Picosecond radical kinetics. Rate constants for ring openings of (2-alkoxy-3-phenylcyclopropyl)methyl radicals

Marie-Hélène Le Tadic-Biadatti and Martin Newcomb *

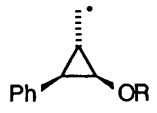
Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

Rate constants for ring openings of the (*trans,trans*-2-methoxy-3-phenylcyclopropyl)methyl radical (1M) and the (*trans,trans*-2-*tert*-butoxy-3-phenylcyclopropyl)methyl radical (1B) have been determined between −21 and 37 °C by indirect kinetics employing benzeneselenol trapping as the competition reaction. Radicals 1 were formed in chain reactions of the appropriate 'PTOC esters', 2-thioxopyridine-*N*-oxy derivatives of the corresponding carboxylic acids, the syntheses of which are reported. Radicals 1 rearrange with rate constants of 8×10^{11} s^{-1} (1M) and 5×10^{11} s^{-1} (1B) at 25 °C with predominant (160:1 and 60:1, respectively) cleavage to give benzylic radical products. The rate constants for ring openings to the minor, alkoxy-substituted radical products represent the first measurements of the kinetic effects of alkoxy substitution on cyclopropylcarbinyl radical ring openings. Precursors to radicals 1 can be employed in mechanistic probe studies that permit differentiation between radical and cationic intermediates.

Mechanistic probes have been widely applied in studies of organic reactions that might proceed *via* radical intermediates. The probe substrate is a precursor to a radical that undergoes a characteristic reaction, most commonly a unimolecular process, and detection of radical-derived products is evidence that a radical intermediate was produced. One potential problem with a radical probe is that the radical indicator reaction might be too slow to compete with processes that intercept the intermediate; for this reason, exceedingly fast radical reactions have been sought. A more subtle problem is that the indicator reaction for a radical intermediate is often not unique to the radical; specifically, these radical reactions usually have analogous cationic reactions. Because cations are inherently more reactive than radicals and because most of the features that accelerate a radical reaction will also accelerate a cation reaction, products of many characteristic 'radical probe' reactions might actually be derived from cationic intermediates.

For probe studies of potential radical intermediates in enzyme-catalysed hydroxylations and for radical clock applications, very fast rearrangements of substituted cyclopropylcarbinyl radicals have been calibrated[1] including ring openings of the bicyclo[2.1.0]pentan-2-yl radical,[2–4] poly-alkyl substituted cyclopropylcarbinyl radicals[4] and aryl substituted cyclopropylcarbinyl radicals.[5–7] In general, radical probes based on these fast rearrangements suffer from the second problem noted above in that one cannot distinguish between a radical and cationic intermediate. We reasoned that such discrimination would be possible in an aryl substituted cyclopropylcarbinyl system that incorporated a cation stabilizing group more powerful than phenyl, an alkoxygroup.[8] In fact, this approach has been shown to be successful. Ring opening of the cyclopropylcarbinyl radicals **1** gave benzylic radicals predominantly, and ring opening of the corresponding cationic intermediates gave oxonium ions exclusively.[8,9] A recent application of the *tert*-butoxy substituted system in a mechanistic study of cytochrome P-450 enzyme catalysed hydroxylation showed that cationic species were produced during the hydroxylation;[9] this feature was the likely origin of confusing results in earlier studies of P-450 oxidations with probes that could not discriminate between cations and radicals.

Whereas mechanistic probes can provide qualitative evidence of an intermediate, substantially more useful information is obtained when the rate constants of the indicator reactions are known allowing the reactions to be used as radical clocks for timing events. In this work, we report the kinetics of ring openings of radicals **1M** and **1B**. Previously, we reported the rate constant for ring opening of **1B** at 37 °C.[9]



1B: R = $C(CH_3)_3$
1M: R = CH_3

Results and discussion

Radical precursors

Aryl-substituted cyclopropylcarbinyl radicals are known to rearrange too fast for direct kinetic studies employing picosecond lasers. In addition, most entries to these radicals involve decarboxylations of acyloxyl radicals, and the decarboxylation step is almost certainly slower than the ring opening reaction.[10,11] Therefore, we employed a competition kinetic method, the PTOC–thiol method,[1,12] using the fast hydrogen transfer trapping agent benzeneselenol.[5,13] The necessary radical precursors are PTOC esters developed originally for synthetic applications by Barton and co-workers.[14]

The synthetic sequence for the radical precursors is outlined in Fig. 1. Reaction of (*Z*)-β-alkoxystyrenes (**2**) with ethyl diazoacetate gave ethyl *trans,trans*-2-alkoxy-3-phenylcyclopropanecarboxylates (**3**) in good yield. The stereochemistry of esters **3** was established by NOE experiments (Fig. 2). Reduction of the ethyl esters with $LiAlH_4$ provided the corresponding alcohols **4** which were subsequently oxidized to aldehydes **5**. Wittig methylenation of the aldehydes provided olefins **6** which were converted into the homologated alcohols **7** by hydroboration–oxidation. Alcohols **7** were oxidized to the homologated acids **8** by a two-stage oxidation sequence which was selected for convenience; direct oxidation of **7** to **8** might be possible, but we did not attempt this conversion. Finally, the PTOC ester precursors **9** were prepared from acids **8**. All intermediates were characterized by NMR spectroscopy. Acids **8** were also characterized by HRMS.

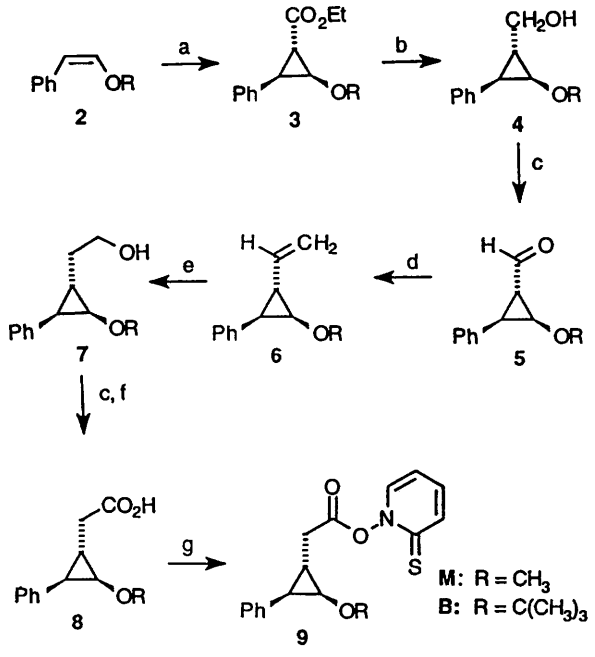


Fig. 1 Synthetic sequence for preparation of PTOC esters **9**: (*a*) ethyl diazoacetate, $CuSO_4$; (*b*) $LiAlH_4$; (*c*) ClCOCOCl, DMSO, Et_3N; (*d*) Ph_3PCH_2; (*e*) 9-BBN, H_2O_2; (*f*) $AgNO_3$, KOH; (*g*) ClCOCOCl, 2-mercaptopyridine *N*-oxide sodium salt

