PERKIN 2

Stannanes as free-radical reducing agents: an *ab initio* study of hydrogen atom transfer from some trialkyltin hydrides to alkyl radicals

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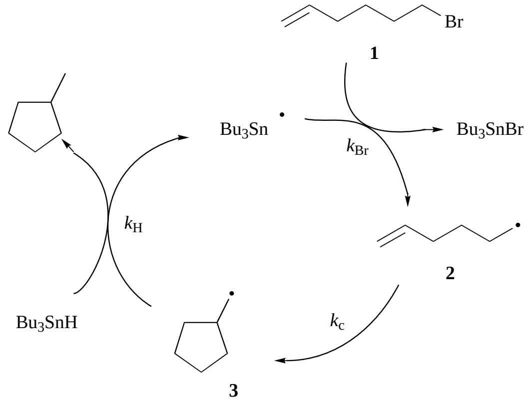
***Ab initio* molecular orbital calculations using a (valence) double-ξ pseudopotential (DZP) basis set, with (MP2, QCISD) and without (SCF) the inclusion of electron correlation, predict that hydrogen atoms, methyl, ethyl, isopropyl and *tert*-butyl radicals abstract hydrogen atoms from stannane and trimethyltin hydride *via* transition states in which the attacking and leaving radicals adopt a colinear arrangement. Transition states in which (overall) Sn–C separations of 3.50 Å have been calculated; these distances appear to be independent of the nature of the attacking radical and alkyl substitution at tin. At the highest level of theory (QCISD/DZP//MP2/DZP), energy barriers ($\Delta E_1^{\ddagger}$) of 18–34 kJ mol^{-1} are predicted for the forward reactions, while the reverse reactions ($\Delta E_2^{\ddagger}$) are calculated to require 140–170 kJ mol^{-1}. These values are marginally affected by the inclusion of zero-point vibrational energy correction. Importantly, QCISD and MP2 calculations predict correctly the relative order of radical reactivity toward reduction by stannanes: *tert*-butyl > isopropyl > ethyl. By comparison, SCF/DZP, AM1 and AM1(CI = 2) calculations perform somewhat more poorly in their prediction of relative radical reactivity.**

Introduction

Free-radical chemistry has benefited enormously from the invention of tin-based chain-carrying reagents.[1–3] Of these, tributyltin hydride and to a lesser extent, triphenyltin hydride, have been the reagents of choice.[1] Their ready availability and favourable rate constants for attack of the corresponding tin-centred radicals at a variety of radical precursors,[4] coupled with useful rate constants for hydrogen transfer[5–8] to alkyl and other radicals, provide for reagents superior to their silicon[9,10] and germanium[6,11] counterparts; only tris(trimethylsilyl)silane rivals trialkyltin hydrides in its synthetic utility.[10] The transformation of 6-bromohex-1-ene (**1**) into methylcyclopentane by the action of tributyltin hydride (Scheme 1) typifies the chemistry in question. A knowledge of rate constants is crucial to the successful design of synthetic procedures involving these reagents. Giese points out that stannane chain-carrying reagents are useful because a knowledge of the important rate constants (k_c, k_H and k_{Br} in Scheme 1) allow, through control of substrate concentration, necessary selectivity criteria to be met.[1] Specifically the hex-5-enyl radical (**2**) must undergo intramolecular addition to form the cyclopentylmethyl radical (**3**), that **3** must abstract a hydrogen atom from tributyltin hydride and that the tributylstannyl radical must abstract the halogen in **1** to form **2**. These processes must proceed faster than any competing side reaction.



