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Cyclopropyl Alkynes as Mechanistic Probes To Distinguish between Vinyl Radical and Ionic Intermediates

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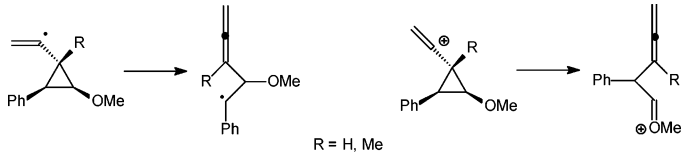

The reactions of (*trans*-2-phenylcyclopropyl)ethyne, **1a**, (*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)-ethyne, **1b**, and (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **1c**, with either aqueous sulfuric acid or tris(trimethylsilyl)silane (or tributyltin hydride) and AIBN have been investigated. Protonation and addition of the silyl (or stannyl) radical occurred at the terminal position of the alkyne giving an α-cyclopropyl-substituted vinyl cation or radical, respectively. Under both reaction conditions, **1a** yielded products derived from ring opening toward the phenyl substituent. Alkynes **1b** and **1c**, however, gave different products depending on whether radical or cationic conditions were used. When radical conditions were employed, products derived from regioselective ring opening toward the phenyl substituent were obtained. In contrast, when cationic conditions were employed, products derived from selective ring opening toward the methoxy substituent were isolated. The corresponding α-cyclopropyl-substituted vinyllithium derivatives were also synthesized and were found to be stable toward rearrangement. An estimate of the rate constants for ring opening of the α-cyclopropylvinyl cations was also made: values of $10^{10}-10^{12}$ s^{-1} were found for the vinyl cations derived from protonation of the terminal carbon of alkynes **1a**−**c**. Based on these results, cyclopropyl alkynes **1a**−**c** can be classified as hypersensitive mechanistic probes for the detection of vinyl radical or cationic intermediates generated adjacent to the cyclopropyl ring and, in the case of **1b** and **1c**, the distinction between a radical or cationic intermediate is possible.

Introduction

The rapid ring-opening rearrangement of cyclopropylcarbinyl radicals is the cornerstone of many effective radical clocks,[1] mechanistic probes,[2] and diverse synthetic methodologies.[3] Despite the versatility of the cyclopropylcarbinyl radical rearrangement, relatively little is known about the reactivity of the analogous α-cyclopropylvinyl radicals. Crandall et al. were the first to examine the reactivity of α-cyclopropylvinyl and the isomeric homoallenyl radicals.[4] Simple derivatives of the radicals

* To whom correspondence should be addressed.

(1) For examples, see: (a) Cooksy, A. L.; King, H. K.; Richardson, W. H. *J. Org. Chem.* **2003**, *68*, 9441. (b) Tanko, J. M.; Blackert, J. F. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1775. (c) Engel, P. S.; Wu, A. *J. Org. Chem.* **1994**, *59*, 3969. (d) Caldwell, R. A.; Zhou, L. *J. Am. Chem. Soc.* **1994**, *116*, 2271. (e) Engel, P. S.; Lowe, K. L. *Tetrahedron Lett.* **1994**, *35*, 2267. (f) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151. (g) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563. (h) Adam, W.; Heil, M. *J. Am. Chem. Soc.* **1991**, *113*, 1730. (i) Campredon, M.; Kanabus-Kaminska, J. M.; Griller, D. *J. Org. Chem.* **1988**, *53*, 5393. (j) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 1313. (k) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860.

(2) For examples, see: (a) Flemmig, B.; Kretzschmar, I.; Friend, C. M.; Hoffmann, R. *J. Phys. Chem. A* **2004**, *108*, 2972. (b) Tong, X.; DiLabio, G. A.; Clarkin, O. J.; Wolkow, R. A. *Nano Lett.* **2004**, *4*, 357. (c) Samuel, M. S.; Baines, K. M. *J. Am. Chem. Soc.* **2003**, *125*, 12702. (d) Samuel, M. S.; Jenkins, H. A.; Hughes, D. W.; Baines, K. M. *Organometallics* **2003**, *22*, 1603. (e) Tokuyasu, T.; Kunikawa, S.; Masuyama, A.; Nojima, M. *Org. Lett.* **2002**, *4*, 3595. (f) Adam, W.; Roschmann, K. L.; Saha-Moller, C. R.; Seebach, D. *J. Am. Chem. Soc.* **2002**, *124*, 5068. (g) Kretzschmar, I.; Levinson, J. A.; Friend, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 12395. (h) Newcomb, M.; Toy, P. H. *Acc. Chem. Res.* **2000**, *33*, 449. (i) Hartshorn, R. M.; Telfer, S. G. *J. Chem. Soc., Dalton Trans.* **1999**, 3565. (j) Dixon, C. E.; Hughes, D. W.; Baines, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 11049. (k) Arasasingham, R. D.; He, G.-X.; Bruice, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 5, 7985. (l) Slama, J. T.; Satsangi, R. K.; Simmons, A.; Lynch, V.; Bolger, R. E.; Suttie, J. *J. Med. Chem.* **1990**, *33*, 824. (m) Suckling, C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 537. (n) Baldwin, J. E.; Adlington, R. M.; Domayne-Hayman, B. P.; Knight, G.; Ting, H.-H. *J. Chem. Soc., Chem. Commun.* **1987**, 1662. (o) Alonso, M. E.; Hernandez, M. I.; Gomez, M.; Jano, P.; Pekerar, S. *Tetrahedron* **1985**, *41*, 2347.

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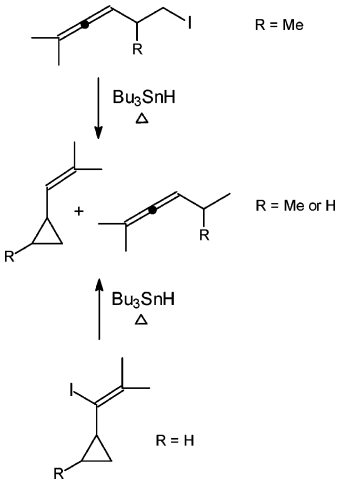
were generated independently by reaction of the appropriate iodides with tributyltin hydride under various conditions. The interconversion between the α-cyclopropylvinyl and the homoallenyl radical was confirmed by the formation of the same products regardless of the starting iodide (Scheme 1). The results suggested that

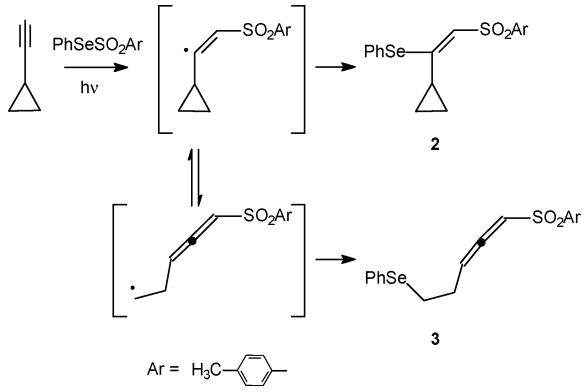
SCHEME 1



the rate constants for the isomerizations are smaller than those between the unsubstituted cyclopropylcarbinyl and homoallyl radicals.

Back et al. studied the free-radical selenosulfonation of cyclopropylacetylene and various vinylcyclopropanes.[5] Cyclopropylacetylene was photolyzed in the presence of *Se*-phenyl *p*-toluenesulfonate yielding compounds **2** and **3**. The formation of the observed products was proposed to involve the initial generation of an α-cyclopropylvinyl radical from the regioselective addition of the $ArSO_2$ radical to the triple bond. The vinyl radical can then either be trapped directly by the PhSe radical or can rearrange to the homoallenyl radical before trapping (Scheme 2). When the analogous vinylcyclopropanes were subjected to the same reaction conditions, only products derived from trapping of the ring-opened homoallyl radical were obtained suggesting that the rate constant

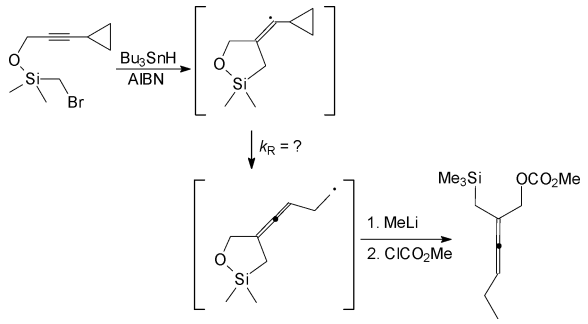
SCHEME 2



for rearrangement of the cyclopropylcarbinyl radical is larger than that of the vinyl analogue.

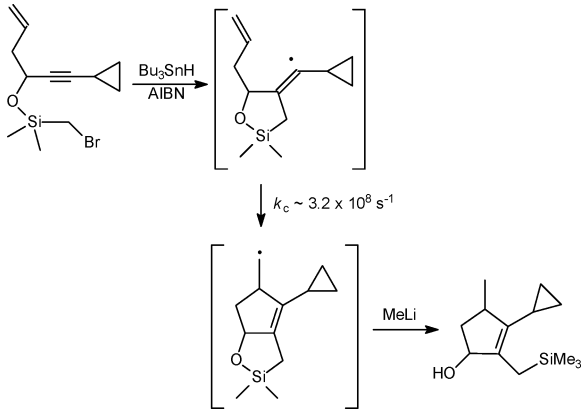
More recently, Mainetti et al. examined the reactivity of α-cyclopropylvinyl radicals derived from the intramolecular addition of a primary radical, generated by reaction of a (bromomethyl)dimethylsilyl ether with tributyltin hydride onto a cyclopropyl-substituted alkyne (Scheme 3).[6] When the α-cyclopropylvinyl radical was

SCHEME 3



generated in the absence of a nearby π-bond, rearrangement of the radical to the corresponding allene occurred. However, when the reaction was carried out using a derivative containing a tethered alkene, radical cyclization occurred in preference to ring opening (Scheme 4).

