chemistry of these novel compounds will be described in a full paper.

Acknowledgment. The diffractometer used in this work was purchased with a National Science Foundation equipment grant. We thank Dr. W. K. Rohwedder and Ronald Plattner for mass spectra and Tim Mueser and Barry Jones for technical assistance. The 470-MHz ^1H NMR spectra were obtained through cooperation of the Purdue University Biological Magnetic Research Laboratory supported in part by the National Institutes of Health, Division of Research Resources, Grant No. RR 01077. We express our appreciation to Drs. J. Otvos and D. M. Doddrell for assistance in obtaining the initial DEPT experimental results.

Registry No. Sesbanimide, 85719-78-4.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, and both ^1H NMR and ^{13}C NMR spectra for sesbanimide (4 pages). Ordering information is given on any current masthead page.

Free-Radical Cyclization of Bromoacetals. Use in the Construction of Bicyclic Acetals and Lactones†

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Received February 8, 1983

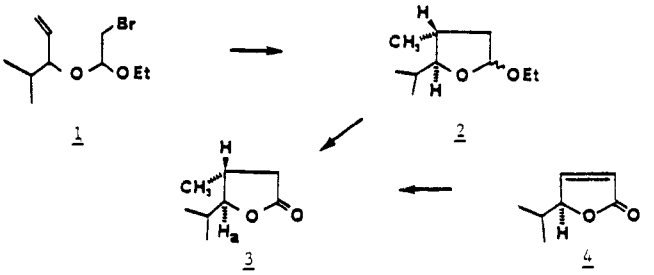
Radical cyclization is rapidly becoming an important method for the formation of bicyclic systems.[1] We recently reported[1b] a general regiospecific synthesis of vinyl radical intermediates by an intramolecular process starting with the bromoacetals of ethynyl carbinols (cf. A → B), and during the course of this work, we

A B

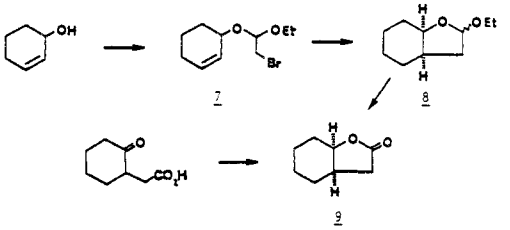
became interested in the cyclization of radicals derived from the bromoacetals of allylic and homoallylic alcohols. Such cyclizations will be especially valuable in the construction of cis-bicyclic systems bearing latent functionality (vide infra). We mention first the simpler synthesis of monocyclic acetals.

Treatment of the mixed bromoacetal **1** (Scheme I) derived from vinylisopropylcarbinol with tri-*n*-butylstannane (1.2 equiv of Bu_3SnH (0.02–0.04 M), AIBN catalyst, 4 h of reflux in benzene; potassium fluoride workup[2]) gave in 81% yield the cyclic acetal **2**, which was oxidized in quantitative yield with Jones reagent (4 equiv; room temperature) to the lactone **3**.[3] NMR as well as GLC analysis showed 97–98% of a major isomer,[4] which had a methyl resonance at δ 1.15 (d, J = 6.6 Hz) and H_a at δ 3.85 (dd, J = 5.6, 6.2 Hz).

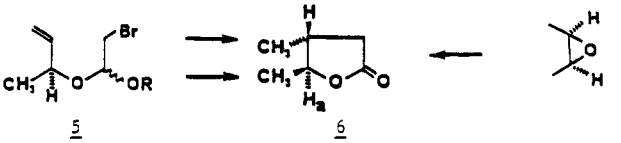
Scheme I



Scheme II



The stereochemistry of the lactone **3** was established to be trans by correlation with the product of lithium dimethylcuprate addition[5] to the butenolide **4**.[4,6] Our stereochemical conclusions are at variance with a report[7] that appeared while our work was being readied for publication[8] and that states that a very similar cyclization starting with the bromoacetal **5** led to the *cis*-4,5-



5 6

dimethyl isomer of **6**. Our expectation that the product of the cyclization of **5** should be trans-4,5-disubstituted (cf. **1** → **2** → **3** above) is clearly correct since the derived lactone **6** is identical with the necessarily *trans*-dimethyl lactone obtained by opening of the epoxide of *cis*-2-butene with malonic ester anion.[9]

Useful as these simple cyclizations may be, we believe that it is in the formation of bicyclic systems that the greater potential lies. The cis fusion of the bicyclic lactol produced by such a process (C → D, n = 0, 1) follows from the expected transition-state

C D

geometry and thus leads to the regio- and stereocontrolled formation of a carbon–carbon bond.

We illustrate the method starting with 2-cyclohexenol (Scheme II). Conversion to the mixed acetal **7** with 1,2-dibromoethyl ethyl ether,[1b,10] followed by treatment with tri-*n*-butylstannane readily gave the bicyclic lactol ether **8** as a mixture of anomers.[11] The

† This paper is dedicated to Professor Edgar Leherer on the occasion of his 75th birthday.

