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Selective Cis–Trans Isomerization of a Tetraene via an Allene Intermediate: Geometric Isomerism via an sp^2 to sp^2 Sigmatropic Hydrogen Shift and Kinetic Isotope Effect Studies

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Abstract: A kinetic investigation in the unlabeled and deuterium-labeled series of the [1,5] sigmatropic hydrogen shift of vinylallene **5** to trienes **7** plus **8** and the [1,7] sigmatropic hydrogen shift of dienallene **6** to tetraenes **9** plus **10** has been completed. The results lead to the proposal that the pathway for geometric isomerism of the terminal double bond of tetraene **9** involves as an intermediate the allene **6**. The allene **6** could in fact be isolated in the case of the isomerization of **9**, and moreover, at long reaction times **6** and **9** are transformed to **10**. For the isomerization of **5** to **7** plus **8**, it was shown that **7** and **8** interconvert with one another, but it is unclear whether allene **5** is an intermediate in their interconversion. The temperature dependencies of the primary deuterium kinetic isotope effects observed for the rearrangement of **5** (via a [1,5] sigmatropic hydrogen shift) and **6** (via the corresponding [1,7]-shift) suggest a tunneling contribution.

Only recently was it firmly established that *cis,cis,cis*-2,4,6-octatriene (**1**) and its cis,cis,trans isomer **3** when heated at 111 °C interconvert with one another via two consecutive [1,7] sigmatropic hydrogen shifts by way of the intermediate *cis,cis*-octa-1,3,5-triene (**2**) (Chart I).[1,2] However, the kinetic data suggest that a second competing pathway between **1** and **3** not involving the intermediate **2** is superimposed on the main path.[1a] In addition, the trans,cis,trans isomer **4** was also detected at longer reaction times.[1a] That direct π-bond rotation (geometric isomerism) of the terminal double bond of the trienes **1** or **3** occurs under such relatively mild conditions is surprising because not only is a relatively low activation energy barrier apparently involved,[3] but also because of the selectivity. The purpose of this article is to report selective geometric isomerization of a terminal double bond of a tetraene and to invoke a pathway involving a sigmatropic hydrogen shift leading to net cis–trans double-bond geometric isomerism. The geometric isomerism of a related triene is also reported.

The genesis of this study stems from an attempt to compare in closely related systems primary deuterium kinetic isotope effects including their temperature dependencies characteristic of [1,5] and [1,7] sigmatropic shifts. No such comparison has been previously made, and when this study was initiated, only a few isotope effect studies of [1,5]-shifts[4] and even fewer studies of [1,7]-shifts[5] had been reported. Substantive experimental input in this area would provide a firm basis for computational probing of these processes, and in this connection, we were able to secure the two closely related unlabeled and labeled allenic systems **5**[4d] and **6**[6] for initiating the study. Accordingly, this article also describes the first side by side comparison of primary kinetic isotope effects characteristic of [1,5] and [1,7] sigmatropic shifts leading to trienes (**7** and **8**) and tetraenes (**9** and **10**), respectively (Chart II).

Chart I

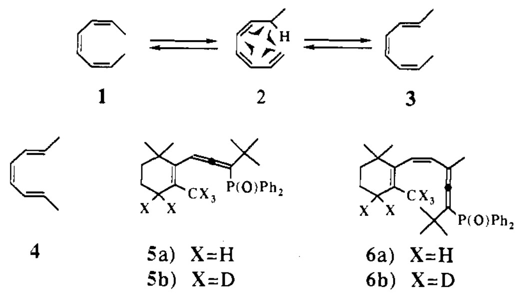


Chart II

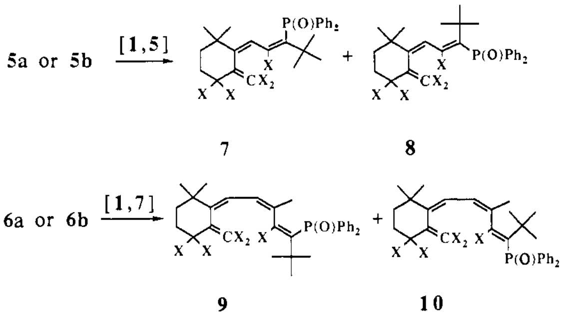
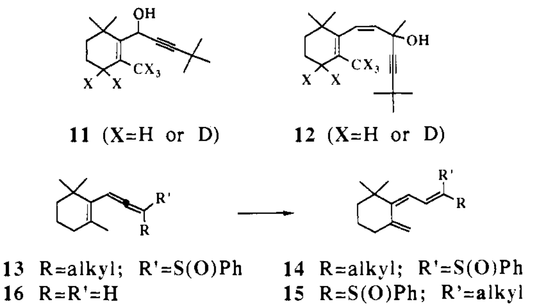


