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Determination of the rate constant for ring opening of an α-cyclopropylvinyl radical

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The rate constant for ring opening of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical, **4**, generated by photolysis of the corresponding vinyl iodide **2**, is reported. The value of the rate constant was determined by the tin hydride method and was found to be $(1.6 \pm 0.2) \times 10^{10}$ s^{-1}, one order of magnitude smaller than the rate constant for rearrangement of the *trans*-2-phenylcyclopropylcarbinyl radical.

Introduction

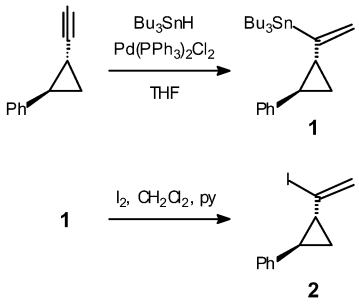
Cyclopropylcarbinyl radical rearrangements have been utilized as both mechanistic probes and radical clocks for over two decades.[1] The success of these radical probes can be attributed, for the most part, to the large and precisely determined rate constants for rearrangement.[2] A particularly useful derivative of these probes contains a phenyl substituent at the 2-position on the cyclopropyl ring. The introduction of the phenyl substituent results in an increase in the rate of rearrangement by three orders of magnitude.[3] These hypersensitive radical probes have been effectively utilized in a variety of mechanistic investigations including studies of the mechanisms of enzyme-catalyzed hydroxylation reactions,[4] of Co(III)-catalyzed autoxidation of alkenes with Et_3SiH,[5] and of the addition of aldehydes to Group 14 dimetallenes.[6]

In contrast to the well known cyclopropylcarbinyl radical system, there are only three reports describing the reactivity of the analogous α-cyclopropylvinyl radicals.[7] The results suggest, at least qualitatively, that the rate constant of ring opening of the vinyl radical is slower than the carbinyl analog. Given the importance of cyclopropylcarbinyl radical rearrangements as well as the widespread occurrence of vinyl radicals in organic chemistry, we believe that the corresponding cyclopropylvinyl radical rearrangement may also be of general interest as a mechanistic probe. To act effectively as a probe, the rearrangement must compete with potentially very fast pseudo-first-order processes, and thus, a large rate constant for rearrangement is necessary. With the aim of developing a hypersensitive probe for vinyl radicals and to evaluate its potential, we have determined the rate constant for the rearrangement of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical, **4**, using an indirect kinetic method. Our results are reported herein.

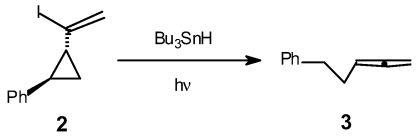
Results and discussion

The most appropriate precursor for generation of the radical **4** was determined to be vinyl iodide **2**. Vinyl iodide **2** was easily synthesized by iodinolysis of 1-(*trans*-2-phenylcyclopropyl)-1-tributylstannylethene, **1**, which was prepared by hydrostannylation of *trans*-2-phenylcyclopropylethyne[8] (Scheme 1). The hydrostannylation reaction yields a mixture of the desired stannylethene **1** and *trans*-2-(*trans*-2-phenylcyclopropyl)-1-tributylstannylethene. Upon chromatography, the latter product undergoes a hydrodestannylation reaction forming *trans*-2-phenylcyclopropylethene, **5**. It was difficult to remove all traces of **5** from the final product.

Irradiation of 1-iodo-(*trans*-2-phenylcyclopropyl)ethene, **2**, at 350 nm in the presence of one equivalent of Bu_3SnH resulted in the formation of 5-phenylpenta-1,2-diene, **3**, in quantitative yield as determined by ^1H NMR spectroscopy (Scheme 2). The ^1H and ^{13}C NMR chemical shifts and the IR spectral data of the allene agreed well with the literature values.[9,10] *trans*-2-Phenylcyclopropylethene, **5**, was also detected in the reaction mixture by gas chromatography (ratio of **3**/**5** = 43 : 1). The alkene was identified by co-injection with an authentic sample prepared by a Wittig reaction of the corresponding aldehyde.[11] No evidence for the formation of the regioisomeric allene, 4-phenylpenta-1,2-diene, was found.



