Intramolecular and Intermolecular Reactions of Alkenylsilyl Radicals

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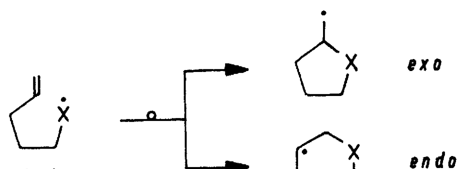
The radicals formed during photolysis of di-t-butyl peroxide and a number of alkenyldimethylsilanes have been examined by e.s.r. spectroscopy. Only carbon-centred radicals were observed. These were either secondary alkyl radicals formed by the addition of the initially formed silyl radical to a double bond and/or allyl radicals formed by hydrogen-atom abstraction from the alkenyl group. In most cases addition to the double bond was an intermolecular process. However, pent-4-enylsilyl radicals undergo intramolecular addition with *endo*-cyclization to form the six-membered ring being strongly favoured over *exo*-cyclization to form the five-membered ring. This preference was confirmed by product studies on 3,3-dimethylpent-4-enyldimethylsilane. The factors that control homolytic *exo*:*endo* cyclization rates for species in which the radical centre is located on a second row element are adumbrated.

Free-radical rearrangements are of growing importance since they can provide new approaches to the synthesis of organic compounds [1] and can also be used to determine the absolute rate constants for intermolecular radical–molecule reactions.[1,2] The most useful and most carefully studied rearrangement is undoubtedly the ring-closure of the hex-5-enyl radical (1; X = CH_2) and related hydrocarbon and hetero-atom-containing species including those in which the initial radical centre, X, is on a nitrogen atom or an oxygen atom.[1,3,4]

In almost all cases, the kinetically favoured product has the five-membered ring structure produced by *exo*-cyclization. If, however, this reaction is reversible [as is generally the situation when the initial radical is resonance stabilized, *e.g.*[5] $\dot{X} = \dot{C}(CN)CO_2Et$], the final products will have the thermodynamically favoured six-membered ring structure formed by *endo*-cyclization.[1,3] The products of the analogous cyclizations of species having the initial radical centre on a second row element [*i.e.*, $\dot{X} = \dot{S}iR_2$, $\dot{P}(OR)_3$, $\dot{S}$] have received comparatively little attention.[1,3] On the basis of rather limited data it has been concluded that *exo*-cyclization is probably generally preferred.[3,6] However, the present results point towards a more complex picture.

In this paper we report the results of an e.s.r. spectroscopic investigation of the intermolecular and intramolecular reactions of several alkenyldimethylsilyl radicals (2) and related species. Our results have an important bearing on the generalization to second row elements of the Baldwin–Beckwith rules [6,7] for radical cyclizations which were developed on the basis of the results obtained with first row elements. The only previous report on the subject of alkenylsilyl radical cyclizations is a brief mention in a review by Sakurai.[8]



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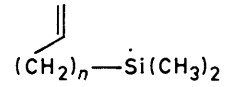
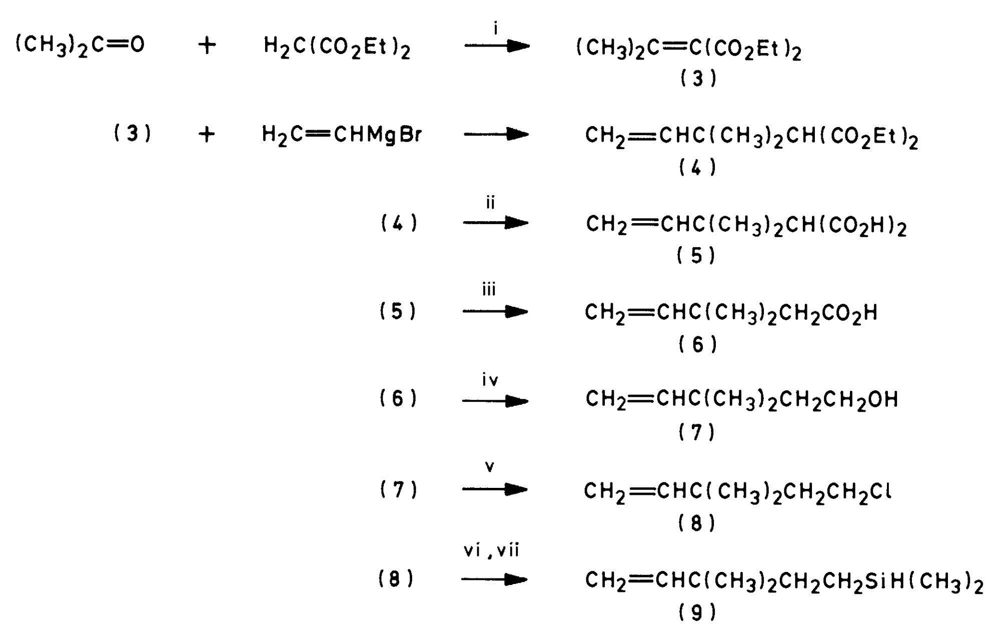