(1) (a) Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. (b) Stork, G.; Mook, R., Jr. *Ibid.*, in press. (c) Hart, D. J.; Tsai, Y.-M. *Ibid.* **1982**, *104*, 1430. (d) Hart, D. J.; Choi, J.-K.; Tsai, Y.-M. *Tetrahedron Lett.* **1982**, *23*, 4765.

(2) Jacobus, J.; Leibner, J. E. *J. Org. Chem.* **1979**, *44*, 449.

(3) The substances referred to in this paper were normally purified by flash chromatography with ethyl acetate–petroleum ether on silica gel.

(4) The minor isomer was the cis isomer of **3**, identical with the major product of the hydrogenation (cf. ref 5) of the 4-methyl derivative of the unsaturated lactone **4**. The methyl and H_a resonances of the cis isomer were at δ 1.09 (d, J = 6.5 Hz) and 3.94 (dd, J = 4.8, 12.5 Hz).

(5) Vigneron, J. P.; Meric, R.; Dhaenens, M. *Tetrahedron Lett.* **1980**, *21*, 2057.

(6) Made by reaction of the disodium salt of ethynylisopropylcarbinol with carbon dioxide, followed by semihydrogenation.

(7) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564.

(8) Some of our work on bromoacetal cyclizations was presented in a plenary lecture at the Fourth International Conference on Organic Synthesis, Tokyo, Aug 1982.

(9) Bystrom, S.; Hogberg, H. E.; Norin, T. *Tetrahedron* **1981**, *37*, 2249. The NMR absorptions due to H_a in the authentic *cis*- and *trans*-dimethyl lactones are very characteristic of their stereochemistry.

(10) Rowlands, D. C.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Org. Chem.* **1952**, *17*, 807.

(11) The yield of purified cyclization product derived from the bromoacetal **7** and from the bromoacetal from **10** (50–55%) may be a lower limit, at least in the case of **8**, because of its volatility.

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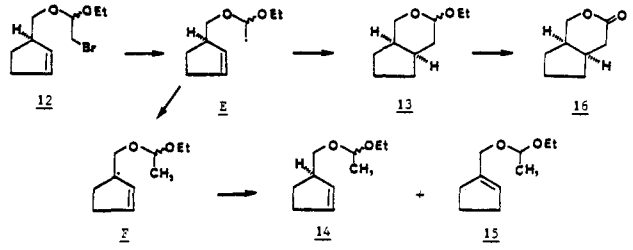
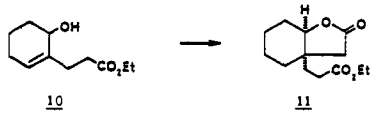
Scheme III



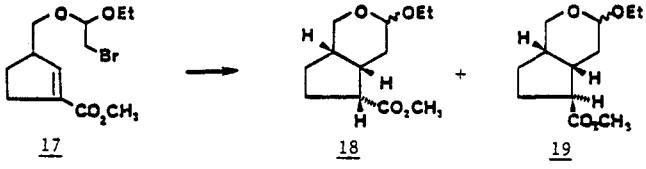
expected cis fusion was established by Jones oxidation (−10 °C, 15 min) to the lactone **9**, which was identical (IR, NMR) with an authentic sample.[12]

As in other cases of radical cyclization processes,[1a,b] quaternary centers are formed with ease. This is illustrated by the transformation **10** → **11**,[11,13] which also shows the expected compatibility with an ester carbonyl.



In many of the cyclization processes described here, 1,4-hydrogen transfer to the initial radical would have led to an allylic tertiary radical of greater stability. That this does not compete with cyclization probably reflects the strain required to achieve the linear arrangement of the relevant centers in the transition state for such a process. When, however, the starting alcohol is homoallylic, the transition state for what is now a 1,5-hydrogen transfer is not so constrained; it is encountered in a host of processes such as the Barton reaction.[14] We have studied the acetal cyclization in such a case, starting with the bromoacetal **12** of 2-cyclopentenemethanol (Scheme III). Reaction of **12** with tri-*n*-butylstannane under typical conditions gave, in 70% yield, a mixture of acetals **13**–**15** in a 73:17:10 ratio (GLC).[15] It is significant that, even in this case, half of the products arise by the desired cyclization path. The structure and stereochemistry of **13** were established by hydrolysis (1:2 10% HCl–THF) followed by Jones oxidation, which gave the known cis-bicyclic lactone **16**.[16]

A simple modification of structure **12** served to make cyclization the exclusive pathway. Bromoacetal **17**[17] led in 90% yield to the bicyclic acetals **18** and **19**[18] (85:15 ratio by GLC), thus demonstrating the favorable effect of an α,β-unsaturated ester acceptor.