SCHEME 4



(3) For examples, see: (a) Ruedi, G.; Hansen, H.-J. *Tetrahedron Lett.* **2004**, *45*, 5143. (b) Cai, Y.; Roberts, B. P. *Tetrahedron Lett.* **2003**, *44*, 4645. (c) Bernard, A. M.; Cadoni, E.; Frongia, A.; Piras, P. P.; Secci, F. *Org. Lett.* **2002**, *4*, 2565. (d) Takekawa, Y.; Shishido, K. *J. Org. Chem.* **2001**, *6*, 8490. (e) Ogawa, A.; Ogawa, I.; Sonoda, N. *J. Org. Chem.* **2000**, *65*, 7682. (f) Takekawa, Y.; Shishido, K. *Tetrahedron Lett.* **1999**, *40*, 6817. (g) Lee, P. H.; Lee, B.; Lee, J.; Park, S. K. *Tetrahedron Lett.* **1999**, *40*, 3427. (h) Kantorowski, E. J.; Borhan, B.; Nazarian, S.; Kurth, M. J. *Tetrahedron Lett.* **1998**, *39*, 2483. (i) Fagnoni, M.; Schmoldt, P.; Kirschberg, T.; Mattay, J. *Tetrahedron* **1998**, *54*, 6427. (j) Ziegler, F. E.; Petersen, A. K. *Tetrahedron Lett.* **1996**, *37*, 809. (k) Tsunoi, S.; Ryu, I.; Muraoka, H.; Tanaka, M.; Komatsu, M.; Sonoda, N. *Tetrahedron Lett.* **1996**, *37*, 6729. (l) Boto, A.; Betancor, C.; Suarez, E. *Tetrahedron Lett.* **1994**, *35*, 5509. (m) Batey, R. A.; Harling, J. D.; Motherwell, W. B. *Tetrahedron* **1992**, *48*, 8031. (n) Clive, D. L.; Daigneault, S. *J. Org. Chem.* **1991**, *56*, 3801. (o) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165. (p) Harling, J. D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1988**, 1380. (q) Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E., Jr.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. (r) Trost, B.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 6556. (s) Moiseenkov, A. M.; Czeskis, B. A. *Collect. Czech. Chem. Commun.* **1986**, *51*, 1316. (t) Mariano, P. S.; Bay, E. *J. Org. Chem.* **1980**, *45*, 1763.

(4) Crandall, J. K.; Tindell, G. L.; Manmade, A. *Tetrahedron Lett.* **1982**, *23*, 3769.

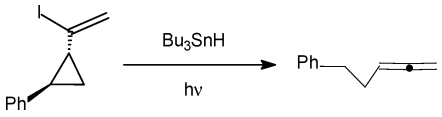
(5) Back, T. G.; Mualidharan, K. R. *J. Org. Chem.* **1989**, *54*, 121.

(6) Mainetti, E.; Fensterbank, L.; Malacria, M. *Synlett* **2002**, *6*, 923.

These results provide an upper limit for the rate constant for ring opening of the α-cyclopropylvinyl radical.[7]

We have recently examined the reactivity of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical, generated by photolysis of the corresponding vinyl iodide in the presence of tributyltin hydride (Scheme 5).[8] Under

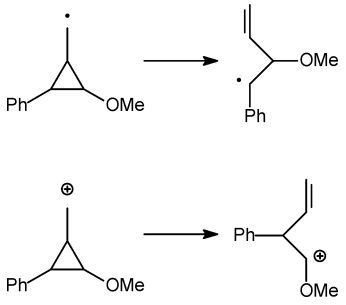
SCHEME 5



our conditions, we found clean rearrangement of the radical to the allene; only traces of the unrearranged alkene were detected. Furthermore, we estimated, for the first time, the rate constant for the ring-opening rearrangement of the radical. As suggested by the early studies, the rate constant, at $(1.6 \pm 0.2) \times 10^{10}$ s^{-1}, is smaller than that of the analogous carbinyl system (3×10^{11} s^{-1})[9] by an order of magnitude.

Cations often undergo the same rearrangements as their radical counterparts. This has led to the development of cyclopropylcarbinyl-based mechanistic probes which are capable of distinguishing between a radical and a cationic intermediate by the judicious placement of appropriate substituents.[10] One strategy, developed by Newcomb and co-workers, incorporates an alkoxy substituent at the 3-position of the cyclopropyl ring.[9,10b] When a cation is formed adjacent to the cyclopropane ring, products derived from regioselective ring opening toward the methoxy group are obtained, whereas when a radical is generated, products are derived from regioselective ring opening toward the phenyl substituent (Scheme 6). Thus, by analyzing the structure of the

SCHEME 6



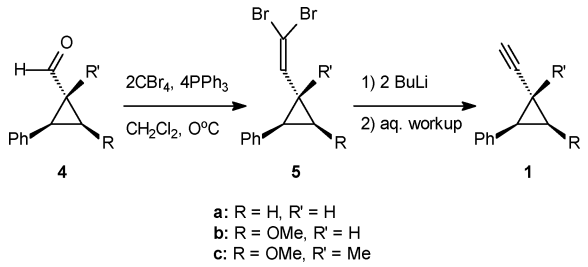
products, one can make conclusions regarding the type of intermediates formed during the course of the reaction.

We are interested in the development of a mechanistic probe for the detection of vinylic intermediates and propose to use cyclopropyl alkynes as precursors.[8] The rate constant for the rearrangement of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical is large enough to effectively use this rearrangement as the basis of a mechanistic probe to detect the formation of vinyl radicals. Since the ring opening of α-cyclopropylvinyl cations to the homoallenyl derivatives and the reverse reaction are well-known,[11] it is necessary to include substituents on the cyclopropyl framework of the probe to enable the discrimination between radical and cationic intermediates. Thus, we now report on the synthesis and reactivity of (*trans*-2-phenylcyclopropyl)ethyne, **1a**, (*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)ethyne, **1b**, and (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethyne, **1c**. For completeness, we have also examined the reactivity of the α-cyclopropylvinyl anion, as modeled by the lithium derivative. Furthermore, during the course of these studies, we were able to estimate rate constants for the ring opening of the α-cyclopropylvinyl cations.

Results and Discussion

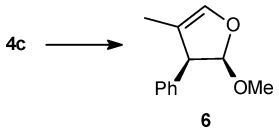
Alkynes **1a**,[12] **1b**, and **1c** were synthesized according to Scheme 7**.** Aldehydes **4a**,**b** were prepared by following

SCHEME 7



the literature procedures,[9,12] and aldehyde **4c** was prepared by a similar procedure starting with the reaction of *β*-methoxystyrene and ethyl 2-diazopropionate. Since aldehyde **4c** quantitatively rearranges to dihydrofuran **6** (Scheme 8) in less than 24 h under ambient conditions,

SCHEME 8



it was used immediately following preparation. Dibromoolefins **5a**−**c** were prepared from aldehydes **4a**−**c** via a Corey−Fuchs reaction. The relative stereochemistry of **5c** was confirmed by X-ray crystallography. Dibromoolefin **5b** isomerizes to cyclopentenone **7** within two weeks when stored under ambient conditions (Scheme 9). In light of this instability, compound **5b** was stored at −20 °C and used within 24 h of preparation.

(7) The rate constant for cyclization of the 1,5-hexadien-1-yl radical was reported to be 3.2×10^8 s^{-1}: Beckwith, A. L. J.; O'Shea, D. M. *Tetrahedron Lett.* **1986**, *27*, 4525.

(8) Milnes, K. K.; Gottschling, S. E.; Baines, K. M. *Org. Biomol. Chem.* **2004**, *2*, 3530.

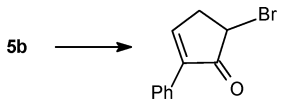
(9) Le Tadic-Biadatti, M.-H.; Newcomb, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1467.

(10) (a) Tian, F.; Battiste, M.-A.; Dolbier, W. R., Jr. *Org. Lett.* **1999**, *1*, 193. (b) Newcomb, M.; Chestney, D. L. *J. Am. Chem. Soc.* **1994**, *116*, 9753.

(11) (a) Alem, K. V.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2002**, *106*, 10681. (b) Salcedo, R.; Olvera, C. *THEOCHEM* **1999**, *460*, 221. (c) Brennenstuhl, W.; Hanack, M. *Tetrahedron Lett.* **1984**, *25*, 3437. (d) Seihl, H. U. *J. Chem. Soc., Chem. Commun.* **1984**, *10*, 635. (e) Apeloig, Y.; Schleyer, P. V. R.; Pople, J. A. *J. Org. Chem.* **1977**, *18*, 3004. (f) Santelli, M.; Bertrand, M. *Tetrahedron* **1974**, *30*, 243. (g) Bergman, R. G.; Sherrod, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 1925. (h) Bergman, R. G.; Kelsey, D. R. *J. Am. Chem. Soc.* **1971**, *93*, 1953. (i) Nishimura, A.; Ohta, M.; Kato, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1530. (j) Sharrod, S.; Bergman, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 2115. (k) Hanack, M.; Häffner, J. *Tetrahedron Lett.* **1964**, *32*, 2191.

(12) Charette, A. B.; Giroux, A. *J. Org. Chem.* **1996**, *61*, 8718.

SCHEME 9



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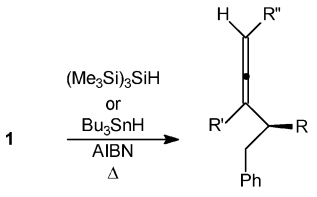
Dibromoolefins **5a**−**c** were converted to the desired alkynes by the addition of 2 equiv of BuLi. Although compound **1a** can typically be prepared very cleanly rendering further purification unnecessary, minor impurities were usually present in the crude reaction mixtures of **1b**,**c**, and thus, silica gel column chromatography was utilized to purify the alkynes. Alkyne **1c** continued to be contaminated with minor amounts of (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)-ethene (6% by GC analysis) even after chromatography. Alkyne **1c** is relatively stable but does undergo a slow decomposition under ambient conditions (12% decomposition after 7 months as determined by GC analysis). The major products of decomposition were identified as benzaldehyde and 5,5-dimethoxy-4-phenylpenta-1,2-diene.

