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Free-Radical Homolytic Substitution: New Methods for Formation of Bonds to Heteroatoms

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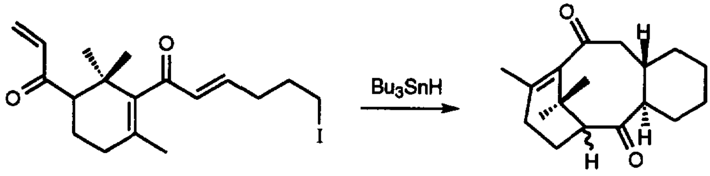
Contents

1. *Radicals in Synthesis*

Over the past twenty years free-radical chemistry has undergone a remarkable transformation. Long gone are the days when free-radicals were considered to give rise only to intractable tars or polymers. With the increased understanding of the factors which govern the reactivity, regio- and stereochemistry of radical addition chemistry comes the emergence of a maturity which has seen the development of several impressive syntheses based on radical chemistry. Several excellent reviews[1] and books[2] on this topic have been written and the reader is referred to these works for further information.

The elegant synthesis of the taxane skeleton (**1**) reported by Pattenden[3] typifies the role that intramolecular homolytic addition chemistry plays in modern synthetic chemistry (Scheme 1). The success of this methodology depends largely on the understanding of the rate constants associated with the various competing radical processes. The preparation of **1** as depicted in Scheme 1 relies on a sequence of radical addition steps and is referred to as a *tandem* or *cascade* radical reaction.

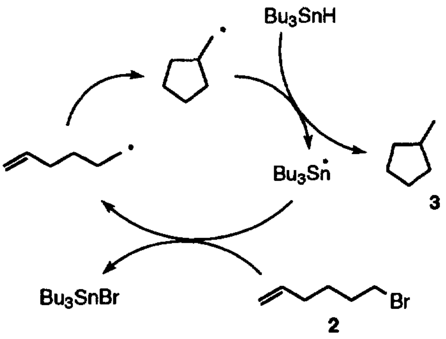
Scheme 1



1

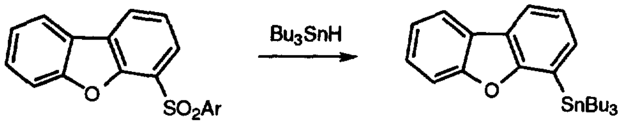
If we turn our attention to the prototypical cyclization reaction, namely the ring-closure of 6-bromo-1-hexene (**2**) to afford methylcyclopentane (**3**) using tributyltin hydride mediated conditions, it is immediately clear that while the key carbon-carbon bond forming reaction is indeed the addition step itself, the radical chain mechanism requires two homolytic substitution reactions for overall success (Scheme 2). Indeed, a large proportion of free-radical sequences involve the use of homolytic addition by carbon-centred radicals to an unsaturated moiety as the key step in the overall strategy. These radicals, in turn, are often generated by intermolecular homolytic substitution of tin, germanium or silicon-centred chain carrying radicals at the chlorine, bromine or iodine atom in alkyl halides. Despite the homolytic substitution reaction being of importance in these sequences, homolytic substitution remains a less well understood process than the more favoured homolytic addition reaction.

Scheme 2



In his 1981 review, Beckwith lists six key reaction types found in free-radical chemistry.[1b] These include bond homolysis, combination, electron transfer, β-scission, homolytic addition and homolytic substitution. Despite the fact that several examples of synthetically useful reactions involving radical combination processes have been documented,[2] homolytic addition and substitution reactions are of most synthetic significance in the formation of bonds because they involve radical-molecule reactions and do not result in the loss of radical character during the course of the overall transformation.

Scheme 3



4 **5**

Many workers have employed homolytic *aromatic* substitution chemistry in synthesis. The transformation of sulfone (**4**) into the stannane (**5**) provides an example of this chemistry (Scheme 3).[4] Transformations of this type are two step processes involving homolytic addition followed by β-scission and are mentioned here for completeness. Free-radical attack at a saturated atom (Y) within a molecule with the expulsion of a leaving radical (L) (Scheme 4) is the topic which is addressed in this report.

Scheme 4

$$A^{\bullet} \quad Y{-}L \longrightarrow A{-}Y + L^{\bullet}$$

Various workers have used symbols such as "S_H2" and "S_Hi" to denote inter- and intra-molecular homolytic substitution reactions respectively. Pryor addresses the validity of the use of the "S_H2" symbol in a short note which appeared in *Nature Physical Science* in 1971.[5] He emphasises that the "S_H2" symbol should be used where the mechanism is known to be a direct, one step displacement reaction which involves Walden inversion. A significant proportion of homolytic substitution reactions proceed with the involvement of hypervalent intermediates or by unknown mechanisms (see later). Consequently, we have chosen to avoid the usage of these symbols, preferring the generic *homolytic substitution* label instead.

Ingold and Roberts provide a comprehensive account of the state of homolytic substitution chemistry prior to 1971.[6] Since that time radical substitution chemistry has featured only as minor components in several reviews. This report is intended to demonstrate that while homolytic addition chemistry plays an important synthetic role, especially in the formation of carbon-carbon bonds, bonds to heteroatoms can be formed conveniently and efficiently through the use of inter- and intramolecular homolytic substitution chemistry as the key bond-forming process. Over the past five years, the synthetic potential of homolytic substitution chemistry has been demonstrated by us and by several groups around the world. In much the same way that a clearer understanding of the details of homolytic addition chemistry gave rise to the rapid increase in the use of that methodology in synthesis, our recent increase in understanding of homolytic substitution processes has the similar potential of providing synthetic chemists with yet further tools for their synthetic endeavours.

2. *Radical Attack at Saturated Carbon and First-Row Heteroatoms*

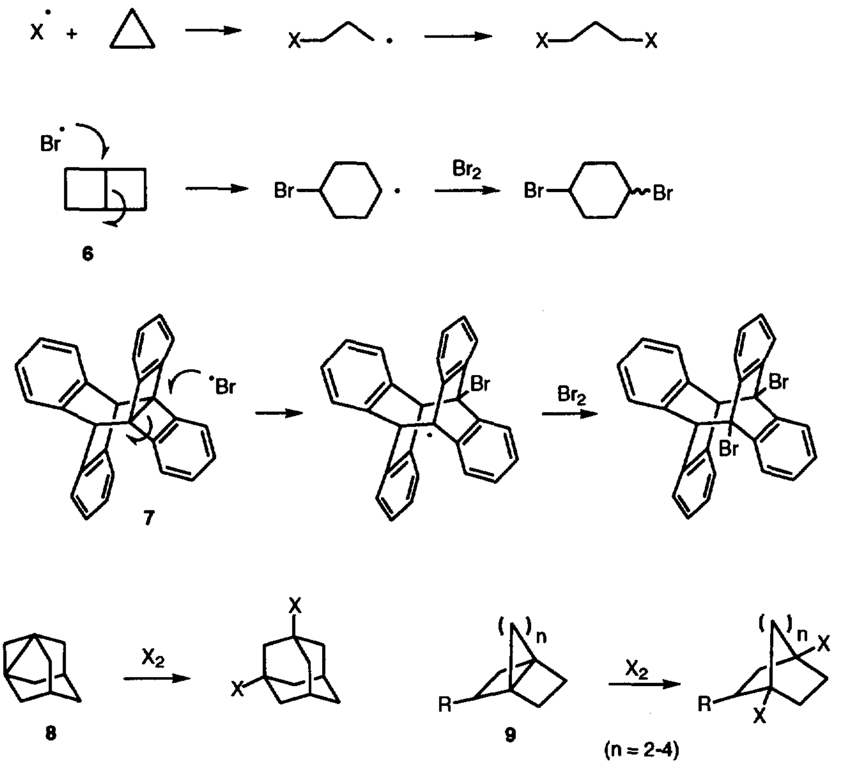
Despite the substantial synthetic potential that free-radical attack at saturated carbon provides, especially in the formation of carbon-carbon bonds, there are relatively few examples of reactions of this type. Those which have been reported involve activation of the carbon atom through strain or involvement of metal leaving groups. While there exist several early reports of intermolecular substitution at unactivated carbon, many of these were subsequently shown to proceed via mechanisms which do not involve radical attack at saturated carbon.[6] The attack of trifluoromethyl radical at the methyl group in neopentane with the formation of 1,1,1-trifluoroethane appears to be the only example of homolytic substitution at an "unactivated" sp^3 carbon (Scheme 5).[7]

Scheme 5

$$\dot{C}F_3 + H_3C{-}C(CH_3)_3 \longrightarrow CF_3CH_3 + (CH_3)_3\dot{C}$$

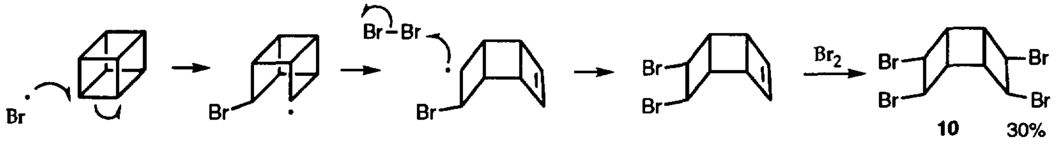
Cyclopropanes, on the other hand, undergo rapid substitution by halogen atom[6,8] and tris(trifluoromethyl)aminyloxyl radical[9] to afford a variety of ring-opened products, while bicyclo[2.2.0]hexane (**6**),[10] 9,10-dehydrodianthracene (**7**),[11] 1,3-dehydroadamantane (**8**)[6] and several [n.2.2]propellanes (**9**)[12] undergo homolytic substitution by bromine or iodine atom at the bridgehead saturated carbon with loss of substantial strain energy to afford a variety of dihalides (Scheme 6).

Scheme 6



Recently, Della, Walton and co-workers demonstrated that cubane undergoes photobromination to afford *cis,cis*-3,4,7,8-tetrabromo-*syn*-tricyclo[4.2.2.$0^{2,5}$]octane (**10**) in a process that is likely to involve homolytic attack by bromine atom at the cubyl carbon followed by β-scission and eventual olefin bromination (Scheme 7).[13]

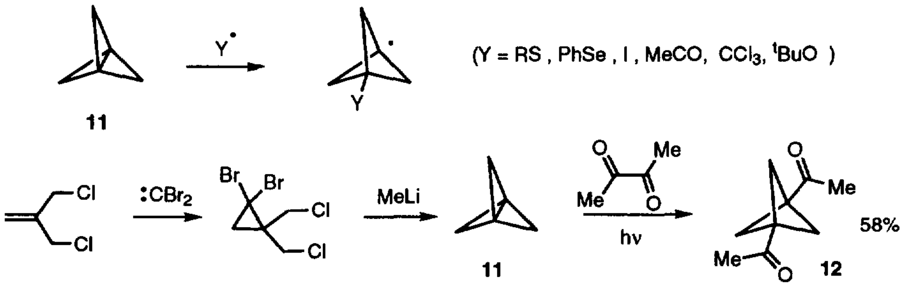
Scheme 7



Several types of radicals have been shown to substitute at the unique bridgehead carbons in [1.1.1]propellane (**11**) (Scheme 8).[14] Whether or not these reactions are homolytic substitution reactions in the true sense is a matter for debate given the ambiguous nature of the transannular bond in **11**.[15]

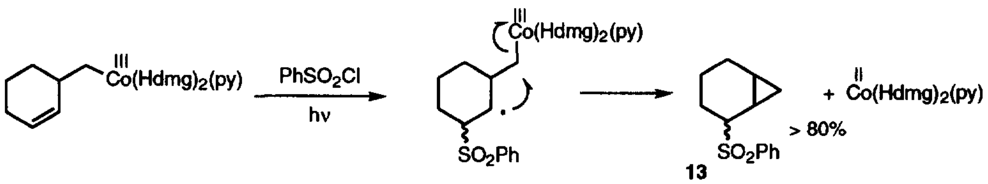
Of preparative significance is the reaction of **11** with biacetyl under photochemical conditions to give 1,3 diacetylbicyclo[1.1.1]pentane (**12**) recently reported by Michl and coworkers.[16] Indeed, the transformation of **11** into **12** possibly represents the only synthetically significant carbon-carbon bond forming reaction in which the key step involves homolytic substitution at carbon.

Scheme 8



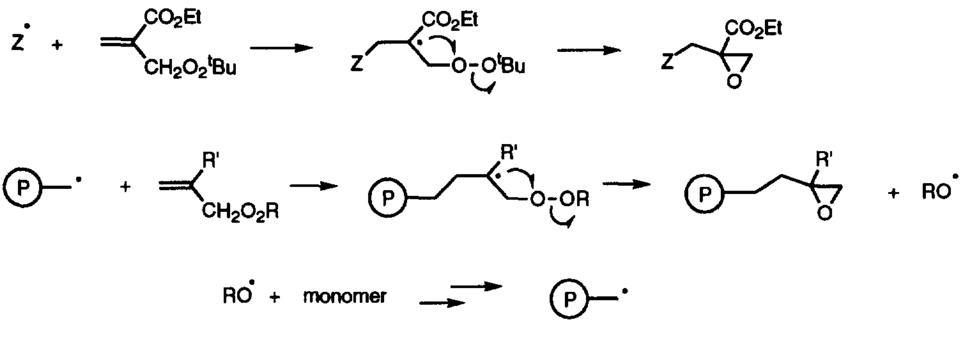
Several workers have demonstrated that cobalt complexes are useful starting materials for the preparation of cyclopropanes.[17] The key step in these transformations would appear to involve homolytic substitution at carbon with expulsion of the metal as the leaving group. The preparation of the bicyclo[4.1.0]hept-2-yl sulfone (**13**) is representative of this chemistry (Scheme 9).

Scheme 9



Of the remaining first-row elements, only oxygen appears to become involved readily in homolytic substitution chemistry. Interestingly, attack at oxygen appears to be unique to peroxides in which the reaction is facilitated by the weak oxygen-oxygen bond. Early examples are well reviewed by Ingold and Roberts.[6] More recently, Maillard and coworkers[18] as well as Thang[19] have shown that homolytic attack by carbon-centred radical at the oxygen atom in peroxyesters is a useful procedure for the preparation of epoxides. (Scheme 10). This chemistry plays an important role in the chain-transfer step during free-radical polymerization and can be used to control chain length.[19]

Scheme 10

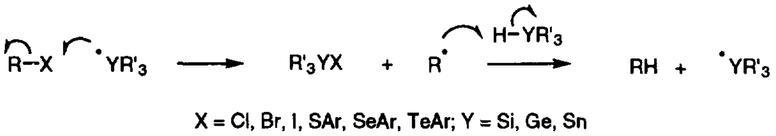


3. *Group Transfer (Translocation) Reactions*

3.1. Bimolecular Reactions

Hydrogen transfer reactions (homolytic substitutions at hydrogen atom) are common processes. They are of fundamental importance in most free-radical sequences which involve reagents such as tributyltin hydride and tris(trimethylsilyl)silane (eg. Scheme 1)[1] and will not be discussed to any great extent in this report.

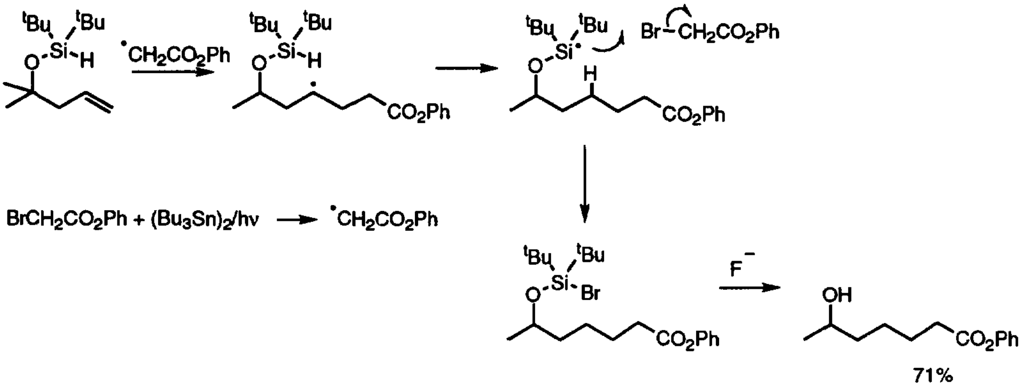
Scheme 11



Reactions of alkyl and aryl halides, sulfides, selenides and tellurides with trialkylstannyl, germyl and silyl radicals (Scheme 11) are commonly used methods for the generation of carbon-centred radicals.[1,20] These carbon-centred radicals, once generated, can react further. In synthesis, tributyltin hydride, and more recently, tris(trimethylsilyl)silane[21] have been the reagents of choice, mainly because of their favourable Sn-H or Si-H bond strengths, which allow for efficient chain propagation via intermolecular hydrogen transfer. Trialkylgermanes have also been employed in synthesis,[1,22] however, the expense associated with germanium-containing compounds can often be prohibitive. Trialkylsilanes are significantly limited in their synthetic applicability; the unfavourable Si-H bond strength associated with most organosilanes often results in inefficient chain propagation.[23] Recently, Curran has overcome some of these difficulties by incorporating intramolecular hydrogen transfer as part of the chain process. Termed Unimolecular Chain Transfer (UMCT) reactions, they allow silanes in general to become synthetically useful.[24] An example is given in Scheme 12.

