for 5 h at room temperature. The precipitate was removed by filtration, the solvent was removed from the filtrate using a rotary evaporator and the residue was distilled under reduced pressure to yield the product as an oil. The yields ranged from 40 to 90% and the characteristics of the products are given below.

Diphenyl(2-methylbut-3-en-2-yloxy)silane 5. Bp 92–95 °C/0.05 Torr; δ_H 1.42 (6H, s, Me_2C), 5.01 (1H, dd, *J* 10.6 and 1.3, 4-H), 5.23 (1H, dd, *J* 17.3 and 1.3, 4-H), 5.56 (1H, s, SiH), 6.00 (1H, dd, *J* 17.3 and 10.6, 3-H), 7.36–7.66 (10H, m, Ph); δ_C 29.7, 75.2, 111.5, 127.9, 130.0, 134.6, 135.9, 145.5; *m*/*z* 268 (M^+, 30%), 253 (30), 199 (73), 183 (100) (Found: C, 75.9; H, 7.4. $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5%).

Diphenyl(2,3-dimethylbut-3-en-2-yloxy)silane 6. Bp 93–95 °C/0.05 Torr; δ_H 1.45 (6H, s, Me_2C), 1.83 (3H, s, 3-Me), 4.80 (1H, s, 4-H), 5.04 (1H, s, 4-H), 5.55 (1H, s, SiH), 7.38–7.66 (10H, m, Ph); δ_C 19.1, 29.1, 77.1, 109.3, 127.8, 129.9, 134.5, 135.9, 150.9; *m*/*z* 282 (M^+, 12%), 267 (14), 199 (100), 183 (81) (Found: C, 76.6; H, 7.9. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

Diphenyl(3-methylbut-3-en-2-yloxy)silane 7. Bp 93–96 °C/0.05 Torr; δ_H 1.32 (3H, d, *J* 6.4, *Me*CH), 1.74 (3H, s, 3-Me), 4.38 (1H, q, *J* 6.4, 2-H), 4.79 (1H, m, 4-H), 4.94 (1H, m, 4-H), 5.44 (1H, s, SiH), 7.36–7.67 (10H, m, Ph); δ_C 17.7, 22.6, 74.3, 110.3, 128.0, 130.3, 134.4, 134.7, 147.7; *m*/*z* 268 (M^+, 11%), 199 (100), 183 (86) (Found: C, 75.8; H, 7.4. $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5%).

Diphenyl(3-methylhepta-1,6-dien-3-yloxy)silane 15. Bp 119–121 °C/0.05 Torr; δ_H 1.39 (3H, s, Me), 1.70 (2H, m, 4-H), 2.14 (2H, m, 5-H), 4.94 (2H, m, 7-H), 5.06 (1H, dd, *J* 10.7 and 1.4, 1-H), 5.25 (1H, dd, *J* 17.3 and 1.4, 1-H), 5.56 (1H, s, SiH), 5.78 (1H, m, 6-H), 5.89 (1H, dd, *J* 17.3 and 10.7, 2-H), 7.35–7.65 (10H, m, Ph); δ_C 27.2, 28.4, 42.0, 77.2, 112.8, 114.1, 127.8, 129.9, 134.5, 135.8, 138.8, 144.0; *m*/*z* 308 (M^+, 1%), 253 (91), 183 (100) (Found: C, 78.2; H, 7.7. $C_{20}H_{24}OSi$ requires 77.9; H, 7.8%).

