Electronic Effects in the Regiochemistry of the Alkenylsilyl Radical Cyclizations

J. Pedro Sarasa, Joan Igual, and Josep M. Poblet *
Departament de Química Física, Facultat de Química de Tarragona, Universitat de Barcelona, P. Imperial Tarraco, 43005, Tarragona, Spain

The intramolecular reaction of alkenylsilyl radicals has been studied by MINDO/3. Partitioning of the total energy into local contributions is used to analyse the different effects competing in *exo–endo* cyclization. The change in the regioselectivity of the dimethylpent-4-enylsilyl and but-3-enylsilylmethyl radical with respect to the hex-5-enyl radical has been studied. The reversal in the regioselectivity of the silyl radical is due to an enthalpy factor caused by electronic effects.

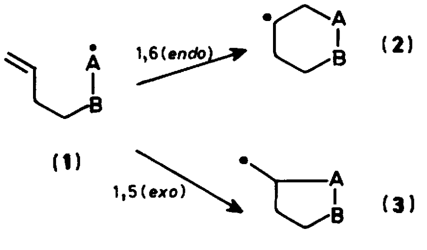
One of the most carefully studied free-radical rearrangement is the ring closure of ω-alkenyl radicals. In particular the hex-5-enyl cyclization of radical and related species with the atom bearing the radical being a first-row element (C, N, or O).[1–5] The rearrangements proceed under kinetic control and they produce the radical of the *exo*-cyclization (**3**), rather than the radical of the *endo*-process,[1] (**2**), although the latter is thermodynamically more favoured.[6,7] If the radical is located on a second-row element two effects are noticeable. First, a strong increase in the cyclization rates is observed.[8] Secondly, a change in the regioselectivity is produced.[8,9] Very recently, the regiochemistry of the dimethylpent-4-enylsilyl radical cyclization has been studied[8,9] (A = Me_2Si, B = CH_2). The cycloaddition reaction demonstrates thermodynamic control favouring 1,6-cyclization with the formation of the six-membered ring over 1,5-cyclization.[8,9] The familiar Baldwin–Beckwith rules[5,10] for homolytic ring closures cannot be extended to these radicals.[8,9] Ingold *et al.*[9] have presented a proposal to explain the determinant factors of the regioselectivity. The study is based on structural factors such as bond lengths and configurations at the radical centres.

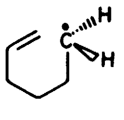
In previous work[11] we showed how the transition state and molecular orbital theories can be used to provide a detailed understanding of the physical origin of the hex-5-enyl and some methyl-substituted radical cyclizations. Analyses of the transition states (TS) and reactants were made by means of the energy partitioning into mono- (E_A) and bi-centric (E_{AB}) local contributions.[12] By this means other inter- and intra-molecular additions were also analysed.[13] The purpose of the present work is to extend the theoretical discussion of the intramolecular reactions of alkenyl radicals to the alkenylsilyl radicals. The non-fulfilment of the Baldwin–Beckwith rules are analysed in two cases, first, when the radical centre is a silicon atom (A = Me_2Si, B = CH_2) and secondly, when the silicon atom is adjacent to the radical centre (A = CH_2, B = SiH_2).

The determination of the activation entropies, which can be important in this type of reaction,[11,14] entails a very accurate search of the transition states involved. Due to the number of degrees of freedom only the use of semi-empirical methods is possible. The MINDO/3 semi-empirical method[15] has been extensively used in the study of intermolecular[16–18] and intramolecular[11,13,14,19] additions, activation energies and kinetic isotope effects being very well reproduced.[16]

Theory

The calculations were carried out by using the unrestricted version (UHF) of MINDO/3 with the standard parameters.[15] The equilibrium geometries were calculated by minimizing the total energy with respect to all geometrical parameters using the Davidon–Fletcher–Powell procedure.[20] The located transition-state structures were found by minimizing the scalar gradient of energy.[21] The stationary points were confirmed by the presence of six near-zero eigenvalues, all the other eigenvalues being positive for minima while a transition state has one negative eigenvalue.





