

Communications to the Editor

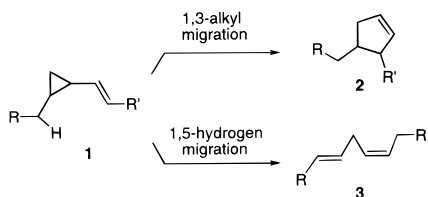
Evidence for a Kinetic Silicon Effect in a Sigmatropic Rearrangement

Yi-Lun Lin and Edward Turos*

Department of Chemistry, University of South Florida
Tampa, Florida 33620

Received June 11, 1998

Of the variety of synthetically useful transformations¹ that vinylcyclopropanes can undergo, the 1,3-alkyl migration (ring expansion) reaction and the 1,5-hydrogen migration (retro-ene) reaction are by far the most common.^{2,3} These processes generally occur competitively at elevated temperatures. However, for *cis*-disubstituted vinylcyclopropanes **1**, the formation of retro-ene product **3** is kinetically favored over the ring expansion product **2**.⁴ In this report, we describe a novel application of this retro-ene reaction for the stereoselective synthesis of *E*-vinylsilanes,⁵ as well as evidence that the silyl substituent ($R = \text{SiR}_3$) can accelerate the sigmatropic process.



Our studies focused on the thermal rearrangements of *cis*-1-silylmethyl-2-vinylcyclopropanes **4**. Upon heating in dilute toluene solution, substrates **4** isomerize readily to vinylsilanes **5** in nearly quantitative yields and, in most cases, with complete stereoselection. The isolated yields of products and reaction half-life times⁶ for these reactions are summarized in Table 1. Initial experiments utilizing compound **4a** indicate that the reaction is

* Corresponding author. Telephone: 813-974-7312. FAX: 813-974-1733. E-mail: eturos@chuma.cas.usf.edu.

- (1) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247.
 (2) (a) Jorgenson, M. J.; Thacher, A. F. *Tetrahedron Lett.* **1969**, *10*, 4651.
 (b) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103. (c) Frey, H. M.; Solly, R. K. *Int. J. Chem. Kinet.* **1969**, *1*, 473. (d) Ando, W. *Tetrahedron Lett.* **1969**, *10*, 929. (e) Jones, H.; Ando, W.; Kulczycki, A. *Tetrahedron Lett.* **1967**, *8*, 1391. (f) Roth, W. R.; Konig, J. *Justus Liebigs Ann. Chem.* **1965**, *688*, 28. (g) Roberts, R.; Landolt, R. *J. Am. Chem. Soc.* **1965**, *87*, 2281. (h) Ellis, R. J.; Frey, H. M. *Proc. Chem. Soc., London* **1964**, *22*. (i) Ogle, C. A.; Black, K. C.; Sims, P. F. *J. Org. Chem.* **1992**, *57*, 3499.
 (3) (a) Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4595. (b) Daub, J. P.; Berson, J. A. *Tetrahedron Lett.* **1984**, *25*, 4463. (c) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981. (d) Hudlicky, T.; Koszyk, F. J. *Tetrahedron Lett.* **1980**, *21*, 2487. (e) Mazzocchi, P. H.; Tamburin, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 555. (f) Baharel, Y.; Cottier, L.; Descotes, G. *Synthesis* **1974**, 118. (g) Paquette, L. A.; Henzel, R. P.; Eizenber, R. F. *J. Org. Chem.* **1973**, *38*, 3257.
 (4) The 1,5-hydrogen migration of *cis*-disubstituted vinylcyclopropanes reportedly has an activation barrier of approximately 30–35 kcal/mol (cf. Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 3547), 15–20 kcal lower than that of the 1,3-alkyl migration, and is generally viewed to be a reversible process (Hudlicky, T.; Kutchan, T. M.; Koszyk, F. J.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020).
 (5) Vinylsilanes have become valuable reagents and intermediates in synthesis. For a review, see: Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.
 (6) Reaction half-lives were measured by ¹H NMR experiments using 1,4-dinitrobenzene as an internal standard.
 (7) The isomerization of *trans*-vinylcyclopropanes to *cis*-vinylcyclopropanes or to cyclopentenes generally takes place at temperatures well-above 200 °C (see ref 1).

Table 1. Thermal 1,5-Hydrogen Rearrangements of Vinylcyclopropanes **4**

The diagram shows a vinylcyclopropane derivative **4** with a silyl group (R₃Si) and a vinyl group. Upon heating at 110 °C in toluene, it undergoes a 1,5-hydrogen migration to form a vinylsilane derivative **5**.

substrate 4	isolated % yield of 5	t _{1/2} (110 °C)
a R = Ph, R ¹ = R ² = R ³ = H	97	3.2 h
b R = Ph, R ¹ = R ² = H; R ³ = CO ₂ Me	97	7.8 h
c R = Ph, R ¹ = R ² = H; R ³ = Ph	96	13 h
d R = Ph, R ¹ = R ³ = H; R ² = Ph	96	17 h
e R = Ph, R ¹ = CO ₂ Me, R ² = H; R ³ = Ph	98	0.7 h
f R = Me, R ¹ = CO ₂ Me, R ² = H; R ³ = Ph	96 ^a	3 h
g R = OEt, R ¹ = CO ₂ Me, R ² = H; R ³ = Ph	94 ^b	2 h