Diphenyl(2-methylpent-4-en-2-yloxy)silane 17. Bp 100–104 °C/0.05 Torr; δ_H 1.31 (6H, s, Me_2C), 2.36 (2H, d, *J* 7.3, CH_2), 5.08 (2H, m, 5-H), 5.60 (1H, s, SiH), 5.94 (1H, m, 4-H), 7.36–7.66 (10H, m, Ph); δ_C 29.3, 49.0, 75.3, 117.5, 127.9, 130.0, 134.5, 134.9, 136.0; *m*/*z* 282 (M^+, 30%), 241 (81), 183 (100) (Found: C, 76.5; H, 7.9. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

Dimethyl(2-methylpent-4-en-2-yloxy)silane 18. Bp 46 °C/78 Torr; δ_H 0.18 (6H, d, *J* 2.8, Me_2Si), 1.24 (6H, s, Me_2C), 2.25 (2H, d, *J* 7.3, CH_2), 4.76 (1H, m, SiH), 5.05 (2H, m, 4-H), 5.88 (1H, m, 4-H); δ_C 0.8, 29.1, 48.8, 74.1, 117.2, 135.1; *m*/*z* 158 (M^+, 1%), 117 (70), 75 (100) (Found: C, 60.5; H, 11.6. $C_8H_{18}OSi$ requires C, 60.7; H, 11.5%).

Diphenyl(4-methylpent-4-en-2-yloxy)silane 19. Bp 98–100 °C/0.05 Torr; δ_H 1.22 (3H, d, *J* 6.1, *Me*CH), 1.67 (3H, s, 4-Me), 2.16 (1H, dd, *J* 13.1 and 6.8, 3-H), 2.36 (1H, dd, *J* 13.1 and 6.1, 3-H), 4.15 (1H, m, 2-H), 4.76 (2H, m, 5-H), 5.47 (1H, s, SiH), 7.35–7.67 (10H, m, Ph); δ_C 22.8, 23.1, 47.8, 69.3, 113.0, 127.9, 130.2, 134.6, 134.7, 142.7; *m*/*z* 282 (M^+, 5%), 227 (77), 183 (100) (Found: C, 76.3; H, 7.7. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

Diphenyl(2,3-dimethylbut-3-en-1-yloxy)silane 20. Bp 100–104 °C/0.05 Torr; δ_H 1.07 (3H, d, *J* 6.9, 2-Me), 1.70 (3H, br s, 3-Me), 2.45 (1H, m, 2-H), 3.64 (1H, dd, *J* 10.0 and 7.1, 1-H), 3.79 (1H, dd, *J* 10.0 and 6.4, 1-H), 4.76 (1H, d, *J* 1.2, 4-H), 4.80 (1H, d, *J* 1.2, 4-H), 5.44 (1H, s, SiH), 7.38–7.68 (10H, m, Ph); δ_C 16.1, 20.4, 43.1, 68.4, 110.7, 128.0, 130.3, 134.7, 135.0, 147.3; *m*/*z* 282 (M^+, 7%), 199 (35), 183 (100) (Found: C, 76.6; H, 7.8. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

Diphenyl(2,2,3-trimethylbut-3-en-1-yloxy)silane 21. Bp 116–118 °C/0.05 Torr; δ_H 1.09 (6H, s, 2-Me), 1.74 (3H, s, 3-Me), 3.61 (2H, s, 1-H), 4.81 (2H, m, 4-H), 5.41 (1H, s, SiH), 7.39–7.64 (10H, m, Ph); δ_C 19.9, 24.0, 41.1, 72.2, 110.4, 127.9, 130.2, 134.2, 134.7, 150.4; *m*/*z* 296 (M^+, 1%), 213 (50), 183 (100) (Found: C, 76.9; H, 8.1. $C_{19}H_{24}OSi$ requires C, 77.0; H, 8.2%).

Diphenyl[(1-isopropenylcyclohexyl)methoxy]silane 38. Bp 158 °C/0.03 Torr; δ_H 1.70 (3H, s, Me), 1.78–1.42 (10H, m, 5 × CH_2), 3.55 (2H, s, OCH_2), 4.89 (1H, br s, C=CH), 5.04 (1H, br s, C=CH), 5.39 (1H, s, SiH), 7.38–7.65 (10H, m, Ph); δ_C 20.2, 22.2, 26.4, 31.3, 44.7, 71.6, 113.6, 127.9, 130.2, 134.3, 134.7, 152.3; *m*/*z* 336 (M^+, 1%), 123 (95), 81 (100) (Found: C, 78.2; H, 8.1. $C_{22}H_{28}OSi$ requires C, 78.5; H, 8.4%).