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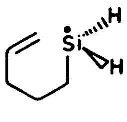

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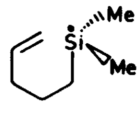

(**6**)

The activation entropies were obtained by means of the vibrational frequencies and inertial moments from the calculated geometries, according to classical methods.[22]

Results and Discussion

Effect on Cyclization when the Silicon Atom is in the Radical Centre. Cyclization of the Dimethylpent-4-enylsilyl Radical.— The direct silyl radical parent of the hex-5-enyl radical (**4**) would be radical (**1**; A = SiH_2, B = CH_2) [≡(**5**)]. Though cyclization of this radical has not been observed, comparison with cyclization of the hex-5-enyl radical should be made with the rearrangement of this radical. Nevertheless, all efforts to obtain transition states with enough accuracy were unsuccessful. The calculated constant matrix had one negative eigenvalue associated with the correct reaction co-ordinate,[21] but it was not possible to separate the rotations from some soft vibrations. This made it impossible to find the true importance of the entropy contribution for this cyclization. In consequence we centre all our discussion on radical (**6**) [≡(**1**; A = Me_2Si, B = CH_2)].

The MINDO/3 transition states for the *exo*- and *endo*-cyclizations of radical (**6**) are shown in Figure 1 and the main structural parameters of the reactant and transition states are reported in Table 1. The calculated force constant matrix for these transition states had just one negative eigenvalue and an associated eigenvector which corresponded to the correct reaction co-ordinate (or transition vector[21]). For this radical

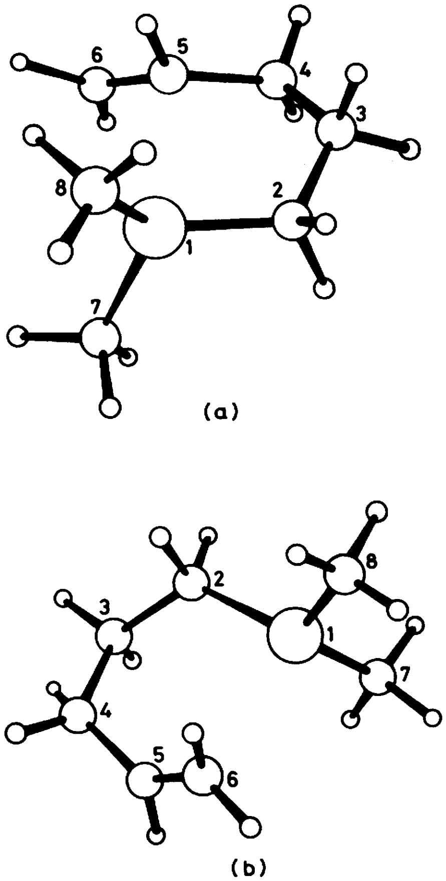

Figure 1. *exo* (a) And *endo* (b) transition states for the dimethylpent-4-enylsilyl radical

Table 1. The main structural parameters calculated by MINDO/3 method for the reactant and transition states of the dimethylpent-4-enylsilyl radical

Parameters[a,b]	Reactant	*exo*-TS	*endo*-TS
Si(1)–C(2)	1.867	1.880	1.882
C(2)–C(3)	1.521	1.521	1.520
C(3)–C(4)	1.520	1.519	1.522
C(4)–C(5)	1.491	1.504	1.491
C(5)–C(6)	1.328	1.357	1.348
C(5)–Si(1)		2.648	
C(6)–Si(1)			2.791
C(7)–Si(1)	1.833	1.848	1.846
C(8)–Si(1)	1.834	1.849	1.848
Si(1)C(2)C(3)	123.7	115.4	122.6
C(2)C(3)C(4)	125.6	117.9	121.2
C(3)C(4)C(5)	120.7		117.2
C(4)C(5)C(6)	131.2	128.9	
C(6)Si(1)C(2)			92.7
C(5)Si(1)C(2)		83.9	
C(7)Si(1)C(2)	117.8	115.4	115.9
C(8)Si(1)C(2)	118.6	115.9	114.8
HC(6)C(5)	124.0	124.0	124.8
H′C(6)C(5)	125.6	124.9	122.7
Si(1)C(2)C(3)C(4)	156.7	−28.8	45.8
C(2)C(3)C(4)C(5)	−133.4		−49.2
C(6)C(1)C(2)C(3)			−33.9
C(5)C(1)C(2)C(3)		10.6	
C(7)Si(1)C(2)C(3)	116.8	124.3	78.1
C(8)Si(1)C(2)C(3)	−90.4	−98.5	−144.8

[a] Distances in Å, angles in degrees. [b] See Figure 1 for notation.

