Substituent Effect Studies on the Thermal [1,5]-Sigmatropic Hydrogen Shifts of Vinylallenes[1]

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Abstract: The vinylallenes **13** were synthesized, and the competitive thermal [1,5]-sigmatropic hydrogen shifts of **13** to **14** plus **15** as a function of various allene end groups (**13a–i**; H, alkyl, and sulfur substituents) were investigated. The presence of the phenylsulfinyl group (**13a–e**) at the allene terminus was determined not only to exert an accelerating effect on their [1,5] hydrogen shifts but also to effect control of π-facial geometric stereoselection in these triene syntheses. In the series **13a–e**, the bulkier the R group the greater the observed selectivity (3/1 to >98/2 favoring **15a–e**). The kinetic results for **13f–i** and **13a** (both diastereomers) indicate that their relative rates for [1,5]-shifts parallel the electron-withdrawing nature of the substituent (SO_2Ph > SOPh > SPh > H or *t*-Bu), but only the sulfoxide (phenylsulfinyl) group exerts significant π-facial selectivity. Kinetic studies of the [1,5]-shifts performed on several selected vinylallene derivatives to determine activation parameters, solvent effects, and kinetic isotope effects (KIE's) reveal results similar to those for classical nonallenic systems. For example, the two diastereomeric sulfoxides of **13a** and their isotopically labeled counterparts **21b** rearrange with primary deuterium KIE's (k_H/k_D) of 7.5–8.4 at 40 °C. The temperature-dependent KIE's of unlabeled **13g** and labeled **21c** were determined over a ca. 50 °C temperature range (between ~40 and 115 °C). When the data were extrapolated to 25 °C, a large k_H/k_D of 12.8 could be calculated. This value is similar to the k_H/k_D value of 12.2 reported by Roth and König for the parent *cis*-1,3-pentadiene, and in fact, there is a striking parallel between the results described here and Roth and König's results over the entire temperature range from room temperature to 200 °C.

Vinylallenes are useful in organic synthesis,[2,3] and they undergo a variety of pericyclic processes[4] that are of mechanistic and theoretical interest. In addition, the vinylallene moiety is a structural component of several unusual natural products.[3] Recently, we were able to establish the efficacy of utilizing a [1,5]-sigmatropic shift of a vinylallene as a key step in the synthesis of the 1α-hydroxyvitamin D analogue **1** and 11-*cis*-vitamin A (**2**) (Chart I).[2]

Thermal [1,5]-sigmatropic rearrangements of nonallenic pentadienyl systems are well-known (**3** $\rightleftarrows$ **4**) (Chart II).[5] The simplest case of a [1,5]-shift was studied through isotopic labeling by Roth and König[6] in (*Z*)-1,3-pentadiene itself. A large primary deuterium kinetic isotope effect of 12.2 at 25 °C was observed for this process, consistent with a highly symmetrical transition state in a concerted process. The activation energy for [1,5]-migration in acylic pentadienes is in the range 30–36 kcal/mol.[5] In comparison, only about 24 kcal/mol is required for the vinylallene to undergo the analogous process **5** → **6**.[7] Translating these activation energies into synthetic terms, typical reaction temperatures for rearranging 1,3-pentadienes of the type **3** range from 250 to 300 °C, whereas approximately 100 °C is required for isomerizing simple vinylallenes related to **5**. These milder reaction conditions render the vinylallene approach highly attractive for synthesizing thermally labile biological polyenes such as vitamins D and A.

The rearrangement of vitamin D type vinylallenes (typified by **7** in which L and S correspond to the CD hydrindane fragment of the steroid) has been studied extensively in this laboratory,[2] and numerous analogues of vitamin D of biological interest have emerged with this methodology (Chart III).[8] It should be noted

Chart I

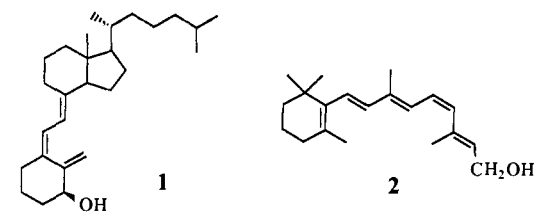


Chart II

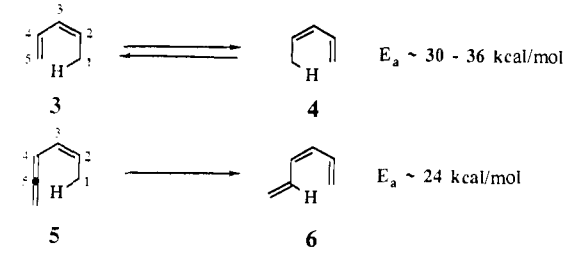


Chart III

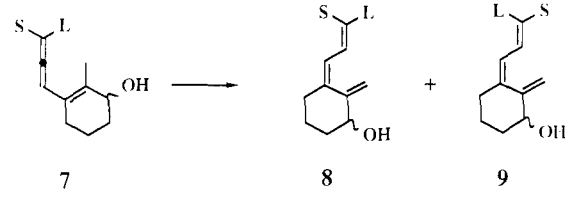
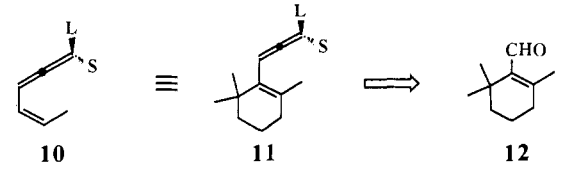


Chart IV



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(2) Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81.
(3) Egenburg, I. Z. *Russ. Chem. Rev. (Engl. Transl.)* **1978**, *47*, 470.
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(5) The [l,j]-sigmatropic rearrangement has been reviewed by: (a) Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187. (b) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103. (c) Gajewski, J. J. In *Mechanisms of Molecular Migrations*; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 4, pp 1–54. (d) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981.
(6) (a) Roth, W. R.; König, J. *Justus Liebis Ann. Chem.* **1966**, *699*, 24. (b) Roth, W. R.; König, J.; Stein, K. *Chem. Ber.* **1970**, *103*, 426.
(7) (a) Skattebøl, L. *Tetrahedron* **1969**, *25*, 4933. (b) Barrack, S. A.; Okamura, W. H. *J. Org. Chem.* **1986**, *51*, 3201. (c) Heimgartner, H.; Zsindely, J.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2924.

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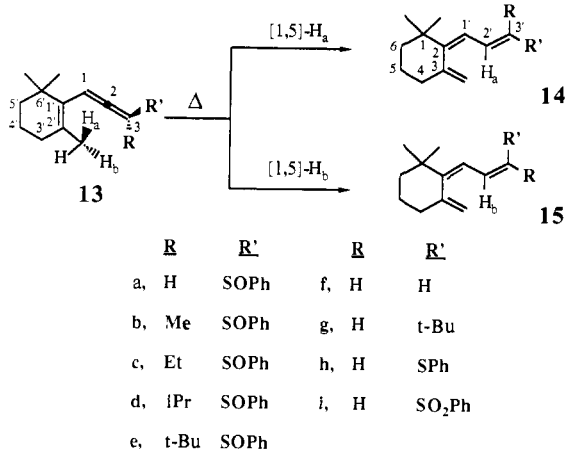
Scheme I



	R	R'		R	R'
a,	H	SOPh	f,	H	H
b,	Me	SOPh	g,	H	t-Bu
c,	Et	SOPh	h,	H	SPh
d,	iPr	SOPh	i,	H	SO_2Ph
e,	t-Bu	SOPh			

that the [1,5]-shift (assuming suprafacial trajectories[6b]) can lead to two possible geometric isomers **8** and **9**, differing in configuration about the double bond bearing the L and S groups. Interestingly, the configurational orientation of the seemingly remote allylic hydroxyl group in **7** controls the ratio of products (**8** versus **9**) formed.[7b,8] The nature of L and S (usually alkyl groups or hydrogen) did not appear to have a significant effect on product geometry. Because of this unusual selectivity, a study was directed toward evaluating in greater detail the effect of the groups on the allene terminus (L and S) on these competing pathways. Accordingly, studies of vinylallenes of the type **10** lacking the allylic hydroxyl were desirable. The β-cyclocitral (**12**) derived system **11** was chosen for study as a model for prototype **10** (Chart IV).