Chart III



Results and Discussion

Treatment of equimolar amounts of **11**[4d] or **12**[6] with Ph_2PCl and 4-(dimethylamino)pyridine in THF (room temperature, 3 h; HPLC purification) afforded **5** or **6**, respectively, in good yields. Using a method similar to that described previously for investigating the rate of rearrangement of vinylallene sulfoxide **13** to

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[1] (a) Baldwin, J. E.; Reddy, V. P. *J. Org. Chem.* **1988**, *53*, 1129. (b) Baldwin, J. E.; Reddy, V. P. *J. Am. Chem. Soc.* **1987**, *109*, 8051. (c) Baldwin, J. E.; Reddy, V. P. *J. Am. Chem. Soc.* **1988**, *110*, 8223.

[2] (a) Marvell, E. N.; Caple, G.; Schatz, B. *Tetrahedron Lett.* **1965**, 385. (b) Vogel, E.; Grimme, W.; Dinnê, E. *Tetrahedron Lett.* **1965**, 391.

[3] Besides ref 1a, see: (a) Doering, W. v. E.; Beasley, G. H. *Tetrahedron* **1973**, *29*, 2231. (b) Egger, K. W.; James, T. L. *Trans. Faraday Soc.* **1970**, *66*, 410.

[4] (a) Roth, W. R.; König, J. *Justus Liebigs Ann. Chem.* **1966**, *699*, 24. (b) Kwart, H.; Brechbiel, M. W.; Acheson, R. M.; Ward, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4671. (c) McLean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555. (d) Shen, G.-Y.; Tapia, R.; Okamura, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 7499. (e) Barrack, S. A.; Okamura, W. H. *J. Org. Chem.* **1986**, *51*, 3201. Only references 4a–d and this study pertain to studies of the temperature dependence of the kinetic isotope effect (TDKIE) of [1,5] sigmatropic shifts.

[5] Besides ref 1, see: (a) Hoeger, C. A.; Johnston, A. D.; Okamura, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 4690. (b) Hoeger, C. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 268. (c) Okamura, W. H.; Hoeger, C. A.; Miller, K. J.; Reischl, W. *J. Am. Chem. Soc.* **1988**, *110*, 973. Only ref 1b,c and this study pertain to studies of the TDKIE of [1,7] sigmatropic shifts.

[6] (a) Chauhan, Y. S.; Chandraratna, R. A. S.; Miller, D. A.; Kondrat, R. W.; Reischl, W.; Okamura, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 1028. (b) Okamura, W. H.; Peter, R.; Reischl, W. *J. Am. Chem. Soc.* **1985**, *107*, 1034. (c) Elnagar, H. Y.; Okamura, W. H. *J. Org. Chem.* **1988**, *53*, 3060.

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Table I.[a]

T^b		$E_a{}^c$	$\Delta H^{\ddagger c}$	$\Delta S^{\ddagger d}$	$\Delta G^{\ddagger e}$	log A^f
50.0–90.0	**5a**	20.5 ± 0.1	19.9 ± 0.1	−19.7 ± 0.3	25.8 ± 0.2	9.0 ± 0.1
50.0–90.0	**5b**	23.1 ± 0.1	22.4 ± 0.1	−16.2 ± 0.3	27.2 ± 0.2	9.7 ± 0.1
50.0–110.0	**6a**	20.9 ± 0.1	20.2 ± 0.1	−22.8 ± 0.2	27.0 ± 0.2	8.3 ± 0.1
70.0–130.0	**6b**	22.5 ± 0.1	21.8 ± 0.1	−21.5 ± 0.3	28.2 ± 0.2	8.6 ± 0.1

[a] The uncertainties are standard deviations. [b] Temperature range studied, °C. [c] kcal/mol. [d] cal/mol·K. [e] kcal/mol at 25 °C. [f] A, s^{-1}.

