which is ca. 10% larger than the observed value. This difference suggests the higher ordering involving the interlocking of TCNQ radical anions.

The LB films exhibited higher conductivities in the lateral direction even without the I_2 vapor treatment. The value of conductivity in the film plane of HTF (3×10^{-5} S cm^{-1}) was larger than that of LTF (7×10^{-7} S cm^{-1}), due to the difference in orientation of TCNQ radical anion. No anisotropy of conductivity was observed in the film plane of HTF in spite of the structural anisotropy. The compacted sample of **1** exhibited a conductivity of 6.1×10^{-10} S cm^{-1}.

The relatively large values of conductivity in the lateral direction result from the highly anisotropic layered structure of LB films: the close stacking of charge-transfer layer sandwiched between layers of insulating long alkyl chains. The conductivity of the order of 10^{-14} S cm^{-1} was obtained in the normal direction for HTF.

These results indicate that the conductivity of films can be controlled by the subphase temperature and demonstrate the feasibility of controlling the orientation of donors and acceptors in the charge-transfer complex by means of LB technique.

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Acetal-Initiated Cyclizations of Vinylsilanes. A General Synthesis of Allylically Unsaturated Oxacyclics

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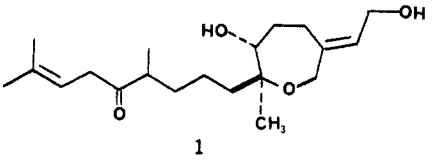
Oxacyclics have been isolated from nearly all sources of natural products,[2] and a number of these contain a single endo- or exocyclic double bond allylic to the oxygen atom.[3] An example of this latter group from plant sources is the unusual diterpene zoapatanol (**1**).[4] A potentially general route to oxacyclics of this



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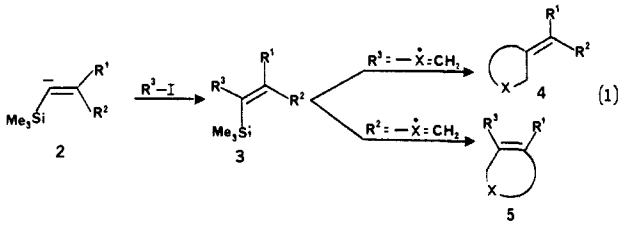
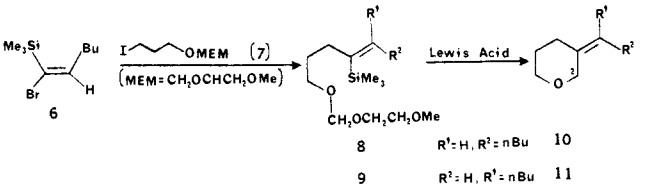
type is outlined in eq 1 (X = O). In this vinyl silane-based



approach, the silicon substituent[5] is utilized to both assist assembly of the cyclization substrate (**2** → **3**) and control the regiochemistry and stereochemistry of the product double bond.[6] In this paper we outline the successful use of this strategy to prepare five-, six-, and seven-membered unsaturated oxacyclics. We also report the unprecedented control that double-bond stereochemistry can exert on the ring size of the cyclization product.

Although cations derived from acetals have been employed for years to initiate cyclizations to form carbocyclic products,[7] it is only recently that Kocienski, Itoh, and others[8] have demonstrated the utility of related cyclization reactions for the synthesis of oxacyclic products. Our initial studies employed (methoxyethoxy)methyl (MEM) ethers,[10] since these mixed acetals had been shown[8a,c,e] to be useful cyclization initiators. Alkylation of the lithium reagent derived from readily available bromide **6**[11] with iodide **7** afforded vinylsilane acetal **8** (80% yield, >99% *Z*[12]), which could be isomerized[13] to provide the more stable (*E*)-vinylsilane **9** (53% yield, 99% *E*).[12] A variety[14] of Lewis acids promote the desired cyclization reactions of **8** and **9**. Yields were best with $SnCl_4$ (2-8 equiv, CH_2Cl_2, -20 °C; quench at -70 °C with aqueous NaOH) which gave the 3-(*Z*)-pentylidenetetrahydropyran (**10**)[12] and the (*E*)-pentylidene isomer **11**[12] in 89% and 92% yields



from **8** and **9**, respectively.[15,16] Quantitative capillary GC analysis demonstrated that the conversions of **8** → **10** and **9** → **11** were both *>99.5% stereospecific*.