^a A 5:1 ratio of 1*E*,4*E*:1*Z*,4*E*-isomers was observed by ¹H NMR.
^b The 1.3:1 ratio of 1*E*,4*E*:1*Z*,4*E*-isomers was observed by ¹H NMR.

complete within several hours at 110 °C, which is nearly 100 °C lower than that reported^{2a} for systems which lack the C₁ silyl group (**1**, R = H). Compounds **4b–d** likewise undergo clean isomerization upon thermolysis to produce 1*E*,4*Z*-dienylsilane **5** as single stereoisomers. The corresponding *trans*-vinylcyclopropane isomers are inert under these reaction conditions and can be recovered unchanged even after 20 days in refluxing xylenes.⁷

The data provided in Table 1 help to define some of the features of this sigmatropic rearrangement process. First, the presence of an electron-withdrawing group located at the C₅ terminus of the vinylcyclopropane, as seen for compounds **4b–d**, has a detrimental effect on the rate of isomerization. This is most likely due to loss of conjugation of the olefin with the C₅ substituent upon forming dienes **5b–d**. It is also interesting that the reactions of *E*-vinylcyclopropane **4c** and its *Z*-isomer **4d** both lead to the 1*E*,4*Z*-vinylsilane product, indicating that the formation of olefin stereochemistry in diene **5** occurs independently of the starting olefin geometry. On the other hand, the fact that the *E*-isomer **4c** rearranges faster than the *Z*-isomer **4d** suggests that the rate of isomerization *does* depend on the *E/Z*-geometry of the vinylcyclopropane.⁸

It is also informative to consider the vastly different reaction half-lives for substrate **4c** (13 h) versus compound **4e** (0.7 h). These data indicate that the presence of a carbomethoxy substituent at C₃ on the ring *enhances* the rate of isomerization, which is opposite to the effect observed in the thermolysis of **4b** which has the electron-withdrawing group at the C₅ olefin terminus. In the case of **4e**, the development of conjugation of the olefin with

(8) Some very early studies briefly described the effect of olefin substitution and *E/Z* geometry on 1,5-hydrogen rearrangements of simple vinylcyclopropane systems. See ref 2.

(9) The observed ratio of products in this case is not the result of thermodynamic equilibration under the reaction conditions. 1*E*,4*Z*- and 1*Z*,4*Z*-vinylsilanes **5f** are each stable in refluxing toluene for several weeks without any crossover to the other stereoisomer or reversion back to the vinylcyclopropane. Slow equilibration of the vinylsilane in **5f** does occur slowly over a period of 10 days in refluxing xylene.

(10) The lower selectivity in this example may suggest a deviation in the reaction mechanism due to the presence of the silyl alkoxy ligands, perhaps through stabilization of a β-radical or cation by the electron pair of the ethoxy oxygen (Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609).

(11) Substituents can alter the electronegativity and hyperconjugation ability of silicon, with the general trend in radical or cation stabilization being (RO)₃Si < Ar₃Si < R₃Si. (Brook, M. A.; Henry, C.; Jefferson, E.; Juschke, R.; Sebastian, T.; Tomaszewski, M.; Wenzel, S. *Bull. Soc. Chem. Fr.* **1995**, *132*, 559.)

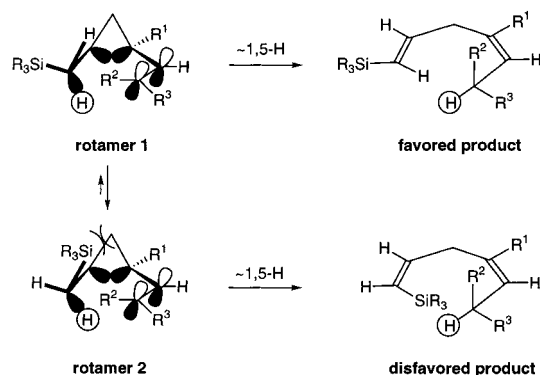


Figure 1.

the C_3 ester group lowers the activation energy for rearrangement. The thermolyses of ester-bearing compounds **4e–g** further reveal that the rate and stereoselectivity of the 1,5-hydrogen migration have a subtle dependence on the nature of the silyl substituents R. For instance, whereas the triphenylsilyl derivative **4e** yields exclusively the *1E,4E*-diene product, the trimethylsilyl compound **4f** produces diene **5f** as a 5:1 mixture of *1E,4E*- and *1Z,4E*-isomers.¹¹ The erosion of stereoselectivity in forming the C_1/C_2 olefin in **5f** suggests that the size of the silyl substituents plays a dominant role in controlling the stereochemistry of hydrogen migration. To our surprise, the isomerization of triethoxysilyl compound **4g** proceeds with almost complete loss of stereocontrol at C_1/C_2 , giving dienes **5g** as a 1.3:1 mixture of *1E,4E*- and *1Z,4E*-isomers.^{9,10} Moreover, the longer half-life times for **4f** and **4g** (3 and 2 h, respectively) compared to **4e** (0.7 h) indicate that the observed order of reactivity ($\text{Me}_3\text{Si} < (\text{EtO})_3\text{Si} < \text{Ph}_3\text{Si}$) is not the result of ligand electronegativity effects.¹¹