(2)

Experimental

Materials.—Alkenyldimethylsilanes which were used in this work were prepared by reaction of the alkenyl Grignard reagent with dimethylsilyl chloride as described by Swisher and Chen.[9] With one exception, the required alkenyl halides were commercially available. The exception was 3,3-dimethylpent-4-enyl chloride (8) which was prepared as indicated in Scheme 1. The isopropylidenemalonate (3) was prepared by the procedure of Cope and Hancock.[10] To a Grignard solution prepared from vinyl bromide (60.5 g, 0.5 mol) and magnesium (12 g, 0.5 mol) in tetrahydrofuran (300 ml) was added a solution of (3) (100 g, 0.5 mol) in ether. The reaction mixture was hydrolysed after stirring overnight and refluxing for 3 h. It gave, after the usual work-up, crude (4) (90 g) which, after vacuum distillation yielded pure (4) (65 g). This distillation is not easy as the major impurities [unchanged (3) and $CH_2{=}C(CH_3)CH(CO_2Et)_2$] have b.p.s close to that of (4). After refluxing (4) (57 g, 0.25 mol) and KOH (1 mol) in ethanol (150 ml) for 4 h, the bulk of the ethanol was removed on a rotary evaporator and the residue was dissolved in the minimum amount of water. This solution was acidified with concentrated HCl (ice-cooling) to a pH of *ca.* 1.0. Extraction with ether yielded the crude malonic acid derivative (5) (33 g) which was placed in a distillation apparatus and heated to 160 °C, at which temperature CO_2 evolution began. This was complete after *ca.* 2 h. Vacuum distillation of the residue yielded (6) (23 g) which was reduced with $LiAlH_4$ in ether in the usual way to give the carbinol (7) (15 g). To a suspension of the Vilsmeier reagent, $[Me_2NCHCl]^+ Cl^-$ (prepared from PCl_5 and dimethylformamide),[11] in hexamethylphosphoramide (50 ml) at 0 °C was added (7) (15 g). The mixture was then heated to 75 °C for 1 h. After cooling, an excess of water was added, the oily layer separated, washed with water, dried ($MgSO_4$), and distilled, yielding (8) (7.8 g). Next, a Grignard solution was prepared from (8) (6 g) and magnesium in ether and to this at room temperature was slowly added Me_2SiHCl in ether. After stirring overnight the mixture was refluxed for 3 h, cooled, and water was added. The separated organic layer was washed with water and dried ($MgSO_4$). After solvent evaporation and distillation the desired silane (9) (5.2 g) was obtained, δ_H ($CDCl_3$) 0.055 [6 H, d, *J* 4.5 Hz, $Si(CH_3)_2$], 0.30—0.60 (2 H, m, $SiCH_2$), 0.97 [6 H, s, $C(CH_3)_2$], 1.19—1.41 (2 H, m, CCH_2C), 3.82 (1 H, ≥ heptet, SiH), 4.76—4.99 (2 H, m, $CH{=}CH_2$), and 5.57—5.92 (m, 1 H, $CH{=}CH_2$); δ_C ($CDCl_3$) − 4.51 [$Si(CH_3)_2$], 8.49 ($SiCH_2$), 26.26 [$C(CH_3)_2$], 37.17 (CCH_2C),



Scheme 1. Reagents: i, $ZnCl_2$; ii, KOH–EtOH; iii, 160 °C, $-CO_2$; iv, $LiAlH_4$; v, DMF–HMPA–PCl_5; vi, Mg; vii, $(CH_3)_2SiHCl$

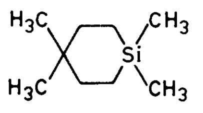
37.57 [$C(CH_3)_2$], 110.60 (H_2C=CH), and 148.49 (H_2C=CH) p.p.m.; *m/e* 141 ([$M - 15]^+$, 6%), 113 (6), 100 (10), 99 (4), 87 (28), 85 (7), 73 (12), 72 (7), 69 (4), 60 (7), and 59 (100).

The alkenyldimethylsilanes, other than (9), prepared for use in this work, are known compounds. Tripent-4-enylsilane was a gift from Professor M. J. Perkins, Chelsea College, and the disilane CH_2=$CHCH_2Si(CH_3)_2SiH(CH_3)_2$ was a gift from Dr. T. J. Barton, Iowa State University. All these compounds were purified by careful distillation followed by preparative g.l.c. Their purity before use was >99.5% by analytical g.l.c. Less pure materials generally gave no e.s.r. spectra or spectra that were too weak to analyse, or caused the build-up of persistent radicals.

