as reagents with improved thermal stability. For comparison, the corresponding yields for $Bu_2Cu(CN)Li_2$ were 95% and 84% in ether.

With their thermal stability established[15] the reactivity and economy of cuprates based on **1**–**3** are illustrated by the examples in Table I. In the first, 6-bromo-3-chloro-1-hexene was added to the reagent prepared with **1** (from **4** and $LiPPh_2$, prepared in situ[8] from $HPPh_2$ and BuLi) and 1.0 equiv of *n*-heptylmagnesium bromide in THF at −20 °C to obtain 87% of an *E*–*Z* mixture (6:4) of 1-bromo-4-tridecenes (**5**) and 11% of 1-bromo-4-vinylundecane (**6**). So that a comparable total yield (97% **5**, <1% **6**) could be obtained, 1.8 equiv of the corresponding homocuprate (prepared from 3.6 equiv of Grignard reagent and 1.8 equiv of **4**) was required. The yield of **5** based upon heptyl in this case is only 27%. In a related example, Macdonald and co-workers[16] treated 9-bromo-3-chloro-1-nonene with 1.0 equiv of the cuprate prepared from 2.0 equiv of *n*-propylmagnesium bromide and 1.0 equiv of **4** to obtain 80% of 1-bromo-7-dodecene (40% based on propyl). Besides the requirement of less Grignard reagent for complete action, the higher reactivity of our reagent is indicated by the presence of **6** from the direct displacement of Cl at a secondary center,[14a] not observed with the homocuprate.

The vinyl cuprate prepared from **3** and vinyllithium reacts with 2-cyclopentenone to afford 83% of 3-vinylcyclopentanone. The yield reported for the (phenylthio)cuprate was 30%.[3] The vinylcuprate prepared from **2** and vinyllithium adds 1,4 to isophorone in 64% yield, compared with 52–58% for acetylenic mixed cuprates.[12,17] While the yields of 3-vinyl adduct from isophorone and 2 equiv of divinylcopper(I) lithium[18] or divinyl(cyano)copper(I) dilithium[14c] are higher based on isophorone (85% and 88%, respectively), the yields based on vinyllithium are significantly lower (21–22%). The conjugate addition of vinyl copper(I) reagents is important because of its relevance to certain prostaglandin syntheses, where the optically active vinyllithium reagent from which the cuprate is made can be more valuable than the cyclopentenone substrate.[19] In such cases it is more valid to calculate yields based on the Li reagent.

Considering the 92% yield from 2-cyclohexenone and $BuCu(NCy_2)Li$, the low yields of isophorone conjugate addition products using cuprates based on **3** (see Table I) are due to steric inhibition of the reaction. In line with this view, the smaller $BuCu(NEt_2)Li$ affords a 60% yield of 3-butyl-3,5,5-trimethylcyclohexanone. This result suggests the possibility of tailoring heterocuprate reactivity by choosing the appropriate amido ligand.

Examples of reactions where thermal stability and reactivity are crucial are the opening of epoxides and the displacement of primary iodides. Cyclohexene oxide yields 62% of *trans*-2-methylcyclohexanol when treated with 5 equiv of Me_2CuLi.[20] (The yield based on Me is but 6%.) With cuprates prepared from **1** and **3**, the yields based on Me (or on cyclohexene oxide) are 35% and 46%, respectively. With use of MeCu(CN)Li to effect this transformation, the yield is 29%;[21] the yield we obtain using 1.0 equiv of Lipshutz's[14b] $Me_2Cu(CN)Li_2$ is 53% (27% per Me). A 97% yield of nonane from octyl iodide and 3 equiv of Me_2CuLi has been reported.[22] On the basis of Me the yield is 16%, compared with 57% from the methyl derivative of **2** and 84% from that of **3**.

As a final example of the high reactivity of these new heterocuprates, $BuCu(PPh_2)Li$ and $BuCu(NCy_2)Li$ are able to open a 1,1-diactivated cyclopropane with the kind of yield (70%) that often requires 2 equiv of R_2CuLi.[23]

We believe that the high thermal stability and reactivity of the new cuprates introduced here will make them valuable reagents for the synthesis of complex molecules.

Acknowledgment. We thank Professors A. Ponaras and J. Schwab (Catholic University of America) for suggesting that we examine the (dicyclohexylamido)cuprates, Dr. Linda Anthony for capillary GLC analysis of the 2-methylcyclohexanol (which established it to be purely trans), A. Mujsce for mass spectral analyses, and Professor B. Lipshutz for an authentic sample of 3-vinyl-3,5,5-trimethylcyclohexanone.

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[15] For a more detailed discussion of the factors influencing thermal stability, see Part IV of our series (ref 1).

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Cavitands: Synthetic Molecular Vessels[1]

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Received April 26, 1982

In host–guest complexation, the concave surface of a host complements the convex surface of a guest.[2] Similarly, the receptor sites of enzymes frequently contain rigid cavities whose internal surfaces complement the convex surfaces of substrates or inhibitors.[3] To imitate nature's complexes, hosts that contain enforced concave surfaces of substantial dimensions must be designed and synthesized. We propose the class name *cavitand* for synthetic organic compounds that contain *enforced cavities* large enough to accommodate simple molecules or ions.

