Pergamon

Tetrahedron Vol. 51, No. 21, pp. 6051-6060, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00263-4

An *Ab Initio* Study of Some Free-Radical Homolytic Substitution Reactions at Sulfur, Selenium and Tellurium[1]

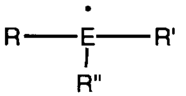
Carl H. Schiesser* and Bruce A. Smart

School of Chemistry, The University of Melbourne, Parkville, Victoria, Australia, 3052

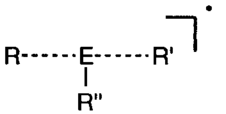
Abstract: Ab initio *molecular orbital calculations using pseudopotential basis sets and electron correlation (MP2, QCISD) predict that homolytic substitution by methyl, silyl, germyl and stannyl radicals at the chalcogen atom in methanethiol, methaneselenol and methanetellurol, with the expulsion of methyl radical, proceeds smoothly. With the exception of dimethyl-λ^4-tellanyl at the MP2 and QCISD levels of theory, no hypervalent (9-E-3) intermediates were located in any of the reactions in this study. Reactions of germyl and stannyl radicals at methaneselenol and methanetellurol are predicted to be reversible.*

Introduction

Over the last 10-15 years, the free-radical chemistry of sulfur-, selenium-, and more recently tellurium-containing compounds has been explored and utilized in many synthetic transformations. While the use of these chalcogen-containing species as precursors of carbon[2], nitrogen[3] and oxygen[4] -centred radicals has been established for some time now, inter- and intramolecular group transfer reactions[5,6] and the preparation of chalcogen-containing heterocycles by intramolecular homolytic substitution at sulfur[7] and selenium[8,9] are illustrative of current work in this area.



1



2 (E = S, Se, Te)

The question of the involvement of hypervalent (9-E-3) intermediates in the homolytic attack of radicals at sulfur, selenium and tellurium has been the subject of recent theoretical interest. It is generally agreed that the reaction at both sulfur and selenium proceeds via either a transient intermediate (**1**) or a T-shaped transition structure (**2**) in which the attacking and leaving groups adopt a near colinear arrangement.[10] Unless radical stabilizing groups are present on sulfur and selenium,[11] *ab initio* calculations using double-ζ basis sets, both with and without electron correlation (MP2) have failed to locate any hypervalent intermediate (**1**) in homolytic substitution reactions at sulfur and selenium.[8,11-14] Interestingly, semiempirical (PM3) calculations predict the involvement of an intermediate in the rearrangement of the 4-phenylthiobut-1-yl radical.[15] In comparison, the similar substitution process at the phosphorus atom in phosphines is predicted to proceed with the involvement of intermediates at all levels of theory.[16]

We recently demonstrated that basis sets of triple-ζ quality and high levels of correlation (QCISD) are neccessary to determine conclusively the nature of stationary points associated with hypervalent (9-E-3) sulfur and selenium containing structures.[17] λ^4-Sulfanyl (SH_3), a species with a measured lifetime of at least 0.56

μs,[18] is predicted to be a transition state even when calculations using QCISD/6-311G(2df,2p) are performed. In comparison, we have shown the pseudopotential basis set of Hay and Wadt[19] to be the basis of choice in calculations involving homolytic substitution at chalcogen.[17] Indeed, in our recent study, only this basis set at the QCISD level of theory was able to predict correctly that nature of λ^4-sulfanyl. Similarly, λ^4-selanyl (SeH_3) was also predicted to be an intermediate in the homolytic attack of hydrogen atom at hydrogen selenide, in agreement with high level (triple-ζ, QCISD) all electron calculations.[17]

These recent data cast doubt on our, and other, previous work.[11-13] We felt that this homolytic substitution chemistry required re-examination and expansion to include tellurium and other common attacking radicals. As such, the potential energy surfaces for the attack of methyl, silyl, germyl and stannyl radicals at the chalcogen atom in methanethiol, methaneselenol and methanetellurol (with the loss of methyl radical) were examined using the pseudopotential basis set of Hay and Wadt, with and without the inclusion of electron correlation, with the aim of providing further mechanistic insight into these free-radical processes.

Methods

All *ab initio* molecular orbital calculations were carried out using the Gaussian 92 program.[20] Geometry optimisations and vibrational frequencies were performed using standard gradient techniques at the SCF and MP2 levels of theory using RHF and UHF methods for closed and open shell systems, respectively.[21] Further single-point QCISD calculations were performed on each of the MP2 optimised structures. When correlated methods were used calculations were performed using the frozen core approximation.

All vibrational frequencies were calculated numerically from analytic first derivatives to determine the nature of all located stationary points. Calculations were performed on all reactants, products and transition states to obtain barriers and energies of reaction.

