with experimental data. For CF_2, these quantities are 3.8 kcal/mol and 6.0 eu, respectively. The experimental values obtained by Giese are $\Delta\Delta H^{\ddagger} = 3.4$ kcal/mol and $\Delta\Delta S^{\ddagger} = 5.0$ eu.[7]

For CCl_2, no significant ΔH barrier and no complex was assumed, but "entropy-controlled" behavior is reproduced, nevertheless. From the functions used to plot the curves for CCl_2 in Figure 1, $\Delta\Delta H^{\ddagger}$(theor) = −0.2 kcal/mol $\Delta\Delta S^{\ddagger}$(theor) = −5.0 eu. Giese's experimental values are $\Delta\Delta H^{\ddagger} = -0.3$ kcal/mol and $\Delta\Delta S^{\ddagger} = -5.3$ eu.[7] When variations in the curvature of the ΔH potential were tested, large variations in $-T\Delta\Delta S^{\ddagger}$ resulted, but $\Delta\Delta H^{\ddagger}$ always remained near zero, as long as $-T\Delta S$ increased linearly with decreasing r. Such behavior mimics the behavior of CCl_2 in cycloadditions to a wide variety of alkenes.[1,7] Even if there were a small enthalpic barrier for this reaction, the TS can occur at a point where ΔH is lower than ΔH of the reactants.

For CBr_2, $\Delta H^{\ddagger}$ at the TS is less favorable for the more electron-rich (more reactive) alkene, but $-T\Delta S^{\ddagger}$ is more favorable. From the functions shown in the figure, values of −1.3 kcal/mol and −7.7 eu are obtained for $\Delta\Delta H^{\ddagger}$(theor) and $\Delta\Delta S^{\ddagger}$(theor), respectively. The experimental values are −2.4 kcal/mol and −11.2 eu, respectively.[7] Negative activation enthalpies will be observed in such a case, and the value of $\Delta H^{\ddagger}$ will increase (become less negative) as the alkene becomes more electron rich. This is a general property of our model, as long as $-T\Delta S$ increases in essentially an exponential fashion in the region of the TS, as shown in the figure for CBr_2. The $-T\Delta S$ term controls reactivity only because of more favorable enthalpy of interaction at any given value of r for the more electron-rich alkene and the absence of a barrier. The more substituted alkene has a more favorable entropy because the transition state occurs earlier,[8] at the point where the rapidly decreasing enthalpy overcomes the unfavorable entropy. Since the enthalpy decreases faster for TME than for DME, the TS occurs earlier for TME.

For CCl_2 and more reactive carbenes, we postulate that no stable complexes are formed, nor will they be observed at low temperatures.[9] The Giese π-complex model predicts that carbene selectivities will reverse at low temperatures, with alkyl substitution eventually diminishing the rate of reaction. By contrast, we predict that reactions of CCl_2, CClBr, and CBr_2 will be unselective and diffusion controlled at low temperature. In general, diffusion-controlled reactions will occur when $\Delta G^{\ddagger}$(diffusion) exceeds the $\Delta G^{\ddagger}$ for reaction. Reactions that are diffusion controlled at some temperature should develop negative activation energies at higher temperatures, when the $\Delta G^{\ddagger}$ for reaction exceeds $\Delta G^{\ddagger}$ for diffusion. Put the other way, reactions in solution that increase in rate as the temperature is lowered ($E_{act} < 0$) will inevitably reach a rate mimimum at some lower temperature, after which diffusion-controlled behavior ($E_{act} > 0$) will be observed. Exactly such behavior has been observed for reactive carbene cycloadditions and for nitrile ylide cycloadditions.[1] Indeed, such behavior should be observed for all bimolecular reactions with negligible enthalpic barriers. For example, related descriptions have been given for the third-body-mediated recombination of radicals in the gas phase.[10]

The normal Bell–Evans–Polanyi-principle or Hammond-postulate reasoning about the relationship between reactivity, the position of the transition state, and reaction exothermicity holds, for example, when comparing the reactions of a single alkene with CF_2, CCl_2, and CBr_2. However, for the reaction of a single carbene with a series of alkenes, the reaction exothermicity does not change to any appreciable extent. Nevertheless, the position of the transition state does change appreciably when there are small or zero enthalpic barriers. In such cases, the more stabilizing the carbene–alkene interaction, the earlier the transition state.