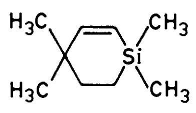
1,1,4,4-Tetramethylsilacyclohexane (10) was synthesized by reaction of dimethyldichlorosilane with the Grignard reagent prepared from 1,5-dibromo-3,3-dimethylpentane. The last named compound was prepared by the method of Meinwald and Smith [12] by the $AlCl_3$ catalysed reaction of ethylene with 1,3-dibromo-3-methylbutane (which was itself prepared from isoprene [12]). Compound (10) had δ_H ($CDCl_3$) −0.01 [6 H, s, $Si(CH_3)_2$], 0.46—0.63 (4 H, m, $SiCH_2$), 0.85 (6 H, s, $C(CH_3)_2$], and 1.37—1.52 (4 H, m, CCH_2); δ_C($CDCl_3$) −3.05 [$Si(CH_3)_2$], 9.87 ($SiCH_2$), 28.49 [$C(CH_3)_2$], 32.43 [$C(CH_3)_2$], and 36.77 (CCH_2C) p.p.m.; *m/e* 156 ([$M]^+$, 13%), 142 (5), 141 (28), 129 (10), 128 (62), 114 (7), 113 (50), 101 (9), 100 (75), 99 (33), 97 (7), 87 (14), 86 (17), 85 (47), 74 (8), 73 (60), 72 (61), 71 (15), 70 (7), 69 (8), 67 (6), 60 (9), 59 (100), 58 (43), 57 (8), 55 (27), and 53 (11).

t-Butyl hyponitrite (TBHN) was prepared by the method of Keifer and Traylor.[13]

Reaction of (9) *with TBHN.*—In an n.m.r. tube an evacuated solution of (9) (175 mg, 1.12 mmol) and TBHN (97 mg, 0.56 mmol) in C_6D_6 (1.05 ml) was heated at 46 °C for 4 days (*ca.* 14 half-lives of the TBHN). At the end of this time (10) and t-butyl alcohol could be seen by n.m.r. to be the major products. The volatile material was separated by trap-to-trap distillation under high vacuum and was analysed by g.c.–m.s. using undecane as an internal standard. The amount of (9) consumed was 1.03 mmol and the hyponitrite had yielded 0.06 mmol of di-t-butyl peroxide and *ca.* 1.1 mmol of t-butyl alcohol. The yield of (10) was 0.36 mmol. Two other g.c. peaks appeared shortly before the peak due to (10). The first, and by far the larger of these two peaks, was identified as the silacyclohexene (11) by its mass spectrum, *m/e* 154 ([$M]^+$, 26%) 140 (8), 139 (56), 127 (12), 126 (10), 112 (16), 111 (87), 109 (11), 99 (17), 98 (5), 97 (17), 95 (13), 85 (13), 83 (19), 81 (6), 79 (7), 74 (7), 73 (71), 72 (9), 71 (7), 69 (9), 67 (9), 59 (56), 58 (13), 55 (15), and 53 (11). The [$M + 1]^+$ and [$M + 2]^+$ ions have the expected 15 and 4% intensity relative to the [$M]^+$ ion. After separation by preparative g.l.c., the ^1H n.m.r. spectrum showed δ_H ($CDCl_3$) 0.04 [6 H, s, $Si(CH_3)_2$], 0.06—0.80 (2 H, m, $SiCH_2$), 0.97 [6 H, s, $C(CH_3)_2$], 1.53—1.72 (2 H, m, CCH_2C), 5.48 (1 H, d, *J* 14.1 Hz, CH=CHSi), and 6.41 (d, 1 H, CCH=CH). The yield of (11) was 0.11 mmol.



(10)



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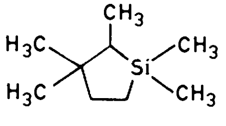


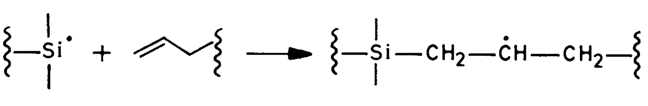
(12)

Between the g.c. peaks due to (10) and (11) [both of which appear soon after that due to (9)] was a minor peak due to a compound which we *tentatively* identify as the silacyclopentane (12) on the basis of its mass spectrum, *m/e* 156 ([$M]^+$, 15%), 141 (6), 129 (19), 128 (100), 114 (13), 113 (88), 99 (23), 88 (5), 87 (23), 86 (95), 85 (12), 73 (38), 72 (6), 71 (6), 70 (5), 69 (5), 60 (6), 59 (56), 58 (77), 55 (15), and 53 (5); the [$M + 1]^+$ and [$M + 2]^+$ ions have the expected intensity relative to the [$M]^+$ ion). The yield of (12) was 0.01 mmoles.