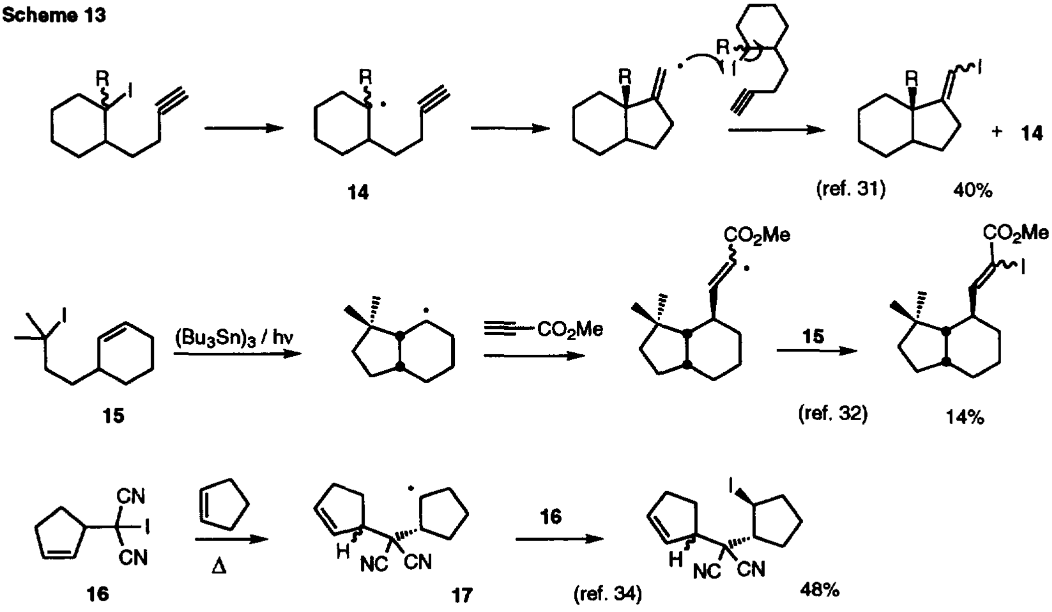
Intermolecular transfer of bromine, iodine, phenylselenide and aryltelluride between carbon-centred radicals has commonly been employed in synthesis. These transformations, referred to as *group* or *atom transfer* reactions (unlike reactions involving stannane, germane or silane chain transfer reagents) have the advantage that functionality is not lost during the course of the reaction. In all cases, success in group transfer chemistry relies on a disparity in reactivity between attacking and leaving radicals.

Scheme 12

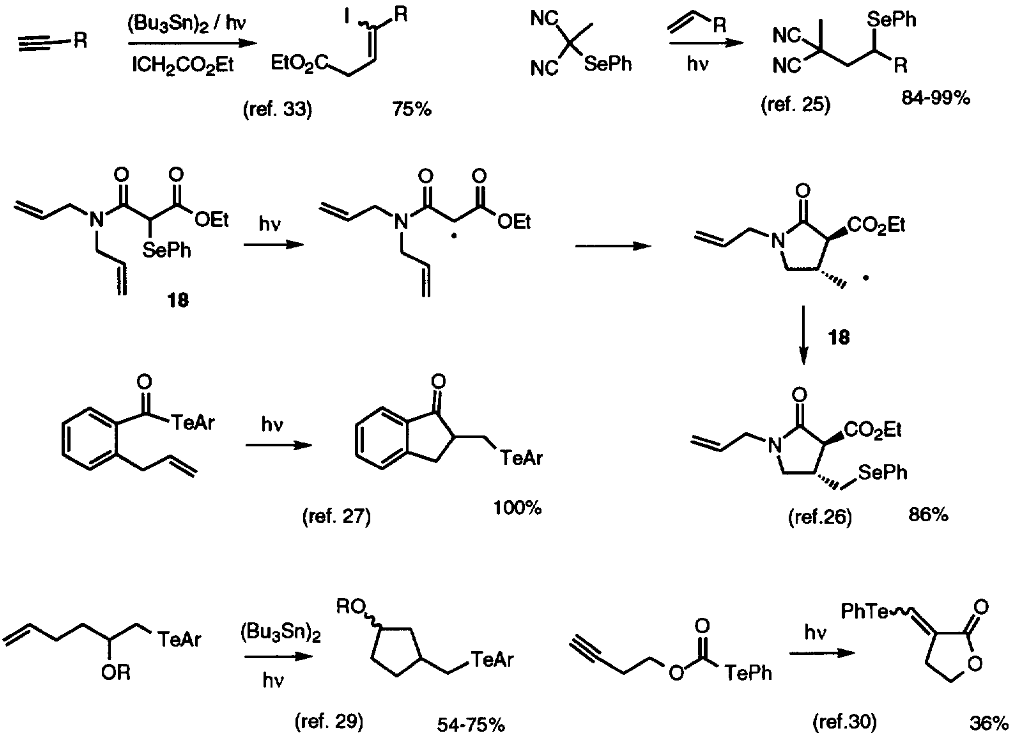


The reader is referred to the excellent account of many efficient bromine and iodine transfer reactions provided by Curran in his 1988 review.[1e] Transfer of phenylselenide has been shown to proceed readily by Curran[25] and other workers,[26] while work reported by Crich,[27] Barton,[28] Engman[29] and experiments performed in our laboratories[30] have utilised aryltelluride transfer as the key step in several synthetic strategies. Many of these transformations involve tandem addition/substitution processes. Selected recent examples are highlighted in Scheme 13. Sometimes transformations of this type afford the required product in low yield due to competing hydrogen abstraction processes.[32] In many cases, the favourable disparity between the rates of homolytic substitution and intramolecular addition can be used to good effect. Reaction of iodide (**16**) provides such an example; intermediate radical (**17**) undergoes preferential intermolecular homolytic substitution at the iodine atom in **16** rather than cyclization.[34]

Scheme 13



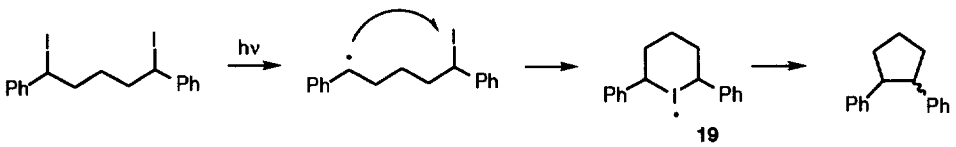
Scheme 13 (cont.)



3.2. Intramolecular Reactions

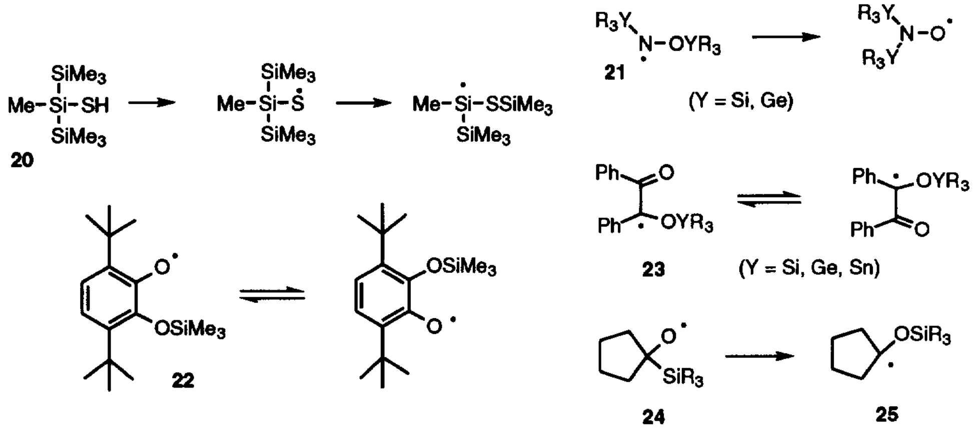
Apart from a recent report by Scaiano in which the existence of hypervalent iodine radical intermediates (eg. **19**) during laser flash and laser-drop experiments is suggested (Scheme 14),[35] there appear to be no reported examples of intramolecular group transfer reactions involving selenium, tellurium or halogen. This is most likely due to the geometric constraints imposed in the transition states involved in homolytic substitution reactions at these atoms. There appears to be one example involving intramolecular transfer of phenylthio and is discussed in some detail below (Scheme 23) while there appear to be several examples involving the transfer of trialkylsilyl and stannyl groups. The mechanistic implications of these observations are discussed later.

Scheme 14



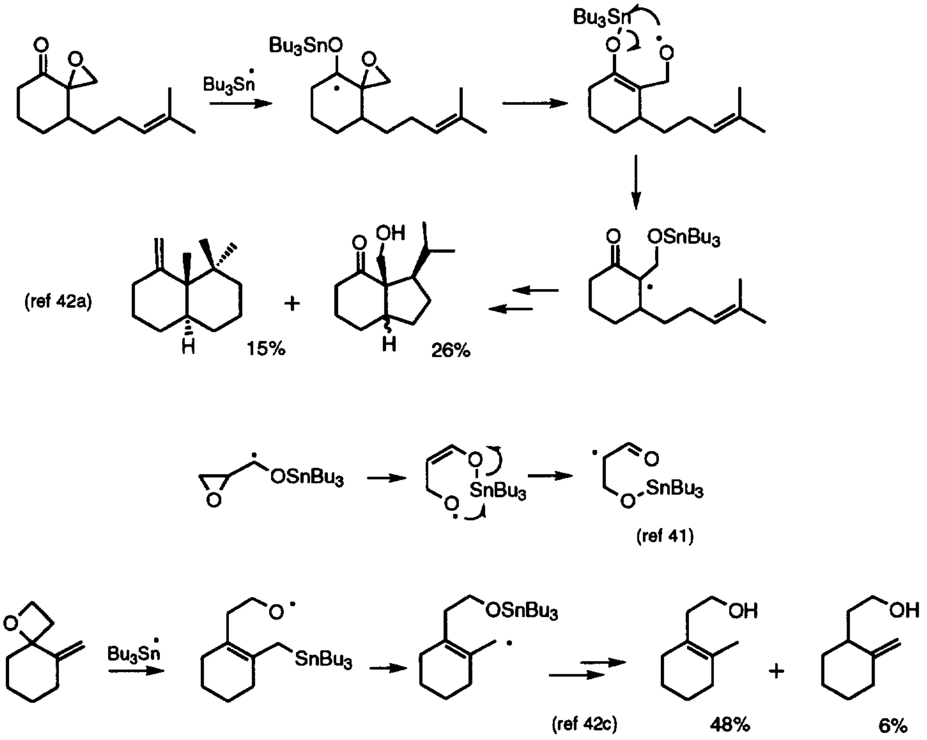
There are several early reports of intramolecular radical migrations of organosilyl and germyl groups involving 1,2 shifts. Pitt and Fowler reported a radical catalyzed rearrangement of trisilanethiols (**20**),[36] while other workers have investigated similar shifts in organosilyl and germyl nitroxides (eg. **21**).[37] Several groups reported tautomerism in silicon, germanium and tin containing radicals (eg. **22**, **23**),[38] while 1,2-silyl transfer appear to be the key step in the radical Brook rearrangement (eg. **24** --> **25**).[39,40]

Scheme 15

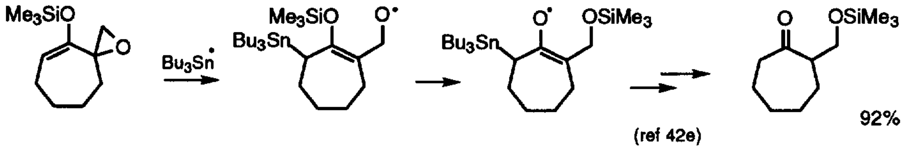


Intramolecular 1,5 and 1,6 transfers of stannyl and silyl groups have been put to good use by Davies and coworkers,[41] as well as Kim and his associates.[42] Selected examples are highlighted in Scheme 16.

Scheme 16



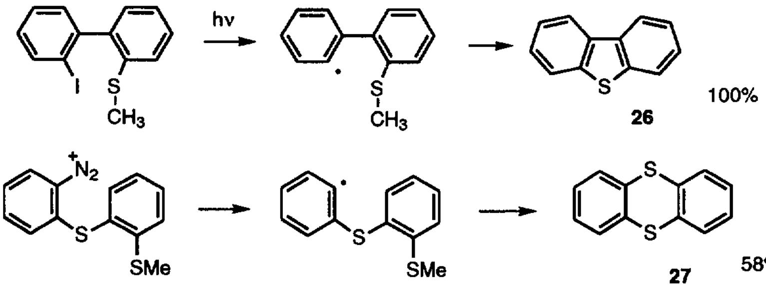
Scheme 16 (cont.)



4. *Radical Ring Closure (Formation of Higher Heterocycles)*

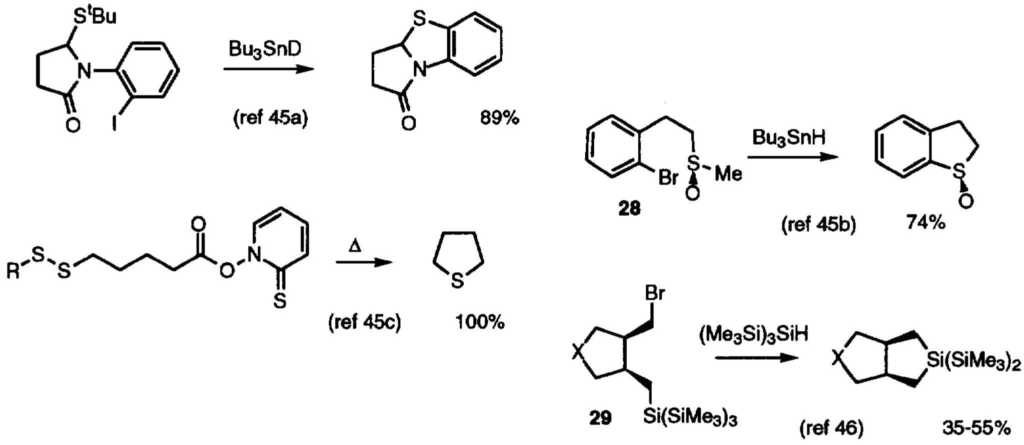
Intramolecular radical attack at higher heteroatoms with the expulsion of a suitable leaving radical can be envisaged to afford higher heterocycles. Over the past thirty years, this chemistry has been used in the preparation of sulfur-containing, and more recently, selenium-containing heterocycles. Early reports by Kampmeier[43] as well as Tundo[44] include the formation of dibenzothiophene (**26**) and thianthrene (**27**) by intramolecular homolytic substitution (Scheme 17).

Scheme 17

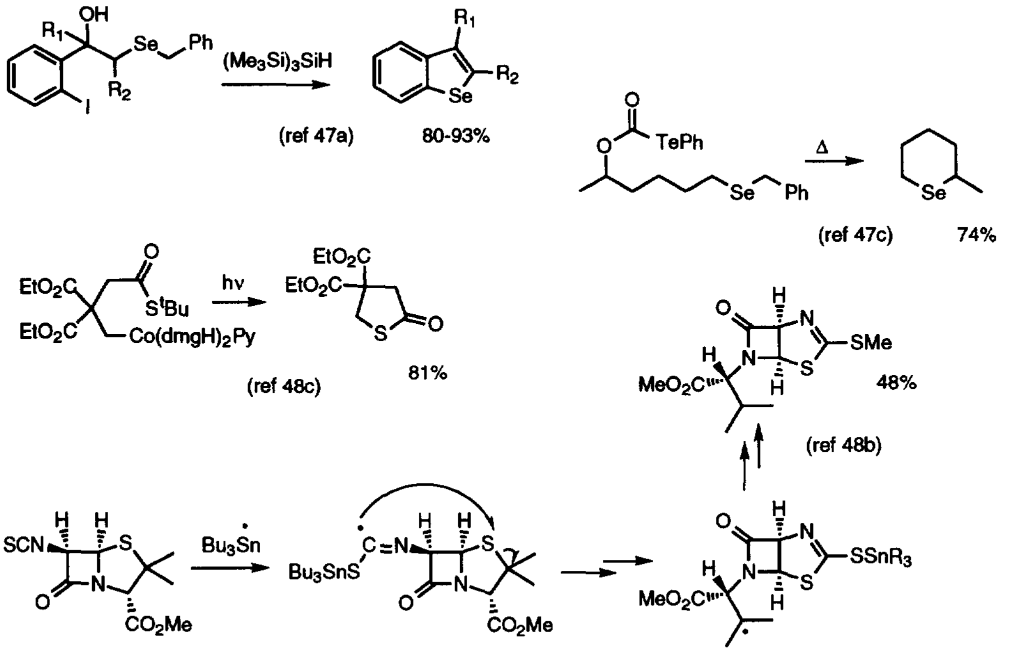


Intramolecular homolytic substitution by alkyl and aryl radicals at the sulfur atom in alkyl sulfides and sulfoxides, the selenium atom in alkyl selenides and the silicon atom in some silanes (**29**) has been demonstrated by Beckwith,[45] Giese,[46] ourselves[47] and others[48] to offer efficient alternatives to traditional chemistry for the formation of higher heterocycles. Selected examples are displayed in Scheme 18.