Table 2. Activation energy for the cyclization of several radicals (in kcal mol^{-1})

Radical	*exo*-TS	*endo*-TS
Hex-5-enyl (**4**)	16.5	16.5
Dimethylpent-4-enylsilyl (**6**)	10.3	9.2
But-3-enylsilylmethyl (**7**)	21.9	19.5

there is no problem in reaching the convergence necessary in the transition states. This is due to the curvature of the potential surface being greater for radical (**6**).

The activation enthalpies for the 1,5- and 1,6-cyclizations are 10.4 and 9.2 kcal mol^{-1} respectively while the corresponding value for the hex-5-enyl radical was 16.5 for both modes[14] (Table 2). This decrease is in excellent agreement with the strong increase of the rate constants for the cyclization of (**6**) with respect to (**4**).[1,8] The activation entropy favours *exo* cyclization by only 0.4 cal mol^{-1} K^{-1}. Nevertheless, the enthalpy contribution is more important, making the *endo* mode the faster process. This result is also in good agreement with the experimental data. So in the analysis of these results two points should be considered: first, the decrease produced in the activation energy and secondly, the inversion in the regioselectivity of this radical.

To discuss the above points we begin by making some comments about the structural parameters of the reactants and transition states. It must be remarked that not all conformations have been studied for radical (**6**). For this type of radical it is possible to find several structures with similar energy, as shown by the hex-5-enyl radical.[23] The conformation which is probably most stable has been studied. If this is compared with the preferred structure for radical (**4**), the only noticeable difference is the longer distance between the radical centre and the adjacent atom. The value of the Si(1)–C(2) distance is 1.867 Å whereas for C(1)–C(2) bond it is 1.454 Å.[23] In spite of these minor changes, in the transition states an important event occurs. The incipient bonds are longer than those found in the hex-5-enyl radical (2.648 *versus* 2.200 Å in the *exo* mode and 2.791 *versus* 2.265 Å in the *endo* mode). Nevertheless, in the olefinic bonds the changes are negligible.

To take into account the new bond it is possible to assume that for radical (**6**) the transition states are produced early on the reaction co-ordinate. But as the main electronic event in a radical addition is the transfer of the unpaired electron from the incoming radical centre to the non-attacked olefinic bond,[11] we will compare this transfer in the first stage of the reaction (in the transition state) for both radical cyclizations under discussion. For the 1,6-cyclization (the favoured process) the polarization of the olefin is small for the hex-5-enyl radical, *i.e.* there is a small shift of β spin density toward the attacked carbon (Table 3). The transfer of α spin density is small when the radical atom is silicon (0.126 *versus* 0.167 in the *endo* TS). Similar results can be found for the *exo* path. Therefore, from electronic considerations it can be concluded that the *endo* and *exo* transition states in the dimethylpent-4-enylsilyl radical (**6**) are produced earlier than the hex-5-enyl radical (**4**).

How is the above result interpreted from an energy point of view? The origin of the decrease in the activation enthalpy can be revealed by energy-partitioning analysis. The main geometrical effect is minor deformation of the chain of the radical. So, we can partition the main interactions in the radical chain into three groups. The first is associated with the interactions between the radical centre and the double bond. The second is associated with the alkyl fragment C(2)–C(4). The

Table 3. Electron and spin densities for the initial radical and transition states of the hex-5-enyl, dimethylpent-4-enylsilyl, and but-3-enylsilylmethyl radical cyclizations