Scheme 1



Scheme 2

We employed the tin hydride competition method, outlined in Scheme 3, to determine the rate constant for rearrangement, k_R, of the α-cyclopropylvinyl radical **4**. The rate constant for the competition reaction, k_H, abstraction of a hydrogen atom from Bu_3SnH by radical **4**, is not known, and thus it was necessary to use a comparable value from the literature. The rate constant for reaction of the 2,2-dimethylvinyl radical, formed by photolysis of the corresponding diacyl peroxide, with tributyltin hydride has been reported[12] and appears to be an appropriate choice. However, it was later demonstrated that decarboxylation of the related aroyloxy radicals is a relatively slow process,[13] and thus the actual rate constant reported for the reaction of the 2,2-dimethylvinyl radical with Bu_3SnH is likely the rate constant for reaction of the vinyl-substituted carboxyl radical instead.[14] There are no other reports concerning the rate constants for the reaction of a vinyl radical with a tin hydride; however, the rate constant for the reaction of aryl radicals with Bu_3SnH has been determined using two independent methods;[13] the recommended value is 7.8×10^8 $M^{-1}s^{-1}$. Given that the vinyl and the phenyl radicals are both σ-radicals located at an sp^2-hybridized carbon,

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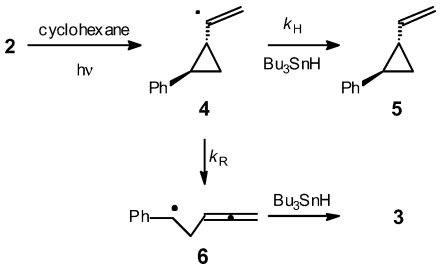
we, and others,[14] believe that the rate constant for the reaction of a vinyl radical with Bu_3SnH should be very similar to that of an aryl radical. To conclude that radical **4** is a reasonable model for the phenyl radical, it is necessary to assume that the α-phenylcyclopropyl substituent will not greatly influence the rate constant for the abstraction of a hydrogen atom by the σ-radical. The available evidence suggests that the analogous assumption is valid in the related cyclopropylcarbinyl system: that is, that the cyclopropylcarbinyl radical is a reasonable model for the primary alkyl radical in fast trapping reactions.[15] Finally, we have also assumed that solvent effects on these radical reactions will be minimal. With these assumptions, we have utilized 7.8×10^8 $M^{-1}s^{-1}$ as the rate constant for the competition reaction, k_H, in this study. The error in the basis reaction was incorporated into the precision calculations of this study.

Photolyses of 1-iodo-(*trans*-2-phenylcyclopropyl)ethene, **2**, were performed at 350 nm in cyclohexane in the presence of Bu_3SnH (1 M to 2 M) at 20 °C. All runs proceeded to 100% conversion; the reactions were extremely clean; only allene **3** and alkene **5** were detected as products. The identities of the products were confirmed by comparison of GC retention times or by coinjection of authentic samples. During the course of these studies, it was found that the injector temperature of the GC must be kept well below 200 °C since at elevated temperatures *trans*-2-phenylcyclopropylethene, **5**, is in equilibrium with its *cis*-isomer.[16] Furthermore, the *trans*-isomer also rearranges at elevated temperatures to give 4-phenylcyclopentene.[16] To avoid the formation of these compounds, the GC injector temperature was maintained at 100 °C.



Scheme 3

According to the kinetic expression, $([\mathbf{5}]/[\mathbf{3}]) = (k_H/k_R)[Bu_3SnH]_{avg}$, the ratio of the unrearranged to the rearranged products, [**5**]/[**3**], and the concentration of Bu_3SnH provide the ratio of the rate constants for the direct trapping, k_H, and the ring opening, k_R, reactions; the results are presented graphically in Fig. 1. Given that k_H is 7.8×10^8 $M^{-1}s^{-1}$ (*vide supra*), the rate constant for the rearrangement of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical, **4**, k_R, was found to be $(1.6 \pm 0.2) \times 10^{10}$ s^{-1}. The error includes the competition reaction rate constant error[13] as well as the random error of the method. The value of the rate constant for ring-opening is within an order of magnitude of that reported for the rearrangement of the *trans*-2-phenylcyclopropylcarbinyl radical (3×10^{11} s^{-1}).[3] The plotted data have a non-zero intercept indicating that the ring opening rearrangement of vinyl radical **4** to benzyl radical **6** is reversible.[2a] As such, one would expect to observe the formation of *cis*-2-phenylcyclopropylethene due to non-stereoselective ring closure of benzyl radical **6**. No evidence for the formation of *cis*-2-phenylcyclopropylethene was observed during the course of these studies as noted by the comparison of GC retention times with an authentic sample.[11] The reversibility of the ring opening rearrangement of **4** to **6** does not affect the rate constant of the forward reaction. The rate constant of the reverse reaction was estimated to be 1.6×10^4 s^{-1}.[2a]