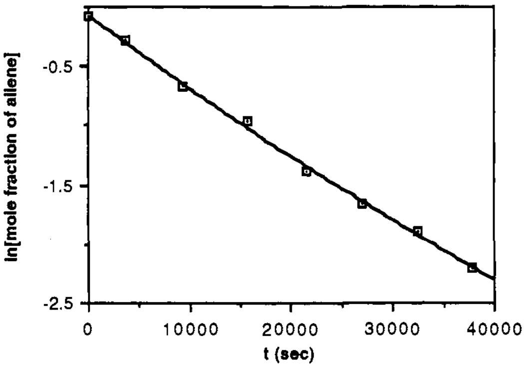

Figure 1. Thermolysis of the allene **6a** in benzene-d_6 followed over 3 half-lives at 90.0 °C.

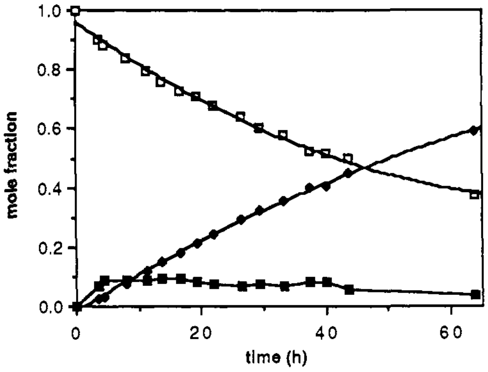

Figure 2. Action plot for the thermolysis of tetraene **9a**. The relative amounts of tetraenes **9a** (open squares) and **10a** (closed diamonds) and allene **6a** (closed squares) were followed over 3 days at 90.0 °C.

14 (major) plus **15** (minor) (Chart III),[4d,7] a detailed kinetic investigation of the rearrangement of **5** to **7** plus **8** and of **6** to **9** plus **10** [both in the unlabeled (**a**) and labeled (**b**) series] was carried out.

When the rate of disappearance of **6** (labeled or unlabeled) was followed for more than 1 half-life, a deviation from the expected irreversible, first-order behavior was noted. For example, Figure 1 depicts a typical plot of ln (mole fraction starting allene) versus time showing a negative slope with a noticeable upward curvature.[8a] A clue to the mechanistic scenario was obtained by individually heating the product tetraenes **9** and **10**. First, tetraene **10a** proved to be stable even after 20 h at 160 °C. Second, under similar conditions, **9a** was completely transformed into **10a**. Finally, in a separate experiment, when **9a** was heated at 90 °C, a mixture of **9a**, **10a**, and the dienallene **6a** was observed (76:14:10 ratio, respectively, after 13.5 h as judged by ^{1}H NMR integration). The action plot for this experiment is shown in Figure 2. The presence of **6a** (as well as labeled **6b** when **9b** was heated) was confirmed by its isolation from the reaction mixture in a preparative-scale experiment. The recovery of allene **6** by heating **9** can thus most simply be represented as a surprisingly facile sp^2 to sp^2 [1,7] sigmatropic hydrogen shift. Thus, what emerges is a new mechanistic pathway for cis–trans geometric isomerism. The presence of two large end groups attached to the polyene system probably facilitates the detection of **6** in the thermolysis of **9**, by attenuating their relative thermodynamic stabilities making possible the detection of allene **6** along this pathway. What is surprising is the observation that **10** is significantly more stable than **6** and **9**.

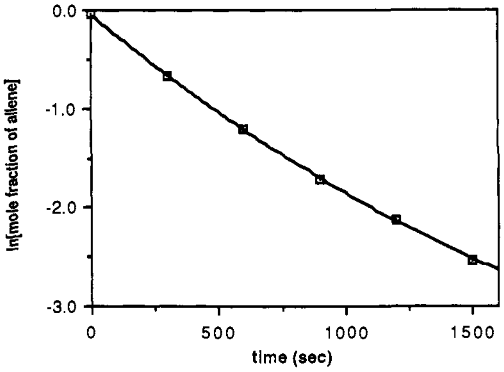

Figure 3. Thermolysis of the allene **5a** in benzene-d_6 followed over 5 half-lives at 110.0 °C.