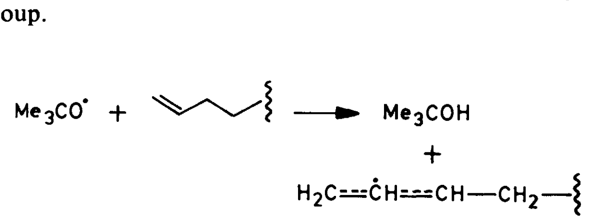
Results

E.s.r. Spectroscopic Studies.—Photolysis of solutions of alkenylsilanes and di-t-butyl peroxide in cyclopropane generally yielded rather weak spectra, the individual lines being quite broad. Silyl radicals were never observed, all the radicals being carbon-centred. This must be due to the presence of the double bond(s) in the alkenyl group(s) because silanes such as $CH_3(CH_2)_2SiH(CH_3)_2$ and $(CH_3)_2CH(CH_2)_2SiH(CH_3)_2$ gave strong spectra of their respective trialkylsilyl radicals under similar conditions.

The hyperfine splittings (h.f.s.) obtained for most of the alkenylsilanes studied in this work and the structures of the radicals to which they are assigned are given in the Table. The major radicals derived from silanes (13)—(16) are secondary alkyls. These are clearly formed by an intermolecular addition reaction involving the expected silyl radical and the parent silane.



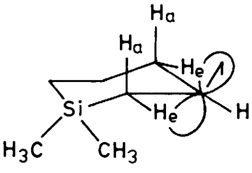
The two pairs of silanes (13) and (14), and (15) and (16) yield radicals with virtually the same h.f.s. As might be expected, the radical obtained by photolysis of triethylsilane, di-t-butyl peroxide, and hex-1-ene in cyclopropane had h.f.s. that were very similar [*viz.* a^H 17.7 (2 H), 20.5 (1 H), and 25.5 G (2 H) at 200—310 K] to those of the radicals derived from (15) and (16). The four silanes (13)—(16) showed no signs of intramolecular reaction, *i.e.*, there was no e.s.r. signal that could be attributed to a cyclized radical. However, both (15) and (16) did show very weak spectra from a second radical. The parameters for the second radicals allow their structures to be unambiguously assigned to allylic species, $RCH_2CH{\cdots}\dot{C}H{\cdots}CH_2$. Such radicals are obviously not formed *via* the silyl radical, but must instead be produced by a direct hydrogen-atom abstraction by t-butoxyl from the allylic methylene group.



The intensities of the spectra due to these allylic radicals, relative to those from the secondary alkyl radicals formed by the intermolecular silyl radical addition reaction, increased as the temperature was raised.

Compound (17), which could yield a silicon-centred analogue of hex-5-enyl gave more than one radical, most of which could not be identified, and polymeric material was formed upon prolonged photolysis. The 'cleanest' spectrum from (17) was obtained at 214 K, at which temperature the predominant species appeared to be an allyl radical.

The silane (18) which could also yield a silicon-centred analogue of the hex-5-enyl radical, also gives mainly an allyl radical at *ca.* 270—295 K. However, as the temperature is decreased a new radical makes its appearance and, below 240 K, dominates (if such a word should be applied to such a weak e.s.r. signal) the spectrum. We assign to this low temperature species a *six*-membered ring structure, *i.e.*, the radical observed is that resulting from an *endo*-cyclization.[*] The e.s.r. spectrum of this new radical shows h.f.s. by only two out of its four β-hydrogen atoms. These are presumably the two axial hydrogens H_a, the equational hydrogens H_e lying too close to the C_α $2p_z$ nodal plane to be resolved [see (19)]. The lines in the spectrum of (19) are rather broad (ΔH_{pp} 1.8 G). This could be due to ring motions and/or unresolved long range h.f.s.



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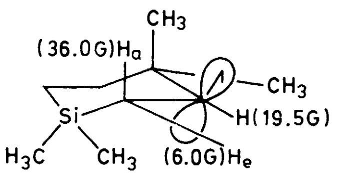

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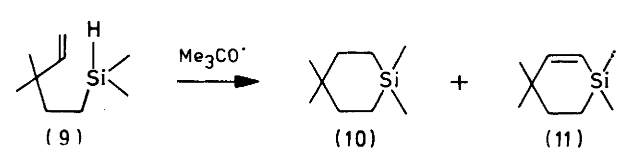

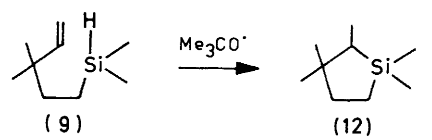

Behaviour similar to that of (18) was observed with $CH_2{=}CH(CH_2)_3SiH_3$ and with $CH_2{=}CH(CH_2)_3SiCl_2H$. That is, allyl radical spectra were produced above *ca.* 270 K and a radical having a six-membered ring analogous to (19), appeared to be formed at low temperatures. However, the e.s.r. spectra were even weaker than those obtained from (18), and so these silanes were not studied in further detail.