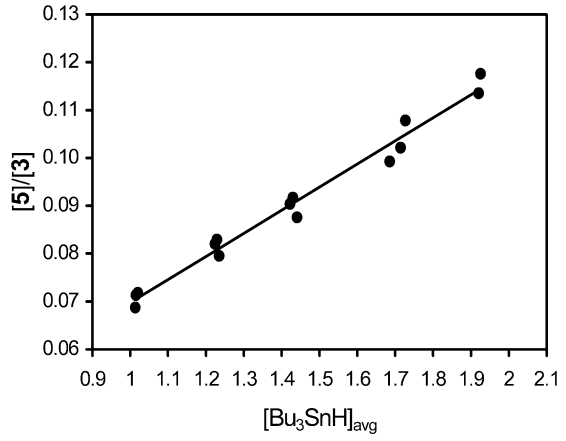
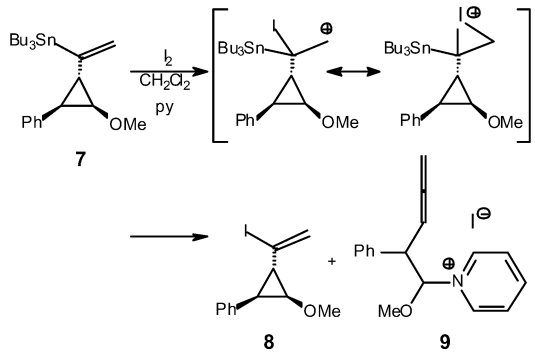


Fig. 1 Plot of the ratio of [**5**]/[**3**] *vs.* $[Bu_3SnH]_{avg}$ at 20 °C.

Incorporation of an alkoxy group at the unsubstituted carbon of phenyl-substituted cyclopropylcarbinyl probes allows for the discrimination between the formation of radical and cationic intermediates.[17] The alkoxy group does not significantly influence the rate constant for rearrangement of the radical.[3b] To investigate the influence of a 3-alkoxy substituent on the rate constant for rearrangement for ring-opening of radical **4**, the preparation of 1-iodo-1-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)ethene, **8**, was attempted. Stannylethene **7** was prepared as described above for stannylethene **1**; however, iodinolysis of **7** only gave a low yield of impure vinyl iodide **8** (Scheme 4). The major product formed is a diastereomeric mixture of allene **9**. Iodide **8** is likely the result of tributyliodostannane elimination from the putative β-stannyl cation. Presumably, the methoxy substituent provides anchimeric assistance which results in concurrent rearrangement of the intermediate cation to give an oxonium ion which is trapped by pyridine. Subsequent elimination of tributyliodostannane would result in the formation of allene **9**. Thus, we were unable to synthesize the iodide precursor in the required amounts and purity to complete the kinetic study on this molecule.



Scheme 4

Conclusions

We have determined the rate constant for rearrangement of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical, **4**. Based on the qualitative behavior of α-cyclopropylvinyl radicals,[7] it was expected that the value of the rate constant for the vinyl radical rearrangement would be less than that of the analogous carbinyl system; however, it is only one order of magnitude smaller. We believe this very fast radical rearrangement will find general use by organic, bioorganic, organometallic and surface chemists as a mechanistic probe.