The (valence) double-ζ pseudopotential basis sets of Hay and Wadt[19] supplemented with a single set of d-type polarisation functions were used for the heteroatoms in this study (exponents d(ζ) as recommended by Höllwarth and co-workers[22] were used for Si, Ge, Sn; exponents d(ζ) of 0.60, 0.38 and 0.30 were used for S, Se, Te respectively[17]) while the double-ζ all-electron basis sets of Dunning[23] with an additional set of polarisation functions (exponents $d(\zeta)_C = 0.75$ and $p(\zeta)_H = 1.00$) were used for C and H.

Results and Discussion

Reaction of Methyl Radical with Methanethiol, Methaneselenol and Methanetellurol

The hypervalent dimethyl-λ^4-chalcogenyl species (**3**, **4**), which include dimethyl-λ^4-sulfanyl (Me_2SH), dimethyl-λ^4-selanyl (Me_2SeH) and dimethyl-λ^4-telluryl (Me_2TeH) were located on their respective potential energy surfaces. Calculated geometries are displayed in Figure 1, while the energy barriers ($\Delta E^{\#}$) for the reactions as depicted in Scheme 1 are listed in Table 1. Calculated energies of all structures in this study are listed in Table 3.

Structures (**3**) are predicted to be of C_{2v} symmetry and to correspond to transition states at the SCF level of theory. When electron correlation (MP2) is introduced into the calculation, structures (**3**) are predicted to deviate somewhat from planarity to geometries of C_s symmetry. Additionally, dimethyl-λ^4-tellanyl (Me_2TeH) is found to correspond to a hypervalent (9-Te-3) intermediate at the MP2 level; this structure is calculated to lie some 4.4 kJ.mol^{-1} ($\Delta E_2^{\#}$) below the transition state (**4**) for its formation, which in turn is predicted to lie 29.7 kJ.mol^{-1} above the reactants (CH_3 + MeTeH). When single-point QCISD calculations are performed on the

MP2 structure (QCISD//MP2), (**4**) is found to be 1.2 kJ.mol^{-1} lower in energy than (**3**), which is calculated to lie some 27.2 kJ.mol^{-1} above the reactants. Since the transition state geometry for EH_3 structures is known to change substantially when the level of theory is improved,[17] it is likely that the structures of (**3**) and (**4**) need to be optimized using QCISD to obtain reliable data, a task which is beyond our current resources. The value of 27.2 kJ.mol^{-1} can only be taken as an approximate QCISD energy barrier.

Scheme1

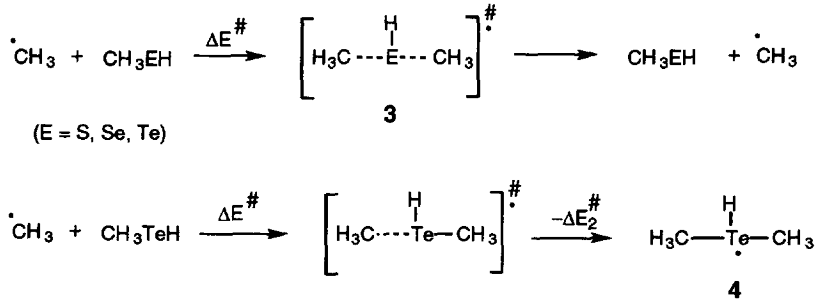


Table 1. SCF, MP2 and QCISD//MP2 Calculated Energy Barriers[a] ($\Delta E^{\#}$) for the Homolytic Substitution Reactions of Methyl Radical at the Chalcogen in Methanethiol, Methaneselenol and Methanetellurol (Scheme 1).

Transition State	SCF	MP2	QCISD//MP2
	$\Delta E^{\#}$	$\Delta E^{\#}$	$\Delta E^{\#}$
Me_2SH	127.3	87.9	89.1
Me_2SeH	96.9	63.1	63.0
Me_2TeH[b]	68.4	29.7	26.0

[a]Energies in kJ.mol^{-1}. For details of the basis set used, see text. [b]Structure (3) at the SCF level, structure (4) at the MP2 and QCISD levels.