When the rate of disappearance of **5** was followed for more than 1 half-life, as in the case of **6**, a similar deviation from the expected irreversible, first-order behavior was also noted. Figure 3 depicts a typical plot of ln (mole fraction starting allene) versus time. Other pertinent observations include the fact that the rate constant showed no change when the initial concentration of **5a** was varied from 0.04 M to 0.2 M, ruling out a second-order contribution.[8b] In addition, when trienes **7** and **8** were individually heated, they interconverted with one another (10% conversion after 10 h at 100 °C). Although the interconversion of **7** and **8** might be considered a direct cis to trans geometric isomerism of a terminal double bond, the kinetic behavior (Figure 3) was inconsistent with what was the assumed mechanism, namely, irreversible, competitive formation of **7** and **8** from **5**. Upon careful reexamination of both ^{1}H NMR spectra and HPLC data, we fully verified that allene **5** was absent during experiments involved in heating **7** or **8**. While the interconversion of **7** and **8** may involve a direct geometric isomerism, the observed curvature exhibited in Figure 3 cannot be explained by the intervention of this process.[9a] The

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(7) Shen, G.-Y. Ph.D. Thesis, University of California, Riverside, 1986.

(8) (a) The rate constant for the kinetic run at 90.0 °C shown in Figure 1 was 5.62 × 10^{-5} s^{-1} (±1.2 × 10^{-6}; correlation coefficient, 0.998) when all the data points are considered in the linear regression analysis. Considering only the first three points from Figure 1 (corresponding to less than 1 half-life), a value of ~6 × 10^{-5} s^{-1} can be estimated, in reasonable agreement with the value 5.46 × 10^{-5} s^{-1} extrapolated to 90.0 °C from the Arrhenius data. Thus, the difference between a simple irreversible first-order process and the pathway proposed herein is slight. For a classic example of this kind, see: Bateman, L. C.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1940**, 974. (b) The experimental rate constants for the thermolysis of **5a** at 65.0 °C were essentially the same over the 5-fold difference in concentration range studied [4.83 × 10^{-5} (0.04 M), 5.25 × 10^{-5} (0.08 M) and 5.00 × 10^{-5} (0.2 M)].

(9) (a) Reversible interconversion of **7** and **8** by way of two consecutive six-electron electrocyclizations will also not lead to the observed curvature (Figure 3). See, for example: Okamura, W. H.; de Lera, A. R.; Reischl, W. *J. Am. Chem. Soc.* **1988**, *110*, 4462, and references cited therein. (b) We are very grateful to two reviewers for critically analyzing the original version of this paper. Most significantly, our computations reveal that some allene should have been detected (up to 2–4%) in the interconversion of **7** and **8**. Several thermal experiments were repeated in an attempt to detect allene **5a** or some other species by heating **7a** for at least 5.5 h (100 °C), but neither HPLC nor ^{1}H NMR analysis revealed the presence of any allene (in contrast to the experiment depicted in Figure 2). The same result was obtained for **8a** (^{1}H NMR analysis). On prolonged heating however, a new, unidentified species was detected (after 9 h). The latter, which could not be obtained pure, continued to increase at the expense of **7a** and **8a** over a >3-week period (all at 100 °C). Thus, the curvature typified by that shown in Figure 3 can be explained by invoking a systematic flaw in our experimental sampling method (at longer reaction times) or by intervention of an as of yet undetected pathway that affects the mole fraction of allene **5a** present over time. See footnote 8b and the text for additional discussion.

observed rate data for **5a** to **7a** plus **8a** suggest that up to 4% **5a**[9b] should have been produced and therefore detected, but we were unable to detect the allene.[10,11] Thus, it is possible that another kinetically significant pathway analogous to that involved in the interconversion of **9** to **10** is involved in the interconversion of **7a** and **8a**, but we have been unable to verify this possibility (i.e., an sp^2 to sp^2 [1,5] sigmatropic hydrogen shift[10,11]). Nevertheless, the [1,7] sigmatropic shift results clearly demonstrate the intervention of the involvement of consecutive sp^2 to sp^2 hydrogen shifts in the geometric isomerization of **9** to **10**.