Scheme 18



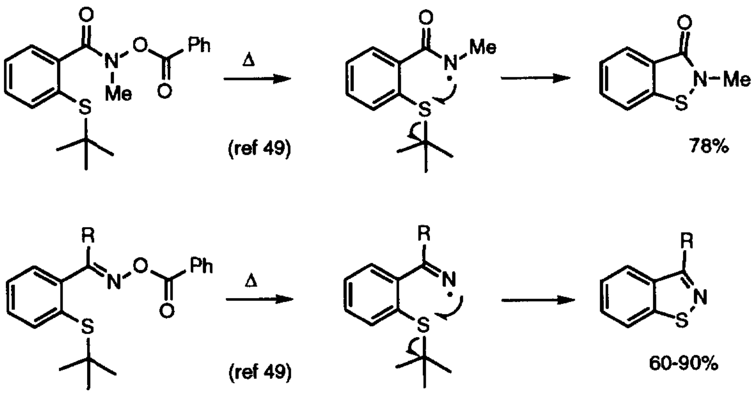
Scheme 18 (cont.)



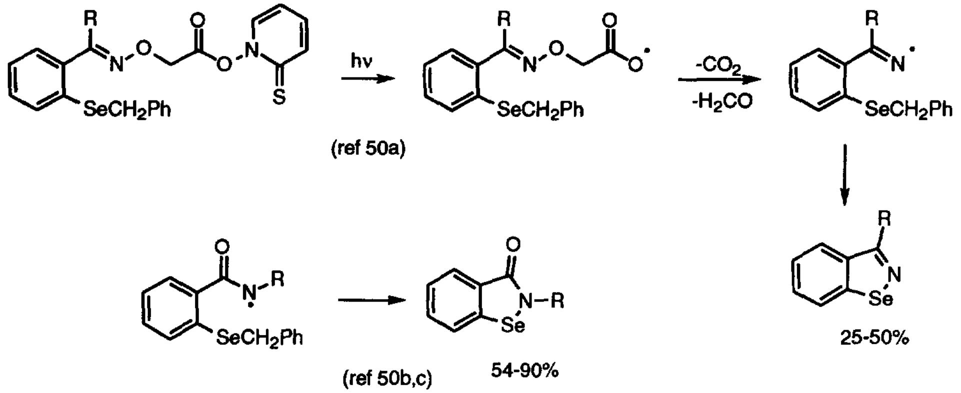
Iminyl and amidyl radicals have also been shown to become involved in intramolecular homolytic substitution chemistry at sulfur[49] and selenium[50] (Scheme 19).

At this time, we are unaware of any reports of the formation of higher heterocycles through the use of intramolecular homolytic substitution chemistry at other higher heteroatoms.

Scheme 19



Scheme 19 (cont.)

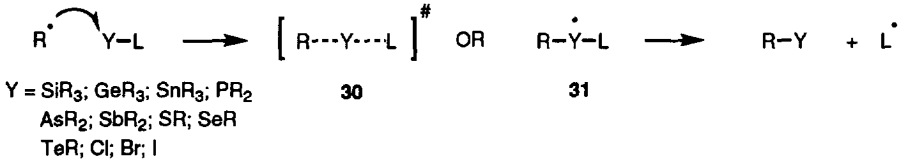


5. *The Mechanism of Homolytic Substitution*

5.1. Hypervalency in Homolytic Substitution?

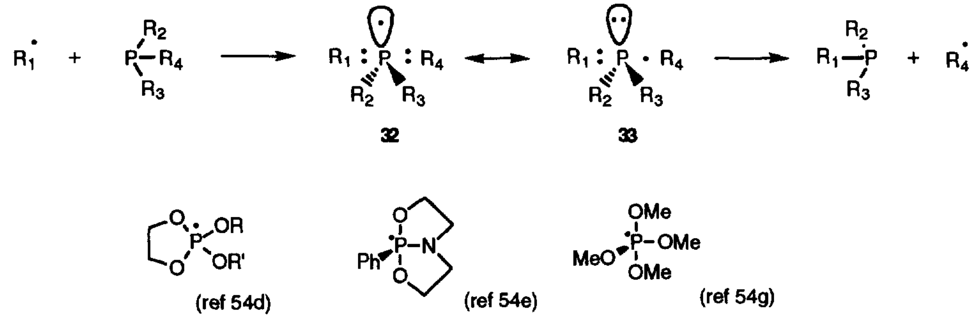
It is generally agreed that homolytic substitution by a radical (R•) at a group (Y) proceeds via either a transition state (**30**) in which the attacking and leaving groups adopt a co-linear (or nearly so) arrangement resulting in Walden inversion, or with the involvement of a hypervalent intermediate (**31**) which may or may not undergo pseudorotation prior to dissociation.[6,51]

Scheme 20

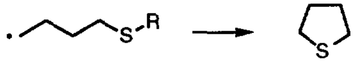


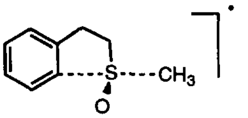
Since they were first proposed as transient reaction intermediates,[52] several research groups have sought evidence for the intermediacy of hypervalent, nine-electron, tetravalent (9-P-4) phosphoranyl radicals in homolytic substitution chemistry (Scheme 21). The chemistry of phosphoranyl radicals is now well established and has been reviewed on several occasions.[53] ESR studies have been particularly useful in establishing the structural details and isomerization kinetics for a large variety of phosphoranyl radicals.[54] The vast majority of these species prefer to adopt a trigonal bipyramidal geometry (**32**) in which the vacant equatorial site is occupied by the unpaired electron or (**33**) in which the apical ligands are bonded by three-electron, three-centre bonds and the vacant equatorial site is occupied by the lone pair , although there is some debate concerning structural details,[55] especially when low-lying σ^* phosphorus-ligand orbitals are involved.[56] Indeed, (**32**) and (**33**) would be expected to contribute to the overall resonance description of these systems. Some examples of phosphoranyl radicals are displayed in Scheme 21.

Scheme 21



Experimental rate studies cast doubt on the existence of a hypervalent intermediate in the ring closure by the alkyl radical at the sulfur atom in **34**.[48a] However, there appear to be several ESR examples of reactions involving hypervalent (9-S-3) sulfuranyl radicals in homolytic substitution reactions when stabilizing groups are present on sulfur[6,57] and some examples involving (9-Se-3) selenuranyl radicals.[58] Selected structures are given in Scheme 22. On the other hand, the strict inversion of configuration observed when a chiral sulfoxide (**28**) is employed[45b] (Scheme 18) provides strong evidence for the involvement of a single transition state (**35**) or an intermediate (**36**) which is too short lived to undergo pseudorotation prior to dissociation. The sulfuranyl radical (SH_3) itself has been observed during neutralization-reionization spectroscopy.[59]


34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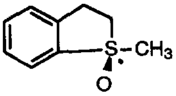
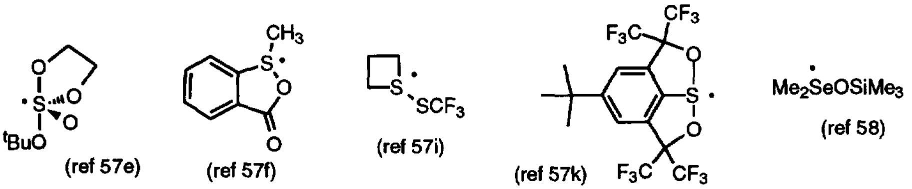
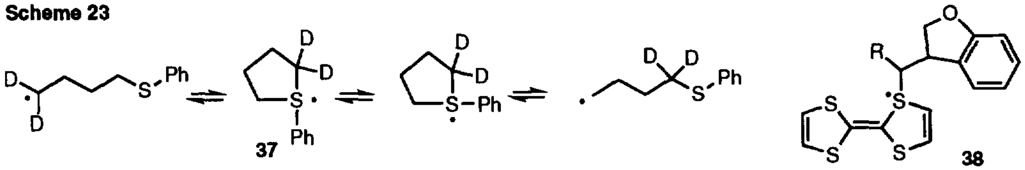

36

Scheme 22



Scheme 23



High-level *ab initio* calculations suggest that trialkylsulfuranyl radicals (SR_3) correspond to transition states during homolytic substitution reactions (see later). At this time we are aware of only two examples of sulfuranyl radicals in which all ligands at sulfur are carbon. Radical rearrangement studies in our laboratories provide evidence for the existence of a hypervalent intermediate (**37**) (which undergoes pseudorotation prior to dissociation) during the rearrangement of the 1,1-dideuterio-4-phenylthiobutyl radical (Scheme 23),[60] while

Murphy has speculated at the possible involvement of hypervalent species (**38**) during radical reactions involving tetrathiafulvalene.[61] While **37** and **38** are examples of sulfuranyl radicals containing all-carbon ligands, one or all of the ligands at sulfur would nevertheless provide considerable stabilization to the radical centre in each case.

Curran and Newcomb postulate that homolytic substitution by alkyl radical at the selenium atom in a series of alkyl selenides occurs without the involvement of intermediates in order to explain the pronounced leaving group effects they observe.[62] Other than the speculated intermediacy of the iodinyl radical intermediate (**19**) during laser-flash experiments, we are unaware of experimental evidence in support of nine-electron hypervalent structures involving silicon, germanium, arsenic, antimony, selenium, tellurium, chlorine or bromine.

5.2. Rates of Homolytic Substitution

There exist limited rate data for intramolecular homolytic substitution reactions. Data which are available[45c,47a,48a] are listed in Table 1 and include values of 3.7 x 10^4 s^{-1} at 80° for the homolytic cyclization of the 4-(benzylthio)butyl radical (**39**) and about 3 x 10^7 s^{-1} at 80° for the ring closure of **40**. Beckwith indicates that intramolecular attacks of aryl radicals on sulfide sulfur typically have rate constants of 10^7 s^{-1} at ordinary temperatures.[45c] These data are to be compared with the value of 1.4 x 10^6 s^{-1} (25°) for the ring closure of the 5-hexenyl radical (**41**).[63] The reader is also referred to the excellent compilation of free-radical rate constant data found in the Landolt-Börnstein series.[64]

Table 1. Selected Rate Constant Data for Homolytic Ring Closure of Some Sulfides and Selenides.

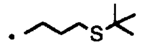
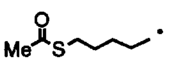
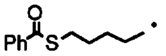
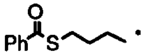
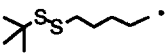
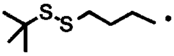
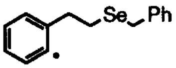
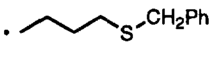
Radical	Temp (°C)	k (s^{-1})	Reference
	25°	18.2	48a
	25°	2.7 x 10^2	48a
	25°	3.9 x 10^3	48a
	104°	ca. 2.3 x 10^2	45c
	104°	ca. 1.1 x 10^3	45c
	50°	ca. 2.0 x 10^2	45c
	50°	ca. 7.0 x 10^3	45c
	50°	6.2 x 10^5	45c
	50°	3.3 x 10^8	45c
	50°	1.7 x 10^7	45c
	80°	ca. 3 x 10^7	47a

Table 2. Selected Rate Constant Data for Intermolecular Homolytic Substitution by Alkyl Radicals At the Halogen or Chalcogen Atoms in Alkyl Halides and Chalcogenides

Radical	Halide / Chalcogenide	Temp (°C)	k ($M^{-1}s^{-1}$)	Reference
$CH_3(CH_2)_6\dot{C}H_2$	$(CH_3)_3CI$	50°	3×10^6	65a
	$(CH_3)_2CHI$	50°	5.6×10^5	65a
	$c\text{-}C_6H_{11}I$	50°	5.1×10^5	65a
	CH_3CH_2I	50°	1.7×10^5	65a
	Cl_3CBr	80°	2.6×10^8	65b
	Cl_3CBr	80°	1.3×10^9	65b
$Ph^{\bullet}$	Cl_3CBr	80°	1.6×10^9	65b
	Cl_3CBr	25°	2.8×10^9	65b
$CH_3(CH_2)_6\dot{C}H_2$	$(CH_3)_3CBr$	50°	4.6×10^3	65a
	$(CH_3)_2CHBr$	50°	1.2×10^3	65a
	$c\text{-}C_6H_{11}Br$	50°	8×10^2	65a
	$CH_3(CH_2)_3Br$	50°	6×10^2	65a
	$(CH_3)_3CCl$	50°	6×10^2	65a
	CCl_4	50°	2.4×10^5	65a
	CCl_4	27°	5.8×10^4	65c
	CCl_4	27°	5.0×10^3	65c
${}^tBu^{\bullet}$	CCl_4	27°	3.1×10^4	65c
$R\dot{C}H_2$	$ICMe(CO_2Et)_2$	50°	1.8×10^9	66
	ICH_2CN	50°	1.7×10^9	66
	$ICMe_2CO_2Et$	50°	6×10^8	66
	ICH_2CO_2Et	50°	2.6×10^7	66
	$BrCMe(CO_2Et)_2$	50°	1.0×10^6	66
	$BrCH_2CO_2Et$	50°	7×10^4	66
$CH_3(CH_2)_9\dot{C}H_2$	MeSSMe	25°	6×10^4	62
	PhSSPh	25°	2×10^5	62
	$MeSCMe(CN)_2$	25°	8×10^4	62
	$MeSCBu(CN)_2$	25°	7×10^4	62
	$PhSCMe(CN)_2$	25°	2.3×10^5	62
$CH_3(CH_2)_6\dot{C}H_2$	$PhSCMe(CN)_2$	50°	6×10^5	62
	PhSeSePh	50°	2.6×10^7	67
	$PhSeCH_2CO_2Et$	50°	1×10^5	62
	$PhSeCMe_2CO_2Et$	50°	2.3×10^5	62
	$PhSeCH_2CN$	50°	2.3×10^5	62
	$p\text{-}MeOPhSeCH_2CN$	50°	2.3×10^5	62

Radical	Halide / Chalcogenide	Temp (°C)	k ($M^{-1}s^{-1}$)	Reference
$CH_3(CH_2)_6\dot{C}H_2$	p-$ClPhSeCH_2CN$	50°	3.0×10^5	62
	$PhSeCMe(CO_2Et)_2$	50°	8×10^5	62
	$PhSeCMe(CN)_2$	50°	8×10^6	62
	PhTeTePh	50°	1.1×10^8	67
	$PhTeCH_2CO_2Et$	50°	2.3×10^7	62

On the basis of these data, homolytic substitution reactions at the sulfur atom in sulfides and the selenium atom in selenides would be expected to be efficient methods for the preparation of rings containing these heteroatoms and has been demonstrated to be so in the numerous examples provided previously (Schemes 18 and 19).



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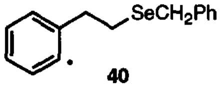

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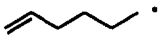

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Rate constant data for intermolecular homolytic substitution reactions between carbon centres are also rather limited. Table 2 provides a list of representative rate constants. Examples include values of 3×10^6 $M^{-1}s^{-1}$ for abstraction of iodine atom from *tert*-butyl iodide by primary alkyl radicals at 50°, 5×10^3 $M^{-1}s^{-1}$ for the similar abstraction of bromine atom from *tert*-butyl bromide, and 6×10^2 $M^{-1}s^{-1}$ for abstraction of chlorine atom from *tert*-butyl chloride at 50°.[65a] Chalcogen transfer rate constants (25°) include values of 2.3×10^5 $M^{-1}s^{-1}$ for attack of undecyl radical at the sulfur atom in **42**, 8×10^6 $M^{-1}s^{-1}$ for attack of octyl radical at the selenium atom in **43** and 2.3×10^7 $M^{-1}s^{-1}$ for the similar attack at the tellurium atom in **44**.[62]

$PhSC(Me)(CN)_2$	$PhSeC(Me)(CN)_2$	$PhTeCH_2CO_2Et$
42	**43**	**44**

Inspection of the data in Table 2 reveals some interesting trends. When the attacking radical is primary alkyl and given similar leaving groups on the heteroatom undergoing substitution, it would appear that chlorine and sulfur have similar reactivities. Bromine and selenium are also similar and react approximately ten times more rapidly than chlorine or sulfur, while iodine and tellurium react approximately 1000 times more rapidly than chlorine or sulfur.

