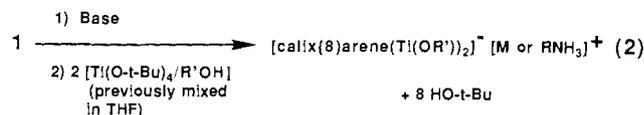(*R*)-(+)-1-(1-naphthyl)ethylamine enhances the diastereomeric ratio to 3:1 (**2e**). A 10:1 mixture of diastereomers is observed upon changing the α-methyl substituent in the latter amine to an isopropyl group (**2f**). Chiral recognition in these systems is proposed to result from the following interactions between the calixarene skeleton and the ammonium ion: (1) a hydrogen bond between an ammonium ion hydrogen and a phenolate oxygen and (2) the stacking[9] of one calixarene aryl ring with the naphthyl ring of the chiral amine. Evidence for the latter interaction is indicated by an upfield shift of one calixarene *tert*-butyl resonance per diastereomer (ca. 0.5 ppm for the minor and 1.0 ppm for the major diastereomer). This is not observed in the analogous sodium or potassium salts (**2a,b**). Furthermore, many of the resonances associated with these ammonium ions (e.g., methine, α-alkyl and naphthyl ring hydrogens) are shifted upfield (up to 1.3 ppm), relative to their analogous hydrochloride salts. Steric repulsion between the metallacalixarene frame and the α-alkyl substituent on the chiral amine would account for the third interaction necessary for chiral recognition.

The crystal structure together with space-filling models indicate that the shape and size of the cavities in **2** should prevent the synthesis of analogous dititanacalix[8]arene complexes containing sterically demanding alkoxide ligands. We have in fact observed that using Ti(O-*t*-Bu)$_4$ in place of Ti(O-*i*-Pr)$_4$ in eq 1 leads to a compound that is *not* structurally related to the isopropoxide complexes discussed above (deduced by ^{1}H NMR). However, reaction of this material with 2 equiv of isopropyl alcohol provides the isopropoxide complex in quantitative yield. This observation leads to a convenient and practical synthesis of a variety of dititana(alkoxy)calix[8]arene complexes as shown in eq 2.[14] The ^{1}H NMR spectra of the crude products from these reactions (after removal of the solvent in vacuo) indicate that these compounds may be used in further reactions without purification.

$$1 \xrightarrow[\substack{\text{2) 2 [Ti(O-t-Bu)}_4\text{/R'OH]}\\ \text{(previously mixed}\\ \text{in THF)}}]{\text{1) Base}} [\text{calix(8)arene(Ti(OR'))}_2]^- \text{ [M or RNH}_3]^+ \quad (2)$$
$$+ \text{ 8 HO-t-Bu}$$

Finally, we have also prepared zirconium(isopropoxy)calix-[8]arene and vanadium(oxo)calix[8]arene complexes[10] by substituting Zr(O-*i*-Pr)$_4$(HO-*i*-Pr) and V(O)(O-*i*-Pr)$_3$, respectively, as the metal reagents in eq 1.

A search employing other chiral amines (especially those derived from the chiral pool[11]) should lead to a synthesis of homochiral dimetallacalixarenes.[12] The reaction chemistry[13] of these complexes as well as their potential applications as resolving agents, protecting groups, and chiral auxiliaries in organic synthesis are also being explored.

Supplementary Material Available: NMR, mass spectral data, and elemental analysis information for all dimetallacalixarenes

(9) (a) Rebek, J., Jr.; Askew, B.; Ballester, P.; Buhr, C.; Jones, S.; Nemeth, D.; Williams, K. *J. Am. Chem. Soc.* **1987,** *109,* 5033. (b) Hamilton, A. D.; Van Engen, D. *J. Am. Chem. Soc.* **1987,** *109,* 5035.

(10) On the basis of the similarities between the ^{1}H and ^{13}C NMR and IR spectra of these compounds and the dititanacalixarene complexes.

(11) Scott, J. W. In *Asymmetric Synthesis;* Morrison, J. S., Scott, J. W., Eds.; Academic Press: New York, NY, 1984; Vol. 4, p 1.

(12) We have already isolated some homochiral complexes by selective crystallization of one diastereomer from a mixture.

(13) Alcohol exchange with the alkoxy ligands in **2** has been observed. For example, 2 equiv of 4-nitrophenol react with **2a** to give the analogous 4-nitrophenolate complex in high yield.

