Table II. Vibrational Frequencies for CaCp and SrCp in cm^{-1}

state	CaCp	SrCp
$\tilde{X}^2A_1$	312^a	223
$\tilde{A}^2E_1$	325	259
$\tilde{B}^2A_1$	300	260

^{a} $\omega_e x_e$ = 8.9 cm^{-1}.

transition of the 0–0 (v'–v'') vibrational band. The partially resolved peak to the right is the 0–0 $\tilde{A}^2E_{1(1/2)}$–$\tilde{X}^2A_1$ transition. The pair of features between 6700 and 6750 Å correspond to the two spin components of the $\tilde{A}$ state in the v' = 1 level of the 1–0 transition. Only one mode is Franck–Condon active, and sequence structure was not resolved. The unequal intensities of the two spin components is due to incomplete collisional relaxation. In the laser excitation spectrum these two features have the same intensity, as expected for two spin components. If the $\tilde{A}^2E_{1(1/2)}$ component is excited then the intensity of the $^2E_{1(1/2)}$ spin components is enhanced. Thus, at our pressure of 1–2 torr there is some evidence of resonance fluorescence. The major part of the observed emission is produced by collisional relaxation, accounting for the observation of the 2–0 and 1–0 bands when the 0–0 band is pumped. This collisional redistribution of population in the excited electronic state is observed for all of the larger radicals[13] that we have prepared.

The corresponding spectra of the $\tilde{A}^2E_1$–$\tilde{X}^2A_1$ and $\tilde{B}^2A_1$–$\tilde{X}^2A_1$ transitions of SrCp were also observed. For SrCp the vibrational frequency accidentally matches the spin–orbit splitting so the vibrational and spin–orbit structures are overlapped. For example, the $^2E_{1(3/2)}$–$^2A_1$ 0–0 band overlaps the $^2E_{1(1/2)}$–$^2A_1$ 1–0 band at 7262 Å. The centers of the observed CaCp and SrCp bands are provided in Table I for both the $\tilde{B}$–$\tilde{X}$ and $\tilde{A}$–$\tilde{X}$ transitions.

The attribution of our spectra to CaCp and SrCp and the spectral assignments rest on the close similarily with the alkaline-earth monohalide, monohydroxide,[8-11] and monoalkoxide[12,13] spectra. The observed $\tilde{A}^2E_1$ spin–orbit splittings are 55 ± 5 cm^{-1} (CaCp) and 258 ± 5 cm^{-1} (SrCp) compared to 67 cm^{-1} for CaOH[9] and 264 cm^{-1} for SrOH.[10] The presence of five off-axis carbons and hydrogens hardly quenches the spin–orbit coupling and there is no evidence of a Jahn–Teller effect. This is probably because the molecular orbital for the $\tilde{A}^2E_1$ state (like the alkaline earth monohalide A state[17-19]) is polarized away from the ring so that the unpaired electron is separated from the Cp$^-$ ring by the M^{2+} core.

The strongest features in the $\tilde{A}$–$\tilde{X}$ and $\tilde{B}$–$\tilde{X}$ transitions were attributed to the 0–0 vibrational band because of Franck–Condon arguments. The observed vibrational frequencies (ω_e's) are listed in Table II with estimated ±5-cm^{-1} errors. For the other alkaline-earth derivatives the metal–ligand stretch always had the largest Franck–Condon factor. Therefore we assign the observed mode to the M–Cp stretch of a_1 symmetry. The only possible alternate assignment is to the M–Cp tilt of e_1 symmetry. Since the bend is doubly degenerate only $\Delta v_B = \pm 2$ bands would appear, although a Jahn–Teller effect would allow electronic transitions with $\Delta v_B = \pm 1$.[20]

The techniques we have utilized in the discovery of the CaCp and SrCp molecules are quite general. Any metal can be vaporized by heating or by sputtering in an electrical discharge,[21] and any appropriate oxidant can be added to the system. One laser drives the chemistry by making M* from M while the second laser interrogates the product molecules formed by reaction of M* with the oxidant. It is very likely that many gas-phase metal alkyls, alkoxides, cyanates, cyanides, carboxylates, and cyclopentadienides can be synthesized and identified in this way.

