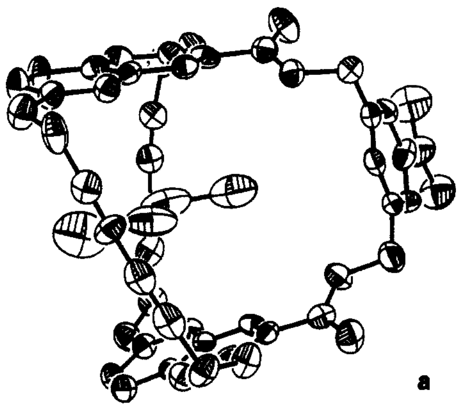
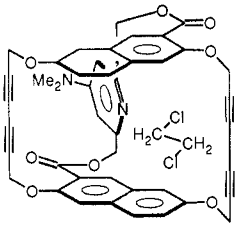
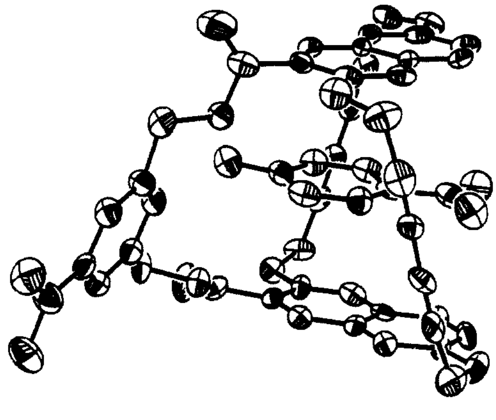
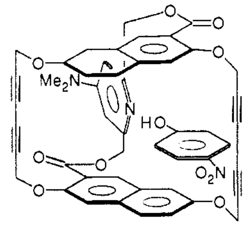




1 : EDC complex





1 : PN complex

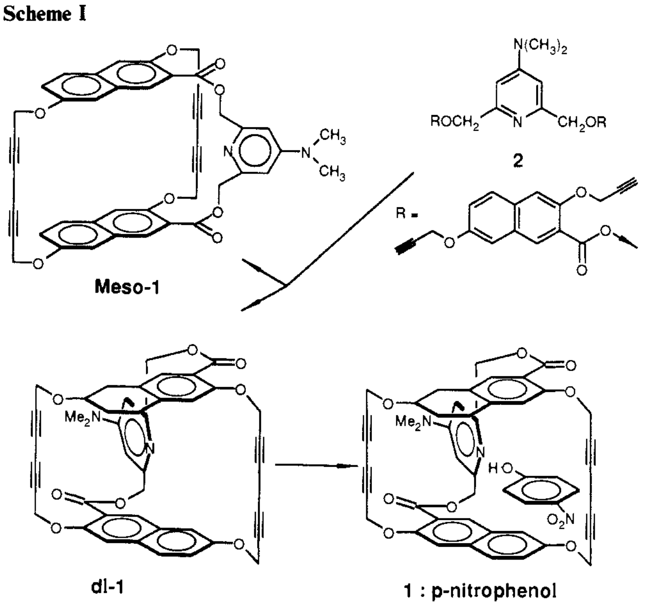
Figure 1. (a) X-ray structure of **1**/ethylene dichloride complex. (b) X-ray structure of **1**/*p*-nitrophenol complex.

with no apparent incavitation of the anion. This is consistent with requirement of an *optimum* ΔpK_A relating acid and base in this type of complex. Although of little precedent,[10] this idea seems reasonable when one considers those cases of "hydrogen bonding" when extremely large ΔpK_A's are involved.

A high degree of cooperativity between hydrogen bonding and intracavity interactions is indicated. We suggest that this is consistent with Menger's hypothesis[11] concerning temporal effects and intramolecular interactions.

Conclusions. One may construct host molecules possessing a rigidly defined cavity with concave functionality. These exhibit guest complexation characterized by large association constants in *nonaqueous* media and an exceptionally high but little-understood guest selectivity. The implications of this for the design of sequence-selective DNA intercalators and "artificial" enzymes is clear.[12]

Scheme I



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[10] Rubin, J.; Senkowski, B. Z.; Panson, G. S. *J. Phys. Chem.* **1964**, *68*, 1601.