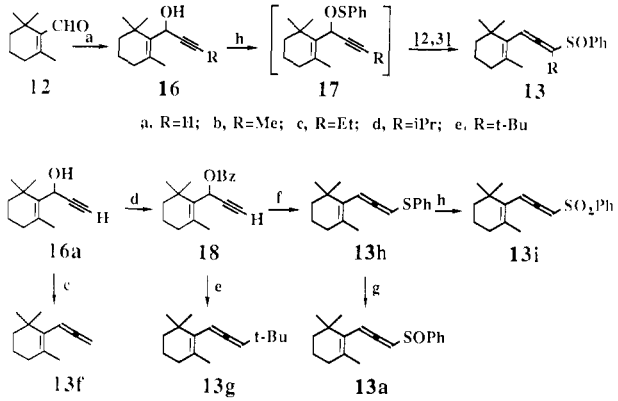
In the preliminary report,[1] we described the syntheses of vinylallenes **13a–i** and their thermal isomerization at 40.0 °C (Scheme I). It was found that in the thermal rearrangement of **13** to **14** plus **15** the sulfoxide substituent not only exerts an acceleration of the [1,5]-shift but also can effect control of π-facial stereoselection in these triene syntheses. For the sulfoxides **13a–e**, the ratio of **15** to **14** was found to vary from **4**:1 to >98:2 as the size of the R group was increased (H, Me, Et, *i*-Pr, *t*-Bu). That is, path H_b in Scheme I was favored. In striking contrast, alkyl, sulfide, and sulfone substituents on the allene, as in **13g–i**, respectively, imparted little selectivity on the competing trajectories, H_a versus H_b in Scheme I. The remarkable influence of the sulfoxide substituent (the phenylsulfinyl group) on the course of this classical pericyclic process encouraged more detailed investigations.

It is the purpose of this article to describe the complete experimental details of the preliminary report[1] on isomerization of **13** to **14** plus **15** and also to report on new experiments. Most notably, a comprehensive kinetic study of the isomerization processes involving **13a–i** as shown in Scheme I, including a temperature dependence kinetic isotope effect (TDKIE) study of **13g** and its deuteriated derivative, is described.

Results and Discussion

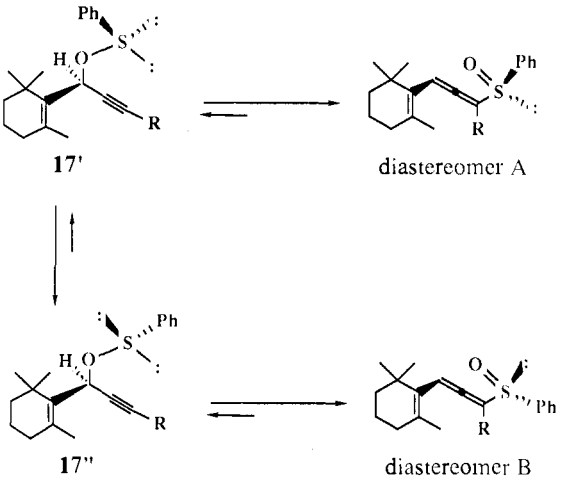
Preparation of Vinylallenes and Structural Characterization of Their Thermally Rearranged Products. The syntheses of the vinylallenes **13a–i** utilized in this stereochemical and kinetic investigation are shown in Scheme II. Reaction of β-cyclocitral (**12**) with the corresponding lithium acetylides (RC_2Li)[9] gave the propargyl alcohols **16a–e** in excellent yields (>90%). The propargyl alcohols **16** were then treated with PhSCl[10] in the presence of Et_3N in THF at −78 °C and warmed to room temperature to afford, after standing at room temperature for approximately 10 h, the completely isomerized triene sulfoxides **14a–e** and **15a–e** (Scheme I). Each triene was separated and characterized as described below. By processing the phenylsulfenyl chloride reactions (Scheme II) at or below room temperature, each vinylallene sulfoxide **13a–e** could be isolated and characterized and shown to rearrange to the corresponding **14** and **15**. Each of the five vinylallene sulfoxides formed in the [2,3]-sigmatropic shift process (**17** → **13** in Scheme II) exists as diastereomeric pairs, which are separable by HPLC. Small amounts of the rearranged products (**14a–e** and **15a–e**) were also isolated during the HPLC purification of the vinylallene sulfoxides **13a–e**.

Scheme II[a]



[a] Reagents and conditions: (a) RC_2Li, THF, −78 °C; (b) PhSCl, Et_3N, THF, −78 °C; (c) 3:1 $LiAlH_4$:$AlCl_3$, ether; (d) *n*-BuLi, PhCOCl, ether, −4 °C; (e) $(t\text{-Bu})_2Cu(CN)Li_2$, ether, −78 °C; (f) $PhSCuP(OMe)_3$, LiBr, THF; (g) 1 equiv of *m*-CPBA, CH_2Cl_2, −20 °C; (h) 2 equiv of *m*-CPBA, CH_2Cl_2, −20 °C.

Scheme III



The two diastereomeric vinylallene sulfoxides (labeled throughout as less polar diastereomer A and more polar diastereomer B) were found to be formed in unequal amounts (**13a**, A/B = 1/8; **13b**, A/B = 1/22; **13c**, A/B = 1/22; **13d**, A/B = 1/18; **13e**, A/B = 2/1). As to a rationale for this diastereoselectivity, it is hypothesized that the [2,3]-sigmatropic shift of the sulfenate

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(10) (a) Cinquini, M.; Colonna, S.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 256. (b) Cinquini, M.; Colonna, S.; Cozzi, F.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2061. (c) Horner, L.; Binder, V. *Justus Liebigs Ann. Chem.* **1972**, *757*, 33. (d) Braverman, S.; Stabinsky, Y. *Isr. J. Chem.* **1967**, *5*, 125. (e) Smith, G.; Stirling, C. J. M. *J. Chem. Soc. C* **1971**, 1530. (f) Bickard, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869. (g) Tang, R.; Mislow, K. *Ibid.* **1970**, *92*, 2100. (h) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (i) Van Rheenen, V.; Shephard, P. K. *J. Org. Chem.* **1979**, *44*, 1582.

ester **17** (Scheme II) occurs preferentially as shown in Scheme III via the less hindered conformation **17″** to give the major isomer B; the hindered conformation **17′** leads to the minor isomer A. Note that in **17′** the phenyl and the β-ionylidene ring are syn to one another (more hindered), but in **17″** these two groups reside in a less hindered anti arrangement. The [2,3]-sigmatropic rearrangement that occurs via a transition state corresponding to **17′** should give the minor vinylallene sulfoxide isomer A. Similarly, the transition state corresponding to **17″** should give the major isomer B. Whether the A and B series of diastereomers correspond in their relative configuration to those depicted in Scheme III is not known however.

For **17a–c**, where R equals H, Me, and Et, the [1,5]-shift proved faster (vide infra) than the reverse [2,3]-shift, which would have otherwise resulted in interconversion of diastereomers B and A (Scheme III), a process well-known for optically active allenyl sulfoxides.[10a,b] In the case where R equals *i*-Pr (**13d**), [1,5]- and [2,3]-sigmatropic shifts are competitive to some extent (diastereomer A of **17d** is detectable by NMR during thermolysis of pure diastereomer B of **17d**). And when R equals *t*-Bu (**13e**), the reversible [2,3]-shift (Scheme III) is faster than the [1,5]-shift. Thus, except for the *t*-Bu case (**13e**), the selectivity of formation of diastereomer B is high (A/B, 1/8–1/22).

Other vinylallenes of the general structure **13** such as the hydrocarbons **13f** and **13g** and the sulfur oxidation state derivatives **13h** and **13i** were synthesized as shown in Scheme II above. Reduction of the propargyl alcohol **16a** with 3/1 of $LiAlH_4/AlCl_3$ in dry ether at room temperature gave the vinylallene **13f**.[11] Conversion of the benzoate **18** (prepared from **16a** in 82% yield) into the *t*-Bu-substituted vinylallene **13g** could be accomplished in 89% yield via a S_N2' type reaction with $(t\text{-Bu})_2Cu(CN)Li_2$[12] in ether at −78 °C.

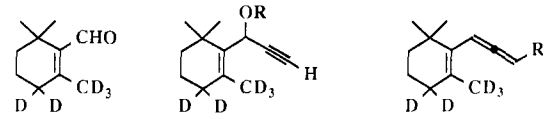
The synthesis of sulfide **13h** was accomplished in 96% yield by treating the benzoate **18** with $PhSCuP(OMe)_3$ and LiBr in THF.[13] Oxidation of the vinylallene sulfide **13h** with 1 equiv of MCPBA afforded the separable vinylallene sulfoxide distereomers **13a** (diastereomer ratio A/B = 1/1.3), while the use of 2 equiv of MCPBA gave the vinylallene sulfone **13i**.