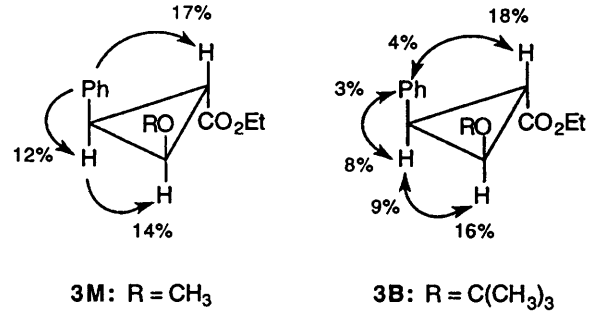
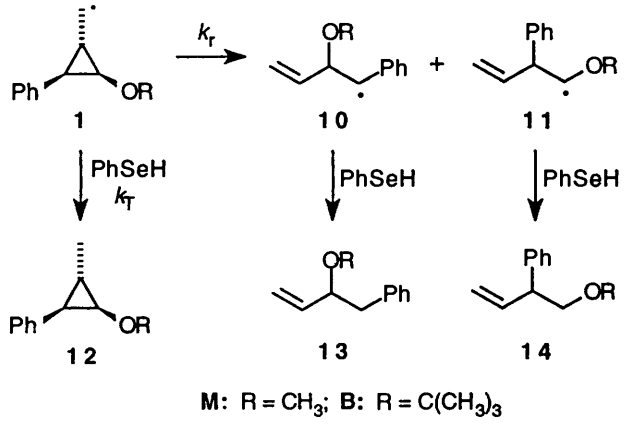


Fig. 2 Percentage NOE observed for esters 3



Scheme 1

In the competition kinetic studies (Scheme 1), radicals **1** were produced in radical chain reactions of PTOC esters **9**. Radicals **1** can ring open in two directions to give benzylic radicals **10** and alkoxy-substituted radicals **11** in addition to being trapped before ring opening. Therefore, hydrogen atom transfer trapping experiments will result in three possible products in each case, compounds **12**–**14**.

Authentic samples of all of the possible products were synthesized for GC and GC–MS comparisons with the products of the radical reactions. The cyclopropylmethanes **12** were prepared from alcohols **4** by conversion into the mesylates and reduction with $LiBEt_3H$. The mesylates from **4** could not be isolated due to their high ionic reactivity, and substantial amounts of ring-opened products were obtained even when the mesylation and reduction reactions were conducted at low temperatures. The by-products formed in this sequence are 4-alkoxy-3-phenylbut-1-enes (**14**) from ionic ring opening and, ultimately, hydride capture, and these isomers of compounds **12** could not be removed from the desired products readily. Therefore, the reaction mixtures were treated with *m*-chloroperbenzoic acid to epoxidize the by-products **14**, and pure compounds **12** were obtained by column chromatography. An authentic sample of compound **14B** was prepared simply by running the mesylation–reduction sequence with alcohol **4B** at a relatively high temperature, and a sample of **14M** was prepared by the previously reported method.[8] The major products from ring openings of radicals **1** are benzylic radicals, so we employed the radical ring opening reactions in the synthesis of authentic samples of 3-alkoxy-4-phenylbut-1-enes (**13**). Reactions of PTOC esters **9** in the presence of thiophenol gave compounds **13** contaminated with a small amount of isomers **14**, and column chromatography afforded pure samples of **13**. All of the products **12**–**14** were characterized by NMR spectroscopy and HRMS.

Kinetics

For fast radical reactions, the PTOC–thiol kinetic method can be employed with benzeneselenol as a trapping agent. Rate constants for reaction of PhSeH with the cyclopropylcarbinyl radical are known.[5,13] With the assumption[1] that the cyclopropylcarbinyl radical and substituted cyclopropylcarbinyl radicals react with the selenol with the same rate constants, one can use the product distributions and concentrations of PhSeH to calculate the rate constants for ring opening of radicals **1**.

Reactions of PTOC esters **9** in THF in the presence of PhSeH were conducted between −21 and 37 °C, and the results are collected in Table 1. Products **12**–**14** were obtained in all reactions in both the methoxy and *tert*-butoxy series as determined by GC–MS comparison of the radical-derived products to authentic samples. Ring-opened products **13**, the ultimate products from opening to give benzylic radicals, predominated by far, and the yields of **13** were effectively the total yields of the reactions. In order to determine the ratios of products **13** and **14** to product **12** reasonably accurately, mixtures of authentic samples of the various products in the approximate amounts observed in the radical reactions were prepared for GC calibrations. Nevertheless, the large product ratios resulted in considerable random errors.

The total yields of hydrocarbon products **12**–**14** from reactions of PTOC esters **9** were generally in the 50–70% range. Two interfering reactions can limit the yields of hydrocarbon products from PTOC esters: nucleophilic substitution at the activated carbonyl group of the precursor[15] and trapping of the acyloxyl radical by the reactive hydrogen donor in competition with the decarboxylation step.[3] The former reaction apparently limited the yields of **12**–**14** in our case. A 500 MHz NMR analysis of the crude reaction mixture from a preparative-scale reaction of **9B** in the presence of 2 M PhSH indicated that a new derivative of **8B**, presumed to be the phenylthio ester, was present. Another possible competing reaction, 'self-trapping' of alkyl radicals by a PTOC ester, is known to be two or three orders of magnitude less rapid than reactions of radicals with PhSH or PhSeH,[1] and the concentrations of PhSeH and PhSH exceeded those of the PTOC esters by at least an order of magnitude. Therefore, no 'self-trapping' to give 2-pyridyl sulfides was expected, and the above NMR analysis of the crude product mixture showed no vinyl proton signals other than those from **13B** and **14B**. The reduced overall yields may limit the precision of the kinetic measurements, but they do not affect the kinetics which are based solely on the partitioning of radicals **1**.

