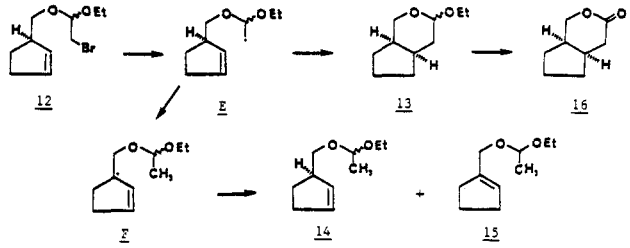
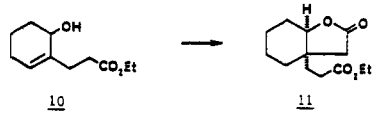
Scheme III



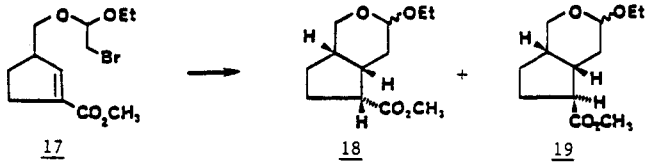
expected cis fusion was established by Jones oxidation (−10 °C, 15 min) to the lactone **9**, which was identical (IR, NMR) with an authentic sample.[12]

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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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 ($MCl_2 \cdot nNH_3$).[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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Table I. Heats of Reaction at 25 °C in Kilocalories per Mole

reaction	ΔH° [a]	ref
$ANH_2(s) + AN(s) + 2NH_3(aq) + Ba(OH)(aq) \rightarrow Ba(NH_3)_2(AN)_2(s) + 2H_2O(l)$	+95.9 ± 2.9	this work
$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)(aq) + H_2(g)$	−101.94	6
$AN(s) + H_2(g) \rightarrow ANH_2(s)$	−17.0	7
$2NH_3(g) \rightarrow 2NH_3(aq)$	−17.1	8
$Ba(s) + 2NH_3(g) + 2AN(s) \rightarrow Ba(NH_3)_2(AN)_2(s)$	−40.1 ± 3.2	

[a] The standard deviations were obtained from the standard deviation in the slope of the line in Figure 1, and the errors reported in ref 6-8.

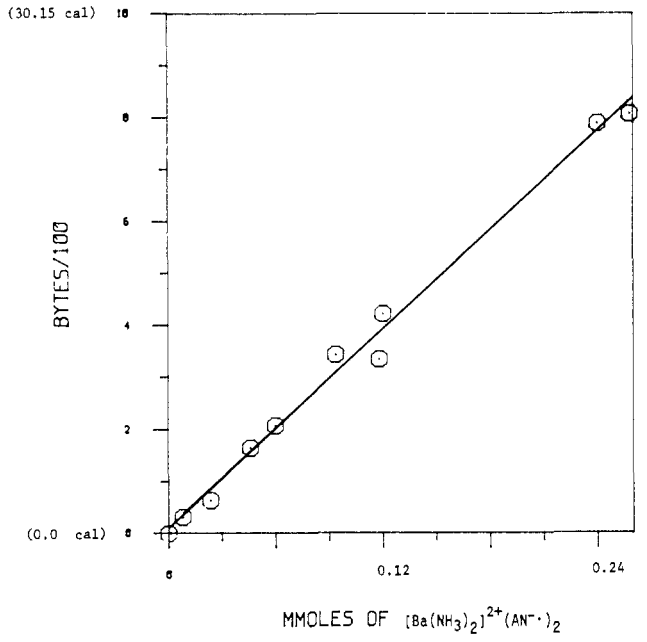

Figure 1. Plot of the change in the temperature of the calorimeter (in computer bytes) vs. the millimoles of the barium complex in the glass bulbs. Multiplying the slope of this line (3.181 ± 0.097 bytes/millmol) by the capacity of the calorimeter (0.03015 cal/byte) yields the enthalpy of reaction 1. When the contents of the calorimeter are titrated, a millimole of HCl is used for each millimole of ammonia and each half millimole of barium hydroxide.

the calorimeter vs. the millimoles of salt in the glass bulbs is linear, Figure 1, and it yields an enthalpy for reaction 1 of 95.9 ± 2.9 kcal/mol (Table I).