The hydrocarbon allenes **13f** and **13g** could be obtained pure. However, all the sulfur-substituted vinylallenes prepared as described above and then purified by HPLC were contaminated with varying amounts of the corresponding [1,5] hydrogen shifted products **14** plus **15**. Nevertheless, the spectral data together with their thermal behavior provided ample evidence for the assigned allenic structures **13a–i**. The spectral data for these substances are given in detail as supplemental material. Although most of the sulfur-substituted vinylallenes were contaminated to varying extents by [1,5]-shifted products, the irreversible first-order kinetic behavior of these allenes facilitated the kinetic analysis.

The stereochemistry about the terminal double bond in **14a** and **15a** (Scheme I) was established by comparison of their ^1H NMR vicinal coupling constants (between H_2' and H_3'). The isomer **15a** exhibits a smaller coupling constant ($J \sim 9.3$ Hz) than does **14a** ($J \sim 15.1$ Hz), and they are therefore assigned as the 2(1′),2′-*ZZ* and 2(1′),2′-*ZE* isomers, respectively. The geometry of **15e** was confirmed indirectly. The *tert*-butyl derivative **15e** was desulfurized [$Ni(acac)_2$/*i*-PrMgCl/THF][14] in 41% yield to a single hydrocarbon identified as 2(1′),2′-*ZE* isomer **14g**, which exhibits $J_{2',3'} \sim 15.6$ Hz, while the 2(1′),2′-*ZZ* isomer **15g** (analyzed by ^1H NMR as the mixture of **14g** and **15g** obtained from thermolysis of hydrocarbon **13g** described below) exhibits $J_{2',3'} \sim 11.7$ Hz. It has been established in many cases that desulfurization under similar conditions occurs with retention of configuration at the sulfur-bearing carbon.[14] The geometric assignments of the remaining trienes (**14b–d** and **15b–d**) were then based on comparison of the chemical shifts of their vinylic protons H_1' and H_2' with those of **14a**, **15a**, **14e**, and **15e** (see Table VII in the supplementary material).[15] Finally, the *Z* geometry of the central $\Delta^{2(1')}$ double bond of **14** and **15** was assigned on the basis of their mode of formation via the [1,5]-sigmatropic hydrogen shift.

For the kinetic isotope effect (KIE) studies, the deuteriated vinylallenes **21** were prepared according to the synthetic sequences described in Scheme II. The pentadeuterio-β-cyclocitral (**19**), which is readily available from the base-catalyzed hydrogen–deuterium exchange of β-cyclocitral itself,[16] was used as the starting material (Chart V). The pentadeuteriovinylallene sulfoxides **21b** (both diastereomers in an A/B ratio of 1/1.2) were obtained in four steps (**19** → **20a** → **20b** → **21a** → **21b**) in an overall yield of 37%. Unlike the unlabeled vinylallenes **13a** (diastereomers A and B), the ^1H NMR spectra of the deuteriated vinylallenes **21b** (A and B) show no contamination by rearranged products. This greater stability is ascribed to the slower [1,5]-shift

Chart V



19 **20 a**, R = H; **b**, R = Bz **21** a, R = SPh; b, R = SOPh; c, R = t-Bu

Table I. Relative Rates for Thermal Rearrangement of Monosubstituted Vinylallenes

entry	compd	$\tau_{1/2}$,[a,b] min	k_{rel}	ratio of **15**/**14**
1	**13f**	5010 ± 80	1	
2	**13g**	6780 ± 180	0.74	39/61
3	**13h**	123 ± 3	41	50/50
4	**13a**[c]	38.5 ± 1.8	131	75/25
5	**13a**[d]	48.3 ± 0.7	104	82/18
6	**13i**	7.0 ± 0.1	717	53/47

[a] Determined at 40.0 ± 0.1 °C in benzene-d_6. [b] The uncertainties are absolute deviations. [c] Diastereomer A, less polar isomer. [d] Diastereomer B, more polar isomer.

Table II. Relative Rates and Geometric Selectivity for Thermal Rearrangement of the Sulfoxide-Substituted Vinylallenes

entry	compd	$k \times 10^4$,[a] s^{-1}	k_{rel}	ratio of **15**/**14**
1	**13a**	2.39	1.0	82/18
2	**13b**	3.39	1.4	92/8
3	**13c**	2.58	1.1	92/8
4	**13d**	2.50	1.0	93/7
5	**13e**	3.17	1.3	>98/2[b]

[a] Determined at 40.0 ± 0.1 °C in benzene-d_6 for diastereomer B in all cases. [b] No **14e** was detected from ^1H NMR.

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Table III. Activation Parameters for the Thermal [1,5]-Sigmatropic Hydrogen Shift of Vinylallenes **13a**, **13g**, **13h**, and **13i** in Benzene-d_6 Compared at 40 °C[a]

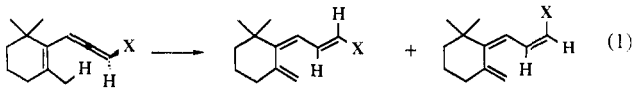
T,[b] °C		E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol·K)	$\Delta G^{\ddagger}$, kcal/mol	log A, s^{-1}
35.0–49.3	**13a**[c] → **14a**	20.2 ± 0.5	19.5 ± 0.5	−15.1 ± 0.4	24.3 ± 0.6	9.9 ± 0.3
	13a → **15a**	19.4 ± 0.3	18.7 ± 0.3	−15.4 ± 0.3	23.6 ± 0.4	9.9 ± 0.2
35.0–49.3	**13a**[d] → **14a**	19.8 ± 0.3	19.2 ± 0.3	−17.4 ± 0.2	24.6 ± 0.3	9.4 ± 0.1
	13a → **15a**	19.9 ± 0.6	19.2 ± 0.6	−14.2 ± 0.4	23.7 ± 0.7	10.1 ± 0.3
40.0–100.0	**13g** → **14g**	22.1 ± 0.8	21.5 ± 0.8	−17.1 ± 0.6	26.9 ± 1.0	9.5 ± 0.3
	13g → **15g**	22.7 ± 0.7	22.0 ± 0.7	−16.4 ± 0.5	27.1 ± 0.9	9.7 ± 0.3
40.0–53.9	**13h** → **14h**	22.2 ± 0.7	21.6 ± 0.7	−9.6 ± 0.3	24.6 ± 0.8	11.2 ± 0.4
	13h → **15h**	22.8 ± 0.9	22.2 ± 0.8	−7.6 ± 0.3	24.6 ± 0.9	11.6 ± 0.4
28.4–40.0	**13i** → **14i**	20.3 ± 1.4	19.7 ± 1.4	−9.9 ± 0.7	22.8 ± 1.6	11.1 ± 0.8
	13i → **15i**	19.8 ± 1.7	19.2 ± 1.6	−11.3 ± 1.0	22.7 ± 1.9	10.8 ± 0.9

[a] The uncertainties are standard deviations. [b] Temperature range studied. [c] Diastereomer A, less polar isomer. [d] Diastereomer B, more polar isomer.

of the deuteriated materials rendering them easier to handle. The deuteriated *tert*-butylvinylallene hydrocarbon **21c** was prepared by *tert*-butylation of the benzoate **20b** using $(t\text{-Bu})_2(CN)Li_2$[12] in an overall yield of 72% from **19**.

Relative Rates at 40.0 °C and Geometric Selectivities for the Thermal Rearrangement of Vinylallenes. For each kinetic run, the appropriate vinylallene was thermolyzed separately as 0.05–0.2 M solutions in benzene-d_6 (or other solvents) in NMR tubes or sealed ampules. In each case, the reaction was monitored for the disappearance of starting material and formation of products by ^1H NMR. Irreversible first-order kinetic behavior was observed in every case, and the product ratios from the thermolyses were also determined to ascertain that this ratio was invariant during each kinetic run. Moreover, in selected cases, the individually purified triene products were shown to be stable to the conditions of the kinetic runs. The detailed procedures and kinetic results are presented in the Experimental Section and the supplementary material. The most pertinent comparisons of the data are summarized in Tables I and II.

Table I compares the relative rates for thermal rearrangement of monosubstituted vinylallenes as depicted in eq 1 in which X is varied from H, *t*-Bu, SPh, SOPh (diastereomers A and B), to SO_2Ph. The data in Table I reveal the following: (a) The sulfur

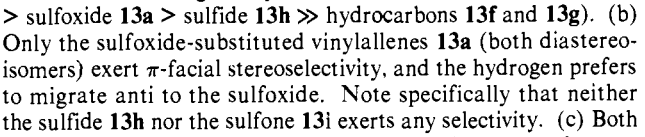


(1)

13a,f-i **14a,f-i** **15a,f-i**

substituents markedly accelerate the [1,5] hydrogen shift relative to hydrocarbon substituents, and the acceleration follows the electron-withdrawing ability order of the substituents (sulfone **13i** > sulfoxide **13a** > sulfide **13h** ≫ hydrocarbons **13f** and **13g**). (b) Only the sulfoxide-substituted vinylallenes **13a** (both diastereoisomers) exert π-facial stereoselectivity, and the hydrogen prefers to migrate anti to the sulfoxide. Note specifically that neither the sulfide **13h** nor the sulfone **13i** exerts any selectivity. (c) Both diastereomers A and B of sulfoxide **13a** show similar reaction rate and stereoselectivity, showing that sulfur chirality has a negligible effect on the reaction.