Diphenyl(2-methylhex-5-en-2-yloxy)silane 40. Bp 108–110 °C/0.05 Torr; δ_H 1.30 (6H, s, Me_2C), 1.63 (2H, m, 3-H), 2.16 (2H, m, 4-H), 4.95 (2H, m, 6-H), 5.55 (1H, s, SiH), 5.82 (1H, m, 5-H), 7.34–7.62 (10H, m, Ph); δ_C 28.8, 29.5, 43.5, 75.4, 114.1, 127.9, 130.0, 134.6, 136.1, 139.2; *m*/*z* 296 (M^+, 1%), 241 (49), 183 (100) (Found: C, 77.1; H, 8.1. $C_{19}H_{24}OSi$ requires C, 77.0; H, 8.2%).

Typical procedure for radical-chain cyclisation

Diphenyl(2-methylbut-3-en-2-yloxy)silane **5** (0.30 g, 1.1 mmol) and hexane (4 cm^3) were introduced into a dry, argon-filled 25 cm^3 two-necked conical flask containing a magnetic stirrer bar and fitted with a condenser, with argon flowing slowly downwards through it. *tert*-Dodecanethiol (TDT, 6.5 μl, 2.5 mol%, based on **5**) and TBHN (4.8 mg, 2.5 mol%, based on **5**) were added to the mixture through the side arm, which was then

closed with a stopper, and the flask was immersed in an oil bath pre-heated to 60 °C. The mixture was stirred under argon for 1 h and further amounts of TDT (2.5 mol%) and TBHN (2.5 mol%) were then added, before stirring was continued for a further 2 h. The reaction mixture was allowed to cool to room temperature, the solvent was removed using a rotary evaporator and the residue was purified by chromatography on silica gel, using petroleum–diethyl ether (98:2) as eluent, to give 2,2-diphenyl-5,5-dimethyl-1-oxa-2-silacyclopentane **8** (0.97 mmol, 88%) as a clear oil; δ_H 1.34 (2H, t, *J* 7.7, 3-H), 1.39 (6H, s, Me_2C), 1.97 (2H, t, *J* 7.7, 4-H), 7.37–7.64 (10H, m, Ph); δ_C 9.9, 29.8, 38.0, 80.7, 127.8, 129.9, 134.5, 135.4; *m*/*z* 268 (M^+, 22%), 253 (100), 199 (44) (Found: C, 76.3; H, 7.4. $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5%).

Other cyclisation reactions were carried out in a similar way and the characteristics of the products are given below; all were oils and the yields are given in Tables 1 and 2.

2,2-Diphenyl-4,5,5-trimethyl-1-oxa-2-silacyclopentane 9. δ_H 1.10 (3H, d, *J* 6.9, 4-Me), 1.11 (1H, dd, *J* 14.8 and 12.7, 3-H), 1.17 (3H, s, 5-Me), 1.39 (1H, dd, *J* 14.8 and 6.5, 3-H), 1.44 (3H, s, 5-Me), 2.14 (1H, m, 4-H), 7.36–7.65 (10H, m, Ph); δ_C 18.8, 23.7, 29.3, 43.3, 82.8, 127.8, 129.9, 134.5, 134.6, 135.4, 135.7; *m*/*z* 282 (M^+, 8%), 239 (100), 105 (86) (Found: C, 76.3; H, 7.7. $C_{18}H_{22}Osi$ requires C, 76.5; H, 7.9%).