	Electron density			Spin density		
	Initial radical	*exo*-TS	*endo*-TS	Initial radical	*exo*-TS	*endo*-TS
			Hex-5-enyl radical			
C(1)	4.090	4.047	4.048	1.118	0.935	0.951
C(5)	4.032	3.966	4.013	0.000	−0.437	0.469
C(6)	3.990	4.043	3.994	0.000	0.582	−0.397
			Dimethylpent-4-enylsilyl radical			
Si(1)	3.889	3.874	3.880	0.920	0.769	0.794
C(5)	3.988	3.963	3.994	0.000	−0.388	0.381
C(6)	4.033	4.041	4.010	0.000	0.588	−0.299
			But-3-enylsilylmethyl radical			
C(1)	4.113	4.099	4.099	1.158	0.952	1.003
C(5)	4.033	3.957	4.017	0.000	−0.471	0.516
C(6)	3.992	4.044	3.990	0.000	0.650	−0.426

third is associated with bicentric interactions between atoms 1 and 2, and between atoms 4 and 5. From a consideration of the bi- and mono-centric terms the major contribution to the decrease of the activation energy is mainly due to the third group and principally to the small destabilization of the (1)–(2) bond during cyclization. In the *endo* TS the $\dot{\mathrm{C}}(1)$–C(2) deformation is 9.0 kcal mol^{-1} greater than that of $\dot{\mathrm{S}}\mathrm{i}(1)$–C(2). The difference in the alkyl chain is also important (3.7 kcal mol^{-1}). Nevertheless, the interaction between the radical centre and the double bond only gives a difference of 1.7 kcal mol^{-1}. The inexact reproduction of the global energy change is because not all interactions have been considered in this analysis. For instance, the electronic deformation of the methyl groups in radical (**6**), which are greater than the corresponding hydrogen deformations in the hex-5-enyl radical (**4**), have not been included.

At this point there is still a question: why are the transition states earlier? There are two effects to consider. First, the stabilizing energy due to new bond formation is produced at an earlier stage if the radical centre is a silicon atom. At long distances the Si···C overlap is more efficient. Secondly, the Si(1)–C(2) bond is less stable than the corresponding C(1)–C(2) bond in the hex-5-enyl radical and consequently its deformation energy will be small and the transition states can be reached early.

A final remark can be made about the activation enthalpy of this type of cyclization. For the intermolecular addition of alkyl radical to olefin the activation energies are in the range 3—10 kcal mol^{-1}.[24] In the intramolecular additions of ω-alkenyl radicals the activation energies are greater (10—30 kcal mol^{-1}).[1,11] This increase is mainly due to the strain in the chain. When the radical centre is a silicon atom the chain effects are small and the reaction is similar to an intermolecular addition.

Regioselectivity in the cyclization process can also be studied through energy-partitioning analysis. The main mono- and bi-centric contributions are associated with the interactions of the radical centre with the double bond rather than the adjacent bond [C(4)–C(5)] fragment. These contributions are collected in Table 4. The energy difference between the *exo*- and *endo*-TS is quite well reproduced by the sum of the differences between the local contributions ($\Delta_{endo\text{-TS}-exo\text{-TS}}$) in Table 4 (0.9 kcal mol^{-1}). The global difference is 1.1 kcal mol^{-1} more favourable to the *endo*-TS.

Table 4. Energy-partitioning analysis of the dimethylpent-4-enylsilyl radical cyclization. Energies in eV

Energy terms[a]	Initial radical	*exo*-TS	*endo*-TS	$\Delta_{endo\text{-TS}-exo\text{-TS}}$
*E*Si(1)–C(5)		−1.957		
*E*Si(1)–C(6)			−1.297	0.660[b]
*E*C(5)–C(6)	−24.990	−22.753	−23.459	−0.706
*E*C(4)–C(5)	−15.897	−15.549	−15.871	−0.322
*E*C(5)	−101.249	−101.523	−101.717	−0.194
*E*C(6)	−101.757	−102.560	−101.905	0.655
*E*C(1)	−80.009	−79.871	−79.998	−0.127

[a] See Figure 1 for notation. [b] Difference between *E*Si(1)–C(6) (*endo*-TS) and *E*Si(1)–C(5) (*exo*-TS).