To obviate the problems caused by the reversibility in both systems, the kinetic studies were conducted over less than 1 half-life. The results are summarized in Table I (see the supplementary material for further details). The activation parameters for the [1,5] sigmatropic shift of **5a** are very similar to those reported previously for the vinylallene **13**.[4d] The diphenylphosphinoyl group is less effective at activating the [1,5]-shift than the phenylsulfinyl, as reflected by the smaller enhancement observed in the rate of the rearrangement when compared with the parent system **16** (relative rates for the [1,5]-shift of **16**/**5a**/**13**, 1:2.1:135 at 40 °C). The diphenylphosphinoyl group also exerts less control than the phenylsulfinyl over the facial selectivity of the reaction (*E*/*Z* ratio of 20:80 from **5a** as compared to a *E*/*Z* ratio of 2:98 from **13**).[12] For the [1,7] sigmatropic shift, the activation parameters are also similar to those reported by Baldwin for the thermolysis of **2** to give **1** and **3**.[1b] These results suggest that the diphenylphosphinoyl group does not effect a significant alteration in the mechanism of the [1,*n*] sigmatropic shift. As for the comparison between the two systems **5** and **6**, the [1,5] sigmatropic shift proved to be faster than the [1,7]-shift, and its primary kinetic isotope effect was also found to be more temperature dependent ($k_H/k_D = 12.4$ and 5.3 at 25 and 100 °C, respectively, for **5**; and 7.7 and 4.4 for **6** at the corresponding temperatures).

The values for ΔE_a, 2.5 kcal/mol for **5** and 1.6 kcal/mol for **6**, together with the corresponding values for A_H/A_D, 0.2 for **5** and 0.5 for **6**, to the extent that these parameters represent suitable criteria,[13] indicate a tunneling contribution in both systems. In light of previous isotope effect studies of [1,5] sigmatropic hydrogen shifts,[4] it seems that the temperature dependence of the k_H/k_D varies from system to system and even upon changes of substituents. There is at present a paucity of related information on [1,7]-shifts.[5]

Aside from a need for additional examples of kinetic isotope effect data for these hydrogen-transfer processes, further insight regarding the predilection of *simpler* hydrocarbon polyenes toward geometric isomerism via allene intermediates is desirable. Studies in the latter direction are under way.

Experimental Section

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-4,4-dimethyl-3-(diphenylphosphinoyl)-1,2-pentadiene (5a). To a solution of propargyl alcohol **11a** (1.00 g, 4.18 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (512 mg, 4.20 mmol) in THF (20 mL) was slowly added chlorodiphenylphosphine (1.00 g, 4.55 mmol) under a nitrogen atmosphere at 0 °C. The reaction mixture was stirred at room temperature for 4 h, quenched with water (5 mL), and extracted with ether (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and then concentrated under vacuum. The residue was subjected to column chromatography (silica gel, 40% EtOAc/hexanes) to afford **5a** (1.07 g, 60%) as an amorphous solid.

1-[3′,3′-Dideuterio-6′,6′-dimethyl-2′-(trideuteriomethyl)-1′-cyclohexen-1′-yl]-4,4-dimethyl-3-(diphenylphosphinoyl)-1,2-pentadiene (5b). This compound was prepared in the same manner as the protio allene **5a**, except that pentadeuterio propargyl alcohol **11b** reported previously[4d] was used to afford the labeled allene **5b** as an amorphous solid (60% yield).

(*Z*)-5-(Diphenylphosphinoyl)-3,6,6-trimethyl-1-(2′,6′,6′-trimethylcyclohex-1′-en-1′-yl)hepta-1,3,4-triene (6a). A solution of the propargylic alcohol **12a** (223 mg, 0.81 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (150 mg, 1.23 mmol) in ether (10 mL) was stirred at 0 °C under nitrogen. Chlorodiphenylphosphine (0.22 mL, 1.22 mmol) was added dropwise to the alcohol solution. The starting alcohol was completely consumed within 0.5 h as determined by ^{1}H NMR. The reaction mixture was stirred at room temperature for 3 h and then quenched with water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic layers were dried (Na_2SO_4) and filtered through a short column of silica gel (200–425 mesh) using 1:1 EtOAc/hexanes as eluant to remove solid material. Solvent evaporation under reduced pressure followed by vacuum drying on an oil pump afforded 315 mg (85%) of the allene **6a** as an oil.

