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## An *ab initio* study of some free radical homolytic substitution reactions at selenium \*

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### Abstract

*Ab initio* molecular orbital calculations at the HF/3-21G(\*) and HF/HUZ-SV\*\* levels of theory predict that homolytic substitution by alkyl and other radicals at the selenium atom in alkyl selenides proceeds via a T-shaped transition structure in which the attacking and leaving radicals are colinear, or nearly so. The calculated energy barriers suggest that the nature of the leaving group is important in these reactions, whereas the nature of the attacking alkyl radical is not. HF/HUZ-SV\*\* calculations put the energy barrier for the attack on methaneselenol by the alkyl radicals in this study at 96–105 kJ mol<sup>-1</sup>. MP2 single-point correlation correction reduces most of these barriers to about 71–80 kJ mol<sup>-1</sup>, while approximately 68 kJ mol<sup>-1</sup> is obtained using the MP4 correction. Formation of methyl radical from methaneselenol by reaction with silyl radical is predicted to be extremely favourable with an MP4/HUZ-SV\*\*//HF/HUZ-SV\*\* calculated barrier of only 12.6 kJ mol<sup>-1</sup>, reinforcing the importance of this type of reaction in generating alkyl radicals.

### Introduction

Recently, work in our laboratories has been directed towards the development of free-radical methods of forming carbon–heteroatom bonds in synthesis. In this context we reported that carbon-centred radicals undergo intramolecular homolytic substitution at the Se atom in alkyl selenides to afford selenium-containing rings in good yield [1]. We are aware of only two other reports in which homolytic substitution by carbon-centred radicals at selenium has been employed. Newcomb *et al.* used diphenyldiselenide to trap alkyl radical [2] while Byers *et al.* demonstrated that alkyl phenylselenides become involved in atom transfer reactions [3].

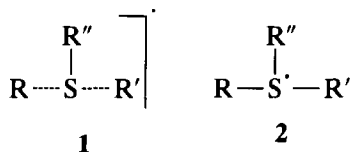
Homolytic substitution by tributylstannyl [4,5] and tributylgermyl [6] radicals on alkyl phenylselenides has been used as a method of generating alkyl radicals. More recently, Chatgililoglu and coworkers [7] have generated alkyl radicals from

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phenylselenides by use of tris(trimethylsilyl)silane and have suggested that an intermediate is involved in the attack of tris(trimethylsilyl)silyl radical at selenium.

The question of intermediate *versus* transition state in homolytic substitution reactions is a topic of current interest. In order to explain the strict inversion of configuration they observe in chiral sulphoxides, Beckwith and Boate [8] argue that homolytic substitution at the S atom in sulphoxides proceeds via a transition state in which the attacking and leaving radicals adopt a colinear arrangement (such as 1) or an intermediate (such as 2) in which the rate of pseudo-rotation is slow with respect to the rate of departure of the leaving group.



Franz *et al.* [9] suggest that their data rule out the rate-determining formation of a 9-S-3 (nine-electron, trivalent sulphur) intermediate in their study of homolytic substitution in sulphides. Other workers report that stable 9-S-3 species are formed in ESR experiments when a perester with a neighbouring sulphenyl group is photolysed [10] or when trialkylsulphonium salts are electrochemically [11] or conventionally [12] reduced. Significantly, radical stabilizing groups were present on sulphur in each of these experiments.

We have recently demonstrated [13] that homolytic substitution at the S atom by alkyl radical can occur in systems where the "required" colinear arrangement of attacking and leaving groups is physically impossible to achieve and postulated the existence of an intermediate in the rearrangement of 1,1-dideuterio-4-(phenylthio)butyl radical to 4,4-dideuterio-4-(phenylthio)butyl radical.

In order to shed some light on the mechanistic details of homolytic substitution at the Se atom, we have examined the reactions of several free radicals with various alkyl selenides by *ab initio* molecular orbital theory. Our calculations predict that all the reactions in this study proceed via a colinear transition state (such as 1) rather than a 9-Se-3 intermediate.

## Methods

*Ab initio* molecular orbital calculations were performed using the Gaussian 90 system of programs [14] on a SUN SparcStation + 1 or SparcStation 2 computer. Structures were optimized to minima or saddle points using gradient-optimization techniques [15] and proven as corresponding to the appropriate stationary point by evaluation of the complete set of harmonic force constants in each case. Structures were optimized by the restricted Hartree-Fock (RHF) method for closed-shell systems and the unrestricted Hartree-Fock (UHF) method for open-shell systems. In certain systems single-point correlation correction was applied using Møller-Plesset perturbation theory at the MP2 and MP4 levels [15].