Experimental

Reactions were performed under ambient conditions unless otherwise noted. THF and CH_2Cl_2 were purged with N_2 and passed through an alumina column prior to use. Cyclohexane was distilled from $LiAlH_4$, and then purged with Ar prior to use. Tributyltin hydride was purchased

from Aldrich Chemical Co. *trans*-2-Phenylcyclopropylethyne[8] and *trans*-2-phenylcyclopropylethene[11] were prepared according to the literature procedures. A mixture of *cis*/*trans*-2-phenylcyclopropylethene was prepared by initial formation of the isomeric ethyl 2-phenylcyclopropylcarboxylates by $CuSO_4$-catalyzed cyclopropanation of styrene with ethyl diazoacetate, reduction of the esters to the alcohols using $LiAlH_4$ and oxidation to the aldehydes using Swern oxidation conditions. The mixture of aldehydes was then converted to the alkenes by a Wittig reaction. ^1H and ^{13}C NMR spectral data of *cis*-2-phenylcyclopropylethene agreed well with the literature values.[11]

NMR spectra were recorded on Varian Mercury 400 or Varian Inova 400 spectrometers. The standards used were as follows: residual C_6D_5H (7.15 ppm), residual $CHCl_3$ (7.24 ppm), residual $CDHCl_2$ (5.32 ppm) for ^1H NMR spectra; C_6D_6 central transition (128.00 ppm), $CDCl_3$ central transition (77.00 ppm) for ^{13}C NMR spectra. *J* values are given in Hz. Mass spectra were obtained on a Finnegan MAT model 8400 mass spectrometer with an ionizing voltage of 70 eV (reported in mass-to-charge units, *m*/*z*, with ion identity and intensities relative to the base peak in parentheses). IR spectra were recorded (cm^{-1}) on a Perkin-Elmer System 2000 FT IR spectrometer. Ultraviolet spectra were recorded on a Varian Cary 100 UV-Visible Spectrophotometer. Gas chromatographic analyses were performed on a dimethylpolysiloxane column on an Agilent 6850 Series GC. Photolyses were performed in a Rayonet Photochemical Reactor. The temperature within the reactor was maintained at 20 °C using an Endocal model ULT-70 low temperature external bath circulator to force cooled (20 °C) methanol through a vacuum-jacketed Pyrex immersion well.

Synthesis of 1-(*trans*-2-phenylcyclopropyl)-1-tributylstannylethene (1)

A solution of tributyltin hydride (18.1 mL, 67 mmol) dissolved in THF (50 mL) was added dropwise to a solution of *trans*-2-phenylcyclopropylethyne (9.6 g, 67 mmol) and $Cl_2Pd(PPh_3)_2$ (0.94 g, 1.34 mmol) dissolved in THF (150 mL). Upon complete addition, the reaction mixture appeared opaque and brown. The solvent was removed by rotary evaporation yielding a brown oil consisting of a mixture of stannylethene **1**, and *trans*-2-(*trans*-2-phenylcyclopropyl)-1-tributylstannylethene (54 : 46) as determined by ^1H NMR spectroscopic analysis. Upon column chromatography (silica gel, 9 : 1 hexanes–CH_2Cl_2) *trans*-2-(*trans*-2-phenylcyclopropyl)-1-tributylstannylethene undergoes hydrodestannylation yielding 1-(*trans*-2-phenylcyclopropyl)ethene, **5**. Minor amounts of **5** were always present in the final product. Stannylethene **1** was obtained as a clear colourless oil (5.89 g, 20% yield). ν_{max}(film)/cm^{-1} 2956 s, 2926 s, 2870 m, 2852 m, 1603 m, 1501 m, 1460 m, 782 m, 695 m; δ_H (400 MHz, C_6D_6) 7.09–7.14 (2H, m, *m*-Ph*H*), 6.99–7.02 (1H, m, *p*-Ph*H*), 6.97-6.99 (2H, m, *o*-Ph*H*), 5.78 (1H, dd, C=C(H)H_{trans}, *J* 1.8, 1.2, $^3J_{119Sn-H}$ 138, $^3J_{117Sn-H}$ 132), 5.25 (1H, d, C=C(H)H_{cis}, *J* 2.4, $^3J_{119Sn-H}$ 64, $^3J_{117Sn-H}$ 60), 1.92 (1H, t, C(*H*)C(Sn)=C, *J* 7.2), 1.92 (1H, t, C(*H*)Ph, *J* 7.2), 1.52-1.60 (6H, m, $SnCH_2CH_2$), 1.33 (6H, tq, $SnCH_2CH_2CH_2$, *J* 7.2, 7.2), 1.26-1.30 (1H, m, $CH_{2cycloprop}$), 1.04-1.10 (1H, m, $CH_{2cycloprop}$), 0.96-1.00 (6H, m, $SnCH_2$, *J* 7.2), 0.89 (9H, t, $SnCH_2CH_2CH_2CH_3$, *J* 7.4); δ_C (100 MHz, C_6D_6) 155.0 (Sn*C*=C), 143.2 (*i*-Ph*C*), 128.6 (*m*-Ph*C*), 125.9 (*o*-Ph*C*), 125.8 (*p*-Ph*C*), 122.6 (SnC=*C*, $^2J_{119/117Sn-C}$ 29), 33.2 (*C*C=C, $^2J_{119/117Sn-C}$ 50), 29.5 ($SnCH_2CH_2$, $^2J_{119/117Sn-C}$ 20), 27.8 ($SnCH_2CH_2CH_2$, $^3J_{119/117Sn-C}$ 55), 26.9 (*C*(H)Ph, $^3J_{119/117Sn-C}$ 11), 16.9 (CH_2, $^3J_{119/117Sn-C}$ 17), 13.9 ($SnCH_2CH_2CH_2CH_3$), 10.0 ($SnCH_2$, $^1J_{119Sn-C}$ 329, $^1J_{117Sn-C}$ 314); *m*/*z* (CI) 435 (M + H^+, 1.3%), 377 ($C_{19}H_{29}{}^{120}Sn$ (M^+ − Bu), 94), 291 ($C_{12}H_{27}{}^{120}Sn$ (Bu_3Sn), 100), 235 ($C_8H_{18}{}^{120}Sn$ (Bu_2Sn), 33), 177 ($C_4H_9{}^{120}Sn$ (BuSn), 22), 128 ($C_{10}H_8$ (M^+ − Bu_3Sn-CH_3), 17), 91 (C_7H_7 (M^+ − Bu_3Sn-C_4H_4), 7); high resolution MS (CI) for $C_{23}H_{39}{}^{120}Sn$ (M + H^+) calcd 435.2073, found: 435.2070.

