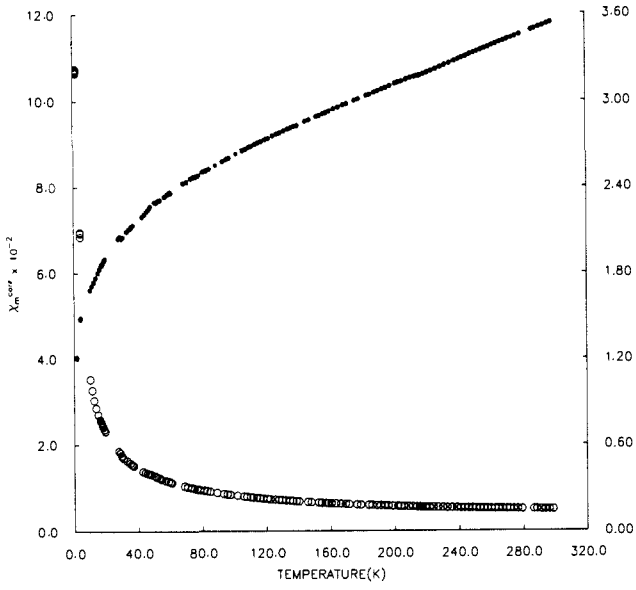

Figure 3. Molar magnetic susceptibility (χ_m, open circles) and effective magnetic moment (μ_{eff}, filled circles) of chromium trimer **3**.

Cr1, and C2 lie on the mirror plane), but the three chromium atoms form an almost perfect equilateral triangle. Sitting atop this triangle is a μ_3-CH group, presumably formed by multiple abstraction of hydrogen from a methyl ligand. Three chloride ligands, each bridging between two chromium atoms, and three cyclopentadienyl groups complete the molecule.

Common to both **1** and **3** is a pseudooctahedral coordination environment around Cr(III) consisting of a cyclopentadienyl ring, two chloride ligands, and an alkyl group. Edge sharing of two such fragments generates **1**, and condensation of three of these units in a doubly edge sharing arrangement results in **3**. Despite these similarities, the structures are remarkably different. Whereas **1** exhibits a Cr-Cr distance of 3.29 Å, that distance decreases to an average value of 2.82 Å in **3**. This is well within the range of distances typical of Cr-Cr single bonds (2.65-2.97 Å).[9] Another manifestation of this shortening is the decrease in the Cr-Cl-Cr angle from 88.5° in **1** to an average value of 73.6° in **3**.[10] The question then arises whether **3** is a true chromium cluster. Does it contain M-M bonds, or is it merely a polynuclear complex with unusually short M-M contacts?

Metal-metal bonding implies spin pairing, and we have therefore studied the magnetic behavior of **3** (Figure 3). The effective magnetic moment of **3** is temperature dependent, indicating an antiferromagnetic interaction between the chromium atoms.[5,11] The phenomenon of molecular antiferromagnetism does not depend on direct metal-metal bonding, as the observation of such interaction in **1** demonstrates. However, in a recent series of papers, Pasynskii et al. have proposed the occurrence of antiferromagnetism in Cr-Cr bonded systems.[12] Their sole criterion for the presence of such bonding seems to be the observed metal-metal distance. We prefer to think of these systems as weakly interacting, i.e., occupying an intermediate position in the spectrum ranging from isolated metal centers to true metal-metal bonds.[13]

There remains the question what, if not metal-metal bonding, is the cause of the drastic contraction of the Cr-Cr distance in **3**? A comparison with other structurally characterized μ_3-CH complexes provides a possible clue.[14] The M-C-M angles in this—albeit small—sample are typically smaller than 90° (ranging from 81.5 to 87.5°). The corresponding average angle of 93.3° in **3** represents a deviation from the preferred hybridization of the μ_3-CH ligand. It may be this structural "clamp" that is responsible for the short Cr-Cr contacts. It remains to be seen whether this situation affects the reactivity of the μ_3-CH group.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation (CHE-8451670 and CHE-8512710), the Camille and Henry Dreyfus Foundation, the Atlantic Richfield Foundation, Dow Chemical Co., Rohm and Haas Co., and Cornell University.

Supplementary Material Available: Tables of X-ray structure determinations of **1** and **3** (17 pages); tables of structure factors for **1** and **3** (11 pages). Ordering information is given on any current masthead page.

