Thermal [1,7]-Sigmatropic Hydrogen Shift versus Electrocyclization of Dienylallene Sulfoxides

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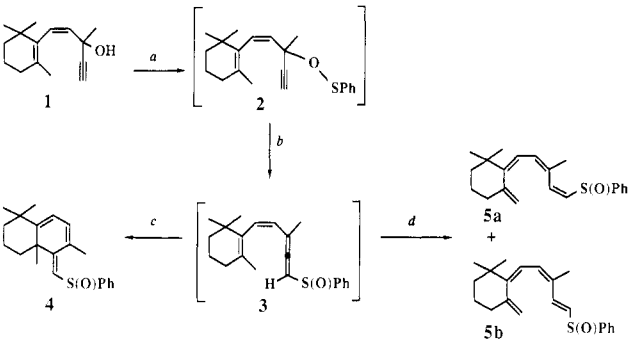
Treatment of dienylpropargyl alcohol **9** with phenylsulfenyl chloride and base produces dienylallene sulfoxide **10**, which undergoes competitive pericyclic processes: six-electron electrocyclization leads to drimatriene sulfoxides **11** and **12** while [1,7]-sigmatropic hydrogen shift leads to tetraene sulfoxides **13** and **14**. In the absence of a very sterically demanding substituent at the allene terminus bearing the phenylsulfinyl group, the electrocyclization process was found to be favored. Furthermore, the sulfoxide moiety was observed to influence the stereochemical mode of electrocyclic ring closure as well as the [1,7]-sigmatropic hydrogen shift. Of the two possible modes of disrotatory electrocyclization (inward–inward versus outward–outward), the stereochemistry of the sulfoxide plays a decided role in the control of one of these two modes. Of the two possible antarafacial modes of the [1,7]-sigmatropic shift involving **10d**, the phenylsulfinyl group exerts a small syn directive effect.

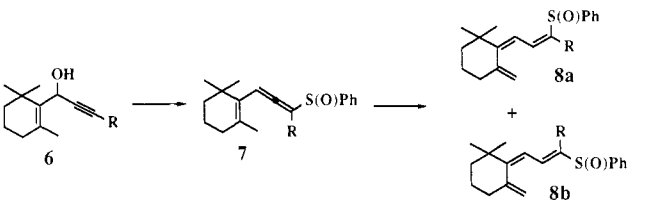
cis-Dienylpropargyl alcohol **1** is transformed to drimatriene **4** (Scheme I) in a spontaneous, multistep one-pot process under mild conditions ($PhSCl/Et_3N$, −78 °C to room temperature).[1] Through stereochemical studies,[1b] insight into the mechanistic pathway of this process has been discerned. This reaction is believed to proceed through initial formation of sulfenate ester **2**, which undergoes a [2,3]-sigmatropic shift to afford allenyldiene sulfoxide **3** in a manner stereospecific with respect to allene configuration,[1,2] but with little selectivity at sulfur. The allene sulfoxide **3**, a species not directly observed, is then considered to undergo a stereospecific, six-electron electrocyclization in only one disrotatory sense to afford the observed product **4** as a pair of sulfoxide diastereomers. Had **3** undergone the alternative, allowed disrotatory electrocyclic ring closure, the opposite exocyclic double-bond geometric isomer of **4** would have resulted. It was originally anticipated (vide infra) in connection with vitamin A related studies[3] that the [1,7]-sigmatropic shifted products **5a** and **5b** rather than electrocyclization product **4** would be observed. Nevertheless, the serendipitous finding that cyclization product **4** is produced preferentially is interesting and the process has synthetic potential. For example, it has been demonstrated with an optically active derivative of **1** (vide infra) that this process occurs with complete stereospecificity. Thus, this process provides a means for the enantiospecific synthesis of chiral building blocks.

An investigation of the competitive [1,7]-sigmatropic hydrogen shift of the kind represented by the isomerization of **3** to geometric isomers **5a** plus **5b**, besides being of possible use in our vitamin A studies, would have been of considerable interest in connection with our attempts to evaluate the effect of substituents on $4n$ versus $4n + 2$ pericyclic processes.[4] Such a process is closely related to the [1,5]-sigmatropic hydrogen shift of the allene sulfoxide **7** (prepared in a similar way from propargyl alcohol **6**) to **8a** plus **8b** (Scheme II).[5] In the latter study, it was discovered that the sulfoxide had a profound effect on rate and on the geometric course of the hydrogen shift. An allylic methyl hydrogen of **7** was shown to migrate to the central carbon of the allene preferentially in a manner anti to the sulfoxide, affording an excess of **8a** over **8b** (3:1 to >98:2 depending on the nature of R). Thus, it was of interest to determine whether the antarafacial,[4] $4n$-electron process **3** → **5a** + **5b** would favor **5b** in preference to **5a**. The former, **5b**, results from migration of the allylic hy-

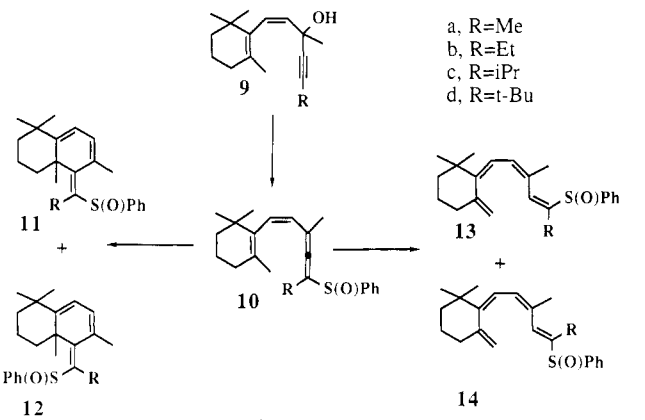
Scheme I



Scheme II



Scheme III



(1) (a) Reischl, W.; Okamura, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 6115. (b) Okamura, W. H.; Peter, R.; Reischl, W. *Ibid.* **1985**, *107*, 1034.
(2) (a) Braverman, S.; Stabinsky, Y. *Isr. J. Chem.* **1967**, *5*, 125. (b) Cinquini, M.; Colonna, S.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 256. (c) Cinquini, M.; Colonna, S.; Cozzi, F.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2061.
(3) 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.
(4) (a) Hoeger, C. A.; Johnston, A. D.; Okamura, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 4690. (b) Hoeger, C. A.; Okamura, W. H. *Ibid.* **1985**, *107*, 268.
(5) (a) Okamura, W. H.; Shen, G.-Y.; Tapia, R. *J. Am. Chem. Soc.* **1986**, *108*, 5018. (b) Shen, G.-Y.; Tapia, R.; Okamura, W. H. *Ibid.* **1987**, *109*, 7499.