Synthesis of 1-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)-1-tributylstannylethene (7)

A solution of tributyltin hydride (2.8 mL, 10.5 mmol) dissolved in THF (20 mL) was added dropwise to a solution of *trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropylethyne[18] (1.80 g, 10.5 mmol) and $Cl_2Pd(PPh_3)_2$ (152 mg, 0.2 mmol) in THF (35 mL). After stirring at RT for 15 min, the solution was dark brown in colour. The solvent was removed to yield a dark brown oil. A mixture of stannylethene **7** and *trans*-2-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)-1-tributylstannylethene (70 : 30) was obtained as determined by ^1H NMR spectroscopic analysis. Chromatographic separation (silica gel, 1 : 1 hexanes–CH_2Cl_2) of the crude reaction mixture yielded stannylethene **7** as a clear, colourless oil (3.1 g, 63%). ν_{max}(film)/cm^{-1} 2955 s, 2925 s, 1603 m, 1496 m, 1460 m, 1219 m, 697 s; δ_H (400 MHz, C_6D_6) 7.35 (2H, d, *o*-Ph*H*, *J* 7.4), 7.18 (2H, t, *m*-Ph*H*, *J* 7.4), 7.06 (1H, t, *p*-Ph*H*, *J* 7.2), 5.71 (1H, br t, C=C(H)H_{trans}, *J* 1.8, $^3J_{119Sn-H}$ 137, $^3J_{117Sn-H}$ 131), 5.26 (1H, d, C=C(H)H_{cis}, *J* 2.0, $^3J_{119Sn-H}$ 64, $^3J_{117Sn-H}$ 60), 3.42 (1H, dd, C*H*OMe, *J* 6.6, 3.5), 2.98 (3H, s, OMe), 2.39 (1H, dd, C(*H*)C(Sn)=C, *J* 6.6, 3.5), 2.16 (1H, t, C(*H*)Ph, *J* 6.6), 1.56-1.61 (2H, m, $SnCH_2CH_2$), 1.34 (2H, tq, $SnCH_2CH_2CH_2$, *J* 7.6, 7.3), 0.99-1.02 (2H, m, $SnCH_2$), 0.90 (3H, t, CH_2CH_3, *J* 7.2); δ_C (100 MHz, C_6D_6) 152.8 (Sn*C*=C) 138.2 (*i*-Ph*C*), 128.3, 128.2 (*o*,*m*-Ph*C*), 125.9 (*p*-Ph*C*), 123.0 (SnC=*C*), 67.7 (*C*OMe), 57.8 (OMe), 36.2 (*C*C=C), 32.9 (*C*(H)Ph, $^3J_{119/117Sn-C}$ 15), 29.5 ($SnCH_2CH_2$, $^2J_{119/117Sn-C}$ 21), 27.8 ($SnCH_2CH_2CH_2$, $^3J_{119Sn-C}$ 57, $^3J_{117Sn-C}$ 54), 13.9 ($SnCH_2CH_2CH_2CH_3$), 9.9 ($SnCH_2$, $^1J_{119Sn-C}$ 330, $^1J_{117Sn-C}$ 315); *m*/*z* (CI) 464 (M^+, 1.2%), 432 (M^+ − MeOH, 3.5), 407 (M^+ − Bu, 17), 291 (Bu_3Sn^+, 91), 265 (50), 235 (40), 179 (45), 142 (M^+ − Bu_3Sn-OMe, 100); high resolution MS (CI) for $C_{24}H_{40}O^{120}Sn$ (M^+) calcd 464.2101, found 464.2104.

