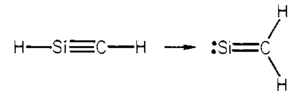
atoms, as were d functions on carbon (α = 0.75) and silicon (α = 0.6). The technical specification of this double-ζ plus polarization (DZ + P) basis is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s1p/2s1p). Although heavy-atom d functions are known[14] to be important for such systems, it was also thought that the p functions on hydrogen (particularly those on the migrating hydrogen) might lower the predicted barrier.

The transition-state geometry for the silaethylene rearrangement was determined here at the DZ + P self-consistent-field (SCF) level of theory and is seen in Figure 1 along with the analogous DZ + P SCF structure for the reactant molecule. Comparison with the earlier DZ SCF transition state[7] shows the two structures to be qualitatively similar. The appropriate total energies are −329.05439 (silaethylene) and −328.98320 (transition state) hartrees, yielding a predicted barrier of 44.7 kcal, only 0.3 kcal below the DZ SCF barrier height.[7] Thus it is seen that at the SCF level the addition of polarization functions has little effect on either the reaction mechanism or energetics.

With the full DZ + P basis set, CI including all single and double excitations was carried out, with the restriction that the core molecular orbitals (Si 1s, 2s, $2p_x$, $2p_y$, $2p_z$ and C 1s) were deleted. For silaethylene in point group C_{2v} there are 9003 configurations while the transition state, with no elements of symmetry (point group C_1), the CI involved 32 131 configurations. The variational energies obtained for silaethylene and the rearrangement transition state are −329.29703 and −329.22858 hartrees, respectively, yielding a barrier of 43.0 kcal. Appendage of the Davidson correction[17] for unlinked clusters yields a final prediction of 40.6 kcal for the classical barrier.

One surprising result of this research is that the most reliable predicted barrier height for reaction 1 is qualitatively the same as the 45.0 kcal predicted[7] at the relatively simple DZ SCF level. As noted earlier, polarization basis functions and correlation effects typically provide a considerable reduction in such predicted barriers.[9–12] That is to say, relative minima on a potential surface are typically treated more correctly at a simple level of theory than are transition states. The invalidation of this trend in the present case is almost certainly due to the relative inability of the simple methods to describe the silaethylene ground state. That is, silaethylene is just as difficult to describe electronically as is its transition state to methylsilylene. Interestingly, the same qualitative result has been found for the related silacetylene rearrangement



$$H{-}Si{\equiv}C{-}H \longrightarrow :Si{=}CH_2 \qquad (3)$$

There Gordon and Pople[18] find that polarization functions and correlation effects actually *increase* the rearrangement barrier.

Unless there exists a different, lower energy pathway for reaction 2, it would appear that alternate interpretations of the experiments of Conlin and Wood[15] and of Drahnak, Michl, and West[16] should be sought.[19,20]

Acknowledgment. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. W-7405-ENG-48. We thank Professors Conlin and Michl for bringing their work[15,16] to our attention prior to its publication and Dr. John. D. Goddard for many helpful discussions.

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(17) S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974).

(18) M. S. Gordon and J. A. Pople, *J. Am. Chem. Soc.*, **103**, 2945 (1981).

(19) The seemingly remote possibility remains (suggested by DMW[16]), of course, that the additional methyl group in reaction 2 could provide a qualitative difference between reactions 1 and 2.

(20) The transition state seen in Figure 1 was determined via analytic gradient techniques, beginning from the earlier determined[7] DZ SCF transition state structure. Since both structures contain no elements of symmetry (point group C_1), there are no constraints on the geometrical optimization.