Scheme 1

Recently, our interests in the development of modified stannanes for use in free-radical synthesis necessitated our computer modelling of the radical reactions of stannanes and stannyl radicals through the use of *ab initio* molecular orbital theory. We recently published the results of high-level *ab initio* investigations into the attack of silyl, germyl and stannyl radicals at the halogen atom in halomethanes and the chalcogen atom in the analogous sulfides, selenides and tellurides.[12] These studies predicted that, in accordance with expectation, stannyl radicals react with halogen and chalcogen containing substrates in the order $\mathrm{I} \geqslant \mathrm{Te} \gg \mathrm{Br} \geqslant \mathrm{Se} \gg \mathrm{Cl} \geqslant \mathrm{S}$. In addition, reactions involving tellurides are calculated to be reversible, a prediction we have recently verified.[13]

To the best of our knowledge there are no *ab initio* reports detailing hydrogen atom transfer from tin to carbon (or any other) centred radical. Beckwith and Zavitsas reported the results of AM1 (semiempirical) calculations on reactivity and diastereoselectivity during stannane reduction of several dioxolanyl radicals.[14] These calculations suggest that AM1 is capable of reproducing experimentally observed diastereoselectivities with good levels of correlation with experimentally available data.

In order to provide further insight into the intimate details of hydrogen atom transfer from stannanes, we have examined the potential energy surfaces for the attack of hydrogen atom, methyl, ethyl, isopropyl and *tert*-butyl radicals at the hydrogen atom in stannane (SnH_4) with expulsion of stannyl radical, and the analogous reaction of hydrogen atom and methyl radical with trimethyltin hydride (Me_3SnH) by *ab initio* molecular orbital theory and, for comparision in some cases, AM1 (semiempirical) calculations.

Methods

All *ab initio* molecular orbital calculations were carried out using the Gaussian 92[15] or Gaussian 94[16] program. Geometry optimisations 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.[17] 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. Vibrational frequencies were calculated on each SCF-calculated structure and at the MP2 level on the reactants, products and transition states involved in the reaction of hydrogen atom and methyl radical with stannane (SnH_4). Where appropriate, zero-point vibrational energy (ZPE) corrections have been applied.

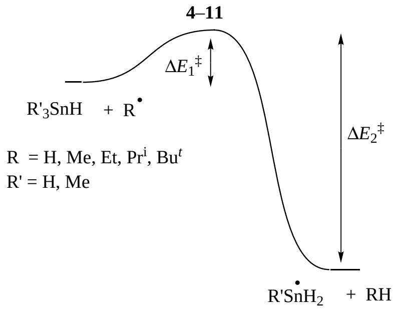
All *ab initio* calculations were performed using the previously published DZP basis set[12] on a Sun SparcStation 5, Cray Y-MP4E/364 or Cray J916 computer.

AM1 and AM1(CI = 2) calculations were performed within Gaussian 92 or AMPAC 5.0[18] on a Sun SparcStation 2 or Sun SparcStation 5.

Results and discussion

Reaction of hydrogen atom with stannane (SnH_4) and trimethyltin hydride (Me_3SnH)

Species of C_{3v} symmetry (**4**, **5**) were located on the SnH_5 and Me_3SnH_2 potential energy surfaces at the SCF/DZP and MP2/DZP levels of theory. These structures were found to correspond to the transition states for transfer of hydrogen atom from the tin centre to hydrogen atom (Scheme 2; R = H) and are displayed in Fig. 1, while the calculated energy barriers for these reactions are listed in Table 1 together with the calculated (imaginary) stretching frequency associated with the reaction coordinate in each case. Calculated energies of all structures in this study are listed in Table 2.



Scheme 2

The data displayed in Table 1 reveal calculated energy barriers of 39.8 (SCF/DZP), 27.3 (MP2/DZP) and 20.6 kJ mol^{-1} (QCISD/DZP//MP2/DZP) for the abstraction of hydrogen atom from stannane ($\Delta E_1^{\ddagger}$) with barriers for the reverse reaction ($\Delta E_2^{\ddagger}$) of 139.6, 146.6 and 150.1 kJ mol^{-1} at increasing levels of theory respectively. Inclusion of zero-point vibrational energy correction (ZPE) serves to lower slightly the forward barriers ($\Delta E_1^{\ddagger}$) by a maximum of 2.2 kJ mol^{-1}, while the reverse barriers ($\Delta E_2^{\ddagger}$) are also lowered by 6.8–8.8 kJ mol^{-1}. These data clearly emphasise the need for inclusion of zero-point energies in reactions of this type.