In dynamics terminology, the temperature effects upon the kinetic behavior of reactive species such as carbenes are dictated by how fast the floor of the entrance channel slopes downward and by how fast the walls of the entrance channel narrow. The TS occurs at that point where the downward slope of ΔH equals the upward slope of $-T\Delta S$. For similar reactions with barriers that are large, the position of the TS is near the position of ΔH_{max}, and $\Delta H^{\ddagger}$ is a positive quantity. For reactions with no significant barriers, the TS occurs when the decrease in ΔH overcomes the unfavorable entropy effects, and $\Delta H^{\ddagger}$ is negative even when no complex is formed.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-8213329 to K.N.H. and equipment grant to the University of Pittsburgh) for financial support of this research, and to J. A. Pople, B. Giese, P. S. Skell, and C. Doubleday, Jr., for helpful comments.

Registry No. CF_2, 2154-59-8; CCl_2, 1605-72-7; CBr_2, 4371-77-1; DME, 115-11-7; TME, 563-79-1.

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High Threo Diastereoselectivity via Europium(III)-Catalyzed Cyclocondensation of a Silyloxy Diene with α-Alkoxy Aldehydes. Synthesis of (−)-Pestalotin

M. Mark Midland* and Richard S. Graham

Department of Chemistry, University of California
Riverside, California 92521

Received February 27, 1984
Revised Manuscript Received May 25, 1984

Lewis acid catalyzed cyclocondensation of silyloxy dienes with dieneophiles has become a powerful method of constructing complex structures in a single step.[1] The cyclocondensation of the appropriately substituted diene with an aldehyde or ketone provides a potentially efficient and convergent method of synthesizing a variety of δ-lactones.[2] Since our research group is interested in the asymmetric synthesis of γ- and δ-lactones,[3] we chose to investigate the cyclocondensation of 1,3-dimethoxy-1-(silyloxy)butadiene with carbonyl compounds. Herein we report the use of this diene to prepare substituted δ-lactones and the stereochemical aspects of this cyclocondensation with substituted aldehydes.

Danishefsky and co-workers have clearly illustrated the usefulness of aldehydes as heterodieneophiles to provide γ-pyrones.[4] However, simple aryl and alkyl ketones have received very little attention as possible dieneophiles. In general, only highly elec-

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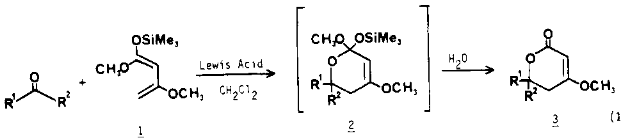
0002-7863/84/1506-4294$01.50/0

trophilic carbonyl groups undergo the cyclocondensation process.[1d] We have found that under Lewis acid catalyzed conditions 1,3-dimethoxy-1-(silyloxy)butadiene (Brassard's diene)[5] (**1**) condenses with aldehydes and *unactivated ketones* in a regiospecific manner to provide, after hydrolysis, the desired substituted δ-lactone in good yield (eq 1). Although the orthoester intermediate **2** is readily hydrolyzed to the lactone **3**, we did isolate **2** derived from the diene and acetophenone. The isolation of cycloadduct **2** adds support to a pericyclic mechanism.[6] Typical conditions used an aldehyde:diene ratio of 1.0:1.1 at −78 °C in methylene chloride (1 M) containing 1 equiv of anhydrous zinc chloride or boron trifluoride etherate. The reaction was allowed to warm to room temperature while being stirred overnight, then hydrolyzed, and extracted with ether to provide the δ-lactone **3**. Stronger Lewis acids such as titanium tetrachloride, aluminum trichloride, or tin tetrachloride afford **3** in lower yield along with a variety of decomposition products.