Cucurbituril

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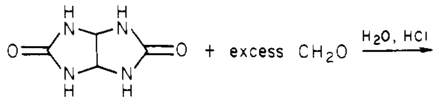
Some 75 years ago Behrend et al. reported materials from acidic condensation of glycoluril (**1**) with an excess of formaldehyde.[1] The initial product so obtained should probably be regarded as a cross-linked, aminal-type polymer by virtue of its physical properties (amorphous character, insolubility in all common solvents). In seeking a more tractable material from this precipitate, the previous workers resorted to treatment with hot, concentrated sulfuric acid, which eventually dissolves the substance (as we have confirmed). When such solution is diluted with cold water, filtered, and subsequently boiled, a crystalline precipitate (**2**) is obtained, which Behrend characterized as $C_{10}H_{11}N_7O_4 \cdot 2H_2O$. Although no structure for **2** was offered, the substance proved exceedingly stable toward a number of potent reagents. Also, a series of crystalline complexes incorporating a surprising variety of metal salts and dye stuffs was recorded.[1]



1

$$\text{precipitate} \xrightarrow[110\ ^\circ\text{C}]{\text{concentrated } H_2SO_4} \text{solution} \xrightarrow{H_2O} \text{solution} \xrightarrow{\Delta} \mathbf{2}\ (\text{precipitate})$$

Intrigued by this report, we repeated the preparation and obtained **2** without difficulty in somewhat less than the specified yield (40–70%). Spectral characterization enhanced our curiosity. In the infrared region, the carbonyl absorption (1720 cm^{-1}, KBr) suggested retention of the glycoluril nucleus. The proton NMR spectrum, containing only three signals of equal intensity, indicated a nonaromatic structure of high symmetry: δ^{Me_4Si} (90% HCOOH) 5.75 (s, glycoluril methines), and 4.43, 5.97 (d, $|J|_{gem}$ = 15.6 Hz, nonequivalent methylene hydrogens, $N{-}CH_aH_b{-}N$). This evidence implies the stoichiometry $nC_4H_6N_4O_2 + 2nCH_2O \rightarrow (C_6H_6N_4O_2)_n + 2nH_2O$, which is in reasonable agreement with elemental analysis of **2** (as a hydrate).[1,2] However, the material proved insufficiently volatile for mass spectral molecular weight determination, even by the technique of field desorption ionization. Consequently, an X-ray crystallographic structure determination was undertaken.

Although the parent substance proved unsuitable for this purpose, satisfactory crystals of a calcium bisulfate complex of **2** were obtained from sulfuric acid solution. This material was of composition $(C_6H_6N_4O_2)_3 \cdot CaSO_4 \cdot H_2SO_4 \cdot (H_2O)_{6.5}$ and crystallized in the triclinic system with a = 11.948 (3) Å, b = 10.391 (3) Å, c = 15.667 (5) Å, α = 92.15 (8)°, β = 115.18 (5)°, γ = 109.66 (6)°. The observed density was consistent with two of the above formulas per unit cell. The structure was solved in space group $P\bar{1}$ by direct methods (MULTAN). The solution, based on 3686 observed, absorption-corrected, unique data, has been refined to a conventional R of 0.0673.

The organic moiety (**2**) is a cyclic hexamer of dimethanoglycoluril as shown in Figure 1.[3] Fuller details of the crystal structure will be provided elsewhere. Briefly, however, the organic macrocycle encircles a crystallographic center of symmetry, with calcium ions coordinated to urea carbonyl oxygen atoms of adjacent molecules of **2**. Octacoordination of the metal is completed with water and sulfate ligands. The center of each hexamer is

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(1) Behrend, R.; Meyer, E.; Rusche, F. *Liebigs Ann. Chem.* **1905**, *339*, 1.

(2) Found: C 40.92, H 4.17, N 30.17 (Galbraith); C 36.66, H 4.53, N 30.08 (Behrend et al.,[1] average values).

(3) The spectral evidence previously cited is quite in accord with this structure. Magnetic nonequivalence of the methylene protons arises from endo- and exocyclic orientations.