It is interesting to note that methyl substitution on tin in moving from stannane to trimethyltin hydride serves to lower the barrier for the forward reaction ($\Delta E_1^{\ddagger}$) by only 0.4 to 3.1 kJ mol^{-1}, with reductions in the reverse barrier ($\Delta E_2^{\ddagger}$) of approximately 10 kJ mol^{-1} at each level of theory. Despite this, these reactions are predicted to be significantly exothermic at each level of theory.

These data are to be compared with the energy barriers calculated for homolytic substitution by a hydrogen atom at the tin atom in stannane and methylstannane with expulsion of hydrogen atom and methyl radical, respectively.[19] Barriers of between 68.9 kJ mol^{-1} (QCISD/DZP + ZPE) and 116.9 kJ mol^{-1} (SCF/DZP + ZPE) for the former reaction with values ranging from 95.3 kJ mol^{-1} (QCISD/DZP) to 109.3 kJ mol^{-1} (SCF/DZP + ZPE) for the latter reaction indicate strongly that, as expected,[1] hydrogen abstraction is preferred over homolytic substitution at the tin atom in each case.

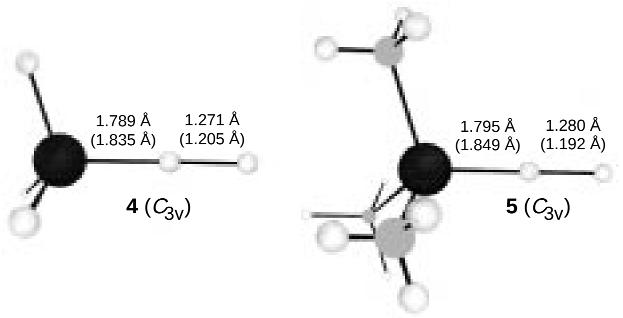


Fig. 1 MP2/DZP calculated transition states (**4**, **5**) (SCF data in parentheses) for hydrogen abstraction by hydrogen atoms from stannane and trimethylstannane

Inspection of Fig. 1 reveals a pleasing level of correlation between the SCF and MP2 generated transition state structures (**4**, **5**). At the lower level, H–H separations of 1.205 (**4**) and 1.192 Å (**5**) are predicted, while Sn–H$_{TS}$ separations of 1.835 and 1.849 Å are calculated for **4** and **5**, respectively. Inclusion of electron correlation (MP2) serves to marginally alter the position of the transferring hydrogen atom in each transition state without altering the overall gross transition state structure. Separations of 1.271 and 1.280 Å (H–H in **4** and **5**, respectively), coupled with Sn–H$_{TS}$ distances of 1.789 (**4**) and 1.795 Å (**5**) lead to overall Sn–H$_{attack}$ distances of 3.060 and 3.075 Å in structures **4** and **5**, respectively. These values are very similar to those calculated at the SCF level of theory, namely 3.040 and 3.041 Å.

We also examined the AM1 potential energy surfaces for the reactions described above. Unfortunately, AM1 calculations provided data of questionable quality; values of $\Delta E_1^{\ddagger}$ were calculated to be 0.04 and 0.01 kJ mol^{-1} for reactions involving transition states **4** and **5**, respectively. Beckwith and Zavitsas also report poor results for the reaction of hydrogen atom with H_2, where a negative activation energy is predicted by AM1.[14] It seems that AM1 may have problems modelling reactions involving the hydrogen atom in general. Accordingly, we urge caution in the use of AM1 under these circumstances.

