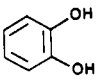
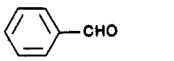
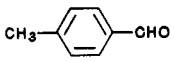
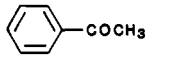
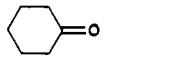
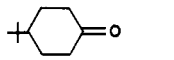
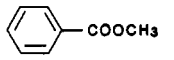
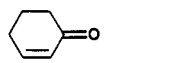
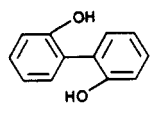
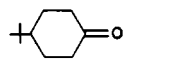
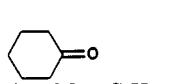
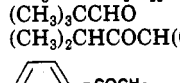
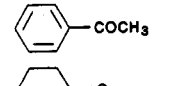
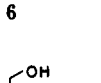
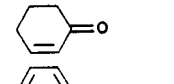
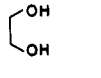
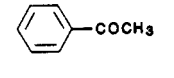
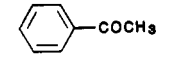
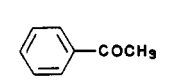
Table I. Reduction of Carbonyl Compounds with Bis(diolato)hydridosilicate

alcohol	carbonyl compd	conditions	% yield[a]
 5		0 °C, 2 h	96
5		0 °C, 2 h	96
5		0 °C, 2 h	98
5		0 °C, 2 h	95
5		0 °C, 2 h	92[b]
5		rt,[g] 12 h	0
5		0 °C, 2 h	85[c]
 6		rt, 5 h	92[d]
6		rt, 5 h	100
6	CH_3CO-*n*-C_5H_{11}	rt, 5 h	90
6	$(CH_3)_3CCHO$	rt, 5 h	92[e]
6	$(CH_3)_2CHCOCH(CH_3)_2$	rt, 30 h	50[e]
6		rt, 5 h	97
6		rt, 5 h	91[f]
		rt, 12 h	50[e]
		rt, 12 h	50[e]
EtOH		reflux, 24 h	0
PhOH		reflux, 40 h	0

[a] Isolated by TLC or distillation. [b] Cis/trans = 44/56 as determined by GLC. See text. [c] 2-Cyclohexenol was the sole product. [d] Cis/trans = 67/33 as determined by GLC. [e] Determined by GLC. [f] 2-Cyclohexenol/cyclohexanone = 97/3. [g] rt = room temperature.

the alcohol with a cis/trans ratio of 10/90,[10] whereas stereically bulky reducing reagents such as LiAlH(*i*-Bu)$_2$-*t*-Bu,[11] NaBH(OCHMe$_2$)$_3$,[10] and LiBH(*sec*-Bu)$_3$[12] gave the product in ratios of 49/51, 20–25/75–80, and 96.5/3.5, respectively. Judging from these data, **4** and **7** are the reducing reagents of fairly large steric bulkiness.

Next, the structure and reactivity relationship in the reduction was examined with substituted benzaldehydes. To **7** prepared first at −78 °C in THF was added a mixture of benzaldehyde (10 equiv) and a substituted benzaldehyde (10 equiv). After being kept at 26 °C for 5 h, the yields of both unsubstituted and substituted benzyl alcohols were analyzed by GC. The result is shown graphically in Figure 1. Excellent Hammett plots for the relative reactivities were obtained. Very recently, Yang and Tanner have

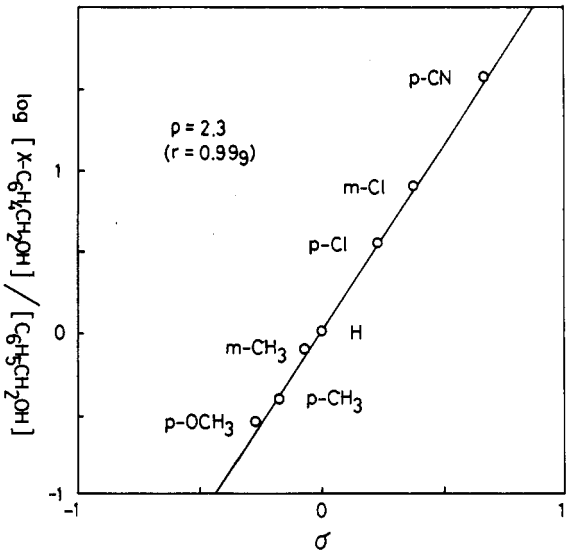


Figure 1. Hammett plots for the reduction of substituted benzaldehydes with bis(biphenyl-2,2′-diolato)hydridosilicate at 26 °C.

suggested that the single electron transfer (SET)–hydrogen atom abstraction mechanism should be involved in the fluoride ion catalyzed reduction of carbonyl compounds with phenyldimethylsilane.[13] However, an excellent linear Hammett plot with a large positive ρ value (2.3, $r = 0.99_9$) indicates that the hydride transfer step should be involved in the rate-determining step at least in the present system. Further works are in progress.