5.3. Computational Data

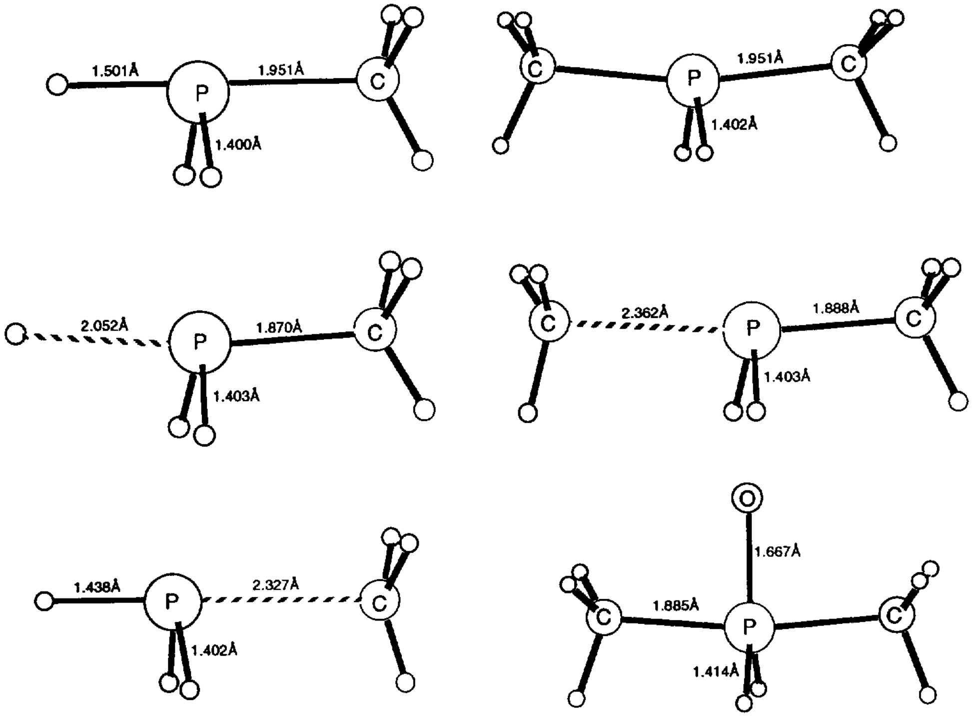
The past fifteen years has seen computational data provide significant insight into the nature of chemical reactions in systems of increasing sophistication. Molecular orbital methods, both semiempirical and *ab initio* can provide physical details of transition states and transient intermediates not readily observable by experimental techniques. These computer methods are well suited to exploring the intimate details of homolytic substitution chemistry with the aim of providing insight into the existence of hypervalent intermediates.

Tables 4 and 5 detail calculated reaction profiles for a wide cross-section of homolytic substitution reactions. The preface to these tabulated data also discusses briefly the computational methods employed.

5.3.1. *Phosphorus, Arsenic and Antimony*

Early *ab initio* molecular orbital calculations (HF/4-31G) predict that the phosphoranyl radical (PH_4) is a transition state on the reaction pathway for attack of hydrogen atom at phosphine.[68] This result is almost certainly an artefact arising from the lack of polarization functions in the 4-31G basis set. Simple inclusion of a set of d-functions on phosphorus has a dramatic effect. HF/3-21G$^{(*)}$ calculations suggest that PH_4 corresponds to a hypervalent species with a barrier of 9.0 kJ.mol^{-1} to dissociation.[69] Higher level calculations (MP5/6-31G**//MP2/6-31G**) predict that this barrier is more substantial at some 25.3 kJ.mol^{-1}.[70]

Figure 1. MP2/6-31G** Calculated structures of some phosphoranyl radicals and transition states for their formation in reactions involving hydrogen atom and methyl radical.



Ab initio molecular orbital calculations for attack of methyl,[70] and other[71] radicals at the phosphorus atom in alkyl phosphines and phosphine oxides[72] predict the involvement of hypervalent species, in good agreement with experimental observations (see previous). For example, the dimethylphosphoranyl radical (Me_2PH_2) is predicted to be constrained by a barrier of 13.9 kJ.mol^{-1} and to lie some 14.9 kJ.mol^{-1} above the reactants at the MP4/6-31G**//MP2/6-31G** level of theory.[70] In addition, Cramer reported that hydroxyphosphoranyl and fluorophosphoranyl radicals also correspond to intermediates.[71] Selected calculated phosphoranyl radical intermediates and transition states for their formation are displayed in Figure 1, while Tables 4 and 5 attempt to provide a comprehensive list of calculational data for a variety of homolytic substitution reactions.

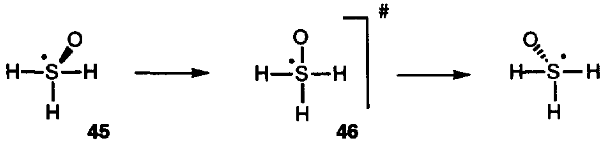
Low-levels of theory also predict the involvement of hypervalent intermediates in free-radical attack by hydrogen atom at the arsenic atom in arsine (AsH_3) and the antimony atom in stibine (SbH_3).[69] At HF/3-21G$^{(*)}$ level of theory, AsH_4 is predicted to constrained by a barrier of only 1.6 kJ.mol^{-1}, while the similar barrier for SbH_4 is predicted to be 12.2 kJ.mol^{-1}. At the HF/HUZ-SV** level,[69,73] these barriers are reduced slightly to 0.8 and 10.7 kJ.mol^{-1} respectively.

5.3.2. *Sulfur, Selenium and Tellurium*

The choice of basis set may be crucial in predicting correctly the nature of hypervalent species involved in homolytic substitution chemistry. We showed recently that the (valence) double-ζ pseudopotential basis set (DZP) of Hay and Wadt[74,75] (with the inclusion of polarization functions[75]) is a reliable basis in calculations involving homolytic substitution at chalcogen.[73] Some other pseudopotential basis sets were shown to be less reliable.[75] In particular QCISD/DZP calculations predict correctly the nature of SH_3, a species with a measured lifetime of at least 0.56 μs.[59] In contrast, SH_3 is predicted to be a transition state in every other reported theoretical study, even when calculations using large all-electron basis sets and substantial electron correlation [QCISD/6-311G(2df,2p)] are performed.[75]

Attack of hydroxyl radical at the sulfur atom in dimethylsulfide is predicted to proceed without the involvement of a hypervalent intermediate at the MP4/6-31G* level of theory.[76] Similarly attack of alkyl radicals at the sulfur atom in sulfides is predicted to proceed without the involvement of an intermediate at all reported levels of theory, including MP2/DZP, strongly suggesting that homolytic substitution at sulfur atoms which contain no radical-stabilizing ligands do not involve hypervalent intermediates.[77] The transition states involved in these reactions are calculated to be of C_{2v} symmetry at SCF levels of theory, but deviate somewhat (but not greatly) from co-linearity with the inclusion of electron correlation.[77] At the QCISD/DZP//MP2/DZP level, the barrier for the attack of methyl radical at the sulfur atom in methanethiol with expulsion of methyl radical was calculated to be 87.4 kJ.mol^{-1}.[77c] Selected sulfuranyl radical transition states are displayed in Figure 2, while other selected data are listed in Tables 4 and 5.

Scheme 24

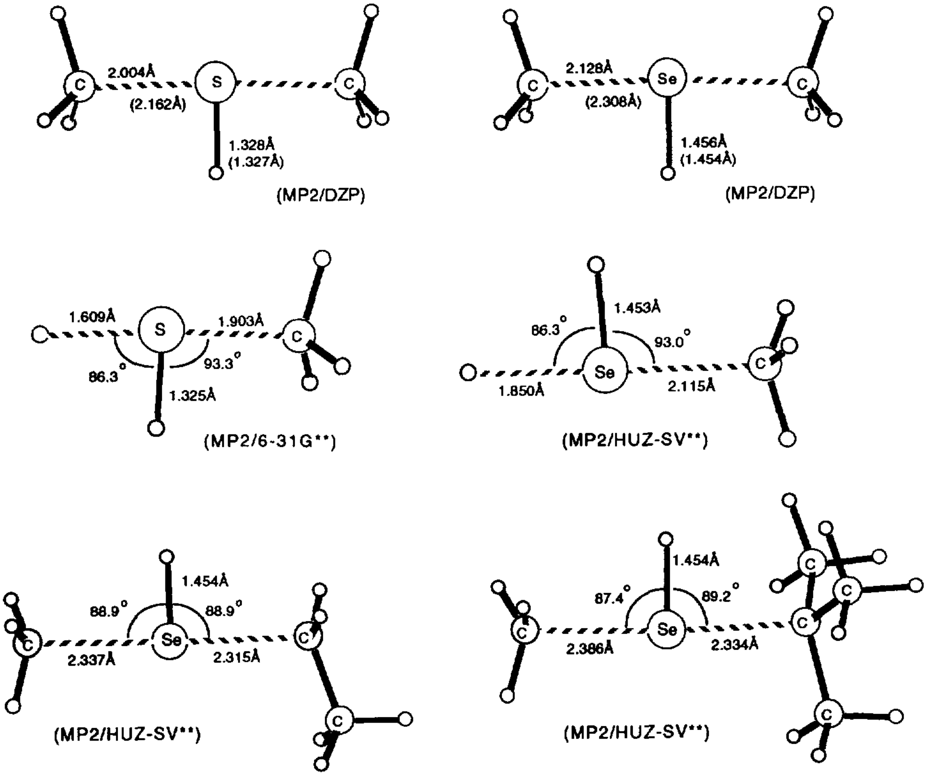


In contrast, homolytic attack by hydrogen atom and methyl radical at the sulfur atom in sulfoxides is predicted to lead to the formation of hypervalent intermediates.[77a] These, in turn are calculated to be constrained with barriers of only 0.3-4.5 kJ.mol^{-1} at the MP2/6-31G** level of theory. It seems reasonable to propose, therefore, that the inversion of configuration observed in the ring closure of **28** (Scheme 18) involves an intermediate which is too short lived to undergo racemization processes prior to dissociation. Indeed, inversion of intermediate **45** (Scheme 24) through the square-planar transition state (**46**) is calculated to require

64.1 kJ.mol^{-1} (MP2/6-31G**).[77a] With such small barriers to dissociation, the intermediates involved in these reactions are more likely to resemble transition states.[77a]

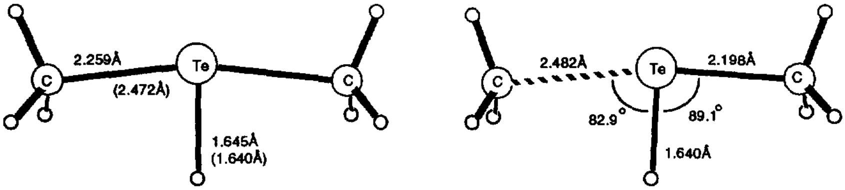
Like its sulfur analogue, H_3Se is predicted to correspond to a transient intermediate when MP2/DZP and QCISD/DZP levels of theory are used.[75] In contrast, homolytic substitution at the selenium atom in a range of alkyl selenides is predicted to proceed without the involvement of (9-Se-3) intermediates at all reported levels of theory.[47e,73, 77c,d] Once again the transition states involved in these reactions are predicted to deviate slightly from co-linearity at the higher levels of theory. At the MP2/HUZ-SV**//UHF/HUZ-SV** level[73] the activation barriers for the attack of variety of alkyl radicals at methaneselenol with the expulsion of methyl radical are predicted to be largely independent of the nature of the attacking radical with calculated energy barriers of approximately 75 kJ.mol^{-1} in all cases studied. At the QCISD/DZP//MP2/DZP level, the barrier for the attack of methyl radical at the selenium atom in methaneselenol with expulsion of methyl radical was calculated to be 61.3 kJ.mol^{-1}.[77] Selected transition states are displayed in Figure 2, while other selected data are listed in Tables 4 and 5.

Figure 2. *Ab initio* calculated structures of some transition states involved in homolytic substitution at sulfur and selenium.



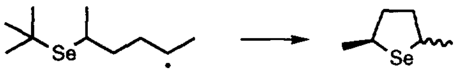
Homolytic attack by hydrogen atom at the tellurium atom in H_2Te or methyl radical at methanetellurol with the expulsion of hydrogen atom or methyl radical respectively is predicted to proceed with the involvement of hypervalent intermediates at most reported levels of theory.[75,77c,d] At the SCF/DZP level Me_2TeH is calculated to correspond to a transition state.[77c] The intermediates resemble slightly-distorted T-shapes and are predicted to be contained within shallow wells with barriers to dissociation of 4.4-7.5 kJ.mol^{-1} at the MP2/DZP level of theory, rising to 12.3 kJ.mol^{-1} when QCISD/DZP calculations are performed on the reaction involving H_3Te.[75] At the QCISD/DZP//MP2/DZP level, the barrier for the attack of methyl radical at the tellurium atom in methanetellurol with expulsion of methyl radical was calculated to be 25.5 kJ.mol^{-1}.[77c,d] MP2/DZP calculated structures of Me_2TeH and the transition state for its formation are displayed in Figure 3, while other selected data are listed in Tables 4 and 5.

Figure 3. MP2/DZP calculated structures of Me_2TeH and the transition state for its formation.



Molecular mechanics calculations have been used to gain insight into the stereochemistry of some cyclization reactions at selenium.[47b] For example the 5-(*tert*-butylseleno)hex-2-yl radical (**47**) was predicted to ring close with essentially no stereochemical control, in excellent agreement with experimental observations (Scheme 25).[47b]

Scheme 25



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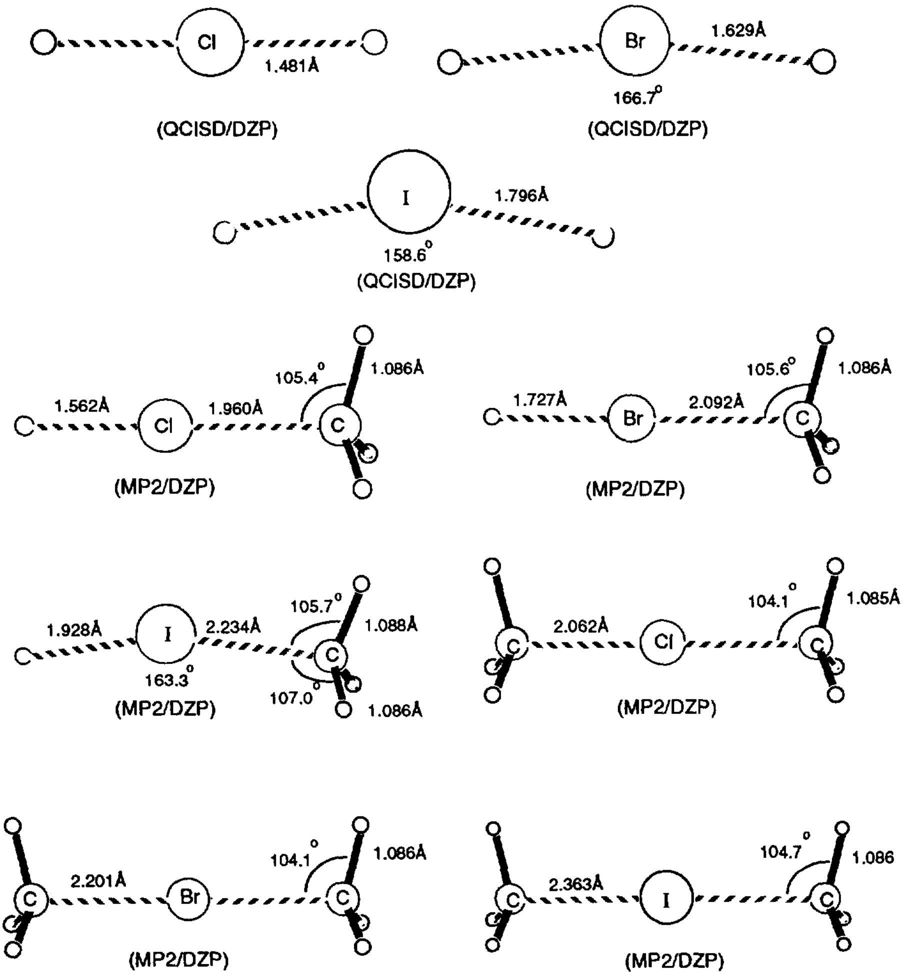
(cis:trans 1:1)

5.3.3. *Chlorine, Bromine and Iodine*

Transfers of halogen atoms between hydrogen atoms and/or methyl radicals are representative of intermolecular group transfer chemistry. We reported recently that calculations involving the DZP basis sets with and without the inclusion of electron correlation predict that these reactions proceed without the involvement of hypervalent intermediates in all cases studied.[78] QCISD/DZP energy barriers for attack of hydrogen atom with expulsion of hydrogen atom range from 104.8 kJ.mol^{-1} (Cl) to 74.3 kJ.mol^{-1} (Br) and 47.2 kJ.mol^{-1} (I). Similar data (QCISD/DZP//MP2/DZP) for attack of methyl radical (with expulsion of methyl) range from 115.9 kJ.mol^{-1} (Cl) to 82.2 kJ.mol^{-1} (Br) and 51.5 kJ.mol^{-1} (I). Selected calculated transition structures are displayed in Figure 4, while other selected data are listed in Tables 4 and 5.