(14) Representative alcohols are as follows: cyclopentanol, geraniol, 4-*tert*-butylcyclohexanol, 4-nitrophenol, ethanol, ($\pm$)-3-butyn-2-ol, (*R*)-*sec*-phenethyl alcohol, α-methyl-2-naphthalenemethanol.

and crystallographic details and tables of atomic positional and thermal parameters for **2a** (26 pages); tables of observed and calculated structure factors (74 pages). Ordering information is given on any current masthead page.

Intramolecular Cyclization of an Allyl Cation. The Formation of 11-Membered Carbocyclic Rings *via* Cationic Processes

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Although cationic cyclization processes have been proposed as part of the biosynthetic pathway to a variety of large-ring terpenes, such as humulene and cembrene,[2] little experimental evidence exists in support of such entropically unfavorable cyclization processes.[3,4] As part of our continuing interests in both the intramolecular[5] and intermolecular[6] cyclization reactions of allyl cations, we have explored the intramolecular addition of an allyl cation to a vinylcyclopropane moiety. We now report that 11-membered rings, similar to that of humulene, can be formed in good yield through entropically unfavorable cationic cyclization reactions at low temperature.

In a typical procedure, a dry methylene chloride solution of **1a**[7,8] was treated with 2 mol % of triflic acid at 0 °C for 3 min. Quenching of the acid catalyst with excess triethylamine, followed

(1) National Science Foundation Fellow, 1984–1987.

(2) For general discussions, see: *Natural Products Chemistry;* Nakanishi, K., Goto, T., Ito, S., Natori, S., Nozoe, S., Eds.; University Science Books: Mill Valley, CA, 1974; 1983; Vol. 1 and 3. Cane, D. E. In *Biosynthesis of Isoprenoid Compounds;* Porter, J. W., Spurgeon, S. L., Eds.; John Wiley and Sons: New York, 1981; Vol. 1. West, C. A. In *Biosynthesis of Isoprenoid Compounds;* Porter, J. W., Spurgeon, S. L., Eds.; John Wiley and Sons: New York, 1981; Vol. 1.

(3) For an intramolecular acylation reaction to form a 14-membered ring, see: Kato, T.; Suzuki, M.; Kobayashi, T.; Moore, B. P. *J. Org. Chem.* **1980,** *45,* 1126. Kato, T.; Suzuki, M.; Nakazima, Y.; Shimizu, K.; Kitahara, Y. *Chem. Lett.* **1977,** 705. Kitahara, Y.; Kato, T.; Kobayashi, T.; Moore, B. P. *Chem. Lett.* **1976,** 219. Kato, T.; Kobayashi, T.; Kitahara, Y. *Tetrahedron Lett.* **1975,** 3299.

(4) See, also: Baker, P. M.; Bycroft, B. W.; Roberts, J. C. *J. Chem. Soc. C* **1967,** 1913. von Hans Gerlach, V. *Helv. Chim. Acta* **1977,** 3039. Huisgen, R.; Rietz, Y. *Tetrahedron* **1958,** *2,* 271. Smith, A. B., III; Guaciaro, M. A.; Schow, S. R.; Wovkulich, P. M.; Toder, B. H.; Hall, T. W. *J. Am. Chem. Soc.* **1981,** *103,* 219. Nishimura, J.; Yamada, N.; Ueda, E.; Ohbayashi, A.; Oku, A. *Tetrahedron Lett.* **1986,** *27,* 4331. Nichimura, J.; Hashimoto, K.; Okuda, T.; Hayami, H.; Mukai, Y.; Oku, A. *J. Am. Chem. Soc.* **1983,** *105,* 4758. Overman, L. E.; Blumenkopf, T. A.; Castañeda, A.; Thompson, A. S. *J. Am. Chem. Soc.* **1986,** *108,* 3516. Overman, L. E.; Thompson, A. S. *J. Am. Chem. Soc.* **1988,** *110,* 2248. Cockerill, G. S.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. 1* **1985,** 2093, 2101. Marshall, J. A.; DeHoff, B. S.; Crooks, S. L. *Tetrahedron Lett.* **1987,** *28,* 527.

(5) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984,** *106,* 6085. Gassman, P. G.; Singleton, D. A. *J. Org. Chem.* **1986,** *51,* 3075.

(6) Gassman, P. G.; Singleton, D. A.; Wilwerding, J. J.; Chavan, S. P. *J. Am. Chem. Soc.* **1987,** *109,* 2182. Gassman, P. G.; Chavan, S. P. *J. Org. Chem.* **1988,** *53,* 2392.