Registry No. **4**, 106469-05-0; **5**, 120-80-9; **6**, 1806-29-7; **7**, 106469-06-1; $HO(CH_2)_2OH$, 107-21-1; $HOC(CH_3)_2C(CH_3)_2OH$, 76-09-5; C_6H_5CHO, 100-52-7; 4-$H_3CC_6H_4CHO$, 104-87-0; $C_6H_5COCH_3$, 98-86-2; $C_6H_5CO_2CH_3$, 93-58-3; $H_3CCOC_5H_{11}$, 110-43-0; $(CH_3)_3CCHO$, 630-19-3; $(CH_3)_2CHCOCH(CH_3)_2$, 565-80-0; $C_6H_5CH_2OH$, 100-51-6; 4-$H_3CC_6H_4CH_2OH$, 589-18-4; $C_6H_5CH(OH)CH_3$, 98-85-1; $(CH_3)_3CCH_2OH$, 75-84-3; $(CH_3)_2CHCH(OH)CH(CH_3)_2$, 600-36-2; $H_3CCH(OH)C_5H_{11}$, 543-49-7; 4-butylcyclohexanone, 98-53-3; cyclohexanone, 108-94-1; 2-cyclohexen-1-one, 930-68-7; cyclohexanol, 108-93-0; *cis*-4-(1,1-dimethylethyl)cyclohexanol, 67590-15-2; *trans*-4-(1,1-dimethylethyl)cyclohexanol, 675901-13-0; 2-cyclohexen-1-ol, 822-67-3.

(10) Eliel, E. L.; Senda, Y. *Tetrahedron* **1970**, *26*, 2411.
(11) Kovacs, G.; Galambos, G.; Juvancz, Z. *Synthesis* **1977**, 171.
(12) Walker, E. R. H. *Chem. Soc. Rev.* **1976**, 23.
(13) Yang, D.; Tanner, D. D. *J. Org. Chem.* **1986**, *51*, 2267.

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Received August 7, 1986

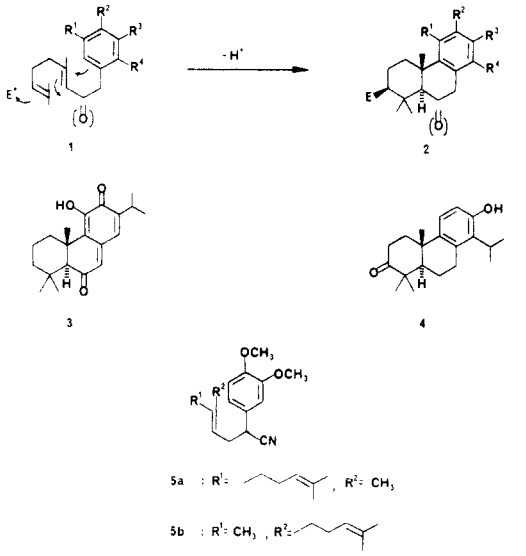
On the Direct Formation of Episulfonium Ions from Alkenes. An Application to the Synthesis of Higher Order Carbocycles via Episulfonium Ion Initiated Polyene Cyclizations

Summary: The use of methyl benzenesulfenate–Lewis acid binary systems for effecting biomimetic polyene cyclizations initiated by episulfonium ions has been demonstrated. The efficiency of higher order annulation is related to the stereostructure of the polyene as well as the nature of the Lewis acid promoter.