Reaction of methyl, ethyl, isopropyl and *tert*-butyl radicals with stannane (SnH_4) and trimethyltin hydride (Me_3SnH)

Extensive searching of the potential energy surfaces for the hydrogen atom transfer reactions involving stannane and methyl, ethyl, isopropyl and *tert*-butyl radicals, as well as trimethyltin hydride and the methyl radical (Scheme 2; R ≠ H), located structures (**6**–**11**) as stationary points at each level of theory. These structures proved to be transition states for the transfer of hydrogen atom and were found to adopt colinear arrangements of attacking and leaving radicals (C_{3v} symmetry) in reactions involving methyl and *tert*-butyl radical (**6**, **7**, **8**, **11**). In the remaining cases (**9**, **10**), slight deviations from colinearity are predicted (C_s symmetry) with Sn–H$_{TS}$–C angles ranging from 174.7 to 178.1°. The MP2/DZP calculated transition structures are displayed in Fig. 2.

Apart from transition state **6** which prefers to adopt an eclipsed conformation, all structures were found to prefer staggered conformations, except for **9** at the AM1 level of theory, where the eclipsed conformation proved to be of lower energy.†

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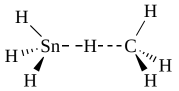
† The eclipsed conformation of **8**–**11** proved to correspond to second-order saddle-points at the SCF/DZP level of theory.

Table 1 Calculated energy barriers[a] for the forward ($\Delta E_1^‡$) and reverse ($\Delta E_2^‡$) hydrogen atom abstraction reactions of hydrogen atom with stannane (SnH_4) and trimethyltin hydride (Me_3SnH) (Scheme 2, R = H) and transition state (imaginary) frequency (ν)[b] of structures (**4**, **5**)

R	R′	TS	Method	$\Delta E_1^‡$	$\Delta E_1^‡$ + ZPVE[c]	$\Delta E_2^‡$	$\Delta E_1^‡$ + ZPVE[c]	ν
H	H	**4**	SCF/DZP	39.8	37.7	139.6	132.5	1766i
			MP2/DZP	27.3	26.1	146.6	139.8	1436i
			QCISD/DZP[d]	20.6	[19.4]	150.1	[143.3]	—
H	Me	**5**	SCF/DZP	39.4	37.2	130.4	121.6	1711i
			MP2/DZP	24.2	(22.0)	136.8	(128.0)	—
			QCISD/DZP[d]	18.1	(15.9)	140.2	(131.4)	—

[a] Energies in kJ mol^{-1}. [b] Frequencies in cm^{-1}. [c] Values in parentheses are estimates based on SCF/DZP ZPE corrections. Values in square brackets are estimates based on MP2/DZP ZPE corrections. [d] QCISD/DZP//MP2/DZP.



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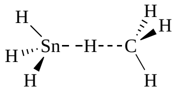

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It is interesting to note that two transition states (**6**, **7**) were identified for the reaction of the methyl radical with stannane. The eclipsed conformation (**6**) is predicted to be more stable than the staggered structure (**7**) by only 0.05 kJ mol^{-1} (SCF/DZP) while AM1 calculations suggest a preference of 0.01 kJ mol^{-1} for **6**. These data suggest significant free rotation during the course of this reaction. In this work, we have extensively examined the eclipsed conformation (**6**).