Table II compares the relative rates and geometric selectivities for the thermal rearrangement of sulfoxide-substituted vinylallenes as depicted in eq 2. Diastereomers B are compared in each case

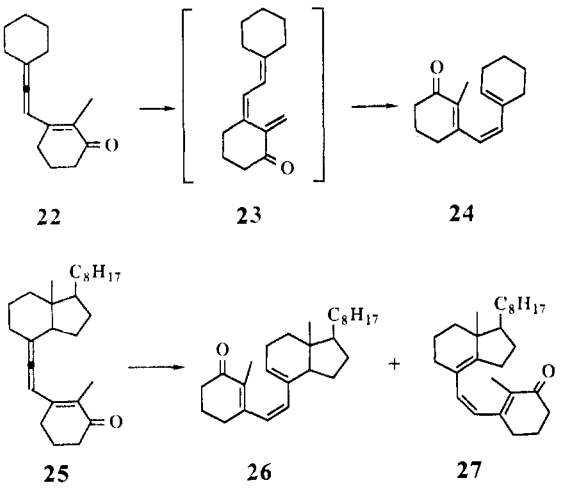


(2)

13a-e **14a-e** **15a-e**

in which one of the substituents is a phenylsulfinyl group and the other substituent R is varied from H, Me, Et, *i*-Pr, to *t*-Bu. The data in Table II reveal the following: (a) It is significant that the rate of isomerization for each sulfoxide is essentially the same, irrespective of the size of the R group, and the major product is always the *ZZ* isomer **15**. (b) As the size of the alkyl group increases, the π-facial selectivity increases. Thus, the ratio increases from 82/18 for the parent case (R = H) to >98/2 for the bulkiest alkyl group case (R = *t*-Bu).

Scheme IV



22 **23** **24**

25 **26** **27**

Further Mechanistic Studies. Prior to the present study, only the earliest investigations of Skattebøl (vide supra),[7a] the studies of *o*-arylallenes by Hansen and Schmid,[7c] and the studies by this laboratoray concerning rearrangement of vitamin D type allenes **22** and **25** (Scheme IV—wherein a rate-limiting [1,5]-sigmatropic shift is followed by a fast [1,7]-sigmatropic shift affording **24** and **26**/**27**, respectively)[7b] concerned kinetic studies of [1,5]-shifts of allenes. The exceptional behavior of the sulfoxide substituent on the π-facial stereoselection of the [1,5] hydrogen shift in these vinylallenes prompted a more detailed mechanistic study. In particular, we report activation parameters, solvent effects, and kinetic isotope effects (including a TDKIE in one case) for the vinylallenes described in this study. These results are compared with the classical [1,5]-sigmatropic shift of (nonallenic) pentadienyl systems.[5]

Activation Parameters. The activation parameters for the thermal rearrangement of vinylallenes **13a** (both diastereomers), **13g**, **13h**, and **13i** in benzene-d_6 are summarized in Table III. The procedure was analogous to that described for rate measurements at 40 °C described above. Note that the observed rate constants may be dissected into the sum of two rate constants from the product ratios, since the rearrangement involves competitive, irreversible formation of two geometric isomers **14** and **15**. Accordingly, the activation parameters listed in Table III are for each of the competing processes taken separately.

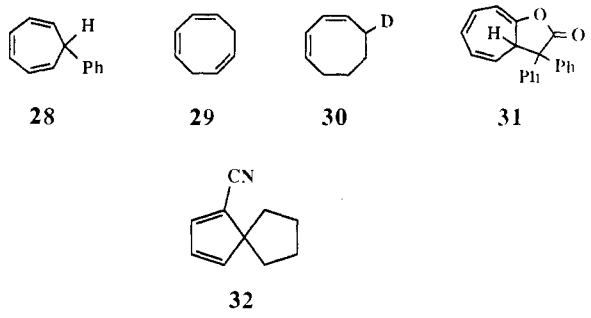
It is instructive to compare the activation parameters obtained in this study (Table III and entry 1 in Table IV) with data obtained in other studies of [1,5]-sigmatropic shifts (Table IV). The range of values obtained for the preexponential factor (log A) and entropy of activation ($\Delta S^{\ddagger}$) terms is relatively uniform for a variety of systems previously studied. These include [1,5]-sigmatropic shifts of vinylallenes (entries 2 and 3), arylallenes (entry 4), simple acyclic pentadiene (entry 5), and a cyclic pentadiene (entry 6). In fact, for seven separate examples of

Table IV. Comparison of Activation Parameters at 40.0 °C[a]

entry	compd	E_a, kcal/mol	log A, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol·K)
1	**13a** (2 diast), **13g**, **13h**, **13i**[b]	19.4–22.8	9.4–11.6	22.7–27.7	18.7–22.2	−7.6 to −17.4
2	5-methyl-1,2,4-hexatriene[c]	24.6	10.3	28.2	24.0	−13.3
3	**22**[d]	24.9	10.6	28.0	24.3	−12.0
4	arylallenes[e]	28.4–30.2	10.4–10.9	31.9–33.3	27.8–29.6	−10.6 to −13.0
5	**33**[f]	36.1	11.3	38.2	35.5	−8.7
6	**35**[g]	20.1	11.3	22.3	19.5	−9.0

[a] Literature data were extrapolated to 40 °C. [b] This study. [c] Reference 7a. [d] Reference 7b. [e] Reference 7c. [f] Reference 6a. [g] Reference 21.

Chart VI



28 **29** **30** **31** **32**

[1,5]-shifts of *acyclic* pentadienes summarized in the review article by Spangler,[5a] the log A and $\Delta S^{\ddagger}$ terms fall in the range summarized in Table IV. Thus, even for the heteroatom-bearing vinylallenes **13a** (both diastereomeric sulfoxides), **13h** (sulfide), and **13i** (sulfone), the vinylallene variant of this hydrogen shift process is mechanistically parallel to that occurring in nonallenic systems.

As indicated earlier, the sulfoxide-substituted vinylallenes **13a** (diastereomers A or B) exhibit significant π-facial selectivity (~3/1 to **4**/1) in their rearrangement to **15** and **14**. The corresponding sulfide (**13h**) and sulfone (**13i**) do not. We note here only that the $\Delta S^{\ddagger}$ term is significantly more negative (−14.2 to −17.4) for the sulfoxide than for the sulfide (−7.6 and −9.6) or sulfone (−9.9 and −11.3) (see Table III). However, we cannot offer a satisfactory interpretation of the activation parameter data in terms of the π-facial selectivity unique to the two sulfoxide cases **13a** (especially since either diastereomeric sulfoxide results in geometric selectivity in the same stereochemical direction, **15a** > **14a**).

Solvent Effects. As indicated in Table I (entry 5), diastereomer B of sulfoxide **13a** isomerizes at 40.0 °C in benzene-d_6 (dielectric constant, ϵ, 2.3) to **14a** plus **15a** with a half-life of $\tau \sim 48.3 \pm 0.7$ min. In the more polar solvents pyridine-d_5 (ϵ 12.3) and acetonitrile-d_3 (ϵ 37.5), this same vinylallene sulfoxide exhibits half-lives for isomerization of $\tau \sim 37.8 \pm 0.8$ min and 50.2 ± 0.6 min, respectively, leading to the same product distribution (±3%) in each case. Thus, like other [1,5]-sigmatropic hydrogen shifts, there is a lack of a significant dependence of rate on solvent polarity.

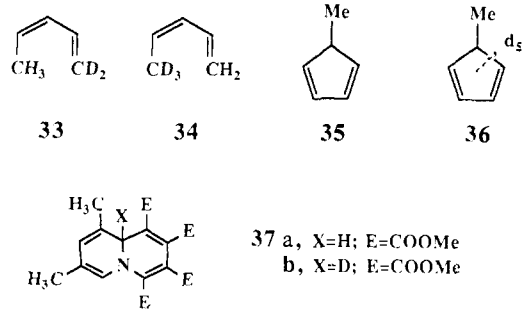
Previous studies of medium effects on [1,5]-sigmatropic hydrogen shifts include the rearrangement of the cycloheptatriene **28** by Kloosterziel,[17a] the 1,3,6-cyclooctatriene **29** by Roth,[17b] the 1,3-cyclooctadiene **30** by Winstein,[17c] and the cycloheptatriene lactone **31** by Kende (Chart VI).[18] More recently, Carpenter[19] reported that [1,5]-sigmatropic *carbon* shift of cyano-substituted spirocyclopentadiene **32** occurs four times faster in isopropyl alcohol than in isooctane at 150 °C. However, medium effects on the rate of [1,5]-sigmatropic hydrogen shifts of **13a** and **28–31** are significantly smaller, attesting to a general lack of polar character in these rearrangements.