The 'blocked' alkenylsilane (9) was synthesized so that t-butoxyl radical would, to all intents and purposes, be forced to attack the Si–H bond. This strategy succeeded in that a 'clean' e.s.r. spectrum of the silacyclohexyl radical (20) was obtained above *ca.* 250 K. At lower temperatures there was, however, some evidence for an intermolecular addition process.

Though the e.s.r. h.f.s. served to identify (20) unambiguously the lines in its spectrum are very broad (ΔH_{pp} 2.5 G) and a spectrum of relatively poor quality results. However, this is not due to any inefficiency in the formation of the silyl radical since the addition of ethyl bromide (*ca.* 5.7M) to the system gave a strong ethyl radical signal. At 173 K the intensity of this ethyl radical spectrum was comparable to that obtained when a saturated silane such as $(CH_3)_2CH(CH_2)_2SiH(CH_3)_2$ was used in place of (9). In this connection, it should be added that the cyclizations of the silicon-centred radicals derived from (9) and (18) will not be reversible under our conditions. The reluctance of β-silylalkyl radicals to undergo β-scission can be illustrated by the following observation. Photolysis of di-t-butyl peroxide and tetraethylsilane gives both $(CH_3CH_2)_3Si\dot{C}HCH_3$ and $(CH_3CH_2)_3SiCH_2\dot{C}H_2$ radicals. Upon the addition of C_2H_5Br (*ca.* 3.4M) to this system the ethyl radical is not produced at temperatures as high as 310 K, which indicates that the reaction $(C_2H_5)_3SiCH_2\dot{C}H_2 \longrightarrow (C_2H_5)_3Si\cdot + H_2C{=}CH_2$ does not occur.

Product Studies.—The conclusion that the silyl radical derived from (9) undergoes *endo*-cyclization predominantly was confirmed by product studies. t-Butoxyl radicals generated thermally at 319 K in C_6D_6 reacted with (9) to yield (10) in 35% yield and (11) in 11% yield based on the quantity of (9) consumed (see Experimental section). The *exo*-cyclized pro-

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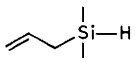
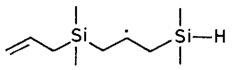
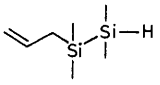
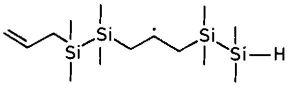
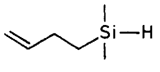
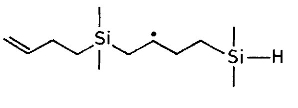
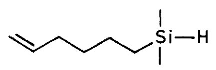
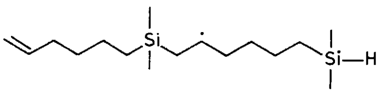
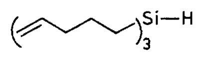
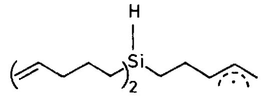
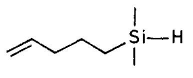
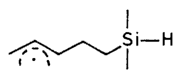
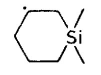
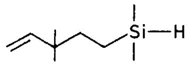
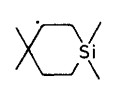
[*] *N.b.* The chloroplatinic acid catalysed cyclization of silanes which are structurally analogous to (18) favours five-membered ring formation.[8]

E.s.r. hyperfine splittings and structures assigned to the principal radicals observed on photolysis of some alkenylsilanes and di-t-butyl peroxide in cyclopropane

Alkenylsilane	Structure assigned to radical	a^H/G	T/K
 (13)		17.3 (4 H) 19.5 (1 H)	295—225
 (14)		17.6 (4 H) 19.6 (1 H)	150—370 [a]
 (15)		17.5 (2 H) 20.5 (1 H) 25.2 (2 H)	295—225 [b]
 (16)		17.0 (2 H) 21.0 (1 H) 26.5 (2 H)	150—255 [b]
 (17)		4.0 (1 H) 13.5 (4 H) 14.5 (1 H)	214
 (18)		4.0 (1 H) 13.8 (4 H) 14.5 (1 H)	295
		20.7 (1 H) 38.5 (2 H)	240
 (19)		6.0 (1 H) 19.5 (1 H) 36.0 (1 H)	200—250 [c]

[a] From 315—370 K tridecane was used as the solvent. [b] Some allyl radical formed by hydrogen-atom abstraction may also be present. [c] At lower temperatures there may be some intermolecular addition.

duct (12) was only tentatively identified. If produced, it is formed in only 1% yield.