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Sulfoxide Induced Acceleration and Enhancement of Geometric Selectivity of a [1,5]-Sigmatropic Hydrogen Shift

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The experimental delineation of the effects of substituents on the stereochemical course and on the rate of pericyclic processes is of utility in synthesis as well as in developing an understanding of the mechanism and theory of these processes. It is the purpose of this paper to describe the profound influence of a sulfoxide moiety, more specifically the phenylsulfinyl group, on the course of the vinylallene variant of the [1,5]-sigmatropic hydrogen shift.[1] The system chosen for study involved the competitive isomerization of vinylallene **1** to the conjugated trienes **2** plus **3** (Scheme I).

In typical initial preparative experiments,[2] a solution of PhSCl (0.28 mmol) in THF (0.25 mL) was added dropwise to a stirred solution of alkenynol **4** (0.25 mmol; prepared by reacting β-cyclocitral with the corresponding acetylide, RC$_2$Li[3]) and triethylamine (0.5 mmol) in dry THF (1 mL) cooled to −78 °C. After 1 h at −78 °C and 10 h at room temperature followed by workup, the observed products proved to be mainly the rearranged trienes **2a–e** (major) plus **3a–e** (minor) in a ratio which ranged from ~4:1 to >98:2 (63–91%). These triene sulfoxides are formed via the intermediacy of vinylallene **1** (formed via [2,3]-sigmatropic shift[4] of sulfenate ester **5** and isolable by rapid handling at or below room temperature) and these examples to our knowledge constitute the most facile examples of neutral, *acyclic* [1,5]-sigmatropic hydrogen shifts yet recorded. By way of comparison, the hydrocarbon **1g** is undetectably rearranged after 2 days of standing at room temperature; after 9 days it is only 23% rearranged to a mixture of **3g** plus **2g** with significantly lower geometric selectivity (~2:1 ratio).

Preparation of the hydrocarbon vinylallenes **1f** and **1g** and the derivatives **1h** and **1i**, which differ from **1a** only with respect to the oxidation level at sulfur, are shown in Scheme II.

In order to more quantitatively assess the nature of the unprecedented sulfoxide effect, a kinetic investigation of these isomerizations was undertaken. Table I compares the data for the sulfoxides **1a–1e**, with that of the hydrocarbons **1f** and **1g** as well as the phenyl sulfide **1h** and phenyl sulfone **1i**. The following are evident from the data in Table I: (a) The sulfoxide substituent imparts a significant directing group on the trajectory of the [1,5]-hydrogen shift[1a,5] (H favors migration anti to the sulfoxide).

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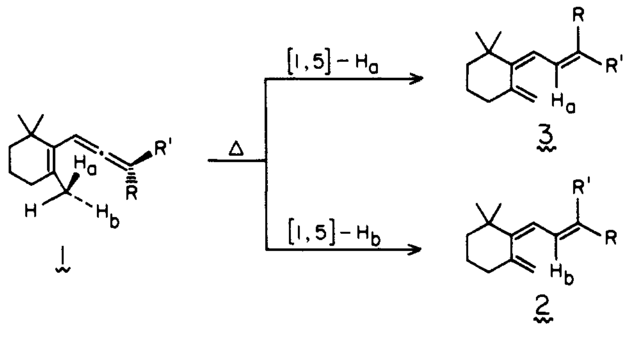
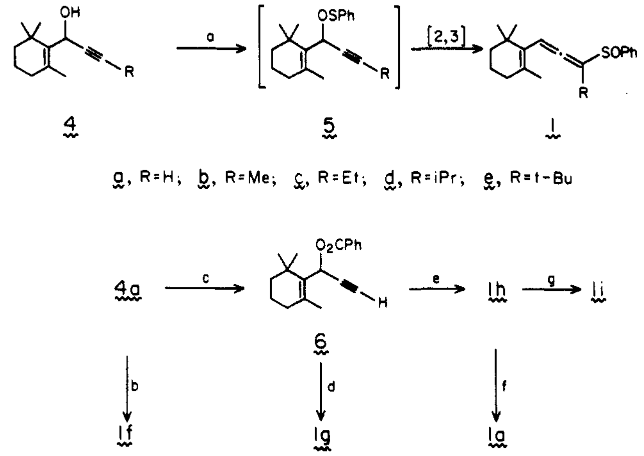
Scheme I