Table 1 Products from reactions of radicals **1**

Radical	T/°C[a]	[PhSeH][b]	% Yield	**13**/**12**	(k_{r1}/k_T)/M[c]	**14**/**12**	(k_{r2}/k_T)/M[d]
1M	−21	0.48	49	428	205	1.7	0.82
	−10	0.48	58	540	259	2.5	1.20
	−10	0.98	55	271	265	1.4	1.37
	−1	0.46	54	503	232	2.5	1.15
	−1	0.95	52	306	291	1.6	1.52
	10	0.48	45	665	319	3.8	1.82
	10	0.98	59	298	291	1.5	1.47
	24	0.46	51	641	295	4.7	2.16
	37	0.46	52	599	275	4.5	2.07
	37	0.95	54	414	392	2.1	2.00
	37	0.98	58	402	392	2.6	2.55
	37	1.45	31	303	438	1.8	2.61
1B	−16	0.41	59	333	137	3.5	1.44
	−16	0.83	58	153	127	1.4	1.11
	−4	0.41	64	349	143	4.2	1.72
	−4	0.83	57	151	125	1.8	1.49
	8	0.41	63	442	181	6.5	2.66
	37	0.43	65	517	222	11	4.73
	37	0.91	68	240	218	5	4.55

[a] ± 1 °C. [b] Mean concentration of PhSeH. [c] Relative rate constants for ring opening to radical **10** *versus* trapping. [d] Relative rate constants for ring opening to radical **11** *versus* trapping.

Table 2 Activation parameters for ring openings of radicals **1**

Reaction	Relative Arrhenius function[a]	Absolute Arrhenius function[a]	$k_{(25)}$/s^{-1}[b]
1M→**10M**	(3.52 ± 0.47) − (5.7 ± 2.6)/θ	(14.55 ± 0.48) − (15.2 ± 2.6)/θ	8×10^{11}
1M→**11M**	(2.08 ± 0.44) − (10.2 ± 2.5)/θ	(13.11 ± 0.45) − (19.7 ± 2.6)/θ	5×10^{9}
1B→**10B**	(3.51 ± 0.40) − (6.9 ± 2.1)/θ	(14.54 ± 0.41) − (16.4 ± 2.1)/θ	5×10^{11}
1B→**11B**	(3.45 ± 0.52) − (16.5 ± 2.7)/θ	(14.48 ± 0.52) − (26.0 ± 2.8)/θ	8×10^{9}

[a] $\theta = 2.3RT$ in kJ mol^{-1}. [b] Rate constant at 25 °C.

The ratios of rearranged to unrearranged products and the concentration of PhSeH provide relative rate constants for the ring opening and trapping reactions (k_r/k_T) which are listed in Table 1. From these relative rate constants, relative Arrhenius functions for each ring opening reaction were calculated, and these relative Arrhenius functions were then added to the Arrhenius function for PhSeH trapping of the cyclopropylcarbinyl radical in THF[13] to give the Arrhenius functions for ring openings of radicals **1** (Table 2). The errors in these functions include the errors in the relative studies performed here as well as those from the initial calibration of PhSeH against the cyclopropylcarbinyl radical ring opening.

One reaction of radical **1B** was conducted in the presence of thiophenol. At 34 °C in the presence of 2.0 M PhSH, PTOC ester **9B** reacted to give **13B** in 76% yield, **14B** in about 2% yield, and a trace of **12B**. The product ratio **13B**:**14B**:**12B** was 1550:33:1. Using a rate constant of 1.5×10^8 M^{-1} s^{-1} for PhSH trapping of radical **1B** at 34 °C,[16] one calculates approximate rate constants of 5×10^{11} s^{-1} and 1.0×10^{10} s^{-1} for ring opening of **1B** to **10B** and **11B**, respectively. These rate constants compare quite favorably with those calculated from the Arrhenius functions in Table 2 for reactions at 34 °C of 6×10^{11} and 1.0×10^{10} s^{-1}, respectively.

Several aryl substituted cyclopropylcarbinyl radical ring openings have been calibrated by the PTOC–thiol method with PhSeH trapping (Fig. 3).[5–7] The rate constants for ring openings of **1M** and **1B** to give the benzylic radicals **10** are slightly greater than those for ring opening of the parent in this series, radical **16**, perhaps reflecting a somewhat increased strain in radicals **1** due to the *cis* substitution of the phenyl and alkoxyl groups.

Unlike the case with phenyl substituted cyclopropylcarbinyl radicals, rate constants for ring openings of alkoxy substituted cyclopropylcarbinyl radicals have not been reported previously. Despite the fact that the alkoxy substituted radicals **11** are minor products from ring openings of **1**, the cleavage reactions

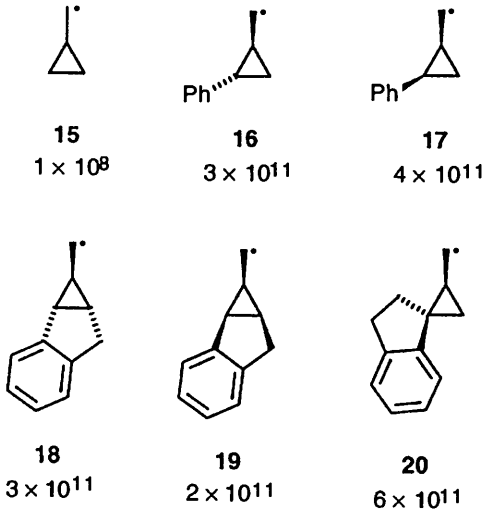


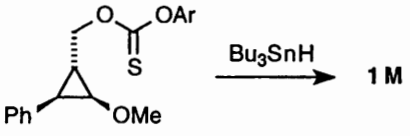
Fig. 3 Rate constants for ring openings of cyclopropylcarbinyl radicals at 25 °C in units of s^{-1} from Refs. 1, 5–7

that give **11** are considerably faster than ring openings of the unsubstituted cyclopropylcarbinyl radical (**15**), cleavage of one bond, which occurs with a rate constant of 5×10^7 s^{-1} at 25 °C.[17] Thus, the incipient alkoxy stabilization accelerates the bond cleavages producing the α-alkoxy radicals by about two orders of magnitude at room temperature. Given that the rearrangements of radicals **1** leading to benzylic radicals are only slightly faster than that of radical **16**, it is reasonable to conclude that the ring openings of **1** to α-alkoxy radicals **11** are likely to be only slightly faster than rearrangements of (2-alkoxycyclopropyl)methyl radicals.