The importance of polarization functions [15] in adequately reproducing the structural features of compounds containing chalcogens has been documented [16].

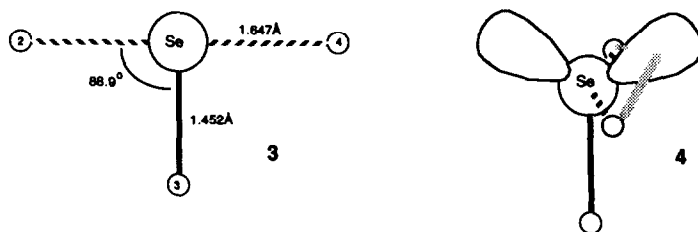


Fig. 1. UHF/HUZ-SV\*\* calculated transition structure for homolytic substitution by H atom on hydrogen selenide.

For this reason we chose to use the 3-21G(\*) basis set of Dobbs and Hehre [17] for the third row and that of Pople and coworkers [18] for the second row as our “moderate” basis set. As standard “larger” basis sets are not generally available for selenium, we chose to construct Huzinaga’s [19] Se/43321/4321/41//Si/4321/421/1//B, C, O, N/421/31/1 split valence and polarization with the Dunning/Huzinaga D95V [20] valence double zeta and polarization on H basis set. The d basis is a set of six Cartesian Gaussians in all cases. We have termed this basis set HUZ-SV\*\* by analogy with the work of Duke [21]. This basis set offers greater flexibility than 3-21G(\*) without the significant use of processor time associated with the recently reported [22] 641(d) basis set and has been shown to reliably reproduce molecular properties [23].

## Results and discussion

### *Reaction of hydrogen atom with hydrogen selenide*

A comprehensive study of the  $\text{H}_3\text{Se}$  potential energy surface indicates the existence of a T-shaped transition structure (3) in the reaction of hydrogen atom with hydrogen selenide at both UHF/3-21G(\*) and UHF/HUZ-SV\*\* levels of theory. Inspection of Fig. 1 and Table 1 clearly reveals that 3 is predicted to have a colinear arrangement of attacking and leaving groups at both levels of theory. Inclusion of electron correlation (MP2/HUZ-SV\*\*) in the optimization of 3 resulted in only minor changes to the geometry.

Table 1

Optimized data <sup>a</sup> for the transition structure 3 in the reaction of hydrogen atom with hydrogen selenide

	UHF/3-21G(*)	UHF/HUZ-SV**	MP2/HUZ-SV**	MP4/HUZ-SV**
$r(1, 2)$	1.648	1.647	1.620	—
$r(1, 3)$	1.460	1.452	1.456	—
$\theta(2, 1, 3)$	87.9	88.9	87.5	—
$\omega(2, 1, 3, 4)$	203.1	198.2	203.0	—
$E^b$	-2390.304798	-2399.315166	-2399.464158	-2399.480795 <sup>c</sup>

<sup>a</sup> Distances in ångströms, angles in degrees. <sup>b</sup> Energies in hartrees (1 H = 2625.5 kJ mol<sup>-1</sup>).  
<sup>c</sup> MP4/HUZ-SV\*\*//MP2/HUZ-SV\*\*.

The transition structure **3** is calculated to lie 67.4 and 73.6 kJ mol<sup>-1</sup> above the energy of the reactants \* at the 3-21G(\*) and HUZ-SV\*\* levels respectively. Inclusion of correlation has an important effect in that the energy barriers are lowered to 53.6 kJ mol<sup>-1</sup> at the MP2/HUZ-SV\*\* level and to 44.8 kJ mol<sup>-1</sup> using single-point MP4/HUZ-SV\*\*//MP2/HUZ-SV\*\* correction.

Close inspection of Table 1 reveals that **3** is predicted to be slightly deviated from colinearity with a dihedral angle ( $\omega(2, 1, 3, 4)$ ) of 203.1, 198.2 and 203.0° at each progressively higher level. This deviation from linearity is displayed in structure **4** (Fig. 1).

Examination of the molecular orbitals generated at the HUZ-SV\*\* level of theory provides an explanation for this phenomenon. The transition structure derives stability through the interaction of the hydrogen *s*-orbitals on the attacking and leaving groups and one of the lone pairs of electrons on selenium. This interaction is akin to hyperconjugation observed in alkyl radicals.