Inspection of Figure 4 reveals that reactions involving attack of hydrogen atom at halogen are predicted to deviate somewhat from the expected co-linear arrangement of attacking and leaving groups, while reactions not involving hydrogen atom are calculated to be exactly co-linear in each case. This phenomenon has also been observed for H_3S, H_3Se and H_3Te,[73,75] and has been explained in terms of hyperconjugative stabilization of those species containing hydrogen in the apical position of the (hypothetical) trigonal bipyramid due to overlap between the lone-pairs of electrons on the central heteroatom and the hydrogen s-orbital.[73]

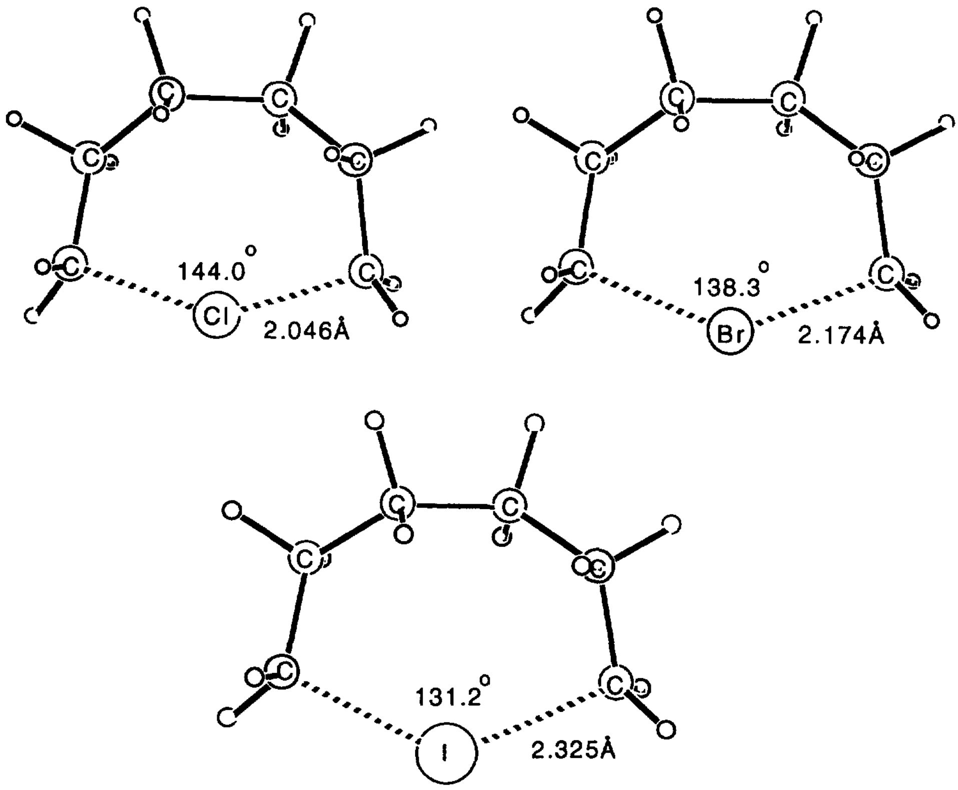
Figure 4. *Ab initio* calculated structures of some transition states involved in homolytic substitution at chlorine, bromine and iodine.



It would appear that homolytic substitution reactions by alkyl radicals at halogen prefer to proceed via transition states in which the attacking and leaving groups are co-linear, or nearly so. As a result of this co-linear requirement, intramolecular halogen transfer reactions might be expected to be difficult; indeed, as previously mentioned, we are unaware of any intramolecular reactions of this type.

In order to provide further insight, we are currently examining the details of intramolecular homolytic halogen transfer reactions through the use of *ab initio* molecular orbital calculations. At this time we report that the transition states involved in the 1,6- transfer of halogen in the 6-halohex-1-yl radicals are calculated at the SCF/DZP and MP2/DZP levels of theory to be substantially deviated from the ideal co-linear arrangement of attacking and leaving group, as depicted in Figure 5.[72] This deviation, as expected, is most pronounced for iodine transfer and results in a substantial increase in the reaction barriers in all cases. For example, 1,6-chlorine transfer is predicted to be accompanied with a barrier of 170.5 kJ.mol^{-1} at the MP2/DZP level, while the equivalent processes at bromine and iodine have calculated barriers of 149.3 and 135.2 kJ.mol^{-1} repectively.[72]

Figure 5. MP2/DZP Calculated transition states for homolytic 1,6-halogen transfer reactions.



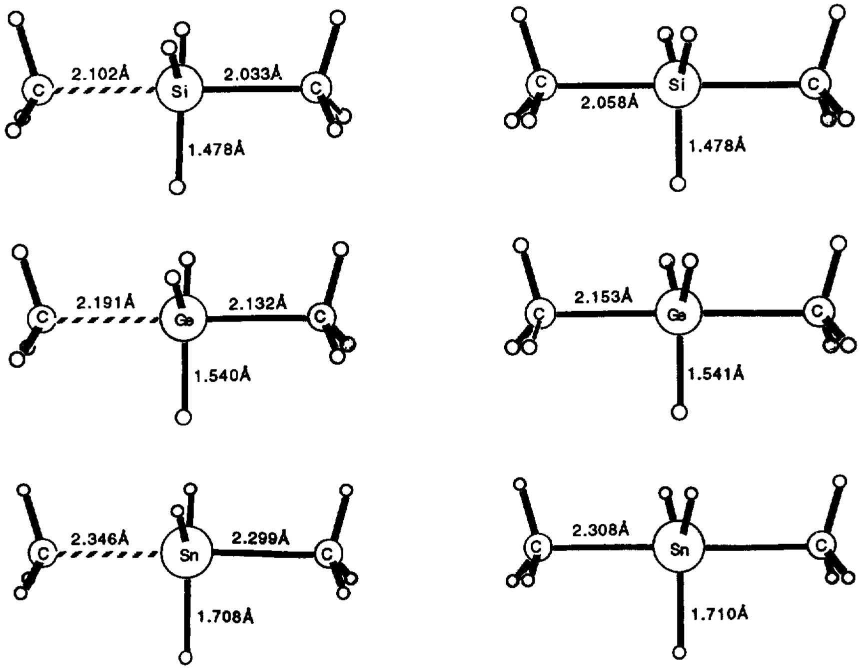
Calculations have provided considerable mechanistic insight into homolytic substitution reactions at halogen and chalcogen; these transfers between carbon centres would appear to prefer a co-linear (or nearly so) arrangement of attacking and leaving radicals, tellurium is predicted to undergo transfer most efficiently and with the involvement of a short-lived hypervalent (9-Te-3) intermediate. The following order of reactivity for homolytic substitution by methyl radical is predicted: Cl < S < Br < Se < I < Te.

5.3.4. *Silicon, Germanium and Tin*

At this time we are unaware of any published computational data pertaining to homolytic substitution at silicon, germanium or tin. We are, however, able to provide some preliminary results obtained within our laboratories.[79]

QCISD/DZP + ZPVE calculations predict that homolytic substitution by hydrogen atom at the heteroatom in silane, germane and stannane with expulsion of hydrogen atom proceeds without the involvement of hypervalent intermediates. Energy barriers for these reactions are calculated to be 72.0, 76.9 and 68.9 kJ.mol^{-1} for attack at silicon, germanium and tin respectively. Similar results are obtained for attack at methylsilane, methylgermane and methylstannane with expulsion of methyl radical at the QCISD/DZP//MP2/DZP level of theory. Energy barriers are calculated to be 68.9, 67.7 and 56.3 kJ.mol^{-1} for attack at silicon, germanium and tin respectively. Further calculated data are displayed in Table 4.

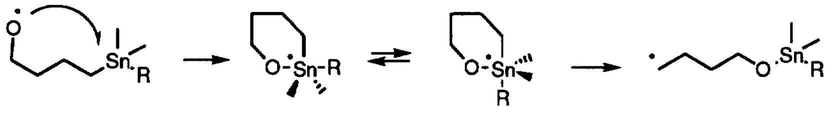
Figure 6. Calculated transition states and intermediates involved in some homolytic substitution reactions at silicon, germanium and tin.



At the QCISD/MP2//MP2/DZP level of theory, attack of methyl radical at the heteroatom in methylsilane, methylgermane and methylstannane are predicted to proceed with the involvement of hypervalent intermediates which are calculated to lie in shallow wells, with barriers to dissociation of 2.0 - 2.8 kJ.mol^{-1}. Energy barriers associated with these reactions are calculated to be 105.5, 103.5 and 86.9 kJ.mol^{-1} for attack at silicon, germanium and tin respectively. With energy barriers of this magnitude, it is not surprising that homolytic transfer between carbon centres of groups containing these heteroatoms has not been reported. Selected transition states and intermediates are displayed in Figure 6.

It is likely that involvement of radical stabilizing groups on the heteroatom will have the effect of lowering both the activation barriers associated with these reactions and the energy of the hypervalent intermediate. Given the co-linear geometric requirement of the transition states involved in homolytic substitution at silicon, germanium and tin (Figure 6), it seems unlikely that the intramolecular group transfer reactions reported by Davies,[41]Kim[42] and others[37-40] (see previous) proceed via single (smooth) transition states. It seems plausible that these reactions involve intermediates which undergo pseudorotation prior to dissociation (eg. Scheme 26). Interestingly, some years ago Symons and coworkers reported ESR data for a radical species formed upon reaction of Me_4Sn with methyl radical which they assign to be Me_5Sn.[80] Work in our group is currently examining the effect of stabilizing groups on the course of these reactions by *ab initio* molecular orbital calculations.

Scheme 26

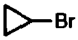
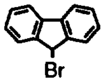
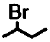


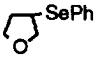
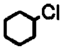
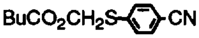
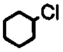
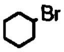
5.4. Silyl, Germyl and Stannyl Radicals

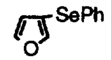
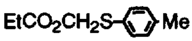
It is interesting to compare the mechanistic details of homolytic substitution by carbon centred radicals at chalcogen and halogen with the analogous reactions involving silicon, germanium and tin centred radicals. These reactions are of fundamental importance in synthesis. As mentioned previously, alkyl and aryl halides, phenylselenides and aryltellurides are often used as radical precursors (Scheme 11). We recently reported that *ab initio* calculations (QCISD/DZP//MP2/DZP) on the reactions of silyl (SiH_3), germyl (GeH_3) and stannyl (SnH_3) radicals at the heteroatom in alkyl halides, methanethiol, methaneselenol and methanetellurol with the expulsion of methyl radical, proceed without the involvement of hypervalent intermediates.[77c,d,78] Representative transition states involved in these reactions are displayed in Figure 7. Activation energies for the forward reactions range from 9.6 kJ.mol^{-1} (Si/Te) to 80.3 kJ.mol^{-1} (Sn/Cl) and are listed in Table 4.

These calculational data are to be compared with available rate constant data, which are listed in Table 3. There are few rate data for homolytic substitution by silicon, germanium or tin -centred radicals at chalcogens or halogens with the expulsion of methyl radical. Available data include rate constants of 8.1 x 10^9 and 2.5 x 10^9 $M^{-1}s^{-1}$ (25°) for attack of triethylsilyl and tributylstannyl radicals at the iodine atom in iodomethane, a factor of 3.2 in favour of the triethylsilyl radical. The QCISD/DZP//MP2/DZP energy barriers of 21.8 and 27.2 kJ.mol^{-1} for attack of silyl (SiH_3) and stannyl (SnH_3) radicals respectively at iodomethane translates into a rate factor of approximately 8 (25°) in favour of the silyl radical. Other comparisons between calculated data and available rate constants have been made.[77c] The reader is also referred to the excellent compilation of free-radical rate constant data found in the Landolt-Börnstein series.[64]

Table 3. Selected rate constant data for homolytic substitution by silicon, germanium and tin -centred radicals at alkyl halides and chalcogenides.

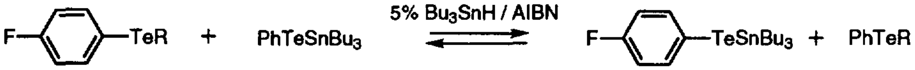
Radical	Substrate	Temp (°C)	k ($M^{-1}s^{-1}$)	Reference
$Et_3Si^\bullet$	$(CH_3)_2CHI$	ca. 27°	1.4×10^{10}	81
	CH_3CH_2I	ca. 27°	4.3×10^9	81
	CH_3I	ca. 27°	8.1×10^9	81
	PhI	ca. 27°	1.5×10^9	81
	$PhCH_2Br$	ca. 27°	2.4×10^9	81
		ca. 27°	1.5×10^9	81
	^tBuBr	ca. 27°	1.1×10^9	81
		ca. 27°	5.4×10^8	81
		ca. 27°	3.4×10^8	81
	PhBr	ca. 27°	1.1×10^8	81
	CCl_4	ca. 27°	4.6×10^9	81
		ca. 27°	2.4×10^7	81
	$PhCH_2Cl$	ca. 27°	2.0×10^7	81
	^tBuCl	ca. 27°	2.5×10^6	81
		ca. 27°	3.1×10^5	81
	PhCl	ca. 27°	6.9×10^5	81
$Me_3Si\dot{S}iMe_2$	^tBuBr	21°	2.6×10^8	82
		21°	1.6×10^8	82
	^tBuCl	21°	4.2×10^5	82
$(Me_3Si)_3Si^\bullet$		20°	2.1×10^9	86
	$PhCH_2Br$	20°	9.6×10^8	86
	^tBuBr	20°	1.2×10^8	86
	$C_{10}H_{21}SePh$	21°	9.6×10^7	21
		20°	4.6×10^7	86
		20°	2.0×10^7	86
	CCl_4	20°	1.7×10^8	86
	$CHCl_3$	20°	6.8×10^6	86
	$C_{10}H_{21}SPh$	21°	$\leq 5 \times 10^6$	21
$Bu_3\dot{G}e$	$PhSeCH_2CO_2Et$	25°	9.2×10^8	22
	^tBuBr	27°	8.6×10^7	83
		27°	4.6×10^7	83
	$C_8H_{17}Br$	25°	4.6×10^7	22
	$BuOCH_2SePh$	25°	2.3×10^7	22

Radical	Substrate	Temp (°C)	k ($M^{-1}s^{-1}$)	Reference
$\mathrm{Bu_3\dot{G}e}$	$BuCO_2CH_2SePh$	25°	2.0×10^7	22
		25°	1.6×10^7	22
	$ClCH_2CO_2Et$	25°	1.8×10^6	22
	$PhCH_2Cl$	25°	1.3×10^6	22
	$PhSCH_2CO_2Et$	25°	8.5×10^5	22
	$PrCO_2CH_2Cl$	25°	1.1×10^5	22
	^tBuCl	27°	$< 5 \times 10^4$	83
	$BuOCH_2SPh$	25°	1.6×10^4	22
		25°	1.2×10^4	22
		25°	1.0×10^4	22
	$PrCO_2CH_2SPh$	25°	4.5×10^3	22
$\mathrm{Me_3\dot{S}n}$	^tBuCl	25°	5.9×10^3	84
		25°	4.9×10^2	84
$\mathrm{Ph_3\dot{S}n}$	^tBuCl	25°	2.0×10^4	84
$\mathrm{Bu_2H\dot{S}n}$	^tBuCl	25°	4.7×10^3	84
$\mathrm{Bu_2Cl\dot{S}n}$	^tBuCl	25°	3.9×10^3	84
$\mathrm{Bu_3\dot{S}n}$	CH_3I	25°	2.5×10^9	84
	$PhCH_2Br$	25°	1.5×10^9	83
	^tBuBr	20°	1.7×10^8	83
	$PhSeCH_2CO_2Et$	25°	1.0×10^8	85
	$C_8H_{17}Br$	25°	3×10^7	85
	^tBuBr	25°	8.5×10^7	84
		20°	2.6×10^7	83
		25°	2.2×10^7	84
		25°	1.9×10^7	84
	$BuOCH_2SePh$	25°	6×10^6	85
	$BuCO_2CH_2SePh$	25°	3×10^6	85
	$PhCH_2Cl$	25°	2×10^6	85
	$PhCH_2Cl$	20°	1.1×10^6	83
	$PhCH_2Cl$	25°	6.4×10^5	84
	$ClCH_2CO_2Et$	25°	1×10^6	85

Radical	**Substrate**	**Temp (°C)**	**k ($M^{-1}s^{-1}$)**	**Reference**
$Bu_3Sn^\bullet$		25°	7 x 10^5	85
	$PhSCH_2CO_2Et$	25°	2 x 10^5	85
		25°	2 x 10^5	85
	$BuOCH_2Cl$	25°	1 x 10^5	85
	$PrCO_2CH_2Cl$	25°	4 x 10^4	85
	^tBuCl	20°	2.7 x 10^4	83
	$C_{11}H_{21}Cl$	25°	7 x 10^3	85
		20°	1.4 x 10^3	83
	$BuOCH_2SPh$	25°	1 x 10^3	85
		25°	8.5 x 10^2	84
	$PrCO_2CH_2SPh$	25°	4 x 10^2	85

Of some importance are the barriers for the reverse reactions, namely attack of methyl radical at the chalcogen or halogen centre with expulsion of the silyl, germyl or stannyl radical (Table 2). In particular QCISD/DZP//MP2/DZP calculations suggest that methyl radical is capable of displacing stannyl radical from sulfur, selenium and tellurium, with calculated activation energies of 62.4, 48.1 and 26.3 kJ.mol^{-1} respectively.[77c,d,78] These data suggest that stannane reductions of alkyl selenides and tellurides are reversible while reactions at alkyl sulfides are endothermic.