Table V. Rate Constants and Deuterium Kinetic Isotope Effects for **13a** and **21b**[a]

substrate	$k \times 10^4$,[b,c] s^{-1}	k_H/k_D[c]
	Diastereomer A	
13a → **14a**	0.742 ± 0.03	
21b → **14a** (d_5)	0.091 ± 0.0009	8.2 ± 0.3
13a → **15a**	2.28 ± 0.11	
21b → **15a** (d_5)	0.306 ± 0.003	7.5 ± 0.4
	Diastereomer B	
13a → **14a**	0.426 ± 0.007	
21b → **14a** (d_5)	0.051 ± 0.001	8.4 ± 0.3
13a → **15a**	1.97 ± 0.03	
21b → **15a** (d_5)	0.236 ± 0.005	8.3 ± 0.4

[a] Complete details are presented in the Experimental Section and supplementary materials. [b] Data are for 40.0 °C in benzene-d_6. [c] All uncertainties listed are absolute deviations from the mean.

Chart VII



33 **34** **35** **36**

37 a, X=H; E=COOMe
b, X=D; E=COOMe

Deuterium Kinetic Isotope Effects. As summarized in Table V, the primary deuterium kinetic isotope effect (KIE) data, k_H/k_D, were determined in benzene-d_6 for diastereomers A and B of vinylallene sulfoxides **13a**/**21b** at 40.0 °C. Secondary isotope effects have been ignored. The only previous determinations of k_H/k_D for the [1,5]-sigmatropic hydrogen shift of vinylallenes were those recently reported by this laboratory for vitamin D type vinylallenes **22** and **25** (Scheme IV) and the alcohol corresponding to ketone **22**. At 98.4 °C, k_H/k_D values of 6.3, 7.6, and 7.0, respectively, were obtained for these substrates. Thus, although not determined entirely at the same temperature, the KIE data determined in this study (Table V) are large and in accord with the conclusion reached earlier for the rearrangement of vitamin D type vinylallenes.[7b] These large KIE's are characteristics of highly symmetrical hydrogen-transfer processes. Thus, the vinylallene variant of the [1,5]-sigmatropic hydrogen shift is mechanistically completely analogous to the corresponding nonallenic variant of this thermal isomerization. To the extent that hydrogen shifts of *cis*-1,3-pentadienes are considered to be concerted, there is no reason to believe that vinylallene systems behave otherwise.

There is a more global aspect to the study of KIE's of [1,5]-sigmatropic hydrogen shifts, however, and this concerns the interpretation of the temperature dependence of the isotope effects (TDKIE). As discussed earlier, Roth[6a] previously reported a k_H/k_D value of 12.2 for the thermal rearrangement of the parent *cis*-1,3-pentadienes **33** and **34** (Chart VII). On the basis of this large KIE value of 12.2 (determined by Roth by extrapolation

(17) (a) terg Borg, A. P.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 741. (b) Roth, W. R. *Justus Liebigs Ann. Chem.* **1964**, *671*, 25. (c) Glass, D. S.; Boikess, R. S.; Winstein, S. *Tetrahedron Lett.* **1966**, 999.

(18) (a) Kende, A. S. *Tetrahedron Lett.* **1967**, 2661. The thermal rearrangement studied by Kende actually involved **31**, not the cyclobutanone structure reported. See: (b) Gomper, R.; Studeneer, A.; Elser, W. *Tetrahedron Lett.* **1968**, 1019. (c) Sugiyama, S.; Takeshita, H. *Chem. Lett.* **1986**, 1203.

(19) Replogle, K. S.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 5751.

of data obtained at 185–211 to 25 °C), Kwart[20] proposed that the [1,5]-sigmatropic hydrogen shift must involve a linear, symmetrical transfer of hydrogen. In the cyclopentadienes **35** and **36**, wherein the ring necessarily constrains the suprafacial [1,5]-sigmatropic hydrogen shift to proceed in a nonlinear but presumably symmetrical, bent manner, McLean[21] has shown that the KIE values are significantly smaller. Similarly, the heterocycle **37** also requires a bent transfer of hydrogen. It should be noted that **33–37** appear to be the only substrates to have been studied in terms of a TDKIE (vide infra).[6a,20a,21,22] Even for the acyclic dienes **33** and **34**, Kwart's proposal, regarding a linear transfer of hydrogen, seemed stereoelectronically unreasonable, and no fewer than five theoretical studies[23–27] have recently addressed this matter.

Both Hess and Schaad[23] and Rondan and Houk,[24a] on the basis of ab initio computations, estimated that the classical suprafacial, bent transition structure for the [1,5] hydrogen shift is significantly lower in energy than the linear transition structure proposed by Kwart.[20] Dormans and Buck[28] from their calculations also proposed that the [1,5] hydrogen shift occurs via a linear transition state. However, this was recently challenged by Jensen and Houk,[24b] Dewar[26] and Dormans[28] suggested that tunneling may play a significant role in these [1,5] hydrogen shift processes, thus further complicating Kwart's interpretation.[20] One difficulty with the recent theoretical considerations,[23–28] however, is the fact that most of the discussion centers around the data of Roth[6a] who, as mentioned above, reported the TDKIE for **33/34**, leading to the well-quoted value of 12.2 for the k_H/k_D at 25 °C. There is less discussion of the data of Kwart and Acheson,[20a] who reported a seemingly more exhaustive investigation of the TDKIE for **37** and showed that k_H/k_D was *independent* of temperature over a very large 60 °C temperature range (kinetic measurements in the range 66–126 °C). By contrast, both Roth (for **33/34**) and McLean (for **35/36**) reported a temperature *dependence* of k_H/k_D over a smaller, ca. 20 °C, temperature range. Thus, extensive experimental TDKIE data on the [1,5]-sigmatropic hydrogen shift is limited to only these three studies,[6a,20a,21] and only Roth's results pertain to an acyclic system.

There exists the possibility that the Roth's data lack the precision to allow accurate extrapolation of high-temperature data to ambient temperatures. Note again that Roth's k_H and k_D values were determined over only a 20 °C temperature range, 190–211 °C, and then extrapolated to room temperature. Since labeled material in our vinylallene series was available, a TDKIE study seemed appropriate, and we elected to study the *tert*-butyl-substituted vinylallene **13g** and its deuteriated counterpart **21c**. The hydrocarbon vinylallenes (**13g/21c**) are less prone to deterioration than the allene sulfoxides (**13a/21b**), thus allowing the kinetic measurements to be made over a much wider temperature range, comparable with the work of Kwart and Acheson.[20a]

The computed k_H/k_D values at various selected temperatures from this investigation together with the corresponding values at the same temperatures from the TDKIE studies of Roth[6a] and McLean[21] are compared in Table VI (Kwart and Acheson[20a] obtained for **37** a constant k_H/k_D value of 5.113 ± 0.016 over the entire temperature range, 66–126 °C). The nearly complete parallel between Roth's results for the parent *cis*-1,3-pentadiene (**33/34**) and our data for the acyclic vinylallene (**13g/21c**) is striking. Moreover, McLean's k_H/k_D values for the cyclic system as reported earlier are smaller.

Table VI. Temperature Dependent k_H/k_D[a]

T, °C	33/34[b]	35/36[c]	13g/21c[d]
200[e]	5.10 (4.96)	1.30 (1.44)	4.68
98.4[f]	7.66 (7.81)	2.62 (2.78)	7.49
68.2[f]	9.06 (9.42)	3.50 (3.65)	9.09
40[g]	10.9 (11.6)	4.83 (4.93)	11.3
25	12.2 (13.2)	5.87 (5.93)	12.8
ΔE_a	1.40 (1.56)	2.42 (2.27)	1.62
A_H/A_D	1.15 (0.932)	0.0988 (0.129)	0.835

[a] Data in parentheses are our recalculated values by linear regression analysis of the rate constants reported in ref 5a and 21. [b] The temperature range of the kinetic study was 185–205 °C (g) for k_H and 190–211 °C (g) for k_D.[5a] [c] The temperature range of the kinetic study was 6–25 °C (CCl_4) for k_H and 19–40 °C (CCl_4) for k_D.[21] [d] In this study, the temperature range was 40–100 °C (C_6D_6) for k_H and 69–115 °C (C_6D_6) for k_D. These represent the k_H/k_D values for **13g/21c** leading to **15**(*Z*) plus **14**(*E*) as depicted in Scheme I. [e] This temperature corresponds to the kinetic study temperature utilized by Roth.[5a] [f] These temperatures correspond to the boiling points of isooctane and hexanes, respectively, often used in our synthetic studies.[2,8] [g] The temperature utilized in most of the kinetic comparisons described in this article.