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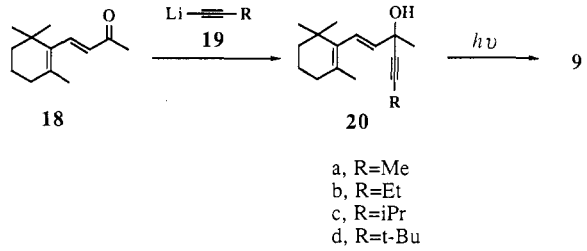
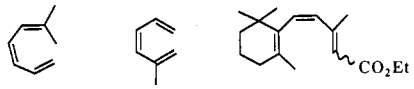
Scheme IV



a, R=Me
b, R=Et
c, R=iPr
d, R=t-Bu

drogen of **3** syn to the sulfoxide group. The possibility that a substituent (sulfoxide) could induce the opposite π-facial selectivity when comparing a $4n + 2$ ([1,5] shift) with a $4n$ ([1,7] shift) process has its origin in a single precedent reported by this laboratory.[4a] Although **3** was not observed to afford **5**, we now find that a bulky substituent at the allene terminus (*tert*-butyl group geminal to the PhSO as in **10d** in Scheme III) of **3** diverts its rearrangement to [1,7]-shifted (e.g., **13** and **14**) rather than electrocyclized products (e.g., **11** and **12**). This latter result therefore allows a study of the effect of a substituent on the geometric course (π-facial selectivity[6]) of the [1,7]-sigmatropic shift.

There have been conflicting reports in the literature regarding the thermally preferred reaction pathway for 1,3,5-heptatrienes. In 1979, Spangler and co-workers[7] concluded that electrocyclic ring closure is preferred over [1,7]-sigmatropic hydrogen shift in the thermolysis of (*Z*)-6-methylhepta-1,3,5-triene (**15**). On the other hand,



15 16 17

Skattebøl found that a much higher temperature was required to achieve complete ring closure[8] of *cis*-2-methyl-1,3,5-hexatriene (**16**). In a separate study[9] Crowley concluded that the fastest initial thermal reaction in unhindered 1,3,5-heptatrienes is the [1,7] hydrogen shift. In a system closely related to ours, Fråter found that triene **17** undergoes electrocyclization at elevated temperature. At a lower temperature, however, only [1,7]-sigmatropic hydrogen-shifted products were observed.[10] In order to develop a better understanding of factors that influence the competition between [1,7] shifts and electrocyclizations, as well as the effect of substituents on π-facial selectivity in the pericyclic processes mentioned above, we report the results of a systematic study of the isomerization of allene sulfoxides **10** derived from propargyl alcohols **9** (Scheme III).

Results and Discussion

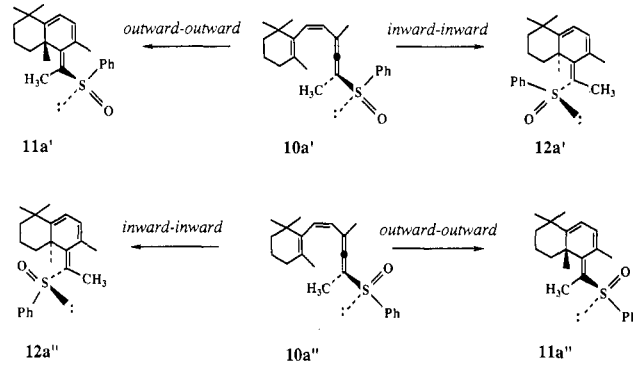
The cis alcohols **9a–d** were prepared by reaction of the corresponding lithiated acetylene derivatives **19** with β-ionone (**18**) to yield the trans alcohols **20**. One-way, triplet-sensitized photoisomerization[1,11] of the latter affords **9** (Scheme IV). The cis alcohols **9** were treated with phenylsulfenyl chloride to afford the products summarized in Table I. As indicated above, the pathway for formation of these products can be considered to involve competing pericyclization of the allene intermediates **10** (Scheme III).

Table I. Product Distribution from the Rearrangement of 9 to 11–14[a]

reactant	R	% 11	% 12	% 13	% 14
9a	Me	30 (**11a**)	14 (**12a**)	nd	nd
9b	Et	32 (**11b**)	26 (**12b**)	nd	nd
9c	*i*-Pr	nd	6 (**12c**)	10 (**13c**)	9 (**14c**)
9d	*t*-Bu	nd	nd	18 (**13d**)	42 (**14d**)

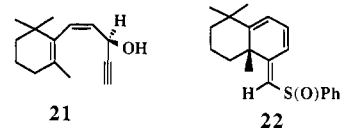
[a] Absolute yields of purified (HPLC, ^1H and ^{13}C NMR) products are given. In each case, not detected (nd) refers to the fact that each HPLC-detectable component was collected (detected on the refractive index detector) preparatively and examined spectroscopically for the presence of **11–14**. Details are presented in the Experimental Section.

Scheme V



The Methyl and Ethyl Derivatives. For the dienylallene **10a** where R = Me, the bicyclic products **11a** plus **12a** resulting from competing six-electron electrocyclization processes were obtained exclusively. The *E* isomer **11a** was the major isomer (for R = Me, **11a**:**12a** = 2:1). A similar result was obtained for the ethyl derivative **10b**, the *E* isomer **11b** being only slightly favored (**11b**:**12b** = 1.2:1.0). It is noteworthy that for both the methyl and ethyl cases, efforts to detect diastereomeric sulfoxides for each geometric isomer were unsuccessful. That this observation is quite unusual is discussed next.

As mentioned above, the [2,3]-shift process that generates the reactive allene sulfoxide is stereospecific with respect to the allene configuration,[1,2] but not particularly selective at sulfur. For example, in the specific case shown in Scheme I, **4** is produced as a 60:40 diastereomeric mixture of sulfoxides. In the study of optically active **21** (84% ee), **22** was produced as a 1:1 diastereomeric mixture



21 22

of sulfoxides (wherein the chirality transfer from the secondary center in **21** to the bridgehead center in **22** was stereospecific). It is therefore anticipated that **10** should be produced as a pair of diastereomeric sulfoxides, **10a'** and **10a"** (Scheme V), each of which is capable of undergoing two thermally allowed modes of disrotatory six-electron electrocyclization, namely inward–inward or outward–outward rotation. Because of the kind of analysis

(6) See footnote 22 in ref 4a for additional leading references.
(7) Spangler, C. W.; Keys, B.; Bookbinder, D. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 810. Despite the suggestion that electrocyclization of **15** is faster than the competing [1,7]-sigmatropic hydrogen shift process, the evidence provided by Spangler et al. is not compelling. The activation parameters suggest that the [1,7]-shift step is unlikely to be rate limiting. For example, see ref 4a and the references cited.
(8) Skattebøl, L. *Tetrahedron* **1969**, *25*, 4933.
(9) (a) Crowley, K. J.; Traynor, S. G. *Tetrahedron Lett.* **1975**, 3555. (b) Crowley, K. J.; Traynor, S. G. *Tetrahedron* **1978**, *34*, 2783.
(10) Fråter, G. *Helv. Chim. Acta* **1974**, *57*, 2446.
(11) Ramamurthy, V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. *J. Org. Chem.* **1973**, *38*, 1247.