(7) The synthesis of **1a** involved treatment of glutaraldehyde with 1,1-dimethylethyl triphenylphosphoranylideneacetate to give 1,1-dimethylethyl (2*E*)-7-oxoheptenoate in 78% yield. Treatment of this aldehyde with 1-triphenylphosphoranylidene-2-propanone gave 91% of 1,1-dimethylethyl (2*E*,7*E*)-9-oxodecadienoate. Reaction of this keto ester with dimethylsulfoxonium ylid yielded 32% of 1,1-dimethylethyl [2*E*(1*S**,2*S**)]-6-(2-acetylcyclopropyl)hexenoate. The acetyl group of this ester was treated with triphenylphosphoranylidenemethane to give 92% of 1,1-dimethylethyl [2*E*-(1*S**,2*S**)]-6-[2-(1-methylethenyl)cyclopropyl]hexenoate. Addition of methyllithium to this ester gave 70% of **1a**. Treatment of **1a** with potassium hydride followed by methyl iodide gave 93% of **1b**.

(8) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds. All compounds described had IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data which were consistent with the assigned structures.

Figure 1. ORTEP drawing of **4c**.
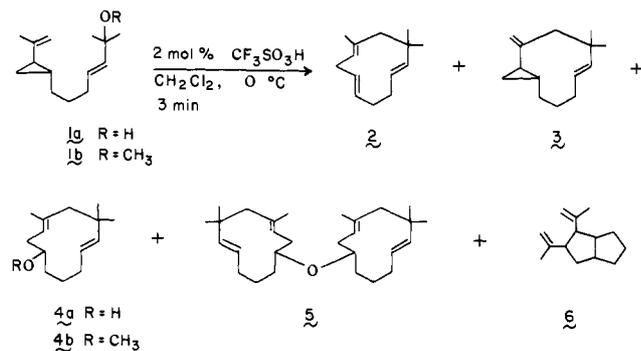
by workup and chromatographic isolation of the products, gave compounds **2–6**, plus trace amounts of monomeric ethers. When the concentration of **1a** was 0.001 M, we obtained 35% of **2**, 18% of **3**, 6% of **4a**, trace amounts of **5**, and trace amounts of **6**. When the concentration of **1a** was increased to 0.005 M, the corresponding yields were **2**, 22%; **3**, 10%; **4a**, 16%; **5**, 8%; and trace amounts of **6** in addition to small amounts of several monomeric ethers. When the temperature of the reaction was increased to 25 °C and the concentration of **1a** was maintained at 0.001 M, **2** was obtained in 46% yield, and **4a** was present in 3% yield. Under these conditions, **3** was not observed.

Similar treatment of **1b** (0.005 M) in methylene chloride at −23 °C with 5 mol % triflic acid gave 35% of **4b**, 6% of **2**, plus an assortment of acyclic monoethers and diethers. The alcohol **4a** was converted into **4b** in 94% yield through treatment with potassium hydride followed by methyl iodide. The structure of **4a** was unequivocally established through conversion of **4a** into its *p*-nitrobenzoate, **4c** (R = PNB, mp 126–127 °C), followed by single-crystal X-ray analysis. Figure 1 shows an ORTEP drawing of **4c**.[9,10]

Although elemental analyses, exact mass molecular weights, ^{1}H NMR, ^{13}C NMR, COSY and HETCOR NMR studies, and IR spectroscopy all supported the structural assignments made in this investigation, we desired to tie as many products as possible to **4c** via **4a** and **4b**. Thus, a variety of chemical correlation studies were carried out. Treatment of **3** with 2 mol % of triflic acid in methylene chloride containing 5 equiv of methanol for 20 min at 0 °C gave an 84% yield of **4b** interrelating **3** and **4**. Treatment of **3** with 2 mol % of triflic acid in methylene chloride for 5 min at −23 °C gave a 40% yield of **2** in addition to unreacted **3**. When **3** was treated under these conditions for 15 min, a mixture of **2** and **7** was obtained. Equilibration of **2** and **7** resulted in a 1:6 ratio, respectively.
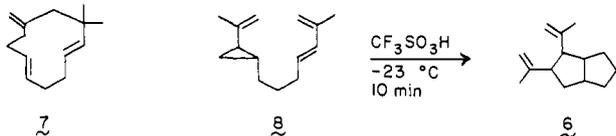
The presence of **6** was thought to be related to the conversion of **1** into **8**. When **8** was treated with 5 mol % of triflic acid in methylene chloride at −23 °C for 10 min, **6** was obtained as the

major product. We believe this to be the result of the productive protonation of the vinylcyclopropane moiety in preference to the butadiene moiety of **8**.

