Organic & Biomolecular Chemistry

PAPER

Cite this: *Org. Biomol. Chem.*, 2025, **23**, 4106

Rate constants and Arrhenius parameters for H-atom abstraction from Bu_3SnH by the 2,2-dimethylvinyl radical in PhMe. Kinetic evidence for an entirely free radical mechanism for the O-directed hydrostannation of alkynols with stannanes and Et_3B/O_2†‡

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Received 14th November 2024,
Accepted 7th March 2025

DOI: 10.1039/d4ob01846j

rsc.li/obc

Using the 2,2-dimethylvinyl radical **6** as a horological calibrant for the α-cyclopropyl-β-tributylstannylvinyl radicals **2a** and **13** in PhMe, the *k* values and Arrhenius parameters for their cyclopropane ring-openings have been estimated by competition kinetics over a 293–353 K temperature range. The high log *A* values (14.95 and 14.55) for these reactions only satisfactorily align with a unimolecular, β-scissive, E_H1 radical ring-opening being rate-determining, and the radicals **3a** (R = Bu) and **14** undergoing H-atom abstraction from the stannane to give **4a** and **15**. The log *A* data for these two reactions only endorse a totally free radical mechanism for the O-directed free radical hydrostannation of dialkyl acetylenes with stannanes and Et_3B/O_2. An estimated $k_{\text{H-atom abstraction Bu}_3\text{SnH PhMe 293 K}}$ of 1.96×10^8 mol^{-1} s^{-1} is proposed for **6** in PhMe, along with an estimated $k_{\text{H-atom abstraction Ph}_3\text{SnH PhMe 293 K}}$ of 1.36×10^9 mol^{-1} s^{-1}.

Introduction

Quantifying the rate constants and Arrhenius parameters for solution-phase free radical reactions of established synthetic worth is often a highly rewarding endeavour, since such information can frequently guide the design of efficient new synthetic pathways based upon those processes,[1] while also providing important new mechanistic insights[2] into the detailed inner workings of such reactions.

In that very connection, we recently had cause to kinetically re-investigate the mechanism[3] of the O-directed free radical hydrostannation reaction of dialkyl acetylenes[4] using "radical clock" competition methods,[5] due to a recent series of papers[6] having postulated that O_2-generated stannylvinyl cations are key synthetic intermediates in these reactions; these forming from stannylvinyl radical precursors by single electron transfer (SET) to O_2, and subsequently undergoing facile ionic reduction by the stannane, to provide the allylically-oxygenated trisubstituted (*Z*)-vinylstannane products alongside regenerated O_2 (see section 1.6 of the ESI‡ for more detail).

It was felt that if the O-directed free radical hydrostannation of alkynols **1** and **12** (Schemes 1 and 2) could be studied with Bu_3SnH and cat. Et_3B/O_2 in PhMe, over a fairly wide temperature range, the product allenyltin : vinyltin ratios might yield rate constants and log *A* values for the ensuing cyclopropane ring-openings. The magnitude of that log *A* data might then give important clues as to the molecularity of the rate-determining step of these ring-openings, and reveal whether the mechanistic pathway to **4a** and **15** was unimolecular, and exclusively free radical in its nature,[3] or whether it proceeded *via* a putative α-cyclopropyl β-stannylvinyl cation and a cationic reduction, as would be advocated by the proponents[6] of the stannylvinyl cation theory.

A key assumption in doing such work would be that the intermediary stannylvinyl radicals[4d] **2a** (Scheme 1) and **13** (Scheme 2) would be calibratable with the $k_{\text{H-atom abstraction}}$

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† Dedicated to the memory of Dr Clive W. Bird FRSC, former Reader in Chemistry at King's College London (University of London); a truly outstanding organic chemist of extraordinary chemical insight and teaching ability. Clive was a genuinely good human being who helped all around him. He was inventor of the now famous "Bird Aromaticity Index".

‡ Electronic supplementary information (ESI) available: Full experimental details, calculations and NMR data supporting the work. See DOI: https://doi.org/10.1039/d4ob01846j

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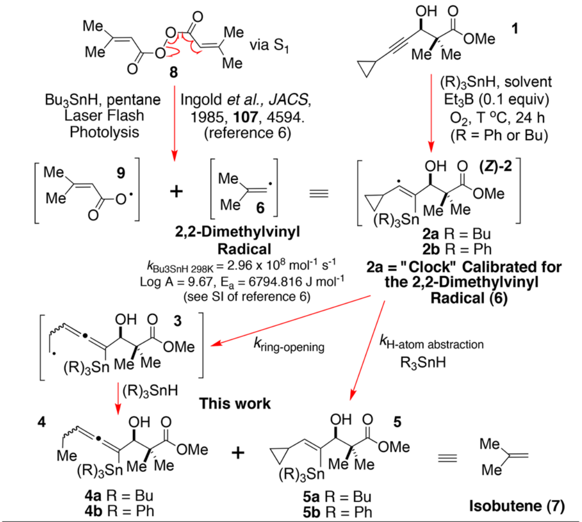
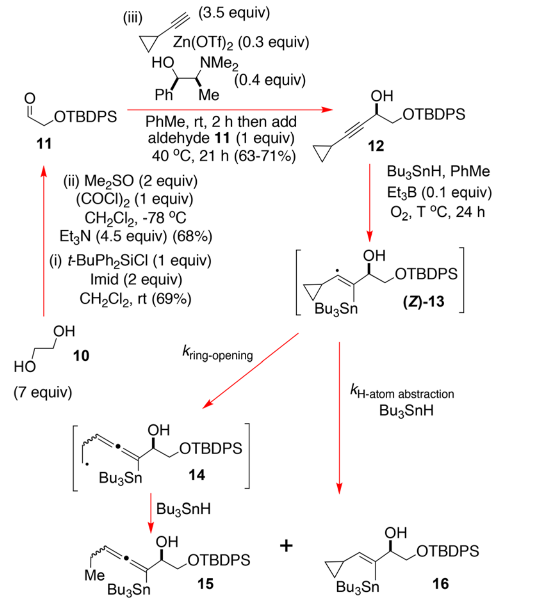


Entry	Solvent	[R3SnH]	R	T in K (°C)	Averaged Value of **4**:**5**	**(Z)-2** → **3** $k_{\text{ring-opening}}$[a] s^{-1}	**(Z)-2** → **5** (**6** → **7**) $k_{\text{H-atom abstraction}}$[a] $mol^{-1}\ s^{-1}$
1	pentane	0.2 M	Bu	293 (20 °C)	1.50 : 1	8.64×10^7	2.88×10^8 [b]
2	pentane	0.2 M	Bu	298 (25 °C)	1.60 : 1	9.47×10^7	2.96×10^8
3	pentane	0.2 M	Bu	303 (30 °C)	2.06 : 1	1.30×10^8	3.15×10^8 [b,c]
4	PhMe	0.2 M	Bu	293 (20 °C)	2.24 : 1	8.78×10^7	1.96×10^8
5	PhMe	0.2 M	Bu	298 (25 °C)	2.50 : 1	1.01×10^8	2.01×10^8
6	PhMe	0.2 M	Bu	303 (30 °C)	2.82 : 1	1.20×10^8	2.15×10^8
7	PhMe	0.2 M	Bu	313 (40 °C)	4.33 : 1	2.01×10^8	2.32×10^8 [d]
8	PhMe	0.2 M	Bu	333 (60 °C)	10.03 : 1	5.43×10^8	2.71×10^8 [d]
9	PhMe	0.2 M	Bu	353 (80 °C)	20.73 : 1	1.29×10^9	3.11×10^8 [d]
10	PhMe	0.2 M	Ph	293 (20 °C)	1 : 4.71	5.77×10^7	1.36×10^9
11	PhMe	0.2 M	Ph	313 (40 °C)	1 : 1.92	—	—
12	PhMe	0.2 M	Ph	333 (60 °C)	1.56 : 1	—	—
13	PhMe	0.2 M	Ph	353 (80 °C)	2.93 : 1	—	—

[a] This estimated or calculated rate constant should only be regarded as accurate to one decimal place.
[b] A rate constant calculated from the Ingold, $k_{\text{H-atom abstraction}}$, log A and E_a data of reference 7.
[c] This rate constant replaces and revises the original $3.5 \times 10^8\ mol^{-1}\ s^{-1}$ $k_{\text{H-atom abstraction 303K}}$ value that was previously reported by Ingold *et al.* in reference 7, which is typographically incorrect.
[d] A rate constant calculated from the log A and E_a data generated from the data in entries 4-6.

Scheme 1 Use of the radical **6** as a calibrating free radical "clock" for α-cyclopropyl-β-stannylvinyl radical probe **2a** (R = Bu).