The preparation of a representative group of oxacyclics by similar cyclizations is summarized in Table I. In all cases only a single C-C double bond positional isomer was obtained. Both 3-alkylidenetetrahydrofurans and 3-alkylideneoxepanes can be prepared also in this way. Entries 1 and 2 represent, to our knowledge, the first examples of vinylsilane cyclizations that form seven-membered ring products. The clean formation[17] of the (*E*)-3-alkylideneoxepane **12** (entry 2) is particularly significant since it supports the potential viability of an oxacyclization approach for the synthesis of zoapatanol (**1**) and congeners. The

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(7) (a) For a review of the pioneering efforts of W. S. Johnson and his colleagues, as well as other literature in this area, see: Bartlett, P. A. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 5. (b) Acetal-initiated cyclizations of vinylsilanes that occur in the exocyclic mode to form cyclohexene products have been described by Fleming: see: Chow, H.-F.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1815. See also: Tius, M. A. *Tetrahedron Lett.* **1981**, *22*, 3335.

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(11) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623.

(12) (a) Yields refer to pure (>98%) material isolated by chromatography (silica gel) or distillation. (b) Isomer ratios and product purities were determined by capillary GC analysis.

(13) Zweifel, G.; On, H.-P. *Synthesis* **1980**, 803.

(14) The most effective are $TiCl_4$, $TiCl_3O$-*i*-Pr, $EtAlCl_2$, $SnCl_4$, and $ZnBr_2$.

(15) Stereochemical assignments for the 3-alkylidene products followed directly from the diagnostic[16] ^{13}C NMR shifts of C-2: e.g., 67.1 ppm for **10** and 75.0 ppm for **11**.

(16) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 112-118.

(17) Cyclization of analogues of the substrates described in Table I entries 1 and 2 but lacking the *gem*-dimethyl substituent are more complex.

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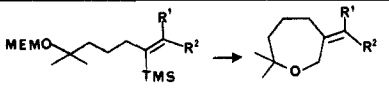
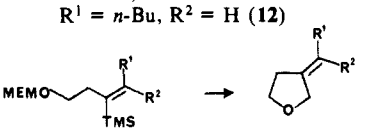
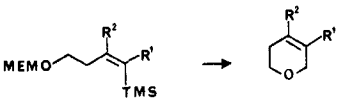
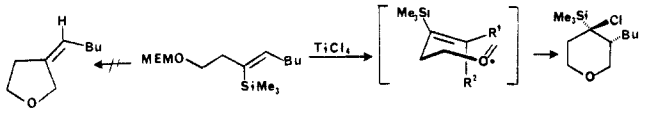
Table I. Acetal-Vinylsilane Cyclizations

entry	conversion	reactn condtn[a]	yield, %[b]	stereochem[c]
				
1	R^1 = H, R^2 = *n*-Bu	−15 °C, 12 h	71	>98% *Z*
2	R^1 = *n*-Bu, R^2 = H (**12**)	−15 °C, 24 h	57	>98% *E*
				
3	(**13**) R^1 = *n*-Bu, R^2 = H (**14**)	−5 °C, 12 h	81	97% *E*
4	R^1 = Et, R^2 = *n*-Bu	−10 °C, 6 h	86	~60% *Z*[d]
5	R^1 = *n*-Bu, R^2 = Et	−10 °C, 6 h	89	~60% *Z*[d]
				
6	R^1 = Br, R^2 = H	−60 °C, 2 h[e]	78	
7	R^1 = $(CH_2)_3Ph$, R^2 = H	−20 °C, 2 h[f]	83	
8	R^1 = R^2 = H	−20 °C, 1 h	71	
9	R^1 = H, R^2 = Me	−20 °C, 1 h	65	