***cis*-2,2-Diphenyl-4,5-dimethyl-1-oxa-2-silacyclopentane 10-*cis*.** This compound (t_r 4.2 min) and its *trans* isomer (t_r 7.1 min) were isolated by HPLC on the reversed-phase column using methanol–water (75:25) as eluent; δ_H 1.03 (3H, d, *J* 6.9, 4-Me), 1.06 (1H, dd, *J* 14.8 and 9.6, 3-H), 1.20 (3H, d, *J* 6.5, 5-Me), 1.40 (1H, dd, *J* 14.8 and 6.8, 3-H), 2.46 (1H, m, 4-H), 4.42 (1H, qd, *J* 6.5 and 6.2, 5-H), 7.34–7.66 (10H, m, Ph); δ_C 17.4, 17.5, 18.1, 36.8, 78.1, 127.8, 130.0, 134.4, 134.5, 135.3, 135.6 (Found: C, 76.4; H, 7.4. $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5%).

***trans*-2,2-Diphenyl-4,5-dimethyl-1-oxa-2-silacyclopentane 10-*trans*.** δ_H 1.01 (1H, dd, *J* 14.8 and 11.9, 3-H), 1.12 (3H, d, *J* 6.5, 4-Me), 1.39 (3H, d, *J* 6.0, 5-Me), 1.48 (1 H, dd, *J* 14.8 and 6.5, 3-H), 1.90 (1H, m, 4-H), 3.77 (1H, m, 5-H), 7.36–7.64 (10H, m, Ph); δ_C 19.8, 20.5, 21.5, 41.2, 81.4, 127.8, 127.9, 130.0, 130.1, 134.5, 134.6, 135.1, 135.2 (Found: C, 76.4; H, 7.4. $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5%).

2,2-Diphenyl-6,6-dimethyl-1-oxa-2-silacyclohexane 22. This compound (t_r 7.8 min) and the five-membered-ring isomer **24** (t_r 4.5 min) were isolated by normal-phase HPLC, using hexane as eluent; δ_H 1.16 (2H, t, *J* 6.9, 3-H), 1.32 (6H, s, 6-Me), 1.67 (2H, m, 4-H), 1.94 (2H, m, 5-H), 7.31–7.62 (10H, m, Ph); δ_C 10.5, 18.0, 30.8, 41.2, 74.4, 127.7, 129.5, 134.2, 137.5; *m*/*z* 282 (M^+, 20%), 267 (100), 199 (62) (Found: C, 76.5; H, 7.8. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

2,2-Dimethyl-6,6-dimethyl-1-oxa-2-silacyclohexane 23. δ_H 0.13 (6H, s, 2-Me), 0.58 (2H, t, *J* 6.9, 3-H), 1.24 (6H, s, 6-Me), 1.50 (2H, m, 4-H), 1.81 (2H, m, 5-H); δ_C 1.4, 12.7, 17.8, 30.7, 41.0, 73.3.

2,2-Diphenyl-3,5,5-trimethyl-1-oxa-2-silacyclopentane 24. δ_H 1.08 (3H, d, *J* 7.2, 3-Me), 1.32 (3H, s, 5-Me), 1.52 (3H, s, 5-Me), 1.62 (1H, apparent t, *J* 12.7, 4-H), 1.92 (1H, m, 3-H), 2.16 (1H, dd, *J* 12.7 and 7.7, 4-H), 7.39–7.67 (10H, m, Ph); δ_C 14.6, 18.0, 29.4, 31.2, 47.9, 79.7, 127.7, 127.9, 129.8, 130.0, 133.4, 134.5, 134.9, 135.2; *m*/*z* 282 (M^+, 18%), 240 (100), 199 (54) (Found: C, 76.5; H, 7.9. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

2,2-Dimethyl-3,5,5-trimethyl-1-oxa-2-silacyclopentane 25. δ_H 0.08 (3H, s, 2-Me), 0.21 (3H, s, 2-Me), 1.05 (3H, d, *J* 7.0, 3-Me), 1.17 (3H, s, 5-Me), 1.28 (1H, m, 3-H), 1.30 (3H, s, 5-Me), 1.39 (1H, apparent t, *J* 12.0, 4-H), 1.99 (1H, dd, *J* 12.0 and 7.1, 4-H); δ_C 1.4 (2C), 14.1, 18.3, 29.4, 31.5, 47.8, 78.7.