Entry	[Bu3SnH]	T	T °K	Averaged Value of **15**:**16**	**(Z)-13** → **14** $k_{\text{ring-opening}}$[a] s^{-1}	**(Z)-13** → **16** $k_{\text{H-atom abstraction}}$[a,b] $mol^{-1}\ s^{-1}$
1	0.2 M	40 °C	313	0.87 : 1	4.04×10^7	2.32×10^8 [b]
2	0.2 M	50 °C	323	1.45 : 1	7.28×10^7	2.51×10^8 [b]
3	0.2 M	60 °C	333	1.99 : 1	1.08×10^8	2.71×10^8 [b]
4	0.2 M	70 °C	343	2.64 : 1	1.53×10^8	2.91×10^8 [b]
5	0.2 M	80 °C	353	4.29 : 1	2.66×10^8	3.11×10^8 [b]

[a] This estimated or calculated rate constant should only be regarded as accurate to one decimal place.
[b] A calculated rate constant from the log A and E_a data at hand obtained experimentally for **(Z)-2** in PhMe between 20 and 30 °C. These *k* values have been used or the purpose of calibrating **(Z)-13**.

Scheme 2 Synthesis of probe **12** and its $k_{\text{ring-opening}}$ values.

value for a typical vinyl radical such as **6** from Bu_3SnH in pentane and PhMe.

Although rate constants have long been known for the abstraction of a H-atom from Bu_3SnH by several vinylic radicals,[7,8] only one set of Arrhenius parameters has so far emerged from such studies.[7] That work is due to Ingold *et al.*[7] who measured the rate at which the 2,2-dimethylvinyl radical (**6**) abstracted a H-atom from Bu_3SnH in pentane; a solvent rarely used in free radical chemistry.

Importantly, Ingold's study[7] yielded a $k_{\text{H-atom abstraction 298 K}}$ value of $2.96 \times 10^8\ mol^{-1}\ s^{-1}$, an E_a of 1.624 ± 0.407 kcal mol^{-1}, and a $\log A$ of 9.67 ± 0.33 ($A = 4.67 \times 10^9\ mol^{-1}\ s^{-1}$) for this process[7] (see Scheme 1 and the Ingold ESI‡[7]). Ingold generated his 2,2-dimethylvinyl radical **6** by laser flash photolysis (LFP) of 3-methyl-but-2-enoyl peroxide (**8**) at 308 nm;[7] a process now widely accepted[9–12] to produce the highly reactive **6** alongside the much more delocalised and less reactive 3,3-dimethylacryloyloxy radical (**9**). Both radicals are thought to emerge from a *concerted* two-bond homolytic cleavage reaction occurring within the photoexcited S_1 form of peroxide **8** ($[(Me)_2C{=}C(H){-}C(O)O]_2$), on a reaction timescale of 0.4 ps, given recent LFP and CIDNP-NMR studies of related acyl peroxides.[9–12]

Most importantly, Ingold's $k_{\text{H-atom abstraction Bu}_3\text{SnH 298 K}}$ value[7] for **6** aligned very well with Branchi, Galli and Gentili's[8] independent k determination of $3.7 \times 10^8\ mol^{-1}\ s^{-1}$ for the encounter of a fluorenyl vinyl radical with Bu_3SnH at 298 K in MeCN : MeOH (40 : 60 v/v); the latter radical itself having been generated from a vinylic bromide precursor by LFP. This means that Ingold's $\log A$, E_a and $k_{\text{H-atom abstraction Bu}_3\text{SnH}}$ data[7] for **6** can be relied upon for k calculations and radical probe calibrations (accepting a 25% level of error in the E_a).

Given the dependability of Ingold's Arrhenius parameters for the 2,2-dimethylvinyl radical (**6**) in pentane,[7] we set about using these to horologically calibrate the two stannylvinyl radical reporter probes **2a**[3b,c] (R = Bu) and **13** as free radical "clocks"[5] in PhMe, for a series of competition experiments aimed at establishing the relative rates of the two competing reactions shown in Schemes 1 and 2. Namely: (a) the E_H1 stannylvinyl radical-induced cyclopropane ring-opening of radicals **2a** and **13** and (b) the S_H2 H-atom abstraction event involving Bu_3SnH and radicals **2a** and **13**, to give the vinyltins **5a** and **16**.

While conceptually analogous to the novel k determinations of Baines,[13] Newcomb[14] and Crich[15] using other free radical "clocks",[5] the two reporter probes, (*Z*)-**2a** (R = Bu) (Scheme 1) and **13** (see Scheme 2) are themselves unique and conceptually new, having been purposely designed to allow an estimate of the k values for an event that has hitherto resisted k quantification by other means, namely, the radical ring-opening of α-cyclopropyl-β-tributylstannylvinyl radicals.

Results and discussion

Our precise experimental method is detailed here. It used the 2,2-dimethylvinyl radical (**6**) as a horological calibrant for the α-cyclopropyl-β-tri-*n*-butylstannylvinyl radical **(*Z*)-2a** (R = Bu) *in pentane*, with **2a**[3b,c] itself being generated by an O-directed free radical hydrostannation[4,5,16–19] of the alkynol **1**[3b,c] with Bu_3SnH/cat. Et_3B[3b,4b,6] over a temperature range of 20–30 °C. Accordingly, at 298 K (25 °C), the radical **2a** (R = Bu) was assigned Ingold's $k_{\text{H-atom abstraction}}$ value for the reaction of **6** with Bu_3SnH in pentane,[7] which is 2.96×10^8 mol^{-1} s^{-1}. From Ingold's $\log A$ of 9.67 and his E_a of +1.624 kcal mol^{-1} (6794.816 J mol^{-1}) for **6**,[7] the corresponding Bu_3SnH $k_{\text{H-atom abstraction}}$ values were *calculated* for **6**/**2a** in pentane at 293 K and 303 K. These *calculated* values were then used alongside Ingold's experimentally-determined $k_{\text{H-atom abstraction}}$ value at 298 K, to allow a reasonably accurate experimental quantification of the $k_{\text{ring-opening}}$ values (Scheme 1) for the α-cyclopropyl-β-tri-*n*-butylstannylvinyl radical **2a** (R = Bu) *in pentane* at 293, 298 and 303 K using Baines' proven method for α-cyclopropylvinyl radicals.[13] The Baines formula of eqn (1) equates the ratio of the vinyltin : allenyltin products in such radical "clock" experiments[5] to the ratio of the k values for H-atom abstraction and cyclopropane ring-opening:

$$\frac{[\text{Vinyltin}]}{[\text{Allenyltin}]} = [(\text{R})_3\text{SnH}] \times \frac{k_{\text{H-atom abstraction}}}{k_{\text{ring-opening}}} \quad (1)$$

Of course, the latter expression rearranges to that in eqn (2):

$$k_{\text{ring-opening}} = [(\text{R})_3\text{SnH}] \times k_{\text{H-atom abstraction}} \times \frac{[\text{Allenyltin}]}{[\text{Vinyltin}]} \quad (2)$$

Following collation of the three experimentally-derived values (Scheme 1 entries 1–3) for the $\log k_{\text{ring-opening } \mathbf{2a} \text{ in pentane}}$ v $1/T$ in the form of an Arrhenius plot (see ESI‡), it was possible to deduce a $\log A$ of 13.274 (frequency factor $A = 1.88 \times 10^{13}$ s^{-1}) for the ring-opening of **2a** (R = Bu) in pentane, and a mean E_a of +7.18 kcal mol^{-1}. The high magnitude of the $\log A$ for this ring-opening of **2a** (R = Bu) unambiguously confirmed that it was a unimolecular E_H1 free radical ring cleavage process that was leading to the radical **3a** (R = Bu), which then H-atom abstracted from the Bu_3SnH. Such a $\log A$ most definitely did not align with a stannylvinyl cation E1-ring-opening/reduction mechanism having led to **4a**,[6] nor a bimolecular S_N2 stannylvinyl cation reduction, as would be invoked by advocates of the stannylvinyl cation mechanistic theory[6] (see ESI‡).

Significantly, however, our experimentally-derived $k_{\text{ring-opening}}$ value of 9.47×10^7 s^{-1} for **2a** (R = Bu) in pentane at 298 K, and its accompanying $\log A$ of 13.274, did align very satisfactorily with Newcomb's $k_{\text{ring-opening}}$ value[14a] of 1.0×10^8 s^{-1} for the cyclopropylcarbinyl radical in THF at 298 K, and the $\log A$ of 13.15 that these workers reported for this process, which lends considerable confidence to the entirely free radical mechanistic proposal that is being advanced here (see Scheme 1).