Studies by Laser Flash Photolysis.—Recently we reported [14,15] that a number of silyl radicals have observable optical absorption spectra, *e.g.*, $(CH_3CH_2)_3Si\cdot$ has a weak absorption below 340 nm with ε_{308} *ca.* 360 l mol^{-1} cm^{-1}. An attempt was therefore made to observe the silyl radical derived from (9) and monitor its cyclization to (20). A sample containing (9) and di-t-butyl peroxide in iso-octane (1 : 1 : 4 v/v) was irradiated with the pulse from a nitrogen laser in the equipment previously described.[16] No transient absorbing above 300 nm was observed which suggests that cyclization of the silyl radicals to form (20) occurs on a time scale shorter than that for their formation, *i.e.* on a time scale shorter than that for hydrogen atom abstraction from the silane by t-butoxyl (which is *ca.* 170 ns).

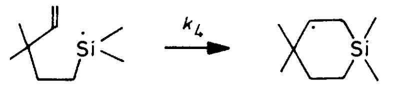
Discussion

Our results provided us with the first indication that t-butoxyl radicals abstract hydrogen from silicon and from allylic methylene groups at comparable rates. This qualitative observation has since been confirmed by direct and quantitative measurements of the rate constants for the two different processes. At 300 K $k_1 = 5.7 \times 10^6$ l mol^{-1} s^{-1} [15,17] and k_2 can be calculated to be *ca.* 1.1×10^6 l mol^{-1} s^{-1}.[18] In view of these (approximate) rate constants for the different positions at

$$Me_3CO^{\cdot} + (CH_3CH_2)_3SiH \xrightarrow{k_1} Me_3COH + (CH_3CH_2)_3Si^{\bullet} \quad (1)$$

$$Me_3CO^{\cdot} + RCH_2CH_2CH{=}CHCH_2R' \xrightarrow{k_2} Me_3COH + RCH_2CH{\cdots}\overset{\bullet}{C}H{\cdots}CHCH_2R' \quad (2)$$

$$(CH_3CH_2)_3Si^{\cdot} + CH_2{=}CH(CH_2)_3CH_3 \xrightarrow{k_3} (CH_3CH_2)_3SiCH_2\overset{\bullet}{C}H(CH_2)_3CH_3 \quad (3)$$



(4)

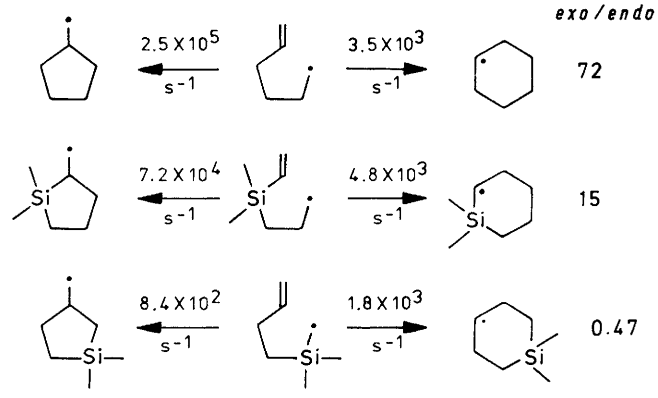
which t-butoxyl can attack it is not surprising that an allyl radical was a minor product from most alkenyldimethylsilanes, nor that it appeared to be the predominant product from the tripent-4-enylsilane (17). The observation that the allyl radical concentration was relatively larger at higher temperatures implies that the activation energy for hydrogen-atom abstraction by t-butoxyl from a silane (2.64 kcal mol^{-1} for Et_3SiH)[15] is less than that for hydrogen-atom abstraction from an allylic position.

The silyl radicals that are produced from most alkenylsilanes undergo an intermolecular addition with unreacted silane. For the analogous addition of triethylsilyl radicals to hex-1-ene [reaction (3)] the rate constant $k_3 = 4.8 \times 10^6$ l mol^{-1} s^{-1} at 300 K.[19] At the silane concentrations employed in our experiments the intermolecular addition is sufficiently rapid to preclude all hope of observing the alkenylsilyl radicals themselves. Only in the case of the pent-4-enylsilanes (9) and (18) is the intermolecular addition intercepted by an even more ready intramolecular addition.

E.s.r. spectroscopy shows that *endo*-cyclization predominates over *exo*-cyclization for the silyl radicals derived from (9) and (18). This was confirmed for (9) by product studies since it seems reasonable to assume that the ratio of six-membered ring products to five-membered ring products, *i.e.*, [(10)] + [(11)]/[(12)], should to some extent reflect the ratio of the rates of *endo*- to *exo*-cyclization. Of course, the six-ring : five-ring product ratio (47 : 1 at 319 K) is not necessarily equal to the *endo* : *exo* rate constant ratio since the yield of volatile products was only 47%, which suggests that some of the secondary (*endo*) and primary (*exo*) alkyl radicals were lost in radical coupling reaction and other processes leading to involatile products.