***cis*-2,2-Diphenyl-4,6-dimethyl-1-oxa-2-silacyclohexane 26.** This compound (t_r 10.5 min) and its *trans* isomer **27** (t_r 6.9 min) were isolated by reversed-phase HPLC, using methanol–water (80:20) as eluent; δ_H 0.76 (1H, dd, *J* 14.6 and 12.9, 3-H_{ax}), 1.08 (3H, d, *J* 6.5, 4-Me), 1.21 (1H, ddd, *J* 13.7, 11.6 and 11.2, 5-H_{ax}), 1.31 (1H, dd, *J* 14.6 and 2.2, 3-H_{eq}), 1.32 (3H, d, *J* 6.2, 6-Me), 1.64 (1H, ddd, *J* 13.7, 2.2 and 2.1, 5-H_{eq}), 1.91 (1H, m, 4-H), 4.10 (1H, m, 6-H), 7.32–7.70 (10H, m, Ph); δ_C 19.6, 24.9, 27.1, 29.5, 46.0, 71.1, 127.8, 128.0, 129.7, 129.9, 134.3, 135.2, 135.9; *m*/*z* 282 (M^+, 22%), 225 (48), 204 (100) (Found: C, 76.7; H, 8.0. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

***trans*-2,2-Diphenyl-4,6-dimethyl-1-oxa-2-silacyclohexane 27.** δ_H 0.94 (1H, dd, *J* 14.7 and 8.9, 3-H equatorial **27a**, axial in **27b**), 1.06 (3H, d, *J* 6.8, 4-Me), 1.28 (3H, d, *J* 6.5, 6-Me), 1.38 (1H, dd, *J* 14.7 and 4.9, 3-H axial in **27a**, equatorial in **27b**), 1.63 (2H, apparent t, *J* 5.4, 5-H), 2.29 (1H, m, 4-H), 4.48 (1H, m, 6-H), 7.36–7.65 (10H, m, Ph); δ_H 18.9, 23.8, 24.6, 24.7, 43.0, 68.4, 127.7, 127.8, 129.6, 134.1, 134.2, 137.1; *m*/*z* 282 (M^+, 22%), 225 (57), 204 (100) (Found: C, 76.7; H, 8.0. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

***cis*-2,2-Diphenyl-4,5-dimethyl-1-oxa-2-silacyclohexane 28.** This compound (t_r 10.8 min) and its *trans* isomer **29** (t_r 13.2 min) were isolated by reversed-phase HPLC, using methanol–water (75:25) as eluent; δ_H 1.03 (3H, d, *J* 7.0, 4-Me), 1.05 (3H, d, *J* 7.3, 5-Me), 1.07 (1H, dd, *J* 14.9 and 11.4, 3-H), 1.18 (1H, dd, *J* 14.9 and 4.3, 3-H), 1.74 (1H, m, 4-H), 2.14 (1H, m, 5-H), 3.96 (1H, dd, *J* 11.1 and 3.8, 6-H), 4.05 (1H, dd, *J* 11.1 and 2.6, 6-H), 7.35–7.67 (10H, m, Ph); δ_C 10.7, 15.3, 22.6, 32.5, 37.5, 70.3, 127.9, 128.0, 129.9, 130.0, 134.1, 134.3, 135.2, 135.9 (Found: C, 76.8; H, 7.7. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

***trans*-2,2-Diphenyl-4,5-dimethyl-1-oxa-2-silacyclohexane 29.** δ_H 0.82 (3H, d, *J* 6.2, 4-Me), 0.94 (1H, dd, *J* 14.8 and 12.1, 3-H_{ax}), 1.09 (3H, d, *J* 5.9, 5-Me), 1.32 (1H, dd, *J* 14.8 and 3.0, 3-H_{eq}), 1.57 (2H, m, 4- and 5-H), 3.59 (1H, dd, *J* 11.5 and 10.5, 6-H_{ax}), 4.00 (1H, dd, *J* 11.5 and 3.1, 6-H_{eq}), 7.33–7.69 (10H, m, Ph); δ_C 15.1, 20.1, 24.4, 35.3, 40.9, 71.3, 127.8, 128.0, 129.9, 130.0, 134.1, 134.2, 134.8, 135.6 (Found: C, 76.8; H, 7.7. $C_{18}H_{22}OSi$ requires C, 76.5; H, 7.9%).

