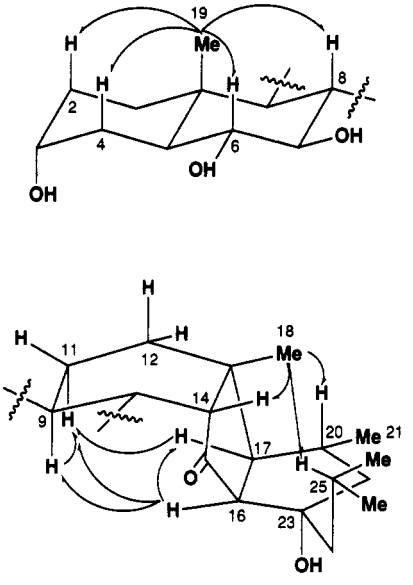
in C_3 was confirmed to be α-oriented from the broad singlet-like signal at δ 4.35 and the upfield shift of the C_3 signal (δ 65.3). The coupling constants of H_6 (dd, J = 10.0, 10.0 Hz) and H_7 (dd, J = 10.0, 10.0 Hz) determined the α- and β-oriented hydroxyl groups, respectively. The cis C/D ring junction was determined as follows: H_{14} appeared as a broad singlet-like signal at δ 3.42 and the NOE was observed between H_{18} and H_{14} but not between H_{16} and H_{14}. The NOE between H_{18} and H_{20} indicated the C_{20} R configuration. The two α-oriented hydrogens at C_{16} and C_{17} were confirmed by the NOE between H_{16} and H_{17} and H_{16} and H_9. The NOE was detected between H_{18} and H_{25}, but not between H_{21} and H_{25}, confirming the C_{23} S configuration. Furthermore, the NOE was observed between H_{17} and H_{11}, H_{16} and H_{11}, and H_9 and H_{11}, but not between H_9 and H_{12}, indicating a boat conformation of the ring C.



NOE correlations for 1

Xestobergsterol B (2) was obtained as an amorphous white powder.[5] The molecular formula of 2 was determined to be $C_{27}H_{44}O_7$ (FABMS $(M + Na)^+$ 503, HREIMS, and LREIMS), differing from the molecular formula of 1 in addition of O_2. Comparison of physicochemical data of 2 with those of 1 revealed that the only difference was 2 having hydroxyl groups at the C_1 and C_2 positions. These aspects were confirmed by six carbon signals connected to oxygen atoms in the δ 65–82 region in the ^{13}C NMR spectrum. The connectivity of the COSY and HMBC experiments supported the assumed structure of 2.

The NOE between H_9 and H_1 established the β-hydroxyl group in the C_1 position. The β-hydroxyl group configuration in C_2 was determined by the broad singlet-like signal at δ 4.46. The other configurations of asymmetric carbons were determined by NOE experiments and coupling constants and found to be the same as in 1.

Biogenetically, 1 and 2 are considered most likely to be produced by an intramolecular aldol-type reaction in the organism. The possibility that 1 and 2 are artifacts arising during the isolation process was excluded, because silica gel TLC of the original methanol/toluene extract showed the presence of 1 and 2 as major spots and because no base or no acid was employed in the present experiment. Very recently, R. J. Andersen et al. reported contignasterol from the sponge *Petrosia contignata* as the first steroid with cis C/D ring junction from marine organisms.[6] To the best of our knowledge, this is the first isolation of steroids posessing five carbocyclic rings and cis C/D ring junction.

In the present study, 1 and 2 strongly inhibited histamine release from rat peritoneal mast cells induced by anti-IgE in the dose-dependent manner.[7] The IC_{50} values of 1 and 2 were 0.05 and 0.10 μM, respectively. The inhibitory effect of 1 was about 5200 times more potent than that of disodium cromoglycate (DSCG), which is a well-known antiallergic drug (IC_{50} = 262 μM). IgE binding is a key event in Type I immediate hypersensitivity, and histamine release from mast cells and basophils relates the allergic reaction.[8] Effective inhibitors of histamine release from rat mast cells are used in the treatment of allergy and asthma. From these results, it is suggested that 1 and 2 are hopeful for an antiallergic drug. Detailed clarification of the pharmacological properties of 1 and 2 is in progress.