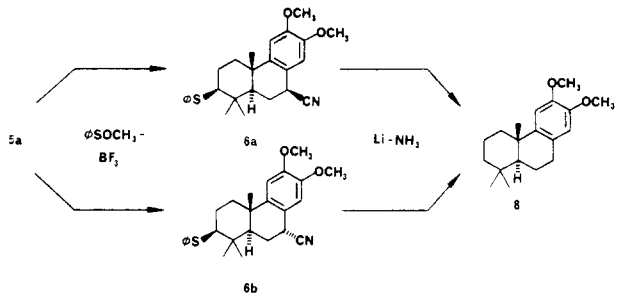
Sir: Cationic polyene cyclizations have become widely utilized for the synthesis of naturally occurring ring systems.[1] There are, however, relatively few methods which

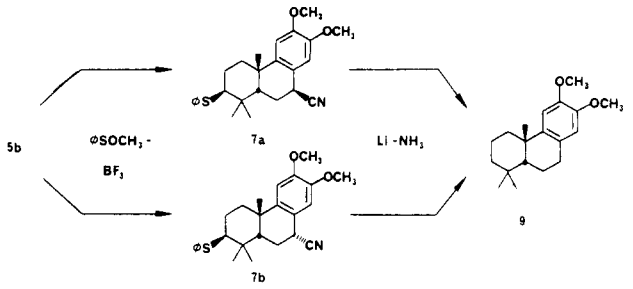
0022-3263/87/1952-0949$01.50/0

are *generally* useful for effecting these cascade reactions via the activation of simple external alkenes (e.g., **1** → **2**).[2,3] Our interest in this mode of initiation was stimulated by its potential application to the synthesis of the tricyclic ketoditerpenes taxodione (**3**)[4] and totarolone (**4**).[5] Recently, we described a direct method for the annulation of simple carbocycles via sulfenylative arene–alkene cyclizations.[6] In this communication we report the first examples of biomimetic polyene cyclizations initiated by pendent episulfonium and episelenonium ions[7,8] formed in situ from alkenes.

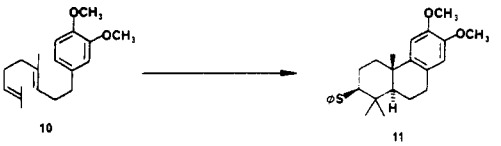


The precyclization substrates **5a** and **5b** were conveniently prepared by the lithiation of (3,4-dimethoxyphenyl)acetonitrile followed by alkylation with the requisite 1-bromo 2,6-diene.[9] Treatment of the ((*E*)-3,7-dimethylocta-2,6-dien-1-yl)phenylacetonitrile **5a** with 1.05 equiv of methyl benzenesulfenate ($PhSOCH_3$) in the presence of 2.10 equiv of BF_3 (as a 0.80 M solution in CH_3NO_2)[10] [CH_3NO_2, −30 °C (1 h)] furnished the diastereomeric octahydrophenanthrenes **6a** and **6b** (**6a**/**6b** = 1) as the exclusive products in 85% chromatographic yield.[11] Similarly, sulfenylative cyclization of the ((*Z*)-3,7-dimethylocta-2,6-dien-1-yl)phenylacetonitrile **5b** [1.05 equiv of $PhSOCH_3$, 2.10 equiv of BF_3, −30 °C (1 h)] provides the tricyclic adducts **7a** and **7b** as a 1:1 mixture of diastereomers in 59% isolated yield.[11,12] Support for the stereochemical assignments of **6a**,**b** and **7a**,**b** was provided by the following experiments. Reductive cleavage of the phenylthio and cyano moieties from the individual diastereomers **6a** and **6b** (Li, NH_3–*t*-BuOH–THF, −78 °C, 5 min) provided the common octahydrophenanthrene **8**. Reduction of the individual diastereomers **7a** and **7b** in an identical way gave a single new product **9** which was distinct from **8**.[13] The 300-MHz NMR spectrum of the reduction product **9** exhibited signals for the methyl substituents at 0.40, 0.92, and 1.14 ppm. The strongly shielded resonance for the 4-α methyl centered at 0.40 ppm is characteristic for octahydrophenanthrenoids which possess a cis-fused A/B ring junction.[14] By way of contrast, the 300-MHz NMR spectrum for **8** revealed rather unexceptional methyl signals at 0.91, 0.94, and 1.18 ppm as would be expected for members of this series which possess a trans-A/B ring junction.[14]





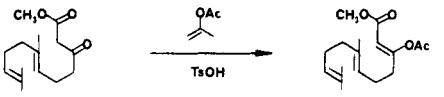
The inductive effect of the nitrile function was found to play a minor role in determining the site selectivity of initiation for substrates possessing an internal (*E*)-alkene. Accordingly, cyclization of the reductively decyanated aryl diene **10** [$PhSOCH_3$-BF_3, CH_3NO_2, −30 °C (1 h)] provided the corresponding octahydrophenanthrene **11** (mp 146–148 °C) in 58% recrystallized yield.[15]