Thermolysis of **1a** or **1b** in the presence of tris-(trimethylsilyl)silane and a catalytic amount of AIBN yielded a single compound (**8a** or **b**, respectively, Scheme 10), whereas thermolysis of **1c** in the presence of tributyltin hydride and a catalytic amount of AIBN yielded a mixture of diastereomers (57:43, **8c**). All products were readily identified by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. A strong absorption at ∼1930 cm^{-1} in the IR spectrum of all products as well as a signal at ∼210 ppm in the ^{13}C NMR spectra are consistent with the presence of an allene moiety. The regiochemistry of **8a**−**c** was established using ^{1}H, ^{13}C, gCOSY, gHSQC, and gHMBC NMR spectroscopy. For example, the ^{1}H NMR spectrum of **8b** contains two doublets of doublets at 2.94 (J = 7.6, 13.6 Hz) and 2.79 ppm (J = 5.6, 13.6 Hz); the coupling constant of 13.6 Hz as well as the observation of a correlation in the ^{13}C−^{1}H gHSQC NMR spectrum between both of these signals and the signal at 42.6 ppm establishes that the two ^{1}Hs giving rise to these signals are geminal to one other. The chemical shifts of these two ^{1}H signals (2.94 and 2.79 ppm) are consistent with the presence of a geminal phenyl and a vicinal alkoxy substituent. These chemical shifts are not consistent with the regioisomer in which the methoxy and phenyl groups are interchanged.[13] A multiplet at 3.95 ppm (1H) was also observed in the ^{1}H NMR spectrum of **8b**. The chemical shift is consistent with a ^{1}H geminal to an alkoxy group and vicinal to an sp^2 hybridized carbon.[13] In agreement with the assigned regiochemistry, a correlation was observed between the signals at 2.94 and 2.79 ppm in the ^{1}H dimension and the signals at 138.6 and 129.7 ppm, assigned to the *ipso* and *ortho* phenyl carbons, respectively. Similar results were obtained for **8a** and **8c**.

SCHEME 10



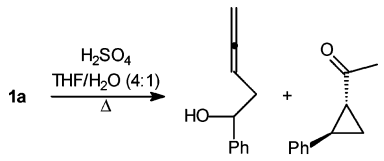
8

a: R = H, R' = H, R" = $Si(SiMe_3)_3$
b: R = OMe, R' =H, R" = $Si(SiMe_3)_3$
c: R = OMe, R' = Me, R" = $SnBu_3$

The formation of **8a**−**c** can easily be explained. The generated silyl (or stannyl) radical adds regioselectively to the terminal end of the alkyne forming an α-cyclopropylvinyl radical. The α-cyclopropylvinyl radical then rearranges to give the benzyl radical, followed by abstraction of a hydrogen atom yielding **8a**−**c**. The regioselective addition of the tris(trimethylsilyl)silyl radical to the terminal end of an alkyne has previously been reported.[14] There was no evidence (by ^{1}H NMR spectroscopy) for the formation of products derived from ring opening toward the methoxy substituent or from direct abstraction of a hydrogen by the putative vinyl radical.

Hydrolysis of **1a** in aqueous acidic THF yielded allene **9** (Scheme 11). The structure of **9** was clearly established by ^{1}H, ^{13}C, gCOSY, gHSQC, and gHMBC NMR and IR spectroscopy and mass spectrometry. Most notably, a correlation in the ^{13}C−^{1}H gHMBC NMR spectrum of **9** was observed between the triplet (1H) at 4.77 ppm in the ^{1}H dimension and the signals at 125.7 and 143.4 ppm in the ^{13}C dimension, assigned to the *ortho* and *ipso* phenyl carbons, respectively. The chemical shift and multiplicity of the ^{1}H signal and the observed correlations to the phenyl clearly places the hydroxyl and the phenyl substituents on the same carbon and adjacent to a methylene group. Furthermore, a correlation was observed between the pseudo triplet of triplets at 2.46 ppm (2H) in the ^{1}H dimension, assigned to the methylene group and the signal at 209.2 ppm in the ^{13}C dimension assigned to the central allenic carbon. These correlations are completely consistent with the assigned structure. The allene is likely formed by protonation of the alkyne at the terminal end to give the α-cyclopropylvinyl cation. Ring-opening rearrangement toward the phenyl group and subsequent hydration would give the observed product **9**. (*trans*-2-Phenylcyclopropyl)ethanone[15] was also observed in the ^{1}H NMR spectrum of the crude product, indicating that hydration of the vinyl cation competes with ring opening (**9**/ethanone = 10.7:1).

SCHEME 11



9

In contrast, hydrolysis of **1b** cleanly afforded a 2:1 mixture of 2-phenylcyclopent-2-enone,[16] **10**, and *E*-2-

(13) The chemical shifts for ^{A}H and $^{B/C}$H$_2$ in $(Me_3Si)_3SiCH{=}C{=}CHC^{A}H(X)C^{B/C}H_2Y$ were calculated using the ACD Inc, I-Lab service. For X=OMe and Y=Ph, the chemical shifts were calculated to be 4.14, 2.93, and 2.78 ppm, respectively. For comparison, the chemical shifts in the regioisomer: X=Ph and Y=OMe were calculated to be 3.95, 3.94 and 3.77 ppm, respectively.

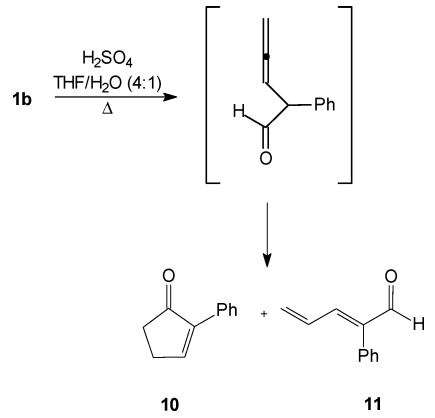
(14) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994.

(15) Solladié-Cavallo, A.; Isarno, T. *Tetrahedron Lett.* **1999**, *40*, 1579.

(16) Kerr, W. J.; McLaughlin, M.; Pauson, P. L.; Robertson, S. M. *J. Organomet. Chem.* **2001**, *630*, 104.

phenylpenta-2,4-dienal, **11** (91% recovered yield; Scheme 12). The *E* configuration of **11** was confirmed by NOESY

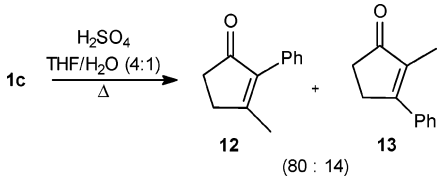
SCHEME 12



analysis; a correlation was observed between the aldehydic proton and the β-vinylic proton. Apparently, protonation at the terminal position of the alkyne generates an α-cyclopropylvinyl cation, which undergoes regioselective ring opening to give the methoxonium ion followed by addition of water to give the hemiacetal. Hydrolysis of the hemiacetal would yield the corresponding homoallenic aldehyde which, under the reaction conditions, is converted to a mixture of **10** and **11**.

Hydrolysis of **1c** under similar conditions yielded a mixture of 3-methyl-2-phenylcyclopent-2-enone,[17] **12**, 2-methyl-3-phenylcyclopent-2-enone,[17] **13**, in a 80:14 ratio, respectively (Scheme 13). Again, formation of the

SCHEME 13

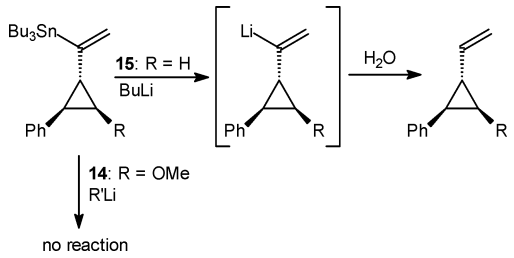


isomeric cyclopentenones **12** and **13** is easily understood in terms of initial protonation of the alkynyl moiety to give an α-cyclopropylvinyl cation. In this case, direct hydration of the vinyl cation effectively competes with ring opening. Hydration of the cation would yield the corresponding ketone which could undergo an acid-catalyzed ring opening to eventually yield the aldehyde. Finally, an acid-catalyzed aldol condensation followed by double-bond isomerization would give **13**. Alternatively, ring opening of the vinyl cation would result in the formation of an allenic oxonium species. Hydrolysis and double-bond isomerization would yield the conjugated aldehyde, and finally, an acid-catalyzed cyclization would yield the observed **12**. *E*- and *Z*-3-methyl-2-phenylpent-2-enal[18] were also present in the hydrolysis product mixture in a 1:1 ratio accounting for 6% of the total product. *E*- and *Z*-3-methyl-2-phenyl-pent-2-enal are likely formed from an acid-catalyzed ring-opening rearrangement of the minor amounts of (*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethene which contaminate alkyne **1c**.

Clearly, the presence of the methoxy substituent has a profound influence on the regiochemistry of the ring-opening reaction of the vinyl cation produced by protonation of the cyclopropyl alkynes. In the absence of the methoxy substituent, the α-cyclopropylvinyl cation will undergo ring opening toward the phenyl substituent, as in the case of **1a**. However, if a methoxy substituent is present on the ring as in the case of **1b** and **1c**, regioselective ring opening toward the methoxy substituent is observed.