The observed ratios of products **13** to **14** (Table 1) confirm the desired high discrimination between radicals and cations in

systems **1**. Radical ring openings towards the phenyl group are faster than those towards the alkoxyl groups by approximately factors of 160 (**1M**) and 60 (**1B**) at ambient temperature. We reported previously that, for both systems, cationic ring openings of the mesylates derived from alcohols **4** occurred with exclusive (to the limit of detection) ring openings towards the alkoxy groups.[8,9]

Using the Arrhenius functions for ring opening of radical **1M**, one predicts that the ratio of products (**13M** : **14M**) formed at 80 °C will be about 125 : 1. When radical **1M** was produced at 80 °C from the thioxocarbonate **21** in a Bu_3SnH-mediated reaction, the observed product ratio was 170 : 1.[8] Given that the predicted product ratio for 80 °C requires extrapolation of Arrhenius functions with relatively large errors in the activation parameters, the agreement between the predicted and observed ratio, to within a factor of 1.4, is good. This is an important observation because the radical **1M** was produced by different reactions, an acyloxyl radical decarboxylation involving C–C bond cleavage and a thioxocarbonate adduct fragmentation involving C–O bond breaking, in the two studies. We have tacitly assumed that, despite the very short lifetimes of aryl-substituted cyclopropylcarbinyl radicals such as **1**, these intermediates behave in a statistical rather than deterministic kinetic manner, and the agreement in relative rate constants when **1M** was produced from two sources provides some support for this assumption.



21: Ar = *p*-C_6H_4F

The embodiment of the phenyl and alkoxy groups into cyclopropane probe systems was shown to provide fast radical probes that can differentiate between radical and cationic intermediates.[8,9] The kinetic values for ring openings of radicals **1** reported here permit quantitative applications of these systems in radical studies. With lifetimes in the 1–3 ps range at ambient temperatures, no radical reaction can suppress the ring openings of phenyl-substituted cyclopropylcarbinyl radicals to the point that these products are undetectable, and these intermediates can even be applied to study the details of nuclear motions in transition structures.[9]

Experimental

General

Reagents were purchased from Aldrich and used as received unless otherwise noted. All air- and moisture-sensitive reactions were performed in flame-dried glassware under an atmosphere of N_2. Benzeneselenol was prepared and handled as previously described.[3] Tetrahydrofuran (THF) and ether were distilled from sodium and benzophenone ketyl. Methylene chloride was distilled from P_2O_5. Benzene and hexanes were distilled from CaH_2. NMR spectra were obtained at 300 MHz (^1H) and 75 MHz (^{13}C). Analytical GC was accomplished on flame ionization detector equipped Varian 3400 chromatographs (bonded phase Carbowax and low polarity silicone oil, 5% phenyl, wide-bore capillary columns 15 m × 0.54 mm from Altech) and on a Hewlett-Packard model 5890 GC interfaced to an HP model 5971 mass selective detector (15 m × 0.25 mm capillary bonded phase Carbowax column from Altech). Radial chromatography was performed on a Chromatotron® model 7294T (Harrison Research Corp.) using plates coated with 2 mm of TLC grade silica gel (Merck) with gypsum binder and fluorescent indicator. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. High resolution mass spectral analyses were performed by the Central Instrument Facility at Wayne State University.

cis-β-*tert*-Butoxystyrene (2B)

2B was prepared by reaction of potassium *tert*-butoxide with 0.5 equiv. of phenylacetylene in dry *N*,*N*-dimethylformamide (DMF) under N_2 at 135–140 °C for 4 days (80%) and by reaction of 0.4 equiv. of potassium *tert*-butoxide with phenylacetylene in 5.4 equiv. of *tert*-butyl alcohol at reflux ($CaCl_2$ drying tower) for 6 days (73%). The reaction mixtures were treated with water and extracted with ether. The ethereal layers were dried ($MgSO_4$) and concentrated. Residual phenylacetylene was distilled at reduced pressure to leave a residue of crude product which was a 96 : 4 mixture of *cis* and *trans* isomers and contained no other impurities according to NMR spectroscopy. The crude mixture was used in the next step. δ_H 1.40 (9 H, s), 5.32 (1 H, d, J = 7.2 Hz), 6.50 (1 H, d, J = 7.2 Hz), 7.15–7.18 (1 H, m), 7.25–7.45 (2 H, m) and 7.65–7.75 (2 H, m); δ_C 28.1, 105.7, 125.4, 128.1 (4 carbons), 137.0 and 141.0 (quaternary C not observed).

Ethyl *trans*,*trans*-2-*tert*-butoxy-3-phenylcyclopropanecarboxylate (3B)

A mixture of crude *cis*-β-*tert*-butoxystyrene (**2B**) (4.5 g, 25.6 mmol) and 0.42 g of anhydrous $CuSO_4$ in 10 ml of benzene was heated at 75 °C as a solution of 5.4 ml (51.2 mmol) of ethyl diazoacetate in 20 ml of benzene was added dropwise over 2 h. The mixture was heated at reflux for an additional 2 h and allowed to cool to room temperature. Stirring was continued for 12 h. The reaction mixture was treated with water, and the resulting phases were separated. The aqueous layer was extracted with ether, and the combined organic phases were extracted with water and saturated aqueous NaCl solution and dried ($MgSO_4$). Concentration of the organic phase at reduced pressure gave a residue which contained a mixture of **3B** and ethyl *cis*,*cis*-2-*tert*-butoxy-3-phenylcyclopropanecarboxylate. Separation of the mixture by column chromatography (silica gel; ethyl acetate–hexanes) gave **3B** (3.4 g, 51%) as an oil. The structure of **3B** was confirmed by NOE experiments (see Fig. 2). δ_H 1.15 (9 H, s), 1.27 (3 H, t, J = 7 Hz), 2.13 (1 H, dd, J = 6.2, 3 Hz), 2.59 (1 H, dd, J = 7, 6.2 Hz), 3.87 (1 H, dd, J = 7, 3 Hz), 4.16 (2 H, q, J = 7 Hz) and 7.18–7.32 (5 H, m); δ_C 14.3, 27.7, 30.1, 32.0, 59.2, 60.7, 75.8, 126.2, 127.8, 128.3, 136.1 and 172.6; *m*/*z* 206 (16%), 188 (48), 178 (16), 177 (100), 161 (12), 149 (15), 133 (39), 132 (18), 131 (70), 115 (19), 104 (15), 103 (23), 91 (7), 77 (14) and 57 (97). HRMS: calc. for $C_{12}H_{14}O_3$ $(M - 56)^+$, 206.0943; found, 206.0938.