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(11) (a) Attempts to fit the χ_m data with the HDVV model as applied to an equilateral triangle of $S = {}^3/_2$ ions proved unsatisfactory. However, the room temperature moment of **3** (μ_{eff}(300 K) = 3.55 μ_B) is consistent with $J \approx -110$ cm^{-1}; see ref 11d. (b) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48. (c) Wucher, J.; Gijsman, H. M. *Physica (Amsterdam)* **1954**, *20*, 361. (d) Earnshaw, A.; Figgis, B. N.; Lewis, J. *J. Chem. Soc. A* **1966**, 1656.

(12) (a) Pasynskii, A. A.; Eremenko, I. L.; Rakitin, Yu. V.; Novotortsev, V. M.; Kalinnikov, V. T.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 57. (b) Pasynskii, A. A.; Eremenko, I. L.; Orazsakhatov, B.; Rakitin, Y. V.; Novotortsev, V. M.; Ellert, O. G.; Kalinnikov, V. T. *Inorg. Chim. Acta* **1980**, *39*, 91. (c) Eremenko, I. L.; Pasynskii, A. A.; Gasanov, G. Sh.; Orazsakhatov, B.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *275*, 71 and references therein.

(13) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

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Stereochemistry of the Intramolecular Enamine/Enal (Enone) Cycloaddition Reaction and Subsequent Transformations

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Received August 12, 1986

The [4 + 2] cycloaddition reaction of electron-rich olefins with α,β-unsaturated carbonyl compounds is an important transformation in organic synthesis.[1] Enamines are particularly reactive heterodienophiles that often react with heterodienes at room temperature or below. The reaction course is highly dependent on enamine and heterodiene structure and can result in the formation of dihydropyrans, cyclobutanes, and alkylated enamines.[2] We have found the intramolecular reaction of certain enamine/enal (enone) combinations, generated in situ by the action of a secondary alkyl or aryl amine on an aldehyde/enal (enone), proceeds stereoselectively under mild conditions to provide [4 + 2] cycloadducts.[3] Furthermore, the dihydropyran products can

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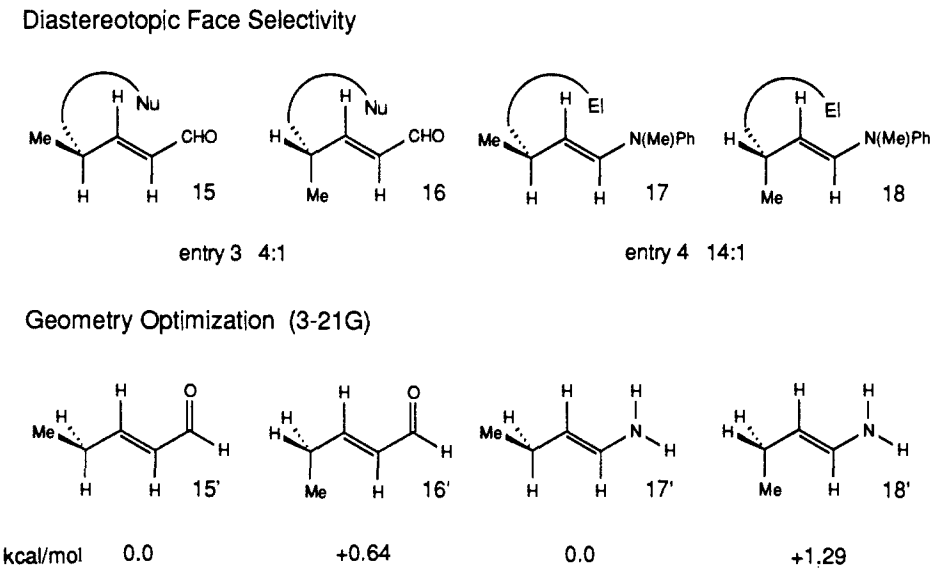
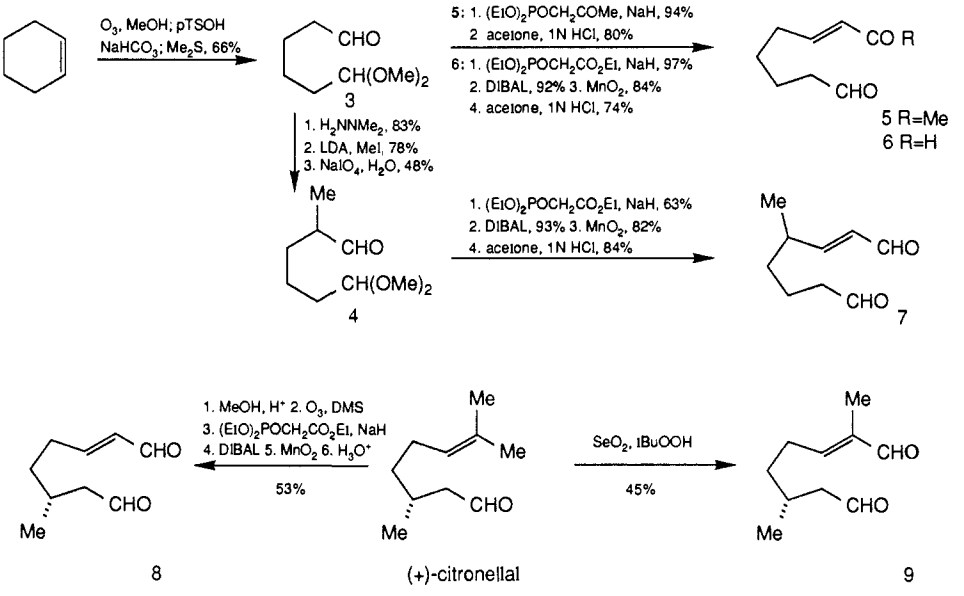
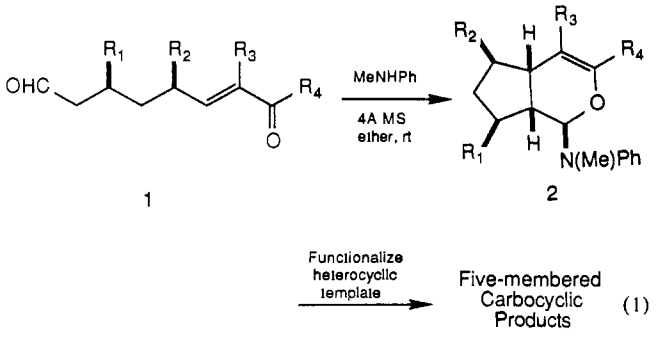