By comparing the experimentally-derived vinyltin : allenyltin ratios **5a** : **4a** (R = Bu) for the hydrostannation of **1** in pentane at 273, 298 and 303 K with the corresponding data gathered in PhMe, we were able to show that the rate of H-atom abstraction from Bu_3SnH by the stannylvinyl radical **2a** (R = Bu)/**6** is approximately 1.47 times slower in PhMe than it is in pentane, which confirmed a noticeable solvent effect. Moreover, when the experimentally-determined rate constants obtained for **2a** (R = Bu)/**6** in PhMe were collated in the form of an Arrhenius plot (see ESI‡), this led to an E_a of +1.599 kcal mol^{-1} (*i.e.* 1.6 kcal mol^{-1}) or 6693.84 J mol^{-1} being determined for the H-atom abstraction event involving **6**/**2a** and Bu_3SnH in PhMe. The resulting $\log A$ of 9.4826 ($A = 3.04 \times 10^9$ mol^{-1} s^{-1}) also allowed a $\Delta S^{\ddagger}_{298\text{K}}$ of −17.148 e.u. or −71.75 J K^{-1} mol^{-1} to be deduced, which showed that the rate-determining step for this H-atom transfer was bimolecular and S_H2.

From the experimentally-derived $\log A$ (9.4826 *i.e.* 9.48) and E_a (6693.84 J mol^{-1}) data gathered on **2a** (R = Bu) in PhMe, the theoretical $k_{\text{H-atom abstraction}}$ values could now be calculated for the reaction of the 2,2-dimethylvinyl radical **6**/**2a** with Bu_3SnH in PhMe at the higher temperatures of 313, 333 and 353 K (see Scheme 1). The availability of this $\log A$ and these $k_{\text{H-atom abstraction}}$ values now allowed a complete experimental determination of the $k_{\text{ring-opening}}$ values for the α-cyclopropyl-β-tri-*n*-butylstannylvinyl radical **2a** (R = Bu) in PhMe over the temperature range 20–80 °C (293–353 K) at 0.2 M Bu_3SnH concentration, and this k data is tabulated in Scheme 1.

An Arrhenius plot of the experimentally-derived $\log k_{\text{ring-opening}}$ data for **2a** (R = Bu) in PhMe *vs.* $1/T$ gave a straight line output (see Fig. 1 and ESI‡) from which a $\log A$ of 14.951 ($A = 8.93 \times 10^{14}$ s^{-1}) and an E_a of +9.47 kcal mol^{-1} (*i.e.* 9.5 kcal mol^{-1}) could both be deduced for the ring-opening of **2a** over the 293–353 K temperature range studied. The high mean $\log A$ for this cyclopropane ring-opening, and its substantially sized positive entropy of activation at 333 K ($\Delta S^{\ddagger}_{333\text{K}}$ = +32.09 J K^{-1}

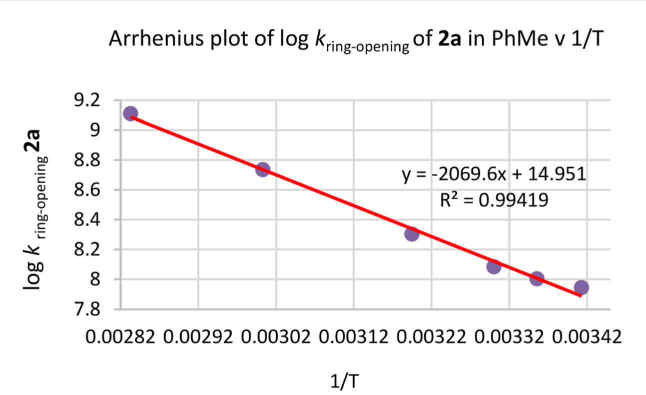


Fig. 1 Arrhenius plot of $\log k_{\text{ring-opening}}$ of **2a** *vs.* $1/T$ from the reaction of **1** with Bu_3SnH/cat. Et_3B/O_2 in PhMe over 293–353 K.

mol^{-1} or +7.67 e.u.) both immediately *ruled out a stannylvinyl cation E1-ring-opening/reduction or a bimolecular ionic reduction mechanism*[6] *as having led to* ***4a*** (see section 1.6 of the ESI‡ for an in depth discussion of these two invalid ionic mechanisms). Observations that were further supported by our previous unsuccessful cation-trappings with H_2O in 4 : 1 THF : H_2O.[3b,c]

Instead, our newly derived kinetic parameters only satisfactorily aligned with an entirely homolytic, unimolecular, E_H1 fissive mechanism operating in the rate-determining step (Scheme 1), in which a very loose activated complex of the radical **2** was singularly transforming into the radical **3a** *via* a product-like transition state in which cyclopropane bond-cleavage was already very advanced. The resulting stannylhomoallenyl radical **3a** then H-atom abstracted from the Bu_3SnH to ultimately yield **4a**.

Critically, the $\log A$ for this ring-opening of the α-cyclopropyl-β-stannylvinyl radical **2a** (R = Bu) in PhMe aligned very well with the typical $\log A$ values (13.29–16.11) recorded by Frey[20] for the unimolecular *gas phase* pyrolytic C–C bond homolyses of various cyclopropanes, which are always associated with large positive $\Delta S^{\ddagger}$ values, due to the increased bond-loosening and much greater mobility that is experienced by such activated cyclopropane rings as they fissively transit into their initial biradical products.

We next elected to synthesize the sterically less encumbered chiral cyclopropylpropargylic alcohol **12** by the route shown in Scheme 2. This featured a catalytic Carreira alkynylation[21] as a key step. The alkynol **12** was then subjected to an O-directed hydrostannation[4,6,16–19] with Bu_3SnH/cat. Et_3B in PhMe, to generate **13**, which now permitted an *estimate* of the $k_{\text{ring-opening}}$ for its cyclopropane ring over a range of temperatures (Scheme 2).

Once again, it was assumed that the $k_{\text{H-atom abstraction}}$ values for **13** would very closely mirror those for **2a**/**6**. If one is prepared to accept this key kinetic assumption, with the usual experimental caveats of course, then an Arrhenius plot of the resulting $\log k_{\text{ring-opening}}$ data *v* $1/T$ (see Fig. 2) reveals a $\log A$ of 14.549 ($A = 3.54 \times 10^{14}$ s^{-1}), a $\Delta S^{\ddagger}_{333K}$ of +24.39 J K^{-1} mol^{-1} (+5.83 e.u.), and an E_a of +9.92 kcal mol^{-1} (*i.e.* +9.9 kcal mol^{-1}).

Critically, the above $\log A$ and $\Delta S^{\ddagger}_{333K}$ data definitively *ruled out* a stannylvinyl cation reduction mechanism[6] as having afforded **15** (see section 2.2 of the ESI‡ for a more detailed and in depth discussion of this point).

Significant also was the fact that our experimentally derived E_a of +9.9 kcal mol^{-1} was close in magnitude to the E_a of +10.7 kcal mol^{-1} calculated by Guo *et al.*[22] for the closely related unimolecular radical-induced ring-opening[22] of radical **17** (Scheme 3).

While it is tempting to try to estimate the *k* values for the reaction of the β-triphenylstannylvinyl radical **2b** (R = Ph) (Scheme 1) with Ph_3SnH at different temperatures, by assuming that the $k_{\text{ring-opening}}$ values for **2a** and **2b** would be identical, current EPR evidence suggests that β-triphenylstannylvinyl radicals are much more highly stabilised[3d] *and potentially far less reactive* than their β-trialkylstannylvinyl radical counterparts, which are generally unobservable by low temperature EPR spectroscopy.[23]

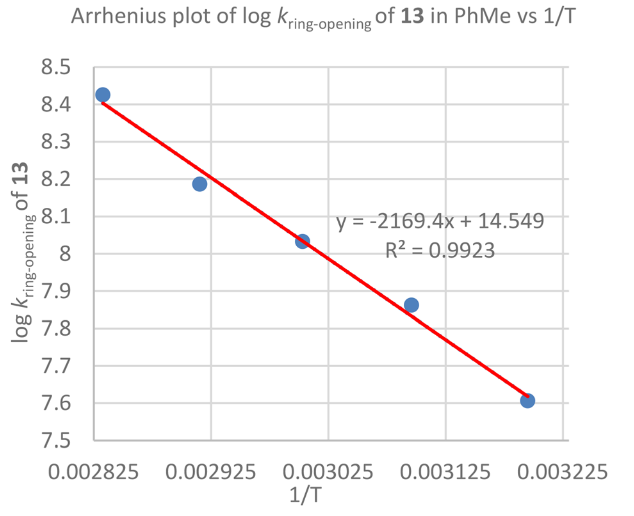
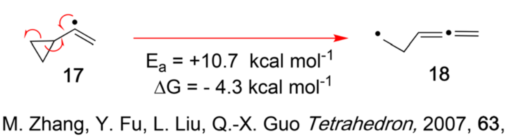


Fig. 2 Arrhenius plot of $\log k_{\text{ring-opening}}$ of **13** *vs.* $1/T$ from the reaction of **12** with Bu_3SnH/cat. Et_3B/O_2 in PhMe over 313–353 K.