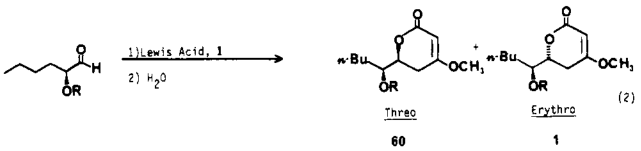


(1)

R^1	R^2	%
Ph	H	70
Ph	CH_3	40
CH_3	CH_3	67
CH_3	$\equiv\!-CH_3$	63
$-(CH_2)_5-$		52

The recently reported[4] mild Lewis acid catalysts Eu(fod)$_3$ and Eu(hfc)$_3$ are also excellent catalysts for this reaction. Although Eu(hfc)$_3$ has been reported[7] to induce asymmetry in the cyclocondensations of Danishefsky's diene (a 1,3-dialkoxy diene) with aldehydes, we observed no asymmetric induction or kinetic resolution in the cyclocondensation of Brassard's diene (a 1,1,3-trialkoxy diene) with carbonyl compounds. These results indicate that substitutents at the 1-position of the diene may be important in contributing to the asymmetric induction.

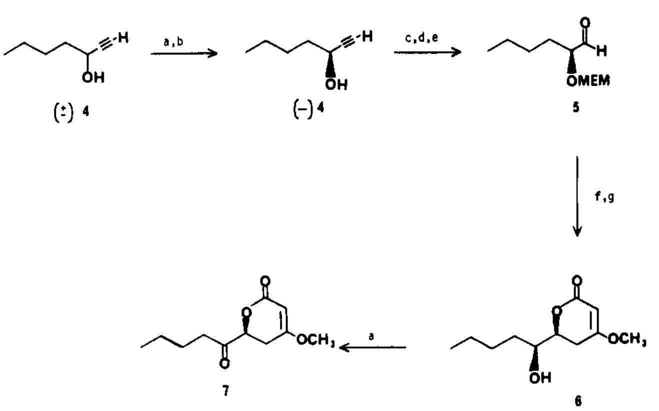
Recent studies have shown that α or β chiral centers can provide high diastereoselections during the addition of nucleophilic or electrophilic agents to carbonyl groups or olefins[8] (eq 2). Our initial attempts to achieve chelation controlled cyclocondensation of Brassard's diene with 2-alkoxyhexanal in the presence of zinc chloride, boron trifluoride etherate, or magnesium bromide were disappointing. Each gave the chelation control product (threo isomer) with a diastereoselectivity of 2.0:1. *However, a very dramatic improvement in diastereoselectivity was established when europium(III) complexes were used as Lewis acid catalysts.* The cyclocondensation of **1** with either 2-[((methoxyethoxy)methyl)oxy]- or 2-(benzyloxy)hexanal gave excellent threo diastereoselection (>60:1). These results are in sharp contrast to the recently reported[8] findings that magnesium bromide and titanium tetrachloride (but not lanthanides) provide excellent stereochemical control. Again the 1,1-dialkoxy substitution pattern of Brasard's diene vs. the single alkoxy group at the 1-position of Danishefsky's diene appears to be responsible for the change.



(2)

Although the α-alkoxy aldehydes provide excellent diastereoselection, our initial attempts with β-alkoxy aldehydes were unsuccessful (threo selectivity ~2:1). Likewise, aldehydes with α-chiral centers that do not allow for chelation, such as 2-phenylpropionaldehyde, gave the Cram product (erythro) as the major condensation product (~3:1).

Scheme I[a]



[a] (a) Jones' oxidation, (b) (*S*)-Alpine-Borane, (c) H_2, Pd/BaSO$_4$, (d)MEMCl,[12] (e) O_3,[13], (f) Eu(hfc)$_3$ and **1**, (g) TiCl$_4$.