	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	SO2Ph
e,	t-Bu	SOPh			

Scheme II[a]



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

Note particularly that neither the sulfide **1h** nor the sulfone **1i** exerts significant geometric selectivity and that for the sulfoxides, both diastereomers afford similar results. (b) For the sulfoxides, the geometric selectivity increases as the size of R increases (4:1 to >98:2) but reactivity is not affected. (c) Sulfur substituents accelerate the [1,5]-hydrogen shift relative to hydrocarbon substituent and the reactivity order parallels the electron-withdrawing ability of the substituents (sulfone > sulfoxide > sulfide >> H, *t*-Bu). (d) The polarity of the solvent (benzene, pyridine, acetonitrile) has little effect on the rate and selectivity of the reaction, which is characteristic of other [1,5]-sigmatropic shifts.[6]

In summary, we have discovered that the sulfoxide group is a useful substituent which not only exerts an acceleration of the [1,5]-shift but also can effect control of π-facial stereoselection in these triene syntheses.[7] Although the origin of this effect is as of yet uncertain, the results should further enhance the utility of vinylallenes in stereoselective syntheses of sensitive polyenes bearing useful functional groups.

Table I. Half-Lives, Relative Rates, and Product Ratios for the Thermal Rearrangement of Vinylallenes

	$\tau_{1/2}$, min[a,b]	k_{rel}	**2/3**[c]
1a′[d]	38.5 ± 1.8	131	75/25
1a[e]	48.3 ± 0.7	104	82/18
1b[e]	34.2 ± 1.7	147	92/8
1c[e]	44.8 ± 1.2	112	92/8
1d[e]	46.2 ± 0.4	110	93/7
1e[e]	36.4 ± 0.1	138	> 98/2[f]
1f	5010 ± 80	1	
1g	6780 ± 180	0.74	39/61
1h	123 ± 3	41	50/50
1i	7.0 ± 0.1	717	53/47
1a[e,g]	37.8 ± 0.8	133	81/19
1a[e,h]	50.2 ± 0.6	100	79/21

[a] These were determined at 40.0 ± 0.1 °C in benzene-d_6 (dielectric constant, ϵ 2.3) unless otherwise noted. Details are provided as Supplementary Material. [b] The uncertainties are absolute deviations. [c] Measured by ^1H NMR and confirmed by HPLC. The product ratios remained constant (±1%) during the kinetic runs and individual product isomers were stable to the reaction conditions. Assignments of geometric configuration were based on NMR and other data. [d] Less polar diastereomer, minor isomer. [e] More polar diastereomer, major isomer. [f] No isomer 3 detected by ^1H NMR. [g] In pyridine-d_5 (ϵ 12.3). [h] In acetonitrile-d_3 (ϵ 37.5).

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Supplementary Material Available: Spectral and analytical data and details of kinetic studies including a table of rate constants and *Z*/*E* ratios. (36 pages). Ordering information is given on any current masthead page.

Synthesis of Punaglandin 3 and 4. Revision of the Structures

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The structures of a series of chlorinated prostanoids punaglandins[1] (PUGs) isolated from the Hawaiian octocoral *Telesto riisei* have been reported by Scheuer and his colleagues. To PUG 3 and 4, which have higher antitumor activity[1,2] than the related marine prostanoids clavulones[3] (claviridenones[4]) (isolated from the Japanese octocoral *Clavularia viridis*), formula **1** and **2**

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