Scheme 3 Guo's calculations for the ring-opening of radical **17**.[22]

This is not the case with β-triphenylstannylvinyl radicals[3d] generated by the O-directed alkyne hydrostannation with Ph_3SnH/cat. Et_3B/O_2.[4] A process that has now allowed many such radicals to be routinely observed by EPR spectroscopy at low temperatures in PhMe and THF,[3d] due to the much greater lifetimes of β-triphenylstannylvinyl radicals in solution, even in the presence of excess Ph_3SnH.

Possibly this enhanced longevity and much greater stability of β-triphenylstannylvinyl radicals is due to increased negative hyperconjugation (SOMO → $\sigma^*_{\text{C–Sn}}$) in such radicals (due to the electron-withdrawing Ph groups present on the Sn), as well as the reduced positive $\sigma_{\text{C–Sn}}$ → SOMO hyperconjugation they experience.[17e,f,g]

Now even though it is not possible to reliably use the $k_{\text{ring-opening}}$ values for **2a** to directly calibrate **2b**, a simple relative comparison of the **4b** : **5b** product ratio of entry 10 in Scheme 1 with the ratio of **4a** : **5a** obtained in entry 4, does suggest that the 2,2-dimethylvinyl radical **6** will likely react with Ph_3SnH at a rate which is *at least* 6.95 times faster than the corresponding reaction with Bu_3SnH in PhMe at 20 °C. This, in turn, points to a $k_{\text{H-atom abstraction}}$ value of *no less than* 1.36×10^9 mol^{-1} s^{-1} for **6** and **2b** from Ph_3SnH in PhMe (Scheme 1). While this relative $k_{\text{H-atom abstraction}}$ value for Ph_3SnH can only ever be considered tentative, and a conservative minimal *estimate* at best, it does nevertheless confirm that such H-atom transfers do proceed at a very fast rate that is approximately an order of magnitude less than a diffusion-controlled reaction in PhMe ($k_{\text{diffusion PhMe 293 K}} = 1.101 \times 10^{10}$

$mol^{-1}\ s^{-1}$). The availability of this $k_{\text{H-atom abstraction }Ph_3SnH}$ value for **2b**/**6** has allowed a tentative estimate of the $k_{\text{ring-opening}}$ value for **2b**, which has clearly confirmed that the radical **2b** has a lower level of reactivity with respect to its unimolecular ring-opening than **2a**.

Our collective findings to date do very strongly suggest that it is the fast rate of formation and trapping of β-triphenylstannylvinyl radicals, and *their much lower tendency to β-scissively revert back into the starting propargyloxy O-co-ordinated tin radical*, that is responsible for Ph_3SnH *generally* outperforming Bu_3SnH[6,18] as a hydrostannylating reagent with most propargylically-oxygenated dialkylacetylene substrates under the rt Et_3B-initiated reaction conditions.

It is also pertinent to point out that just because β-tributylstannylvinyl radicals are far less stable and more reactive than their β-triphenylstannylvinyl radical counterparts, this does not necessarily impose on them the requirement to preferentially engage in a fast *bimolecular* H-atom abstraction event with Bu_3SnH. Such enhanced reactivity for β-tributylstannylvinyl radicals could manifest itself in other ways, such as through increased *unimolecular* β-scissive dissociation back into the starting alkyne in the form of its O-complexed Bu_3Sn radical. This, in turn, might explain the generally lower levels of conversion[4a,b,24] that one typically sees with Bu_3SnH/cat. Et_3B in most O-directed[4] and non-directed[24] alkyne free radical hydrostannations.

Although the latter may be synthetically detrimental to a significant number of intended applications,[4] equally well, the enhanced reactivity of many β-tributylstannylvinyl radicals might sometimes be of direct benefit to certain tandem radical cyclisation processes.[17] One case in point is Alabugin's brilliant O-directed hydrostannylative route to benzofluorenes from oligoalkynes,[17a] where Bu_3SnH/AIBN was found to vastly outperform Ph_3SnH/AIBN in PhMe in the tandem stannylvinyl radical cyclisation process conducted on a diyne model test substrate (86% yield *vs*. 40% yield). However, for *most* rt O-directed[4] and non-directed[24] dialkylacetylene hydrostannations with Et_3B initiation, it is Ph_3SnH[4a,b] that usually outperforms Bu_3SnH, and this enhanced performance is almost certainly attributable to the higher stability of most β-triphenylstannylvinyl radical intermediates, which allows for their much more effective bimolecular trapping by the Ph_3SnH at the fast, near diffusion-controlled, rates that we are seeing here.

Of further note in our current studies is the significant 5-fold rate acceleration seen for the ring-opening of **2a** at 80 °C ($k_{\text{ring-opening}} = 1.29 \times 10^9\ mol^{-1}\ s^{-1}$) relative to **13** ($k_{\text{ring-opening}} = 2.66 \times 10^8\ mol^{-1}\ s^{-1}$). Such a marked increase in the rate of ring-opening of **2a** possibly points to the potential constant recurrence of temporary *transient* internal MeO–C=O: → Sn electron-donating events helping to accelerate the E_H1 cyclopropane ring-opening event, by strongly reinforcing the $\sigma_{C-Sn} \rightarrow$ SOMO positive hyperconjugative interaction.[17] Such Thorpe–Ingold-induced internal coordination in **2a** might also be impeding the aforementioned reverse unimolecular β-scissive $(R)_3Sn^\bullet$ elimination back into the starting alkyne O-coordinated tin radical. Also, the much lower tendency of the stannylvinyl radical **2b** (R = Ph) to engage in E_H1 elimination to give the ring-cleaved **3b** might simply be a reflection of the much higher stability of **2b**, reduced conformational mobility induced by the Ph_3Sn group, and the superior H-donor power of Ph_3SnH. While our $k_{\text{ring-opening}}$ and $k_{\text{H-atom abstraction}}$ data for **2a** and **13** in PhMe are all based on Ingold's k and $\log A$ data for **6** in pentane,[7] clearly, our values will potentially be modifiable in the future, should improved k calibration data appear.

Conclusions

We expect that our new $k_{\text{H-atom abstraction}}$ data for the reaction of the 2,2-dimethylvinyl radical (**6**) with Bu_3SnH and Ph_3SnH in PhMe will aid much future synthetic planning with vinyl radicals in the commonly used solvent PhMe.

Significantly, our new kinetic and $\log A$ work on the cyclopropane ring-openings of the β-stannylvinyl radicals derived from the probes **1** and **12** have further ruled out the hypothesised intermediacy of stannylvinyl cations[6] in these Et_3B/O_2 radical-initiated alkyne hydrostannation reactions and, as such, the present work has confirmed an entirely free radical mechanism[3] for the O-directed free radical hydrostannation of propargylically-oxygenated dialkylacetylenes (see sections 1.5 and 1.6 of the ESI‡ for more detailed discussion).[4]

In the paper that accompanies this,[25] other probe trapping studies will be described in THF : H_2O that further invalidate the stannylvinyl cationic mechanistic theory[6] of alkyne hydrostannation under the Et_3B/O_2-initiated reaction conditions. This work and the EPR studies that accompany it[25] provide further new insights into the complex mechanistic events that proceed alongside these highly stereoselective, *entirely free radical*, O-directed hydrostannation reactions.[3a,26]

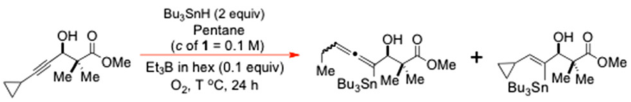
Experimental

General information

Unless stated otherwise, all reactions were run in dry solvents under an N_2 atmosphere. Dry pentane was freshly distilled from CaH_2 under an N_2 atmosphere and dry PhMe was used as supplied by Sigma-Aldrich. Both anhydrous solvents were taken out by dry syringe under an N_2 atmosphere. Ph_3SnH was purchased from Sigma-Aldrich and used as supplied; it was always handled in a glove-bag under N_2. Bu_3SnH was purchased from Alfa and was used as supplied. It was also periodically tested on a known thiocarbonyl imidazolide substrate that typically deoxygenates in >95% yield; if a yield of this magnitude was obtained, then the Bu_3SnH was used for the experiments reported. SiO_2 flash chromatography was carried out using Fluorochem silica gel 60 Å, and petrol refers to the 40–60 °C b.p. fraction; it was distilled prior to use for chromatography. HPLC grade EtOAc was used for all chromatographic purifications. TLC analysis and preparative TLC were performed on Merck glass-backed TLC plates coated with silica gel 60 F_{254}. NMR analyses were carried out using the QUB School of Chemistry Bruker Avance III HD Ascend 600 instrument operating at a frequency of 600.1337 MHz. Although the 600.13 MHz ^{1}H spectra of **4a** and **5a** in $CDCl_3$ (referenced upon tetramethylsilane (TMS) at δ 0.00 ppm, residual $CHCl_3$ at δ 7.23 ppm) were previously published in ref. 3*c* (see: H. A. Watson, S. Manaviazar, H. G. Steeds and K. J. Hale, *Tetrahedron*, 2020, **76**, 131061), we have included these spectra here *in considerably abridged form*, along with some of the previous spectra of **4b** and **5b**, in order to allow the readers of the present paper to conveniently gauge the new kinetic ratio determinations that we are presenting here *for the very first time*. Clearly, there are *minor* changes in the chemical shifts observed, in the new spectra, as one would expect.