[a] In CH_2Cl_2 (substrate concentration = 0.03–0.05 M). The catalyst was $SnCl_4$ (distilled from P_2O_5 and stored under argon) unless otherwise noted. The equivalents of catalyst were not optimized: 2 equiv were employed for entries 1 and 2, and 5 equiv for entries 3–5, 8, and 9. [b] Reference 12. [c] By capillary GC analysis except for entries **4** and 5 which were determined from the 250-MHz ^1H NMR spectrum of the crude product. [d] The origin of the lack of stereospecificity in these cases will be discussed in a subsequent full account of this work. [e] $TiCl_4$ (3 equiv, freshly distilled from Cu powder) was employed. [f] $TiCl_3$ (O-*i*-Pr) (3 equiv) was employed.

preparation of the 3- and 4-substituted 5,6-dihydro-2*H*-pyrans (entries 6–9) demonstrates the success of acetal–vinylsilane cyclizations that are also endocyclic[9] with respect to the vinylsilane terminator.

In marked contrast to the successful preparation of the (*E*)-alkylidenetetrahydrofuran **14** (entry 3), cyclization of the (*Z*)-vinylsilane acetal **15** with $TiCl_4$ did not afford **16** but gave almost exclusively tetrahydropyran **17**.[12,18-20] The conversion of **15** →



16 15 18 17

17 was quite rapid and occurred readily at −55 °C (2 h, 81% yield of **17**). The observation that the stereochemistry of an alkene can completely control whether a cyclization reaction occurs in an endo- or exocyclic sense with respect to this component is, to our knowledge, without precedent. We rationalize this startling observation by suggesting that the rate of cyclization to form the five-membered product is insensitive to the stereochemistry at the alkene terminus, while the rate of cyclization to form the six-membered product is highly dependent on the orientation of the terminal substituent. Specifically, cyclization of **15** → **17** is facile since the butyl group would adopt a favored quasi-equatorial orientation in a chairlike[7a] cyclization transition state **18** (R^1 = *n*-Bu), while the similar mode of cyclization of substrates with an (*E*)-vinylsilane substituent (entries 3–5) is disfavored since an alkyl group would occupy a quasi-axial position (**18**, R^2 = alkyl).[21]

In summary, acetal–vinylsilane cyclizations should prove to be a useful addition to the methods currently available for preparing five-, six-, and seven-membered ring oxygen heterocycles. These cyclization reactions provide the first route for preparing 3-alkylidene oxacyclics in a stereocontrolled fashion.

Acknowledgment. This study was supported by PHS Grant GM-30859. NMR and mass spectra were determined with spectrometers purchased with the assistance of NSF Departmental Instrumentation Grants.

Supplementary Material Available: Full experimental details and characterization data for the preparation of **10**, **11**, and **17** (4 pages). Ordering information is given on any current masthead page.

(18) The tetrahydropyran structure of **17** is firmly based on fully decoupled ^1H and ^{13}C NMR spectra (see supplementary material). Alternate tetrahydrofuran structures [e.g., 3-(trimethylsilyl)-3-(bromochloromethyl)tetrahydrofuran] are rigorously excluded.

(19) This and other examples[20] suggest that the energy difference between a β-silyl secondary cation and an α-silyl tertiary cation may be small.

(20) Mikami, H.; Kishi, H.; Nakai, T. *Tetrahedron Lett.* **1983**, *24*, 795.

(21) We suggest that a terminal substituent which is cis to the connecting atoms of a nascent ring should in general disfavor cyclization in an endocyclic sense as a result of the steric interactions between this substituent and the forming ring.[7a]

The Taylor Vortex: The Measurement of Viscosity in NMR Samples

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Nuclear relaxation, molecular motion, and solution viscosity are intimately linked through hydrodynamic models.[1-3] NMR T_1 relaxation times provide detailed information about molecular properties.[4-6] In this paper a method for measuring viscosity in NMR samples is introduced. NMR images of coherent periodic flow are presented.

The transition from laminar to turbulent flow is specified by the Reynolds number—a function of viscosity. That such a transition generates cyclic vortices has been known since ancient times.[7] In his classic 1923 paper, Taylor[8] established the con-

[†] National Hispanic Scholarship Fund recipient 1984.

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