Synthesis of 1-iodo-1-(*trans*-2-phenylcyclopropyl)ethene (2)

A solution of I_2 (1.41 g, 5.55 mmol) in CH_2Cl_2 (200 mL) was added dropwise to a solution of stannylethene **1** (2.41 g, 5.55 mmol) and pyridine (2 mL, 25 mmol) in CH_2Cl_2 (50 mL). After addition, the reaction mixture was allowed to stir for 0.5 h and was then quenched with a saturated solution of $Na_2S_2O_3$. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, the solids were removed by gravity filtration and the solvent was removed by rotary evaporation yielding a yellow oil. Hexanes were added to the crude product. The salts were removed by gravity filtration and the hexanes removed from the filtrate by rotary evaporation. The product was dissolved in EtOAc (20 mL) and an aqueous solution of excess KF was added. The biphasic solution was allowed to stir vigorously for 18 h. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, the solids were removed by gravity filtration and the solvent was removed by rotary evaporation. The product was triturated with CH_3CN to remove any remaining KF. The product was further purified by column chromatography (silica gel, 8 : 2 hexanes–CH_2Cl_2) yielding 1-iodo-1-(*trans*-2-phenylcyclopropyl)ethene, **2**, as a clear, colorless oil (0.78 g, 52%, 96% by GC). The amount of 1-(*trans*-2-phenylcyclopropyl)ethene, **5**, present was determined to be 1% by GC. λ_{max} (cyclohexane)/nm 219 (ε/$dm^3mol^{-1}cm^{-1}$ 8520); ν_{max}(film)/cm^{-1} 3084 w, 3064 w, 3025 w, 3002 w, 2924 w, 2847 w, 1604 s, 1495 s, 1456 m, 1196 m, 1169 m, 1095 s, 1076 m, 885 m, 750 s, 695 s; δ_H (400 MHz, C_6D_6) 7.03-7.08 (2H, m, *m*-Ph*H*), 6.97-7.02 (1H, m, *p*-Ph*H*), 6.81-6.85 (2H, m, *o*-Ph*H*), 5.71 (1H, br t, C=C(H)H_{trans}, *J* 1.2), 5.54 (1H, dd, C=C(H)H_{cis}, *J* 1.6, 0.4), 1.99 (1H, ddd, C(*H*)Ph, *J* 4.4, 6.0, 9.2), 1.50-1.56 (1H, m, C(*H*)C(I)=C), 1.06 (1H, ddd, $CH_{2cycloprop}$, *J* 5.2, 5.6, 9.2), 0.86 (1H, ddd, $CH_{2cycloprop}$, *J* 4.8, 6.0, 8.4); δ_C (100 MHz, C_6D_6) 141.0 (*i*-Ph*C*), 128.6 (*m*-Ph*C*), 126.5 (*o*-Ph*C*), 126.3 (*p*-Ph*C*), 123.9 (IC=*C*), 113.4 (I*C*=C), 35.6 (*C*C=C), 27.2 (*C*(H)Ph), 18.3 (CH_2); *m*/*z* (EI) 270 (M^+, 19%), 192 (M^+ − C_6H_6, 6), 143

($M^+ - {}^{127}I$, 100), 128 ($C_{10}H_8$, 89), 115 (27). High resolution MS (EI) Calc. for $C_{11}H_{11}{}^{127}I$ (M^+): 269.9865, found 269.9913.