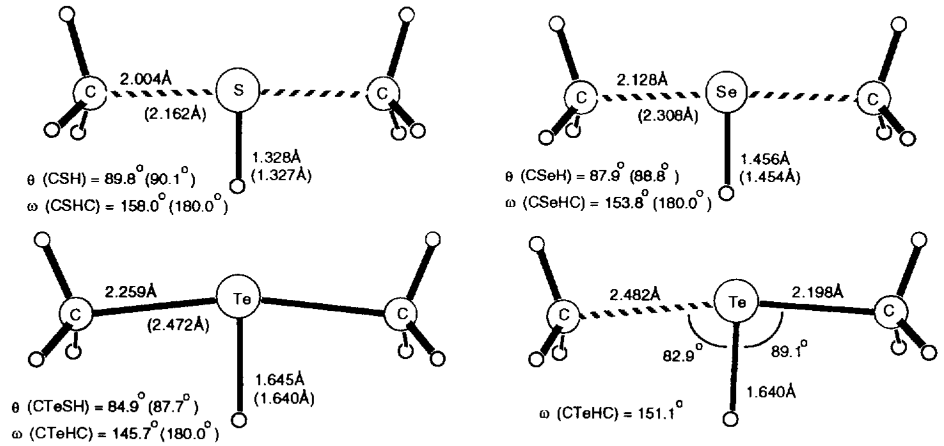
The structures (**3**) depicted in Figure 1 are to be compared with the transition structures, calculated using the same basis set, for the homolytic substitution of methyl radical at the halogen atom in halomethanes which are predicted to have a colinear arrangement of attacking and leaving groups at both levels of theory.[24] For example, the MP2-calculated C-E distance of 2.004Å (S), 2.129Å (Se) and 2.259Å (Te) are slightly shorter than the corresponding C-X distances of 2.062Å (Cl), 2.201Å (Br) and 2.363Å (I) and are consistent with the smaller covalent radii associated with the chalcogens.

Calculated energy barriers are somewhat lower than for the corresponding attack of methyl radical at halogen. For example, QCISD//MP2 calculations predict energy barriers of 117.6, 81.9 and 53.2 kJ.mol^{-1} for attack at the chlorine, bromine and iodine atoms respectively in halomethanes,[24] compared with 89.1, 63.0 and 26.0 kJ.mol^{-1} for the similar attack at sulfur, selenium and tellurium respectively at the same level of theory.

The reactions depicted in Scheme 1 are representative of *group transfer* reactions and their synthetic utility has been discussed previously.[5,6] The calculations reported in this work provide mechanistic insight into these reactions; chalcogen transfer between carbon centres would appear to prefer a bent arrangement of attacking and leaving radicals, tellurium is predicted to undergo transfer most efficiently and with the involvement of a short-lived hypervalent (9-Te-3) intermediate. These data are in agreement with the conclusions drawn by Curran and coworkers in their study of leaving group effects in intramolecular phenylseleno group transfer reactions which appear to be consistent with direct displacement reactions.[6]

The following order of reactivity for homolytic substitution by methyl radical is therefore suggested: Cl < S < Br < Se < I < Te and is in qualitative agreement with available rate data for the attack of a variety of carbon-centred radicals at both halogens and chalcogens.[6,25]

Figure 1. MP2 Calculated Geometries[a] of the Structures (**3**, **4**) involved in the Homolytic Substitution of Methyl Radical at the Chalcogen in Methanethiol, Methaneselenol and Methanetellurol (SCF Data in Parentheses).

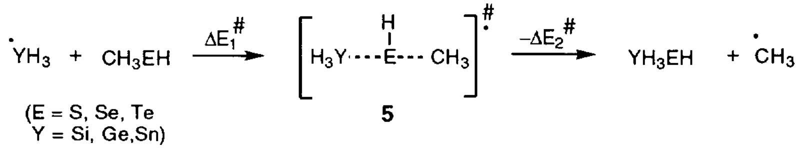


[a] For description of basis set used, see text. Full geometries are available from the authors on request.

Reaction of Silyl, Germyl and Stannyl Radical with Methanethiol, Methaneselenol and Methanetellurol.

We next turned our attention to the attack of silyl (•SiH_3), germyl (•GeH_3) and stannyl (•SnH_3) radicals at the chalcogen atom in methanethiol, methaneselenol and methanetellurol (Scheme 2). Alkyl phenylsulfides and selenides are commoly used as precursors for the formation of carbon-centred radicals; chain-carrying radicals such as tributyltin are often used in these processes.[2] These calculations should, therefore provide mechanistic insight into homolytic substitution reactions involving these species.

Scheme 2



$$\dot{Y}H_3 + CH_3EH \xrightarrow{\Delta E_1^{\#}} \left[H_3Y\cdots\overset{H}{\underset{|}{E}}\cdots CH_3 \right]^{\#\,\bullet} \xrightarrow{-\Delta E_2^{\#}} YH_3EH + \dot{C}H_3$$

(E = S, Se, Te
Y = Si, Ge,Sn)

5

At both SCF and MP2 levels of theory, only transition stuctures (**5**) could be located on the appropriate potential energy surfaces, strongly suggesting that these chain-carrying radicals abstract sulfur, selenium and tellurium from alkyl chalcogenols via smooth transitions states. Inspection of Figure 2 reveals that apart from the attack of silyl radical at selenium, MP2 calculations predict a colinear arrangement of attacking and leaving species in reactions involving sulfur and selenium, with transition structures of C_s symmetry.