Experimental procedures for generating α-stannylvinyl radical 2a and stannyl homoallenyl radical 3a *en route* to 4a and 5a

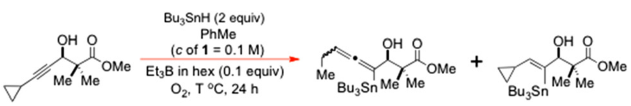
General procedure for the O-directed hydrostannation of 1 with Bu_3SnH in pentane at various temperatures to obtain the 4a : 5a ratio.



1 4a 5a

To a round-bottomed flask containing a well-stirred solution of the cyclopropylacetylenic alcohol **1** (196.2 mg, 1 mmol) in dry pentane (10 mL) under N_2 was added Bu_3SnH (0.54 mL, 2 mmol) dropwise *via* syringe over 1 min. To this stirred mixture at the desired temperature (20, 25 and 30 °C) was successively added Et_3B (0.1 mL, 1 M in hex, 0.1 mmol, 0.1 equiv.) dropwise *via* syringe followed by air (5 mL) from a syringe 5 min later. The reactants were stirred at the requisite temperature for 24 h, after which, the reaction flask was transferred to a rotary evaporator and the solvent removed *in vacuo*. A ^{1}H NMR spectrum was recorded of a portion of the crude reaction mixture in $CDCl_3$ to ascertain the crude ratio of products. Each reaction temperature was examined a minimum of three times and the average product ratio of **4a : 5a** was taken to determine of the rate constant $k_{\text{ring-opening}}$ for the **(*Z*)-2a→3a** (R = Bu) conversion at the designated temperature.

General procedure for the O-directed hydrostannation of 1 with Bu_3SnH in PhMe at various temperatures to obtain the 4a : 5a ratio.

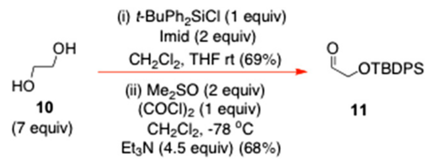


1 4a 5a

To a small round-bottomed flask containing a well-stirred solution of the cyclopropylacetylenic alcohol **1** (196.2 mg, 1 mmol) in dry PhMe (10 mL) under N_2 was added Bu_3SnH (0.54 mL, 2 mmol) dropwise *via* syringe over 1 min. To this stirred mixture at the desired temperature (20, 25, 30, 40, 60 and 80 °C) was successively added Et_3B (0.1 mL, 1 M in hex, 0.1 mmol) (0.1 equiv.) dropwise *via* syringe followed by air (5 mL, from a syringe) 5 min later. The reactants were then maintained at the desired temperature with stirring for 24 h, after which, the reaction flask was transferred to a rotary evaporator and solvent removed *in vacuo*. A ^{1}H NMR spectrum was recorded of a portion of the crude reaction mixture in $CDCl_3$ to ascertain the crude ratio of products. Each reaction temperature was examined a minimum of 2–4 times and the average product ratio of **4a : 5a** (R = Bu) was taken to determine of $k_{\text{ring-opening}}$ for the **(*Z*)-2a→3a** conversion in PhMe at the designated temperature.

Synthetic route to the (*R*)-1-(*tert*-butyldiphenylsilyloxy)-4-cyclopropylbut-3-yn-2-ol (12)

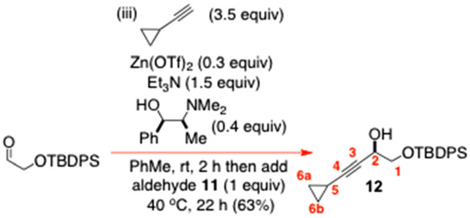
Synthesis of aldehyde 11.



To a round-bottomed flask containing ethylene glycol (20 mL, 357.7 mmol, 7 equiv.) in dry CH_2Cl_2 (200 mL) under N_2 was added imidazole (6.69 g, 102.2 mmol, 2 equiv.) in one portion with vigorous stirring. THF (40 mL) was then added *via* syringe, and the reaction mixture was cooled to 0 °C using an ice bath. *t*-Butyldiphenylsilyl chloride (13.3 mL, 51.146 mmol, 1 equiv.) was then added dropwise over 30 min *via* syringe. When the addition was complete, the ice bath was removed and the reactants were allowed to stir at rt for 18 h before the reaction was diluted with CH_2Cl_2 (200 mL) and quenched with saturated aq. $NaHCO_3$ solution (100 mL) and H_2O (200 mL). The aqueous layer was washed with CH_2Cl_2 (50 mL × 3) and the combined organic layers were dried with $MgSO_4$, filtered and concentrated *in vacuo*. The oily residue was purified by gradient elution SiO_2 flash chromatography with petrol–EtOAc (50 : 1 → 25 : 1 → 20 : 1 → 10 : 1 → 5 : 1) to give the O–silyl ether **17** (10.67 g, 69%) as a slightly impure oil. This technical grade alcohol **17** was then used directly for the oxidation step.

To a stirred −78 °C solution of $(COCl)_2$ (2.83 mL, 33.05 mmol, 1 equiv.) in dry CH_2Cl_2 (187 mL) under N_2 was added DMSO (4.7 mL, 66.1 mmol, 2 equiv.) dropwise *via* syringe over 3 min. Stirring was continued at −78 °C for a further 30 min before a solution of the aforementioned alcohol **17** (9.93 g, 33.05 mmol, 1 equiv.) in dry CH_2Cl_2 (20 mL) was added dropwise *via* syringe over 15 min. After a further 7 min of stirring at −78 °C, Et_3N (20.7 mL, 148.717 mmol, 4.5 equiv.) was added dropwise over 3 min and the reaction mixture then allowed to warm from −78 °C to rt, whereupon it was stirred for 2 h. The solvents were then removed *in vacuo* on the rotary evaporator. The crude residue of the aldehyde **11** was then suspended in petrol–EtOAc (4 : 1, 500 mL), and the solid Et_3NHCl filtered off under vacuum. The filtrate was concentrated *in vacuo* and the syrupy residue was purified by gradient elution SiO_2 flash chromatography with petrol–EtOAc (20 : 1 → 10 : 1) to give the aldehyde **11** (6.73 g, 68%) as an oil.

(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-4-cyclopropylbut-3-yn-2-ol (12).

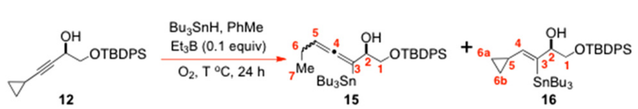


To solid $Zn(OTf)_2$ (2.05 g, 5.649 mmol, 0.3 equiv.) and (−)-*N*-methylephedrine (1.35 g, 7.532 mmol, 0.4 equiv.) in a small pear-shaped flask under N_2 was successively added PhMe (20 mL) and Et_3N (3.94 mL, 28.246 mmol, 1.5 equiv.) by syringe. Cyclopropylacetylene (5.62 mL, 66.284 mmol, 3.52 equiv.) was then added by syringe maintaining the N_2 atmosphere throughout. The reactants were stirred vigorously at rt for 2 h whereafter a solution of aldehyde **11** (5.62 g, 18.831 mmol) (which had been pre-dried by coevaporation from PhMe × 2) in PhMe (7.1 mL) was added *via* syringe, along with a 1 mL rinse of the flask with more dry PhMe. The flask containing the reactants was next transferred to an oil bath and vigorously stirred at 40 °C for 22 h. The reaction mixture was then quenched by the addition of saturated aq. NH_4Cl solution (50 mL) and diluted with EtOAc (50 mL). The organic extract was separated, and the aqueous layer was further extracted with more EtOAc (2 × 50 mL). The combined organic extracts were washed with H_2O (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography with petrol–EtOAc (25 : 1) to give the alkynol **12** (4.33 g, 63%) as a thick oil. ^{1}H NMR of **12** (600.13 MHz, $CDCl_3$) δ: 7.73–7.64 (m, 4H, –Ph), 7.46–7.34 (m, 6H, Ph), 4.43 (m, 1H, H2), 3.765–3.75 (dd, *J* = 10.2, 3.6 Hz, 1H, H1a), 3.67 (dd, *J* = 10.2, 6.6 Hz, 1H, H1b), 2.58 (d, *J* = 5.4 Hz, 1H, –OH), 1.23 (m, 1H, H5), 1.07 (s, 9H, *t*-Bu), 0.74 (m, 1H, H6a), 0.66 (m, 1H, H6b). ^{13}C NMR of **12** (150.9 MHz, $CDCl_3$) δ: 135.6 (*m*-CH of Ph), 135.5 (*m*-CH of Ph), 133.0 (q of Ph), 132.9 (q of Ph), 129.9 (*p*-CH of Ph), 129.8 (*p*-CH of Ph), 127.8 (*o*-CH of Ph), 127.77 (*o*-CH of Ph), 89.4 (C3), 73.2 (C4), 67.9 (C2), 63.2 (C1), 26.8 (Me groups of *t*-Bu), 26.6 (C5), 19.2 (q carbon of *t*-Bu), 8.11 (C6a), 8.10 (C6b) ppm.