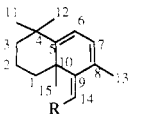
shown in Scheme V (racemic materials indicated in all cases), the observation that only two drimatriene isomers were produced from **9a** initially suggested to us that the products were the outward–outward disrotation products (±)-**11a′** and (±)-**11a″**. This seemed reasonable because for each geometric isomer two sulfur diastereomers were expected ((±)-**11a′**/(±)-**11a″** or (±)-**12a′**/(±)-**12a″**; and it seemed logical that since only two isomers were obtained, outward rotation of sulfoxide (where sulfoxide is viewed as being larger than the geminal methyl) would be preferred. In the event, it proved (vide infra) that **9a** afforded geometric isomers, (±)-**11a″**/(±)-**12a′** or (±)-**11a′**/(±)-**12a″** [assuming that the allenyl sulfoxide is a mixture of (±)-**10a′** plus (±)-**10a″**], as the products. Since no sulfoxide diastereomers were detected for either isomer, it must be concluded that each of the diastereomeric sulfoxides of **10a** preferentially undergoes disrotatory cyclization in the opposite sense, one sulfoxide (±)-**10a′** affording (±)-**11a′** and the other (±)-**10a″** affording (±)-**12a″** [or vice versa: (±)-**10a′** affording (±)-**12a′** and (±)-**10a″** affording (±)-**11a″**]. The same result obtains for the ethyl derivative **10b**, for which only a single sulfoxide diastereomer of **11b** as well as a single sulfoxide diastereomer of **12b** was produced. The implication is clear. The sulfoxide stereochemistry is influencing the sense of disrotatory electrocyclization (inward–inward vs outward–outward).

It is interesting that Kahn and Hehre have recently examined in some detail by theoretical methods the effect of sulfoxides on the π-facial course of Diels–Alder reactions and other processes.[12a] The Kahn–Hehre theory on the effect of sulfoxides on the π-facial stereoselective course of Diels–Alder reaction has recently been questioned however.[12b] As indicated in Scheme II, it is known from our studies of [1,5]-sigmatropic shifts involving vinylallene intermediate **7** that the phenyl sulfoxide substituent leads to **8a** in preference to **8b**.[5] For R = H the **8a**:**8b** ratio is 4:1; for R = alkyl, the ratio ranges from >10:1 to 50:1. Although the origin of this effect remains unclear, it does not appear to be steric in nature. Finally, the recent studies by Houk and others[13] indicate that donor–acceptor substituents can strongly influence the stereochemistry of the conrotatory electrocyclization (inward–outward vs outward–inward) in the 1,3-butadiene–cyclobutene, 4*n*-electron interconversion.

The Isopropyl Case. The situation is different when the R group in **9** (Scheme III) is the more bulky isopropyl group. In this case, products resulting from competing electrocyclization and [1,7]-sigmatropic shift processes result. Only a single electrocyclization product, the diastereomerically homogeneous *E* isomer **12c**, was obtained. However, two tetraene sulfoxides, **13c** and **14c**, which result from competing [1,7] shifts, were produced. Although only one electrocyclization product **12c** was obtained in the isopropyl case (unlike the methyl and ethyl cases where two geometric isomers **11** and **12** were observed), there is a most reasonable trend in the ratio of **11** and **12** in this series. The ratio of **11** to **12** was 2.1 (30%/14%) and 1.2 (32%/26%) for the methyl and ethyl cases, respectively. The higher proportion of **12** in the ethyl case compared to the methyl case is explicable on the basis that the R group in **12** occupies a sterically less encumbered site than in **11**. Thus, for the isopropyl case, it can be conjectured that the size of R has reached the point where electrocyclization to **11** is precluded. Like the methyl and ethyl cases, only a single sulfoxide of **12c** could be detected. Unfortunately, difficulty was encountered in purifying the individual components of the product mixture derived from isopropyl derivative **9c**. Thus, definitive conclusions regarding the significance of product ratios is difficult. However, only in the isopropyl case was there observed *both* [1,7]-shifted and electrocyclized products. For the isomerization of allene **10**, it is reasonably discerned that a simple steric effect diverts a normally preferred electrocyclization to the [1,7]-shift process.

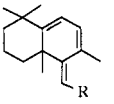
The *tert*-Butyl Case. For the sterically demanding *tert*-butyl substituent, no cyclization products were detected. Only the [1,7]-shifted products, the two possible geometric isomers, **13d** and **14d**, were obtained. The two tetraene sulfoxides were obtained in 60% yield with the 4′*Z* isomer (**14d**) being the major product (2.3–2.6:1). The observed major isomer **14d** results from a hydrogen migration syn to the sulfoxide group. As mentioned earlier, this is opposite to what was previously observed for the corresponding [1,5] shift in vinylallene sulfoxides (Scheme II).[5] In comparison to the isopropyl case where both modes of pericyclization were detected, it is suggested that the electrocyclization process is now completely inhibited because of steric factors; the bulky *tert*-butyl group blocks carbon–carbon bond formation entirely.

Reduction of Sulfoxides to Hydrocarbons: Evidence for Geometry. The geometric configuration of all the vinyl sulfoxides obtained in this study was verified by reduction to the corresponding hydrocarbons, which could be characterized more definitively by ^{1}H NMR (including NOE studies in several cases as summarized in the supplementary material). Recently, we reported a mild method for stereospecifically reducing vinyl sulfoxides in the presence of a proton source using *t*-BuLi.[14] With this new procedure, the bicyclic 14*E* sulfoxides **11a** and **11b** were reduced to hydrocarbons **23a** and **23b**, respectively, and the 14*Z* sulfoxides **12a** and **12b** were similarly reduced to the corresponding hydrocarbons **24a** and **24b**, respectively.



23

a, R=Me
b, R=Et



24

a, R=Me
b, R=Et
c, R=iPr

NOE experiments were performed to confirm the geometry of **23a** and **24a**. Upon irradiation of the C_8-methyl signal of **23a** and that of **24a** the C_{14}-hydrogen signal was enhanced in **23a** while that in **24a** was not affected. The vinyl sulfoxide **12c** was similarly reduced to triene **24c**.