Scheme 27



48 **49** **50** **51**

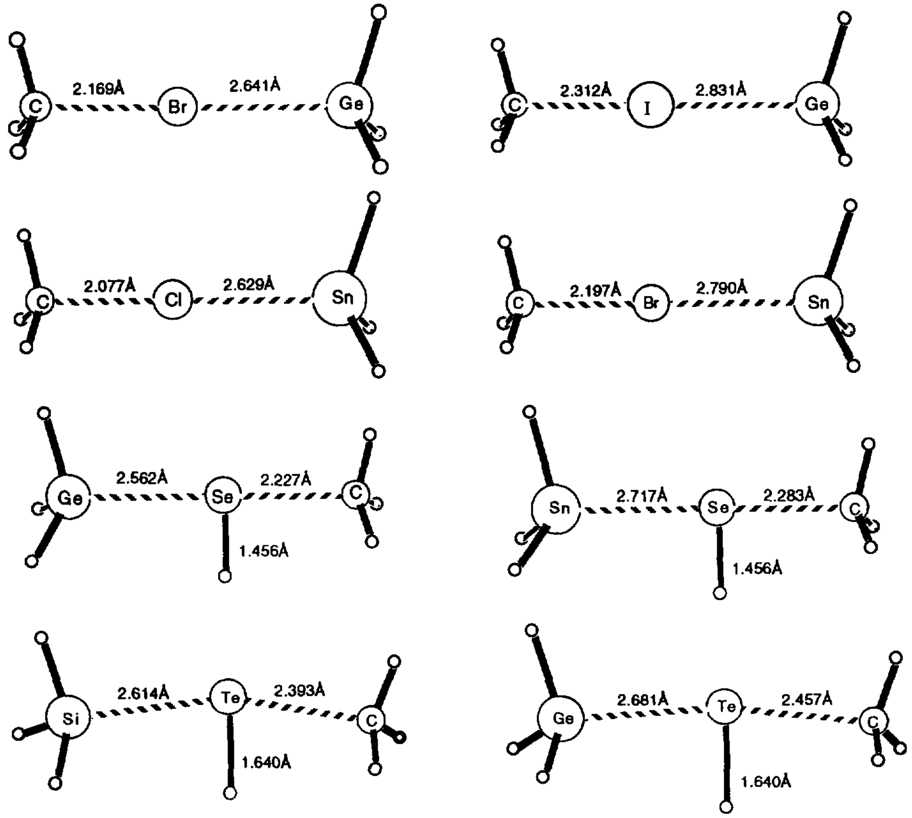
R = Me, Et, i-Bu

This predicted reversibility is certainly unexpected and to us seemed contra-intuitive. In order to provide experimental evidence in support of the calculational data, we examined the reactions of substituted alkyl aryl tellurides (**48**) with phenyltellurotributyltin (**49**) in the presence of a catalytic amount of tributyltin hydride (AIBN initiator) (Scheme 27).[87] The appearance of the ligand-exchange products (**50**, **51**) by ^{119}Sn and ^{125}Te NMR spectroscopy[87] provides strong evidence that methyl, primary and secondary alkyl radicals are capable of displacing stannyl radicals from tellurium, in agreement with the calculational data.

6. *Concluding Remarks*

In this report we have attempted to provide an overview of homolytic substitution chemistry with particular reference to the formation of bonds to heteroatoms. There now exist synthetic, kinetic, mechanistic and computational data to provide chemists with sufficient information for the design of synthetic methods based on this chemistry. We hope that the reader will be encouraged to use this free-radical methodology and that future years sees this chemistry unfold into a useful and commonly used alternative to the more traditional methods based on free-radical addition reactions.

Figure 7. MP2/DZP optimized transition states involved in homolytic substitution by silyl, germyl and stannyl radicals at some methyl chalcogenols and methyl halides.



7. *Tables of Computational Data*

We have attempted to provide a comprehensive compilation of computational data for homolytic substitution reactions by a variety of radicals at several heteroatoms. Table 4 details energy barriers for reactions which are predicted not to involve intermediates, while Table 5 lists data for reactions which are calculated to proceed with the involvement of intermediates. Some reactions are listed in both tables because the nature of the potential energy surface is dependent on the level of theory employed.

The calculations reported in this section have generally been performed using *ab initio* techniques. Until more recently, these calculations employed small all-electron basis sets (3-21G, 4-31G) and were performed at the Hartree-Fock (HF, SCF) level of theory. The inclusion of polarization functions was shown early on to be important in order to adequately reproduce the properties of molecules containing second and third-row heteroatoms; without the inclusion of these functions the results have proven to be of questionable reliability. When polarization functions are included (3-21G$^{(*)}$, 6-31G*, 6-31G**, D95**, 6-311G**, HUZ-SV** etc.) more reliable data are obtained. The inclusion of diffuse functions appears to be much less important.[75]

With recent advances in computer technology, it has become possible to routinely perform calculations which include the effects of electron correlation. Calculations utilizing moderate basis sets (eg. D95**, 6-31G*, 6-311G**) together with correlation correction (MP2, MP4, MP5, QCISD etc.) demonstrated that electron correlation is also important in describing accurately both the nature and properties of hypervalent structures involving higher heteroatoms. Clearly, the best results would be expected from calculations which include a high level of correlation with a good quality basis augmented with polarization functions (eg. QCISD/6-311G**).

Unfortunately, despite modern advances in technology, some calculations are still prohibitive because of the size of the molecule or individual atoms in question. Calculations involving tellurium and iodine are clear examples of systems for which data are difficult to obtain using reliable levels of theory. Fortunately, the advent of pseudopotential (effective core potential) basis sets in which core electrons are replaced with functions which simulate both electronic and relativistic effects, has largely alleviated these problems. The (valence) double-ζ pseudopotential basis reported by Hay and Wadt for higher heteroatoms,[74] when augmented with polarization functions appears to perform well for many homolytic substitution reactions.[75] Of course, when electron correlation is included, this basis would be expected to provide superior results. When combined with the D95** basis set for first-row elements, this basis has been referred to (by us) as the DZP basis set. Often zero-point vibrational energy correction (ZPVE) is also included in the calculation in order to provide a more accurate estimate of energy barriers.

Pople and co-authors provide an excellent overview of *ab initio* molecular orbital techniques in their 1986 book.[88]

Table 4. Calculated energy barriers (kJ.mol^{-1}) for homolytic substitution reactions not involving intermediates.

$$\dot{A} + Y\text{-}L \xrightarrow{\Delta E_1} \left. A\text{---}Y\text{---}L \right]^{\#\bullet} \xrightarrow{\Delta E_2} A\text{-}Y + \dot{L}$$

Reaction	Transition state	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$PH_3 + H^{\bullet} \longrightarrow PH_3 + H^{\bullet}$	$^{\bullet}PH_4$	54.3	54.3	HF/4-31G	68
$H_2S + H^{\bullet} \longrightarrow H_2S + H^{\bullet}$	$H_3S^{\bullet}$	64.9	64.9	MP2/6-31G**	77a
$H_2S + Me^{\bullet} \longrightarrow MeSH + H^{\bullet}$	$Me\dot{S}H_2$	95.8	52.7	MP2/6-31G**	77a
$MeSH + Me^{\bullet} \longrightarrow MeSH + Me^{\bullet}$	$Me_2\dot{S}H$	81.2	81.2	MP2/6-31G**	77a
		126.9	126.9	SCF/DZP	77c,d
		85.9	85.9	MP2/DZP	77c,d
		87.4	87.4	QCISD/DZP//MP2/DZP	77c,d
$Me_2S + Me^{\bullet} \longrightarrow Me_2S + Me^{\bullet}$	$Me_3S^{\bullet}$	80.3	80.3	HF/4-31G* + ZPVE	77e
		55.3	55.3	MBPT(2)/4-31G*//HF/4-31G* + ZPVE	77e
		66.4	66.4	MBPT(3)/4-31G*//HF/4-31G* + ZPVE	77e
		55.0	55.0	SDTQ-MBPT(4)/4-31G*//HF/4-31G* + ZPVE	77e

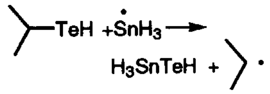
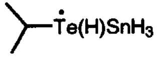
Reaction	Transition state	ΔE1	−ΔE2	Level of Theory	Ref.
$\mathrm{Me_2S} + \dot{\mathrm{O}}\mathrm{H} \longrightarrow \mathrm{MeSOH} + \mathrm{M\dot{e}}$	$\mathrm{Me_2\dot{S}OH}$	306	243	HF/6-31G* + ZPVE	76
		170	158	MP2/6-31G*//HF/6-31G* + ZPVE	76
		193	169	MP4/6-31G*//HF/6-31G* + ZPVE	76
$\mathrm{H_2Se} + \mathrm{H}^{\bullet} \longrightarrow \mathrm{H_2Se} + \mathrm{H}^{\bullet}$	$\mathrm{H_3S\dot{e}}$	67.4	67.4	HF/3-21G(*)	73
		73.6	73.6	HF/HUZ-SV**	73
		53.6	53.6	MP2/HUZ-SV**//HF/HUZ-SV**	73
		44.8	44.8	MP4/HUZ-SV**//HF/HUZ-SV**	73
$\mathrm{H_2Se} + \mathrm{M\dot{e}} \longrightarrow \mathrm{MeSeH} + \mathrm{H}^{\bullet}$	$\mathrm{Me\dot{S}eH_2}$	110.9	49.4	HF/3-21G(*)	73
		136.0	49.9	HF/HUZ-SV**	73
		87.4	45.2	MP2/HUZ-SV**//HF/HUZ-SV**	73
		92.0	33.5	MP4/HUZ-SV**//HF/HUZ-SV**	73
$\mathrm{MeSeH} + \mathrm{M\dot{e}} \longrightarrow \mathrm{MeSeH} + \mathrm{M\dot{e}}$	$\mathrm{Me{-}{-}\underset{\mathrm{H}}{\dot{\mathrm{S}}\mathrm{e}}{-}{-}Me}$	78.2	78.2	HF/3-21G(*)	73
		96.5	96.5	SCF/DZP	77c,d
		95.4	95.4	HF/HUZ-SV**	73
		76.6	76.6	MP2/HUZ-SV**//HF/HUZ-SV**	73
		67.8	67.8	MP4/HUZ-SV**//HF/HUZ-SV**	73
		61.1	61.1	MP2/DZP	77c,d
		61.3	61.3	QCISD/DZP//MP2/DZP	77c,d

Reaction	Transition state	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$MeSeH + \dot{Me} \longrightarrow Me_2Se + H^{\bullet}$	$Me\text{--}\underset{Me}{\dot{Se}}\text{--}H$	110.9	51.9	HF/3-21G(*)	73
		136.8	53.6	HF/HUZ-SV**	73
		76.6	41.4	MP2/HUZ-SV**//HF/HUZ-SV**	73
		80.8	28.9	MP4/HUZ-SV**//HF/HUZ-SV**	73
$Me_2Se + \dot{Me} \longrightarrow Me_2Se + Me^{\bullet}$	$Me_3\dot{Se}$	87.4	87.4	HF/3-21G(*)	73
		105.0	105.0	HF/HUZ-SV**	73
		79.9	79.9	MP2/HUZ-SV**//HF/HUZ-SV**	73
$EtSeH + \dot{Me} \longrightarrow MeSeH + Et^{\bullet}$	$Me\text{--}\underset{H}{\dot{Se}}\text{--}Et$	74.1	79.1	HF/3-21G(*)	73
		89.5	96.2	HF/HUZ-SV**	73
		73.6	72.4	MP2/HUZ-SV**//HF/HUZ-SV**	73
$^tBuSeH + \dot{Me} \longrightarrow MeSeH + {}^t\dot{Bu}$	$Me\text{--}\underset{H}{\dot{Se}}\text{--}{}^tBu$	68.2	78.7	HF/3-21G(*)	73
		79.5	103.3	HF/HUZ-SV**	73
$MeSeH + \dot{C}H_2OH \longrightarrow HOCH_2SeH + \dot{Me}$	$Me\text{--}\underset{H}{\dot{Se}}\text{--}CH_2OH$	80.8	68.2	HF/3-21G(*)	73
		95.4	80.8	HF/HUZ-SV**	73
		81.6	65.3	MP2/HUZ-SV**//HF/HUZ-SV**	73

Reaction	Transition state	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$\mathrm{MeSeH + \dot{C}H_2BH_2 \longrightarrow H_2BCH_2SeH + \dot{M}e}$	$\mathrm{Me{\cdot}{\cdot}\underset{\overset{\vert}{H}}{\dot{S}e}{\cdot}{\cdot}CH_2BH_2}$	72.0	29.7	HF/3-21G(*)	73
		97.9	54.8	HF/HUZ-SV**	73
		56.5	23.8	MP2/HUZ-SV**//HF/HUZ-SV**	73
$\mathrm{MeSeH + \dot{N}H_2 \longrightarrow NH_2SeH + \dot{M}e}$	$\mathrm{Me\dot{S}e(H)NH_2}$	107.9	73.2	HF/3-21G(*)	73
		131.4	73.6	HF/HUZ-SV**	73
		115.9	80.3	MP2/HUZ-SV**//HF/HUZ-SV**	73
		112.5	63.2	MP4/HUZ-SV**//HF/HUZ-SV**	73
$\mathrm{MeTeH + \dot{M}e \longrightarrow MeTeH + \dot{M}e}$	$\mathrm{Me_2\dot{T}eH}$	68.0	68.0	SCF/DZP	77c,d
$\mathrm{MeSH + \dot{S}iH_3 \longrightarrow H_3SiSH + \dot{M}e}$	$\mathrm{Me\dot{S}(H)SiH_3}$	86.0	149.7	SCF/DZP	77c,d
		64.3	94.7	MP2/DZP	77c,d
		60.3	95.2	QCISD/DZP//MP2/DZP	77c,d

Reaction	Transition state	ΔE1	-ΔE2	Level of Theory	Ref.
$\mathrm{MeSeH} + \dot{\mathrm{S}}\mathrm{iH_3} \rightarrow \mathrm{H_3SiSeH} + \dot{\mathrm{M}}\mathrm{e}$	$\mathrm{Me\dot{S}e(H)SiH_3}$	41.4	123.8	HF/3-21G(*)	73
		44.4	114.2	HF/HUZ-SV**	73
		19.7	120.9	MP2/HUZ-SV**//HF/HUZ-SV**	73
		12.6	58.2	MP4/HUZ-SV**//HF/HUZ-SV**	73
		59.3	125.0	SCF/DZP	77c,d
		40.6	71.5	MP2/DZP	77c,d
		35.5	72.0	QCISD/DZP//MP2/DZP	77c,d
$\mathrm{MeTeH} + \dot{\mathrm{S}}\mathrm{iH_3} \rightarrow \mathrm{H_3SiTeH} + \dot{\mathrm{M}}\mathrm{e}$	$\mathrm{Me\dot{T}e(H)SiH_3}$	36.5	92.9	SCF/DZP	77c,d
		19.1	37.6	MP2/DZP	77c,d
		9.6	37.2	QCISD/DZP//MP2/DZP	77c,d
$\mathrm{MeSH} + \dot{\mathrm{G}}\mathrm{eH_3} \rightarrow \mathrm{H_3GeSH} + \dot{\mathrm{M}}\mathrm{e}$	$\mathrm{Me\dot{S}(H)GeH_3}$	92.8	126.1	SCF/DZP	77c,d
		77.5	75.5	MP2/DZP	77c,d
		71.8	74.5	QCISD/DZP//MP2/DZP	77c,d

Reaction	Transition state	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$\mathrm{MeSeH} + \mathrm{\dot{G}eH_3} \longrightarrow \mathrm{H_3GeSeH} + \mathrm{\dot{M}e}$	$\mathrm{Me\dot{S}e(H)GeH_3}$	63.5	106.0	SCF/DZP	77c,d
		51.1	56.5	MP2/DZP	77c,d
		44.3	55.3	QCISD/DZP//MP2/DZP	77c,d
$\mathrm{MeTeH} + \mathrm{\dot{G}eH_3} \longrightarrow \mathrm{H_3GeTeH} + \mathrm{\dot{M}e}$	$\mathrm{Me\dot{T}e(H)GeH_3}$	39.1	79.9	SCF/DZP	77c,d
		29.0	30.7	MP2/DZP	77c,d
		19.9	28.4	QCISD/DZP//MP2/DZP	77c,d
$\mathrm{MeSH} + \mathrm{\dot{S}nH_3} \longrightarrow \mathrm{H_3SSnH} + \mathrm{\dot{M}e}$	$\mathrm{Me\dot{S}(H)SnH_3}$	96.7	111.5	SCF/DZP	77c,d
		90.4	64.8	MP2/DZP	77c,d
		82.7	62.4	QCISD/DZP//MP2/DZP	77c,d
$\mathrm{MeSeH} + \mathrm{\dot{S}nH_3} \longrightarrow \mathrm{H_3SeSnH} + \mathrm{\dot{M}e}$	$\mathrm{Me\dot{S}e(H)SnH_3}$	66.0	96.8	SCF/DZP	77c,d
		61.2	50.1	MP2/DZP	77c,d
		52.9	48.1	QCISD/DZP//MP2/DZP	77c,d