Why is there an inversion of the regioselectivity for the hex-5-enyl radical cyclization? In previous work we showed the different factors which control the rearrangement of some alkenyl radicals.[11-13] On the other hand in the conversion of free radical into olefins the HOMO–SOMO interaction is dominant in the first steps of the reaction.[17,25,26] Attack takes place at the olefinic carbon with the greater coefficient in HOMO. For instance, in the addition of methyl radical to propene, due to the well known polarization effect of the alkyl groups,[27] attack occurs at the less substituted carbon. However, in hex-5-enyl radical cyclization the orientation of the interacting orbitals is also important.[11] The transition state structures show that in the *exo*-TS the orbitals of the two interacting carbons are better orientated to overlap and this fact counterbalances the effect of the initial polarization of the double bond which favours the *endo*-TS.[11] Now in the silyl radical cyclization, the orbital orientation effect is similar in both TSs, as the HOMO–SOMO interaction dominates the regioselectivity, as happens in intermolecular additions.

Finally, we comment on the role of the activation entropy in these silyl radical cyclizations. The entropy difference between the *exo*- and *endo*-transition states slightly favours the *exo*-TS by only 0.4 kcal mol^{-1} K^{-1}. This value contrasts with that for hex-5-enyl radical of 3.6 cal mol^{-1} K^{-1}.[11] The minor difference found now is because the changes in the transition states are minor and these are more similar to the initial radical and also to each other. So, the effects of the entropy and enthalpy contributions are opposed, but in this case the enthalpy factor is dominant, the 1,6 cyclization being more favoured.

Cyclization of the But-3-enylsilylmethyl Radical. The Silicon Atom is adjacent to the Radical Centre.—When the silicon atom is adjacent to the radical centre 1,6-cyclization is also preferred over the 1,5-cyclization.[8] The MINDO/3 transition states for the but-3-enylsilylmethyl radical (**7**) [≡ (**1**; A = CH_2, B = SiH_2)] are shown in Figure 2 and the main structural parameters of the reactant and transition states are reproduced in Table 5.

The activation enthalpies for the *exo* and *endo* modes are 21.9 and 19.5 kcal mol^{-1} respectively (Table 2). The increase in both paths with respect to the hex-5-enyl (**4**) and dimethylpent-4-enylsilyl (**6**) radicals is in good agreement with the decrease of the rate constants.[8] Nevertheless, the energy increase found by MINDO/3 method is probably too exaggerated, although if in our calculations the methyl groups were considered [B = $SiMe_2$ in (**1**)] the activation energy should be lower.[11] The activation entropy favours the *exo* form by 1.4 cal mol^{-1} K^{-1}. The enthalpy and entropy contributions are in agreement in this case, but it is the energy difference which dominates. The global effect is in excellent agreement with the experimental data.

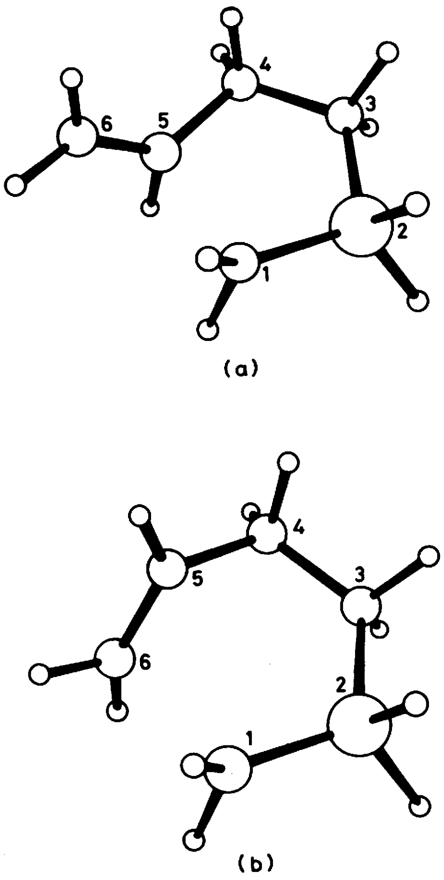

Figure 2. *exo* (a) And *endo* (b) transition states for the but-3-enylsilylmethyl radical