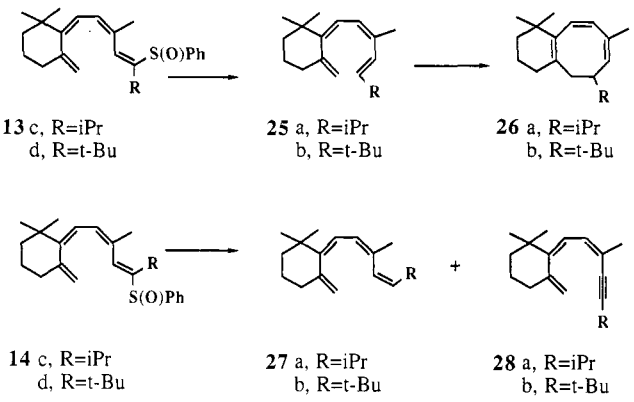
The geometries of the tetraene sulfoxides were established by a similar series of reduction experiments (Scheme VI). The 4′*Z*-tetraenes **13c** and **13d**, after reduction to **25** (detected by ^{1}H NMR), underwent eight-electron electrocyclization at room temperature within a few hours to bicyclic compounds **26a** and **26b**, respectively. The 4′*E* isomers **14c** and **14d** were similarly reduced to **27a** and **27b**,

(12) (a) Kahn, S. D.; Hehre, W. J. *Tetrahedron Lett.* **1986**, *27*, 6041. (b) Koizumi, T.; Arai, Y.; Takayama, H. *Ibid.* **1987**, *28*, 3689. (c) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381. (d) Kahn, S. D.; Pau, C. F.; Hehre, W. J. *Ibid.* **1986**, *108*, 7396. (e) Kahn, S. D.; Hehre, W. J. *Ibid.* **1986**, *108*, 7399.

(13) (a) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (c) Dolbier, W. R., Jr.; Koroniak, H.; Burton, D. J.; Heinze, P. L.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *Ibid.* **1987**, *109*, 219. (d) Dolbier, W. R.; Koroniak, H.; Burton, D. J.; Bailey, A. R.; Shaw, G. S.; Hansen, S. W. *Ibid.* **1984**, *106*, 1871. (e) Breulet, J.; Schaefer, H. F., III. *Ibid.* **1984**, *106*, 1221.

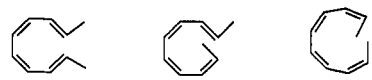
(14) Theobald, P. G.; Okamura, W. H. *Tetrahedron Lett.* **1987**, *28*, 6585.

Scheme VI



respectively. In contrast to the thermal lability of tetraenes **25**, the latter tetraene hydrocarbons **27** were stable even in boiling benzene for 21 h. The reductions of **14c** and **14d** afforded besides **27** a side product resulting from elimination of a β hydrogen and the sulfoxide moiety, namely the trienynes **28a** and **28b**, respectively.

In the case of tetraenes **27a** and **27b**, the presence of the bulky isopropyl or *tert*-butyl group at the tetraene terminus with *Z* configuration inhibits the cyclization process. This observation is consistent with the tetraene, eight-electron electrocyclization studies of Marvell and Huisgen.[15] In their work, it was found that increasing steric congestion at the termini of the tetraene system resulted in an increase in the temperature required for electrocyclization. Whereas *EZZE* isomer **29** cyclized to a cy-



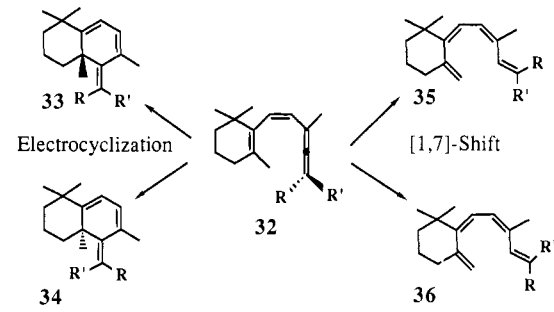
29 30 31

clooctatriene (and the corresponding bicyclooctadiene) below room temperature (−10 °C), the terminally more hindered *ZZZZ* isomer **31** required heating (65 °C) to effect similar cyclization. The *EZZZ* isomer **30** expectedly cyclized at an intermediate temperature (+9 °C). All three isomers (**29–31**) underwent conrotatory cyclization. Thus, that the terminally less hindered (*ZZE*)-**25** is more prone than the terminally more hindered (*ZZZ*)-**27** toward electrocyclization is not unexpected.

Summary

Regarding the relative facility of [1,7] shifts versus disrotatory, thermal electrocyclizations in non-allenic, heptatrienyl systems (such as **15–17**), [1,7] shifts are preferred,[7–10,16] notwithstanding a conflicting report by Spangler.[7] The results obtained in this study of dienylallenes of the type **32** reveal that just the opposite situation prevails. Electrocyclization is preferred in the absence of overriding steric congestion at the allene terminus (Scheme VII). For **32**, where R, R′ = Me, PhS(O) or R, R′ = Et, PhS(O), electrocyclization to **33** plus **34** is preferred even though these decalin systems appear highly sterically congested even on cursory inspection of models. However, introduction of both a *t*-Bu and PhS(O) group at the allene terminus in **32** diverts it entirely to the [1,7]-sigmatropic

Scheme VII



shift pathway, the isopropyl–PhS(O) case being the crossover point between electrocyclization and [1,7] shift. The intrinsic preference for electrocyclization can be attributed to the greater thermodynamic advantage gained in forming a new carbon–carbon bond as reflected in the transition state leading to the decalin (drimatriene) systems **33–34**. The process leading from **32** to **35** plus **36** is more nearly thermoneutral in that no new carbon–carbon bonds are produced. Apparently, in non-allenic cases such as **15–17**, the presence of sp^2 centers at both reacting termini introduces steric inhibition to electrocyclization, rendering the [1,7] shift more facile. In the allene **32**, the reacting termini in the electrocyclization involve one sp^2 center and a sterically less constrained sp center.[17]

The finding that the phenyl sulfoxide group is a syn-directing group in the [1,7]-sigmatropic shift (i.e., in the rearrangement of **10d** to **13d** plus **14d**, the latter is preferred) nicely complements our previous finding that this same substituent is an anti-directing group in the [1,5]-sigmatropic shift (i.e., in the rearrangement of **7** to **8a** plus **8b**, the former is preferred). This alternation in π-facial selectivity between a $4n + 2$ and $4n$ process exerted by a common substituent [PhS(O)] is only the second such case reported.[4,18] However, the effect observed here is so small (2.3–2.6:1, syn:anti), especially when compared to the corresponding [1,5]-shift case (>50:1, anti:syn for analogous substituents), that steric effects may be adequate to explain the syn selectivity.