(*Z*)-5-(Diphenylphosphinoyl)-3,6,6-trimethyl-1-[3′,3′-dideuterio-6′,6′-dimethyl-2′-(trideuteriomethyl)cyclohex-1′-en-1′-yl]hepta-1,3,4-triene (6b). This compound was prepared in the same manner as the unlabeled **6a** except that pentadeuterio propargyl alcohol **12b** was used to afford **6b** as an oil (72% yield).

(7*Z*)-9-(3′,3′-Dimethyl-1′-butynyl)-4,4,18,18,18-pentadeuterio-*β*-ionol (12b). This substance was prepared in the manner previously described[6] for unlabeled **12a** except that (7*E*)-9-(3′,3′-dimethyl-1′-butynyl)-4,4,18,18,18-pentadeuterio-*β*-ionol was used to afford **12b** as a clear oil, (82% yield).

Rates of Thermal [1,7] Sigmatropic Rearrangement of (*Z*)-5-(Diphenylphosphinoyl)-3,6,6-trimethyl-1-(2′,6′,6′-trimethylcyclohex-1′-en-1′-yl)hepta-1,3,4-triene (6a). The general procedure for the kinetic studies was followed by integrating the ^{1}H NMR (benzene-d_6) proton resonances of one or both of the *gem*-dimethyl groups corresponding to the starting material and the rearranged products. These appear at 1.03 ppm for the starting dienallene **6a**, 1.14 ppm for the *ZZZ* isomer **9a** and 1.11 ppm for the *ZZE* isomer **10a**.

For spectral characterization of the individual tetraene products, samples from the kinetic runs were combined and concentrated and then the residue was subjected to HPLC separation (Whatman Partisil M9 10/50 column, 50% EtOAc/hexanes, 4.0 mL/min). The elution order was as follows: *ZZZ* isomer **9a** (less polar isomer A) and a mixture of *ZZE* isomer **10a** (more polar isomer B) and starting dienallene **6a**. After recycling to separate the remaining vinylallene from the *ZZE* isomer (the latter eluted first), both tetraenes were obtained pure. The ratio of *ZZE* isomer **10a** to *ZZZ* isomer **9a** varied from 61:39 to 52:48 over the temperature range studied.

Rates of Thermal [1,7] Sigmatropic Rearrangement of (*Z*)-5-(Diphenylphosphinoyl)-3,6,6-trimethyl-1-[3′,3′-dideuterio-6′,6′-dimethyl-2′-(trideuteriomethyl)cyclohex-1′-en-1′-yl]hepta-1,3,4-triene (6b). The general procedure for the kinetic studies was followed by integrating (^{1}H NMR, benzene-d_6) the proton resonances of one or both of the *gem*-dimethyl groups corresponding to the starting material and the rearranged products. These appear at 1.03 ppm for the starting dienallene **6b**, 1.14 ppm for the *ZZZ* isomer **9b** and 1.11 ppm for the *ZZE* isomer **10b**.

For spectral characterization, the two rearranged tetraenes were obtained by HPLC purification of samples from the kinetic runs (Whatman Partisil M9 10/50 column, 50% EtOAc/hexanes, 4 mL/min). The elution order was as follows: *ZZZ* isomer **9b** (less polar isomer A) and a mixture of *ZZE* isomer **10b** (more polar isomer B) and starting dienallene **6b**. After recycling to separate the remaining *ZZE* from the dienallene (*ZZE* isomer eluted first), both tetraenes were obtained pure. The ratio of *ZZE* isomer **10b** to *ZZZ* isomer **9b** varied from 59:41 to 55:45 over the temperature range studied.

Rates of Thermal [1,5] Sigmatropic Rearrangement of 1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-4,4-dimethyl-3-(diphenylphosphinoyl)-1,2-pentadiene (5a). The general procedure for the kinetic studies was followed by integrating the ^{1}H NMR (benzene-d_6) proton resonances of the *gem*-dimethyl groups corresponding to the starting material and the rearranged products. These appear at 0.67 and 0.79 ppm for the starting vinylallene **5a**, 0.48 ppm for the *ZZ* isomer **7a**, and 1.06 ppm for the *ZE* isomer **8a**.