Acknowledgment. We thank Mr. Z. Nagahama for help with collections. We are indebted to Dr. M. Toyota and Ms. I. Okamoto for measurements of mass spectra.

(5) ^1H NMR (400 MHz, pyridine-d_5) δ 4.29 (H1), 4.46 (H2), 4.64 (H3), 2.85 (H4), 2.36 (H4), 2.60 (H5), 3.92 (H6), 5.15 (H7), 2.12 (H8), 2.01 (H9), 2.98 (H11), 2.21 (H11), 1.46 (H12), 1.21 (H12), 3.54 (H14), 2.73 (d, J = 10.3 Hz, H16), 1.71 (dd, J = 10.3, 10.3 Hz, H17), 1.22 (s, H18), 1.49 (s, H19), 2.63 (H20), 1.10 (d, J = 5.9 Hz, H21), 2.10 (H22), 1.33 (dd, J = 12.5, 12.5 Hz, H22), 1.98 (dd, J = 13.9, 5.1 Hz, H24), 1.60 (dd, J = 13.9, 6.6 Hz, H24), 2.21 (H25), 1.06 (d, J = 8.1 Hz, H26), 1.04 (d, J = 8.1 Hz, H27); ^{13}C NMR (100 MHz, pyridine-d_5) δ 77.0 (d, C1), 76.2 (d, C2), 70.6 (d, C3), 26.3 (t, C4), 42.0 (d, C5), 75.0 (d, C6), 75.0 (d, C7), 39.4 (d, C8), 48.3 (d, C9), 43.5 (s, C10), 25.0 (t, C11), 39.1 (t, C12), 38.1 (s, C13), 52.0 (d, C14), 217.6 (s, C15), 62.8 (d, C16), 58.0 (d, C17), 20.0 (q, C18), 10.0 (q, C19), 34.7 (d, C20), 20.8 (q, C21), 52.4 (t, C22), 82.2 (s, C23), 52.0 (t, C24), 25.0 (d, C25), 24.9 (q, C26), 25.3 (q, C27).

(6) Burgoyne, D. L.; Andersen, R. J.; Allen, T. M. *J. Org. Chem.* **1992**, *57*, 525.

(7) (a) Saeki, K. *Jap. J. Pharmac.* **1964**, *14*, 375. (b) Nemeth, A.; Rohlich, P. *Eur. J. Cell. Biol.* **1980**, *20*, 272. (c) Takei, M.; Matsumoto, T.; Endo, K.; Muramatsu, M. *Agents Actions* **1988**, *25*, 17. (d) Shoji, N.; Umeyama, A.; Takei, M.; Endo, K.; Arihara, S. *J. Pharm. Sci.*, in press.

(8) Coombs, R. R. A.; Gell, P. G. H. *Clinical Aspects of Immunology*, Blackwell Scientific: Oxford, 1975; p 761.

On the Mechanism of the Lewis Acid Mediated Cleavage of Chiral Acetals

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Received February 14, 1992

Summary: The $TiCl_4$-promoted cleavage of acetals has been shown to proceed by different mechanisms depending on the structure of the acetal, making it difficult to draw firm conclusions about the mechanism of related acetals based on model studies.

We have initiated a program to study methods for the asymmetric addition of nucleophiles to carbonyl deriva-

0022-3263/92/1957-2997$03.00/0

Scheme I

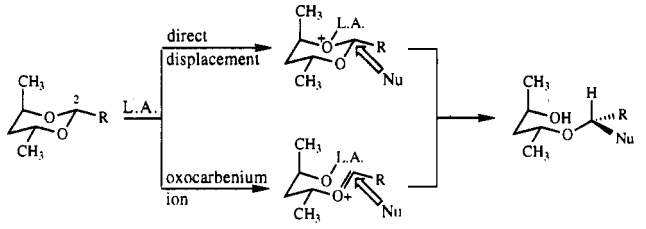
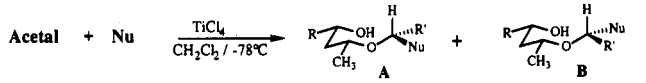
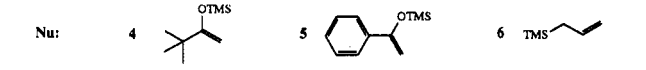