When run under identical conditions on 1 g (3.351 mmol) scale, with respect to aldehyde **11**, the yield of **12** (0.87 g) was found to improve to 71%, possibly due to improved stirring.

General procedure for the O-directed hydrostannation of alkynol 12 with Bu_3SnH in PhMe at various temperatures to obtain the 15 : 16 ratio

For each of these kinetic runs, a 1 M solution of Et_3B in PhMe was freshly prepared by addition of Et_3B (0.2 mL, 1 M solution in hexanes) to dry PhMe (2 mL) under N_2; an aliquot of that solution was then taken and used as the reaction initiator, adhering to the general procedure set out below.

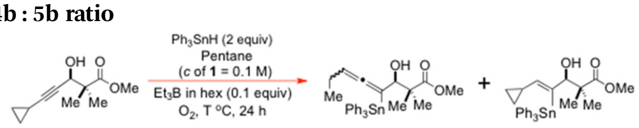


A small pear-shaped flask was charged with the alkynol **12** (100.0 mg, 0.275 mmol) and the contents of this flask were co-evaporated twice from dry PhMe (5 mL). After the second evaporation had taken place, a N_2 atmosphere was introduced into the flask, whilst it was attached to the rotary evaporator. Whilst maintaining the counter-flow of N_2 from the N_2-filled balloon connected to the rotary evaporator, an open 3-way tap, fitted with an N_2-filled balloon emitting N_2, was used to cap the reaction flask that was being removed, to preserve the N_2 atmosphere inside the flask. That flask was then placed under high vacuum for 30 min, whereafter a N_2 atmosphere was re-introduced by means of the 3-way tap (which now had a rubber septum fitted to its vertical gas inlet). To that dried residue of the **12** was added dry PhMe (2.64 mL) *via* syringe, followed by Bu_3SnH (0.15 mL, 0.55 mmol), and the reactants were stirred at rt to ensure proper mixing. The flask containing **12**, Bu_3SnH and PhMe was then placed in an oil bath at the requisite temperature between 40 and 80 °C, and a small aliquot of Et_3B (0.1 mL, 1 M solution in hex, *ca.* 0.1 equiv.) was added dropwise over several seconds. Air (5 mL) from a syringe was then introduced into the reaction vessel, whilst the N_2 atmosphere was maintained. The reactants were then stirred at the requisite temperature for reaction times that varied between 19–21 hours, before they were concentrated *in vacuo*. In all cases, TLC analysis indicated that the reactions did not progress much further after 1.5–2 h, and starting alkynol **12** always remained at reaction end, but the prolonged heating did help to decompose the tin and borane by-products, to make the crude NMR analysis easier. The allenyltin and vinyltin products **15** and **16** were much faster-moving than the starting alkynol **12**, and the allenyltin diastereomers **15** were themselves slightly faster-moving than the vinyltin product **16** on TLC. The ratio of **15 : 16** in the crude concentrated reaction mixture was then determined by high field NMR spectroscopy in $CDCl_3$ and this ratio was subsequently used alongside the theoretical or experimentally determined $k_{\text{H-atom abstraction}}$ values in Scheme 2, to determine the $k_{\text{ring-opening}}$ values for the conversion of **13** into **14**. Each reaction temperature was examined a minimum of 2–4 times and the average product ratio of **15 : 16** was taken to determine of $k_{\text{ring-opening}}$ for the **13** into **14** conversion in PhMe at the designated temperature.

In an attempt to obtain analytically pure samples of the two products **15** and **16**, several of the aforementioned crude reaction mixtures were combined and partially purified by gradient-elution SiO_2 flash chromatography using petrol–EtOAc (80 : 1 → 40 : 1 → 20 : 1 → 10 : 1) as the eluent. A second flash chromatographic purification of this partially purified mixture (enriched in the stannylallene **15**) was then performed with petrol–Et_2O (150 : 1 → 100 : 1) as the eluent, to isolate **15** in reasonably pure condition. A third analytical column with neat CH_2Cl_2 was then performed to allow isolation of the allene **15** as a 1 : 1 diastereomeric mixture in near pure condition. The spectral data for this mixture of the two diastereosiomers of **15** is reported now in full: ^{1}H NMR of **15** (600.13 MHz, $CDCl_3$) δ: 7.71–7.63 (m, 4H, Ph), 7.46–7.34 (m, 6H, Ph), 4.77 (td, *J* = 6.6 and 3.0 Hz, 1H, H5 geometric isomer 1), 4.715 (td, *J* = 6.6 and 3.0 Hz, 1H, H5 geometric isomer 2), 4.383 (complex m, 1H, H2 both diastereomers), 3.68 (dd, J = 10.2, 3.0 Hz, 1H, H1a diastereomer 1) partially superimposed upon 3.66 (dd, J = 10.2, 3.6 Hz, 1H, H1a diastereomer 2), 3.49 (dd, J = 8.4, 4.8 Hz, 1H, H1b, diastereomer 1) partially superimposed upon 3.48 (dd, J = 8.4, 4.8 Hz, 1H, H1b diastereomer 2), 2.71 (d, J = 3.0 Hz, 1H, OH, diastereomer 1) superimposed upon 2.706 (d, J = 3.0 Hz, 1H, OH, diastereomer 2), 1.64 and 1.45 (m, 2H, H6a, H6b both diastereomers), 1.40–1.23 (complex m, 18 H, $-CH_2-$ regions of Bu_3Sn, both diastereomers), 1.066 and 1.064 (2 × s, 9H, *t*-Bu, TBDPS, both diastereomers), 0.92 (t, J = 7.8 Hz, 9H, Me of Bu_3Sn, superimposed upon m, 3H, H7, diastereomer 1), 0.86 (t, J = 7.2 Hz, 9H, Me of Bu_3Sn, superimposed upon m, 3H, H7, diastereomer 2) ppm. ^{13}C NMR of **15** (150.9 MHz, $CDCl_3$) δ: 200.77 and 200.64 (1 × C4, both diastereomers), 135.56 and 135.54 (2 × *m*-CH of Ph, both diastereomers), 133.3 (1 × quaternary C of Ph, both diastereomers), 129.74 and 129.72 (1 × *p*-CH of Ph, both diastereomers), 127.71 (2 × *o*-CH of Ph carbons of both diastereomers) 96.28 and 96.22 (1 × C5, both diastereomers), 86.17 and 86.07 (1 × C3, both diastereomers), 72.94 and 72.73 (C2, both diastereomers), 68.74 and 68.43 (1 × C1, both diastereomers), 29.0, 27.84 and 27.28 ($-CH_2-$ groups of Bu_3Sn, both diastereomers), 26.86 and 26.83 (*t*-Bu, both diastereomers), 21.65 and 21.60 (C6, of both diastereomers), 19.2 (quaternary C, *t*-Bu), 17.51 ($-CH_2-$ groups of Bu_3Sn, $^1J^{119}Sn^{13}C$ = 336.5 Hz, $^1J^{117}Sn^{13}C$ = 321.4 Hz, $-Sn\underline{C}H_2-$ of Bu_3Sn, both diastereomers), 14.0 and 13.9 (C7–Me of both diastereomers) 13.69, 13.65 and 13.59 (Me groups of Bu_3Sn groups, both diastereomers), 10.88 and 10.83 (CH_2- of Bu_3Sn, both diastereomers) ppm.