The finding that the sulfoxide moiety at the allene terminus in **10** (Scheme V) is capable of controlling the mode of electrocyclic ring closure was unexpected. These electrocyclizations are conjectured here to reflect a balance between a steric effect and the π-facial selectivity (an asymmetric induction) exerted by the sulfoxide moiety. *In the absence of the methyl group geminal to the sulfoxide*,[1] the steric factor dominates and only outward–outward disrotation is observed (i.e., as in **3** to **4**, Scheme I). Apparently, the geometric disposition of the sulfoxide group cis to the allylic, ring methyl group as in **4** is not as sterically encumbering as would have been the case if **3** had disrotated in the opposite disrotatory sense, which would have disposed the sulfoxide group toward the quaternary bridgehead center. *In the presence of the methyl group geminal to the sulfoxide* as in **10**, outward–outward or inward–inward rotation is viewed as resulting in nearly the same steric congestion whether the exocyclic double is disposed as in **11** or **12** (Scheme V). Thus, with steric effects balanced, we suggest that the sense of disrotation

(15) (a) Huisgen, R.; Dahmen, A.; Huber, H. *J. Am. Chem. Soc.* **1967**, *89*, 7130. (b) Marvell, E. N.; Seubert, J. *Ibid.* **1967**, *89*, 3377. See also: (c) Woodward, R. B.; Hoffmann, R. *Ibid.* **1965**, *87*, 395. (d) Marvell, E. N. *Thermal Electrocyclic Reactions*; Academic: New York, 1980.

(16) For a review on [1,*j*]-sigmatropic rearrangements, see: Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187. See also footnote 4 above for leading references.

(17) (a) The electrocyclization process of dienylallenes described herein is viewed as a classical, concerted process. The possibility of the involvement of a pseudopericyclic mechanism is discussed in ref 1b. For a definition of pseudopericyclic reactions, see: Ross, J. A.; Seiders, R. P.; Lemal, D. M. *J. Am. Chem. Soc.* **1976**, *98*, 4325. (b) For a recent theoretical discussion; see: Henriksen, U.; Synder, J. P.; Halgren, T. A. *J. Org. Chem.* **1981**, *46*, 3767.

(18) Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81.

of **10** is sensitive to and hence controlled by the chirality of the sulfoxide moiety.

Experimental Section

General Procedure. See supplementary material.

(7*Z*)-9-(1′-Propynyl)-β-ionol (9a). A solution of trans propargylic alcohol **20a** (1.15 g, 4.95 mmol) and 2′-acetonaphthone (46 mg, 0.27 mmol) dissolved in benzene (85 mL) was added to a water-cooled Pyrex immersion apparatus. The solution was deoxygenated by the passage of a stream of nitrogen and irradiated for 21 h with a 450-W Hanovia medium-pressure mercury lamp. After the solvent was evaporated under reduced pressure, the residue was subjected to chromatographic purification (silica gel, 10% EtOAc/low-boiling petroleum ether) and vacuum-dried to give 0.86 g (75%) of cis alcohol **9a**.

(7*Z*)-9-(1′-Butynyl)-β-ionol (9b). A solution of trans propargylic alcohol **20b** (1.77 g, 7.19 mmol) and 2′-acetonaphthone (81 mg, 0.48 mmol) in benzene (90 mL) was photolyzed and then worked up as described for the preparation of **9a**. There was obtained 1.55 g (88%) of cis alcohol **9b**.

(7*Z*)-9-(3′-Methyl-1′-butynyl)-β-ionol (9c). A solution of trans propargylic alcohol **20c** (1.314 g, 5.05 mmol) and 2′-acetonaphthone (65 mg, 0.38 mmol) in benzene (90 mL) was irradiated and then processed as described for the preparation of **9a**. There was obtained 1.069 g (81%) of the cis alcohol **9c**.

(7*Z*)-9-(3′,3′-Dimethyl-1′-butynyl)-β-ionol (9d). A solution of trans propargylic alcohol **20d** (2.199 g, 8.01 mmol) and 2′-acetonaphthone (104 mg, 0.62 mmol) in benzene (90 mL) was irradiated and then worked up as described for the preparation of **9a** to afford 1.824 g (83%) of the cis alcohol **9d**.

(*E*)- and (*Z*)-14-Methyl-14-(phenylsulfinyl)drima-5,7,9-(14)-triene (11a and 12a). To a solution of cis propargyl alcohol **9a** (105 mg, 0.45 mmol) and Et_3N (0.25 mL, 1.8 mmol) in CH_2Cl_2 (5 mL) cooled to −78 °C under a nitrogen atmosphere was added a CCl_4 solution of phenylsulfenyl chloride (1.83 M, 0.26 mL, 0.48 mmol; prepared by addition of chlorine in CCl_4 to diphenyl disulfide in CCl_4). After stirring for 0.5 h at −78 °C, the reaction mixture was allowed to warm to room temperature over 0.5 h and then quenched with water (5 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated, and chromatography (HPLC, Whatman Partisil ODS-2 M9 reverse-phase column, 20% acetone in acetonitrile) led to separation of two isomeric products. The major product **11a** (*E* isomer; **isomer A**, eluted first, mp 145 °C, crystallized from hexanes) was obtained in 30% yield (46 mg) and the minor product **12a** (*Z* isomer; **isomer B**, eluted second, viscous oil) in 14% yield (22 mg).

(*E*)- and (*Z*)-14-Ethyl-14-(phenylsulfinyl)drima-5,7,9-(14)-triene (11b and 12b). To a solution of cis alcohol **9b** (189 mg, 0.77 mmol) and triethylamine (0.20 mL, 1.4 mmol) in dichloromethane (5 mL) at −78 °C under a nitrogen atmosphere was added phenylsulfenyl chloride (2.6 M in CCl_4, 0.44 mL, 1.1 mmol). The reaction mixture was stirred for 2 h, then allowed to warm to room temperature, and left to stand overnight. The reaction was quenched with water (4 mL), the organic layer was separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and then concentrated under vacuum. Passage of the residue though a short silica gel column (EtOAc–hexanes) followed by HPLC separation (reverse phase, 9:1 acetonitrile/acetone) afforded two compounds: **isomer A** (eluted first; *E* isomer **11b**), mp 142–143 °C (87 mg, 32%); **isomer B** (eluted second; *Z* isomer **12b**), viscous liquid (70 mg, 26%).