(*trans*,*trans*-2-*tert*-Butoxy-3-phenylcyclopropyl)methanol (4B)

A mixture of ester **3B** (3.4 g, 13 mmol) and $LiAlH_4$ (1.0 g, 26 mmol) in 50 ml of ether was heated at reflux for 12 h. The mixture was cooled to 0 °C, and excess hydride reagent was quenched by sequential addition of 1 ml of water, 1 ml of 15% aqueous NaOH solution and 3 ml of water. The ethereal solution was filtered, and the solid residue was triturated with ether. The combined organic solutions were washed with saturated aqueous NaCl solution and dried ($MgSO_4$). Solvent was removed at reduced pressure, and the residue was purified by column chromatography (silica gel; ethyl acetate–hexanes) to give **4B** (2.67 g, 95%) as a white solid; mp 65 °C, δ_H 1.05 (9 H, s), 1.64–1.72 (2 H, m), 1.87 (1 H, t, J = 6.6 Hz), 3.46 (1 H, dd, J = 6.6, 3.3 Hz), 3.61–3.75 (2 H, m) and 7.14–7.29 (5 H, m); δ_C 27.7, 28.2, 29.1, 56.7, 64.2, 75.1, 125.3, 127.6, 128.0 and 138.4; *m*/*z* (relative intensity), 220 (M^+, 2), 189 (5), 164 (16), 146 (45), 133 (71), 117 (73), 105 (12), 91 (30), 77 (12), 57 (100), 41 (34) and 29 (15). HRMS: calc. for $C_{14}H_{20}O_2$, 220.1463; found, 220.1458.

(*trans,trans*-2-*tert*-Butoxy-3-phenylcyclopropanecarbaldehyde (5B)

To a solution of oxalyl chloride (436 μl, 5.0 mmol) in 15 ml of dichloromethane at −78 °C was added dropwise dimethyl sulfoxide (DMSO) (777 μl, 10.9 mmol). This mixture was stirred for 10 min, and a solution of alcohol **4B** (1.0g, 4.54 mmol) and Et_3N (3.1 ml, 22.7 mmol) in 8 ml of dichloromethane was added dropwise *via* cannula. The reaction was monitored by thin layer chromatography. After 15 min, the mixture was allowed to warm to room temperature and was subsequently treated with water. The resulting phases were separated. The aqueous layer was extracted with dichloromethane, and the combined organic phases were extracted with water and saturated aqueous NaCl solution and dried ($MgSO_4$). Concentration of the organic phase at reduced pressure gave the aldehyde **5B** as a yellow oil with traces of triethylammonium salts. The salts were precipitated by treatment with ether, and the resulting mixture was filtered. Concentration of the filtrate at reduced pressure gave aldehyde **5B** (0.99 g, 100% yield) which was used without further purification. δ_H 1.17 (9 H, s), 2.50–2.54 (1 H, m), 2.85 (1 H, t, J = 6.6 Hz), 4.00 (1 H, dd, J = 6.9, 2.9 Hz), 7.21–7.30 (5 H, m), 9.81 (1 H, d, J = 2.7 Hz); δ_C 27.6, 33.8, 39.9, 61.5, 76.1, 126.5, 127.9, 128.4, 135.5 and 199.1.

(*trans,trans*-2-*tert*-Butoxy-3-phenylcyclopropyl)ethylene (6B)

A stirred solution of methyltriphenylphosphonium bromide (2.05 g, 5.7 mmol) in 25 ml of THF was cooled at 0 °C as a solution of *n*-butyllithium (2.04 ml of a 2.5 M solution in hexanes) was added dropwise. After 15 min, a solution of aldehyde **5B** in 10 ml of THF was added *via* cannula, and the reaction was stirred overnight. The mixture was treated with water, the phases were separated, and the aqueous layer was extracted thrice with ether. The combined organic phases were washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and concentrated at reduced pressure. Purification of the residue by column chromatography (silica gel; ethyl acetate–hexanes) gave the desired alkene **6B** (734 mg, 75%) as a yellow oil. δ_H 1.13 (9 H, s), 1.86–1.92 (1 H, m), 2.01 (1 H, t, J = 6.6 Hz), 3.47 (1 H, dd, J = 6.8, 3.6 Hz), 4.97 (1 H, dd, J = 10.4, 1.6 Hz), 5.08 (1 H, dd, J = 17.1, 1.6 Hz), 5.58–5.70 (1 H, m) and 7.11–7.28 (5 H, m); δ_C 27.8, 31.6, 32.0, 59.5, 75.1, 113.2, 125.4, 127.6, 128.1, 137.9 and 138.2.

2-(*trans,trans*-2-*tert*-Butoxy-3-phenylcyclopropyl)ethanol (7B)

A solution of alkene **6B** (734 mg, 3.4 mmol) in 15 ml of THF was added *via* cannula to a solution of 9-borabicyclo[3.3.1]nonane (9-BBN) (10.2 ml of a 0.5 M solution in hexanes, 5.1 mmol) in 30 ml of THF. The reaction was monitored by thin layer chromatography. After complete disappearance of the alkene, the reaction mixture was quenched by slow addition of 3.7 ml of ethanol, 2.5 ml of aqueous 3 M NaOH solution and 2.5 ml of 30% aqueous H_2O_2 solution. The mixture was heated at reflux for 1 h. After cooling, the two phases were separated, and the aqueous layer was extracted thrice with ether. The combined organic phases were washed with saturated aqueous NaCl solution, dried ($MgSO_4$), and concentrated at reduced pressure. Purification of the residue by column chromatography (silica gel; ethyl acetate–hexanes) gave alcohol **7B** (765 mg, 96%) as a clear, colourless oil. δ_H 1.05 (9 H, s), 1.31–1.38 (1 H, m), 1.49–1.64 (2 H, m), 1.71 (1 H, t, J = 6.4 Hz), 1.76–1.85 (1 H, m), 3.33 (1 H, dd, J = 6.4, 3.6 Hz), 3.75 (2 H, t, J = 6.1 Hz), 7.14–7.27 (5 H, m); δ_C 24.0, 27.8, 30.2, 35.4, 58.6, 62.1, 74.8, 125.1, 127.5, 127.9 and 139.2.