The reactivity of the α-cyclopropylvinyl anion was examined using the corresponding vinyllithium as a model. Vinyllithium species are readily synthesized by transmetalation of vinylstannanes with alkyllithium reagents.[19] It was, therefore, envisioned that an α-cyclopropylvinyllithium species could be generated from the corresponding α-cyclopropylvinylstannane. BuLi was added to a solution of 1-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)-1-tributylstannylethene,[8] **14**, under varying conditions (Table 1, Scheme 14). When BuLi was

SCHEME 14



added to a solution of **14** in THF at −78 °C or at room temperature (entries 1 and 2), starting material was recovered in high yield. The addition of the coordinating cosolvent, TMEDA (Entries 3 and 4), had no effect on the reaction; starting material was recovered in high yield even after 17 h of reflux. Attempts to form the vinyllithium by using the noncoordinating, nonpolar solvent hexanes were also unsuccessful. When *t*-BuLi was used as the reagent, starting material was again recovered in good yield (entries 6 and 7). Beavers and Wilson[20] have reported that the addition of BuLi to vinylcyclopropane dissolved in THF and TMEDA resulted in deprotonation at several positions on the cyclopropyl ring and the vinyl substituent. To determine the extent of deprotonation (if any) of **14**, a portion of one of the reactions was quenched with D_2O (entry 1). ^1H NMR spectroscopic analysis of the recovered **14** showed no decrease in the intensity of any signals indicating no significant deuterium incorporation.

For comparative purposes, the reaction of 1-(*trans*-2-phenylcyclopropyl)-1-tributylstannylethene,[8] **15**, with BuLi

(17) Kobayashi, T.; Koga, Y.; Narasak, K. *J. Organomet. Chem.* **2001**, *624*, 73.

(18) Dana, G.; Gharbi-Benarous, J. *Can. J. Chem.* **1980**, *58*, 1451.

(19) Examples of lithium−tin exchanges can be found in the following references: (a) Reich, H. J.; Gudmundsson, B. O.; Green, D. P.; Bevan, M. J.; Reich, I. L. *Helv. Chim. Acta* **2002**, *85*, 3748. (b) Oprunenko, Y. F.; Akhmedov, N. G.; Laikov, D. N.; Malyugina, S. G.; Mstislavsky, V. I.; Roznyatovsky, V. A.; Ustynyuk, Y. A.; Ustynyuk, N. A. *J. Organomet. Chem.* **1999**, *583*, 136. (c) Beaudet, I.; Launay, V.; Parrain, J.-L.; Quintard, J.-P. *Tetrahedron Lett.* **1995**, *36*, 389. (d) Kang, K.-T.; Ryu, D. C.; Sung, T. M.; Kim, J. G. *Bull. Chem. Soc. Jpn.* **1994**, *15*, 926. (e) Yang, Y.; Wong, H. N. C. *J. Chem. Soc., Chem. Commun.* **1992**, *23*, 1723.

(20) Beavers, W. A.; Wilson, S. E. *Tetrahedron Lett.* **1979**, *19*, 1678.

TABLE 1. Addition of Alkyllithium Reagents to 14

entry	RLi	equiv	solvent	time (h)	*T* (°C)	result
1	BuLi	1.1	THF	1	−78	no reaction[a]
2	BuLi	1.1	THF	1.5	rt	recovered **14** (91%)
3	BuLi	3.0	THF/TMEDA (5:1)	1	rt	no reaction[a]
4	BuLi	3.0	THF/TMEDA (5:1)	17	reflux	recovered **14** (98%)[b]
5	BuLi	2.0	hexanes	21	rt	recovered **14** (94%)[b]
6	*t*-BuLi	2.0	THF	2	−78 °C (1 h) → rt (1 h)	no reaction[a]
7	*t*-BuLi	2.0	THF	19	rt	recovered **14** (98%)[b]

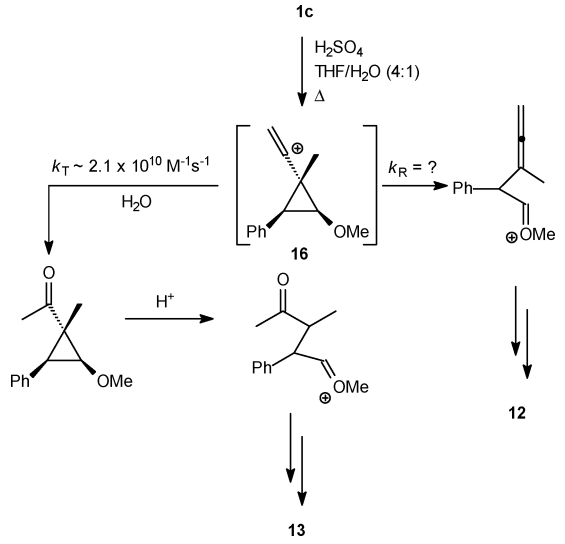
[a] Based on ^{1}H NMR spectroscopic analysis of a quenched aliquot after aqueous workup. [b] Based on ^{1}H NMR spectroscopic analysis of isolated material after aqueous workup of entire reaction.

was also investigated. When **15** was allowed to react with BuLi at −78 °C for 1 h followed by the addition of water, (*trans*-2-phenylcyclopropyl)ethene was obtained in good yield (76%). Presumably, the vinyllithium is an intermediate in the formation of the alkene (Scheme 14). There was no evidence for the formation of any ring-opened products, and thus, it was concluded that the vinyllithium does not rearrange under the reaction conditions. This result is in agreement with previous reports concerning the reactivity of cyclopropylvinyllithium and Grignard species.[20,21] The difference in reactivity between vinylstannanes **14** and **15** toward BuLi is puzzling. It appears to be the result of electronic effects of the methoxy substituent, although the nature of this electronic effect is unclear.

Estimation of Rate Constants of Ring Opening of α-Cyclopropylvinyl Cations. To assess the potential of alkynes **1a**−**c** to act as mechanistic probes, determination of the rate constants for rearrangement of the α-cyclopropylvinyl intermediates was necessary. We have recently reported the rate constant for the rearrangement of the 1-(*trans*-2-phenylcyclopropyl)ethen-1-yl radical.[8] The reported value of $(1.6 \pm 0.2) \times 10^{10}$ s^{-1} is only 1 order of magnitude smaller than the rate constant for ring opening of the analogous α-cyclopropylcarbinyl radical.[9,22] In order for the rearrangement to be used as a mechanistic probe, the rearrangement must be able to compete effectively with other processes that may take place during the course of the reaction; with a rate constant for rearrangement on the order of 10^{10} s^{-1}, the α-cyclopropylvinyl radicals can be considered as hypersensitive radical probes. We believe that the rate constant for ring opening of the analogous radicals from **1b** and **1c** will be comparable; the remote methoxy and methyl group will not greatly influence the rate constant of rearrangement.

An approximate rate constant for the ring-opening rearrangement of the 1-(*trans*,*trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethen-1-ylium cation, **16**, can also be estimated if the hydrolysis of **1c** (vide supra) is analyzed by competition kinetics (eq 1). The acid-catalyzed hydrolysis of alkyne **1c** yielded products from two competing reactions: the direct hydration of the α-cyclopropylvinyl cation as well as from ring opening followed by hydrolysis of the oxonium ion (Scheme 15). According to competition

SCHEME 15



kinetics, the ratio of the rate constant of rearrangement of the cation (k_R) and trapping of the cation (k_T) by hydration is equal to the ratio of the rearranged product (RT) and the trapped product (UT) times the concentration of the trapping agent (T) (eq 1). For this rough estimate we have assumed that the water trapping reactions are irreversible. The ratio of the two products formed (**12** and **13**) was determined by ^{1}H NMR spectroscopy and the concentration of the trapping agent, water, was known. The rate constant for the competition reaction, the hydrolysis of a cyclopropyl substituted vinyl cation (k_T), has not been determined. However, even in the presence of a strong cation-stabilizing substituent such as the *p*-methoxyphenyl substituent, vinyl cations do not persist long enough (<20 ns) to permit an evaluation of the rate constant for hydrolysis.[23] Although there is some debate in the literature regarding the relative ability of a cyclopropyl or phenyl substituent to stabilize a vinyl cation,[24] we believe it is reasonable to assume that the rate constant for hydrolysis of an α-cyclopropylvinyl cation will approach or be at the diffusion limit. Using the value of 2.1×10^{10} M^{-1} s^{-1} reported by Newcomb[25] for the rate constant for diffusion in THF as the rate constant for the competition reaction (i.e., hydrolysis of an α-cyclopropylvinyl cation), a value

(21) (a) Emme, I.; Redlich, S.; Labahn, T.; Magull, J.; de Meijere, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 786. (b) Crandall, J. K.; Ayers, T. A. *J. Org. Chem.* **1992**, *57*, 2993. (c) Maerker, A.; Girreser, U. *Angew. Chem.* **1990**, *120*, 718. (d) Mislankar, D. G.; Mugrage, B.; Darling, S. D. *Tetrahedron Lett.* **1981**, *22*, 4619. (e) Richey, H. G., Jr.; Kossa, W. C., Jr. *Tetrahedron Lett.* **1969**, *9*, 2313.

(22) Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varick, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10915.

(23) Cozens, F. L.; Kanagasabapathy, V. M.; McClelland, R. A.; Steenken, S. *Can. J. Chem.* **1999**, *77*, 2069.

(24) (a) Allen, A. D.; Chiang, Y.; Kresge, A. J.; Tidwell, T. T. *J. Org. Chem.* **1982**, 775. (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *18*, 3004. (c) Alem. K. v.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2002**, *106*, 10681.

(25) Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662.