Table VI also gives the ΔE_a and A_H/A_D values calculated from the data obtained in the three studies. At least for Roth's and our studies, it is assumed that a significant tunneling contribution to the KIE's is negligible (on the basis of the magnitudes of ΔE_a and A_H/A_D),[29] contrary to recent suggestions concerning a tunneling contribution.[26,28] By contrast, the highly attenuated A_H/A_D ratio of ~0.1 obtained by McLean suggests a tunneling contribution for the [1,5]-sigmatropic hydrogen shift of **35/36**.[21,29b] As regards whether our (and Roth's) large k_H/k_D values of 12–13 reflect a linear transfer of hydrogen as proposed by Kwart, theoretical calculations[23,24] suggest that this is not the case. Moreover, the use of TDKIE studies as a criterion for transition-state structure has been questioned.[25,30]

The strikingly close parallel between Roth's and our extrapolated k_H/k_D, ΔE_a, and A_H/A_D is intuitively surprising. This is because we would have anticipated somewhat attenuated k_H/k_D values for the [1,5]-sigmatropic shift of the vinylallene system, since our system is more exothermic and intrinsically less symmetrical (hydrogen transfer from a sp^3 to sp carbon) than Roth's system. In Roth's parent system study involving **33** and **34**, hydrogen transfer involves an essentially thermal neutral process, and at the transition state, both carbon termini should be equivalently hybridized, approximately midway between sp^3 and sp^2.

Summary and Conclusions. The precise interpretation of the TDKIE results described in this study awaits further theoretical study. The results however provide additional experimental insight into the [1,5]-shift processes and would at least support the experimental validity of Roth's original data. But clearly our acyclic systems differ significantly from the cyclic systems of McLean[21] and Kwart and Acheson.[20a]

Returning to the matter of the extraordinary sulfoxide π-facial selectivity effect on the geometric course of the [1,5]-sigmatropic hydrogen shift (Scheme I and Tables I and II), compelling new information regarding the origin of this selectivity remains elusive. The accelerating effect caused by substituents of increasing electron-withdrawing ability (Table I) is explicable on the basis of a hydride-like (as opposed to a proton-like) [1,5]-sigmatropic hydrogen shift,[31] but it remains for future studies to elaborate

(20) (a) Kwart, H.; Brechbiel, M. W.; Acheson, R. M.; Ward, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4671. (b) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

(21) McLean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555.

(22) For other studies on the primary kinetic deuterium isotope effects (at a single temperature), see the citations in: Reference 5a.

(23) (a) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185. (b) Hess, B. A., Jr.; Schaad, L. J.; Pancíř, J. *J. Am. Chem. Soc.* **1985**, *107*, 149.

(24) (a) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 2519. (b) Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

(25) McLennan, D. J.; Gill, P. M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2971.

(26) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 166.

(27) For earlier theoretical studies of [1,5]-hydrogen shifts, see: (a) Bouma, W. J.; Vincent, M. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767. (b) Castenmiller, W. A. M.; Buck, H. M. *Tetrahedron* **1979**, *35*, 397.

(28) Dormans, G. J. M.; Buck, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 3253.

(29) (a) For a recent example, see: Chrisope, D. R.; Beak, P. *J. Am. Chem. Soc.* **1986**, *108*, 334. (b) For a more general discussion, see: Melander, L.; Sanders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 144, 157.

(30) Anhede, B.; Bergman, N. *J. Am. Chem. Soc.* **1984**, *106*, 7634.

further on facial selectivity effects for a wider variety of substituents on pericyclic processes in general.

Experimental Section[32]

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3-(phenylsulfinyl)-1,2-propadiene (13a), Method A. To a solution of the (phenylthio)allene **13h** (139 mg, 0.514 mmol) in CH_2Cl_2 (2 mL) was added *m*-chloroperbenzoic acid (111 mg, 80%, 0.514 mmol) in CH_2Cl_2 (2 mL) at −10 °C under a nitrogen atmosphere. The reaction mixture was stirred for 25 min at −10 °C and quenched with 5% Na_2CO_3 solution (1 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic extracts were dried ($MgSO_4$) and then concentrated under vacuum. The residue was subjected to HPLC (Whatman Partisil M9 10/5 column, 20% EtOAc/Skellysolve B) to afford four components in the following order of elution: diastereomer A of **13a** (42 mg, 29%); diastereomer B of **13a** (55 mg, 37%); a mixture of diastereomer B of **13a** and *E*-triene **13a** (28 mg, 19%); *Z*-triene **15a** (22 mg, 15%).

Method B. To a solution of the propargyl alcohol **16a** (261 mg, 1.46 mmol) and triethylamine (0.21 mL, 1.5 mmol) in THF (10 mL) was slowly added PhSCl (0.93 mL, 1.65 M in CCl_4, 1.5 mmol) under a nitrogen atmosphere at −78 °C. After the resultant mixture was stirred for 1 h at −78 °C and 2 h at 0 °C, a 5% Na_2CO_3 aqueous solution (1 mL) was added to quench the reaction. The reaction mixture was extracted with ether (3 × 6 mL), dried ($MgSO_4$), and passed through a short silica gel column (2.5 cm). After removal of solvent, the residue was subjected to HPLC (Whatman Partisil M9 10/50 column, 20% ethyl acetate/Skellysolve B) to give four components in the following order of elution: diastereomer A of **13a** (30 mg, 7%); diastereomer B of **13a** (236 mg, 56%); a small amount of rearranged trienes; a byproduct (127 mg, 30%).

If the [1,5]-shifted conjugated trienes **14a** and **15a** are desired on a preparative scale, method B should be utilized, but no attempt need be made to purify the allene sulfoxides before [1,5]-sigmatropic rearrangement is complete.[33]

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3-(phenylsulfinyl)-1,2-butadiene (13b), Following method B described above, propargyl alcohol **16b** (179.5 mg, 0.933 mmol), triethylamine (261 μL, 1.87 mmol), THF (10 mL), and PhSCl (696 μL, 1.48 M in CCl_4, 1.03 mmol) were reacted. After workup, HPLC purification (Whatman Partisil M9 10/50 column, 15% ethyl acetate/Skellysolve B) afforded three components in the following order of elution: diastereomer A of **13b** (10 mg, 4%); a mixture of diastereomer B of **13b** and the rearranged *Z*-triene **15b** (242 mg, 87%); a small amount of the *E*-triene **14b** (~2 mg). Integration of the appropriate peaks of the ^1H NMR spectrum of the second fraction, a mixture of **13b** (diastereomer B) and *Z*-triene **15b**, gave the ratio of **13b**/**15b** = 10/1.[33]

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3-(phenylsulfinyl)-1,2-pentadiene (13c), Following method B described above, propargyl alcohol **16c** (194 mg, 0.939 mmol), triethylamine (262 μL, 1.88 mmol), THF (10 mL), and PhSCl (0.70 mL, 1.48 M in CCl_4, 1.0 mmol) were reacted. After workup, HPLC purification (Whatman Partisil M9 10/50 column, 15% ethyl acetate/Skellysolve B) afforded four components, eluting in the following order: diastereomer A of **13c** (~7 mg, 2%, less polar); diastereomer B of **13c** (145 mg, 49%, more polar); the rearranged *Z*-triene of **15c** (66 mg, 22%); the rearranged *E*-triene of **14c** (~5 mg, 2%).[33]

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-4-methyl-3-(phenylsulfinyl)-1,2-pentadiene (13d), Following method B described above, propargyl alcohol **16d** (200 mg, 0.907 mmol), triethylamine (253 μL, 1.81 mmol), THF (10 mL), and PhSCl (670 μL, 1.48 M in CCl_4, 1.00 mmol) were reacted. After workup, HPLC purification (Whatman Partisil M9 10/50 column, 15% ethyl acetate/Skellysolve B) afforded **13d** as two diastereomers, A (9 mg, 3%, less polar isomer) and B (159 mg, 53%, more polar isomer), the rearranged *Z*-triene **15d** (71 mg, 24%), and a trace amount of *E*-triene **14d**.[33]