Isopropylvinyl Sulfoxides 12c, 13c, and 14c. A solution of cis propargylic alcohol **9c** (365 mg, 1.40 mmol) and Et_3N (0.30 mL, 2.1 mmol) in dichloromethane (5.0 mL) was cooled to −78 °C (under nitrogen). Phenylsulfenyl chloride (2.9 M in CCl_4, 0.73 mL, 2.1 mmol) was added dropwise to the alcohol solution, and then the reaction mixture was stirred for 1.5 h. The mixture was allowed to warm to room temperature and stirred for an additional 0.5 h. The reaction was quenched with water (10 mL), the organic layer was separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were dried (Na_2SO_4). After removal of solvent, the residue was passed through a short column of silica gel (1:1 EtOAc/hexanes) and dried. HPLC (Whatman Partisil, 9:1 hexanes/EtOAc) afforded first a mixture of the less polar [1,7]-sigmatropic shift isomer **13c** (isomer A) and the electrocyclization compound **12c** and then second the more polar [1,7]-sigmatropic rearrangement isomer **14c** (isomer B; 44 mg, 9%). The former, the mixture of **13c** (isomer A) and **12c** (cyclized product), was then subjected to HPLC (Whatman ODS-5, reverse phase, CH_3CN), leading to the separation of the tetraene **13c** (isomer A, eluted first on reverse phase; 50 mg, 10%) and the cyclized isomer **12c** (eluted second on reverse phase; 31 mg, 6%).

(*Z*)- and (*E*)-Tetraene Sulfoxides 13d and 14d. A solution of cis propargyl alcohol **9d** (45 mg, 0.16 mmol) and Et_3N (0.05 mL, 0.33 mmol) in CH_2Cl_2 (3 mL) was cooled at −78 °C under a nitrogen atmosphere. Phenylsulfenyl chloride (2.9 M, 0.09 mL, 0.25 mmol), prepared as described above, was added dropwise to the alcohol solution, and the mixture was stirred for 1 h. The reaction mixture was allowed to warm to room temperature and then left standing overnight. The reaction was quenched with water (3 mL), the organic layer was separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined organic layers were dried (Na_2SO_4), and chromatography (silica gel, 15% EtOAc/hexanes) led to separation of the two geometric isomers of tetraene sulfoxides. The less polar product (minor, less polar isomer A; 11 mg, 18%) was identified as the *Z* sulfoxide **13d**. The more polar product (major, more polar isomer B, mp 101–102 °C; crystallized from hexanes; 26 mg, 42%) was identified as the *E* sulfoxide **14d**.

(7*E*)-9-(1′-Propynyl)-β-ionol (20a). In a dry 100-mL round-bottom flask was condensed 1-propyne (2.27 g, 54.5 mmol) in dry THF (10 mL) at −78 °C. After a solution of *n*-butyllithium (1.5 M in hexanes, 7.0 mL, 10.5 mmol) was added slowly to the propyne solution and the mixture stirred for 20 min, β-ionone (1.00 g, 5.23 mmol) in THF (3 mL) was added dropwise. The reaction mixture was left to stir for 1 h at −78 °C before it was allowed to warm to room temperature and left to stand overnight. The reaction mixture was worked up by quenching with water (10 mL), extracting with ether (3 × 20 mL), and drying the combined organic layers (Na_2SO_4) followed by solvent evaporation under reduced pressure. Vacuum drying on an oil pump afforded 1.16 g (96%) of alcohol **20a** as a residual oil.

(7*E*)-9-(1′-Butynyl)-β-ionol (20b). To a solution of 1-butyne (4.3 g, 80 mmol) in THF (7.0 mL) was added dropwise a solution of *n*-butyllithium (1.51 M in hexanes, 14.0 mL, 21.1 mmol) at −78 °C and then the mixture was stirred for 1 h. A solution of β-ionone (2.15 g, 11.2 mmol) in THF (10 mL) was added slowly to the alkyne salt solution, and the reaction mixture was stirred for an additional 1 h at −78 °C and then left to stand overnight at room temperature. The reaction mixture was quenched with water 15 (mL), the organic layer was separated, and the aqueous layer was extracted with ether (2 × 10 mL). After the combined organic layer was dried ($MgSO_4$) and concentrated, flash chromatography (silica gel, 9:1 hexanes/EtOAc) was followed by solvent evaporation. Vacuum drying of the residue afforded the alcohol **20b** (2.68 g, 97%) as a residual oil.

(7*E*)-9-(3′-Methyl-1′-butynyl)-β-ionol (20c). To a solution of 3-methyl-1-butyne (3.0 mL, 29 mmol) in THF (15 mL) cooled at −78 °C under a nitrogen atmosphere was added *n*-butyllithium (1.5 M in hexanes, 5.0 mL, 7.5 mmol) dropwise and then the mixture was stirred for 0.5 h. β-Ionone (616 mg, 3.2 mmol) dissolved in THF (2.0 mL) was added to the lithiated alkyne solution, and the mixture was allowed to stir for 1 h at −78 °C and then left to stand overnight at room temperature. The reaction mixture was quenched with water (10 mL), the organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. Vacuum drying afforded 784 mg (99%) of the trans alcohol **20c** as residual oil.

(7*E*)-9-(3′,3′-Dimethyl-1′-butynyl)-β-ionol (20d). To a solution of 3,3-dimethyl-1-butyne (2.68 g, 32.6 mmol) in THF (15 mL) cooled to −78 °C under a nitrogen atmosphere was added dropwise a solution of *n*-butyllithium (1.50 M in hexanes, 9.4 mL, 14.1 mmol) and then the solution was stirred for 0.5 h. A solution of β-ionone (1.36 g, 7.07 mmol) in THF (4 mL) was added slowly to the alkyne salt solution, and the mixture was stirred for 2 h

at −78 °C and then left to stand at room temperature overnight. The reaction mixture was worked up by quenching with water (5 mL), extracting the aqueous layer with ether (3 × 10 mL), and drying the combined organic layers (Na_2SO_4). After flash chromatography (silica gel, 9:1 hexanes/EtOAc), solvent evaporation, and vacuum drying, the alcohol **20d** (1.91 g, 98%) was obtained as a residual oil.

(*Z*)-14-Methyldrima-5,7,9(14)-triene (23a). The (*E*)-vinyl sulfoxide **11a** (64 mg, 0.188 mmol) and *sec*-butyl alcohol (43 μL, 0.469 mmol) were dissolved under nitrogen in ether (5 mL) and the mixture was cooled to −78 °C. A solution of *tert*-butyllithium (1.70 M in pentane, 442 μL, 0.752 mmol) was added and the mixture stirred at −78 °C for 4 min. After warming to room temperature, the reaction mixture was quenched with water (4 mL) and the aqueous layer was extracted with ether (2 × 15 mL). The organic layers were combined, dried ($MgSO_4$), and then filtered. Solvent evaporation followed by chromatographic purification (silica gel, hexanes) afforded after vacuum drying the *Z* hydrocarbon **23a** (23 mg, 58%) as an oil.

(*Z*)-14-Ethyldrima-5,7,9(14)-triene (23b). A solution of *tert*-butyllithium (1.7 M in pentane, 198 μL, 0.34 mmol) was added to a solution of (*E*)-vinyl sulfoxide **11b** (29 mg, 0.08 mmol) and *sec*-butyl alcohol (19 μL, 0.21 mmol) in ether (4 mL) cooled to −78 °C under a nitrogen atmosphere. The reaction mixture was allowed to stir for 2 min and then quenched with water (2 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic layers were dried ($MgSO_4$) and after solvent evaporation, the residue was chromatographically purified (silica gel/hexanes). The residue after vacuum drying afforded 14 mg (73%) of the corresponding *Z* hydrocarbon **23b** as an oil.