(*trans,trans*-2-*tert*-Butoxy-3-phenylcyclopropyl)ethanal

To a solution of oxalyl chloride (314 μl, 3.6 mmol) in 14 ml of dichloromethane at −78 °C was added dropwise DMSO (554 μl, 7.8 mmol). The mixture was stirred for 10 min, and a solution of alcohol **7B** (765 mg, 3.27 mmol) and Et_3N (2.3 ml, 16.4 mmol) in 10 ml of dichloromethane was added dropwise *via* cannula. The reaction was monitored by thin layer chromatography. After 15 min, the mixture was allowed to warm to room temperature and was subsequently treated with water. The resulting phases were separated. The aqueous layer was extracted with dichloromethane, and combined organic phases were extracted with water and saturated aqueous NaCl solution and dried ($MgSO_4$). Concentration of the organic phase at reduced pressure gave the desired aldehyde as a yellow oil with traces of triethylammonium salts. The salts were precipitated by treatment with ether, and the resulting mixture was filtered. Concentration of the filtrate at reduced pressure gave the desired aldehyde (737 mg, 97%) which was used in the next step without further purification. δ_H 1.07 (9 H, s), 1.56–1.65 (1 H, m), 1.80 (1 H, t, J = 6.5 Hz), 2.41 (1 H, ddd, J = 17.0, 7.7, 1.9 Hz), 2.62 (1 H, ddd, J = 17.0, 6.6, 2.2 Hz), 3.38 (1 H, dd, J = 6.6, 3.5 Hz), 7.15–7.27 (5 H, m) and 9.81 (1 H, t, J = 2.0 Hz); δ_C 20.4, 27.7, 29.9, 46.2, 57.9, 75.0, 125.5, 127.6, 128.0, 138.0 and 200.9.

(*trans,trans*-2-*tert*-Butoxy-3-phenylcyclopropyl)ethanoic acid (8B)

A solution of silver nitrate (1.0 g, 5.89 mmol) in 3 ml of water was added to a solution of the above aldehyde (683 mg, 2.94 mmol) in 25 ml of ethanol. A 1 M KOH aqueous solution (826 mg in 14.7 ml of H_2O, 14.7 mmol) was then added dropwise. The heterogeneous mixture was stirred for 2 h at room temperature. The precipitated salts were filtered and washed several times with water. The basic solution was extracted thrice with ether. The aqueous solution was then acidified with concentrated HCl and extracted thrice with chloroform. The combined chloroform phases were washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and concentrated at reduced pressure to give acid **8B** (700 mg, 96%) as a yellow solid; mp 88–90 °C, δ_H 1.07 (9 H, s,), 1.62–1.71 (1 H, m), 1.82 (1 H, t, J = 6.5 Hz), 2.40 (1 H, dd, J = 15.9, 7.2 Hz), 2.52 (1 H, dd, J = 15.9, 6.9 Hz), 3.38 (1 H, dd, J = 6.7, 3.5 Hz) and 7.16–7.28 (5 H, m); δ_C 22.3, 27.7, 29.9, 36.8, 57.9, 75.1, 125.4, 127.6, 128.1, 138.1 and 177.9; m/z 248 (M^+, 2%), 192 (20), 175 (26), 146 (9), 145 (10), 133 (16), 132 (11), 117 (27), 115 (18), 105 (13), 104 (17), 91 (21), 78 (13) and 57 (100). HRMS: calc. for $C_{15}H_{20}O_3$, 248.1412; found, 248.1414.

1-(*trans,trans*-2-*tert*-Butoxy-3-phenylcyclopropylethanoyloxy)-pyridine-2(1*H*)-thione (9B)

To a solution of acid **8B** (300 mg, 1.21 mmol) in 10 ml of benzene at room temperature was added a catalytic amount of DMF (2 drops) and oxalyl chloride (211 μl, 2.42 mmol). The solution was stirred for 3 h, and the solvent and excess oxalyl chloride were distilled at reduced pressure using a base trap. The residual acid chloride was dissolved in 20 ml of benzene. The remaining portions of this procedure were conducted with minimal room lighting. The benzene solution was added *via* cannula to a cooled (5 °C) suspension of the sodium salt of 2-mercaptopyridine *N*-oxide (207 mg, 1.39 mmol, Olin Chemical, prepared and dried as previously described)[18] and 4-dimethylaminopyridine (15 mg, 0.12 mmol) in 20 ml of benzene. The stirred reaction was allowed to warm to room temperature. After 1 h, the mixture was washed with saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution, dried ($MgSO_4$) and concentrated at reduced pressure. The brown residue was purified by rapid column chromatography (silica gel; ethyl acetate–hexanes) to give the desired PTOC ester **9B** (343 mg, 79%) as a yellow orange oil. δ_H 1.09 (9 H, s), 1.72–1.79 (1 H, m), 1.97 (1 H, t, J = 6.6 Hz), 2.75 (1 H, dd, J = 16.8, 7.7 Hz), 3.01 (1 H, dd, J = 16.8, 6.7 Hz), 3.52 (1 H, dd, J = 6.7, 3.5 Hz), 6.58 (1 H, dt, J = 6.8, 1.8 Hz), 7.15–7.29 (6 H, m), 7.50 (1 H, dd, J = 7.6, 1.7 Hz) and 7.68 (1 H, dd, J = 8.8, 1.7 Hz).

Ethyl *trans,trans*-2-methoxy-3-phenylcyclopropanecarboxylate (3M)

3M was prepared from the commercially available β-methoxystyrene (mainly *cis*) by a procedure similar to that given above for the preparation of **3B**. Purification by column chromatography (silica gel; ethyl acetate–hexanes) gave **3M** (23%) as an oil. The structure of **3M** was confirmed by NOE experiments (see Fig. 2). δ_H 1.28 (3 H, t, J = 7.2 Hz), 2.21 (1 H, dd, J = 6.3, 2.7 Hz), 2.69 (1 H, t, J = 6.6 Hz), 3.29 (3 H, s), 3.83 (1 H, dd, J = 7.2, 2.7 Hz), 4.16 (2 H, q, J = 7.2 Hz) and 7.20–7.32 (5 H, m); δ_C 14.2, 28.1, 32.4, 58.5, 60.7, 65.9, 126.6, 128.1, 128.3, 134.7 and 172.0.

(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)methanol (4M)

4M was prepared from ester **3M** by a procedure similar to that given above for **4B**. Purification by column chromatography (silica gel; ethyl acetate–hexanes) gave **4M** as a clear colourless oil (100%). δ_H 1.77–1.82 (1 H, m), 1.85 (1 H, br s), 1.97 (1 H, t, J = 6.6 Hz), 3.15 (3 H, s), 3.38 (1 H, dd, J = 6.6, 3.3 Hz), 3.57–3.70 (2 H, m) and 7.18–7.32 (5 H, m); δ_C 27.7, 28.6, 58.2, 63.8, 64.1, 125.8, 127.9, 128.0 and 136.9.