Attack of silyl radical at selenium is predicted to involve a structure of C_s symmetry at the SCF level of theory, and to deviate somewhat from the colinear arrangement of apical ligands at the higher level of theory with an MP2-calculated dihedral angle ω(CSeHSi) of 159.8°. In contrast, all transition states involving tellurium are predicted to deviate from colinearity at the MP2 level, with dihedral angles ω(CTeHY) ranging from 152.3° to 161.7. Only very slight deviations from colinearity are predicted at the at the lower level.

Calculated transition states (**5**) are displayed in Figure 2, calculated energy barriers ($\Delta E_1^{\#}$, $\Delta E_2^{\#}$) for the forward and reverse reactions are listed in Table 2, while calculated energies of **5** are listed in Table 3.

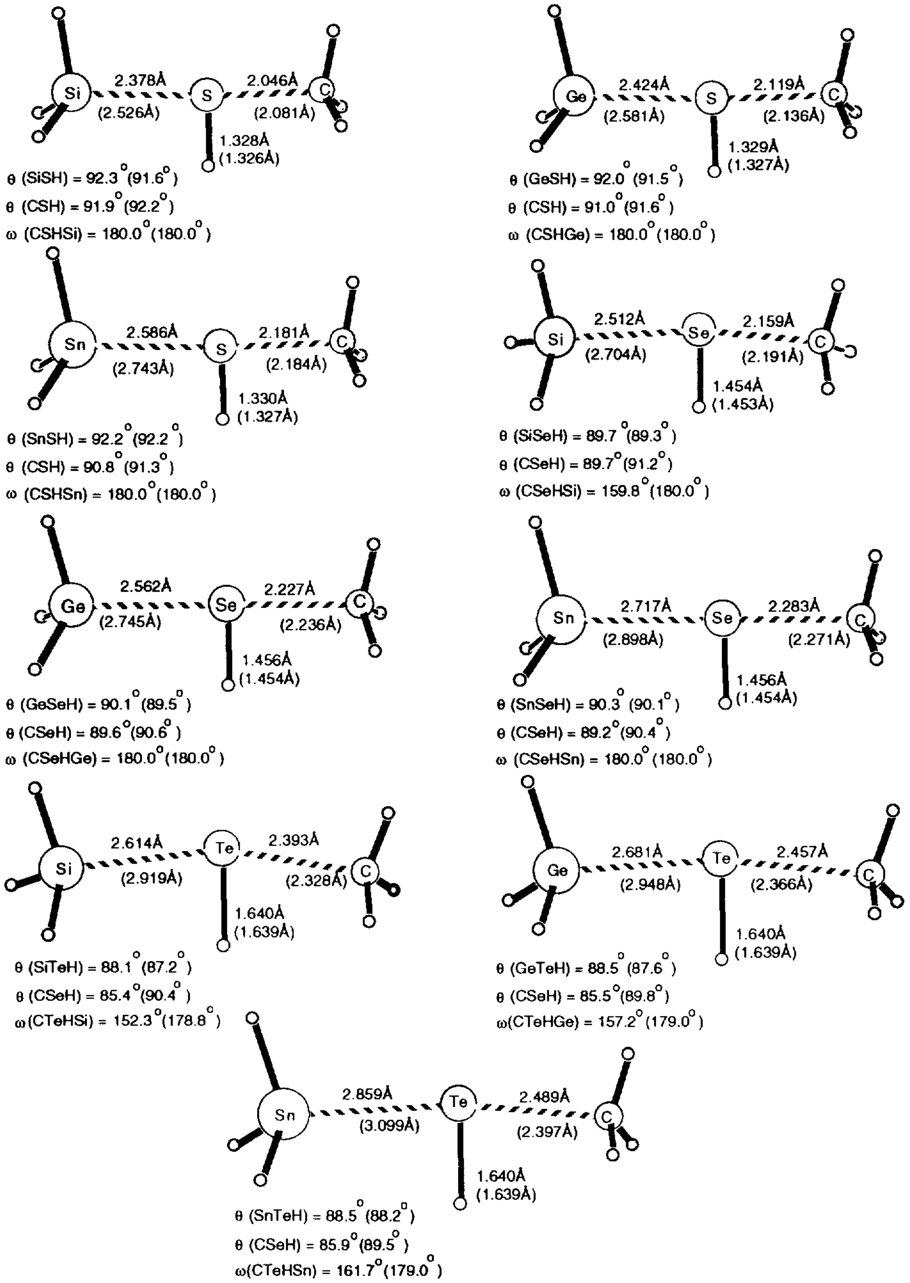
Inspection of Table 2 reveals some interesting features. For each abstracting radical, tellurium, as expected, is the easiest of the chalcogens to abstract, while sulfur is the most difficult. QCISD//MP2 Calculated energy barriers range from 82.7 kJ.mol^{-1} for the abstraction of sulfur by stannyl to 9.6 kJ.mol^{-1} for the abstraction of tellurium by silyl. On the other hand, silyl is predicted to be to be a better chalcogen abstractor than germyl which, in turn, is better than stannyl. The low barriers for reactions at selenium and tellurium are undoubtedly responsible for the success which silicon, germanium and tin-centred reagents have had in the generation of alkyl radicals from alkylselenides and tellurides. The higher barriers for attack at sulfur are consistent with the lack of reactivity of primary phenylsulfides toward abstraction by tributylstannyl radicals.[26] While the reactions involving silyl radical are calculated to be substantially exothermic in all cases, with QCISD//MP2 calculated exothermicities ($\Delta E_2^{\#}$-$\Delta E_1^{\#}$) of 36.6 kJ.mol^{-1} (S), 38.2 kJ.mol^{-1} (Se) and 29.3 kJ.mol^{-1} (Te), the same can not be said for the homolytic attack of germyl and stannyl radicals at sulfur, selenium and tellurium; germyl is calculated to react far less exothermically than silyl, with exothermicities of 4.4 kJ.mol^{-1} (S), 12.7 kJ.mol^{-1} (Se) and 10.2 kJ.mol^{-1} (Te) at the same level of theory.