Table I. Stereochemistry of Acetal Opening with Nucleophiles[a]

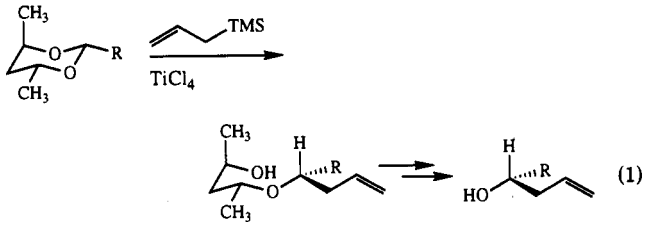


acetal	Nu	A:B	acetal	Nu	A:B	acetal	Nu	A:B
1s	4	4:1	**1s**	5	2:1	**1s**	6	4:1
1a	4	3:1	**1a**	5	2:1	**1a**	6	3:1
2s	4	7:1	**2s**	5	8:1	**2s**	6	3:1
2a	4	1:1	**2a**	5	1:1	**2a**	6	1:1
3s	4	8:1	**3s**	5	7:1	**3s**	6	3:1
3a	4	2.5:1	**3a**	5	2:1	**3a**	6	2:1

[a] Reactions were run at −78 °C in CH_2Cl_2 using 2 equiv of nucleophile and 2 equiv of $TiCl_4$. Ratios were determined by either ^1H NMR, ^{13}C NMR, HPLC, or a combination of the three.



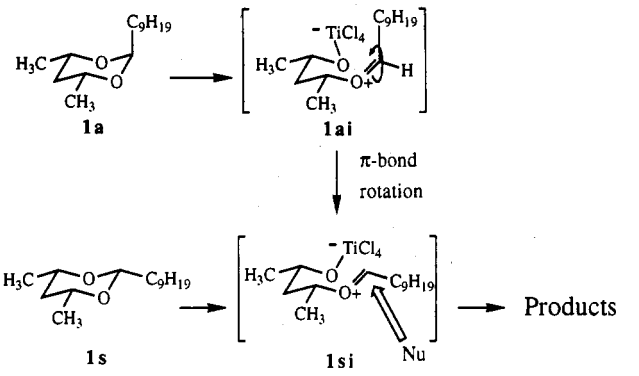
tives. The chiral acetals developed by Johnson and Kishi (eq 1) are used for this purpose and have been the subject of numerous investigations.[1] We are interested in understanding the mechanism of this reaction, particularly regarding the origin of the stereoselection, in order to design new systems that accomplish this transformation more efficiently. Recent publications by Heathcock, Bartlett, Yamamoto, and co-workers[2] and by Denmark and Almstead[3] on the mechanism of acetal cleavage reactions have prompted us to disclose our mechanistic results at this time.

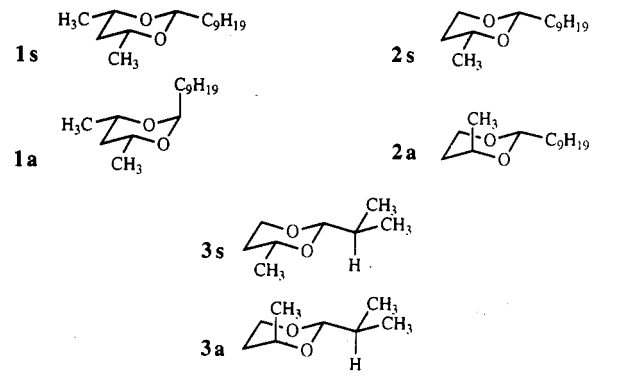


(1)

There are two extreme mechanisms one can draw for the above process, ranging from direct nucleophilic displacement of a Lewis acid–ether complex to prior formation of an oxocarbenium ion intermediate that subsequently undergoes attack by a nucleophile (Scheme I).[4] If the reaction proceeds by way of a cationic intermediate that can undergo rearrangement before nucleophilic attack, then acetals that are diastereomeric at the 2-position will be able to access a common intermediate and provide the same ratio of products. However, if the reaction proceeds by direct nucleophilic displacement of a Lewis acid–ether complex, then diastereomeric acetals will stereospecifically provide diastereomeric products. In order to distinguish between these two mechanisms, we have synthesized the isomeric pairs of 1,3-dioxane derivatives shown below[5] and subjected these substrates to $TiCl_4$-mediated nucleophilic addition with a variety of nucleophiles. The results are shown in Table I.