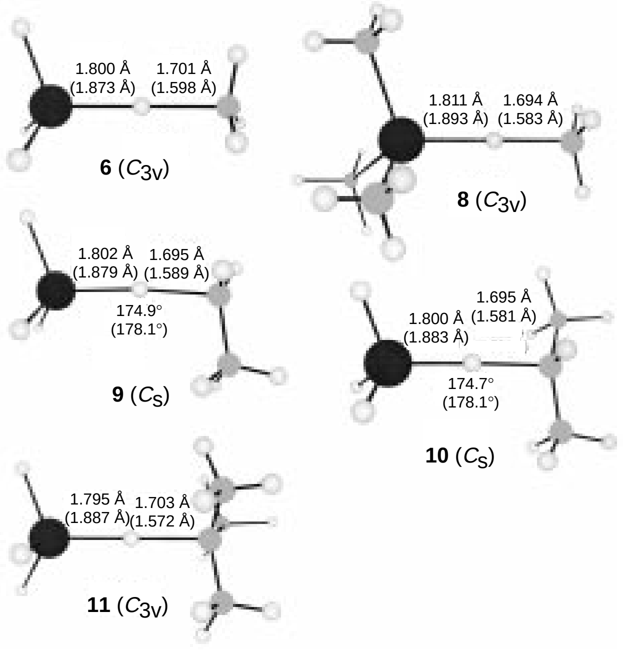
Ab initio calculated energy barriers for these hydrogen atom transfer reactions ($\Delta E_1^‡$, $\Delta E_2^‡$, Scheme 2; $R' \neq H$) are listed in Table 3, while the calculated energies of all structures in this study are found in Table 2. AM1 generated data are included for comparison with the work of Beckwith and Zavitsas.[14]

Inspection of Table 3 reveals a pleasing degree of convergence in the forward energy barriers ($\Delta E_1^‡$). For example, attack of the methyl radical at stannane is predicted to have associated barriers of 63.3 (SCF/DZP), 31.5 (MP2/DZP) and 31.7 kJ mol^{-1} (QCISD/DZP//MP2/DZP), suggesting that the MP2 level of theory is able to provide acceptable data; improvement in the level of correlation leads to only a minor decrease in $\Delta E_1^‡$. Similar trends are observed for the other reactions in this study, with QCISD calculated values of $\Delta E_1^‡$ lying within 5.8 kJ mol^{-1} of the corresponding MP2 value. We speculate that in some cases the QCISD/DZP calculated potential energy surface may differ enough from the MP2/DZP surface to lead to slight discrepancies in the (single-point) QCISD/DZP//MP2/DZP data.

All reactions are predicted to be significantly exothermic, with reverse barriers ($\Delta E_2^‡$) ranging from 167.7 (**6**) to 129.7 kJ mol^{-1} (**11**) at the QCISD level. As was observed for reactions involving hydrogen atom, zero-point vibrational energy correction (ZPE) leads to slight changes in the predicted values of $\Delta E_1^‡$ (−0.9 to 3.9 kJ mol^{-1}), while the reverse reactions ($\Delta E_2^‡$) are affected more strongly (−16.2 to −18.7 kJ mol^{-1}).

Comparing these data with those associated with homolytic substitution by the methyl radical at the tin atom in SnH_4 and $MeSnH_3$ with expulsion of a hydrogen atom and methyl radical, respectively, once again suggests that attack at tin is not competitive with hydrogen abstraction. Energy barriers of around 90 kJ mol^{-1} (QCISD/DZP//MP2/DZP) are predicted for methyl radical attack at tin.[19]

Inspection of Fig. 2 reveals that the overall structures of transition states **6**–**11** are relatively unaffected by alkyl substitution on either tin or carbon radical centres, or indeed the level of theory employed. The greatest effect appears to be on the absolute position of the hydrogen atom in the transition state during delivery. For example, at the MP2 level of theory, while the $Sn-H_{TS}$ separation is found to vary between 1.873–1.893 Å and the $C-H_{TS}$ distance is predicted to lie in the range 1.572–1.598 Å, the overall Sn−C separation is found to lie in the narrow range of 3.464–3.476 Å.



AM1 - Optimised Structures

TS	$r(Sn-H_{TS})$/Å	$r(C-H_{TS})$/Å	$\theta(Sn-H_{TS}-C)$/°
6	1.676	1.764	180.0
8	1.676	1.777	180.0
9[a]	1.697	1.712	173.4
10	1.718	1.674	174.5
11	1.740	1.649	180.0

[a]Eclipsed conformation (see text).