***trans,trans*-2-Methoxy-3-phenylcyclopropanecarbaldehyde (5M)**

5M was prepared from alcohol **4M** by a procedure similar to that given above for **5B** (82%). δ_H 2.56 (1 H, dt, J = 6.0, 2.7 Hz), 2.94 (1 H, dd, J = 7.2, 6.3 Hz), 3.34 (3 H, s), 3.92 (1 H, dd, J = 7.2, 2.4 Hz), 7.22–7.34 (5 H, m) and 9.78 (1 H, d, J = 2.7 Hz); δ_C 34.2, 37.8, 58.9, 68.3, 126.9, 128.2, 128.4, 134.3 and 198.4.

(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethylene (6M)

6M was prepared from aldehyde **5M** by a procedure similar to that given above for **6B**. Purification by column chromatography (silica gel; ethyl acetate–hexanes) gave **6M** (79%) as a yellow oil. δ_H 2.01–2.06 (1 H, m), 2.10 (1 H, t, J = 6.3 Hz), 3.20 (3 H, s), 3.43 (1 H, dd, J = 6.9, 3.6 Hz), 4.98 (1 H, dd, J = 10.5, 1.2 Hz), 5.11 (1 H, d, J = 17.1 Hz), 5.59–5.71 (1 H, m) and 7.15–7.31 (5 H, m); δ_C 30.22, 31.69, 58.15, 66.72, 113.55, 125.75, 127.90, 127.93, 136.92 and 137.46.

2-(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethanol (7M)

7M was prepared from alkene **6M** by a procedure similar to that given above for **7B**. Purification by column chromatography (silica gel; ethyl acetate–hexanes) gave **7M** (93%) as a clear colourless oil. δ_H 1.43–1.51 (1 H, m), 1.63 (2 H, q, J = 6.6 Hz), 1.80 (1 H, t, J = 6.3 Hz), 1.92 (1 H, s), 3.12 (3 H, s), 3.26 (1 H, dd, J = 6.6, 3.3 Hz), 3.74 (2 H, t, J = 6.4 Hz) and 7.14–7.29 (5 H, m); δ_C 23.5, 29.7, 34.8, 58.0, 62.0, 65.9, 125.5, 127.7, 127.9 and 137.7.

(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethanal

This was prepared from alcohol **7M** by a procedure similar to that given above for the corresponding *tert*-butoxy compound (92%). δ_H 1.66–1.74 (1 H, m), 1.89 (1 H, t, J = 6.6 Hz), 2.42–2.59 (2 H, m), 3.19 (3 H, s), 3.30 (1 H, dd, J = 6.9, 3 Hz), 7.17–7.29 (5 H, m) and 9.82 (1 H, t, J = 1.8 Hz); δ_C 19.47, 29.66, 45.84, 58.20, 65.17, 125.92, 127.96, 127.99, 136.67 and 200.53.

(*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethanoic acid (8M)

8M was prepared from the above aldehyde by a procedure similar to that given above for **8B** (89%). δ_H 1.71–1.79 (1 H, m), 1.91 (1 H, t, J = 6.6 Hz), 2.38 (1 H, dd, J = 16.5, 7.8 Hz), 2.52 (1 H, dd, J = 16.5, 6.6 Hz), 3.18 (3 H, s), 3.32 (1 H, dd, J = 6.6, 3.0 Hz) and 7.16–7.29 (5 H, m); δ_C 21.4, 29.7, 36.4, 58.2, 65.1, 125.9, 128.0, 128.1, 136.6 and 177.9; m/z 206 (M^+, 7%), 191 (3), 175 (5), 174 (34), 161 (5), 160 (6), 148 (10), 147 (86), 146 (36), 145 (10), 131 (21), 130 (29), 129 (79), 128 (31), 117 (53), 116 (22), 115 (100), 105 (15), 104 (16), 103 (19), 91 (76) and 77 (35). HRMS: calc. for $C_{12}H_{14}O_3$, 206.0943; found, 206.0945.

1-(*trans,trans*-2-Methoxy-3-phenylcyclopropylethanoyloxy)pyridine-2(1*H*)-thione (9M)

9M was prepared from acid **8M** by a procedure similar to that given above for **9B**. Purification by rapid column chromatography (silica gel; ethyl acetate–hexanes) gave the desired PTOC ester **9M** as a yellow orange oil (88%). δ_H 1.82–1.90 (1 H, m), 2.06 (1 H, t, J = 6.9 Hz), 2.77–2.94 (2 H, m), 3.24 (3 H, s), 3.45 (1 H, dd, J = 6.9, 3.1 Hz), 6.62 (1 H, dt, J = 6.9, 1.8 Hz), 7.17–7.28 (6 H, m), 7.56 (1 H, dd, J = 7.2, 1.2 Hz) and 7.69 (1 H, dd, J = 9.0, 1.8 Hz).

2-*trans*-3-*cis*-1-*tert*-Butoxy-2-methyl-3-phenylcyclopropane (12B)

Alcohol **4B** (0.2 g, 0.9 mmol) was converted into its mesylate by reaction with 77 μl of freshly distilled methanesulfonyl chloride (1 mmol) and Et_3N (190 μl, 1.36 mmol) in 10 ml of dry THF at −20 °C for 1 h. The temperature was maintained at −20 °C as the mixture was treated with $LiEt_3BH$ (3.6 ml of a 1 M solution in THF, 3.6 mmol). The mixture was stirred at −20 °C for 2 h, at −10 °C for 1 h, and at room temperature for 12 h. Unreacted hydride reagent was quenched by slow addition of 2.2 ml of aqueous 3 M NaOH solution. The mixture was treated with 2.2 ml of 30% H_2O_2 solution (slow addition), and the mixture was heated at reflux for 1 h. After cooling, the layers were separated, and the aqueous layer was extracted thrice with ether. The combined organic phases were washed with saturated aqueous NaCl solution, dried ($MgSO_4$) and concentrated at reduced pressure. Purification of the residue by radial chromatography (silica gel; ethyl acetate–hexanes) gave a 2:1 mixture of the desired **12B** and 4-*tert*-butoxy-3-phenylbut-1-ene (**14B**). The mixture was allowed to react with 78 mg of *m*-chloroperbenzoic acid in 5 ml of dichloromethane for 12 h. The solution was washed with saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution and concentrated at reduced pressure. Radial chromatography (silica gel; ethyl acetate–hexanes) gave **12B** (100 mg, 54%) which solidified on standing; mp 33–34 °C, δ_H 1.06 (9 H, s), 1.17 (1 H, d, J = 6.0 Hz), 1.25–1.31 (1 H, m), 1.61 (1 H, t, J = 6.3 Hz), 3.23 (1 H, dd, J = 7.2, 15.9 Hz) and 7.11–7.29 (5 H, m); δ_C 16.9, 21.9, 27.8, 31.6, 59.9, 74.6, 124.9, 127.5, 127.9 and 139.6; m/z 204 (M^+, 2%), 148 (84), 133 (20), 146 (45), 133 (71), 131 (10), 117 (9), 115 (9), 105 (26), 91 (52), 78 (10) and 57 (100). HRMS: calc. for $C_{14}H_{20}O$, 204.1514; found, 204.1510.