Reaction	Transition state	ΔE1	−ΔE2	Level of Theory	Ref.
$MeTeH + \dot{Sn}H_3 \longrightarrow H_3SnTeH + \dot{Me}$	$Me\dot{Te}(H)SnH_3$	41.1	74.4	SCF/DZP	77c,d
		40.3	28.8	MP2/DZP	77c,d
		30.1	26.3	QCISD/DZP//MP2/DZP	77c,d
$EtTeH + \dot{Sn}H_3 \longrightarrow H_3SnTeH + \dot{Et}$	$Et\dot{Te}(H)SnH_3$	34.8	80.4	SCF/DZP	87
		33.1	26.7	MP2/DZP	87
		30.6	88.3	SCF/DZP	87
		30.1	22.7	MP2/DZP	87
$HCl + H^{\bullet} \longrightarrow HCl + H^{\bullet}$	$H_2\dot{Cl}$	139.5	139.5	SCF/DZP	77d,78
		122.4	122.4	MP2/DZP	77d,78
		104.8	104.8	QCISD/DZP//MP2/DZP	77d,78
$HBr + H^{\bullet} \longrightarrow HBr + H^{\bullet}$	$H_2\dot{Br}$	101.9	101.9	SCF/DZP	77d,78
		90.3	90.3	MP2/DZP	77d,78
		74.3	74.3	QCISD/DZP//MP2/DZP	77d,78
$HI + H^{\bullet} \longrightarrow HI + H^{\bullet}$	$H_2\dot{I}$	74.3	74.3	SCF/DZP	77d,78
		64.4	64.4	MP2/DZP	77d,78
		47.2	47.2	QCISD/DZP//MP2/DZP	77d,78

Reaction	Transition state	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$\mathrm{MeCl} + \mathrm{H}^{\bullet} \longrightarrow \mathrm{HCl} + \mathrm{Me}^{\bullet}$	$\mathrm{Me\overset{\bullet}{Cl}H}$	97.5	197.2	SCF/DZP	77d,78
		92.5	162.5	MP2/DZP	77d,78
		72.7	160.8	QCISD/DZP//MP2/DZP	77d,78
$\mathrm{MeBr} + \mathrm{H}^{\bullet} \longrightarrow \mathrm{HBr} + \mathrm{Me}^{\bullet}$	$\mathrm{Me\overset{\bullet}{Br}H}$	62.4	155.0	SCF/DZP	77d,78
		65.5	122.0	MP2/DZP	77d,78
		44.0	123.7	QCISD/DZP//MP2/DZP	77d,78
$\mathrm{MeI} + \mathrm{H}^{\bullet} \longrightarrow \mathrm{HI} + \mathrm{Me}^{\bullet}$	$\mathrm{Me\overset{\bullet}{I}H}$	38.3	124.9	SCF/DZP	77d,78
		45.6	93.2	MP2/DZP	77d,78
		23.4	96.2	QCISD/DZP//MP2/DZP	77d,78
$\mathrm{MeCl} + \mathrm{Me}^{\bullet} \longrightarrow \mathrm{MeCl} + \mathrm{Me}^{\bullet}$	$\mathrm{Me_2Cl}^{\bullet}$	140.7	140.7	SCF/DZP	77d,78
		125.9	125.9	MP2/DZP	77d,78
		115.9	115.9	QCISD/DZP//MP2/DZP	77d,78
$\mathrm{MeBr} + \mathrm{Me}^{\bullet} \longrightarrow \mathrm{MeBr} + \mathrm{Me}^{\bullet}$	$\mathrm{Me_2Br}^{\bullet}$	99.3	99.3	SCF/DZP	77d,78
		91.4	91.4	MP2/DZP	77d,78
		80.2	80.2	QCISD/DZP//MP2/DZP	77d,78
$\mathrm{MeI} + \mathrm{Me}^{\bullet} \longrightarrow \mathrm{MeI} + \mathrm{Me}^{\bullet}$	$\mathrm{Me_2I}^{\bullet}$	67.6	67.6	SCF/DZP	77d,78
		63.0	63.0	MP2/DZP	77d,78
		51.5	51.5	QCISD/DZP//MP2/DZP	77d,78

Reaction	Transition state	ΔE1	-ΔE2	Level of Theory	Ref.
$MeCl + \dot{S}iH_3 \rightarrow H_3SiCl + \dot{Me}$	$Me\dot{Cl}SiH_3$	95.8	211.4	SCF/DZP	77d,78
		98.2	181.2	MP2/DZP	77d,78
		73.7	159.0	QCISD/DZP//MP2/DZP	77d,78
$MeBr + \dot{S}iH_3 \rightarrow H_3SiBr + \dot{Me}$	$Me\dot{Br}SiH_3$	61.6	168.1	SCF/DZP	77d,78
		52.0	124.1	MP2/DZP	77d,78
		44.3	119.6	QCISD/DZP//MP2/DZP	77d,78
$MeI + \dot{S}iH_3 \rightarrow H_3SiI + \dot{Me}$	$Me\dot{I}SiH_3$	36.7	129.8	SCF/DZP	77d,78
		30.3	89.2	MP2/DZP	77d,78
		21.8	84.9	QCISD/DZP//MP2/DZP	77d,78
$MeCl + \dot{G}eH_3 \rightarrow H_3GeCl + \dot{Me}$	$Me\dot{Cl}GeH_3$	98.1	178.7	SCF/DZP	77d,78
		85.7	131.3	MP2/DZP	77d,78
		78.8	127.1	QCISD/DZP//MP2/DZP	77d,78
$MeBr + \dot{G}eH_3 \rightarrow H_3GeBr + \dot{Me}$	$Me\dot{Br}GeH_3$	63.2	144.3	SCF/DZP	77d,78
		56.6	100.3	MP2/DZP	77d,78
		48.3	95.6	QCISD/DZP//MP2/DZP	77d,78

Reaction	Transition state	ΔE1	−ΔE2	Level of Theory	Ref.
$MeI + \dot{G}eH_3 \longrightarrow H_3GeI + \dot{M}e$	$MeI\dot{G}eH_3$	37.6	113.7	SCF/DZP	77d,78
		33.6	72.3	MP2/DZP	77d,78
		24.7	67.7	QCISD/DZP//MP2/DZP	77d,78
$MeCl + \dot{S}nH_3 \longrightarrow H_3SnCl + \dot{M}e$	$MeCl\dot{S}nH_3$	96.2	166.6	SCF/DZP	77d,78
		87.5	117.4	MP2/DZP	77d,78
		80.3	113.2	QCISD/DZP//MP2/DZP	77d,78
$MeBr + \dot{S}nH_3 \longrightarrow H_3SnBr + \dot{M}e$	$MeBr\dot{S}nH_3$	62.1	138.4	SCF/DZP	77d,78
		59.2	92.7	MP2/DZP	77d,78
		50.4	87.7	QCISD/DZP//MP2/DZP	77d,78
$MeI + \dot{S}nH_3 \longrightarrow H_3SnI + \dot{M}e$	$MeI\dot{S}nH_3$	37.2	111.8	SCF/DZP	77d,78
		36.7	68.5	MP2/DZP	77d,78
		27.2	63.5	QCISD/DZP//MP2/DZP	77d,78
$SiH_4 + H^{\bullet} \longrightarrow SiH_4 + H^{\bullet}$	$\dot{S}iH_5$	117.4	117.4	HF/6-311G** + ZPVE	79
		77.5	77.5	MP2/6-311G** + ZPVE	79
		62.4	62.4	QCISD/6-311G** + ZPVE	79
		124.9	124.9	SCF/DZP + ZPVE	79
		86.8	86.8	MP2/DZP + ZPVE	79
		72.0	72.0	QCISD/DZP + ZPVE	79

Reaction	Transition state	ΔE1	−ΔE2	Level of Theory	Ref.
$GeH_4 + \dot{H} \rightarrow GeH_4 + \dot{H}$	$\dot{G}eH_5$	127.4	127.4	SCF/DZP + ZPVE	79
		93.3	93.3	MP2/DZP + ZPVE	79
		76.9	76.9	QCISD/DZP + ZPVE	79
$SnH_4 + \dot{H} \rightarrow SnH_4 + \dot{H}$	$\dot{S}nH_5$	116.9	116.9	SCF/DZP + ZPVE	79
		89.0	89.0	MP2/DZP + ZPVE	79
		68.9	68.9	QCISD/DZP + ZPVE	79
$SiH_4 + \dot{Me} \rightarrow MeSiH_3 + \dot{H}$	$Me\dot{S}iH_4$	180.9	127.9	HF/6-311G** + ZPVE	79
		102.6	94.9	MP2/6-311G** + ZPVE	79
		99.2	64.4	QCISD/6-311G**//MP2/6-311G**	79
		182.8	132.6	SCF/DZP + ZPVE	79
		107.3	99.1	MP2/DZP + ZPVE	79
		101.3	68.9	QCISD/DZP//MP2/DZP	79
$GeH_4 + \dot{Me} \rightarrow MeGeH_3 + \dot{H}$	$Me\dot{G}eH_4$	183.6	125.6	SCF/DZP + ZPVE	79
		112.9	98.9	MP2/DZP + ZPVE	79
		106.6	67.7	QCISD/DZP//MP2/DZP	79
$SnH_4 + \dot{Me} \rightarrow MeSnH_3 + \dot{H}$	$Me\dot{S}nH_4$	170.0	109.3	SCF/DZP + ZPVE	79
		105.0	90.9	MP2/DZP + ZPVE	79
		95.3	56.3	QCISD/DZP//MP2/DZP	79

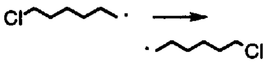
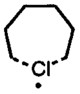
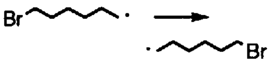
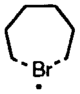
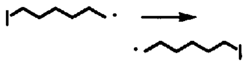
Reaction	Transition state	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$MeSiH_3 + Me^{\bullet} \longrightarrow MeSiH_3 + Me^{\bullet}$	$Me_2\dot{Si}H_3$	184.2	184.2	HF/6-31G**	79
		182.7	182.7	SCF/DZP	79
$MeGeH_3 + \dot{Me} \longrightarrow MeGeH_3 + \dot{Me}$	$Me_2\dot{Ge}H_3$	173.4	173.4	SCF/DZP	79
$MeSnH_3 + \dot{Me} \longrightarrow MeSnH_3 + \dot{Me}$	$Me_2\dot{Sn}H_3$	152.6	152.6	SCF/DZP	79
		185.5	185.7	3-21G$^{(*)}$ + ZPVE	72
		216.6	216.6	SCF/DZP + ZPVE	72
		170.5	170.5	MP2/DZP	72
		165.1	165.1	3-21G$^{(*)}$ + ZPVE	72
		191.1	191.1	SCF/DZP + ZPVE	72
		149.3	149.3	MP2/DZP	72
		165.1	165.1	3-21G$^{(*)}$ + ZPVE	72
		174.0	174.0	SCF/DZP + ZPVE	72
		135.2	135.2	MP2/DZP	72

Table 5. Calculated energy barriers (kJ.mol^{-1}) for homolytic substitution reactions involving intermediates.

$$\dot{A} + Y\text{-}L \xrightarrow{\Delta E_1} \left[A\cdots Y\text{—}L\right]^{\#\bullet} \xrightarrow{\Delta E_2} A\text{—}\dot{Y}\text{—}L$$

Reaction	Intermediate	ΔE1	−ΔE2	Level of Theory	Ref.
$H_2S + H^\bullet$	$H_3S^\bullet$	52.9	0.01	QCISD/DZP	75
$H_2SO + \dot{H}$	$H_3\dot{S}O$	59.8	2.5	MP2/6-31G**	77a
		54.8	2.9	MP4/6-31G**//MP2/6-31G**	77a
$H_2SO + \dot{Me}$	$Me\dot{S}(O)H_2$	57.7	4.5	MP2/6-31G**	77a
$MeS(O)H + H^\bullet$	$Me\dot{S}(O)H_2$	58.6	0.3	MP2/6-31G**	77a
$MeS(O)H + Me^\bullet$	$Me_2\dot{S}(O)H$	61.9	0.8	MP2/6-31G**	77a
$H_2Se + H^\bullet$	$H_3\dot{Se}$	47.2	0.01	MP2/DZP	75
		41.3	8.23	QCISD/DZP	75
$H_2Te + H^\bullet$	$H_3\dot{Te}$	37.6	1.3	HF/3-21G*	69
		38.2	0.4	HF/HUZ-SV**	69
		36.6	0.7	SCF/DZP	75
		24.2	7.5	MP2/DZP	75
		14.2	12.3	QCISD/DZP	75
$MeTeH + \dot{Me}$	$Me_2\dot{Te}H$	27.7	4.4	MP2/DZP	77c,d

Reaction	Intermediate	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$PH_3 + H^{\bullet}$	$^{\bullet}PH_4$	36.1	9.0	HF/3-21G*	69
		34.6	7.3	HF/HUZ-SV**	69
		32.6	12.6	HF/6-31G**	70
		22.4	23.2	MP2/6-31G**	70
		18.7	25.5	MP4/6-31G**//MP2/6-31G**	70
		17.4	25.3	MP5/6-31G**//MP2/6-31G**	70
$PH_3 + \dot{Me}$	$Me\dot{P}H_3$	77.7	0.1	HF/6-31G**	70
		32.1	16.6	MP2/6-31G**	70
		32.7	9.5	MP4/6-31G**//MP2/6-31G**	70
$MePH_2 + \dot{H}$	$Me\dot{P}H_3$	27.8	15.7	HF/6-31G**	70
		17.9	26.7	MP2/6-31G**	70
		14.2	31.0	MP4/6-31G**//MP2/6-31G**	70
$MePH_2 + Me^{\bullet}$	$Me_2\dot{P}H_2$	75.2	1.3	HF/6-31G**	70
		28.5	19.5	MP2/6-31G**	70
		28.8	13.9	MP4/6-31G**//MP2/6-31G**	70
$H_3PO + \dot{H}$	$H_4\dot{P}O$	20.4	15.2	HF/3-21G$^{(*)}$	72
		22.5	9.8	HF/6-31G**	72
		36.5	8.0	MP2/6-31G**	72
		34.1	13.2	MP4/6-31G**//MP2/6-31G**	72
		33.4	16.2	MP5/6-31G**//MP2/6-31G**	72

Reaction	Intermediate	ΔE_1	$-\Delta E_2$	Level of Theory	Ref.
$MeH_2PO + Me^{\bullet}$	$Me_2H_2\dot{P}O$	130.4	44.0	HF/3-21G$^{(*)}$	72
		164.8	31.7	HF/6-31G**	72
		149.6	1.3	MP2/6-31G**	72
		131.7	0.9	MP4/6-31G**//MP2/6-31G**	72
$AsH_3 + H^{\bullet}$	$^{\bullet}AsH_4$	36.3	1.6	HF/3-21G*	69
		18.7	0.8	HF/HUZ-SV**	69
$SbH_3 + H^{\bullet}$	$^{\bullet}SbH_4$	21.0	12.3	HF/3-21G*	69
		18.3	10.8	HF/HUZ-SV**	69
$MeSiH_3 + \dot{Me}$	$Me_2\dot{Si}H_3$	104.4	3.9	MP2/6-311G**	79
		105.3	2.5	MP2/DZP	79
		105.5	2.8	QCISD/DZP//MP2/DZP	79
$MeGeH_3 + \dot{Me}$	$Me_2\dot{Ge}H_3$	104.2	1.3	MP2/DZP	79
		103.5	2.1	QCISD/DZP//MP2/DZP	79
$MeSnH_3 + \dot{Me}$	$Me_2\dot{Sn}H_3$	92.0	2.5	MP2/DZP	79
		86.9	2.0	QCISD/DZP//MP2/DZP	79

References

1. Beckwith, A. L. J.; Ingold, K. U. in *Rearrangements in Ground and Excited States*, **1980**, Vol. 1, p. 161; de Mayo, P. (Ed.), Academic Press, New York. b) Beckwith, A. L. J., *Tetrahedron*, **1981**, *37*, 3073. c) Ramaiah, M., *Tetrahedron*, **1987**, *43*, 3541. d) Curran, D. P., *Synthesis*, **1988**, 417. e) Curran, D. P., *Synthesis*, **1988**, 489. f) Porter, N. A.; Giese, B.; Curran, D. P., *Acc. Chem. Res.*, **1991**, *24*, 296. g) Bowman, W. R. in *Organic Reaction Mechanisms*, **1992**, Chapt. 3, p. 73; Knipe, A. C.; Watts, W. E. (Eds.) Wiley, New York. h) Newcomb, M., *Tetrahedron*, **1993**, *49*, 1151. i) Beckwith, A. L. J., *Chem. Soc. Reviews*, **1993**, 143.

2. a) Giese, B., *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*, **1986**, Pergamon Press, Oxford. b) Regitz, M.; Giese, B., *Radicale, Houben-Weyl Methoden der Organischen Chemie*, **1989**, Vol E 19a, Georg Thieme, Stuttgart. c) Perkins, M. J., *Radical Chemistry*, **1994**, Ellis-Horwood, New York.

3. Hitchcock, S. A.; Pattenden, G., *Tetrahedron Lett.*, **1992**, *33*, 4843.

4. Caddick, S.; Khan, S., *Tetrahedron Lett.*, **1993**, *34*, 7469.

5. Pryor, W. A., *Nature Physical Science*, **1971**, *231*, 181.

6. Ingold, K. U.; Roberts, B. P., *Free-Radical Substitution Reactions*, **1971**, Wiley-Interscience, New York.

7. Jackson, R. A.; Townson, M., *J. Chem. Soc. Perkin Trans. 2*, **1980**, 1452.

8. Tedder, J. M.; Walton, J. C., *Adv. Free-Radical Chem.*, **1980**, *6*, 155.

9. Anpo, M.; Chatgilialoglu, C.; Ingold, K. U., *J. Org. Chem.*, **1983**, *48*, 4104.

10. Walton, J. C.; *J. Chem. Soc. Chem. Commun.*, **1987**, 1252. Walton, J. C., *J. Chem. Soc. Perkin Trans. 2*, **1988**, 1371.