It is interesting to compare these data with those of Minkin and Minyaev [24] who describe nucleophilic substitution at sulphur using semi-empirical methods. Their 10-S-3 species, which are probably transition states [25], have similar T-shaped geometries to that of **3**. Indeed, transition structure **3** resembles many of the known ten-electron hypervalent molecules such as ClF<sub>3</sub>, which have longer apical and shorter equatorial bonds [26]. Interestingly, we were unable to locate any structure that might correspond to a 9-Se-3 intermediate in the homolytic substitution of hydrogen atom on hydrogen selenide.

#### *Homolytic substitution by alkyl radicals on alkyl selenides*

In order to assess the importance of the nature of the attacking alkyl radical and leaving group in homolytic substitution at selenium, reactions between methyl radical and hydrogen selenide, methaneselenol, dimethylselenide, ethaneselenol and tert-buthaneselenol were examined at both levels of theory. T-shaped transition structures were located on the calculated potential energy surface for each reaction. The UHF/HUZ-SV\*\* optimized structures are displayed in Fig. 2 while the important geometric features \*\* and energies of these transition structures are detailed in Table 2. Significantly no structures that correspond to energy minima (9-Se-3 intermediates) were located on the potential energy surface for any of these homolytic processes.

Inspection of the data in Table 2 reveals that transition structures **5** and **7**, namely those involved in the reaction of methyl radical with hydrogen selenide and dimethylselenide respectively, are slightly deviated from planarity. Once again, each transition structure (**5**, **7**) derives “hyperconjugative” stabilization by the overlap of the hydrogen *s*-orbital with one of the lone pairs of electrons on selenium.

Table 2 also reveals the expected trend in geometry as the leaving group stability is increased in moving from H atom through to the tert-butyl radical. The transition state becomes “earlier” as the attacking radical need not approach the selenium atom as closely in order to effect substitution. This is clearly evident in the UHF/HUZ-SV\*\* calculated methyl–selenium separations which increase

\* Calculated energies of reactants and products are displayed in Table 3 below.

\*\* Full geometries (*z*-matrices) are available from the authors on request.

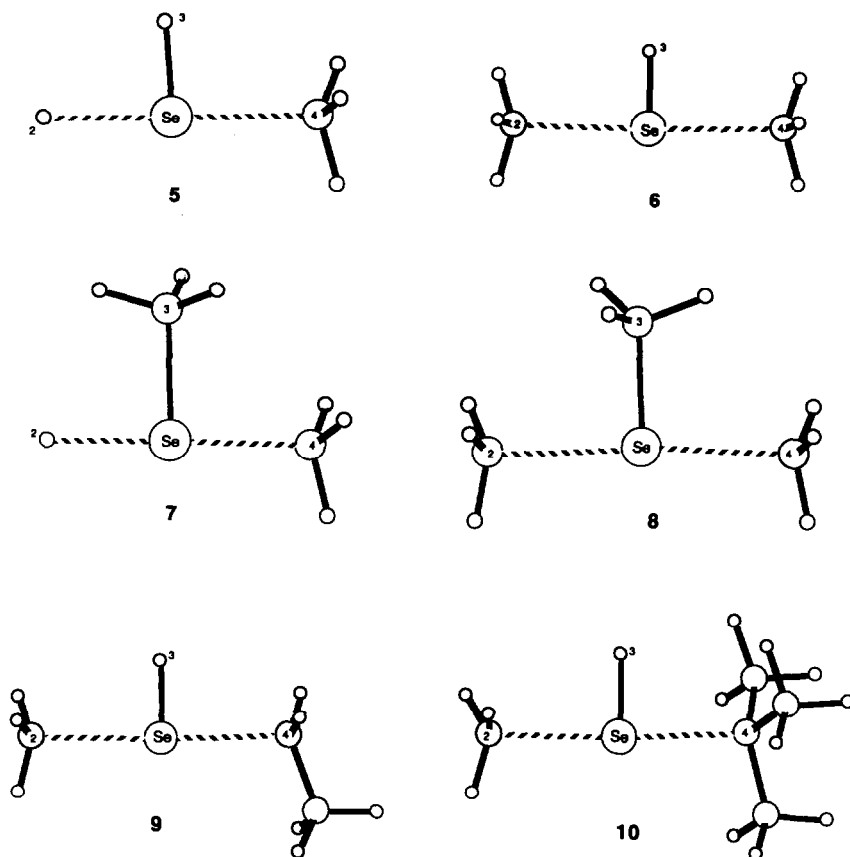


Fig. 2. UHF/HUZ-SV\*\* calculated transition structures for homolytic substitution by methyl radical on hydrogen selenide, methaneselenenol, dimethyldiselenide, ethaneselenol and tert-butaneselenol.