For spectral characterization of the individual rearranged triene products, samples from the kinetic runs were combined and concentrated and then the residue was subjected to HPLC separation (Whatman

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(10) For examples of thermal sp^2 to sp^2 [1,5] hydrogen shifts that have been proposed, see: Bilinski, V.; Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1986**, *69*, 1734. Scott, L. T.; Erden, I. *J. Am. Chem. Soc.* **1982**, *104*, 1147. See also: Smit. A.; Kok, J. G. J.; Geluk, H. W. *J. Chem. Soc., Chem. Commun.* **1975**, 513.

(11) For examples of photochemically induced sp^2 to sp^2 [1,5] sigmatropic hydrogen shifts, see: (a) Bakker, S. A.; Lugtenburg, J.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1459. (b) Havinga, E. *Experientia* **1973**, *29*, 1181, and the references cited therein.

(12) In our reported study of the rate of rearrangement of **13** to **14** plus **15** (ref 4d), it was determined that **14** and **15** did not interconvert with one another under the conditions used for the rate study. The trienes **14** and **15** were not heated at higher temperatures.

(13) See the discussion in ref 1b,c and 4d and the following: Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 144, 157.

Partisil M9 10/50 column, 50% EtOAc/hexanes, 4.0 mL/min). The elution order was as follows: vinylallene **5a**, then the *ZZ* isomer **7a** (less polar isomer A), followed by *ZE* isomer **8a** (more polar isomer B). The ratio of *ZZ* isomer **7a** to *ZE* isomer **8a** varied from 84:16 to 78:22 over the temperature range.

Rates of Thermal [1,5] Sigmatropic Rearrangement of 1-[3′,3′-Dideuterio-6′,6′-dimethyl-2′-(trideuteriomethyl)-1′-cyclohexen-1′-yl]-4,4-dimethyl-3-(diphenylphosphinoyl)-1,2-pentadiene (5b). The general procedure for the kinetic studies was followed by integrating the proton resonances (^{1}H NMR, benzene-d_6) of the *gem*-dimethyl groups corresponding to the starting material and the rearranged products. These appear at 0.67 and 0.79 ppm for the starting vinylallene **5b**, 0.48 ppm for the *ZZ* isomer **7b**, and 1.06 ppm for the *ZE* isomer **8b**.

For spectral characterization of the individual rearranged triene products, samples from the kinetic runs were combined and concentrated and then the residue was subjected to HPLC purification (Whatman Partisil M9 10/50 column, 50% EtOAc/hexanes, 4 mL/min). The elution order was as follows: vinylallene **5b**, then the *ZZ* isomer **7b** (less polar isomer A) and the *ZE* isomer **8b** (more polar isomer B). The ratio of *ZZ* isomer **7b** to *ZE* isomer **8b** varied from 83:17 to 79:21 over the temperature range.

Thermolysis of the Rearranged Products. Control Experiments. (2-(1′)*Z*,2′*Z*,4′*Z*)-1,1-Dimethyl-2-[5′-(diphenylphosphinoyl)-3′,6′,6′-trimethyl-2′,4′-heptadienylidene]-3-methylenecyclohexane (9). A sample of *ZZZ*-tetraene **9a** was subjected to the same conditions as in the kinetic studies. The sample was heated at 90 °C and the reaction was followed by ^{1}H NMR. After 13.5 h, a mixture of *ZZZ*-tetraene **9a** (~76%), *ZZE*-tetraene **10a** (~14%), and a third component (~10%) identical by ^{1}H NMR with the starting dienallene **6a** was observed. To fully characterize the compounds obtained in this control thermolysis experiment, the same experiment was conducted on a semipreparative scale. The *ZZZ*-tetraene **9a** (240 mg) was heated (90 °C, benzene as solvent, sealed tube) as in the ^{1}H NMR experiment, and after 20 h, the solvent was removed and the residue was purified by HPLC (Dynamax Macro column, 40% EtOAc/hexanes, 8 mL/min). The fraction containing a mixture of *ZZE*-tetraene **10a** and allene **6a** was concentrated and reinjected onto the HPLC (Whatman Partisil M9 10/50 column, 50% EtOAc/hexanes, 4 mL/min). A sample was obtained which proved to be spectroscopically (^{1}H NMR, IR) identical with the starting allene **6a**.