(*E*)-14-Methyldrima-5,7,9(14)-triene (24a). A solution of *tert*-butyllithium (1.7 M in pentane, 1.0 mL, 1.72 mmol) was added to a solution of (*Z*)-vinyl sulfoxide **12a** (146 mg, 0.43 mmol) and *sec*-butyl alcohol (98 μL, 1.07 mmol) in dry ether (6 mL) cooled to −78 °C under a nitrogen atmosphere. The reaction mixture was left to stir for 3 min and then quenched with water (5 mL). After the mixture warmed to ambient temperature, the organic layer was separated and the aqueous layer was extracted with ether (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. Flash chromatography (silica gel, hexanes) afforded after vacuum drying of the residue 79 mg (85%) of the *E* hydrocarbon **24a**.

(*E*)-14-Ethyldrima-5,7,9(14)-triene (24b). A solution of *tert*-butyllithium (1.7 M in pentane, 594 μL, 1.0 mmol) was added to a solution of (*Z*)-vinyl sulfoxide **12b** (87 mg, 0.25 mmol) and *sec*-butyl alcohol (58 μL, 0.63 mmol) in ether (6 mL) cooled to −78 °C under nitrogen. The reaction mixture was allowed to stir for 2 min and then quenched with water (4 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic layers were dried ($MgSO_4$) and after solvent evaporation, the residue was subjected to chromatographic purification (silica gel/hexanes). Vacuum drying of the resultant residue afforded 29 mg (51%) of the corresponding *E* hydrocarbon **24b** as an oil.

(*E*)-14-Isopropyldrima-5,7,9(14)-triene (24c). To a solution of (*Z*)-vinyl sulfoxide **12c** (90 mg, 0.24 mmol) and *sec*-butyl alcohol (58 μL, 0.63 mmol) in ether (8 mL) cooled to −78 °C under nitrogen was added *tert*-butyllithium (1.70 M in pentane, 594 μL, 1.01 mmol). The reaction mixture was allowed to stir for 2 min and then quenched with water (5 mL) at −78 °C. After the mixture warmed to ambient temperature, the organic layer was separated and the aqueous layer was extracted with ether (2 × 20 mL). The combined organic layers were dried (Na_2SO_4) and then concentrated. The residue was chromatographed (silica gel/hexanes) and vacuum drying afforded 25 mg (42%) of the pure *E* hydrocarbon **24c** as an oil.

Reduction of (*Z*)-Vinyl Sulfoxide 13c. 6-Isopropyl-4,12,12-trimethylbicyclo[6.4.0]dodeca-1(8),2,4-triene (26a). To a solution of (*Z*)-vinyl sulfoxide **13c** (84 mg, 0.22 mmol) and *sec*-butyl alcohol (50 μL, 0.55 mmol) in ether (6 mL) cooled to −78 °C under nitrogen was added *tert*-butyllithium (1.7 M in pentane, 515 μL, 0.88 mmol). The reaction mixture was allowed to stand for 2 min and then quenched with water (4 mL). The organic layer was separated and the aqueous layer was extracted with ether (2 × 15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The ^1H NMR (200 MHz, $CDCl_3$) of this crude vacuum-dried material indicated the presence of the open-chain tetraene hydrocarbon **25a** and the bicyclic hydrocarbon **26a** (ca. ∼50:50 mixture). The following signals were assigned to the tetraene **25a**: δ 4.67 (1 H, H_E of exo methylene, d, J ∼ 2.9 Hz), 5.07 (1 H, H_Z of exo methylene, m), 5.76 (1 H, $H_{4'}$, dd, J ∼ 16.1, 7.3 Hz; obscured partially by the signals of the bicyclic hydrocarbon **26a**), 6.27 (1 H, $H_{2'}$, d, J ∼ 11.7 Hz), 6.37 (1 H, $H_{1'}$, d, J ∼ 11.7 Hz), 6.66 (1 H, $H_{5'}$, br d, J ∼ 16.1 Hz); the high-field signals of the tetraene were badly obscured by those of its rearrangement product. Chromatographic purification by HPLC (Whatman Partisil column, hexanes) afforded three fractions A–C. Fractions A and B could not be cleanly separated and were therefore identified as a mixture of the open-chain hydrocarbon **25a** (ca. ∼10%) and bicyclic hydrocarbon (ca. ∼90%). Fraction C, present in only small amounts, could not be identified. On standing overnight at room temperature, the combined fractions A and B were completely converted to the bicyclic hydrocarbon **26a** (40 mg, 71%).

Reduction of (*Z*)-Vinyl Sulfoxide 13d. 6-*tert*-Butyl-4,12,12-trimethylbicyclo[6.4.0]dodeca-1(8),2,4-triene (26b). A solution of *tert*-butyllithium (1.7 M in pentane, 396 μL, 0.67 mmol) was added to a solution of (*Z*)-vinyl sulfoxide **13d** (62 mg, 0.17 mmol) and *sec*-butyl alcohol (39 μL, 0.42 mmol) in ether (5 mL) cooled to −78 °C under nitrogen. The reaction mixture was stirred for 2 min, quenched with water (4 mL), and warmed. The organic layer was separated and the aqueous layer was extracted with ether (2 × 20 mL). After the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated, HPLC purification (Whatman Partisil column, hexanes) afforded four fractions A–D, which were individually collected and examined by ^1H NMR spectroscopy. Fractions A and D appeared to be solvent related and were discarded. Fraction B was the bicyclic product **26b** while C was assigned as the open-chain tetraene, which could not be fully characterized because of its ready isomerization to **26b**. After fraction C was allowed to stand overnight at room temperature, it was combined with fraction B to afford a total of 36 mg (88%) of the bicyclic hydrocarbon **26b**.

The intermediate tetraene **25b** (fraction C, immediately after HPLC collection) was characterized by ^1H NMR spectroscopy (the presence of electrocyclization product, ca. ∼60% tetraene **25b** and ∼40% bicyclic hydrocarbon **26b**, was already apparent). The following ^1H NMR (200 MHz, $CDCl_3$) signals were assigned to tetraene **25b**: δ 4.68 (1 H, H_E of exo methylene, d, J ∼ 2.9 Hz), 5.07 (1 H, H_Z of exo methylene, m), 5.75 (1 H, $H_{4'}$, d, J ∼ 15.8 Hz), 6.28 (1 H, $H_{2'}$, br d, J ∼ 11.7 Hz), 6.39 (1 H, $H_{1'}$, d, J ∼ 11.7 Hz), 6.63 (1 H, $H_{5'}$, d, J ∼ 15.8 Hz).