from 2.115 Å in **5** to 2.311 Å in **6**, 2.337 Å in **9** and 2.386 Å in **10**. The data also indicate that the presence of a methyl group instead of a hydrogen atom at the non-reacting position (i.e. **5** vs. **7**; **6** vs. **8**) has little effect on the geometry except to increase the angles  $\theta(2, 1, 3)$  and  $\theta(3, 1, 4)$  as expected on the basis of increased steric bulk.

The 3-21G(\*) and HUZ-SV\*\* calculated energies of reactants and products in the homolytic processes of this study are displayed in Table 3 while the calculated barriers\* to the formation of transition structures **5**–**10** are listed in Table 4.

The data clearly show that the nature of the leaving group is important in these reactions. At all levels of theory, the H atom is the worst leaving group. For example, a barrier of 137.7 kJ mol<sup>-1</sup> for substitution by methyl radical on hydrogen selenide is calculated using HF/HUZ-SV\*\*. At this same level, the barrier for expulsion of a methyl radical is about 96–105 kJ mol<sup>-1</sup>, depending on steric factors, while it costs only 89.5 and 79.5 kJ mol<sup>-1</sup> to expel the ethyl and tert-butyl radicals respectively. While inclusion of electron correlation results in a

\* UHF energy of transition structure less (RHF + UHF) ground state energies.

Table 2

Important calculated geometrical features <sup>a</sup> of the transition structures 5–10 in the reactions of methyl radical with alkyl selenides

Structure (symmetry)		UHF/3-21G(*)	UHF/HUZ-SV**
5(C <sub>1</sub> )	r(1, 2)	1.821	1.850
	r(1, 3)	1.460	1.453
	r(1, 4)	2.110	2.115
	θ(2, 1, 3)	85.7	86.3
	θ(3, 1, 4)	91.9	93.0
	ω(2, 1, 3, 4)	196.1	182.1
	E <sup>b</sup>	-2429.134699	-2438.315699
	E(MP2) <sup>c</sup>	-	-2438.596870
E(MP4) <sup>d</sup>	-	-2438.638871	
6(C <sub>2v</sub> )	r(1, 2)	2.279	2.311
	r(1, 3)	1.461	1.454
	θ(2, 1, 3)	88.6	88.9
	E <sup>b</sup>	-2467.969929	-2477.322532
	E(MP2) <sup>c</sup>	-	-2477.738337
	E(MP4) <sup>d</sup>	-	-2477.801885
7(C <sub>1</sub> )	r(1, 2)	1.777	1.803
	r(1, 3)	1.959	1.957
	r(1, 4)	2.096	2.094
	θ(2, 1, 3)	88.3	89.8
	θ(3, 1, 4)	93.0	93.8
	ω(2, 1, 3, 4)	203.3	197.7
	E <sup>b</sup>	-2467.957541	-2477.306603
	E(MP2) <sup>c</sup>	-	-2477.738490
E(MP4) <sup>d</sup>	-	-2477.797084	
8(C <sub>s</sub> )	r(1, 2)	2.264	2.301
	r(1, 3)	1.964	1.963
	r(1, 4)	2.264	2.292
	θ(2, 1, 3)	91.9	90.7
	θ(3, 1, 4)	91.9	93.7
	ω(2, 1, 3, 4)	172.8	180.0
	ω(2, 1, 3, 4)	90.0	180.0
	E <sup>b</sup>	-2506.790479	-2516.311204
E(MP2) <sup>c</sup>	-	-2516.877374	
9(C <sub>s</sub> )	r(1, 2)	2.297	2.337
	r(1, 3)	1.461	1.454
	r(1, 4)	2.271	2.315
	θ(2, 1, 3)	88.2	88.4
	θ(3, 1, 4)	89.1	88.9
	E <sup>b</sup>	-2506.790609	-2516.318191
E(MP2) <sup>c</sup>	-	-2516.879176	
10(C <sub>s</sub> )	r(1, 2)	2.315	2.386
	r(1, 3)	1.461	1.454
	r(1, 4)	2.260	2.334
	θ(2, 1, 3)	87.6	87.4
	θ(3, 1, 4)	89.1	89.2
	E <sup>b</sup>	-2584.436291	-2594.310010