2-*trans*-3-*cis*-1-Methoxy-2-methyl-3-phenylcyclopropane (12M)

12M was prepared from alcohol **4M** by a procedure similar to that given above for **12B**. Purification by radial chromatography (silica gel; ether–pentane) gave a 3:1 mixture of the desired **12M** and 4-methoxy-3-phenyl-1-butene (**14M**). The mixture was allowed to react with *m*-chloroperbenzoic acid and was worked-up as described above. Radial chromatography of the residue (silica gel; ether–pentane) gave **12M** (66%) as a clear, colorless oil. δ_H 1.15 (3 H, d, J = 6.3 Hz), 1.37–1.47 (1 H, m), 1.69 (1 H, t, J = 6.3 Hz), 3.10 (3 H, s), 3.17 (1 H, dd, J = 6.3, 3.6 Hz) and 7.11–7.28 (5 H, m); δ_C 16.8, 21.1, 31.2, 58.0, 67.4, 125.3, 127.6, 127.8 and 138.2; m/z 162 (M^+, 73%), 161 (18), 147 (100), 131 (29), 129 (37), 117 (33), 116 (14), 115 (68), 91 (64) and 77 (15). HRMS: calc. for $C_{11}H_{14}O$, 162.1045; found, 162.1043.

3-*tert*-Butoxy-4-phenylbut-1-ene (13B)

PTOC ester **9B** (160 mg, 0.45 mmol) was dissolved in 9 ml of dry THF in a flask wrapped in aluminum foil, and 0.92 ml of thiophenol was added. The foil was removed, and the reaction mixture was irradiated with a 150 W tungsten filament lamp. After 1 h, ether was added, and the organic solution was extracted thrice with 3 M aqueous NaOH solution, washed with saturated aqueous NaCl solution, and dried ($MgSO_4$). Concentration at reduced pressure gave a 47:1 mixture of the desired **13B** and 4-*tert*-butoxy-3-phenylbut-1-ene (**14B**). Purification by column chromatography (silica gel; ether–pentane)

gave **13B** (68 mg, 74% yield) as an oil. δ_H 1.04 (9 H, s), 2.66–2.81 (2 H, m), 4.09 (1 H, br q, J = 6.5 Hz), 5.02 (1 H, d, J = 10.5 Hz), 5.12 (1 H, dt, J = 17.1, 1.5 Hz), 5.82–5.94 (1 H, m) and 7.17–7.30 (5 H, m); δ_C 28.3, 44.2, 74.1, 74.3, 113.9, 126.0, 127.9, 129.9, 139.0 and 141.7; m/z 148 (12%), 131 (19), 113 (40), 92 (32), 91 (20), 58 (63) and 57 (100). HRMS. Calc. for $C_{10}H_{12}O$ $(M - 56)^+$, 148.0888; found, 148.0893.

3-Methoxy-4-phenylbut-1-ene (13M)

13M was prepared from PTOC ester **9M** by a procedure similar to that given above for **13B**. Purification by column chromatography (silica gel; ether–pentane) gave the desired **13M** (57%). δ_H 2.78 (1 H, dd, J = 13.8, 6.3), 2.94 (1 H, dd, J = 13.8, 6.9 Hz), 3.28 (3 H, s), 3.78 (1 H, br q, J = 6.6 Hz), 5.11–5.21 (2 H, m), 5.65–5.77 (1 H, m) and 7.18–7.32 (5 H, m); δ_C 42.1, 56.4, 83.8, 117.4, 126.1, 128.1, 129.5, 138.0 and 138.3; m/z 162 (M^+, 2%), 129 (4), 128 (3), 115 (3), 91 (13) and 71 (100). HRMS: calc. for $C_{11}H_{14}O$, 162.1045; found, 162.1046.

4-*tert*-Butoxy-3-phenylbut-1-ene (14B)

When the reaction employed for the synthesis of **12B** was conducted at −5 °C, **14B** was the major product. Purification by radial chromatography as for **12B** gave **14B** and **12B** (31%) as a 95 : 5 mixture as an oil. δ_H 1.16 (9 H, s), 3.50–3.61 (3 H, m), 5.05–5.15 (2 H, m), 6.02–6.14 (1 H, m) and 7.21–7.35 (5 H, m); δ_C 27.5, 50.3, 65.6, 72.8, 115.6, 126.3, 128.1, 128.2, 139.5 and 142.2; m/z 204 (M^+, 2%), 203 (3), 174 (18), 146 (9), 131 (17), 118 (53), 117 (35), 115 (18) and 57 (100). HRMS: calc. for $C_{14}H_{20}O$, 204.1514; found, 204.1511.

4-Methoxy-3-phenyl-1-butene (14M)

14M was prepared as previously reported.[8] δ_H 3.35 (3 H, s), 3.60–3.65 (3 H, m), 5.07–5.17 (2 H, m), 5.97–6.08 (1 H, m), 7.19–7.24 (3 H, m) and 7.29–7.35 (2 H, m); δ_C 49.7, 58.8, 76.2, 115.9, 126.6, 127.9, 128.5, 138.9 and 141.4; m/z 162 (M^+, 14%), 118 (14), 117 (100), 115 (29) and 91 (15). HRMS: calc. for $C_{11}H_{14}O$, 162.1045; found, 162.1041.

Kinetic studies

These followed the general procedures previously reported.[6] A stock solution of PhSeH was prepared in benzene and the concentration of this solution was determined by GC analysis. Reaction mixtures in THF were prepared in flame-dried tubes wrapped in aluminum foil and maintained at −78 °C. The PTOC concentrations were *ca.* 0.05 M. The tubes were sealed under vacuum and equilibrated at the appropriate temperature for several minutes before radical chain reactions were initiated by irradiation with visible light. Following irradiation for 45 min, the tubes were cooled to −78 °C and opened. A standard (octadecane) was added, and the reaction mixtures were analysed by GC. Yields were determined relative to the standard. GC response factors for **12B**, **12M**, **13B**, **13M**, **14B** and **14M** were determined with authentic samples. The mean concentration of PhSeH was the average of the initial and final concentrations of PhSeH where the final concentration was calculated as the initial concentration of PhSeH minus the initial concentration of PTOC ester.

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