Figure 1.

Scheme I



be functionalized by several stereoselective protocols that provide substituted five-membered carbocycles (eq 1). The details of these studies are reported in this paper.



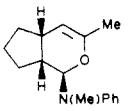
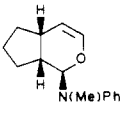
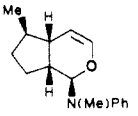
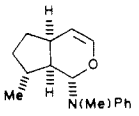
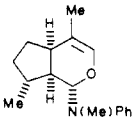
The substrates for the carbocyclization reaction were prepared from cyclohexene (**5**–**7**) and (+)-citronellal (**8**, **9**). Cyclohexene (66 g) was converted to the terminally differentiated product **3** in 66% yield (86 g) by a slight modification of the previously reported method.[4] Aldehyde/enone **5** and aldehyde/enals **6** and **7** were prepared from **3** by standard transformations. (+)-Citronellal ($[\alpha]^{27}_D$ +13.6°, ether) was degraded and homologated to **8** and oxidized, according to the procedure of Sharpless,[5] to **9** (Scheme I).

The results of the cyclization reactions are reported in Table I. Several secondary alkyl amines have been examined and shown to be effective as reagents that promote adduct formation. Among the achiral amines that were examined, *N*-methylaniline provided optimal results with regard to both the yield and stability of the products. Each reaction proceeded with complete relative face selectivity (*ul*) to provide cis-fused products. The reactions of substrates **7**–**9** illustrate internal asymmetric induction by a stereogenic center at the allylic carbon of the enal (entry 3) and enamine (entries 4 and 5). When these reactions were stopped after cyclization was complete (30 min) the indicated ratio of products was obtained. If the same reactions were allowed to proceed for longer periods of time (10 h) a slower thermodynamic equilibration was established and resulted in a high degree of diastereoselection in each case. Silica gel appears to promote equilibration as well, a result that prevented isolation of the minor methyl epimers by silica gel chromatography. Nevertheless, we were able to establish that equilibration takes place (as opposed

(4) Methanol was employed as solvent, see: (a) Schreiber, S. L.; Claus, R. E.; Reagan, J. *Tetrahedron Lett.* **1982**, *23*, 3867. (b) Schreiber, S. L.; Claus, R. E. *Organic Syntheses*; Wiley: New York, 1984; Vol. 64, p 150.