Table 2. SCF, MP2 and QCISD/MP2 Calculated Energy Barriers[a] ($\Delta E_1^{\#}$, $\Delta E_2^{\#}$) for the Forward and Reverse Homolytic Substitution Reactions of Silyl (·SiH_3), Germyl (·GeH_3) and Stannyl (·SnH_3) Radicals at the Chalcogen Atom in Methanethiol, Methaneselenol and Methanetellurol (Scheme 2).

Transition State (5)	SCF		MP2		QCISD//MP2	
	$\Delta E_1^{\#}$	$\Delta E_2^{\#}$	$\Delta E_1^{\#}$	$\Delta E_2^{\#}$	$\Delta E_1^{\#}$	$\Delta E_2^{\#}$
$H_3SiS(H)CH_3$	86.0	150.1	64.3	96.7	60.3	96.9
$H_3GeS(H)CH_3$	92.8	126.5	77.5	77.5	71.8	76.2
$H_3SnS(H)CH_3$	96.7	111.9	90.4	66.8	82.7	64.1
$H_3SiSe(H)CH_3$	59.3	125.4	40.6	73.5	35.5	73.7
$H_3GeSe(H)CH_3$	63.5	106.4	51.1	58.5	44.3	57.0
$H_3SnSe(H)CH_3$	66.0	97.2	61.2	52.1	52.9	49.8
$H_3SiTe(H)CH_3$	36.5	93.3	19.1	39.6	9.6	38.9
$H_3GeTe(H)CH_3$	39.1	80.3	29.0	32.7	19.9	30.1
$H_3SnTe(H)CH_3$	41.1	74.8	40.3	30.8	30.1	28.0

[a] Energies in kJ.mol^{-1}. For details of the basis set used, see text.

Figure 2. MP2 Calculated Geometries[a] of the Transition States (5) involved in the Homolytic Substitution of Silyl (SiH_3), Germyl (GeH_3) and Stannyl (SnH_3) Radical at the Chalcogen in Methanethiol, Methaneselenol and Methanetellurol (SCF Data in Parentheses).



---

[a] For description of basis set used, see text. Full geometries are available from the authors on request.

To our surprise, homolytic substitution by stannyl radical at the sulfur atom in methanethiol (with the expulsion of methyl) is predicted to be endothermic by some 18.6 kJ.mol^{-1} at the QCISD//MP2 level of theory; the barrier for the forward reaction is calculated to be some 82.7 kJ.mol^{-1}, while the reverse reaction is calculated to have a barrier of only 64.1 kJ.mol^{-1}. Similar conclusions can be drawn from the MP2 data. In comparison, the similar process, namely attack of stannyl radical at selenium is predicted at the highest level of theory to be endothermic by only 3.1 kJ.mol^{-1}, while attack at tellurium is predicted to be endothermic to the tune of 2.1 kJ.mol^{-1}.

The small relative barriers for reactions of stannyl and germyl radicals at selenium and tellurium, which range between 19.9 and 52.9 kJ.mol^{-1} (QCISD//MP2) together with similar barriers to reversibility (28.0 - 57.0 kJ.mol^{-1}) are strongly suggestive of equilibrium processes.