2,2-Diphenyl-4,5,5-trimethyl-1-oxa-2-silacyclohexane 33. δ_H 0.83 (3H, s, 5-Me), 1.02 (3H, d, *J* 6.7, 4-Me), 1.04 (3H, s, 5-Me), 1.05 (1H, dd, *J* 15.1 and 13.2, 3-H), 1.18 (1H, dd, *J* 15.1 and 4.1, 3-H), 1.78 (1H, m, 4-H), 3.66 (2H, br s, 6-H), 7.35–7.69 (10H, m, Ph); δ_C 16.5, 17.2, 20.6, 24.8, 36.4, 37.8, 75.9, 127.9, 128.0, 129.9, 130.0, 134.2, 134.4, 134.8, 135.7; *m*/*z* 296 (M^+, 4%), 254 (19), 211 (49), 199 (100), 181 (77) (Found: C, 77.3; H, 8.1. $C_{19}H_{24}OSi$ requires C, 77.0; H, 8.3%).

2-Oxa-3-silaspiro[5.5]undecane 39. δ_H 0.95 (3H, d, *J* 6.9, 5-Me), 1.05 (1H, dd, *J* 15.2 and 8.6, 4-H), 1.30 (1H, dd, *J* 15.2 and 5.1, 4-H), 1.65–1.20 (10H, m, 5 × CH_2), 1.96 (1H, m, 5-H), 3.59 (1H, d, *J* 11.6, 1-H), 4.19 (1H, d, *J* 11.6, 1-H), 7.34–7.61 (10H, m, Ph); δ_C 15.3, 18.6, 21.2, 21.6, 26.4, 27.2, 32.4, 36.8, 37.9, 68.9, 127.8, 127.9, 129.7, 129.8, 134.0, 134.2, 135.6, 136.3; *m*/*z* 336 (M^+, 1%), 294 (9), 199 (100), 181 (65) (Found: C, 78.6; H, 8.4. $C_{22}H_{28}OSi$ requires C, 78.5; H, 8.4%).

2,2-Diphenyl-7,7-dimethyl-1-oxa-2-silacycloheptane 41. δ_H 1.14 (2H, m, 3-H), 1.44 (6H, s, 7-Me), 1.78 (6H, m, 3 × CH_2), 7.27–7.61 (10H, m, Ph); δ_C 15.1, 23.6, 25.8, 31.0, 43.1, 75.4, 127.6, 129.3, 134.2, 137.9; *m*/*z* 296 (M^+, 2%), 199 (94), 123 (100) (Found: C, 76.7; H, 8.2. $C_{19}H_{24}OSi$ requires C, 77.0; H, 8.3%).

EPR spectroscopy

EPR spectra were recorded during continuous UV irradiation of samples positioned in a standard variable temperature insert in the microwave cavity of a Varian E-109 or a Bruker ESP-300 spectrometer operating at 9.1–9.4 GHz, as described previously.[30] Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (3 mm id, 0.5 mm wall). The temperature of the sample during photolysis was determined, using the method described previously;[30a] the heating effect at full light intensity varied between 5 and 7 °C depending on conditions. Di-*tert*-butyl peroxide (98%, Aldrich) was passed down a column of basic alumina (activity 1) and distilled (bp 46–47 °C/76 Torr); cyclopropane (Union Carbide) was used as received.

Computer simulations of spectra were obtained using a modified version of ESRSPEC2,[49] extended to handle com-

posite spectra from up to four radicals with different centres, second-order shifts for coupling to single nuclei with $I > \frac{1}{2}$, and lineshapes continuously variable between 100% Gaussian and 100% Lorentzian.