<sup>a</sup> Distances in ångströms, angles in degrees. Full geometries (z-matrices) available from the authors on request. <sup>b</sup> Energies in hartrees (1 H = 2625.5 kJ mol<sup>-1</sup>). <sup>c</sup> MP2/HUZ-SV\*\*//UHF/HUZ-SV\*\*. <sup>d</sup> MP4/HUZ-SV\*\*//UHF/HUZ-SV\*\*.

Table 3

Calculated energies <sup>a</sup> for reactants and products in the homolytic substitution reactions of this study

Structure	3-21G(*)	HUZ-SV**	MP2 <sup>b</sup>	MP4 <sup>c</sup>
H <sup>•</sup>	-0.496198	-0.497637	-	-
•CH <sub>3</sub>	-39.342610 <sup>d</sup>	-39.521842	-39.651153	-39.673819
•CH <sub>2</sub> CH <sub>3</sub>	-78.163647	-78.517973	-78.790355	-
•C(CH <sub>3</sub> ) <sub>3</sub>	-155.809101 <sup>e</sup>	-156.512345	-	-
•CH <sub>2</sub> OH	-133.77382 <sup>f</sup>	-114.299665	-114.612015	-
•CH <sub>2</sub> BH <sub>2</sub>	-64.461904	-64.755825	-64.959812	-
•NH <sub>2</sub>	-55.245376	-55.505773	-55.651393	-55.671132
•SiH <sub>3</sub>	-289.166164	-290.203103	-290.285363	-290.307540
H <sub>2</sub> Se	-2389.834299 <sup>g</sup>	-2398.845643	-2398.979038	-2399.000158
CH <sub>3</sub> SeH	-2428.657109 <sup>g</sup>	-2437.836951	-2438.116424	-2438.153937
CH <sub>3</sub> SeCH <sub>3</sub>	-2467.481139 <sup>h</sup>	-2476.829353	-2477.256600	-
<sup>t</sup> BuSeH	-2545.119694	-2554.818539	-	-
BH <sub>2</sub> CH <sub>2</sub> SeH	-2543.760273	-2463.054514	-2463.409645	-
NH <sub>2</sub> SeH	-2444.546665	-2453.798870	-2454.103176	-2454.135408
SiH <sub>3</sub> SeH	-2675.511998	-2688.544855	-2688.766532	-2688.804945

<sup>a</sup> Energies (UHF for open-shell; RHF for closed-shell) in hartrees (1 H = 2625.5 kJ mol<sup>-1</sup>). Full geometries (z-matrices) are available from the authors on request. <sup>b</sup> MP2/HUZ-SV\*\*//HF/HUZ-SV\*\*. <sup>c</sup> MP4/HUZ-SV\*\*//HF/HUZ-SV\*\*. <sup>d</sup> Ref. 27. <sup>e</sup> Ref. 28. <sup>f</sup> Ref. 29. <sup>g</sup> Ref. 17. <sup>h</sup> Ref. 16.

lowering of these barriers using both MP2 and MP4 correction, the trend observed in the uncorrelated data is still apparent.

Interestingly, the reverse reactions show no such trend. While it is clear that hydrogen atom is the best attacking species, with an MP4/HUZ-SV\*\*//HF/HUZ-SV\*\* calculated barrier of only 28.9 kJ mol<sup>-1</sup> for the expulsion of the methyl group in methaneselenol, the remaining radicals all appear to have similar energy requirements in their respective homolytic substitution reactions on either methaneselenol or dimethylselenide with the loss of methyl radical. HF/HUZ-SV\*\* calculations predict an energy barrier of 96–105 kJ mol<sup>-1</sup> regardless of whether the attacking radical is methyl, ethyl or tert-butyl. These calculated barriers are reduced somewhat to about 71–80 kJ mol<sup>-1</sup> when single-point MP2 correlation correction is applied; however, due to size constraints, no correlated data are available for the reaction involving transition structure **10**. This

Table 4

Calculated energy barriers <sup>a</sup> for homolytic substitution of methyl radical on some alkyl selenides