The Woodward–Hoffmann rules¹² classify the concerted 1,5-hydrogen migration as a thermally allowed suprafacial process. Earlier studies on the vinylcyclopropane 1,5-hydrogen rearrangement have found that the ring-opening provides the 1,4-pentadiene product with exclusive *cis*-stereochemistry at C_4/C_5 .^{2a,b} The high stereochemical control and silyl rate accelerating effect observed in our examples can best be explained by considering the two conformational isomers 1 and 2 shown in Figure 1.¹³ The arrangement in rotamer 1 allows the silyl group and the axial ring hydrogen to avoid the steric interactions present in rotamer 2 and enables the C–Si bond to be antiperiplanar¹⁴ to the cleaving C–C bond of the ring. This latter feature provides the opportunity

(12) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511.

(13) Our model is supportive of Berson's earlier theoretical experiments which suggest that hydrogen migration occurs preferentially on the face *anti* to the cyclopropyl ring (see refs 3a,b).

for the C–Si bond to assist the ring cleavage through hyperconjugation,¹⁵ a phenomenon which has been well-documented for electrophile-promoted additions to silylmethylcyclopropanes¹⁶ and allylsilanes⁵ but which has not been previously observed in sigmatropic reactions.^{17,18} The presence of an electron-withdrawing substituent R^1 such as CO_2Me (**4e–g**) may help to polarize the cyclopropyl C–C bond to enhance this hyperconjugation effect and thus the rate of isomerization. It is also evident in Figure 1 that decreasing the steric bulk of the silyl substituents, as seen in the thermolysis of trimethylsilyl derivative **4f**, reduces the severity of the unfavorable interactions within conformer 2. Consequently, the strong conformational bias favoring rotamer 1 needed for high stereoselection may be diminished in this case.

In summary, new methodology for the stereoselective synthesis of *E*-vinylsilanes has been developed on the basis of the thermal 1,5-hydrogen migration reaction of *cis*-1-silylmethyl-2-vinylcyclopropanes. The stereochemical results indicate that the hydrogen transfer occurs in a concerted, suprafacial manner through a highly defined transition structure having the carbon–silicon bond antiperiplanar to the breaking carbon–carbon bond of the ring. This conformation allows the silyl substituent to facilitate the rearrangement through hyperconjugation. Experiments are now underway to further define this silicon substituent effect in terms of its synthetic utility and its potential for controlling the course of other sigmatropic processes.

Supporting Information Available: Experimental procedures and characterization data for compounds **4** and **5** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9820339

(14) Glass, D. S.; Boikess, R. S.; Winstein, S. *Tetrahedron Lett.* **1966**, *7*, 999.

(15) For reviews on hyperconjugation effects of silicon, see: (a) Lambert, J. B.; Wang, G.-t.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (b) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, C. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715.

(16) Silylmethylcyclopropanes have pronounced reactivity towards electrophilic ring-opening, to give adducts which lack the silyl group. (a) Ryu, I.; Harai, A.; Suzuki, H.; Sonoda, N.; Murai, S. *J. Org. Chem.* **1990**, *55*, 1409. (b) Ochiai, M.; Sumi, K.; Fujita, E. *Chem. Pharm. Bull.* **1983**, *31*, 3931. (c) Grignon-Dubois, M.; Dunogues, J.; Calas, R. *Can. J. Chem.* **1981**, *59*, 802. (d) Grignon-Dubois, M.; Dunogues, J.; Calas, R. *J. Chem. Research (S)* **1979**, *6*. (e) Wilson, S. R.; Zucker, P. A. *J. Org. Chem.* **1988**, *53*, 4682.

(17) Vinylcyclopropanes having a silyl group directly attached to the ring undergo ring expansion to vinylsilanes at high temperature (flash vacuum conditions). However, the authors do not mention whether the silicon moiety influences the rate of rearrangement. (a) Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T. H. *Tetrahedron Lett.* **1982**, *23*, 263. (b) Yan, T. H.; Paquette, L. A. *Tetrahedron Lett.* **1982**, *23*, 3227.

(18) Heteroatomic and anionic substituents are known to accelerate the vinylcyclopropane–cyclopentene ring expansions (for examples, see: Richey, H. G., Jr.; Shull, D. W. *Tetrahedron Lett.* **1976**, *20*, 575 and ref 1), but the effects of these substituents on the 1,5-hydrogen migration in vinylcyclopropanes have not been investigated.