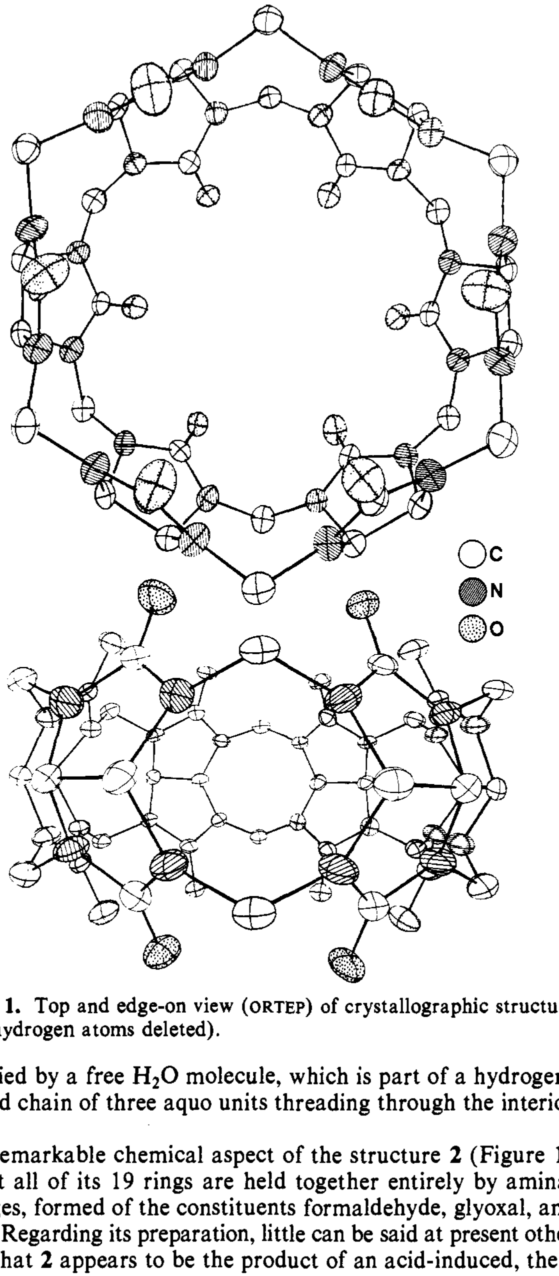

Figure 1. Top and edge-on view (ORTEP) of crystallographic structure of **2** (hydrogen atoms deleted).

occupied by a free H_2O molecule, which is part of a hydrogen-bonded chain of three aquo units threading through the interior of **2**.

A remarkable chemical aspect of the structure **2** (Figure 1) is that all of its 19 rings are held together entirely by aminal linkages, formed of the constituents formaldehyde, glyoxal, and urea. Regarding its preparation, little can be said at present other than that **2** appears to be the product of an acid-induced, thermodynamically controlled rearrangement of an initially formed macromolecular condensation product of **1** and formaldehyde. Aside from its enigmatic spontaneous synthesis, the most captivating feature of **2** is the presence of an internal cavity of approximately 5.5-Å diameter within the relatively rigid macrocyclic structure, to which access is provided by 4-Å diameter portals situated among the carbonyl groups. We have obtained NMR evidence pertinent to this feature of the structure. Apparently the interior of **2** comprises a magnetic shielding region, for the proton resonances of sterically unencumbered aliphatic amines undergo upfield shifts of 0.6–1.0 ppm in the presence of 1 molar equiv of **2** in acid solution. We suggest that this is indicative of formation of a molecular inclusion complex wherein the cationic head of the alkylammonium ion associates with the negative ends of the carbonyl dipoles of **2** and in which the hydrocarbon tail extends into the core of the cage structure. The stoichiometry of this complexation (1:1) is conveniently measurable by NMR integration. The specificity of binding appears quite remarkable. For example, cyclopentanemethylamine is held quite tightly ($K_d \sim 10^{-6}$ M at 40 °C in aqueous formic acid solution), but cyclohexanemethylamine evidently is excluded from the internal cavity of **2** by its size. A comprehensive survey of the host–guest chemistry of **2** will be reported subsequently.

We propose the trivial name cucurbituril for **2**.[4]

Acknowledgment. We thank K. L. Loening (Chemical Abstracts Service) and W. H. Pirkle (University of Illinois at Urbana-Champaign) for nomenclature assistance, K. L. Rinehart (University of Illinois at Urbana-Champaign) for mass spectral data, and J. M. Williams of the Argonne National Laboratory, where some of the crystallographic calculations were performed.