In principle, a variety of alternative moieties could serve as terminators for episulfonium ion initiated polyene cyclizations. Appropriate terminators must, however, exhibit resistance toward premature sulfenylation. In light of this constraint, the sulfenylative cyclization of the (*Z*)-acetoxy enoate **13** was initially examined. The (*Z*)-acetoxy enoate **13** was prepared by the acylation of the corresponding

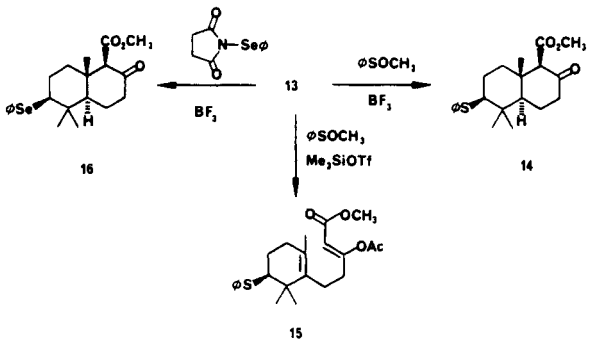
(1) Bartlett, P. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 341.
(2) McMurry, J. E.; Erion, M. D. *J. Am. Chem. Soc.* **1985**, *107*, 2712.
(3) Activation via mercuronium ions has been used to initiate polyene cyclizations in relatively electron rich substrates: Nishizawa, M.; Takenaka, H.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 806 and references therein.
(4) (a) The use of a tertiary allylic cation as a initiator in a biomimetic synthesis of taxodione has been reported: Johnson, W. S.; Shenvi, A. B.; Boots, S. *Tetrahedron* **1981**, *38*, 1397. (b) The synthesis of this natural product by nonbiomimetic pathways has also been described previously: Stevens, R. V.; Bisacchi, G. S. *J. Org. Chem.* **1982**, *47*, 2396 and references therein.
(5) Chow, Y. L.; Erdtman, H. *Acta Chem. Scand.* **1960**, *14*, 1852.
(6) Edstrom, E. D.; Livinghouse, T. *J. Am. Chem. Soc.* **1986**, *108*, 1334.
(7) Edstrom, E. D.; Livinghouse, T. *Tetrahedron Lett.* **1986**, *27*, 3483.
(8) The use of *N*-(phenylseleno)phthalimide and $SnCl_4$ to promote a diene cyclization involving the keto ester **12** has recently been reported: Ley, S. V. *Chem. Ind. (London)* **1985**, *4*, 101. In this instance, closure of the B ring occurred via cationic interception of the carbonyl oxygen.
(9) Skeean, R. W.; Trammell, G. L.; White, J. D. *Tetrahedron Lett.* **1976**, 525.
(10) Boron trifluoride ether complex is comparatively ineffective as a Lewis acid promoter for sulfenylative cyclizations.
(11) All new compounds have been fully characterized by 300-MHz NMR, ^{13}C NMR, and IR spectrometry and possess satisfactory (C, H) analyses or exact mass.
(12) In addition, 16% of a product arising from initiation at the internal alkene was isolated.
(13) The stereochemical purity of the octahydrophenanthrenes **8** and **9** was established by capillary gas chromatography.
(14) Wenkert, E.; Afonso, A.; Beak, P.; Carney, R. W. J.; Jeffs, P. W.; McChesney, J. D. *J. Org. Chem.* **1965**, *30*, 713.
(15) Preliminary experiments suggest that the inductive influence of the cyano function may be more important in governing the site selectivity of cyclization for substrates containing an internal (*Z*)-alkene.