[11] Menger, F. M. *Acc. Chem. Res.* **1985**, *18*, 128-134.

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Synthesis of Tricyclo[3.3.1.0^{3,7}]non-3(7)-ene, a Highly Pyramidalized Olefin

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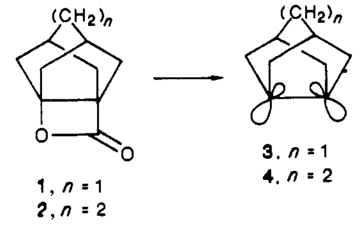
Alkenes in which the carbons forming the double bond are highly pyramidalized are a very interesting but not well-studied class of compounds.[1] We recently reported the generation of one member (**4**) of a homologous series of pyramidalized alkenes by pyrolysis of β-lactone **2**,[2] and, subsequently, the spectroscopic characterization of **4** in matrix isolation was described.[3] Herein



we communicate the results of our attempts to generate **3**, a more highly pyramidalized member of this series, by pyrolysis of β-lactone **1**, and we report the successful formation of this alkene at low temperatures in solution from a different precursor.

β-Lactone **1**[2] proved very resistant to pyrolytic loss of CO_2. Flash vacuum pyrolysis (FVP) of **1** at 550 °C led to only about

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[1] Review: Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, p 299.

[2] Renzoni, G. E.; Yin, T.-K.; Miyake, F.; Borden, W. T. *Tetrahedron* **1986**, *42*, 1581.

[3] Radziszewski, J. G.; Yin, T.-K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544.

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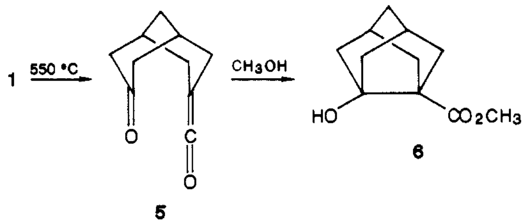
50% decomposition. However, even at this temperature CO_2 extrusion did not occur, for the product was keto ketene **5**, formed by cleavage of the β-lactone ring in **1** in the undesired sense. The keto ketene was identified by its IR spectrum (2125 and 1720 cm^{-1})[4] and by its conversion to hydroxy ester **6**[5,6] on addition of methanol.

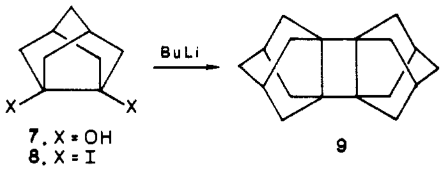


This mode of β-lactone cleavage is, to the best of our knowledge, unprecedented. From the heats of formation of the products,[7] fragmentation of the parent 2-oxetanone to ethylene plus CO_2 is computed to be enthalpically more favorable than cleavage to formaldehyde plus ketene by 39.3 kcal/mol. In addition, loss of CO_2 from **1** is entropically more favorable than its cleavage to **5**. The fact that formation of keto ketene **5** is, nevertheless, the preferred reaction pathway of β-lactone **1** at 550 °C is thus indicative of the very high energy of the pyramidalized alkene **3** that would be formed by extrusion of CO_2 from **1**.

At temperatures above 550 °C, CO_2 loss from **1** was observed. However, only a very small amount of the dimer of **3** was isolated. The major product (>95%) was an isomer of **3**.[8] From its ^{1}H NMR spectrum [($CDCl_3$) δ 1.48 (t, 2 H, J = 1.5 Hz), 2.00 (d of d, 2 H, J = 16.2, 1.5 Hz), 2.26 (d of d, 2 H, J = 16.2, 4.4 Hz), 2.48 (d of d, 1 H, J = 4.4, 1.5 Hz), 3.15 (br s, 1 H), 4.62 (s, 2 H), 4.92 (s, 2 H)] and ^{13}C NMR spectrum [($CDCl_3$) δ 36.48, 36.87, 39.97, 55.31, 102.91, 152.41] this hydrocarbon was identified as 2,6-dimethylenebicyclo[2.2.1]heptane. Based on studies of the thermal chemistry of alkene **4**,[9] the mechanism for formation of this isomer of **3** appears to involve a reverse vinylcyclopropane rearrangement, followed by subsequent bond reorganization in the strained intermediate that is thus generated.