The preference of pent-4-enylsilyl radicals for *endo*-cyclization has not been predicted [3,6] but is not entirely unexpected. That is, Sakurai [8] has reported that the ratios of the yields of five- to six-membered ring products formed in the reaction of $CH_2{=}CH(CH_2)_3Si(X,Y)H$ with t-butoxyl radicals at 303 K are: 0.15, X = Me, Y = Ph; 0.26, X = Y = Ph; and 2.9, X = Me, Y = Cl. However, the total yields of cyclized products were only 10.95, 15.7, and 6.4%,* respectively, presumably in part because of extensive t-butoxyl attack on the allylic hydrogens.

An attempt to measure the rate constant k_4 for the *endo*-cyclization of the silyl radical from (9) by the kinetic e.s.r. method [2] was unsuccessful. This method relies on the simultaneous observation of both the unrearranged and rearranged radicals. At the temperature where this occurs the rearrangement rate constant is always *ca.* 10^3 s^{-1}.[2] Reaction (4) must be rapid because the silyl radical could not be detected at temperatures as low as 200 K.



Scheme 2

An upper limit can be put on k_4 from the results of the experiment with ethyl bromide. Thus, at 173 K the rate constant for bromide atom abstraction from a primary alkyl bromide by triethylsilyl radicals has a value of 2.5×10^8 l mol^{-1} s^{-1}.[20] Since the signal due to the ethyl radical had about the same intensity when (9) was used as the silyl radical source as when trialkylsilanes were employed and since the concentration of ethyl bromide was *ca.* 5.7M, k_4 must be $<10^9$ s^{-1} at this temperature. The fact that the lifetime of the silyl radical is shorter than the time required for its formation in the laser flash experiment (170 ns) puts a lower limit on k_4 of 10^7 s^{-1} at room temperature. This limit is supported by the fact that silyl radicals from (9) appeared not to add to some simple olefins; the rate constants for the addition of Et_3Si radicals to these olefins are all *ca.* 10^6 l mol^{-1} s^{-1} at 300 K.[19]

Our results have an important bearing on the extension of the Baldwin–Beckwith rules [6,7] for homolytic ring-closures by second row element-centred radicals. It is clear that cyclization of pent-4-ene-substituted silyl radicals is a fast reaction and that the formation of the six-membered ring is very strongly favoured. While any explanation of this fact must be somewhat speculative because of the complex factors involved in *endo- versus exo*-cyclizations,[1,3] we will attempt to explain our results and the results of others [21-24] on the basis of bond lengths and configurations at the radical centres.

Wilt's results [24] on the cyclization of two silahex-5-enyl radicals at 298 K are summarized, together with Beckwith's for the cyclizations of the hex-5-enyl radical, in Scheme 2. Rate constants for the individual cyclizations have been revised to fit with recent work on the alkyl radical–tin hydride reaction.[25] Examination of molecular models provides a rationale for the way in which the individual rate constants change and, hence, for *exo*/*endo* ratios. This rationale is based on the stereoelectronic view [1,3] that the preferred direction of approach of the semioccupied orbital to the double bond lies in the plane containing the two olefinic carbon atoms which is orthogonal to the $H_2C{=}CHC$ plane; furthermore the direction of attack is along the line of the bond which will be

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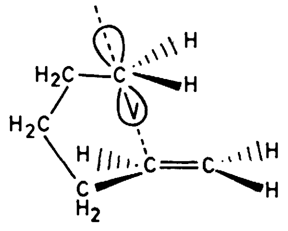
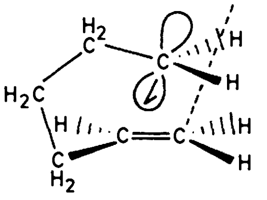
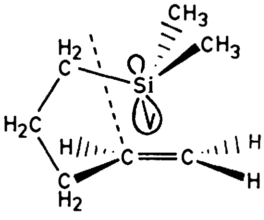
* We confess to some reservations regarding the reported yield (and, hence, to the reported product ratio) for the compound having X = Me, Y = Cl in an analogous reaction at 408 K, *viz.*,[8] 84.2%. For the other pentenylsilanes studied at this temperature the yields were only: 6.11%, X = Me, Y = Ph; 6.84%, X = Y = Ph; and 9.41%, X = Pr^i, Y = Cl.