Iodinolysis of 1-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)-1-tributylstannylethene (7)

A solution of iodine (37 mg, 0.14 mmol) dissolved in CH_2Cl_2 (5 mL) was added to a solution of stannylethene **7** (54 mg, 0.12 mmol) and pyridine (49 μL, 0.60 mmol) dissolved in CH_2Cl_2 (5 mL). After 15 min, the solvent was removed by rotary evaporation to give an orange-brown oil. The oil was triturated with benzene to yield a light brown solid identified as 1-(1-methoxy-2-phenylpenta-3,4-dienyl)pyridinium iodide, **9**, (38 mg, 87%). The product contained minor amounts of tributyltin impurities (~9% as determined by ^{1}H NMR spectroscopy).

The benzene extracts were concentrated by rotary evaporation to yield a brown oil containing 1-iodo-1-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)ethene, **8**, as well as significant amounts of tributyliodostannane and other impurities. Attempts were made to purify crude iodo compound **8** by chromatography (silica gel, 2 : 1 hexanes–CH_2Cl_2); however, the desired compound was never obtained cleanly or in any significant amount. **8**: δ_H (400 MHz, CD_2Cl_2): 7.2-7.3 (5H, m, *o*,*m*,*p*-Ph*H*), 6.12 (1H, t, C=C(H)H_{trans}, *J* 1.8), 5.77 (1H, dd, C=C(H)H_{cis}, *J* 1.8, 0.6), 3.48 (1H, dd, C(*H*)OMe, *J* 7.2, 3.0), 3.29 (3H, s, OMe), 2.41 (1H, t, C(*H*)C(I)=C, *J* 6.6), 2.30-2.35 (1H, m, C(*H*)Ph). **9**: ν_{max}(film)/cm^{-1} diastereomeric mixture: 3034 m, 2956 s, 2924 s, 2854 m, 1953 m, 1623 s, 1476 s, 1456 m, 1211 m, 1150 m, 1097 s, 1024 m, 865 m, 681 s. δ_H (400 MHz, $CDCl_3$), major diastereomer: 8.99 (2H, d, *o*-Py*H*, *J* 5.6), 8.63 (1H, t, *p*-Py*H*, *J* 7.6), 8.00 (2H, t, *m*-Py*H*, *J* 6.7) 7.2-7.4 (5H, m, *o*,*m*,*p*-Ph*H*), 6.58 (1H, d, C(*H*)OMe, *J* 7.3), 5.56 (1H, q, *H*C=C=CH_2, *J* 6.7), 4.79 (1H, ddd, C=C=CH_2, *J* 11.4, 6.7, 2.1), 4.60 (1H, ddd, C=C=CH_2, *J* 11.4, 6.7, 2.1), 3.79-3.87 (1H, m, C(*H*)Ph), 3.65 (3H, s, OMe); minor diastereomer: 9.12 (2H, d, *o*-Py*H*, *J* 5.9), 8.50 (1H, t, *p*-Py*H*, *J* 7.6), 8.11 (2H, t, *m*-Py*H*, *J* 7.0), 7.2–7.4 (5H, m, *o*,*m*,*p*-Ph*H*), 6.77 (1H, d, C(*H*)OMe, *J* 6.7), 5.54 (1H, q, *H*C=C=CH_2, *J* 6.7), 4.86 (1H, ddd, C=C=CH_2, *J* 11.4, 6.7, 2.3), 4.82 (1H, ddd, C=C=CH_2, *J* 11.4, 6.7, 2.3), 3.79–3.87 (1H, m, C(*H*)Ph), 3.54 (3H, s, OMe). δ_C (100 MHz, $CDCl_3$), diastereomeric mixture: 208.7, 208.2 (C=*C*=C), 147.2, 146.9 (*p*-Py*C*), 141.3, 141.2 (*o*-Py*C*), 135.5, 135.5 (*i*-Ph*C*), 128.9, 128.8, 128.7, 128.3, 128.2, 128.1 (*o*,*m*,*p*-Ph*C*), 127.9, 127.8 (*m*-Py*C*), 101.2, 100.4 (*C*(H)OMe), 88.3, 87.6 (H*C*=C=CH_2), 77.7, 77.2 (HC=C=*C*H_2), 59.4, 59.3 (OMe), 52.9, 52.6 (*C*(H)Ph). *m*/*z* (ES) diastereomeric mixture: 631 (2M − I^-, 6%), 252 (M − I^-, 100), 173 (M − I^--C_5H_5N, 4). High resolution MS (ES): Calc. for $C_{17}H_{18}ON$ (M − I^-): 252.1388, found 252.1394.