The facile formation of 10- and 11-membered rings in reactions of **1a** and **1b** with acid illustrates the ease with which an allyl cation can be "trapped" by a vinylcyclopropane.[11] Initial protonation on oxygen, followed by loss of ROH, would produce **9**. In
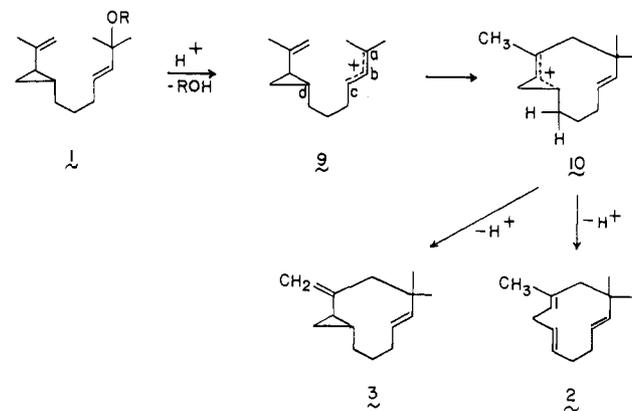
principle, **9** could cyclize to form either an 8-membered ring through attack of carbon "c" of the allylic cation on the vinyl-cyclopropane double bond or a 10-membered ring through attack of carbon "a" of the allyl cation on the olefinic moiety of the vinylcyclopropane. In practice, only a 10-membered transition state is involved, which produces the cyclopropyl carbinyl–hom-oallylic cation **10**.[12] Loss of a proton from the designated methylene group of **10** would produce **2**, while loss of a proton from the designated methyl group of **10** would yield **3**. Obviously, readdition of ROH, which was generated in the first step of the process, to **10** would give **4**.

In summary, we have demonstrated that the vinylcyclopropane moiety is an excellent "trap" for the intramolecular capture of an allyl cation and that an entropically unfavorable transition state can be formed which leads to 10- and 11-membered rings. Whether analogous reactions occur in nature is unknown.

Supplementary Material Available: Spectral (^{1}H NMR, ^{13}C NMR, and IR) and analytical data for **2**, **3**, **4a**, **4b**, **5**, and **6**, tables of bond lengths, bond angles, atomic coordinates, and anisotropic thermal parameters, and an ORTEP drawing of **4c** (13 pages). Ordering information is given on any current masthead page.

(9) The colorless crystals of $C_{21}H_{27}NO_4$ belong to the orthorhombic space group *Pbca*. The measured cell constants $a = 7.358$ (12) Å, $b = 12.573$ (6) Å, $c = 41.432$ (13) Å gave a calculated density of 1.239 g/cm² for eight molecules in the unit cell at −92 °C. Data were collected on a fully automated Enraf-Nonius CAD-4 diffractometer with a variable rate ω–2θ scan technique and graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). After Lorentz polarization corrections, 2433 of 3752 unique reflections (65%) with 2θ ≤ 52° were observed for $[F_o^2 \geq \sigma(F_o^2)]$. A combination of Patterson and Fourier synthesis was used to locate all of the non-hydrogen atoms.[10] The hydrogen atoms were included at idealized positions. All of the non-hydrogen atoms were refined by full-matrix least-squares analysis with anisotropic thermal parameters. The final discrepancy factors were $R = 0.073$ and $R_w = 0.076$.

(10) All calculations were carried out on a PDP 11/34 computer with the Enraf-Nonius SDP programs. This crystallographic computing package is described by the following: Frentz, B. A. In *Computing in Crystallography*; Schenk, H., Oltof-Hazelkamp, R., Von Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.
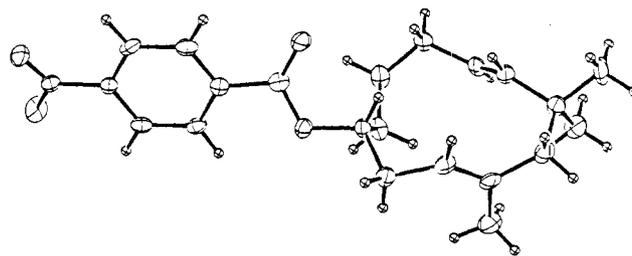
(11) For previous reports of the use of the vinylcyclopropane moiety as a "trap" for carbocations, see: Gassman, P. G.; Riehle, R. J.; Singleton, D. A. Third Chemical Congress of North America, Toronto, Canada, June 5–10, 1988, Abstracts: ORGN 249. Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 6556.

(12) We cannot rule out the possibility that the formation of **6** could result from the electrophilic attack of carbon "c" of **9** on carbon "d" of **9** to form an allyl cation which adds back to carbon "b" to yield a tertiary carbocation at carbon "a".