It is likely that the acetal annulation process described here will prove of considerable use in synthesis. We are exploring its application in prostaglandin construction.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

Registry No. 1, 85710-95-8; **2**, 85710-96-9; **3**, 85710-97-0; **4**, 56767-19-2; **7**, 85710-98-1; **8** (isomer 1), 85710-99-2; **8** (isomer 2), 85711-00-8; **9**, 24871-12-3; **12**, 85711-01-9; **13**, 85711-02-0; **14**, 85711-03-1; **15**, 85711-04-2; **16**, 15773-81-6; 2-cyclohexenol, 822-67-3; 1,2-dibromoethyl ethyl ether, 2983-26-8.

(12) Conveniently made from 2-oxocyclohexaneacetic acid and L-Selectride. Cf.: Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884.

(13) The hydroxy ester **10** was made by sodium borohydride–cerium trichloride reduction of the corresponding keto ester. The precyclization bromoacetal was made in this case from the dibromide derived from 2-chloroethyl vinyl ether.[1b] The lactone **11** was then made by Jones oxidation at 0 °C.

(14) Cf.: Hesse, R. H. *Adv. Free Radical Chem.* **1969**, *3*, 83.

(15) In addition, two regioisomeric dimers of radical F were isolated in 9% yield. The amount of 1,5-hydrogen transfer is thus between 16% and 28%, since some or all of the uncyclized isomer **14** could have arisen by direct hydrogen transfer from tri-*n*-butylstannane to radical E.

(16) Baldwin, S. W.; Crimmins, M. T. *Tetrahedron Lett.* **1978**, 4197. We thank these authors for a sample of lactone **16**.

(17) The (hydroxymethyl)cyclopentenecarboxylic ester precursor of 17 was made from 3-(hydroxymethyl)cyclopentenecarboxaldehyde (Corey, E. J.; Danheiser, R. L. *Tetrahedron Lett.* **1973**, 4477) by cyanide-catalyzed MnO_2 oxidation (Corey, E. J.; Gilman, N. W.; Ganem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616).

(18) The structural assignments shown for **18** and **19** are based on a careful analysis (including decoupling) of their 250-MHz ^1H NMR spectra.

Alkaline Earth Metal–Ammonia–Anion Radical Complexes

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Received February 24, 1983

Alkaline earth metals have long been known to interact strongly with ammonia.[1] In fact they readily form ammoniates that were first thought to be hexammoniates, but it was later realized that nonstoichiometric amounts of ammonia are combined with the metals.[2,3] Even the salts of the alkaline earth metals have a strong affinity for ammonia as evidenced by the fact that the chloride salts absorb ammonia gas to form salt–gas complexes ($MCl_2 \cdot n NH_3$).[3] We have made use of the strong affinity of the alkaline earth cations for ammonia to generate a new class of solid alkaline earth complexes containing hydrocarbon anion radicals that are thermodynamically stable.

When 2 mol of anthracene are reacted with a mole of barium metal in very dry liquid ammonia, a green solution results that yields the ESR signal for the uncomplexed anthracene anion radical. Upon removal of the solvent (NH_3), a dark green solid is left that has the formula $Ba(NH_3)_2(AN)_2$.[4] The composition of this material does not change even during prolonged exposure to high vacuum at room temperature (no noticeable decomposition can be observed after weeks of storage at room temperature under vacuum). Even heating the material to 100 °C for 24 h while exposing it to an open vacuum will not change its composition. The stoichiometry and integrity of the compound were checked in several ways.

(1) Reacting the solid salt with water yields 1 mol of 9,10-dihydroanthracene for each mole of anthracene as organic products.

(2) Boiling the water solution (above) liberates 2 mol of ammonia/mol of Ba.

(3) Heating the salt under vacuum liberates 2 mol of ammonia and 2 mol of anthracene per mol of complex.

The noticeable exothermicity of the reaction of the salt with water, reaction 1, allows for the determination of the thermody-

$$Ba(NH_3)_2(AN^{-\cdot})_2 + 2H_2O_l \rightarrow Ba(OH)_2(aq) + 2NH_3(aq) + ANH_2(s) + AN(s) \quad (1)$$

namic stability of the salt. Thin-walled evacuated bulbs containing the salt were broken under 100 mL of water in a modified Parr solution calorimeter interfaced with a MINC II computer system as previously described.[5] A plot of the temperature change of

(1) Cotrell, F. G. *J. Phys. Chem.* **1914**, *18*, 85.
(2) Marshall, P.; Hunt, H. *J. Phys. Chem.* **1956**, *60*, 732.
(3) Kraus, C. A. *J. Am. Chem. Soc.* **1908**, *30*, 653.
(4) AN = anthracene and ANH_2 = 9,10-dihydroanthracene.
(5) Stevenson, G. R.; Zigler, S. S.; Reiter, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6057.

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