Preparation of 5-phenylpenta-1,2-diene (3)

A solution of vinyl iodide **2** (206 mg, 0.76 mmol) and tributyltin hydride (205 μL, 0.76 mmol) in cyclohexane (2 mL) was irradiated at 350 nm for 80 min. The solvent was removed by trap-to-trap distillation and the product was analyzed by ^{1}H NMR, ^{13}C NMR and IR spectroscopy. The only observable product was allene **3**, the chemical shifts and IR spectral data were comparable to the literature data.[9,10] GC analysis of the product revealed that the product was a mixture of allene **3** and alkene **5** in a ratio of 43 : 1. Alkene **5** was identified by coinjection of an authentic sample.[11]

Kinetic experiments

1-Iodo-1-(*trans*-2-phenylcyclopropyl)ethene, **2**, (for amounts see Table 1) and dodecane (internal standard;10 μL, 0.044 mmol) were added to a vial and sealed with a rubber septum. The contents of the vial were flushed with Ar. Cyclohexane was added to the sealed vial; the volume was adjusted to produce reaction mixtures of varying concentrations (see Table 1). Tributyltin hydride (0.5 mL, 1.8 mmol) was then added to the vial and the contents were irradiated at 350 nm and 20 °C. After 2 min of irradiation the reaction had gone to completion. The reaction mixture was analyzed by GC to determine the ratio of the area of *trans*-2-phenylcyclopropylethene, **5**, to the area of 5-phenylpenta-1,2-diene, **3** (see Table 1). The precursor, 1-iodo-1-(*trans*-2-phenylcyclopropyl)ethene, **2**, was contaminated with alkene **5**, as determined by GC analysis; the ratio of alkene **5** to allene **3** was corrected appropriately. Three independent experiments at each concentration were performed (with the exception of run 5).

Table 1 Ratio of **5**/**3** obtained at varying tributyltin hydride concentrations.

Run	**2**/mmol	V_{cy}/mL	V_{tot}/mL	$[Bu_3SnH]_{avg}$/M	**5**/**3**
1a	0.164	1.2	1.7	1.013	0.069
1b	0.157	1.2	1.7	1.015	0.071
1c	0.141	1.2	1.7	1.020	0.072
2a	0.180	0.9	1.4	1.224	0.082
2b	0.168	0.9	1.4	1.229	0.083
2c	0.150	0.9	1.4	1.235	0.079
3a	0.195	0.7	1.2	1.422	0.090
3b	0.176	0.7	1.2	1.430	0.092
3c	0.150	0.7	1.2	1.441	0.088
4a	0.237	0.5	1.0	1.685	0.099
4b	0.180	0.5	1.0	1.714	0.102
4c	0.155	0.5	1.0	1.727	0.108
5a	0.151	0.4	0.9	1.921	0.113
5b	0.143	0.4	0.9	1.925	0.118

Allene **3** formed in the kinetic runs was identified by comparison of its GC retention time. The identity of *trans*-2-phenylcyclopropylethene, **5**, was confirmed by co-injection of a sample prepared by independent synthesis.[11]

The concentration of Bu_3SnH was the average of the initial and final concentrations of Bu_3SnH (where the final concentration was calculated as [the initial amount of Bu_3SnH (mmol) minus the initial amount of 1-iodo-1-(*trans*-2-phenylcyclopropyl)ethene, **2**, (mmol)] divided by the total volume used).

The GC response factors for 5-phenylpenta-1,2-diene, **3**, and *trans*-2-phenylcyclopropylethene, **5**, were determined to be equal.

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