Scheme II





Some trends are immediately apparent from the data. First, the reaction is *not* stereospecific, as all the substrates examined give mixtures of products. We therefore conclude that the reaction does not proceed exclusively by direct displacement and involves some amount of an oxocarbenium ion intermediate. Furthermore, in the case of substrates **1s** and **1a**, the diastereomeric ratio of prod-

(1) Johnson, W. S.; Harbert, C. A.; Stipanovic, R. D. *J. Am. Chem. Soc.* **1968**, *90*, 5279. Johnson, W. S.; Harbert, C. A.; Ratclif, B. E.; Stipanovic, R. D. *J. Am. Chem. Soc.* **1976**, *98*, 6188. McNamara, J. M.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7371. Sekizaki, H.; Jung, M.; McNamara, J. M.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7372. For a recent review of the chemistry of chiral acetals, see: Alexakis, A.; Mangeney, P. *Tetrahedron: Asymmetry* **1990**, *1*, 447.

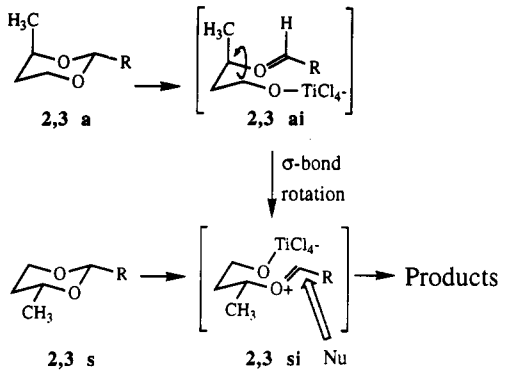
(2) Mori, I.; Ishihara, K.; Flippin, L. A.; Nozaki, K.; Yamamoto, H.; Bartlett, P. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 6107.

(3) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1991**, *113*, 8089. Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1991**, *56*, 6458. Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1991**, *56*, 6485.

(4) For previous mechanistic studies of this type of acetal opening, see: Bartlett, P. A.; Johnson, W. S.; Elliot, J. D.; *J. Am. Chem. Soc.* **1983**, *105*, 2088. Choi, V. M. F.; Elliot, J. D.; Johnson, W. S. *Tetrahedron Lett.* **1984**, *25*, 591. Mori, A.; Fujiwara, J.; Maruoka, K.; Yamamoto, H. *J. Organomet. Chem.* **1985**, *285*, 83. Maruoka, K.; Yamamoto, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 668. Yamamoto, Y.; Nishi, S.; Yamada, J. *J. Am. Chem. Soc.* **1986**, *108*, 7116. Silverman, R.; Edington, C.; Elliot, J. D.; Johnson, W. S. *J. Org. Chem.* **1987**, *52*, 180. Murata, S.; Suzuki, M.; Noyori, R. *Tetrahedron* **1988**, *44*, 4259. Schreiber, S. L.; Wang, Z. *Tetrahedron Lett.* **1988**, *29*, 4085. Denmark, S. E.; Wilson, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 3475. Denmark, S. E.; Willson, T. M.; Almstead, N. G. *J. Am. Chem. Soc.* **1989**, *111*, 9258.

(5) Synthesis of the all-equatorial acetals was accomplished starting from the appropriate diol and aldehyde by azeotropic removal of water. The anti isomers were synthesized by a modification of the procedure of Eliel (Eliel, E. L.; Nader, F. W. *J. Am. Chem. Soc.* **1969**, *91*, 536) by treating the orthoester derived from the diol and trimethylorthoformate with either nonyl Grignard or isopropyl Grignard in dichloromethane. All new compounds gave satisfactory spectral data (^1H and ^{13}C NMR, IR, and mass spectra) and combustion analyses or high-resolution mass spectra consistent with their molecular formula. See supplementary material for details.