Unfortunately, we were never able to obtain a satisfactory ^{1}H NMR spectrum of the pure vinyltin product **16** of the hydrostannation of **12**. Nonetheless, this did not prove especially problematical for the kinetic task at hand, since it was possible to readily determine the crude ratios of **15 : 16** from the ^{1}H NMR spectra run of the crude reaction mixtures. In this regard, the olefinic H4 peak of the vinyltin **16** clearly stood out, it resonating as a dd (J = 10.2 and 1.2 Hz) at δ 5.55 ppm in $CDCl_3$. Its identity was readily confirmed by the small allylic coupling between H4 and H2 (^4J = 1.2 H), and the large J coupling (^3J = 10.2 Hz) with the cyclopropane CH (H5). The vinyltin geometry could be readily assigned from the large $^{119/117}Sn–^1H$ J couplings ($^{119}Sn–^1H$ = 131.4 and 111.6 Hz) that accompanied this resonance.

General procedure for the O-directed hydrostannation of 1 with Ph_3SnH in PhMe at various temperatures to obtain the 4b : 5b ratio



1 4b 5b

A 1 M solution of Ph_3SnH in PhMe was prepared by accurately weighing out Ph_3SnH, into an open-necked round-bottomed flask containing a magnetic stirring bar, *inside a glove bag* filled with dry N_2. The reaction vessel was then capped with a *closed* 3-way tap possessing a Quickfit male joint, while still inside the glove bag. The sealed flask was then removed from the glove bag and connected to a vacuum line *via* a 3-way tap, which was also fitted with an N_2-filled balloon. The reaction flask was then sequentially evacuated and purged with N_2 from the balloon before it was clamped over a magnetic stirrer. Dry PhMe was then added to give a 1 M solution. An aliquot of that freshly prepared solution of Ph_3SnH (2 mL, 1 M in PhMe, 2 mmol) was then added to the flask containing the acetylene **1** (196.2 mg, 1 mmol) and a magnetic stirring bar under N_2. To this stirred mixture of the Ph_3SnH and **1** at the desired temperature (20, 40, 60 and 80 °C) was then added Et_3B (0.1 mL, 1 M in hex, 0.1 mmol) (0.1 equiv.) dropwise *via* syringe, followed by air (5 mL, from a syringe) 5 min later. The reactants were then stirred at the designated temperature for 24 h, after which, the reaction flask was transferred to a rotary evaporator and the solvent removed *in vacuo*. A ^{1}H NMR spectrum was recorded of a tiny portion of the crude reaction mixture in $CDCl_3$ to ascertain the crude ratio of products. The remaining crude concentrated residue was then purified by gradient-elution SiO_2 flash chromatography using initially 3 : 1 → 2 : 1 → 1 : 1 petrol : CH_2Cl_2 to remove excess tin hydride, and then 30 : 1 petrol : EtOAc to yield the allenylstannane product **4b** as a clear oil. Finally the eluent was changed to 25 : 1 petrol : EtOAc to obtain the essentially pure vinylstannane product **5b** as a white amorphous solid. Each reaction temperature was examined a minimum of two/four times and the average product ratio of **4b : 5b** (R = Ph) was taken. This protocol allowed estimation of the $k_{\text{H-atom abstraction } Ph_3SnH}$ (*i.e.* (*Z*)-**2b**→**5b** [R = Ph]) at 293 K (20 °C).

Data availability

The experimental data supporting this article can be found in the Experimental section of this paper and in the ESI.‡ The ESI‡ provides NMR spectra and product ratio determinations for **4a : 5a**, **4b : 5b** and **15 : 16**. The ESI‡ also contains the theoretical rate constant calculations that were performed, and our experimental rate constant determinations, and the Arrhenius Plots that were associated with these studies in Excel format. The ESI‡ also provides details of how the $\log A$, E_a, $\Delta S^‡$ and $\Delta G^‡$ data were calculated from the experimentally-derived data gathered in these plots. Finally, the ESI‡ contains a detailed mechanistic interpretation of the new kinetic data gathered. Citations to references 26–43 can be found in the ESI.‡

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Leverhulme Trust (RPG-2015-438), QUB, LJMU, and the NI DfE for financial support (Ph.D Studentship to HAW), and Dr Joseph S. Vyle of QUB for generous gifts of chemicals.

References

1 S. Z. Zard, *Radical Reactions in Organic Synthesis*, Oxford University Press (OUP), 2003, ch. 1, p. 8.

2 (*a*) H. E. Avery, Theory of Reaction Rates, in *Basic Reaction Kinetics and Mechanism*, Macmillan, 1974, ch. 5, p. 59; H. E. Avery, Reactions in Solution, in *Basic Reaction Kinetics and Mechanism*, Macmillan, 1974, ch. 8, p. 99 (*b*) R. A. Jackson, Kinetics, in *Mechanism: An Introduction to the Study of Organic Reactions*, OUP, 1985, ch. 3, p. 23; (*c*) H. Maskill, The rates of simple chemical reactions, in *The Physical Basis of Organic Chemistry*, Oxford University Press, 1985, ch. 6, p. 216.

3 (*a*) P. Dimopoulos, J. George, D. A. Tocher, S. Manaviazar and K. J. Hale, *Org. Lett.*, 2005, **7**, 5377; (*b*) H. A. Watson, S. Manaviazar, H. G. Steeds and K. J. Hale, *Chem. Commun.*, 2019, **55**, 14454; (*c*) H. A. Watson, S. Manaviazar, H. G. Steeds and K. J. Hale, *Tetrahedron*, 2020, **76**, 131061; (*d*) For the first solution phase EPR spectra of β-triphenylstannylvinyl radicals, see: H. A. Watson, A. J. Fielding and K. J. Hale, *Chem. Commun.*, 2021, **57**, 7449.

4 (*a*) Review: K. J. Hale, S. Manaviazar and H. A. Watson, *Chem. Rec.*, 2019, **19**, 238; (*b*) P. Dimopoulos, A. Athlan, S. Manaviazar, J. George, M. Walters, L. Lazarides, A. E. Aliev and K. J. Hale, *Org. Lett.*, 2005, **7**, 5369; (*c*) S. Manaviazar, K. J. Hale and A. LeFranc, *Tetrahedron Lett.*, 2011, **52**, 2080; (*d*) K. J. Hale, M. Grabski, S. Manaviazar and M. Maczka, *Org. Lett.*, 2014, **16**, 1164; (*e*) K. J. Hale, M. Maczka, A. Kaur, S. Manaviazar, M. Ostovar and M. Grabski, *Org. Lett.*, 2014, **16**, 1168; (*f*) K. Micoine, P. Persich, J. Llaveria, M.-H. Lam, A. Merderna, F. Loganzo and A. Furstner, *Chem. – Eur. J.*, 2013, **19**, 7370.

5 M. Newcomb, Radical Kinetics and Clocks, in *Encyclopedia of Radicals in Chemistry, Biology and Materials*, John Wiley, 2012. DOI: 10.1002/9780470971253.rad007.

6 (*a*) M. S. Oderinde, R. D. J. Froese and M. G. Organ, *Angew. Chem., Int. Ed.*, 2013, **52**, 11334; (*b*) M. S. Oderinde, R. D. J. Froese and M. G. Organ, *Chem. – Eur. J.*, 2014, **20**, 8579; (*c*) M. S. Oderinde and M. G. Organ, *Chem. – Eur. J.*, 2013, **19**, 2615; (*d*) M. S. Oderinde, H. N. Hunter, R. D. J. Froese and M. G. Organ, *Chem. – Eur. J.*, 2012, **18**, 10821; (*e*) M. Alami, A. Hamze and O. Provot, *ACS Catal.*, 2019, **9**, 3437; (*f*) R. Hua, Functionalized Alkenes from Hydrofunctionalization of Alkynes, in *Addition Reactions with Unsaturated Hydrocarbons*, 1st edn, Wiley-VCH, 2022, ch. 3, p. 47.

7 L. J. Johnston, J. Lusztyk, D. D. M. Wagner, A. N. Abeywickreyma, A. L. J. Beckwith, J. C. Scaiano and K. U. Ingold, *J. Am. Chem. Soc.*, 1985, **107**, 4594.

8 B. Branchi, C. Galli and P. Gentili, *Eur. J. Org. Chem.*, 2002, 2844.

9 For Scaiano's observation of phenyl radicals by laser flash photolysis of benzoyl peroxide see: J. C. Scaiano and L. Stewart, *J. Am. Chem. Soc.*, 1983, **105**, 3609.

10 (*a*) C. Reichardt, J. Schroeder, P. Voghringer and D. Schwarzer, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1662; (*b*) C. Reichardt, T. Schafer, J. Schroeder, P. Voghringer and D. Schwarzer, *Ultrafast Phenomena XVI. Springer Series in Chemical Physics*, Springer, Berlin, Heidelberg, 2009, vol. 92. DOI: 10.1007/978-3-540-95946-5_159.