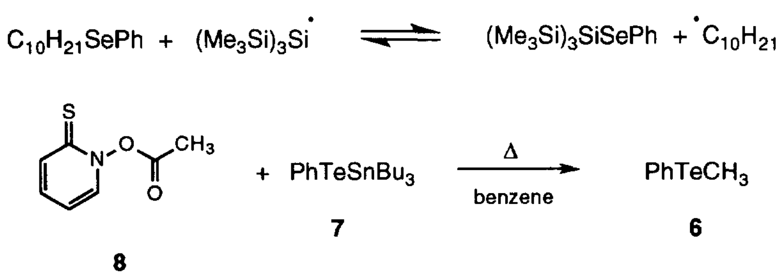
The transition stuctures (**5**) displayed in Figure 2 display the geometrical changes anticipated on the basis of the calculated energy barriers. Reactions involving attack of silyl radical at sulfur, selenium and tellurium are "earlier" than reactions involving the analogous germanium species, which are predicted to be marginally "earlier" than reactions involving the tin species. This is clearly evident in the lengthening of the carbon-chalcogen separation (for a given chalcogen) as one progresses down the group from silicon to germanium and tin. For example, the MP2-calculated carbon-tellurium distance of 2.393Å for attack of silyl, increases to 2.457Å for attack of germyl, and 2.489Å for attack of stannyl. Similar changes are predicted for attack at sulfur and selenium.

These data, together with our previous calculations for the similar process at the halogen atom in halomethanes[24] suggest that these chain-carrying radicals behave quite differently in their homolytic substitution chemistry at chalcogen to halogen. Methyl radical is predicted to be a marginally better leaving radical than stannyl in reactions involving homolytic substitution at either selenium or tellurium and a considerably better leaving group in reactions of stannyl at sulfur.

Recently, Chatgilialoglu and coworkers suggested the involvement of an intermediate in the reaction of 1-phenylselenodecane with tris(trimethylsilyl)silane in order to explain the apparent reversible kinetics they observed.[27] In light of our calculational data, these observations are explainable in terms of an overall reversible reaction; tris(trimethylsilyl)silane is well known to behave much more like the analogous trialkylstannanes,[28] and as such, the tris(trimethylsilyl)silyl radical may well react reversibly with phenylselenodecane (Scheme 3).

Radom and coworkers reported QCISD/6-311G** + ZPVE calculations in which they show that methyl radical behaves quite differently in its addition to alkenes than does *tert*-butyl,[29] suggesting that methyl may not be representative of alkyl radicals in general. We therefore suggest caution in extrapolating our calculational data to reactions involving other alkyl radicals.

Scheme 3



Work within our laboratories is currently providing experimental data for the relative leaving group abilities of methyl versus tin and germanium-centred radicals in their homolytic substitution chemistry at selenium and tellurium. Preliminary work[30] has demonstrated that telluroanisole (**6**) is formed when phenyltelluro tributyltin (**7**) is reacted with the Barton ester[31] of acetic acid in benzene at 80° (Scheme 3).

Presumably, thermal decomposition of the Barton ester (**8**) produces methyl radicals, which subsequently undergo intermolecular homolytic substitution at tellurium atom with expulsion of tributylstannyl. This result is in agreement with our calculational data. We are continuing to examine this intriguing phenomenon.

Table 3. SCF, MP2 and QCISD//MP2 Calculated Energies[a] of the Reactants, Products, Intermediate and Transition States (**3**, **4**, **5**) in this Study.

Structure	SCF	MP2	QCISD//MP2
$\cdot CH_3$	-39.57191	-39.69802	-39.71956
$\cdot SiH_3$	-5.46984	-5.55964	-5.58357
$\cdot GeH_3$	-5.34597	-5.43346	-5.45694
$\cdot SnH_3$	-4.94363	-5.02396	-5.04697
CH_3SH	-50.11713	-50.39418	-50.42944
CH_3SeH	-49.22717	-49.49366	-49.52694
CH_3TeH	-48.04744	-48.29930	-48.33181
H_3SiSH	-16.03962	-16.26900	-16.30813
H_3SiSeH	-15.15044	-15.36864	-15.40619
H_3SiTeH	-13.96715	-14.17021	-14.20770
H_3GeSH	-15.90415	-16.13047	-16.16921
H_3GeSeH	-15.01771	-15.23273	-15.26989
H_3GeTeH	-13.83733	-14.03700	-14.07400
H_3SnSH	-15.49478	-15.71201	-15.75048
H_3SnSeH	-14.61093	-14.81699	-14.85383
H_3SnTeH	-13.43211	-13.62247	-13.65911
Me_2SH	-89.64043	-90.05788	-90.11434
Me_2SeH	-88.76203	-89.16679	-89.22180
Me_2TeH (C_s)	-87.59316	-87.98682	-88.03963
Me_2TeH (C_1)	-	-87.98514	-88.04027
$H_3SiS(H)CH_3$	-55.55421	-55.92935	-55.99007
$H_3GeS(H)CH_3$	-55.42775	-55.79811	-55.85901
$H_3SnS(H)CH_3$	-55.02392	-55.38372	-55.44489
$H_3SiSe(H)CH_3$	-54.67443	-55.03783	-55.09698
$H_3GeSe(H)CH_3$	-54.54897	-54.90764	-54.96701
$H_3SnSe(H)CH_3$	-54.14568	-54.49430	-54.55378
$H_3SiTe(H)CH_3$	-53.50337	-53.85230	-53.91172
$H_3GeTe(H)CH_3$	-53.37852	-53.72171	-53.78117
$H_3SnTe(H)CH_3$	-52.97540	-53.30792	-53.36730