Scheme III



ucts is nearly the same for the syn and anti dioxanes. This suggests either that a common intermediate is accessible from both isomers, or that the isomers are undergoing equilibration prior to reaction. We have ruled out the possibility of equilibration by running substrates **1–3a** to partial conversion using 0.3 equiv of $TiCl_4$ and examining the recovered starting material for isomerization. In all cases less than 5% isomerization was detected by NMR, and the ratio of products was the same as in the case of reactions run to full conversion. We therefore conclude that a common intermediate is accessible from **1a** and **1s**. However, the same reaction performed on substrates **2** and **3** provides different diastereomeric product ratios for the syn and anti dioxanes, indicating that a common intermediate is not accessed in these cases.

It is difficult to explain the results of these experiments with a single mechanism. Clearly, the lack of stereospecificity can be attributed to reaction via an oxocarbenium ion intermediate which undergoes rearrangement. If we assume that all substrates are reacting exclusively by the oxocarbenium ion mechanism, then the varying amounts of rearranged product for the three acetals must be due to different lifetimes for the intermediate oxocarbenium ion or to different rates of rearrangement. However, these possibilities are unlikely for the reasons described below, and we therefore conclude that the substrates do not all react by the oxocarbenium ion mechanism. The C_9 alkyl group on oxocarbenium ion **1ai** (directly derived from dioxane **1a**), and the substituents attached to the cationic oxygen bear a cis relationship to each other (Scheme II). However, there is a trans arrangement for the corresponding substituents in oxocarbenium ion **1si** (directly derived from dioxane **1s**). The cis arrangement is energetically less favored than the trans,[6] however, and to isomerize, **1ai** must undergo what is formally a π-bond rotation about the oxocarbenium ion.[7] It is reasonble to argue that this isomerization is faster than nucleophilic attack, and therefore the product ratio will reflect this and be independent of the geometry of the starting acetal.[8] *It is thus likely that substrates 1s and 1a react by a common oxocarbenium ion mechanism.*

The case of dioxanes **2a** and **3a** is not as straightforward (Scheme III). The lowest energy conformation of these dioxanes is one in which the substituent at the 2-position is equatorial and the methyl group in the 4-position is axial.[9] Ionization of this conformation leads directly to a trans oxocarbenium ion (**2, 3ai**), but not the same trans oxocarbenium ion as derived from substrate **2s** or **3s**.[10] In order to isomerize to the lower energy conformation (**2, 3si**), these molecules must undergo σ-bond rotations about the C–O bond and the C–C bonds. These σ-bond rotations will certainly be lower in energy than the formal π-bond rotation required for substrate **1a**. We would therefore expect that if substrates **2a** and **3a** were reacting via an oxocarbenium ion intermediate then rearrangement would occur at a rate which is faster than that of substrate **1a** and the same ratio of products would be observed for the isomeric acetals. *Given that the same ratio of products is not observed for the isomeric acetals, we must conclude that substrates 2 and 3 do not react exclusively via an oxocarbenium ion mechanism.*

A reasonable explanation for the behavior of these substrates is that there is a delicate balance between a direct displacement mechanism and an oxocarbenium ion mechanism. The more highly strained isomers containing an axial substituent (**2a** and **3a**) are reacting via an equilibrating oxocarbenium ion, leading to a low ratio of products (1–3:1), while substrates **2s** and **3s** react predominantly via a direct displacement mechanism, thus providing a higher ratio of products (7–8:1).[11] The mechanism also appears to be nucleophile dependent. In the case of the weaker nucleophile allylsilane **6**, a lower ratio of products is observed for substrates **2s** and **3s** (3:1) suggesting that there is an increase in the amount of oxocarbenium ion character to the reaction.