We have applied the Lewis acid catalyzed cyclocondensation of 1,3-dimethoxy-1-(silyloxy)butadiene to the asymmetric synthesis of two fungal metabolites, (−)-pestalotin[9] and the oxo analogue of (−)-pestalotin.[10] Scheme I outlines the short, convergent synthesis of these lactones. The key intermediate, (*S*)-2-[((methoxyethoxy)methyl)oxy]hexanal, possesses the necessary chelating ability and proper absolute configuration to provide 1,2 threo *S*,*S* diol. The required propargyl alcohol was conveniently prepared by the asymmetric reduction of 1-heptyn-3-one with (*S*)-Alpine-Borane[11] to give (*S*)-1-heptyn-3-ol, (**4**) in 83% ee. Compound **4** was then readily transformed into aldehyde **5**, which was condensed with **1** to afford exclusively the desired threo product **6** in 50%. One recrystallization (ether/hexane) provides optically pure (−)-pestalotin (**6**) (mp 84–85 °C, $[\alpha]_D$ −91.70° (*c* 1.17, MeOH); literature values[9] mp 84–85 °C, $[\alpha]_D$ −86.2 (*c* 0.14 MeOH)). The oxo metabolite is easily prepared by Jones oxidation of (−)-pestalotin to give optically pure **7** (mp 81–82 °C, $[\alpha]_D$ −30.60 (*c* 1.05, MeOH); literature values[10] mp 83–84 °C, $[\alpha]_D$ −4.3 (*c* 0.266, MeOH). NMR shift study of both lactones indicates only one enantiomer present. Spectral data of both lactones was consistent with literature values.[14]

In conclusion, the Lewis acid catalyzed cyclocondensation of 1,3-dimethoxy-1-((trimethylsilyl)oxy)butadiene with either aldehydes or ketones provides a mild and convergent method of preparing a variety of substituted δ-lactones. Furthermore the europium-catalyzed condensation with α-alkoxy aldehydes undergoes exclusively chelation-controlled addition, an unusual result for lanthanide-catalyzed cyclocondensations of silyloxy dienes. These unusual results point to the importance of the substitution pattern on the diene.

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Acknowledgment. We thank Professor R. M. Carlson for the spectral data of pestalotin. We thank Professor S. Danishefsky for discussions of the stereochemical aspects of the cyclocondensations with his diene. Professor J. J. Sims and S. Castellino have developed a related δ-lactone synthesis.[15] We thank them for helpful discussions. We acknowledge the National Insitutes of Health (GM-24517) for financial support.

Supplementary Material Available: Experimental procedures and NMR data for most compounds (13 pages). Ordering information is given on any current masthead page.

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NMR Isotope Shift as a Probe of Conformation in Carbocations. Determination of Conformation in a Cyclopentyl Cation

Daivd A. Forsyth* and James H. Botkin

Department of Chemistry, Northeastern University
Boston, Massachusetts 02115

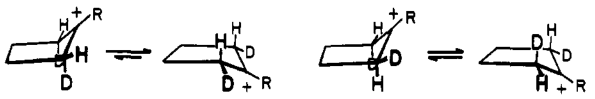
Received March 26, 1984

The isotopic perturbation of degenerate equilibria has been developed into a new method to distinguish between static and equilibrating structures, based on the chemical shift difference (the equilibrium isotope shift) between NMR signals for nuclei which are time averaged to equivalence in the absence of the isotopic perturbation.[1] Another type of equilibrium isotope effect occurs when the magnitude of an intrinsic NMR isotope shift is affected by isotopic perturbation of a rapid equilibrium.[2] We now report a demonstration that the additivity characteristics of the intrinsic isotope shift can serve as a probe of conformation.

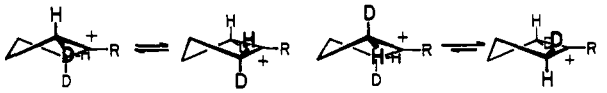
Nonadditivity of isotope shifts is likely to occur if C–H(D) bonds are involved in hyperconjugation or through-space electronic or steric interactions *and* also are conformationally mobile, because of the imposition of an equilibrium isotope effect on the population of conformers which may have different intrinsic NMR isotope shifts. Our example is a cyclopentyl cation, in which the hyperconjugative contributions of the methylene groups adjacent to the cation center can be perturbed by deuterium substitution. Isotopic perturbation of hyperconjugation reduces the electron supply to the cation center, as illustrated by long-range, downfield isotope shifts for nuclei in aryl groups conjugated with the cation center.[2-5]

A cyclopentyl cation could assume a planar, envelope, or twist structure. There would be two equivalent envelope conformations or two equivalent twist conformations. Interconversion between equivalent structures should be a low barrier, rapid process.[6] However, the degeneracy of the proposed equilibria could be removed by appropriate deuterium labeling, which would then lead to nonadditive long-range isotope shifts at any nucleus whose chemical shift depended on charge delocalization from the cation center.