Conclusions

Ab initio calculations predict that homolytic substitution by methyl radical at the sulfur and selenium atoms in methanethiol and methaneselenol with the loss of methyl radical proceeds via symmetrical transition states, while the analogous reaction at the tellurium atom in methanetellurol is predicted to proceed with the involvement of a hypervalent (9-E-3) intermediate. Further calculations predict that homolytic substitutions by silyl, germyl and stannyl radicals at the chalcogen atom in methanethiol, methaneselenol and methanetellurol proceed via mechanisms which do not involve hypervalent 9-E-3 intermediates. These processes adopt either co-linear or bent arrangements of attacking and leaving radicals (depending on the radicals involved) with, as expected, substitution at tellurium being more facile than the analogous reaction at selenium, which in turn is more reactive than sulfur. Reactions involving germyl and stannyl radicals at selenium and tellurium with the loss of methyl are predicted to be reversible processes.

We thank the Australian Research Council for financial support.

References and Notes

1. Part of this work has been published in preliminary form: Schiesser, C. H., Smart, B. A., *J. Chem. Soc. Perkin Trans. 2*, **1994**, 2269.
2. Giese, B., *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, **1986**, Pergamon Press, Oxford; and references cited therein.
3. Beckwith, A. L. J., Maxwell, B. J., Tsanaktsidis, J., *Aust. J. Chem.*, **1991**, *44*, 1809; Maxwell, B. J., Tsanaktsidis,*J. Chem. Soc. Chem. Commun.*, **1994**, 533; Bowman, W. R., Clark, D. N., Marmon, R. J., *Tetrahedron Lett.*, **1991**, *32*, 6441; Bowman, W. R., Clark, D. N., Marmon, R. J., *Tetrahedron Lett.*, **1992**, *33*, 4993.
4. Beckwith, A. L. J., Hay, B. P., *J. Am. Chem. Soc.*, **1989**, *111*, 230.
5. Barton, D. H. R., Bridon, D., Zard, S. Z., *Tetrahedron Lett.*, **1984**, *25*, 5777; Barton, D. H. R., Ozbalik, N., Sarma, J. C., *Tetrahedron Lett.*, **1988**, *29*, 6581; Newcomb, M., Marquardt, D. J., Kumar, M. U., *Tetrahedron*, **1990**, *46*, 2252; Barton, D. H. R., Ramesh, M., *J. Am. Chem. Soc.*, **1990**, *112*, 891; Byers, J. H., Lane, G. C., *Tetrahedron Lett.*, **1990**, *31*, 5697; Byers, J. H., Gleason, T. G., Knight, K. S., *J. Chem. Soc. Chem. Commun.*, **1991**, 354; Curran, D. P., Thoma, G., *J. Am. Chem. Soc.*,**1992**, *114*, 4436; Chen, C., Crich, D., Papadatos, A., *J. Am. Chem. Soc.*,**1992**, *114*, 8313; Barton, D. H. R., Camara, J., Cheng, X., Gero, S. D., Jaszberenyi, J. C., Quinclet-Sire, B., *Tetrahedron*, **1992**, *48*, 9261; Crich, D., Chen, C., Hwang, J.-T., Yuan, H., Papadatos, A., Walter, R. I., *J. Am. Chem. Soc.*, **1994**, *116*, 8937.
6. Curran, D. P., Martin-Esker, A. A., Ko, S.-B., Newcomb, M., *J. Org. Chem.*, **1993**, *58*, 4691.
7. Kampmeier, J. A., Evans, T. R., *J. Am. Chem. Soc.*, **1966**, *88*, 4097; Benati, L., Montevecchi, P. C., Tundo, A., Zanardi, G., *J. Chem. Soc. Perkin Trans. 1*, **1974**, 1272; John, D. I., Tyrrell, N. D., Thomas, E. J., *J. Chem. Soc. Chem. Commun.*, **1981**, 901; Beckwith, A. L. J., Boate, D. R., *J. Chem. Soc. Chem. Commun.*, **1986**, 189; Beckwith, A. L. J., Boate, D. R., *J. Org. Chem.*, **1988**, *53*, 4339; Tada, M., Uetaka, T., Matsumoto, M., *J. Chem. Soc. Chem. Commun.*, **1990**, 1408; Franz, J. A., Roberts, D. H., Ferris, K. F., *J. Orh. Chem.*, **1987**, *52*, 2256; Baldwin, J. E., Adlington, R. M., Bohlmann, R., *J. Chem. Soc. Chem. Commun.*, **1985**, 357; Barton, D. H. R., Bridon, D., Zard, S. Z., *Heterocycles*, **1987**, *25*, 449; Beckwith, A. L. J., Duggan, S. A. M., *J. Chem. Soc. Perkin Trans. 2*, **1994**, 1509.
8. Schiesser, C. H., Sutej, K., *J. Chem. Soc. Chem. Commun.*, **1992**, 57.
9. Benjamin, L. J., Schiesser, C. H., Sutej, K., *Tetrahedron*, **1993**, *49*, 2557; Lyons, J. E., Schiesser, C. H., Sutej, K., *J. Org. Chem.*, **1993**, *58*, 5632; Schiesser, C. H., Fong, M. C., *Tetrahedron Lett.*, **1993**, *34*, 4347; Schiesser, C. H., Sutej, K., *Tetrahedron Lett.*, **1992**, *33*, 5137.