The most likely conformations for the oxocarbenium ion intermediates at equilibrium are **1si** and **2,3si**. These conformations have the carbon bound to the oxonium ion cis to the smaller group (hydrogen), rather than the larger alkyl group, reminiscent of the preferred structure of Lewis acid complexes of aldehydes.[6] They also have the C–H bond of the carbon bound to the oxonium ion eclipsed with the C–O π-bond. Typically, the preferred conformation of sp^3–sp^2 bonds contains one of the ligands of the sp^3 bond eclipsing the π-bond.[12] Recent calculations by Houk and

(6) This is in analogy to the structure of Lewis acid complexes of aldehydes in which the Lewis acid is preferentially bound syn to the hydrogen of the aldehyde. See: Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

(7) Alternatively, the sp^2-oxygen could undergo inversion and arrive at the same product. The two processes are equivalent for our purposes. In any case, the activation barrier for this type of isomerization has been examined theoretically and experimentally and has been found to be in the range of 8–15 kcal/mol, depending on the substitution and concentration of the oxocarbenium ion. See: Cremer, D.; Gauss, J.; Childs, R. F.; Blackburn, C. *J. Am. Chem. Soc.* **1985**, *107*, 2435. Blackburn, C.; Childs, R. F.; Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1985**, *107*, 2442.

(8) For a review of the Curtin–Hammett principle, see: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(9) The *A* value for a methyl group at the 2-position of a 1,3-dioxolane is >3.5 kcal/mol while at the 4-position it is 2.9 kcal/mol (Eliel, E. L.; Knoeber, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 3444). We therefore expected the molecule to exist with the methyl group in the 4-position axial and the C_9-alkyl group equatorial. Molecular mechanics calculation (MM2 force field) on *trans*-2-ethyl-4-methyl-1,3-dioxane indicate that the conformation bearing the axial methyl group at the 4-position and an equatorial ethyl group at the 2-position is favored by approximately 1.3 kcal/mol over that bearing an axial ethyl group at the 2-position and an equatorial methyl group at the 4-position. The NMR spectrum is fully consistent with an axial substituent at the 4-position.

(10) Another possibility is that the molecule undergoes a chair–chair interconversion prior to ionization, providing an oxocarbenium ion intermediate similar to that derived from substrate **1a**. Isomerization of this intermediate would then require a π-bond rotation as is in the case of substrate **1a**.

(11) Denmark has shown that more highly strained acetals can react by a dissociative mechanism, while less strained acetals can react by a direct displacement mechanism. See: Denmark, S. E.; Willson, T. M. *J. Am. Chem. Soc.* **1989**, *111*, 3475. This explanation is similar to that proposed by Johnson regarding the variation in stereoselectivity observed with Lewis acids of different strengths. See: Johnson, W. S.; Crackett, P. H.; Elliot, J. D.; Jagodzinski, J. J.; Lindel, S. D.; Natarajan, S. *Tetrahedron Lett.* **1984**, *25*, 3951.

(12) For a review on this subject, see: Karabatsos, G.; Fenogoli, D. in *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1970; Vol. 5. For recent theoretical studies see: Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035. Dorigo, A. E.; Pratt, D. W.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6591.

co-workers indicate that this conformation is also an energy minimum in oxocarbenium ions.[13] Furthermore, electrostatic attraction between the positively charged oxocarbenium oxygen and the negatively charged $TiCl_4$ alkoxide holds the alkoxide in proximity to the C–O π-bond (tight ion pair). This effectively blocks one face of the oxocarbenium ion and limits attack of the nucleophile to the exposed face. The minor diastereomer could then arise from a conformation in which the C–O π-bond is not eclipsed to the neighboring C–H, but rather is eclipsed to the neighboring C–CH_3 bond, thus exposing the opposite face of the π-system. Alternatively, it could arise from a conformation in which the ion pair is separated by solvent and is no longer effective in blocking one face of the electrophilic carbon.

This study was ostensibly performed to elucidate the mechanism of cleavage of chiral acetals (eq 1). We have seen that seemingly minor perturbations in the structure of the acetal can substantially change the outcome and mechanism of the reaction.[14] It is therefore difficult to draw any firm conclusions regarding the mechanism of other acetal reactions based on these model substrates. However, given that the equilibrating substrates which react by an oxocarbenium ion mechanism display lower selectivity than is observed in the chiral acetal substrates, it is likely that the more selective chiral acetal reactions of Johnson proceed predominantly by a direct displacement mechanism, while the less selective reactions have some amount of an oxocarbenium ion intermediate. Experiments designed to directly test this hypothesis are currently in progress.[15]

Supplementary Material Available: Experimental procedures and compound characterization data (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) Broeker, J. L.; Hoffmann, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006. The preference for the eclipsed conformation in oxocarbenium ions is on the order of about 1–2 kcal/mol depending on the substrate according to these calculations (*O*-methylformaldehyde, 0.95 kcal/mol; *O*-isopropylformaldehyde, 1.83 kcal/mol).