Reaction	Transition structure	321G(*)	HUZ-SV**	MP2 <sup>b</sup>	MP4 <sup>c</sup>
•CH <sub>3</sub> + H <sub>2</sub> Se	<b>5</b>	110.9(49.4)	136.0(49.9)	87.4(45.2)	92.0(33.5)
•CH <sub>3</sub> + CH <sub>3</sub> SeH	<b>6</b>	78.2	95.4	76.6	67.8
•CH <sub>3</sub> + CH <sub>3</sub> SeH	<b>7</b>	110.9(51.9)	136.8(53.6)	76.6(41.4)	80.8(28.9)
•CH <sub>3</sub> + CH <sub>3</sub> SeCH <sub>3</sub>	<b>8</b>	87.4	105.0	79.9	-
•CH <sub>3</sub> + CH <sub>3</sub> CH <sub>2</sub> SeH	<b>9</b>	74.1(79.1)	89.5(96.2)	73.6(72.4)	-
•CH <sub>3</sub> + <sup>t</sup> BuSeH	<b>10</b>	68.2(78.7)	79.5(103.3)	-	-

<sup>a</sup> UHF energy of TS less UHF+RHF energy of GS. Energies in kJ mol<sup>-1</sup>. (Reverse reaction in parentheses.) <sup>b</sup> MP2/HUZ-SV\*\*//HF/HUZ-SV\*\*. <sup>c</sup> MP4/HUZ-SV\*\*//HF/HUZ-SV\*\*.

barrier appears to be even further reduced when MP4 correction is applied. Structure **6** is calculated to lie only  $67.8 \text{ kJ mol}^{-1}$  above the energy of the reactants using MP4/HUZ-SV\*\*//HF/HUZ-SV\*\* single-point correction.

Our data appear to suggest that while the nature of the leaving group is important in homolytic substitution reactions on selenium, the nature of the attacking carbon-centred radical is not.

#### *Homolytic substitution by hetero-substituted radicals on methaneselenol*

Having obtained a better understanding of some of the factors that influence homolytic substitution by carbon-centred radicals on alkyl selenides, we next turned our attention to systems of varying electronic demand. In particular, we were interested in the role that electron-donating and electron-withdrawing groups on the attacking radical plays in the reactions and, as a consequence, we chose to examine the reaction of hydroxymethyl ( $\cdot\text{CH}_2\text{OH}$ ) and boramethyl ( $\cdot\text{CH}_2\text{BH}_2$ ) radicals with methaneselenol. Additionally, our interest in the synthesis of selenazoles and in the use of selenides as free-radical precursors encouraged the investigation of the homolytic substitution by amidogen radical ( $\cdot\text{NH}_2$ ) and silyl radical ( $\cdot\text{SiH}_3$ ) on methaneselenol. In all cases, the leaving group was a methyl radical. Once again, only T-shaped transition structures could be located at both levels of theory in each case. These structures are displayed in Fig. 3 while the important geometric data are displayed in Table 5.

Structures **11–13** reveal that the transition states in the homolytic reactions of stabilized carbon-centred radicals are slightly later than those involving non-stabilized alkyl radicals. This is reflected in the relatively large values for the selenium–methyl separation, calculated to be 2.368 and 2.399 Å at the UHF/HUZ-SV\*\* level of theory for **11** and **12** respectively. The selenium–carbon [ $r(1, 4)$ ] distances of 2.322 (**11**) and 2.360 Å (**12**) at the same level of theory, however, show little change from the values calculated for non-stabilized alkyl

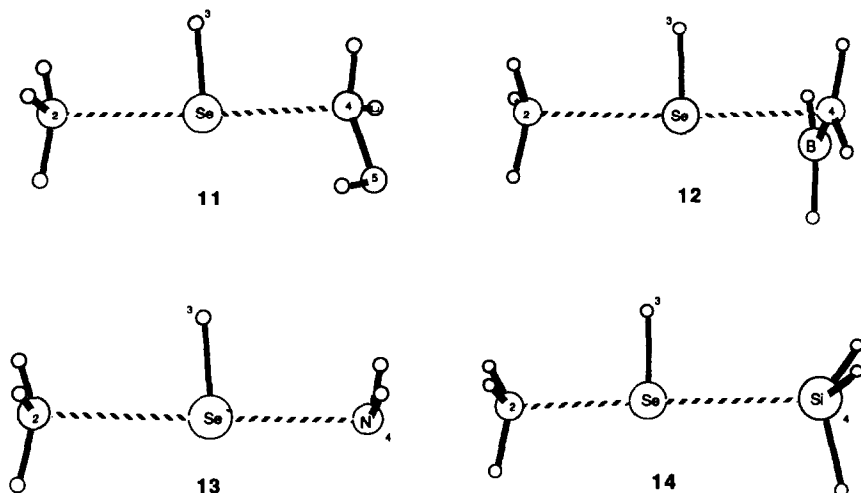


Fig. 3. UHF/HUZ-SV\*\* calculated transition structures for homolytic substitution by hydroxymethyl, boramethyl, amidogen and silyl radicals on methaneselenol.