Although β-lactone **2** is an excellent precursor of **4**, the greater strain in alkene **3** apparently renders **1** a poor source of **3**. This finding prompted us to look for a different precursor of **3**. Toward this end, we succeeded, after trying many different routes, in converting diol **7**[10] to diodide **8**.[8] Heating 200 mg of **7** at 110 °C in 10 mL of 95% phosphoric acid containing 3.0 g of sodium iodide[11] afforded **8**, mp 130–131 °C, in 40% yield after purification by chromatography and sublimation. The ^{1}H and ^{13}C NMR spectra of **8** ($CDCl_3$) showed resonances at respectively δ 1.63 (s, 2 H), 1.90 (s, 2 H), 2.43 (d, 4 H, J = 10.3 Hz), 2.76 (d, 4 H, J = 10.3 Hz) and δ 30.78, 39.45, 53.14, 57.79.

When diiodide **8** was treated with one equivalent of butyllithium in THF at −78 °C, the "2 + 2" dimer of **3** (**9**),[8] mp 211–212 °C, was isolated in almost quantitative yield after chromatography and sublimation. The simplicity of the dimer's 500-MHz ^{1}H NMR spectrum [($CDCl_3$) δ 1.40 (d, 8 H, J = 10.1 Hz), 1.50 (s, 4 H), 1.92 (d, 8 H, J = 10.1 Hz), 2.42 (br s, 4 H)] and ^{13}C NMR spectrum [($CDCl_3$) δ 37.23, 42.34, 44.01, 50.18] was indicative of the high (D_{2h}) symmetry of this hydrocarbon.



In order to provide evidence for the intermediacy of **3** in the dimerization reaction, the reaction was repeated in the presence of diphenylisobenzofuran (DPIBF) as a trap for the pyramidalized olefin. From this reaction was isolated in 90% yield, after chromatography and sublimation, a white solid, 131–132 °C. The product was identified spectroscopically as the expected Diels–Alder adduct of **3** with DPIBF.[8]

The results reported here show that **3** is a highly strained alkene but that it can be generated at low temperatures and chemically trapped before undergoing rearrangement. Attempts to matrix isolate **3** and to obtain its IR and UV spectra for comparison with those of **4**[3] are in progress.

Acknowledgment. We thank the National Science Foundation for support of this research.

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[4] Although the IR spectrum of keto ketene **5** can be obtained in solution at room temperature, the spectrum was first observed in matrix isolation, initially by Dr. Richard A. Hayes and Professor Orville L. Chapman and subsequently by Dr. Juliusz G. Radziszewski and Professor Josef Michl. We thank both groups for performing the matrix-isolation experiments for us.

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[6] A trace amount of the isomeric endo-bicyclic keto ester[5] was also detected. The formation of **6** as the product of kinetic control is consistent with our previous finding that, when the keto ester is treated with base in CH_3OD, capture of the ester enolate at C-7 by the carbonyl group at C-3 is much faster than deuterium incorporation at C-7.[5]

[7] Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

[8] All new compounds gave satisfactory elemental analyses and/or exact masses, and spectral data were in accord with the assigned structures.

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Intramolecular C–H Bond Activation in Aqueous Solution: Preparation of a Unique Cobalt(III)–Alkyl Complex by Deprotonation of an Agostic Intermediate. Crystal Structure of $[\mathrm{Co^{III}}(\mathrm{dacoda}\text{-}C(2))(\mathrm{H_2O})]\cdot 2\mathrm{H_2O}$

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The covalent interaction between an unactivated C–H bond and the central metal in transition-metal complexes, termed an agostic interaction,[2a] has recently received a great deal of attention in relation to the general problem of C–H activation.[2-5] The minimum requirement for the three-center, two-electron M–H–C bond is that the metal center have a suitably oriented low-energy empty orbital to receive the two electrons of the C–H bond.[2a] The quadridentate ligand dacoda (1,5-diazacyclooctane-*N*,*N*′-diacetic acid) forms square-pyramidal five-coordinate $[\mathrm{M^{II}}(\mathrm{dacoda})(\mathrm{H_2O})]$ complexes with Ni(II), Co(II), and Zn(II).[6] A crystal structure

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