(14) For an example where a minor change in the structure of an aminal leads to a reversal of stereoselectivity, see: Burgess, L. E.; Meyers, A. I. *J. Am. Chem. Soc.* **1991**, *113*, 9858.

(15) This work was supported by the National Science Foundation (CHE-9019060), The Camille and Henry Dreyfus Foundation (New Faculty Award to T.S.), and The University of Colorado at Boulder Council on Research and Creative Works (CRCW Junior Faculty Development Award to T.S.). Dr. Greg Fu is gratefully acknowledged for stimulating discussions.

Articles

Intramolecular Diels–Alder Reactions of Pyrimidines and a Computational Study toward Their Structure and Reactivity

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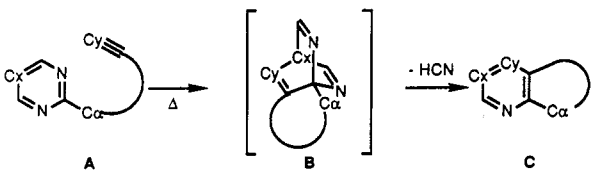
Received October 22, 1991

The syntheses of 2-[(prop-2-ynyloxy)carbonyl]pyrimidine (**1**), 5-[(prop-2-ynyloxy)carbonyl]pyrimidine (**2**), 5-phenyl-2-[2-(1-prop-2-ynylpyrryl)]pyrimidine (**8**), 5-phenyl-2-[2-(1-prop-2-ynylpyrrolidinyl)]pyrimidine (**9**) and 2-[2-(prop-2-ynyloxy)phenyl]-4,6-R_2-5-R_1-pyrimidine (R_1 = H, Cl, Ph; R_2 = H, Me) (**14a–d**) are described. Upon heating, the compounds **1**, **9**, and **14** undergo an intramolecular Diels–Alder reaction and a subsequent retro Diels–Alder reaction to yield the annelated pyridines **15**, **16**, and **17**, respectively. The compounds **2** and **8** did not react. The nonreactivity of the compounds **2** and **8** is ascribed to conjugation of the pyrimidine aromatic system with part of the dienophilic side chain, giving rise to conformations in which the diene and dienophile moieties cannot interact. For the compounds **1**, **9**, and **14** conjugation is absent, due to steric hindrance. To support this, semiempirical (MDNO-PM3) and molecular mechanics (MMX, CHEMX) calculations were performed. The HOMO–LUMO energy seperation of the compounds did not consequently reflect the observed reactivity. However, the probability of the compounds to be in a reactive conformation appeared to correlate with the observed rate of reaction (**9** > **14a** > **1** ≫ **2**, **8**).

Introduction

The study of intramolecular Diels–Alder reactions with inverse electron demand of cyclic aza dienes with a dienophilic side chain has received considerable attention during the last few years.[1-3] The broad scope and relatively mild conditions of these reactions make them very fruitful for synthetic as well as physico-chemical re-

Scheme I. Generalized Ring Transformation Reaction of 2-(ω-Alkynyl)pyrimidines



(1) Recent publications of our group describing intramolecular Diels–Alder reactions of pyridines and pyrazines with a dienophilic side chain. (a) de Bie, D. A.; Geurtsen, G.; van der Plas, H. C. *J. Org. Chem.* **1986**, *51*, 67. (b) de Bie, D. A.; Ostrowicz, A.; Geurtsen, G.; van der Plas, H. C. *Tetrahedron* **1988**, *44*, 2977. (c) Geurtsen, B.; de Bie, D. A.; van der Plas, H. C. *Tetrahedron* **1989**, *45*, 6519. (d) Haider, N.; van der Plas, H. C. *Tetrahedron* **1990**, *46*, 3641.

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