10. Volatron, F., Demolliens, A., Lefar, J.-M., Eisenstein, O., *Chem. Phys. Lett.*, **1986**, *130*, 419; Volatron, F., *J. Mol. Struct. (THEOCHEM)*, **1989**, *186*, 167.

11. Lyons, J. E., Schiesser, C. H., *J. Chem. Soc. Perkin Trans. 2*, **1992**, 1655.

12. Ferris, K. F., Franz, J. A., *J. Org. Chem.*, **1992**, *57*, 777.

13. Lyons, J. E., Schiesser, C. H., *J. Organometal. Chem.*, **1992**, *437*, 165.

14. Demolliens, A., Eisenstein, O. , Hiberty, P. C., Lefour, J. M., Ohanessian, G., Shaik, S. S., Volatron, F., *J. Am. Chem. Soc.*, **1989**, *111*, 5623.

15. Fong, M. C., Schiesser, C. H., *Aust. J. Chem.*, **1992**, *45*, 475.

16. Schiesser, C. H., Wild, L. M., *Aust. J. Chem.*, **1995**, *48*, 175.

17. Smart, B. A., Schiesser, C. H., *J. Comput. Chem.*, (in press).

18. Griffiths, W. J., Harris, F. M., Beynon, J. H., *Int, J. Mass Spectrom. Ion Processes*, **1987**, *77*, 233.

19. Wadt, W. R., Hay, P. J. , *J. Chem. Phys.*, **1985**, *82*, 284; Hay, P. J., Wadt, W. R., *J. Chem. Phys.*, **1985**, *82*, 270; Hay, P. J., Wadt, W. R., *J. Chem. Phys.*, **1985**, *82*, 299.

20. Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E.S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzales, C., Martin, R.L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P., Pople, J. A. **1992**, *Gaussian 92*, Revision F, Gaussian Inc, Pittsburgh, PA. All calculations were performed on either a Sun Sparcserver 10/512.

21. Values of $<S^2>$ never exceeded 0.87 before annihilation of quartet contamination indicating the presence of only moderate spin contamination.

22. Höllwarth, A., Böhme, M., Dapprich, S., Ehlers, A. W., Gobbi, A., Jonas, V., Köhler, K. F., Stegmann, R., Veldkamp, A., Frenking, G., Chem. Phys. Lett., **1993**, *208*, 237.

23. Dunning, T. H., Hay, P. J., *Modern Theoretical Chemistry*, **1976**, Plenum, New York, pp. 1-28 ch. 1.

24. Schiesser, C. H., Smart, B. A., Tran, T.-A., *Tetrahedron* (in press).

25. Newcomb, M., Sanchez, R. M., Kaplan, J., *J. Am. Chem. Soc.*, **1987**, *109*, 1195.

26. Gutierrez, C. G., Summerhays, L. R., *J. Org. Chem.*, **1984**, *49*, 5206.

27. Ballestri, M., Chatgilialoglu, C., Clark, K. B., Griller, D., Giese, B., Kopping, B., *J. Org. Chem.*, **1991**, *56*, 678.

28. Chatgilialoglu, C., Griller, D., Lesage, M., *J. Org. Chem.*, **1989**, *54*, 2492.

29. Wong, W. W., Pross, A., Radom, L., *J. Am. Chem. Soc.*, **1994**, *116*, 11938; Wong, W. W., Pross, A., Radom, L., *J. Am. Chem. Soc.*, **1994**, *116*, 6284.

30 Schiesser, C. H., Laws, M. J., unpublished. In an NMR experiment, 20 mg of (**7**) and approximately 3 equivalents of (**8**) were dissloved in d_6-benzene (2 mL). After heating at 80° for 3h, 300 MHz ^{1}H NMR spectroscopy revealed the presence of (**6**) (compared with an authentic sample).

31. Barton, D. H. R., Crich, D., Motherwell, W. B., *Tetrahedron*, **1985**, *41*, 3901.

(*Received in UK* 21 *March* 1995; *accepted* 31 *March* 1995)