(5) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526.

Table I. Cycloaddition Results[a]

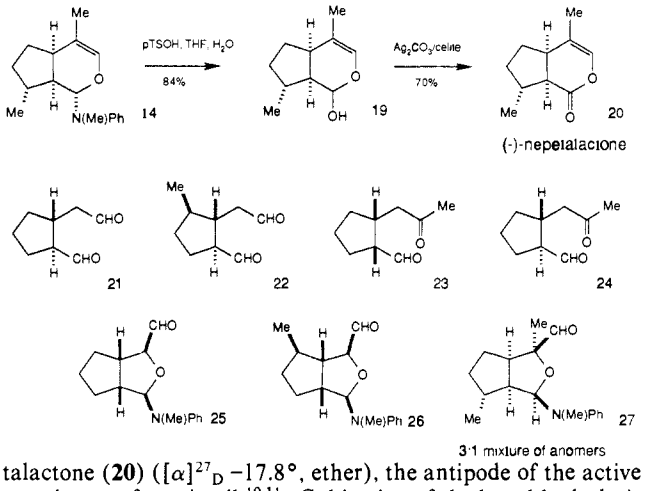
entry	substrate	products	yield	ratio 30 min	ratio 10 h
1	**5**	 (±)-10	73%	>25:1	
2	**6**	 (±)-11	60%	>25:1	
3	**7**	 (±)-12	60%	4:1[d,e]	>25:1
4	**8**	 (-)-13[b]	86%	14:1[d,f]	>25:1
5	**9**	 (-)-14[c]	84%	10:1[d,g]	>25:1

[a] Reactions were conducted in ether at room temperature (30 min and 10 h) with 1.1 equiv of *n*-methylaniline and 4A molecular sieves. [b] $[\alpha]^{27}_D$ −26.0°, ether. [c] $[\alpha]^{27}_D$ −38.3°, ether. [d] Ratios refer to methyl epimers, the major isomer is depicted. [e] Stereochemistry at the carbon-bearing methyl substituent of both isomers was determined by NOEDS. [f] Stereochemistry assigned by analogy to entry 5. [g] Stereochemistry of each isomer of the 10:1 mixture was secured by conversion to nepetalactone and epi (methyl) nepetalactone, respectively.

to selective decomposition) in entry 3 by the use of an internal standard.

The increase in selectivity in entry 4 relative to entry 3 under kinetically controlled conditions is noteworthy. The *E* enamines that are expected as intermediates from **7** and **8** differ only in the location of the methyl substituent (allylic to the enal in **7** and enamine in **8**).[6] The eclipsed conformations **15**–**18** of these allylic systems are depicted in Figure 1. If carbon–carbon bond formation were to take place from these (ground state) low-energy rotamers,[7] the major products would be obtained from **15** and **17** and the minor products from **16** and **18**. The energy differences between pairs of model conformers **15′**–**18′** were calculated via ab initio MO theory. Complete geometry optimization with the 3-21G basis set provided the results shown in the figure. The larger energy difference between **17′** and **18′** relative to **15′** and **16′** is consistent with these local conformations as components of the transition-state structures. The origins of these differences in rotational preferences and the larger details of the transition-state structures are problems that continue to receive our attention.[8]

The hydrolysis of the dihydropyrans **11**–**14** in Table I with *p*-toluenesulfonic acid in aqueous tetrahydrofuran produced unsaturated lactols and a trace amount of the corresponding cis-substituted dials. Thus, **14** gave rise to **19** ($[\alpha]^{27}_D$ +29°, ether) which was oxidized with Fetizon's reagent[9] to provide (−)-nepetalactone (**20**) ($[\alpha]^{27}_D$ −17.8°, ether), the antipode of the active constituent of catnip oil.[10,11] Subjection of the lactol hydrolysis products from **11** and **12** to the action of DBU in THF produced the epimerized dials **21** and **22**, respectively, in 60–65% yield (trans/cis > 25:1) for the two-step operation. The hydrolysis of **10** provided the cis-substituted keto-aldehyde **23** that could be epimerized to the trans isomer **24** (DBU, THF).