11 (*a*) CIDNP-NMR work: A. Kitamura, H. Sakuragi, M. Yoshida and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1393; (*b*) Laser Flash Photolysis work: J. Wang, H. Itoh, M. Tsuchiya, K. Tokumaru and H. Sakuragi, *Tetrahedron*, 1995, **51**, 11967.

12 P. Lebourgeois, R. Arnaud and J. Lemaire, *J. Chim. Phys.*, 1972, **69**, 1633.

13 K. K. Milnes, S. E. Gottschling and K. M. Baines, *Org. Biomol. Chem.*, 2004, **2**, 3530.

14 (*a*) M. Newcomb and A. G. Glenn, *J. Am. Chem. Soc.*, 1989, **111**, 275; (*b*) J. Jin and M. Newcomb, *J. Org. Chem.*, 2007, **72**, 5098.

15 D. Crich and X.-S. Mo, *J. Am. Chem. Soc.*, 1998, **120**, 8298.

16 D. P. Curran and T. McFadden, *J. Am. Chem. Soc.*, 2016, **138**, 7741.

17 (*a*) K. Pati, G. dos Passos Gomes, T. Harris, A. Hughes, H. Phan, T. Banerjee, K. Hanson and I. V. Alabugin, *J. Am. Chem. Soc.*, 2015, **137**, 1165; (*b*) N. P. Tsvetkov, E. Gonzales-Rodriguez, A. Hughes, G. dos Passos Gomes, F. D. White, F. Kuriakose and I. V. Alabugin, *Angew. Chem., Int. Ed.*, 2018, **57**, 3651; (*c*) E. Gonzalez-Rodriguez, M. A. Abdo, G. dos Passos Gomes, S. Ayad, F. D. White, N. P. Tsvetkov, K. Hanson and I. V. Alabugin, *J. Am. Chem. Soc.*, 2020, **142**, 8352; (*d*) C. Hu, L. Kuhn, F. D. Makurvet, E. S. Knorr, X. Lin, R. K. Kawade, F. Mentink-Vigier, K. Hamson and I. V. Alabugin, *J. Am. Chem. Soc.*, 2024, **146**, 4187; (*e*) I. V. Alabugin, G. dos Passos Gomes and M. A. Abdo, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2019, **9**, e1389; (*f*) I. V. Alabugin, K. M. Gilmore and P. W. Peterson, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2011, **1**, 109; (*g*) I. V. Alabugin, *Stereoelectronic Effects: A Bridge Between Structure and Reactivity*, John Wiley & Sons Ltd, Chichester, UK, 2016, ch. 3, p. 42.

18 (*a*) C. Nativi and M. Taddei, *J. Org. Chem.*, 1988, **58**, 820; (*b*) H. E. Ensley, R. R. Buescher and K. Lee, *J. Org. Chem.*, 1982, **47**, 404; (*c*) M. Lautens and A. H. Hudson, *Tetrahedron Lett.*, 1990, **31**, 3105.

19 R. Willem, A. Delmotte, I. De Borger, M. Biesemans, M. Gielen and F. Kayser, *J. Organomet. Chem.*, 1994, **480**, 255.

20 H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103.

21 N. K. Anand and E. M. Carreira, *J. Am. Chem. Soc.*, 2001, **123**, 9687.

22 J. Shi, M. Zhang, Y. Fu, L. Liu and Q.-X. Guo, *Tetrahedron*, 2007, **63**, 12681.

23 K. Suzuki, N. Sugihara, Y. Nishimoto and M. Yasuda, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201883.

24 (*a*) K. Oshima, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 1; (*b*) K. Nozaki, K. Oshima and K. Utimoto, *J. Am. Chem. Soc.*, 1987, **109**, 2547.

25 K. L. E. Hale, A. J. Fielding and K. J. Hale, *Org. Biomol. Chem.*, 2025, **23**, DOI: 10.1039/d4ob01847h.

26 (The relevant citations to references 26–43 can be found in the mechanistic discussions in the accompanying ESI.‡) ref. 26 is: W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, 1935, **3**, 492.
27 E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science, Sausalito, CA, 2006, p. 368.
28 (*a*) J. F. Bunnett and V.I Chapter, The Interpretation of Rate Data, in *Technique of Organic Chemistry, Vol. VIII, Part I, Ed. A. Weissberger, Investigation of Rates and Mechanisms of Reactions, Part I*, ed. S. L. Friess, E. S. Lewis and A. Weissberger, 2nd edn, 1963, p. 177.; (*b*) (See also Jerry March's book for the much more widespread publication of the Bunnett $\Delta S^{\ddagger}$ equation, with due attribution to Bunnett, who made a major contribution to physical organic chemistry with his initial simplifying rearrangement of the original Eyring–Wynne–Jones–Polanyi equation to give the $\Delta S^{\ddagger}$ equation shown). See: . J. March,*Advanced Organic Chemistry. Reactions, Mechanism and Structure*, John Wiley & Sons, 4th edn, 1992, p. 225.
29 R. W. Alder, R. Baker and J. M. Brown, Mechanism and Reactivity, in *Mechanism in Organic Chemistry*, John Wiley & Sons, 1971, ch. 1, pp. 1–77 (see page 5 for their $\Delta S^{\ddagger}$ equation).
30 (*a*) S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, 1971, **93**, 1925; (*b*) S. A. Sherrod and R. G. Bergman, *J. Am. Chem. Soc.*, 1969, **91**, 2115.
31 (*a*) M. Hanack and T. Bassler, *J. Am. Chem. Soc.*, 1969, **91**, 2117; (*b*) For a detailed review by Hanack on cyclopropyl-stabilized vinyl cations, which discusses the special stability of α-cyclopropylvinyl cations, see: M. Hanack, *Acc. Chem. Res.*, 1976, **9**, 364.
32 M. M. Kreevoy, Chapter XXIII, Thermodynamics and Reaction Mechanism, in *Technique of Organic Chemistry, Vol. VIII, Part II, Ed. A. Weissberger, Investigation of Rates and Mechanisms of Reactions, Part II*, ed. S. L. Friess, E. S. Lewis and A. Weissberger, 2nd edn, 1963, p. 1361.
33 K. A. Dill, S. Bromberg and D. Stigter, Chapter 20, Coulomb's Law of Electrostatic Forces, in *Molecular Driving Forces*, ed. K. A. Dill and S. Bromberg, Garland Science, Taylor and Francis Group, New York, 2nd edn, 2010.
34 (*a*) N. Bjerrum, *Kgl. Dan. Vidensk. Selsk. Mat.-Fys. Medd.*, 1926, **7**(9), 1–48; (*b*) For an English Language version of the Introductory Survey of this paper, pages 1–17, see: Neils Bjerrum, *Selected Papers*, Chairmen of Editorial Committee, Neils Bohr, Einar Munksgaard, Copenhagen, 1949. See page 108 of the PDF of this book at: **https://www.royalacademy.dk/Publications/Low/1686_Bjerrum,%20Niels.pdf**. Accessed: 19 June, 2024.
35 R. Moritz, G. Zardalidis, H.-J. Butt, M. Wagner, K. Mullen and G. Houdas, *Macromolecules*, 2014, **47**, 191.
36 S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 1957, **79**, 5937.
37 K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1937, 1183.
38 J. Biordi and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1962, 4291.
39 G. R. Cowie, H. J. M. Fitches and G. Kohnstam, *J. Chem. Soc.*, 1963, 1585.
40 G. Velegraki and M. Stratakis, *J. Org. Chem.*, 2013, **78**, 8880.
41 P. G. Cookson, A. G. Davies and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1976, 1022.
42 (*a*) C. Hu, J. Mena and I. V. Alabugin, *Nat. Rev. Chem.*, 2023, **7**, 405; (*b*) A. M. Hughes, G. does Passos Gomes and I. V. Alabugin, *J. Org. Chem.*, 2019, **84**, 1853.
43 (*a*) For an excellent new 2024 review on alkyne hydrometallation with Group IV metal hydrides, see the following Book Chapter by: T. Wiesner and M. Haas, in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier, 2024. DOI: **10.1016/B978-0-323-96025-0.00125-3**(*b*) For McLaughlan and Roberts' recent highly regiocontrolled $PtCl_2$/XPhos-catalysed hydrostannation of terminal aryl acetylenes and propargylic alcohols, see: D. D. Roberts and M. G. McLaughlin, *Adv. Synth. Catal.*, 2023, **365**, 1602; (*c*) For McLaughlin's recent application of the $PtCl_2$/XPhos/Et_3SiH-catalyst system to the highly regiocontrolled hydroboration of terminal alkyl, aryl and heteroaryl acetylenes with HBPin, see: K. L. E. Hale, D. D. Roberts and M. G. McLaughlin, *Eur. J. Org. Chem.*, 2025, e202401355.