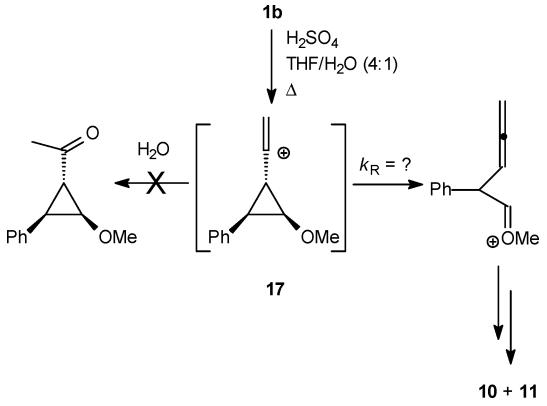
of 4×10^{10} s^{-1} for the rate constant for the ring opening of cation **16** was estimated.

$$RT \xleftarrow{T} R^+ \underset{k_R}{\longleftarrow} U^+ \xrightarrow[k_T]{T} UT$$

$$\frac{k_R}{k_T} = \frac{[RT][T]}{[UT]} \quad (1)$$

By similar analysis, the rate constant for the ring opening of cation **17** can also be estimated. The products formed in the acid-catalyzed hydrolysis of alkyne **1b**, **10** and **11**, were derived exclusively from ring opening of the α-cyclopropylvinyl cation followed by hydrolysis of the oxonium ion (Scheme 16). No products derived from

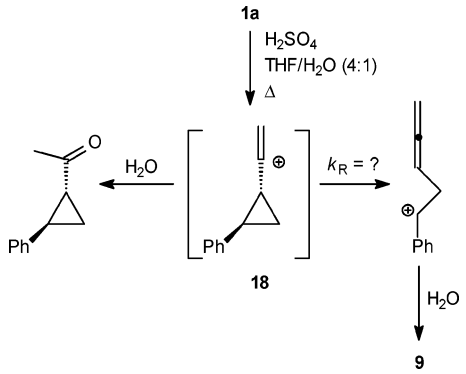
SCHEME 16



hydration of the α-cyclopropylvinyl cation were observed in the ^{1}H NMR spectrum of the crude reaction mixture. Thus, assuming a detection limit of 5% for ^{1}H NMR spectroscopy, the lower limit of the rate constant for the ring opening of the 1-(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)ethen-1-ylium cation, **17**, is estimated to be $\sim 4 \times 10^{12}$ s^{-1}.

Vinyl cation **18** derived from protonation at the terminal position of alkyne **1a**, opens toward the phenyl substituent. Again, a competition exists between direct hydrolysis of the α-cyclopropylvinyl cation to give *trans*-2-phenylcyclopropylethanone and ring opening toward the phenyl substituent, followed by hydration of the benzyl cation to give allene **9** (Scheme 17). The ratio of

SCHEME 17



the two products was determined by ^{1}H NMR spectroscopy; *trans*-2-phenylcyclopropylethanone was not isolated. Based on these data, the rate constant for ring opening of cation **18** was estimated to be 2×10^{12} s^{-1}.

In all cases, the rate constant for the rearrangement of the vinyl cation is estimated to be 10^{10} s^{-1} or greater. Even with due consideration given to the uncertainty in the rate constant and the assumptions made, at this magnitude, the rearrangement should effectively compete with other possible chemical processes, and thus, this rearrangement can be used as a hypersensitive probe for the formation of α-cyclopropylvinyl cations.

Conclusion

Alkynes **1a**−**c** rapidly rearrange when a radical or a cation is generated adjacent to the cyclopropyl ring. Compound **1a** yields products derived from ring opening toward the phenyl substituent under both radical and cationic conditions. Thus, the formation of rearrangement products indicates the presence of a reaction intermediate; however, the structure of the product alone does not allow for the determination of the type of the intermediate. When an anion is generated adjacent to the cyclopropyl ring, no products derived from the opening of the cyclopropyl ring were observed. In contrast, compounds **1b**,**c** gave different products depending on the nature of the reaction intermediate formed adjacent to the ring. Products obtained under radical conditions are derived from ring opening toward the phenyl substituent, whereas products obtained under cationic conditions are derived from ring opening toward the methoxy substituent. The rearrangement of cations **16**, **17**, and **18** were examined using competition kinetics. The rate constants for rearrangement of the cations were crudely estimated to be in the range of 10^{10}−10^{12} s^{-1}. Thus, based on the results herein and our previous work,[8] we conclude that cyclopropyl alkynes **1b**,**c** can indeed act as hypersensitive mechanistic probes which are capable of distinguishing between the formation of a cation, radical or anion at the vinylic position. We believe such versatile probes will find extensive applications in organic, organometallic, biological and materials science. Indeed, we have utilized probe **1c** in the investigation of the mechanism of the cycloaddition of alkynes to disilenes; the results will be reported in due course.

Experimental Section

Preparation of 1,1-Dibromo(*trans*,*trans*-2-methoxy-3-phenylcyclopropyl)ethene (5b). A solution of triphenylphosphine (11.21 g, 42.8 mmol) dissolved in CH_2Cl_2 (30 mL) was added dropwise to a solution of CBr_4 (7.10 g, 21.4 mmol) dissolved in CH_2Cl_2 (12 mL) at 0 °C. The resulting dark orange solution was allowed to stir for 5 min. A solution of aldehyde **4b** (1.89 g, 10.7 mmol) dissolved in CH_2Cl_2 (10 mL) was then added dropwise. The solution was allowed to stir at 0 °C for 1.25 h after which time it had become dark alpine green in color. The reaction mixture was quenched by the addition of distilled H_2O (50 mL). The organic and aqueous layers were separated. The aqueous layer was washed with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and washed with H_2O (50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation to give a pasty solid. The solid was washed with Et_2O (5 × 150 mL). The washes were combined and concentrated to give a yellow jelly, which was then washed with hexanes (5 × 150 mL). The washes were combined and filtered through dry silica. The solvent was removed from the filtrate

by rotary evaporation. The Et_2O and hexanes wash cycle was repeated as needed to maximize the yield. The final product was obtained as a clear, yellow oil (2.96 g, 84%). The product was taken onto the next step without further purification. Upon sitting for 2 weeks, **5b** was found to convert to 1-bromo-3-phenylcyclopent-3-en-2-one, **7**, which was isolated as a crystalline, white solid after chromatographic purification (69%, silica gel, 3:1 hexanes/CH_2Cl_2). Crystals of **7** were grown from a concentrated CH_2Cl_2 solution by slow diffusion of hexanes and then analyzed by X-ray crystallography. Experimental details for the analysis are presented in the Supporting Information. Bond lengths and angles, atomic coordinates, and anisotropic parameters are tabulated.[26] **5b**: IR (cm^{-1}) 3032 (w), 2930 (m) 1691 (m), 1603 (m), 1496 (m), 1445 (m), 1409 (w), 1353 (w), 1240 (w), 1122 (m), 1025 (m), 922 (m), 794 (m), 697 (m); ^1H NMR ($CDCl_3$) δ 7.19−7.29 (m, 5H, Ph*H*), 6.01 (d, 1H, $Br_2C{=}CH$, J = 8.8 Hz), 3.53 (dd, 1H, MeOC*H*, J = 3.2, 6.7 Hz), 3.25 (s, 3H, OMe), 2.23 (t, 1H, PhC*H*, J = 6.7 Hz), 2.20 (ddd, 1H, $Br_2C{=}CHCH$, J = 3.2, 6.7, 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 137.5 ($Br_2C{=}C$), 135.3 (*i*-Ph*C*), 128.0, 128.0 (*o,m*-Ph*C*), 126.2 (*p*-Ph*C*), 88.1 (Br_2C), 65.7 (MeO*C*H), 58.6 (OMe), 32.1 (Ph*C*H), 30.6 ($Br_2C{=}CHCH$); MS (*m/z*) 332 ($C_{12}H_{12}O^{79}Br^{81}Br$, 5), 253 ($C_{12}H_{12}O^{81}Br$, 42), 251 ($C_{12}H_{12}O^{79}Br$, 40), 172 ($C_{12}H_{12}O$, 100); high-resolution MS (CI, isobutane) for $C_{12}H_{13}O^{79}Br^{81}Br$ ($M + H^+$) (*m/z*) calcd 332.9312, found 332.9320. **7**: mp 78−79 °C; IR (cm^{-1}) 3066 (w), 1705 (vs), 1297 (m), 1118 (w), 775 (w), 706 (m); ^1H NMR ($CDCl_3$) δ 7.76 (t, 1H, J = 2.8 Hz, C*H*=CPh), 7.67−7.72 (m, 2H, *o*-Ph*H*), 7.32−7.42 (m, 3H, *m, p*-Ph*H*), 4.52 (dd, 1H, J = 2.4, 6.7 Hz, C*H*Br), 3.43 (ddd, 1H, J = 2.9, 6.7, 20.0, $CH(H_{trans})$), 3.01 (dt, 1H, J = 20.0, 2.9, $CH(H_{cis})$); ^{13}C NMR ($CDCl_3$) δ 200.1 (*C*=O), 154.9 (*C*H=CPh), 140.8 (*C*Ph), 130.5 (*i*-Ph*C*), 128.9, 128.44 (*m*, *p*-Ph*C*) 126.9 (*o*-Ph*C*), 42.5 (*C*HBr), 38.0 (H_2C); MS (*m/z*) 236 (M^+, 24), 157 ($C_{11}H_9O$, 65), 129 ($C_{10}H_9O$, 100), 128 (75), 102 (40); high-resolution MS for $C_{11}H_9O^{79}Br$ (M^+) (*m/z*) calcd 235.9838, found 235.9837.