Supplementary Material Available: A listing of atomic and thermal parameters for **2**·calcium bisulfate (2 pages). Ordering information is given on any current masthead page.

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(4) The proper (current Chemical Abstracts index) name for **2** is dodecahydro-1*H*,4*H*,14*H*,17*H*-2,16:3,15-dimethano-5*H*,6*H*,7*H*,8*H*,9*H*,10*H*,11*H*,12*H*,13*H*,18*H*,19*H*,20*H*,21*H*,22*H*,23*H*,24*H*,25*H*,26*H*-2,3,4a,5a,6a,7a,8a,9a,10a,11a,12a,13a,15,16,17a,18a,19a,20a,21a,22a,23a,24a,25a,26a-tetracosaazabispentaleno[1‴,6‴:5″,6″,7″]cycloocta[1″,2″,3″:3′,4′]pentaleno(1′,6′:5,6,7)cycloocta(1,2,3-*gh*:1′,2′,3′-*g′h′*)cycloocta(1,2,3-*cd*:5,6,7-*c′d′*)dipentalene-1,4,6,8,10,12,14,17,19,21,23,25-dodecone. The trivial name cucurbituril is proposed because of a general resemblance of **2** to a gourd or pumpkin (family Cucurbitaceae), and by devolution from the similarly named (and shaped) component of the early chemists' alembic.

Successive Beckmann Rearrangement–Alkylation Sequence by Organoaluminum Reagents. A Simple Route to *dl*-Pumiliotoxin C

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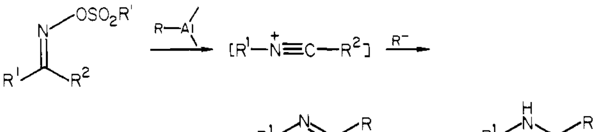
Undoubtedly, the Beckmann rearrangement is the best known and most thoroughly investigated of all azomethine rearrangements because of sustained interest in its mechanism, its application to synthesis, and the industrial interest in it as a step in the manufacture of synthetic polyamides.[1] We wish to disclose that facile alkylation at the intermediary iminocarbonium ion of Beckmann rearrangement is accessible by organoaluminum reagents.[2] The overall transformation is illustrated in eq 1.



(1)

Treatment of a wide variety of oxime sulfonates with several equivalents of alkylaluminum reagents in methylene chloride resulted in formation of the imines, which were directly reduced with excess diisobutylaluminum hydride (DIBAH) to give the corresponding amines (eq 1). This new synthetic approach provides a simple route to many substances hitherto accessible only by lengthy or complicated syntheses.[3] The examples cited in Table I illustrate the preparation of alkylated amines using indicated aluminum reagents and reaction conditions. Several aspects are quite noteworthy. First, a high regioselectivity is seen for rear-

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(1) For reviews, see: Blatt, A. H. *Chem. Rev.* **1933**, *12*, 215. Jones, B. *Chem. Rev.* **1944**, *35*, 335. Moller, F. *Methoden Org. Chem.* (*Houben-Weyl*), *4th Ed.* **1957**, *11*, 892. Donaruma, L. G.; Heldt, W. Z. *Org. React.* (*N.Y.*) **1960**, *11*, 1. Beckwith, A. L. J. In "The Chemistry of Amides"; Zabicky, J., Ed.; Interscience: New York, 1970; p 131. McCarty, C. G. In "Chemistry of the Carbon-Nitrogen Double Bond"; Patai, S., Ed.; Wiley-Interscience: New York, 1970; p 408.

(2) For reviews of aluminum reagents, see: Yamamoto, H.; Nozaki, H. *Angew. Chem., Int. Ed. Engl.*, **1978**, *17*, 169.

(3) The conventional process for accomplishing this transformation consists of several steps, oxime → amide (Beckmann rearrangement) → imino ether (trialkyloxonium tetrafluoroborate) → imine (RLi or RMgX) → amine (reduction), and requires a considerably longer time for execution.

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