The data obtained from Figure 1 can be placed into a thermochemical cycle, Table I, to obtain the heat of formation of the compound from barium metal, ammonia, and anthracene in their standard states, reaction 2. The heat of reaction of barium with

$$Ba(s) + 2NH_3(g) + 2AN(s) \rightarrow Ba(NH_3)_2(AN)_2(s) \quad (2)$$

ammonia and anthracene is about 40% as exothermic as the reaction of barium with water, Table I.

The solid barium complex as well as similar complexes of strontium and calcium are paramagnetic. On the basis of their ESR signals (a single line at $g = 2.0$), the two anthracene molecules exist in the form of the anion radicals. All three of these alkaline earth metal complexes have the same composition relative to anthracene and ammonia, but they differ widely in color ranging from bright yellow for the calcium complex to red brown for the strontium complex. Similar salts can be formed with other organic anion radicals, which are still to be explored. In general there appears to be a myriad of thermodynamically stable alkaline earth metal complexes with the structure $[M(NH_3)_2]^{2+}(\text{anion radical})_2$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. $Ba(NH_3)_2(AN^{-}\cdot)_2$, 85681-26-1; $Sr(NH_3)_2(AN^{-}\cdot)_2$, 85681-27-2; $Ca(NH_3)_2(AN^{-}\cdot)_2$, 85681-28-3.

(6) Keller, R. A. "Basic Tables in Chemistry"; Mcgraw-Hill: New York, 1967.
(7) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organo Metallic Compounds"; Academic Press: London, 1970.
(8) Wertz, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 5316.

2-Oxoazetidine-1-phosphonic Acids: Synthesis and Transesterification

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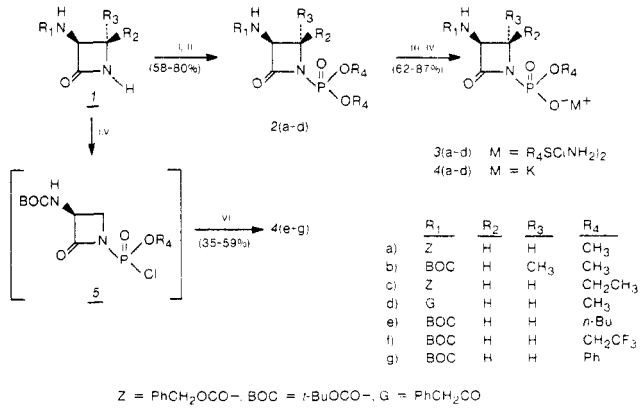
Aztreonam is the first example of a monocyclic β-lactam antibiotic having clinically useful activity.[1] The N-1 sulfonate moiety, characteristic of monobactams provides both activation for the β-lactam ring and the anionic site necessary for enzyme–substrate interaction. Although hexavalent sulfur and pentavalent phosphorus are sterically similar, an N-1 phosphonate moiety should exert less of an inductive effect on the ring compared to sulfonate. However, unlike the sulfur case, tetracoordinate phosphorus provides an extra valence for functionalization. Therefore, the synthesis and chemistry of 2-oxoazetidine-1-phosphonic acids were examined.

Scheme I[a]



	R_1	R_2	R_3	R_4
a)	Z	H	H	CH_3
b)	BOC	H	CH_3	CH_3
c)	Z	H	H	CH_2CH_3
d)	G	H	H	CH_3
e)	BOC	H	H	*n*-Bu
f)	BOC	H	H	CH_2CF_3
g)	BOC	H	H	Ph

[a] Key: (i) *n*-BuLi, THF, −78 °C. (ii) $ClPO(OR_4)_2$, −78 °C. (iii) H_2NCSNH_2, CH_3CN, reflux. (iv) Dowex 50 (K^+ form). (v) $R_4OP(O)Cl_2$, −78 °C. (vi) pH 6 phosphate buffer, dioxane, 0-5 °C.

(1) Sykes, R. B.; Bonner, D. P.; Bush, K.; Georgopapadakou, N. H. *Antimicrob. Agents Chemother.* **1982**, *21*, 85.

0002-7863/83/1505-3743$01.50/0