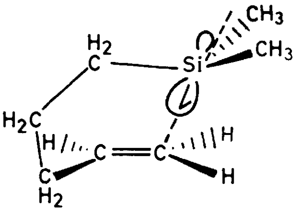
(21)



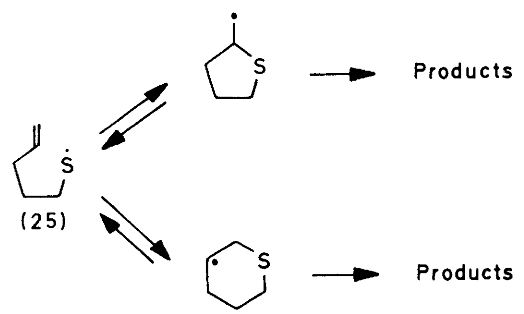
(22)

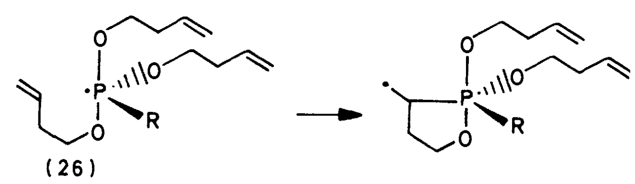


(23)



(24)





(26)
R = Me, EtO

formed. That is, the preferred transition state has the semi-occupied orbital approaching the double bond along the dotted lines in structures (21)—(24). For the hex-5-enyl radical *exo*-cyclization is strongly favoured because such a distribution of atoms, *i.e.*, (21), is readily obtained, while *endo*-cyclization is disfavoured because the optimum orientation cannot be achieved, see (22). Substitution of silicon in the 4- and, even more so, in the 2-position makes a structure analogous to (21) more difficult to achieve because of the longer C–Si bonds, while the structure leading to *endo*-cyclization is only slightly more favoured. However, when the radical centre is on silicon, as in our experiment, a second factor comes into play, namely, the pyramidal configuration of the radical centre. As a consequence of bond length effects *and* configuration effects the *exo*-cyclization is disfavoured, *cf.* (23), and the *endo*-cyclization is favoured, *cf.* (24).

By invoking configurational factors as well as bond lengths effects we are now in a position to use stereoelectronic arguments to explain some other data from the literature. Surzur and his co-workers [22,23] have shown that the pent-4-enylthiyl radical (25) yields both five- and six-membered rings. The six-membered rings were formed in much higher yield than the five-membered rings (*ca.* 10 : 1). Unfortunately, this may not reflect a kinetic preference for *endo*-cyclization since (in contrast to the situation for the silyl radical cyclizations) both of these cyclizations are probably reversible,* the secondary alkyl radical of the six-membered ring being thermodynamically favoured. The occurrence of at least some *exo*-cyclization and the likelihood that it is more important with sulphur (25) than with silicon (23) can be attributed to the fact that for the thiyl radical the semi-occupied orbital will not be tilted out of the preferred direction of approach (as happens with silicon because the radical centre is pyramidal). The *exo*/*endo* cyclization rate constant ratio for (25) needs to be determined.

Davies and his co-workers [21] have shown by e.s.r. spectroscopy that two phosphoranyl radicals (26; R = Me or EtO) undergo exclusive *exo*-cyclization at temperatures as low as 170 K. This can probably be attributed in part to the fact that phosphoranes in which the phosphorus is part of a five-membered ring bridging between apical and equatorial positions often possess higher stability than their acyclic analogues.[28] More important, we believe, is the fact that such phosphoranyl radicals have a quasi-trigonal bipyramidal structure.[29,30] The unpaired electron occupies a molecular orbital composed primarily of an antibonding combination of phosphorus σ atomic orbitals with apical ligand orbitals of appropriate symmetry. For convenience,[29] this class of radical is represented by formulae in which the unpaired electron is shown as an equatorial ' phantom ligand ' as shown in (26). This structure can be considered as a contributing form in a valence bond description of the bonding.[29] Models show that the stereoelectronic properties of a radical having this structure will favour *exo*-cyclization, just as is observed.

Conclusions.—Extension of the Baldwin-Beckwith rules for kinetically controlled homolytic cyclizations to species in which the radical centre is located on a second row element requires consideration of the stereoelectronic consequences for the potential (rival) transition states of: (i) the increased bond lengths involved; (ii) any alteration in the configuration at the radical centre; and (iii) intramolecular steric factors, conformational factors, and ring strain. We are confident that similar guidelines will apply to both homolytic and heterolytic cyclizations since the same stereoelectronic factors should govern both classes of reaction.

Acknowledgements

Tenure of N.R.C.C. Research Associateships is acknowledged by C. C. and H. W. We also thank Messrs. D. A. Lindsay and R. Kolt for valuable technical assistance.

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* Reversibility has been demonstrated in an analogous thiyl radical cyclization in which *endo*-cyclized seven-membered ring products became more favoured relative to *exo*-cyclized six-membered ring products at low thiol concentrations.[26,27]

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Received 29th June 1982; *Paper* 2/1080