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References

1 C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1983, **105**, 3292; C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229.
2 M. Newcomb and S. U. Park, *J. Am. Chem. Soc.*, 1986, **108**, 4132; C. Chatgilialoglu, C. Ferreri and M. Lucarini, *J. Org. Chem.* 1993, **58**, 249.
3 R. P. Allen, B. P. Roberts and C. R. Willis, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1387; J. N. Kirwan, B. P. Roberts and C. R. Willis, *Tetrahedron Lett.*, 1990, **31**, 5093.
4 S. J. Cole, J. N. Kirwan, B. P. Roberts and C. R. Willis, *J. Chem.Soc.*, *Perkin Trans. 1*, 1991, 103.
5 B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 2719.
6 H.-S. Dang and B. P. Roberts, *Tetrahedron Lett.*, 1995, **36**, 2875.
7 K. J. Kulicke and B. Giese, *Synlett*, 1990, 91; M. Ballestri, C. Chatgilialoglu, K. B. Clark, D. Griller, B. Giese and B. Kopping, *J. Org. Chem.*, 1991, **56**, 678; B. Kopping, C. Chatgilialoglu, M. Zehnder and B. Giese, *J. Org. Chem.*, 1992, **57**, 3994; C. Chatgilialoglu, *Acc. Chem. Res.*, 1992, **25**, 188.
8 M. B. Haque and B. P. Roberts, *Tetrahedron Lett.*, 1996, **37**, 9123.
9 I. Ojima, in *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, part 2, ch. 25; T. Hiyama and T. Kusimoto, in *Comprehensive Organic Synthesis*, eds. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991, vol. 8, ch. 3.12.
10 K. Tamao, T. Tanaka, T. Nakajima, R. Sumiya, H. Arai and Y. Ito, *Tetrahedron Lett.*, 1986, **27**, 3377.
11 S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 2121.
12 K. Tamao, T. Nakajima, R. Sumiya, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, 1986, **108**, 6090.
13 K. Tamao, T. Yamauchi and Y. Ito, *Chem. Lett.*, 1987, 171; K. Tamao, Y. Nakagawa, H. Arai, N. Higuchi and Y. Ito, *J. Am. Chem. Soc.*, 1988, **110**, 3712; K. Tamao, T. Tohma, N. Inui, O. Nakayama and Y. Ito, *Tetrahedron Lett.*, 1990, **31**, 7333; K. Tamao, Y. Nakagawa and Y. Ito, *Org. Synth.*, 1995, **73**, 94.
14 S. H. Bergens, P. Noheda, J. Whelan and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 2128; X. Wang and B. Bosnich, *Organometallics*, 1994, **13**, 4131; X. Wang, W. W. Ellis and B. Bosnich, *Chem. Commun.*, 1996, 2561.
15 (*a*) H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 1966, 6163; (*b*) G. D. Mendenhall, *Tetrahedron Lett.*, 1983, **24**, 451; (*c*) H.-T. E. Chen and G. D. Mendenhall, *J. Am. Chem. Soc.*, 1984, **106**, 6375; (*d*) G. D. Mendenhall and H.-T. E.Chen, *J. Phys. Chem.*, 1985, **89**, 2849.
16 D. L. J. Clive and W. Yang, *Chem. Commun.*, 1996, 1605; D. L. J. Clive and M. Cantin, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 319.
17 E. I. Miranda, M. J. Diaz, I. Rosado and J. A. Soderquist, *Tetrahedron Lett.*, 1994, **35**, 3221.
18 T. J. Barton and A. Revis, *J. Am. Chem. Soc.*, 1984, **106**, 3802.
19 C. Chatgilialoglu, H. Woynar, K. U. Ingold and A. G. Davies, *J. Chem. Soc.*, *Perkin Trans. 2*, 1983, 555.
20 J. P. Sarasa, J. Igual and J. M. Poblett, *J. Chem. Soc.*, *Perkin Trans. 2*, 1986, 861.
21 K. Mochida and K. Asami, *J. Organomet. Chem.*, 1982, **232**, 13.
22 A. L. J. Beckwith and K. U. Ingold, in *Rearrangements in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, essay no. 4.