β-keto ester **12** with isopropenyl acetate in the presence of TsOH.[16] Addition of the acetoxy enoate **13** over 1 h



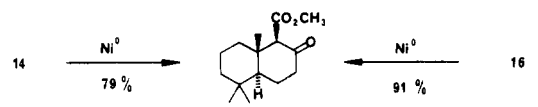
12 13

via a mechanical syringe to 1.10 equiv of $PhSOCH_3$ and 2.20 equiv of BF_3 (as a 0.80 M solution in CH_3NO_2) [CH_2Cl_2–CH_3NO_2 (2:1), −78 °C (1 h)] gave rise to the anticipated cyclized adduct **14** (mp 122–124 °C) in 53% recrystallized yield. In contrast to the results involving cyclization in the presence of BF_3, other Lewis acids proved less effective in promoting the formation of bicyclic products. Accordingly, treatment of **13** with $PhSOCH_3$ and Me_3SiOTf[6] led to the formation of the monocyclic derivative **15** in 46% yield. The existance of the monocycle **15** as an intermediate enroute to **14** in the $PhSOCH_3$·BF_3-mediated cyclization of **13** was ruled out by the exposure of **15** to 2 equiv of BF_3 or BF_3·CH_3OH complex [CH_3NO_2–CH_2Cl_2, −78 °C]. Under these sets of conditions the formation of **14** was not observed and the quantitative recovery of the monocycle **15** was realized.



We have recently disclosed that selenylative carbocycle annulations can be readily accomplished by the treatment of appropriate substrates with *N*-(phenylseleno)succinimide (PSS) in the presence of Lewis acids.[7,8] The utility of PSS–Lewis acid binary systems for initiating representative polyene annulations was demonstrated in the following way. Addition of the (*Z*)-acetoxy enoate **13** over 1 h via mechanical syringe to 1.10 equiv of PSS and 2.20 equiv of BF_3 [CH_2Cl_2–CH_3NO_2 (2:1), −78 °C (1 h)] provided the crystalline bicyclic keto ester **16** (mp 128–130 °C) in 47% chromatographed yield.

Evidence for the equatorial disposition of the pendant phenylthio and phenylseleno moieties of **14** and **16** was provided by the coupling constants observed for the associated C-3 methine protons. Specifically, these methines appeared as doublets of doublets possessing a characteristic *axial* coupling constant in each instance [(**14**: J = *12.3* and 4.6 Hz); (**16**: J = *12.0* and 4.8 Hz)]. The relative stereochemistry at the ring junctions of **14** and **16** was deduced by comparison of the spectral and physical properties of the corresponding reduction product **17** to those reported in the literature (mp **17**: 85–87 °C; lit. mp 85.5–87 °C).[9]



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The foregoing studies clearly indicate the potential that episulfonium and episelenonium ion initiated polyene cyclizations hold for the elaboration of natural products. The application of this methodology to the synthesis of the taxodione and totarolone ring systems will be described in the future.

Acknowledgment. Support for this research by a grant from the National Institutes of Health is gratefully acknowledged. This communication is dedicated to the memory of Professor Robert V. Stevens.

Registry No. **5a**, 106625-34-7; **5b**, 106625-35-8; **6a**, 106625-36-9; **6b**, 106625-37-0; **7a**, 106625-38-1; **7b**, 106625-39-2; **8**, 106708-95-6; **9**, 106708-96-7; **10**, 106625-40-5; **11**, 106625-41-6; **12**, 56523-17-2; **13**, 106625-42-7; **14**, 106625-43-8; **15**, 106625-44-9; **16**, 106625-45-0; **17**, 65794-68-5; $PhSOCH_3$, 1193-82-4.

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Received August 28, 1986

(16) Casey, C. P.; Marten, D. F. *Synth. Commun.* **1973**, *3*, 321.

Stability Relationships of Decalindiones. Modified MM2 Force Field Calculations

Summary: Calculations of the steric energies of decalindiones using standard MM2 parameters lead to predictions of greater stability for the cis isomers. Experimental equilibration studies demonstrate that the trans isomers are favored at equilibrium. Modified MM2 parameters lead to improved predictions of isomer ratios.

Sir: Molecular mechanics is an important and useful technique for the calculation of molecular properties.[1] The technique has seen increasing use in the prediction of favored geometries and the reactive stereochemistry of conformationally mobile systems,[2] transition state geometries,[3] and product vs. reactant energies.[4] The force fields and parameters developed by Allinger and co-workers and utilized through the MM2 program[1] have proven to be powerful tools in synthetic organic chemistry.[5] We wish to report, however, a significant problem with the application of currently available molecular mechanics programs to the calculation of steric energies of cyclic ketones.[6]

Our interest in the area of molecular modeling stems in part from work directed toward the total synthesis of clerodane antifeedant diterpenes.[7] One approach to the clerodanes, compounds featuring substituted decalin structures, involves the use of bicyclic Diels–Alder adducts of general structure **1** as synthetic intermediates.[8] We

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