Table 5

Important calculated geometrical features <sup>a</sup> of the transition structures 11–14 in the reactions of some hetero-substituted alkyl radicals with methaneselenol

Structure (symmetry)	UHF/3-21G(*)	UHF/HUZ-SV**	
11(C <sub>1</sub> )	<i>r</i> (1, 2)	2.237	2.368
	<i>r</i> (1, 3)	1.462	1.455
	<i>r</i> (1, 4)	2.272	2.322
	<i>r</i> (4, 5)	1.404	1.360
	$\theta$ (2, 1, 3)	87.4	87.5
	$\theta$ (3, 1, 4)	89.2	89.3
	$\omega$ (2, 1, 3, 4)	180.0	180.0
	<i>E</i> <sup>b</sup>	-2542.400145	-2552.100313
<i>E</i> (MP2) <sup>c</sup>	-	-2552.697297	
12(C <sub>1</sub> )	<i>r</i> (1, 2)	2.370	2.399
	<i>r</i> (1, 3)	1.458	1.453
	<i>r</i> (1, 4)	2.310	2.360
	<i>r</i> (1, B)	2.507	2.607
	<i>r</i> (4, B)	1.552	1.548
	$\theta$ (1, 3, 4)	78.3	80.8
	$\theta$ (2, 1, 3)	87.1	87.7
	$\theta$ (3, 1, 4)	88.5	89.0
	$\omega$ (2, 1, 3, 4)	172.8	179.0
	<i>E</i> <sup>b</sup>	-2493.091627	-2502.555452
<i>E</i> (MP2) <sup>c</sup>	-	-2503.051774	
13(C <sub>s</sub> )	<i>r</i> (1, 2)	2.356	2.471
	<i>r</i> (1, 3)	1.468	1.460
	<i>r</i> (1, 4)	2.155	2.199
	$\theta$ (2, 1, 3)	85.3	84.6
	$\theta$ (3, 1, 4)	94.8	94.8
	<i>E</i> <sup>b</sup>	-2483.861308	-2493.292631
	<i>E</i> (MP2) <sup>c</sup>	-	-2493.723694
<i>E</i> (MP4) <sup>d</sup>	-	-2493.785148	
14(C <sub>s</sub> )	<i>r</i> (1, 2)	2.140	2.181
	<i>r</i> (1, 3)	1.460	1.453
	<i>r</i> (1, 4)	2.693	2.686
	$\theta$ (2, 1, 3)	91.7	91.7
	$\theta$ (3, 1, 4)	89.1	89.6
	<i>E</i> <sup>b</sup>	-2717.807508	-2728.023151
	<i>E</i> (MP2) <sup>c</sup>	-	-2728.394240
<i>E</i> (MP4) <sup>d</sup>	-	-2728.456671	

<sup>a</sup> Distances in ångströms, angles in degrees. Full geometries (*z*-matrices) available from the authors on request. <sup>b</sup> Energies in hartrees (1 H = 2625.5 kJ mol<sup>-1</sup>). <sup>c</sup> MP2/HUZ-SV\*\*//UHF/HUZ-SV\*\*. <sup>d</sup> MP4/HUZ-SV\*\*//UHF/HUZ-SV\*\*.

radicals. Further to this, the calculated activation barriers (Table 6) indicate, once again, the relative unimportance of the nature of the attacking carbon-centred radical. The HUZ-SV\*\* calculated values of 95.4 and 97.9 kJ mol<sup>-1</sup> for the attack of hydroxymethyl and boramethyl radicals respectively on methaneselenol lie close to the 96–105 kJ mol<sup>-1</sup> range previously determined for the attack of other alkyl

Table 6

Calculated energy barriers <sup>a</sup> for homolytic substitution by some hetero-substituted alkyl radicals on methaneselenol