(2(1′)*Z*,2′*Z*,4′*E*)-1,1-Dimethyl-2-[5′-(diphenylphosphinoyl)-3′,6′,6′-trimethyl-2′,4′-heptadienylidene)-3-methylenecyclohexane (10a). A sample of *ZZE*-tetraene **10a** was subjected to the same conditions as in the kinetic studies. After 20 h at 90 °C, no change was observed in the ^{1}H NMR spectrum of the sample. The *ZZE*-tetraene **10a** proved to be thermally stable even after 20 h at 160 °C.

(2(1′)*Z*,2′*E*)-1,1-Dimethyl-3-methylene-2-[4′,4′-dimethyl-3′-(diphenylphosphinoyl)-2′-pentenylidene]cyclohexane (8a). A sample of *ZE*-triene **8a** was heated at 100 °C under the same conditions as in the kinetic studies. After 1.5 h, a new set of signals corresponding to the *ZZ* isomer **7a** was observed. No changes other than the formation of *ZZ* isomer **7a** were apparent over a 10-h period as determined by ^{1}H NMR (ratio *ZE*/*ZZ*, 91:9).

(2(1′)*Z*,2′*Z*)-1,1-Dimethyl-3-methylene-2-[4′,4′-dimethyl-3′-(diphenylphosphinoyl)-2′-pentenylidene]cyclohexane (7a). A sample of *ZZ*-triene **7a** was subjected to the same conditions as in the kinetic studies. No change was apparent in the ^{1}H NMR spectrum after 1.5 h at 100 °C. After 1.5 h, a small amount of *ZE* isomer **8a** was observed. The thermolysis was followed for 5.5 h, and no species other than the two components (ratio *ZZ*/*ZE*, 90:10) were observed during this period of time.

Thermolysis of Allene 6a. Preparation of (2(1′)*Z*,2′*Z*,4′*Z*)-9a (Isomer A) and (2(1′)*Z*,2′*Z*,4′*E*)-1,1-Dimethyl-2-[5′-(diphenylphosphinoyl)-3′,6′,6′-trimethyl-2′,4′-heptadienylidene]-3-methylenecyclohexane (10a; Isomer B). Allene **6a** (30 mg) was dissolved in benzene (15 mL) and heated under a nitrogen atmosphere for 27 h. The solvent was evaporated under reduced pressure, and HPLC purification of the resulting residue (Whatman Partisil column, 40% EtOAc/SSB) led to separation of two geometrically isomeric tetraenes. The less polar compound **9a** (isomer A, characterized as the 4′*Z* compound) was obtained as the minor isomer (11 mg, 37%) and the more polar compound **10a** (isomer B, identified as the 4′*E* compound) as the major isomer (17 mg, 57%) (total yield, 94%). A trace of the starting allene was also recovered (eluted third).

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Supplementary Material Available: Spectral and kinetic data for **5a,b-10a,b** and **12** (10 pages). Ordering information is given on any current masthead page.

Synthesis of (Sulfodifluoromethyl)phosphonic Acid

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Abstract: (Sulfodifluoromethyl)phosphonic acid, $(HO)_2P(O)CF_2SO_3H$, has been synthesized for the first time. This mixed phosphonic–sulfonic acid was prepared from $(C_2H_5O)_2P(O)CF_2SO_3Na$, which had been synthesized via oxidation of the corresponding sulfinate salt, $(C_2H_5O)_2P(O)CF_2SO_2Na$. The sulfinate salt was prepared from $(C_2H_5O)_2P(O)CF_2X$ (X = Br, I) and $[(C_2H_5O)_2P(O)CF_2SO_2]_2Cd$ precursors.

The incorporation of fluorine into organic compounds has a significant effect on the acidity of the resultant molecule. When the initial substrate is an acid, such as a carboxylic, sulfonic, or phosphonic acid, the acidity is increased several orders of magnitude, and the perfluorinated acid analogues are some of the strongest organic acids known. Acids, such as trifluoroacetic acid and triflic acid, have also become important products of commerce, and derivatives of the longer chain analogues are utilized industrially as surfactants and fabric treatment agents. Although not investigated as extensively as the carboxylic or sulfonic acids, the perfluoroalkanephosphonic acids have recently attracted attention as biological chelating agents[2] and electrolytes.[3]

Mixed analogues, such as $HO_2CCF_2SO_3H$ and $(HO)_2P(O)CF_2COOH$ have also been prepared.[4] However, the parent phosphonic–sulfonic acid analogue, $(HO)_2P(O)CF_2SO_3H$, has thus

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