Stereoselective oxidation of the enol ether present in the cycloadducts was achieved by treatment with mCPBA and $NaHCO_3$ in methanol at 0 °C[12] or catalytic osmium tetraoxide and *N*-methylmorpholine *N*-oxide (NMMO) in tetrahydrofuran at 0 °C.[13] For example, employment of the latter conditions with dihydropyrans **11** and **12** provided the bicyclic tetrahydrofurans **25** and **26**, respectively, in 68–72% yield. The stereochemistry of the oxidation products was determined by NOEDS experiments on **26** and the corresponding primary alcohol obtained by reduction of the formyl group of **25** ($LiAlH_4$, THF, 0 °C). The exo stereochemistry of the formyl groups in **25** and **26** may result from endo (concave) oxidation of the bicyclic dihydropyrans[14] followed by rearrangement to the bicyclic tetrahydrofuran skeleton or by exo (convex) oxidation[15] followed by rearrangement and epimerization of the formyl groups.[16] Attempts to trap an intermediate tetrahydrofuran with an *endo*-formyl substituent in these systems were largely unsuccessful. However, in the case of (−)-**14**, where epimerization of the resultant formyl group is not possible, oxidation (OsO_4, NMMO) was found to take place on the convex face and gave rise to a 3:1 anomeric mixture of products **27** (major anomer depicted) with the formyl substituent on the endo face of the bicycle. The stereochemistry of these products was determined by consideration of *J* values in combination with NOEDS experiments.

Finally, we note that the cyclization reactions of aldehyde/enal **6** respond to several chiral amines with substantial asymmetric induction. The details of these and related studies are currently under investigation and will be reported in due course.

(6) For example, when heptanal was subjected to the reaction conditions, rapid formation of the *E* enamine ensued.

(7) Martin, E.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 5035.

(8) For experimental studies of related "remote" substituent effects on the rotational preferences of the sp^2–sp^3 bond, see: Lessard, J.; Saunders, J. K.; Viet, M. T. P. *Tetrahedron Lett.* **1982**, *23*, 2059.

(9) Fetizon, M.; Golfier, M. *C. R. Acad. Sci., Ser. 3* **1968**, *267*, 900.

(10) Structure determination: Bates, R. B.; Eisenbraun, E. J.; McElvain, S. M. *J. Am. Chem. Soc.* **1958**, *80*, 3420.

(11) Syntheses: (a) Sakan, T.; Fujino, A.; Murai, F.; Suzuki, A.; Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1737. (b) Achmad, S. A.; Cavill, G. W. K. *Proc. Chem. Soc.* **1963**, 166. (c) Trave, R.; Marchesini, A.; Garanti, L. *Gazz. Chim. Ital.* **1968**, *98*, 1132.

(12) Ireland, R. E.; Habich, D. *Tetrahedron Lett.* **1980**, 1389.

(13) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

(14) For examples of anomalous endo (concave) oxidations of cis-fused bicyclic systems, see: (a) Nelson, N. A.; Scahill, T. A. *J. Org. Chem.* **1979**, *44*, 2791. (b) Vedejs, E.; Campbell, J. B.; Gadwood, R. C.; Rodgers, J. D.; Spear, K. L.; Watanabe, Y. *J. Org. Chem.* **1982**, *47*, 1534. (c) Smith, A. B.; Boschelli, D. *J. Org. Chem.* **1983**, *48*, 1217.

(15) For a relevant example of the more common exo (convex) addition, see: Jung, M. E.; Light, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 7614.

(16) For the facile epimerization of formyl substituted furanosides, see: (a) Jones; G. H.; Moffatt, J. G. *Abstracts of Papers*, 158th National Meeting of the American Chemical Society, New York, NY, American Chemical Society: Washington, DC, 1969; CARB 16. (b) Kozluk, T.; Zamoski, A. *Tetrahedron* **1983**, *39*, 805.

Acknowledgment. These investigations were supported by the NIH (GM-30738) to whom we are grateful. Additional support was provided by the NSF (Presidential Young Investigator Award), Alfred P. Sloan Foundation (1985-1987), and the Camille and Henry Dreyfus Foundation, Inc. (Teacher/Scholar Award 1984-1989). Matching funds for the NSF-PYI award were generously provided by American Cyanamid, the Upjohn Co., and Pfizer, Inc. Preliminary experiments in these studies were carried out by R. E. Claus. We thank Professor E. J. Eisenbraun (Oklahoma State University) for providing spectral data of (+)-nepetalactone and Professor Scott E. Denmark (University of Illinois at Urbana—Champaign) for many helpful and stimulating discussions.

Supplementary Material Available: Tables of 3-21G optimized geometries for **16'**, **15'**, **18'**, and **17'** and experimental section including experimental procedures and spectral data (10 pages). Ordering information is given on any current masthead page.