Reaction	Transition structure	3-21G(*)	HUZ-SV**	MP2 <sup>b</sup>	MP4 <sup>c</sup>
·CH <sub>2</sub> OH + CH <sub>3</sub> SeH	<b>11</b>	80.8(68.2)	95.4(80.8)	81.6(65.3)	–
·CH <sub>2</sub> BH <sub>2</sub> + CH <sub>3</sub> SeH	<b>12</b>	72.0(29.7)	97.9(54.8)	56.5(23.8)	–
·NH <sub>2</sub> + CH <sub>3</sub> SeH	<b>13</b>	107.9(73.2)	131.4(73.6)	115.9(80.3)	112.5(63.2)
·SiH <sub>3</sub> + CH <sub>3</sub> SeH	<b>14</b>	41.4(123.8)	44.4(114.2)	19.7(120.9)	12.6(58.2)

<sup>a</sup> UHF energy of TS less UHF+RHF energy of GS. Energies in kJ mol<sup>-1</sup>. (Reverse reaction in parentheses.) <sup>b</sup> MP2/HUZ-SV\*\*//HF/HUZ-SV\*\*. <sup>c</sup> MP4/HUZ-SV\*\*//HF/HUZ-SV\*\*.

radicals. Single-point MP2 correction has the effect of lowering these barriers to 81.6 and 64.0 kJ mol<sup>-1</sup>.

Inspection of the data in Table 5 reveals that the boron is involved in the stabilization of transition structure **12**. Both levels of theory predict a favourable interaction between the selenium lone-pair of electrons and the unoccupied *p*-orbital on boron. This manifests itself in rather short Se–B separations of 2.507 and 2.607 Å calculated with the 3-21G(\*) and HUZ-SV\*\* basis sets respectively and in Se–C–B angles of 78.3 and 80.8° at the lower and higher levels respectively.

The data for the attack of amidogen radical on methaneselenol indicate that this is a rather unfavourable process, with an associated energy barrier of 131.4 kJ mol<sup>-1</sup> at the HF/HUZ-SV\*\* level and values of 115.9 and 112.5 kJ mol<sup>-1</sup> when single-point MP2 and MP4 correction is applied.

The reverse reactions appear to be more favourable in all cases with relatively low MP2/HUZ-SV\*\*//HF/HUZ-SV\*\* calculated barriers for the expulsion of hydroxymethyl (65.3 kJ mol<sup>-1</sup>), boramethyl (23.8 kJ mol<sup>-1</sup>) and amidogen (80.3 kJ mol<sup>-1</sup>) radicals by methyl radical. This is as expected on the basis of leaving group stability. The value of 23.8 kJ mol<sup>-1</sup> calculated for the displacement of boramethyl radical by methyl radical suggests the use of the former as a potential leaving group in synthesis.

Finally, attack of the silyl radical on methaneselenol reveals some interesting features. The transition state is calculated to be quite early, with Si–Se separations of 2.693 and 2.686 Å at the lower and higher levels respectively and with Se–C distances of 2.140 and 2.181 Å. This early transition state is also reflected in the relative ease in which the silyl radical is predicted to attack the selenium centre. The HUZ-SV\*\* calculated energy barrier of 44.4 kJ mol<sup>-1</sup> is reduced to only 12.6 kJ mol<sup>-1</sup> when single-point MP4 correction is applied. This low barrier is undoubtedly responsible for the role that selenides play as precursors to alkyl radicals in reactions involving reagents such as tris(trimethylsilyl)silane. It should be noted that this reaction is predicted to proceed via a T-shaped transition structure, as opposed to an intermediate suggested by Chatgililoglu and coworkers for the attack of tris(trimethylsilyl)silyl radical on alkyl phenyl selenides [7].

## Conclusion

These calculations have shown that homolytic substitution by alkyl and other radicals at the selenium atom in alkyl selenides proceeds via a T-shaped transition

structure in which the attacking and leaving groups are colinear or nearly so. No intermediate was located for any homolytic process in this study. Calculated energy barriers indicate the importance of the nature of the leaving radical in these substitution reactions; however, the nature of the attacking carbon-centred radical would appear to be relatively unimportant.

Finally, an energy barrier of only 12.6 kJ mol<sup>-1</sup> has been calculated at the MP4/HUZ-SV\*\*//HF/HUZ-SV\*\* level of theory for the attack of silyl radical on methaneselenol, reinforcing the importance of reactions of this type for the generation of alkyl radicals.

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