In 1,5-cyclization the increase of 5.4 kcal mol^{-1} in the activation energy with respect to the case in which there is a silicon atom present in the radical chain (**4**) is linked to the deformation energy in the fragment C(1)–XH(2)–C(3) (X = C or Si). To take into account only the mono- and bi-centric energy contributions associated to these five atoms and four bonds the energy difference between the two cyclizations is 6.4 kcal mol^{-1}, very near the total difference. It is necessary to remark that in this energy the main contribution becomes from the X–H bonds. In the hex-5-enyl radical these bonds suffer a great deal of stabilization during the reaction; moreover, when X is a silicon atom only moderate stabilization occurs. For the 1,6-cyclization the change is small and it is not located in a fragment of the molecule.

The energy difference between the *exo* and *endo* paths is also determined in this case by the local contributions associated with the new bond, the olefinic bond, and its adjacent bond [C(4)–C(5)]. Their mono- and bi-centric energies are in Table 6. The global energy difference is well reproduced by the sum of the $\Delta_{endo\text{-TS}-exo\text{-TS}}$ contributions. The failure of the Baldwin–Beckwith rules to this radical can be explained in the same terms as for radical (**6**). The orientation orbital effects between the radical centre and the olefinic carbons are similar for both cyclization modes because of the greater distance between atoms 1 and 2.* Therefore, the HOMO–SOMO interaction dominates the regioselectivity of the reaction.

Table 5. The main structural parameters calculated by MINDO/3 method for the reactant and transition states of the but-3-enylsilylmethyl radical

Parameters[a,b]	Reactant	*exo*-TS	*endo*-TS
C(1)–Si(2)	1.794	1.823	1.823
Si(2)–C(3)	1.877	1.877	1.883
C(3)–C(4)	1.517	1.523	1.525
C(4)–C(5)	1.493	1.509	1.492
C(5)–C(6)	1.327	1.366	1.357
C(5)–C(1)		2.180	
C(6)–C(1)			2.260
C(1)Si(2)C(3)	116.0	103.1	112.3
Si(2)C(3)C(4)	123.5	112.5	120.8
C(3)C(4)C(5)	119.8		119.4
C(4)C(5)C(6)	132.0	127.4	
C(6)C(1)Si(2)			108.3
C(5)C(1)Si(2)		99.1	
HC(6)C(5)	124.2	124.7	122.0
H'C(6)C(5)	125.4	123.8	124.2
C(1)Si(2)C(3)C(4)	−170.0	9.9	22.7
C(6)C(5)C(4)C(3)	119.6	138.5	
C(6)C(1)Si(2)C(3)			−1.7
C(5)C(1)Si(2)C(3)		0.6	

[a] Distances in Å, angles in degrees. [b] See Figure 2 for notation.

Table 6. Energy-partitioning analysis of the but-3-enylsilylmethyl radical cyclization. Energies in eV

Energy terms[a]	Initial radical	*exo*-TS	*endo*-TS	$\Delta_{endo\text{-TS}-exo\text{-TS}}$
*E*C(1)–C(5)		−2.232		
*E*C(1)–C(6)			−1.529	0.703[b]
*E*C(5)–C(6)	−25.009	−22.150	−22.841	−0.691
*E*C(4)–C(5)	−15.813	−15.489	−15.899	−0.410
*E*C(5)	−101.281	−101.752	−102.087	−0.335
*E*C(6)	−101.758	−102.847	−102.066	0.781
*E*C(1)	−105.022	−104.558	−104.746	−0.188

[a] See Figure 2 for notation. [b] Difference between *E*C(1)–C(6) (*endo*-TS) and *E*C(1)–C(5) (*exo*-TS).

In this work we have seen that the rule for the orientation of free radical additions to olefins pointed out previously[17,28] can be extended to radical cyclizations with second-row elements. Nevertheless, this should not be used without some caution. Theoretical analysis of other second-row radicals is now under way.

Acknowledgements

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* From the transition states for (**7**) (Figure 2) it can be seen that the orientation of the p_z orbitals of C(1)—(5) [in (a)] and C(1)—(6) [in (b)] should not be very different.

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