11. Applequist, D. E.; Searle, R., *J. Am. Chem. Soc.*, **1964**, *86*, 1389.

12. Eaton, P. E.; Nyi, K., *J. Am.. Chem. Soc.*, **1971**, *93*, 2786. Eaton, P. E.; Temme, G. H., *J. Am. Chem. Soc.*, **1973**, *95*, 7508.

13. Della, E. W.; Head, N. J.; Mallon, P.; Walton, J. C., *J. Am.. Chem. Soc.*, **1992**, *114*, 10730.

14. Wiberg, K. B.; Waddell, S. T.; Laidig, K., *Tetrahedron Lett.*, **1986**, *27*, 1553. Bunz, U.; Polborn, K.; Wagner, H.-U.; Szeimies, G., *Chem. Ber.*, **1988**, *121*, 1785.

15. Jackson, J. E.; Allen, L. C., *J. Am. Chem. Soc.*, **1984**, *106*, 591.

16. Kaszynski, P.; Michl, J., *J. Org. Chem.*, **1988**, *53*, 4593.

17. Gupta, B. D.; Das, I.; Dixit, V.; *J. Chem. Res. (S)*, **1992**, 306. Gupta, B. D.; Roy, M.; Roy, S.; Kumar, M.; Das, I., *J. Chem. Soc. Perkin Trans. 2*, **1990**, 537. Gupta, B. D.; Roy, S., *J. Chem. Soc. Perkin Trans. 2*, **1988**, 1377. Ashcroft, M. R.; Bury, A.; Cooksey, C. J.; Davies, A. G.; Gupta, B. D.; Johnson, M. D.; Morris, H., *J. Organometal. Chem.*, **1980**, *195*, 89. Davis, D. D.; Ahmed, F. U., *J. Am. Chem. Soc.*, **1981**, *103*, 7653.

18. Degueil-Castaing, M.; Navarro, C.; Ramon, F.; Maillard, B., *Aust. J. Chem.*, **1995**, *48*, 233. Colombani, D.; Maillard, B., *J. Org. Chem.* , **1994**, *59*, 4765. Montaudon, E.; Rakotomanana, F.; Maillard, B., *Tetrahedron*, **1985**, *41*, 2727.

19. Meijs, G. F.; Rizzardo, E.; Thang, S. H., *Polym. Prepr.*, **1992**, *33*, 893.

20. Clive, D.L.J.; Chittattu, G.J.; Farina, V.; Kiel, W.A.; Menchen, S. M.; Russell, C.G.; Singh, A.; Wong, C.K.; Curtis, N.J., *J. Am. Chem. Soc.*, **1980**, *102*, 4438.

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

22. Beckwith, A. L. J.; Pigou, P. E.; *Aust. J. Chem.*, **1986**, *39*, 1151.

23. Chatgilialoglu, C.; Ferreri, C.; Lucarini, M., *J. Org. Chem.*, **1993**, *58*, 249.

24. Curran, D. P.; Xu, J.; Lazzarini, E., *J. Chem. Soc. Perkin Trans. 1*, **1995**, 3049.

25. Curran, D. P.; Eichenberger, E.; Collis, M.; Roepel, M. G., *J. Am. Chem. Soc.*, **1994**, *116*, 4279.

26. Byers, J. H.; Gleason, T. G.; Knight, K. S., *J. Chem. Soc. Chem. Commun.*, **1991**, 354.

27. Crich, D.; Chen, C.; Hwang, J.-T.; Yuan, H.; Papadatos, A.; Walter, R. I., *J. Am. Chem. Soc.*, **1994**, *116*, 8937.

28. Barton, D. H. R.; Ozbalik, N.; Sarma, J. C., *Tetrahedron Lett.*, **1988**, *29*, 6581. Barton, D. H. R.; Ramesh, M., *J. Am. Chem. Soc.*, **1990**, *112*, 891.

29. Engman, L.; Gupta, V., *J. Chem. Soc. Chem. Commun.*, **1995**, 2515.

30. Pulis, J.; Schiesser, C. H., unpublished.

31. Curran, D. P.; Chen, M.-H.; Kim, D., *J. Am. Chem. Soc.*, **1989**, *111*, 6265.

32. Curran, D. P.; Kim, D., *Tetrahedron*, **1991**, *47*, 6171.

33. Curran, D. P.; Kim, D.; Ziegler, C., *Tetrahedron*, **1991**, *47*, 6189.

34. Curran, D. P.; Seong, C. M., *Tetrahedron*, **1992**, *48*, 2175.

35. Banks, J. T.; Garcia, H.; Miranda, M. A.; Perez-Prieto, J.; Scaiano, J. C., *J. Am. Chem. Soc.*, **1995**, *117*, 5049.

36. Pitt, C. G.; Fowler, M. S., *J. Am. Chem. Soc.*, **1968**, *90*, 1928.

37. West, R.; Boudjouk, P., *J. Am. Chem. Soc.*, **1973**, *95*, 3983. Harris, J. M.; MacInnes, I.; Walton, J. C.; Maillard, B., *J. Organometal. Chem.*, **1991**, *403*, C25. Harris, J. M.; Walton, J. C.; Maillard, B.; Grelier, S.; Picard, J.-P., *J. Chem. Soc. Perkin Trans. 2*, **1993**, 2119. Roberts, B. P.; Vazquez-Persaud, A. R., *J. Chem. Soc. Perkin Trans. 2*, **1995**, 1087.

38. Alberti, A.; Hudson, A., *Chem. Phys. Lett.*, **1977**, *48*, 331. Prokof'ev, A. I.; Prokof'eva, T. I.; Belostotskaya, I. S.; Bubnov, N. N.; Solodovnikov, S. P.; Ershov, V. V.; Kabachnik, M. I., *Tetrahedron*, **1979**, *35*, 2471. Barker, P. J.; Davies, A. G.; Hawari, J. A.-A.; Tse, M.-W., *J. Chem. Soc. Perkin Trans. 2*, **1980**, 1488. Davies, A. G.; Hawari, J. A.-A., *J. Organometal. Chem.* **1983**, *251*, 53.

39. Dalton, J. C.; Bourque, R. A., *J. Am. Chem. Soc.*, **1981**, *103*, 699.

40. Tsai, Y.-M.; Cherng, C.-D., *Tetrahedron Lett.*, **1991**, *32*, 3515.

41. Davies, A. G.; Tse, M.-W., *J. Organomet. Chem.*, **1978**, *155*, 25.

42. (a) Kim, S. ; Koh, J. S. *J. Chem. Soc. Chem. Commun.*, **1992**, 1377. (b) Kim, S.; Lee, S.; Koh, J. S., *J. Am. Chem. Soc.*, **1991**, *113*, 5106. (c) Kim, S.; Lim, K. M., *J. Chem. Soc. Chem. Commun.*, **1993**, 1152. (d) Kim, S.; Lim, K. M., *Tetrahedron Lett.*, **1993**, *34*, 4851. (e) Kim, S.; Do, J. Y.; Lim, K. M., *J. Chem. Soc. Perkin Trans. 1*, **1994**, 2517.

43. Kampmeier, J. A.; Evans, T. R., *J. Am. Chem. Soc.*, **1966**, *88*, 4096.

44. Benati, L.; Montevecchi, P. C.; Tundo, A.; Zanardi, G.; *J. Chem. Soc. Perkin Trans. 1*, **1974**, 1272.

45. (a) Beckwith, A. L. J.; Boate, D. R., *J. Org. Chem.*, **1988**, *53*, 4339. (b) Beckwith, A. L. J.; Boate, D. R., *J. Chem. Soc. Chem. Commun.*, **1986**, 189. (c) Beckwith, A. L. J.; Duggan, S. A. M., *J. Chem. Soc. Perkin Trans. 2*, **1994**, 1509.

46. Kulicke, K. J.; Chatgilialoglu, C.; Kopping, B.; Giese, B., *Helv. Chim. Acta.*, **1992**, *75*, 935.

47. (a) Lyons, J. E.; Schiesser, C. H.; Sutej, K., *J. Org. Chem.*, **1993**, *58*, 5632. (b) Benjamin, L. J.; Schiesser, C. H.; Sutej, K., *Tetrahedron*, **1993**, *49*, 2557. (c) Lucas, M. A.; Schiesser, C. H., *J. Org. Chem.*, in press. (d) Schiesser, C. H.; Sutej. K., *Tetrahedron Lett.*, **1992**, *33*, 5137. (e) Schiesser, C. H.; Sutej, K., *J. Chem. Soc. Chem. Commun.*, **1992**, 57.

48. (a) Franz, J. A.; Roberts, D. H.; Ferris, K. F., *J. Org. Chem.* , **1987**, *52*, 2256. (b) John, D. I.; Tyrrell, N. D.; Thomas, E. J., *J. Chem. Soc. Chem. Commun.*, **1981**, 901. (c) Tada, M.; Nakagiri, H., *Tetrahedron Lett.*, **1992**, *33*, 6657. (d) Tada, M.; Uetaka, T.; Matsumoto, M., *J. Chem. Soc. Chem. Commun.*, **1990**, 1408.

49. Lawson, A. J., *Phosphorus Sulfur*, **1982**, *12*, 357.

50. (a) Fong, M. C.; Schiesser, C. H., *Tetrahedron Lett.*, **1993**, *34*, 4347. (b) Fong, M. C.; Schiesser, C. H., *Tetrahedron Lett.*, **1995**, *36*, 7329. Fong, (c) M. C., **1995**, *PhD Thesis*, University of Melbourne.

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

52. Walling, C., Rabinowitz, R., *J. Am. Chem. Soc.*, **1957**, *79*, 5326. Ramirez, F., McKelvie, N., *J. Am. Chem. Soc.*, **1957**, *79*, 5829.

53. Roberts, B. P., *Adv. Free Radical Chem.*, **1980**, *6*, 225 and references cited therein. Bentrude, W. G., *Acc. Chem. Res.*, **1982**, *15*, 117 and references cited therein. Schipper, P., Jansen, E. H. J. M., Buck, H. M., *Top. Phosphorus Chem.*, **1977**, *9*, 407.

54. (a) Krusic, P. J.; Mahler, W.; Kochi, J. K., *J. Am. Chem. Soc.*, **1972**, *94*, 6033. (b) Colussi, A. J.; Morton, J. R.; Preston, K. F., *J. Chem. Phys.*, **1975**, *62*, 2004. (c) Fessenden, R. W.; Schuler, R. H., *J. Chem. Phys.*, **1966**, *45*, 1845. (d) Kokoszka, G. F.; Brinckman, F. E., *J. Am.. Chem. Soc.*, **1970**, *92*, 1199. (e) Hay, R. S.; Roberts, B. P., *J. Chem. Soc. Perkin Trans. 2*, **1978**, 770. (f) Kawashima, T.; Bentrude, W. G., *J. Am. Chem. Soc.*, **1979**, *101*, 3981. (g) De Keijzer, A. E. H.; Buck, H. M., *Phosphorus Sulfur*, **1987**, *31*, 203. (h) McConnachie, G. D. G.; Rai, U. S.; Symons, M. C. R., *J. Mol. Struct.*, **1993**, *300*, 527.

55. Roberts, B. P., *Tetrahedron Lett.*, **1983**, *24*, 3377.

56. Hay, R. S.; Roberts, B. P.; Singh, K.; Wilkinson, J. P. T., *J. Chem. Soc. Perkin Trans. 2*, **1979**, 756. Baban, J. A.; Cooksey, C. J.; Roberts, B. P., *J. Chem. Soc. Perkin Trans. 2*, **1979**, 781. Boekestein, G.; Jansen, E. H. J. M.; Buck, H. M., *J. Chem. Soc. Chem. Commun.*, **1974**, 118.

57. Chapman, J. S.; Cooper, J. W.; Roberts, B. P., *J. Chem. Soc. Chem. Commun.*, **1976**, 835. (b) Cooper, J. W.; Roberts, B. P., *J. Chem. Soc. Chem. Commun.*, **1977**, 228. (c) Gara, W. B.; Roberts, B. P.; Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C., *J. Chem. Res.(S)*, **1977**, 152(S). (d) Gara, W. B.; Roberts, B. P., *J. Organometal. Chem.*, **1977**, *135*, C20. (e) Gara, W. B.; Roberts, B. P.; Kirk, C. M.; Gilbert, B. C.; Norman, R. O. C., *J. Magn. Res.*, **1977**, *27*, 509 (f) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K., *J. Am. Chem. Soc.*, **1980**, *102*, 7753. (g) Baban, J. A.; Roberts, B. P., *J. Chem. Soc. Perkin Trans. 2*, **1978**, 678. (h) Gara, W. B.; Giles, J. R. M.; Roberts, B. P., *J. Chem. Soc. Perkin Trans. 2*, **1979**, 1444. (i) Giles, J. R. M.; Roberts, B. P., *J. Chem. Soc. Perkin Trans. 2*, **1980**, 1497. (j) Perkins, C., W.; Clarkson, R., B.; Martin, J., C., *J. Am. Chem. Soc.*, **1986**, *108*, 3206. (k) Perkins, C., W.; Martin, J., C., *J. Am. Chem. Soc.*, **1986**, *108*, 3211.

58. Giles, J. R. M.; Roberts, B. P.; Perkins, M. J.; Turner, E. S., *J. Chem. Soc. Chem. Commun.*, **1980**, 504.

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

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

61. Murphy, J. A., private communication.

62. Curran, D. P., Martin-Esker, A. A., Ko, S.-B., Newcomb, M., *J. Org. Chem.*, **1993**, *58*, 4691.

63. Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K., *Aust. J. Chem.*, **1983**, *36*, 545.

64. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, **1994**, Vol. II/18, Fischer, H. (ed.), Springer-Verlag, Berlin, 1994.

65. (a) Newcomb, M., Sanchez, R. M., Kaplan, J., *J. Am. Chem. Soc.*, **1987**, *109*, 1195. (b) Mathew, L.; Warkentin, J., *Can. J. Chem.*, **1988**, *66*, 11. (c) Hawari, J. A.; Davis, S.; Engel, P. S.; Gilbert, B. C.; Griller, D., *J. Am. Chem. Soc.*, **1985**, *107*, 4721.

66. Curran, D. P.; Bosch, E.; Kaplan, J.; Newcomb, M., *J. Org. Chem.*, **1989**, *54*, 1826.

67. Russell, G. A.; Tashtoush, H., *J. Am. Chem. Soc.*, **1983**, *105*, 1398.

68. Howell, J. M.; Olsen, J. F., *J. Am. Chem. Soc.*, **1976**, *98*, 7119.

69. Benjamin, L. J.; Schiesser, C. H., unpublished.

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

71. Cramer, C. J. *J. Am. Chem. Soc.*, **1990**, *112*, 7965. Cramer, C. J. *J. Am. Chem. Soc.*, **1991**, *113*, 2439.

72. Schiesser, C. H.; Wild, L. M., unpublished.

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

74. 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.

75. Schiesser, C. H.; Smart, B. A., *J. Comput. Chem.* **1995**, *16*, 1055.

76. Gu, M.; Turecek, F., *J. Am. Chem. Soc.*, **1992**, *114*, 7146.

77. (a) Lyons, J. E., *J. Chem. Soc. Perkin Trans. 2*, **1992**, 1655. (b) Smart, B. A.; Schiesser, C. H., *J. Chem. Soc. Perkin Trans. 2*, **1994**, 2269. (c) Schiesser, C. H., Smart, B. A., *Tetrahedron*, **1995**, *51*, 6051. (d) Schiesser, C. H.; Smart, B. A.; Tran, T.-A., *Tetrahedron*, **1995**, *51*, 10651. (e) Ferris, K. F.; Franz, J. A.; Sosa, C.; Bartlett, R. J., *J. Org. Chem.*, **1992**, *57*, 777.

78. Schiesser, C. H.; Smart, B. A.; Tran, T.-A., *Tetrahedron*, **1995**, *51*, 3327.

79. Schiesser, C. H.; Styles, M. L.; Wild, L. M., *J. Chem. Soc. Perkin Trans. 2*, submitted for publication.

80. Fieldhouse, S. A.; Lyons, A. R.; Starkie, H. C.; Symons, M. C. R., *J. Chem. Soc. Dalton Trans.*, **1974**, 1966.

81. Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C., *J. Am. Chem. Soc.*, **1982**, *104*, 5123.

82. Lusztyk, J.; Maillard, B.; Ingold, K. U., *J. Org. Chem.*, **1986**, *51*, 2457.

83. Ingold, K. U.; Lusztyk, J.; Scaiano, J. C., *J. Am. Chem. Soc.*, **1984**, *106*, 343.

84. Carlsson, D. J.; Ingold, K. U., *J. Am. Chem. Soc.*, **1968**, *90*, 7047.

85. Beckwith, A. L. J.; Pigou, P. E., *Aust. J. Chem.*, **1986**, *39*, 77.

86. Chatgilialoglu, C.; Griller, D.; Lesage, M., *J. Org. Chem.*, **1989**, *56*, 2492.

87. Schiesser, C. H.; Skidmore, M. A., *J. Chem. Soc. Chem. Commun.*, in press.

88. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A., *Ab Initio Molecular Orbital Theory*, **1986**, Wiley, New York.

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