Preparation of (*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethyne (1b). BuLi (11.1 mL, 17.8 mmol) was added dropwise to a solution of **5b** (2.96 g, 8.9 mmol) dissolved in THF (30 mL) at −78 °C. The orange solution was allowed to stir at −78 °C for 2 h, after which time it had become dark brown in color. The solution was allowed to warm to rt and then quenched by the addition of distilled H_2O (30 mL). The resulting pale orange, biphasic solution was diluted with Et_2O (30 mL). The organic and aqueous layers were separated. The aqueous layer was washed with Et_2O (3 × 30 mL). The organic layers were combined and then washed with brine (30 mL). The organic layer was dried over $MgSO_4$ and then filtered. The resulting yellow solution was concentrated by rotary evaporation to give a dark, orange oil (1.46 g, 96%). The oil was purified by column chromatography (silica gel, 1:1 CH_2Cl_2/hexanes) to yield a pale yellow oil identified as (*trans,trans*-2-methoxy-3-phenylcyclopropyl)ethyne, **1b** (1.24 g, 81%, 99% pure by GC). Alkyne **1b** is relatively stable but does undergo decomposition under ambient atmosphere and temperature over time (12% decomposition after 7 months as determined by GC analysis). The major products of decomposition identified were benzaldehyde and 5,5-dimethoxy-4-phenylpenta-1,2-diene which was isolated as a pale yellow oil after chromatography (silica gel, CH_2Cl_2) (28% and 36%, respectively, as determined by GC analysis). **1b**: IR (cm^{-1}) 3288 (s), 3027 (w), 2930 (w), 2822 (w), 2105 (m), 1603 (m), 666 (s); ^1H NMR ($CDCl_3$) δ 7.19−7.31 (m, 5H, Ph*H*), 3.63 (dd, 1H, MeOC*H*, J = 3.1, 6.8 Hz), 3.29 (s, 3H, OMe), 2.35 (t, 1H, PhC*H*, J = 6.6 Hz), 1.94 (d, 1H, C≡C*H*, J = 2.2 Hz), 1.82 (ddd, 1H, C*H*C≡CH, J = 2.3, 3.2, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 135.0 (*i*-Ph*C*), 128.0, 128.0, 126.4 (*o,m,p*-Ph*C*), 83.9 (*C*≡CH), 66.2 (MeO*C*H) 66.0 (C≡*C*H), 58.5 (OMe), 32.9 (Ph*C*H), 14.9 (*C*HC≡CH); MS (*m/z*) 172 (M^+, 100), 157 ($C_{11}H_9O$, 23), 141 ($C_{11}H_9$, 65); High-Resolution MS for $C_{12}H_{12}O$ (M^+) (*m/z*) calcd 172.0889, found 172.0889. **5,5-Dimethoxy-4-phenylpenta-1,2-diene:** IR (cm^{-1}) 3062 (m), 3029 (m), 2935 (s), 2831 (m), 1957 (s), 1726 (s), 1625 (m), 1495 (m), 1452 (s), 1116 (s), 1080 (s), 848 (s), 761 (m), 701 (vs); ^1H NMR ($CDCl_3$) δ 7.19−7.32 (m, 5H, *o,m,p*-Ph*H*), 5.43 (q, 1H, C=C=C*H*, J = 6.8 Hz), 4.71, 4.77 (dd on AB, 2H, $H_2C{=}C{=}C$, J = 10.5, 6.7, 2.3 Hz), 4.51 (d, 1H, MeOC*H*, J = 6.7 Hz), 3.60 (tt, 1H, PhC*H*, J = 2.3, 7.0 Hz), 3.39 (s, 3H, OMe), 3.24 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$) δ 208.8 (C=*C*=C), 140.0 (*i*-Ph*C*), 128.6, 128.2, 126.8 (*o,m,p*-Ph*C*), 106.9 ($CH(OMe)_2$), 90.2 (C=*C*H), 76.0 ($H_2C{=}C$), 54.5 (OMe), 54.2 (OMe), 48.6 (Ph*C*H); MS (*m/z*) 204 (M^+, 0.5), 189 (M^+ − Me, 0.6), 173 (M^+ − MeO, 2.8), 140 (M^+ − 2MeOH, 9), 74 ($C(OMe)_2$, 100); high-resolution MS for $C_{13}H_{16}O_2$ (M^+) calcd 204.1150, found 204.1147.

Synthesis of Ethyl *trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropanecarboxylate. A solution of ethyl 2-diazopropionate (13.0 g, 0.10 mol) dissolved in benzene (40 mL) was added dropwise to a refluxing solution of $CuSO_4$ (1.12 g, 7.0 mmol) and *cis*-β-methoxystyrene (9.1 g, 0.068 mol) dissolved in benzene (100 mL). The suspension was allowed to reflux for 18 h and then quenched by the addition of H_2O (100 mL). The organic and aqueous layers were separated. The aqueous layer was washed with Et_2O (3 × 75 mL). The organic layers were combined and washed with H_2O (75 mL), dried over $MgSO_4$ and filtered. Removal of the solvent by rotary evaporation yielded a dark yellow oil. After purification by column chromatography (silica gel, 4:1 hexanes/EtOAc), a pale yellow oil was obtained (8.91 g, 94% based on reacted β-methoxystyrene, 98% purity by GC analysis). **Ethyl *trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropanecarboxylate:** IR (cm^{-1}) 2976 (w), 2930 (w), 1711 (s), 1450 (w), 1255 (m), 1127 (m), 1025 (m), 707 (m); ^1H NMR ($CDCl_3$) δ 7.18−7.31 (m, 5H, *o,m,p*-Ph*H*), 4.16 (q, 2H, OCH_2CH_3, J = 7.2 Hz), 3.83 (d, 1H, MeOC*H*, J = 7.6 Hz), 3.41 (s, 3H, OMe), 2.75 (d, 1H, PhC*H*, J = 7.6 Hz), 1.28 (t, 3H, OCH_2CH_3, J = 7.2 Hz), 1.10 (s, 3H, CMe); ^{13}C NMR ($CDCl_3$) δ 174.7 (*C*=O), 134.2 (*i*-Ph*C*), 130.6 (*o*-Ph*C*), 128.0 (*m*-Ph*C*), 126.5 (*p*-Ph*C*), 68.0 (MeO*C*H) 60.8 (OCH_2CH_3), 59.1 (OMe), 33.5 (Ph*C*H), 28.2 (*C*Me), 14.3 (OCH_2CH_3), 8.1 (Me); MS (*m/z*) 234 (M^+, 20), 205 (M^+ − Et, 13), 173 (45), 161 ($M^+ - C_3H_5O_2$, 62), 129 (100), 117 (45), 84 (54); high-resolution MS for $C_{14}H_{18}O_3$ (M^+) (*m/z*) calcd 234.1256, found 234.1260.

Synthesis of (*trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)methanol. A solution of ethyl *trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropanecarboxylate (1.65 g, 7.0 mmol) dissolved in Et_2O (20 mL) was added dropwise to a suspension of LAH (797 mg, 21.0 mmol) in Et_2O (30 mL). The reaction mixture was allowed to stir at rt for 4 h, was cooled to 0 °C, and then quenched by the slow addition of H_2O (25 mL). The organic and aqueous layers were separated. The aqueous layer was washed with Et_2O (3 × 25 mL). The organic layers were combined and washed with H_2O (25 mL). The organic layer was dried over $MgSO_4$ and filtered. Concentration of the filtrate by rotary evaporation yielded a cloudy, colorless oil (1.34 g, 99%, 97% pure by GC analysis). **(*trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)methanol:** IR (cm^{-1}) 3384 (bs), 2932 (m), 1599 (w) 1493 (m), 1448 (w) 1236 (m), 1138 (m), 1028 (s), 698 (m); ^1H NMR ($CDCl_3$) δ 7.14−7.31 (m, 5H, Ph*H*), 3.54, 3.47 (AB, 2H, CH_2OH, J = 10.9 Hz), 3.38 (s, 3H, OMe), 3.32 (d, 1H, MeOC*H*, J = 7.1 Hz), 1.90 (d, 1H, PhC*H*, J = 7.1 Hz), 1.23 (broad s, 1H, O*H*) 1.05 (s, 3H, CMe); ^{13}C NMR ($CDCl_3$) δ 136.2 (*i*-Ph*C*), 130.1, 127.9 (*o, m*-Ph*C*), 125.7 (*p*-Ph*C*), 70.5 (CH_2OH), 65.7 ($COCH_3$), 58.9 (OMe), 28.6 (Ph*C*H), 27.7 (*C*Me), 9.8 (Me); MS (CI, Isobutane) (*m/z* (%)) 193 ($M + H^+$, 4), 175 ($M + H^+ - H_2O$, 55), 161 ($M + H^+ - CH_3OH$, 100), 143 ($M + H^+ - CH_3OH - H_2O$, 98); high-resolution MS (CI, Isobutane) for $C_{12}H_{17}O_2$ ($M + H^+$) (*m/z*) calcd 193.1228, found 193.1223.

(26) CCDC 257338 contains the supplementary crystallographic data for compound **7** and CCDC 257339 contains the supplementary crystallographic data for compound **5c**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