Fig. 2 MP2/DZP calculated transition states (**6**, **8**–**11**) (SCF data in parentheses) for hydrogen abstraction by various alkyl radicals from stannane and trimethylstannane. AM1 calculated data are included for comparison.

AM1 calculated structures for transition states **6**–**11** are very similar to those calculated using the *ab initio* techniques, with the exception of **9** which is predicted to prefer an eclipsed conformation. The transition state distances are predicted to be somewhat shorter than those calculated using SCF/DZP or MP2/DZP techniques with $Sn-H_{TS}$ and $C-H_{TS}$ separations lying between 1.676–1.740 and 1.649–1.777 Å respectively, resulting in (overall) Sn−C distances of between 3.389 and 3.453 Å, somewhat shorter than the corresponding *ab initio* separations. The intimate transition state geometries are in agreement with those reported by Beckwith and Zavitsas; C−H and Sn−H distances of 1.720 and 1.699 Å are predicted by AM1 for the transition state involved in the reaction of ethyl radical with trimethyltin hydride.[14]

Of more significance are the calculated energy barriers ($\Delta E_1^‡$ and $\Delta E_2^‡$). Table 3 clearly reveals the AM1 calculated trends in

Table 2 SCF, MP2, QCISD,[a] AM1 and AM1(CI = 2) calculated energies[b] of the reactants, products and transition states (**4**–**11**) in this study

Structure	SCF/DZP	MP2/DZP	QCISD/DZP	AM1[c]	AM1(CI = 2)[c]
H·	−0.49764	—	—	—	—
$\cdot\mathrm{CH_3}$	−39.57176	−39.69727	−39.71891	0.04771	0.01190
$\cdot\mathrm{CH_2CH_3}$	−78.61706	−78.88130	−78.91695	0.02462	0.00691
$\cdot\mathrm{Pr^i}$	−117.66350	−118.06814	−118.11713	0.00562	0.00253
$\cdot\mathrm{Bu}^t$	−156.71009	−157.25730	−157.31890	−0.01031	−0.00111
$\cdot\mathrm{SnH_3}$	−4.94363	−5.02396	−5.04697	0.07916	0.01937
$\cdot\mathrm{SnMe_3}$	−122.09584	−122.60693	−122.66550	−0.02014	0.00551
$\mathrm{CH_4}$	−40.20752	−40.36700	−40.38949	−0.01402	−0.00365
$\mathrm{CH_3CH_3}$	−79.24900	−79.54741	−79.58347	−0.02781	−0.00671
$\mathrm{CH_3CH_2CH_3}$	−118.29208	−118.73143	−118.78035	−0.03876	−0.00930
$\mathrm{(CH_3)_3CH}$	−157.33569	−157.91861	−157.97957	−0.04692	−0.01131
$\mathrm{SnH_4}$	−5.53930	−5.63952	−5.66633	0.06703	0.01590
$\mathrm{Me_3SnH}$	−122.69479	−123.22440	−123.28707	0.01369	0.00315
4	−6.02172	−6.12615	−6.15551	—	—
5	−123.17741	−123.71284	−123.77781	—	—
6	−45.08692	−45.32419	−45.37258	0.11944	0.03093
8	−162.23971	−162.90911	−162.99308	0.06599	0.01858
9	−84.13184	−84.50998	−84.57176	0.10006[d]	0.02623
10	−123.17819	−123.69900	−123.77340	0.08505	0.02257
11	−162.22498	−162.89095	−162.97716	0.07415	0.01991

[a] QCISD/DZP//MP2/DZP. [b] Energies in hartrees (1 E_h = 2626 kJ $\mathrm{mol^{-1}}$). [c] Heat of formation. [d] Eclipsed conformation.