Intramolecular [4 + 2] Cycloadditions of (*Z*)-α,β-Unsaturated Aldehydes with Vinyl Sulfides and Ketene Dithioacetals[1a]

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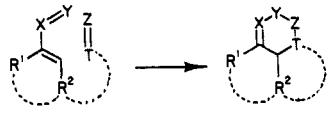
Received August 12, 1986

In the course of our investigations on intramolecular [4 + 2] cycloadditions of nitrosoalkenes[2] (eq 1, X=Y = N=O) we discovered that vinyl sulfides (T=Z = CH=CHSCH$_3$) were superior to enol ethers as electron-rich dienophiles. In contrast to the



(1)

extensive use of enol ethers and enamines in inverse-electron-demand heterodiene cycloadditions,[3,4] vinyl sulfides have received little attention.[5] Indeed, these activated olefins have enjoyed only sparing application in any cycloaddition process[6] despite their synthetic potential.[7] We have now extended our study to include (*Z*)-α,β-unsaturated aldehydes as the 4π-component in these intramolecular cycloadditions.[8] Our rationale for investigating the labile *Z*-geometrical isomers was based on the anticipated higher stereoselectivity of cyclization amply demonstrated in analogous Diels-Alder reactions.[9] We report herein that these reactions operate under kinetic control with Lewis acid catalysis to give exclusively cis-ring-fused products.

Scheme I

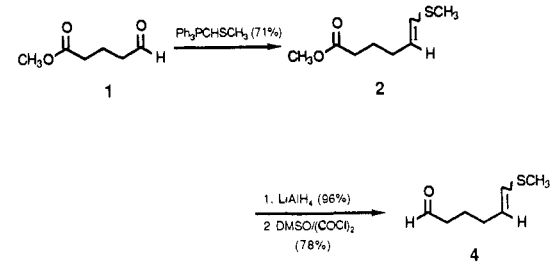
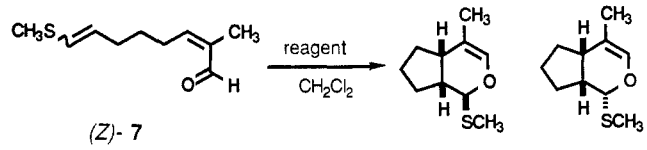


Table I. Cyclization of (*Z*)-**7**[a]

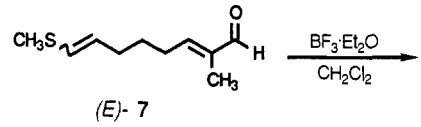


(*Z*)- **7**

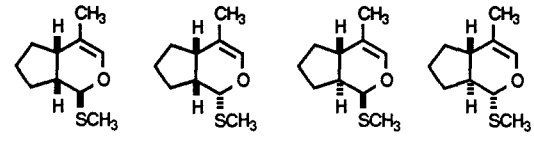
					8a	8b
entry	reagent (equiv)	temp, °C	time	yield, %	**8a:8b**	
1		50	19 h	35	96:4[b]	
2	BF_3·OEt_2 (1.0)	-78	10 min	93	75:25[c]	
3	BF_3·OEt_2 (1.0)	-70	15 min	91	71:29[c]	

[a] The (*Z*)-**7** was a 60:40 *E*:*Z* mixture of vinyl sulfides. [b] Ratio determined by ^{1}H NMR. [c] Ratio determined by capillary GC.

Table II. Cyclization of (*E*)-**7**[a]



(*E*)- **7**



					8a	8b	9a/9b
entry	equiv	temp, °C	time, min	yield, %	**8a:8b:9a/9b**[b]		
1	1.0	-78	15	55	13:44:20/23		
2	1.0	-78	15	38	41:35:24		
3	1.0	-78	45	64	72:28:2		
4	1.0	20	15	48	87:13:0		
5	0.5	-78	30		20:40:22/18[c]		
6	1.5	-78	30		36:39:14/11[c]		

[a] The (*E*)-**7** was a 60:40 *E*:*Z* mixture of vinyl sulfides. [b] The assignment of anomers in **9** is tentative.[21] [c] GC experiments with an internal standard; see text.

(1) (a) Presented at the 190th National Meeting of the American Chemical Society, Chicago, IL, 1985; paper ORGN 139. (b) NSF Presidential Young Investigator 1985-1990, A. P. Sloan Fellow 1985-1987.

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