Reduction of (*E*)-Vinyl Sulfoxide 14c. (2(1′)-*Z*,2′*Z*,4′*Z*)-1,1-Dimethyl-2-(3′,6′-dimethyl-2′,4′-heptadienylidene)-3-methylenecyclohexane (27a) and Trienyne 28a. To a solution of (*E*)-vinyl sulfoxide **14c** (94 mg, 0.26 mmol) in dry ether (6 mL) was added *sec*-butyl alcohol (59 μL, 0.64 mmol) under a nitrogen atmosphere and then the mixture was cooled to −78 °C. A solution of *tert*-butyllithium (1.7 M in pentane, 600 μL, 1.0 mmol) was added and, after the reaction mixture was allowed to stir for 2 min, it was quenched with water (4 mL). The aqueous layer was extracted with ether (2 × 15 mL), and the combined organic layers were dried ($MgSO_4$) and then concentrated. Chromatographic purification by HPLC (Whatman Partisil column, hexanes) afforded 32 mg (52%) of hydrocarbon **27a** (eluted first) and 10 mg (16%) of the alkyne **28a** (eluted second).

Reduction of (*E*)-Vinyl Sulfoxide 14d. (2(1′)-*Z*,2′*Z*,4′*Z*)-1,1-Dimethyl-2-(3′,6′,6′-trimethyl-2′,4′-heptadienylidene)-3-methylenecyclohexane (27b) and Trienyne 28b. The (*E*)-vinyl sulfoxide **14d** (87 mg, 0.23 mmol) was dissolved in dry ether (5 mL), and the solution was cooled to −78 °C. The *sec*-butyl alcohol (50 μL, 0.55 mmol) was added to the sulfoxide solution followed by *tert*-butyllithium (1.7 M in pentane, 534 μL, 0.91 mmol). The reaction mixture was allowed to stir for 2 min before quenching with water (4 mL) and warming to ambient temperature. The aqueous layer was extracted with ether (2 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and then concentrated. HPLC purification (Whatman Partisil column, hexanes) afforded 38 mg (65%) of the corresponding hydrocarbon **27b** (eluted first) and 10 mg (17%) of the trienyne **28b** (eluted second).

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Registry No. (±)-**9a**, 114582-48-8; (±)-**9b**, 114582-50-2; (±)-**9c**, 114582-52-4; (±)-**9d**, 114582-54-6; **11a**, 114582-55-7; **11b**, 114582-56-8; **12c**, 114582-57-9; (±)-**13c**, 114582-58-0; (±)-**13d**, 114582-59-1; (±)-**14c**, 114613-31-9; (±)-**14d**, 114582-60-4; **18**, 79-77-6; (±)-**20a**, 114582-47-7; (±)-**20b**, 114582-49-9; (±)-**20c**, 114582-51-3; (±)-**20d**, 114582-53-5; (±)-**23a**, 114582-61-5; (±)-**23b**, 114582-62-6; (±)-**24a**, 94369-97-8; (±)-**24b**, 114582-63-7; (±)-**24c**, 114594-79-5; **25a**, 114582-64-8; **25b**, 114582-67-1; (±)-**26a**, 114582-65-9; (±)-**26b**, 114582-66-0; **27a**, 114582-68-2; **27b**, 114582-70-6; **28a**, 114582-69-3; **28b**, 114582-71-7; HC≡CMe, 74-99-7; HC≡CEt, 107-00-6; HC≡CPr-*i*, 598-23-2; HC≡CBu-*t*, 917-92-0.

Supplementary Material Available: Spectral and analytical data (31 pages). Ordering information is given on any current masthead page.

Rearrangements of 6-Tricyclo[3.3.0.0^{2,7}]octyl Cations. Factors Influencing the Relative Stabilities of Bridged Carbocations

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The objective of this work was to explore the effect of ring strain on σ delocalization of carbocations. The 6-tricyclo[3.3.0.0^{2,7}]octyl cation (**3**) incorporates 2-norbornyl and 2-bicyclo[2.1.1]hexyl structures in a highly strained molecular framework. Solvolyses of the epimeric brosylates **22** and **23**, as well as nitrous acid deaminations of the analogous amines, **24** and **21**, served to generate **3**. The exo:endo rate ratios of the brosylates and the exo:endo product ratios of the tricyclo[3.3.0.0^{2,7}]octan-6-ols (**19**, **20**) are close to unity. Product distributions and kinetic data suggest a weak k_s contribution at least for the endo brosylate **23**. Several nondegenerate rearrangements of **3** were elucidated: Migration of C-2 from C-7 to C-6 (**3** → **28**) is followed, in part, by fragmentation (**28** → **31**). A minor fraction of **3** undergoes 4,6-hydride shifts (**3** → **37** ⇄ **38**). The degeneracy of **3** was probed with the aid of a 6-^{2}H label. Migration of C-8 from C-7 to C-6 was found to be rapid, as compared to nucleophilic capture, whereas the norbornyl-type Wagner–Meerwein rearrangement (migration of C-4) was not observed. Product and label distributions indicate that the bridged structure (involving C-6, -7, and -8) **3c** is nearly isoenergetic (±0.5 kcal/mol) with the unsymmetrical ion **3a** while products from the norbornyl-type delocalized ion (**3b**) are not observed, so **3b** must be less stable by at least 3 kcal/mol. The exceptional order of relative stabilities is explained in terms of "olefinic strain", i.e., the additional strain resulting from contraction of the basal bond in bridged carbocations.

Many carbocations are known in which the charge is delocalized in two-electron three-center bonds.[1] By Olah's terminology these are carbonium ions as opposed to the charge-localized carbenium ions.[2] These terms actually refer to limiting cases; there can be a continuum of electron delocalization in carbocations.[3] Electronic effects on σ delocalization have been thoroughly studied. For instance, the classical (C_1) structure of the 2-norbornyl cation (**1a**) was found to be favored by charge-stabilizing substituents at C-1 and C-2,[1,4] as well as by electron-withdrawing groups at C-6.[3a,5] The influence of ring strain has received much less attention. Recent solvolytic[6] and computational studies[7] of the 2-bicyclo[2.1.1]hexyl cation (**2**) indicate that the delocalized structure **2b** should be about 3 kcal/mol more stable than **2a** (the exchange of the methylene groups of **2b** must proceed via **2a**). Estimates of the stabilization energy of the 2-norbornyl cation due to bridging (**1b** vs **1a**) are higher: 6–8 kcal/mol from exo:endo rate ratios[1,4] and from heats of ionization;[8] 10–11 kcal/mol from gas phase hydride affinities.[9] However, such estimates depend on the choice of appropriate models.[10] Any conclusion from

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