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-4,4-dimethyl-3-(phenylsulfinyl)-1,2-pentadiene (13e), Following method B described above, propargyl alcohol **16e** (62.1 mg, 0.265 mmol), triethylamine (73.9 μL, 0.530 mmol), THF (2 mL), and PhSCl (151 μL, 1.76 M in CCl_4, 0.265 mmol) were reacted. After workup, HPLC purification (Whatman Partisil M9 10/50 column, 15% ethyl acetate/Skellysolve B, 3.0 mL/min flow rate) afforded **13e** as two diastereomers, A (22 mg, 25%, less polar isomer) and B (14 mg, 16%, more polar isomer), and the rearranged *Z*-triene **15e** (16 mg, 18%).[33]

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-1,2-propadiene (13f). To a solution of lithium aluminum hydride (151 mg, 95%, 3.77 mmol) and aluminum chloride (168 mg, 1.26 mmol) in ether (5 mL) was added slowly **16a** (336 mg, 1.88 mmol) in ether (1 mL) in a nitrogen atmosphere at room temperature. After the mixture was stirred for 1 day at room temperature, saturated NH_4Cl solution (1 mL) was added dropwise to quench the reaction. The organic layer was decanted, and the resulting aqueous paste was extracted with ether (2 × 5 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated. The residue was subjected to HPLC purification (Partisil, 100% Skellysolve B) to afford **13f** (60 mg, 20%) as a colorless oil.

4,4-Dimethyl-1-(2′,6′,6′-trimethyl-1′-cyclohexen-1′-yl)-1,2-pentadiene (13g), To a suspension of CuCN (105 mg, 1.17 mmol) in ether (3 mL) was added slowly *tert*-butyllithium (1.30 mL, 1.8 M in pentane, 2.34 mmol) at −78 °C under a nitrogen atmosphere. The mixture was stirred for 30 min at −78 °C, warmed to 0 °C for 10 min, and then recooled to −78 °C. A solution of the benzoate **18** (165 mg, 0.58 mmol) in ether (1 mL) was added dropwise. The reaction mixture was stirred for 2.5 h at −78 °C, then warmed to room temperature, and quenched with water (2 mL). The organic layer was decanted, and the aqueous phase was extracted with ether (2 × 5 mL). The combined organic extracts were washed with brine (5 mL) and water (5 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was subjected to HPLC purification (Partisil, 100% Skellysolve B, 3 mL/min flow rate) to give 113 mg of **13g** (89%).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3-(phenylthio)-1,2-propadiene (13h), To a solution of $PhSCu{\cdot}P(OMe)_3$ (95.0 mg, 0.320 mmol) and LiBr (55.7 mg, 0.641 mmol) in THF (4 mL) was added the benzoate **18** (90.5 mg, 0.320 mmol) in THF (4 mL) at room temperature in a nitrogen atmosphere. The reaction mixture was stirred for 1.5 h until no benzoate was detected by TLC. Water (2 mL) was added, and the organic layer was separated; the aqueous layer was extracted with ether (2 × 5 mL). The organic extracts were combined, successively washed with saturated $NaHCO_3$ solution (2 mL) and water (2 mL), and dried over magnesium sulfate. After removal of solvent, the residue was subjected to flash chromatographic purification (silica gel, low-boiling petroleum ether) to afford **13h** (83 mg, 96%).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3-(phenylsulfonyl)-1,2-propadiene (13i), To a solution of the sulfide **13h** (41.4 mg, 0.153 mmol) in CH_2Cl_2 (3 mL) was slowly added *m*-chloroperbenzoic acid (66 mg, 80%, 0.31 mmol) in CH_2Cl_2 (2 mL) under a nitrogen atmosphere at −20 °C. After the resultant mixtures was stirred for 20 min at −20 °C, a 5% Na_2CO_3 aqueous solution (1 mL) was added to quench the reaction. All of the workup and subsequent operations were carried out at below room temperature and as rapidly as possible. The organic layer was separated and aqueous layer extracted with CH_2Cl_2 (2 × 3 mL). The combined organic layers were dried over $MgSO_4$ and passed through a short silica gel column (2.5 cm). After removal of solvent, the residue was subjected to HPLC purification (Whatman Partisil M9 10/50 column, 20% ethyl acetate/Skellysolve B) to afford a mixture of **13i** and the rearranged *Z*-(**15i**) and *E*- (**14i**) trienes (24 mg, 51%). The ratio of **13i**/**15i**/**14i** was determined to be 30/37/33 (^1H NMR).

(2(1′)*Z*,2′*E*)- and (2(1′)*Z*,2′*Z*)-1,1-Dimethyl-3-methylene-2-[3′-(phenylsulfonyl)-2′-propenylidene]cyclohexane (14i and 15i, Respectively), Preparation of a mixture of these conjugated triene sulfones is described in the kinetic experiment. However, these geometric isomers were not separable by HPLC (Whatman Partisil, 10% EtOAc/Skellysolve B, 4.0 mL/min). In order to obtain preparatively useful amounts of these isomers, the following experiments were carried out. To a solution of the *Z*-triene sulfoxide **15a** (68 mg, 0.24 mmol) in CH_2Cl_2 (5 mL) was added MCPBA (56 mg, 80%, 0.26 mmol) in CH_2Cl_2 (2 mL) at −20 °C under an argon atmosphere. The reaction mixture was stirred for 20 min followed by addition of water (2 mL). The reaction mixture was extracted with CH_2Cl_2 (2 × 10 mL), and then the organic extracts were washed with brine and water and then dried over $MgSO_4$. After removal of solvent under reduced pressure, the residual product was subjected to HPLC purification (Whatman Partisil M9 10/50 column, 10% EtOAc/Skellysolve B, 4.0 mL/min) to afford the *Z*-triene sulfone **15i** (57.7

(31) Theoretical models at the 3-21G level transition structure of the [1,5]-shifts have been reconstructed: Hehre, W. J.; Kahn, S. D., University of California, Irvine, unpublished observations. Unlike [1,5]-sigmatropic hydrogen shifts of cyclopentadienes, which are thought to involve proton-like transfers, acyclic pentadienes may be polarized in the opposite sense, involving a hydride-like transfer: Kahn, S. D.; Hehre, W. J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291.

(32) Additional general procedures and detailed spectral data are given in the supplementary material.

(33) For preparative purposes for obtaining rearranged trienes (**14**, **15**) the reaction mixture after ether workup was normally allowed to stand at room temperature for >10 h (in ether). The residue after removal of solvent was subjected to HPLC purification (the same condition as described for purification of the corresponding vinylallene sulfoxides) to afford the two conjugated trienes. The yields and *Z*/*E* ratios after separation for each compound were as follows. From **13a**: 63%; **15a**/**14a** = 81/19. From **13b**: 91%; **15b**/**14b** = 92/8. From **13c**: 75%; **15c**/**14c** = 92/8. From **13d**: 80%; **15d**/**14d** = 94/6. From **13e**: 58%; **15e**/**14e** = >98/2.

mg, 80%). The same procedure was used for preparation of *E*-triene sulfone **14i**. By starting from 17 mg of the *E*-triene sulfoxide **14a** (0.06 mmol), there was obtained 16 mg of the *E*-triene sulfone **14i** (95%).