Synthesis of *trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropanecarbaldehyde (4c). A solution of DMSO (5.2 mL, 73 mmol) and CH_2Cl_2 (40 mL) was added dropwise to a solution of oxalyl chloride (3.2 mL, 37 mmol) dissolved in CH_2Cl_2 (120 mL) at −78 °C. The mixture was allowed to stir for 10 min. A solution of (*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)methanol (5.5 g, 29 mmol) and NEt_3 (28 mL, 203 mmol) dissolved in CH_2Cl_2 (80 mL) was added dropwise to the cold solution. The reaction mixture was then allowed to warm to rt and stirred for 2 h. The reaction was quenched by the addition of H_2O (100 mL), and the organic and aqueous layers were separated. The aqueous layer was washed with CH_2Cl_2 (3 × 100 mL), and the combined organic layers were washed with H_2O. The organic layer was dried over $MgSO_4$, filtered, and then concentrated by rotary evaporation to yield a orange-yellow oil. Et_2O (100 mL) was added to the oil to induce precipitation of the NEt_3HCl salt. The precipitate was removed by filtration, and the filtrate was once again concentrated to yield a orange-yellow oil (5.1 g, 94%). Aldehyde **4c** is unstable and rearranges in near quantitative yield to **6** over several days. The rearrangement is accelerated in chloroform and is complete in less than 12 h. It was difficult to obtain a clean sample of **4c** as contamination with dihydrofuran **6** was unavoidable. For this reason, aldehyde **4c** was used without further purification. **4c**: IR (cm^{-1}) 2935 (m), 2827 (m), 2735 (m) 1701 (s) 1603 (m), 1445 (m) 1245 (m), 1091 (m), 1030 (m), 922 (m) 697 (m); ^1H NMR (C_6D_6) δ 9.06 (s, 1H, C*H*O) 7.0−7.25 (m, 5H, *o,m,p*-Ph*H*), 3.38 (d, 1H, MeOC*H*, J = 7.6 Hz), 2.83 (s, 3H, OMe), 2.64 (d, 1H, PhC*H*, J = 7.6 Hz), 1.02 (s, 3H, CMe); ^{13}C NMR (C_6D_6) δ 200.6 (*C*HO), 140.0 (*i*-Ph*C*), 130.9 (*o*-Ph*C*), 128.2 (*m*-Ph*C*), 126.9 (*p*-Ph*C*), 69.0 (MeO*C*H), 58.5 (OMe), 37.3 (*C*Me), 33.5 (Ph*C*H), 6.8 (Me); MS (*m/z*) 190 (M^+, 100), 161 (M^+ − HCO, 78), 129 (M^+ − HCO − CH_3OH, 92), 115 (53), 91 (41); high-resolution MS for $C_{12}H_{14}O_2$ (M^+) (*m*/z) calcd 190.0994, found 190.0994. **6**: ^1H NMR ($CDCl_3$) δ 7.17−7.40 (m, 5H, *o,m,p*-Ph*H*), 6.29 (m, 1H, C*H*=CMe), 5.46 (d, 1H, MeOC*H*, J = 7.6 Hz), 3.99 (broad dq, 1H, PhC*H*, J = 7.6, 1.4 Hz), 3.33 (s, 3H, OMe), 1.48 (t, 3H, CMe, J = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 139.2 (O*C*=C), 135.5 (*i*-Ph*C*), 130.1, 127.8, 126.9 (*o,m,p*-Ph*C*), 112.8 (C=*C*Me), 107.3 (MeO*C*H), 56.5 (OMe), 55.8 (Ph*C*H), 9.9 (CMe); MS (*m/z*) 190 (M^+, 100), 161 (M^+ − HCO, 65), 129 (M^+ − HCO − CH_3OH, 97), 115 (52), 91 (30); high-resolution MS for $C_{12}H_{14}O_2$ (M^+) calcd 190.0994, found 190.0994.

Synthesis of 1,1-Dibromo(*trans,trans*-2-methoxy-1-methyl-3-phenylcyclopropyl)ethene (5c). Compound **5c** was prepared as described for **5b**. Specific experimental details can be found in the Supporting Information. Single crystals of **5c** were grown from a concentrated methylene chloride solution by slow diffusion of acetonitrile and then analyzed by X-ray crystallography. Experimental details for the analysis are presented in the Supporting Information. Bond lengths and angles, atomic coordinates, and anisotropic parameters are tabulated.[26] **5c**: mp 67−69 °C; IR (cm^{-1}) 2928 (s), 2822 (w), 1607 (m), 1497 (s), 1444 (m), 1138 (s), 1077 (m), 698 (s); ^1H NMR ($CDCl_3$) δ 7.36 (pseudo-d, 2H, *o*-Ph*H*, J = 7.8 Hz), 7.26 (pseudo-t, 2H, *m*-Ph*H*, J = 7.2 Hz), 7.19 (pseudo-t, 1H, *p*-Ph*H*, J = 7.2 Hz), 6.65 (s, 1H, Br_2C=C*H*), 3.48 (d, 1H, MeOC*H*, J = 7.2 Hz), 3.44 (s, 3H, OMe), 2.18 (d, 1H, PhC*H*, J = 7.2 Hz), 1.12 (s, 3H, CMe); ^{13}C NMR ($CDCl_3$) δ 141.9 (Br_2C=*C*), 135.4 (*i*-Ph*C*), 130.4 (*o*-Ph*C*), 127.9 (*m*-Ph*C*), 126.1 (*p*-Ph*C*), 92.4 (Br_2C), 67.0 (MeO*C*H), 59.0 (OMe), 32.6 (Ph*C*H), 28.5 (Br_2C=CH*C*), 10.8 (CMe); MS (CI, isobutane) (*m/z*) 347 (M + H^+, 25), 315 (M^+ − CH_3OH, 64), 267 (M^+ − ^{79}Br, 100), 236 (M^+ − ^{79}Br − OMe, 36), 186 (M^+ − ^{79}Br − ^{81}Br, 98); high-resolution MS (CI, Isobutane) for $C_{13}H_{15}O^{79}Br_2$ (M + H^+) (*m/z*) calcd 344.9489, found 344.9495.

Synthesis of (*trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)ethyne (1c). Compound **1c** was prepared as described for **1b**. Specific experimental details can be found in the Supporting Information. **1c**: IR (cm^{-1}) 3283 (s), 2935 (s), 2105 (m), 1603 (m), 1496 (s), 1445 (m), 1199 (m), 1143 (s), 1081 (s), 907 (s), 697 (s); ^1H NMR ($CDCl_3$) δ 7.17−7.32 (m, 5H, *o,m,p*-Ph*H*), 3.62 (d, 1H, MeOC*H*, J = 7.6 Hz), 3.45 (s, 3H, OMe), 2.35 (d, 1H, PhC*H*, J = 7.6 Hz), 1.96 (s, 1H, C≡C*H*), 1.10 (s, 3H, CMe); ^{13}C NMR ($CDCl_3$) δ 134.3 (*i*-Ph*C*), 130.5 (*o*-Ph*C*), 128.0 (*m*-Ph*C*), 126.4 (*p*-Ph*C*), 90.3 (*C*≡CH), 67.9 (MeO*C*H) 64.2 (C≡*C*H, $^1J_{C-H}$ = 264 Hz), 59.0 (OMe), 33.4 (Ph*C*H), 15.8 (*C*C≡CH), 12.4 (CMe); MS (*m/z*)186 (M^+, 69), 171 (M^+ − CH_3, 67), 155 (M^+ − OCH_3, 22), 128 (62), 84 (M^+ − PhC≡CH, 100); high-resolution MS for $C_{13}H_{14}O$ (M^+) (*m/z*) calcd 186.1045, found 186.1046. **(*trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)ethene:** ^1H NMR (C_6D_6) δ 7.41−7.43 (m, 2H, *o*-Ph*H*), 5.47 (dd, 1H, *H*C=CH_2, J = 17.0, 12.5 Hz), 4.97 (dd, 1H, HC=CH(H_{trans}), J = 1.0, 17.0 Hz), 4.91 (dd, 1H, HC=CH(H_{cis}), J = 1.0, 10.5 Hz), 3.12 (d, 1H, MeOC*H*, J = 7.0 Hz), 3.05 (s, 3H, OMe), 1.99 (d, 1H, PhC*H*, J = 7.0 Hz), 1.09 (s, 3H, CMe).

Thermolysis of (*trans*-2-Phenylcyclopropyl)ethyne (1a) with $(Me_3Si)_3SiH$. A solution of **1a** (100 mg, 0.70 mmol), $(Me_3Si)_3SiH$ (346 mg, 1.40 mmol), and AIBN (20 mg, 0.12 mmol) dissolved in toluene (5 mL) was refluxed. The progress of the reaction was monitored by ^1H NMR spectroscopy. The solvent was then removed by rotary evaporation to give a pale, yellow oil (150 mg, 55%), identified as 1-tris(trimethylsilyl)silyl-5-phenylpenta-1,2-diene, **8a**. All attempts to purify **8a** resulted in decomposition. **8a**: IR (cm^{-1}) 3320 (w), 3088 (w), 3065 (w), 3030 (w), 2967 (s), 2897 (s), 1934 (s, C=C=C), 1731 (m), 1263 (s), 1062 (s), 835 (s); ^1H NMR ($CDCl_3$) δ 7.15−7.25 (m, 5H, *o,m,p*-Ph*H*), 4.84 (dt, 1H, SiC*H*=C=CH, J = 3.5, 7.2 Hz), 4.71 (pseudo-q, 1H, SiCH=C=C*H*, J = 6.7 Hz), 2.70 (t, 2H, PhCH_2, J = 8.0 Hz), 2.23−2.32 (m, 2H, $PhCH_2CH_2$), 0.18 (s, 27H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 210.3 (SiCH=*C*=CH) 141.9 (*i*-Ph*C*), 128.3, 128.2, 125.7 (*o,m,p*-Ph*C*), 81.9 (SiCH=C=*C*H), 74.1 (Si*C*H=C=CH), 36.2 (PhCH_2), 30.6 ($PhCH_2CH_2$), 0.8 ($SiMe_3$); MS (CI, Isobutane) (*m/z*) 389 (M^+ − H, 100), 317 (M^+ − $SiMe_3$, 43); high-resolution MS for $C_{20}H_{37}Si_4$ (M^+ − H) (*m/z*) calcd 389.2026, found 389.1966.

Thermolysis of (*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethyne (1b) with $(Me_3Si)_3SiH$. The thermolysis of **1b** was performed as described for **1a**. Specific experimental details can be found in the Supporting Information. **8b**: IR (cm^{-1}) 2951 (s), 2894 (m), 1932 (s), 1257 (m), 1244 (s), 1100 (m), 837 (vs); ^1H NMR ($CDCl_3$) δ 7.19−7.27 (m, 5H, *o,m,p*-Ph*H*), 4.76 (dd, 1H, SiC*H*=C=CH, J = 6.4, 2.0 Hz), 4.70 (t, 1H, SiCH=C=C*H*, J = 7.2 Hz), 3.92−3.97 (m, 1H, MeOC*H*), 3.30 (s, 3H, OMe), 2.94 (dd, 1H, PhCH_2, J = 7.6, 13.6 Hz), 2.79 (dd, 1H, PhCH_2, J = 5.6, 13.6 Hz), 0.17 (s, 27H, $SiMe_3$);^{13}C NMR ($CDCl_3$) δ 209.3 (SiCH=*C*=CH), 138.6 (*i*-Ph*C*), 129.7 (*o*-Ph*C*), 128.0, 126.0 (*m,p*-Ph*C*), 84.4 (SiCH=C=*C*H), 80.6 (MeO*C*H), 75.4 (Si*C*H=C=CH), 56.7 (OMe), 42.6 (PhCH_2), 0.6 ($SiMe_3$); MS (CI, isobutane) (*m/z*) 477 (M^+ + 57, 3), 421 (M + H^+, 9), 389 (M + H^+ − MeO, 100); high-resolution MS for $C_{21}H_{41}OSi_4$ (M + H^+) (*m/z*) calcd 421.2235, found 421.2230.