Scheme I



Scheme II



The 1-(*p*-fluorophenyl)cyclopentyl cation, **1**,[7] was prepared as a mixture of deuterated isotopomers by dissolving labeled 1-(*p*-fluorophenyl)cyclopentanol in 1:1 $FSO_3H:SbF_5$ and SO_2ClF at −78 °C. Varied patterns of labeling were achieved by reacting (*p*-fluorophenyl)magnesium bromide with the appropriately labeled cyclopentanones. Cyclopentanone randomly labeled at the C_2 and C_5 positions to ~70% deuteration was prepared by base-catalyzed (K_2CO_3) exchange in D_2O, and a ~98% labeled sample was obtained by further exchanges. In the randomly labeled sample, the dideuterated species should be present in about 1:1:1 proportions of geminal, cis, and trans patterns of labeling. Geminally labeled cyclopentanone-*2,2-*d_2 was synthesized by a known method from 2-methoxy-1-cyclopentene-1-carboxylic acid.[8] Predominantly trans labeled cyclopentanone-*2,5-*d_2 was prepared by cyclopentanone exchange in D_2O catalyzed by Hine's chiral diamine.[9]

Figure 1 shows two of the ^1H-decoupled 56.2-MHz ^{19}F spectra obtained from various mixtures of labeled and unlabeled **1**. Several mixtures were necessary to assign the signals with certainty. Figure 1a is a spectrum of the randomly labeled **1** mixed with unlabeled **1**. The spectrum in Figure 1b is from a mixture of the randomly labeled cation enriched with *trans*-**1**-*2,5-*d_2. Each deuterated cation gives a different ^{19}F signal with the exception of the precisely overlapping signals for **1**-*2,2-*d_2 and *cis*-**1**-*2,5-*d_2. The downfield isotope shifts at ^{19}F in **1** are as follows: (cation, shift in ppm ± 0.005) **1**, 0.000; **1**-*2-d*, 0.138; *trans*-**1**-*2,5-*d_2, 0.258; *cis*-**1**-*2,5-*d_2, 0.299; **1**-*2,2-*d_2, 0.299; **1**-*2,2,5-*d_3, 0.440; and **1**-*2,2,5,5-*d_4, 0.603.

The isotopomers of the 1-(*p*-fluorophenyl)cyclopentyl cation reveal the preferred conformation to be the twist structure. The key observation is the smaller isotope shift (0.258 ppm) for the trans dideuterated cation than for the cis or geminally dideuterated cations (0.299 ppm). Besides this nonadditive isotope shift, the lack of additivity for the mono- and trideuterated cations is also significant; only the geminal and cis deuterated cations give an isotope shift in relation to the tetradeuterated cation that is proportional to the fractional extent of deuteration. The details of this analysis follow.

The nonadditivity of isotope shifts indicates that the cyclopentyl cation is nonplanar. If the planar structure had been preferred, the long-range isotope shifts at fluorine would have been additive for mono- through tetradeuteration at C_2 and C_5, because each C–H(D) bond would have had the same overlap with the p-orbital of the cation center. However, since the cation assumes a nonplanar conformation, the monodeuterated species exhibits an isotope shift that is less than one-quarter the effect of tetradeuteration, i.e., a nonadditive shift, because an isotope effect on the conformational equilibrium preferentially places the C–D bond out of alignment with the p-orbital. Similarly, the trideuterated cation has an isotope shift that is less than three-quarters of the isotope shift for the tetradeuterated cation, again due to an isotope effect on the conformational equilibrium.

More importantly, of the three dideuterated isotopomers, *trans*-**1**-*2,5-*d_2 exhibits a reduced isotope shift while the remaining *cis*-*2,5-*d_2 isotopomer and the geminally labeled **1**-*2,2-*d_2 have

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