Desulfurization of (2(1′)*Z*,2′*Z*)-1,1-Dimethyl-3-methylene-2-[4′,4′-dimethyl-3′-(phenylsulfinyl)-2′-pentenylidene]cyclohexane (15e). To a solution of the triene sulfoxide **15e** (59.8 mg, 0.175 mmol) in dry THF (5 mL) were added $Ni(acac)_2$ (1 mg) and *i*-PrMgCl (200 μL, 0.52 mmol, 2.6 M solution in ether) at room temperature under a nitrogen atmosphere. The reaction mixture was then heated to reflux for 24 h. After the mixture was cooled to room temperature, a solution of 10% aqueous NH_4Cl was added, and the reaction mixture was extracted with ether. The organic extract was then washed with water, dried over $MgSO_4$, and passed through a short silica gel column. After removal of solvent, the residual product was subjected to HPLC purification (Whatman Partisil M9 10/50 column, 100% Skellysolve B, 2.0 mL/min) to afford the *E*-triene hydrocarbon **14g** (15.5 mg, 41%).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-2-propyn-1-ol (16a). Acetylene was slowly bubbled into a solution of THF (40 mL) at −78 °C in a nitrogen atmosphere; the amount of acetylene (69 mmol) added was calculated by measuring the weight increase. To this acetylene solution was added dropwise *n*-butyllithium (42.0 mL, 0.96 M in hexenes, 40.3 mmol) at −78 °C under a nitrogen atmosphere. The solution was stirred for 30 min, and β-cyclocitral (3.58 g, 23.5 mmol) in THF (5 mL) was added dropwise. The reaction mixture was stirred for 30 min at −78 °C, warmed to room temperature, and quenched with water (8 mL). After the addition of anhydrous K_2CO_3 until the aqueous phase became pasty, the organic layer was decanted, and the solid paste was extracted with ether (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and then concentrated under vacuum. The residue was subjected to Kugelrohr distillation to afford **16a** (3.77 g, 90.0%) as a colorless oil, bp 80–83 °C (1.8 mm).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-2-butyn-1-ol (16b). The procedure described above for the preparation of **16a** was followed. From reaction of propyne (2.5 L, 85%, 86 mmol), THF (40 mL), *n*-butyllithium (45.0 mL, 0.96 M in hexanes, 43.2 mmol), and β-cyclocitral (3.61 g, 23.7 mmol) in THF (6 mL) there was obtained after Kugelrohr distillation **16b** (4.56 g, 100%) as a colorless oil, bp 125–127 °C (1.3 mm).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-2-pentyn-1-ol (16c). The procedure described above for the preparation of **16a** was followed. From reaction of 1-butyne (6.0 g, 110 mmol), THF (50 mL), *n*-butyllithium (70.0 mL, 1.38 M in hexanes, 96.6 mmol), and β-cyclocitral (11.9 g, 78.3 mmol) in THF (10 mL) there was obtained after Kugelrohr distillation **16c** (14.6 g, 90.5%) as a colorless oil, bp 100–102 °C (0.5 mm).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-4-methyl-2-pentyn-1-ol (16d). The procedure described above for the preparation of **16a** was followed. From reaction of 3-methyl-1-butyne (5.00 g, 73.3 mmol), THF (50 mL), *n*-butyllithium (48.0 mL, 1.38 M in hexanes, 66.2 mmol), and β-cyclocitral (9.00 g, 59.1 mmol) in THF (10 mL) there was obtained after Kugelrohr distillation **16d** (12.5 g, 96.0%) as a coloreless oil, bp 120 °C (1.9 mm).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-4,4-dimethyl-2-pentyn-1-ol (16e). The procedure described above for the preparation of **16a** was followed. From reaction of 3,3-dimethyl-1-butyne (4.80 g, 58.4 mmol), THF (40 mL), *n*-butyllithium (36.0 mL, 1.5 M in hexanes, 54.0 mmol), and β-cyclocitral (8.05 g, 52.6 mmol) in THF (10 mL) there was obtained after Kugelrohr distillation **16e** (11.5 g, 92.8%) as a colorless oil, bp 90–92 °C (0.7 mm).

1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-2-propyn-1-yl Benzoate (18). To a solution of the propargyl alcohol **16a** (448 mg, 2.51 mmol) in ether (8 mL) was slowly added *n*-butyllithium (1.70 mL, 1.55 M in hexanes, 2.64 mmol) at −4 °C in a nitrogen atmosphere. The solution was stirred for 20 min, and then freshly distilled benzoyl chloride (292 μL, 2.51 mmol) was added dropwise. The reaction mixture was stirred for 30 min at −4 °C and then 1 h at room temperature. Water (2 mL) was added, and the reaction mixture was stirred for 5 min until a clear solution was obtained. The organic layer was separated, and the aqueous layer was extracted with ether (2 × 5 mL). The combined organic layers were washed with brine (5 mL) and water (5 mL), dried ($MgSO_4$), and concentrated under vacuum. The crude product was chromatographed (Chromatotron; silica gel, 5% EtOAc/low-boiling petroleum ether). Evaporation of solvent afforded **18** (581 mg, 81.8%) as a white solid, mp 66–67 °C.

1-[2′-(Trideuteriomethyl)-6′,6′-dimethyl-3′,3′-dideuterio-1′-cyclohexen-1′-yl]-2-propyn-1-ol (20a). The procedure used in the preparation of **16a** was followed. From reaction of acetylene (1.7 g, 65 mmol), THF (30 mL), *n*-butyllithium (20.0 mL, 1.6 M in hexanes, 32.0 mmol), and pentadeuterio-β-cyclocitral **19** (3.47 g, 22.1 mmol) in THF (5 mL) there was obtained after Kugelrohr distillation **20a** (3.24 g, 80.2%) as a colorless oil, bp 77–80 °C (1.6 mm).

1-[6′,6′-Dimethyl-2′-(trideuteriomethyl)-3′,3′-dideuterio-1′-cyclohexen-1′-yl]-2-propyn-1-yl Benzoate (20b). The procedure used in the preparation of **18** was followed. From reaction of **20a** (1.13 g, 6.19 mmol), dry ether (10 mL), *n*-butyllithium (3.87 mL, 1.6 M in hexanes, 6.19 mmol), and benzoyl chloride (0.80 mL, 6.9 mmol) there was obtained after chromatographic purification (silica gel, 5% EtOAc/low-boiling petroleum ether) the benzoate **20b** (1.55 g, 87.1%) as a white solid, mp 66–67 °C.

1-[6′,6′-Dimethyl-2′-(trideuteriomethyl)-3′,3′-dideuterio-1′-cyclohexen-1′-yl]-3-(phenylthio)-1,2-propadiene (21a). To a solution of $PhSCu·P(OMe)_3$ (211 mg, 0.712 mmol) and LiBr (112 mg, 1.29 mmol) in THF (4 mL) was added the benzoate **20b** (145 mg, 0.504 mmol) in THF (2 mL) at room temperature in a nitrogen atmosphere. The reaction mixture was stirred for 4 h until the benzoate was completely reacted (followed by TLC). Water (2 mL) was added, the organic layer was separated, and then the aqueous layer was extracted with ether (2 × 5 mL). The organic extracts were combined, washed with saturated aqueous $NaHCO_3$ solution (2 mL) and water (2 mL), and dried over magnesium sulfate. After removal of solvent, the residue was subjected to flash chromatographic purification (silica gel, low-boiling petroleum ether) to afford **21a** (140 mg, 100%).

1-[6′,6′-Dimethyl-2′-(trideuteriomethyl)-3′,3′-dideuterio-1′-cyclohexen-1′-yl]-3-(phenylsulfinyl)-1,2-propadiene (21b). To a solution of the allene phenyl sulfide **21a** (49.6 mg, 0.180 mmol) in CH_2Cl_2 (2 mL) was added *m*-chloroperbenzoic acid (31.4 mg, 80%, 0.182 mmol) in CH_2Cl_2 (2 mL) under a nitrogen atmosphere at −20 °C. the reaction mixture was stirred for 20 min at −20 °C, and then the reaction was quenched with 5% Na_2CO_3 aqueous solution (1 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic extracts were then dried over $MgSO_4$ and concentrated under vacuum. The residue was subjected to HPLC purification (Partisil, 20% EtOAc/Skellysolve B) to afford four components in the following order of elution: diastereomer A of **21a** (18 mg, 34%, least polar); diastereomer B of **21a** (22 mg, 42%); a small amount of the rearranged triene products (~5 mg total, ~10%).

4,4-Dimethyl-1-[6′,6′-dimethyl-2′-(trideuteriomethyl)-3′,3′-dideuterio-1′-cyclohexen-1′-yl]-1,2-pentadiene (21c). To a suspension of CuCN (1.54 g, 17.2 mmol) in ether (45 mL) was added slowly *tert*-butyllithium (20.2 mL, 1.7 M in pentane, 17.2 mmol) at −78 °C under a nitrogen atmosphere. The mixture was stirred for 30 min at −78 °C, warmed to 0 °C for 10 min, and then recooled to −78 °C. A solution of the deuteriated benzoate **20b** (2.03 g, 7.1 mmol) in ether (10 mL) was added dropwise. The reaction was stirred for 2 h at −78 °C, then warmed to room temperature, and quenched with water (8 mL). The organic layer was decanted, and the aqueous phase was extracted with ether (2 × 10 mL). The combined organic extracts were washed with brine (10 mL) and water (20 mL), dried ($MgSO_4$), and concentrated under vacuum. The residue was subjected to HPLC purification (Whatman M20 10/50 Partisil, 100% Skellysolve B, 8 mL/min flow rate) to give 1.39 g of **21c** (88%).

General Procedure for the Kinetic Studies. Reactions were followed by ^1H NMR spectroscopy. First-order irreversible kinetic behavior was observed in all cases. The details are given in the supplementary materials. Tables I–VI in the text summarize the pertinent data.

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Supplementary Material Available: Spectral and analytical data, details of kinetic studies, and tables of kinetic data (49 pages). Ordering information is given on any current masthead page.