23 T. V. RajanBabu, *Acc. Chem. Res.*, 1991, **24**, 139.
24 C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, 1959, **81**, 1144.
25 W. Damm, B. Giese, J. Hartung, T. Hasskerl, K. N. Houk, O. Hüter and H. Zipse, *J. Am. Chem. Soc.*, 1992, **114**, 4067.
26 A. S. Dneprovski, B. Z. Pertsikov and V. A. Chertkov, *Russ. J. Org. Chem.*, 1987, **23**, 291.
27 J. Fossey, D. Lefort and J. Sorba, *Top. Curr. Chem.*, 1993, **164**, 99.
28 Y. Guindon, C. Yoakim, V. Gorys, W. W. Ogilvie, D. Delorme, J. Renaud, G. Robinson, J.-F. Lavallée, A. Slassi, G. Jung, J. Rancourt, K. Durkin and D. Liotta, *J. Org. Chem.*, 1994, **59**, 1166.
29 P. L. H. Mok, B. P. Roberts and P. T. McKetty, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 665.
30 (*a*) J. A. Baban and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1981, 161; (*b*) V. Diart and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 1761; (*c*) B. P. Roberts and A. J. Steel, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 2025 (corrigendum, 1993, 1003).
31 D. Griller and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1972, 747; D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317.
32 C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739.
33 J. K. S. Wan and A. J. Elliot, *Acc. Chem. Res.*, 1977, **10**, 161; P. J. Hore, C. G. Joslin and K. A. McLauchlan, *Chem. Soc. Rev.*, 1979, **8**, 29; M. Anpo, K. U. Ingold and J. K. S. Wan, *J. Phys. Chem.*, 1983, **87**, 1674.
34 G. Rauhut, A. Alex, J. Chandrasekhar, T. Steinke, W. Sauer, B. Beck, M. Hutter and T. Clark, VAMP ver. 5.6.0, Erlangen, 1995.
35 S. F. Nelsen, *J. Chem. Soc.*, *Perkin Trans. 2*, 1988, 1005.
36 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.
37 B. P. Roberts and A. J. Steel, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 2411.
38 A. Alberti and G. F. Pedulli, *Rev. Chem. Intermed.*, 1987, **8**, 207; I. G. Green, K. M. Johnson and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1989, 1963; M. Guerra, *J. Am. Chem. Soc.*, 1992, **114**, 2077.
39 H.-S. Dang and B. P. Roberts, *Chem. Commun.*, 1996, 2201; *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 67.
40 M. B. Haque and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 1*, to be published.
41 P. A. Risbood, T. S. Phillips and L. Goodman, *Carbohydrate Res.*, 1981, **94**, 101; M. Spescha, *Helv. Chim. Acta*., 1993, **76**, 1822.
42 J. Y. Corey and R. West, *J. Am. Chem. Soc.*, 1963, **85**, 2430.
43 (*a*) R. August, I. McEwen and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, 1683; (*b*) B. Accot and A. L. J. Beckwith, *Aust. J. Chem*, 1964, **17**, 1342.
44 M. R. Ashcroft, A. Bury, C. J. Cooksey, A. G. Davies, B. D. Gupta, M. D. Johnson and H. Morris, *J. Organomet. Chem.*, 1980, **195**, 89.
45 D. G. H. Crout and S. M. Morrey, *J. Chem. Soc.*, *Perkin Trans. 1*, 1983, 2435.
46 N. C. Yang, D.-D. H. Yang and C. B. Ross, *J. Am. Chem. Soc.*, 1959, **81**, 133.
47 R. A. Schneider and J. Meinwald, *J. Am. Chem. Soc.*, 1967, **89**, 2023.
48 M. Boeykens, N. D. Kimpe and K. A. Tehrani, *J. Org. Chem.*, 1994, **59**, 6973.
49 P. J. Krusic, QCPE no. 210.

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