Table 3 Calculated energy barriers[a] for the forward ($\Delta E_1^\ddagger$) and reverse ($\Delta E_2^\ddagger$) hydrogen atom abstraction reactions of methyl, ethyl, isopropyl and *tert*-butyl radicals with stannane ($\mathrm{SnH_4}$) and trimethyltin hydride ($\mathrm{Me_3SnH}$) (Scheme 2, R ≠ H) and transition state (imaginary) frequency (ν)[b] of structures (**6**–**11**)

R	R′	TS	Method	$\Delta E_1^\ddagger$	$\Delta E_1^\ddagger$ + ZPVE[c]	$\Delta E_2^\ddagger$	$\Delta E_1^\ddagger$ + ZPVE[c]	ν
Me	H	**6**	SCF/DZP	63.3	67.2	168.6	152.4	1688i
			MP2/DZP	31.5	33.7	175.3	158.8	994i
			QCISD/DZP[d]	31.7	[33.9]	167.7	[151.2]	—
			AM1	12.4	—	142.6	—	533i
			AM1(CI = 2)	34.4	—	167.1	—	1464i
Me	Me	**8**	SCF/DZP	70.5	73.7	167.1	148.4	1766i
			MP2/DZP	33.0	(36.2)	170.2	(151.5)	—
			QCISD/DZP[d]	33.9	(37.1)	162.6	(151.2)	—
			AM1	12.0	—	157.2	—	535i
			AM1(CI = 2)	38.8	—	183.7	—	1617i
Et	H	**9**	SCF/DZP	64.2	66.4	159.6	141.9	1688i
			MP2/DZP	26.9	(29.1)	161.2	(143.5)	—
			QCISD/DZP[d]	28.7	(30.9)	154.1	(136.4)	—
			AM1	22.1	—	127.9	—	863i
			AM1(CI = 2)	37.7	—	149.1	—	1488i
$\mathrm{Pr^i}$	H	**10**	SCF/DZP	64.5	65.1	151.0	132.7	1673i
			MP2/DZP	21.1	(21.7)	148.1	(129.8)	—
			QCISD/DZP[d]	24.8	(25.4)	141.6	(123.3)	—
			AM1	32.6	—	117.2	—	1154i
			AM1(CI = 2)	45.6	—	137.4	—	1621i
Bu^t	H	**11**	SCF/DZP	64.0	63.1	142.7	124.2	1652i
			MP2/DZP	13.8	(12.9)	135.5	(117.0)	—
			QCISD/DZP[d]	19.6	(18.7)	129.7	(111.2)	—
			AM1	45.8	—	110.1	—	1364i
			AM1(CI = 2)	56.2	—	130.2	—	1689i

[a] Energies in kJ $\mathrm{mol^{-1}}$. [b] Frequencies in $\mathrm{cm^{-1}}$. [c] Values in parentheses are estimates based on SCF/DZP ZPE corrections. Values in square brackets are estimates based on MP2/DZP ZPE corrections. [d] QCISD/DZP//MP2/DZP.

$\Delta E_1^\ddagger$. Values of 12.4, 22.1, 32.6 and 45.8 kJ $\mathrm{mol^{-1}}$ are predicted for reactions involving transition states **6**, **9**, **10** and **11**, respectively. In other words, in moving from the methyl radical to primary, secondary and tertiary radicals as hydrogen abstracting species, the energy barrier ($\Delta E_1^\ddagger$) is predicted to undergo increases of up to 33.4 kJ $\mathrm{mol^{-1}}$. The value of 22.1 kJ $\mathrm{mol^{-1}}$ for the reaction involving the ethyl radical with $\mathrm{SnH_4}$ compares well with the previously determined value of 21.8 kJ $\mathrm{mol^{-1}}$ for the similar reaction involving trimethyltin hydride.[14]

It is interesting to compare these data with those calculated using *ab initio* techniques. While SCF/DZP calculations suggest that $\Delta E_1^\ddagger$ is about 64–70 kJ $\mathrm{mol^{-1}}$ in all cases, inclusion of electron correlation results in decreases in $\Delta E_1^\ddagger$ in moving through the same set of hydrogen abstracting radicals. Barriers of 31.7, 28.7, 24.8 and 19.6 kJ $\mathrm{mol^{-1}}$ are predicted at the QCISD/DZP//MP2/DZP level for reactions involving transition states **6**, **9**, **10** and **11**, respectively.