Thermolysis of (*trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)ethyne (1c) in the Presence of Tributyltin Hydride. The thermolysis of **1c** was performed as described for 1a, using Bu_3SnH in place of $(Me_3Si)_3SiH$. The specific experimental details can be found in the Supporting Information. **8c**: IR (cm^{-1}): 2955 (s), 2925 (s), 2873 (m), 2848 (m), 1936 (m), 1460 (m), 1378 (w), 1260 (m), 1096 (m), 805 (m), 692 (m); ^1H NMR (C_6D_6) δ major diasteromer 7.31−7.32 (m, 2H, *o*-Ph*H*), 7.19−7.22 (m, 2H, *m*-Ph*H*), 7.07−7.09 (m, 1H, *p*-Ph*H*), 5.17 (dq, 1H, SnC*H*=C=C, J = 0.4, 3.8 Hz, $^2J_{119/117Sn-H}$ = 24.6 Hz), 4.05 (ddd, 1H, MeOC*H*, J = 0.9, 5.3, 8.2 Hz), 3.18 (s, 3H, OMe), 3.11 (dd, 1H, PhCH_2, J = 8.2, 13.8 Hz), 2.90 (dd, 1H, PhCH_2, J = 5.3, 13.8 Hz), 1.75 (d, 3H, Me, J = 3.8 Hz, $^5J_{119/117Sn-H}$ = 19.9 Hz), 1.52−1.59 ($SnCH_2CH_2CH_2$),[27] 1.29−1.38 ($SnCH_2CH_2CH_2CH_2$),[27] 0.85−1.0 ($SnCH_2$),[27] 0.93 (t, CH_2CH_3, J = 7.8 Hz); minor diastereomer 7.24−7.25 (m, 2H, *o*-Ph*H*), 7.15−7.18 (m, 2H, *m*-Ph*H*), 7.06−7.08 (m, 1H, *p*-Ph*H*), 5.04

(27) Some of the signals corresponding to the tributylstannyl ^1Hs of one diastereomer were overlapped by signals of the other diastereomer. Therefore, the chemical shift ranges of both diastereomers have been listed for these signals.

(dq, 1H, SnC*H*=C=C, J = 1.2, 3.8 Hz, $^2J_{119/117Sn-H}$ = 24.9 Hz), 4.07 (ddd, 1H, MeOC*H*, J = 0.9, 6.2, 7.6 Hz), 3.24 (s, 3H, OMe), 3.12 (dd, 1H, PhCH_2, J = 7.6, 13.8 Hz), 2.89 (dd, 1H, PhCH_2, J = 6.2, 13.8 Hz), 1.75 (d, 3H, Me, J = 3.8 Hz, $^5J_{119/117Sn-H}$ = 19.6 Hz) 1.52−1.59 (SnCH$_2$CH_2),[27] 1.29−1.38 (SnCH$_2$CH$_2$CH_2),[27] 0.85−1.0 (SnCH_2),[27] 0.90 (t, CH$_2$CH_3, J = 7.8 Hz); ^{13}C NMR (C_6D_6) δ: 208.0, 207.7 (C=*C*=C), 139.9, 139.7 (*i*-Ph*C*), 129.8, 129.7 (*o*-Ph*C*), 128.5, 128.4 (*m*-Ph*C*), 126.3, 126.3 (*p*-Ph*C*), 87.7, 87.7 (SnCH=C=*C*), 85.3, 85.0 (MeO*C*H), 75.9, 75.5 (Sn*C*H=C=C), 56.1, 55.8 (OMe), 41.2, 41.2 (Ph*C*H$_2$), 29.4, 29.4 (SnCH$_2$*C*H$_2$), 27.6, 27.6 (SnCH$_2$CH$_2$*C*H$_2$), 14.0, 13.9 (CH$_2$*C*H$_3$), 12.8, 12.5 (Me), 10.7 (Sn*C*H$_2$); MS (*m/z*) 478 (M^+, 5), 421 (M^+ − Bu, 41), 291 (Bu_3Sn^+, 64), 265 (100), 235 (55), 179 (49); high-resolution MS for $C_{25}H_{42}O^{120}Sn$ (M^+) (*m/z*) calcd 478.2260, found 478.2263.

Hydrolysis of (*trans*-2-Phenylcyclopropyl)ethyne (1a). Sulfuric acid (0.75 mL of a concentrated (18 M) solution) was added to a solution of **1a** (105 mg, 0.69 mmol) in THF/H_2O (5 mL, 4:1). The solution was heated to reflux and allowed to stir for 83 h. After cooling to rt, Et_2O (5 mL) was added to the reaction mixture and the organic and aqueous layers were separated. The organic layer was dried over $MgSO_4$ and filtered. The solvent was then removed by rotary evaporation to yield a yellow oil which was identified as 1-phenyl-penta-3,4-dien-1-ol, **9** (0.64 mmol, 93%).[28,29] (*trans*-2-Phenylcyclopropyl)ethanone[15] was always present (**9**/ethanone = 10.7:1). **9**: IR (cm^{-1}) 3400 (s, br, OH), 3063 (s), 3032 (s), 2914 (s), 1956 (s, C=C=C), 1685 (s), 1598 (s), 1495 (s); ^{1}H NMR ($CDCl_3$) δ 7.25−7.36 (m, 5H, *o,m,p*-Ph*H*), 5.11 (pseudo-quint, 1H, H$_2$C=C=C*H*, J = 6.8 Hz), 4.77 (t, 1H, C*H*OH, J = 6.4 Hz), 4.71 (dt, 2H, *H*$_2$C=C=CH, J = 6.8, 2.4 Hz), 2.46 (tt, 2H, C=CHC*H*$_2$, J = 2.4, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 209.2 (H$_2$C=*C*=CH) 143.4 (*i*-Ph*C*), 128.3 (*m*-Ph*C*), 127.5 (*p*-Ph*C*), 125.7 (*o*-Ph*C*), 86.1 (H$_2$C=C=*C*H), 75.1 (H$_2$*C*=C=CH), 73.6 (*C*HOH), 38.6 (C=C*H*CH$_2$); MS (*m/z*) 160 (M^+, 24), 145 (13), 117 ($M^+ - C_3H_7$, 100), 115 (55); high-resolution MS for $C_{11}H_{12}O$ (M^+) (*m/z*) calcd 160.0888, found 160.0894.

Hydrolysis of (*trans,trans*-2-Methoxy-3-phenylcyclopropyl)ethyne (1b). The hydrolysis of **1b** was performed as described for **1a**. Specific experimental details can be found in the Supporting information. **11**: IR (cm^{-1}) 2961 (s), 2920 (s), 1731 (s), 1691 (s), 1445 (m), 1260 (s), 1091 (s), 1025 (s), 799 (s), 679 (m); ^{1}H NMR ($CDCl_3$) δ 9.67 (s, 1H, C*H*O), 7.34−7.41 (m, 3H, *m, p*-Ph*H*), 7.19−7.21 (m, 2H, *o*-Ph*H*), 7.05 (d, 1H, C*H*CH=CH$_2$, J = 11.4 Hz), 6.70 (ddd, 1H, C*H*=CH$_2$, J = 10.0, 11.4, 17.0 Hz), 5.81 (ddd, 1H, CH=CH(H_{trans}), J = 0.8, 1.6, 17.0 Hz), 5.59 (ddd, 1H, CH=CH(H_{cis}), J = 0.8, 1.6, 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 193.2 (*C*HO), 149.2 (*C*HCH=CH$_2$), 141.9 (*C*=CHCH=CH$_2$), 132.8 (C=*C*HCH=CH$_2$), 132.1 (*i*-Ph*C*), 129.7 (*o*-Ph*C*), 128.2, 128.1 (*m, p*-Ph*C*), 127.7 (*C*H$_2$); MS (*m/z*) 158 (M^+, 36), 129 ($C_{10}H_9$, 100), 115 (C_9H_9, 40); high-resolution MS for $C_{11}H_{10}O$ (M^+) (*m/z*) calcd 158.0782, found 158.0727.

Hydrolysis of (*trans,trans*-2-Methoxy-1-methyl-3-phenylcyclopropyl)ethyne (1c). The hydrolysis of **1c** was performed as described for **1a**. Specific experimental details can be found in the Supporting Information.

Addition of BuLi to 1-(*trans*-2-Phenylcyclopropyl)-1-tributylstannylethene. BuLi (150 μL of a 1.6 M solution, 0.24 mmol) was added to a solution of stannylethene **15** (53 mg, 0.12 mmol) in THF (5 mL) at −78 °C. The solution was allowed to stir at −78 °C for 1 h 45 min. The reaction mixture became yellow in color with the intensity of the color increasing with time. The cold reaction mixture was quenched by the addition of H_2O (3 mL). The organic and aqueous layers were separated. The organic layer was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to yield a clear, colorless oil (55 mg). The crude reaction mixture was purified by preparative thin-layer chromatography (silica gel, 2:1 hexanes/CH_2Cl_2) to give (*trans*-2-phenylcyclopropyl)ethene[30] (13 mg, 76%).

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Supporting Information Available: NMR spectra and GC chromatograms, where applicable, for all new compounds. General experimental details and the preparation of compounds **5c**, **1c**, **8b**−**c**, and **10**. Experimental details for the X-ray crystallographic analyses including bond lengths and angles, atomic coordinates, and anisotropic parameters for compounds **5c** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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