These data can be compared with experimentally determined activation energies associated with hydrogen abstraction by primary, secondary and tertiary radicals from tributyltin hydride. Laser-flash photolytic (LFP) techniques have determined activation energies of 13.5, 15.3, 14.5 and 12.3 kJ $\mathrm{mol^{-1}}$

for reactions involving methyl, ethyl, isopropyl and *tert*-butyl radicals, respectively in isooctane–*tert*-butyl peroxide.[7] These experimentally determined activation energies are some 7–18 kJ mol^{-1} lower than our QCISD data. These discrepancies may be attributed to either solvent effects or differences in alkyl substitution on the stannanes used in the experimental and computational studies, or both.† Indeed, Ingold and co-workers suggest that 'polar factors' may be responsible for the activation energies for the isopropyl and *tert*-butyl radicals which 'seem to be anomalously low'.[7] Perhaps all of the reactions in question are affected by polar factors which would lead to lower than expected activation energies in the LFP reaction solvent [1 : 1 : 1 *tert*-butyl peroxide : trialkylphosphine (or trialkylarsine) : Bu_3SnH in isooctane].

Encouragingly, the correlated *ab initio* methods are generally (apart from methyl) capable of reproducing the experimentally observed trends in $\Delta E_1^{\ddagger}$, while SCF/DZP and AM1 calculations are unable to successfully reproduce these observations. These results highlight the importance of including electron correlation in calculations of this type.

Inclusion of correlation into AM1 [AM1(CI = 2)] was suggested by Beckwith and Zavitsas to provide 'a useful practicable tool for predicting the relative rates, regioselectivity and diastereoselectivity of radical reactions of relatively complex substrates'.[14] In the reactions examined in this study, AM1(CI = 2) calculations serve only to worsen both activation energies and associated trends. Values of $\Delta E_1^{\ddagger}$ were calculated to range from 34.4 (R = Me) to 56.2 kJ mol^{-1} (R = Bu^t) using AM1(CI = 2). We suggest caution in using AM1 and AM1(CI = 2) in predicting trends associated with hydrogen abstraction reactions from stannanes.

Conclusions

The results presented above indicate that MP2/DZP and QCISD/DZP//MP2/DZP (*ab initio*) calculations are generally capable of modelling the relative reactivities of primary, secondary and tertiary radicals toward hydrogen atom abstraction from stannanes. Activation energies for abstraction of hydrogen atom from stannane and trimethyltin hydride ($\Delta E_1^{\ddagger}$) are predicted to lie between 18 and 34 kJ mol^{-1} (QCISD) and are some 7–18 kJ mol^{-1} higher than experimentally determined activation energies for analogous reactions with tributyltin hydride. These discrepancies may be attributed to solvent or alkyl substitution at tin.

Interestingly, SCF/DZP, AM1 and AM1(CI = 2) methods, while predicting similar transition state geometries to the higher-level *ab initio* methods, perform poorly in predicting energy barriers and relative radical reactivities. We urge caution in the use of these methods in modelling stannane reductions.

While our results are not inconsistent with those reported recently by Beckwith and Zavitsas,[14] we suspect that the success of AM1 and AM1(CI = 2) calculations in predicting diastereoselectivities in stannane reductions of dioxolanyl radicals is partly due to the geometric insensitivity of the transition states for hydrogen transfer to the nature of the attacking radical and the fact that two faces of the same radical are involved. Errors in activation energy are likely to cancel.

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† A referee suggested that tunnelling effects may also reduce the barrier by an amount which may account for the differences between calculated and experimental data.