The spherands,[4] exemplified by **1** (Chart I) are a specific type of cavitand. Unlike the chorands (crowns) or cryptands, they contain rigid cavities formed during their syntheses rather than during their complexation. The spherands's preorganization resulted in the highest binding and selectivity yet observed for the alkali metal ions.[5] Cyclotriveratrylene (**2**), which at 25 °C possesses a rigid saucer shape, is another type of cavitand.[6] Collet et al. have recently reported the elegant synthesis of a cavitand composed of two cyclotriveratrylene units connected by three dimethylene bridges (**3**).[7] Gutsche et al. has recently rigidified calixarene **4** by trimethylsilylation to give a cone-shaped cavitand.[8] We describe here the four new cavitands **7**–**10**, prepared from the conformationally mobile resorcinol–acetaldehyde condensation

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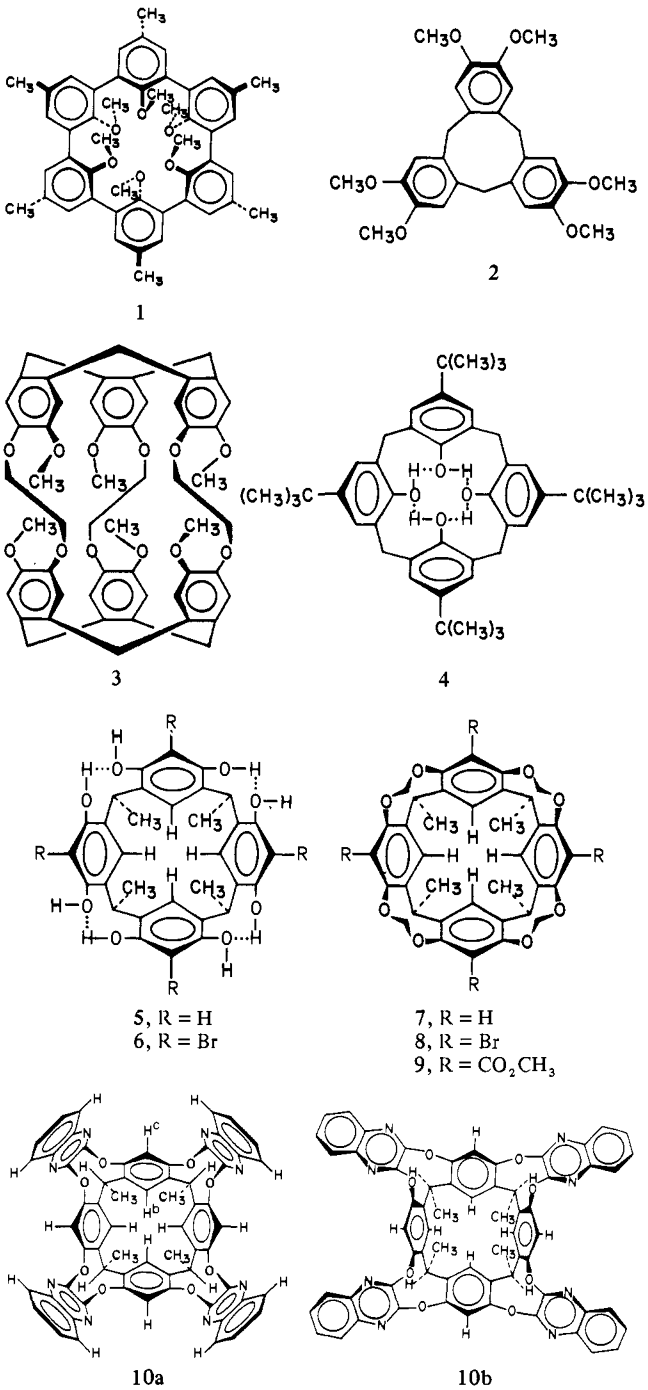
Chart I



1, 2, 3, 4

5, R = H
6, R = Br

7, R = H
8, R = Br
9, R = CO_2CH_3

10a, 10b

product cyclophane **5**, reported by Högberg.[9a]

Cavitand **7**[10] was produced (14%) by treating **5**[9a] with excess CH_2BrCl[11] and base. Similarly, **8**[10] was obtained (42%) from tetrabromide **6**,[10] which had been prepared by NBS bromination (48%) of **5**. Metalation of **8** with BuLi and carbonation of the organometallic produced the corresponding tetracarboxylic acid, which with CH_2N_2 gave the tetraester **9**[10] (56% overall). Cavitands **7** and **10** crystallize only as solvates, whereas **8** and **9** crystallize only free of solvent.

Strain-free molecular models (CPK) of cavitands **7–9** possess no rotational degrees of freedom about their aryl–O bonds. Four new rings can be closed only when **5** is in its bowl-shaped conformation (C_{4v} point group). In **7–9** the four methyl groups and the eight oxygens occupy parallel planes. The aryl–H, aryl–Br, or aryl–CO_2CH_3 bonds fall on an axis intersecting these planes at an angle of ~125°. These conformational constraints impart to **7–9** the shape of a bowl supported on a base of four methyl groups. The NMR spectra of **7–9** confirm the conclusions based on model examination. In models the cavity dimensions of **8** and **9** are large enough to embrace single models of CH_2Cl_2, $CHCl_3$, or $(CH_2)_4O$ or four models of H_2O.

The tall, vase-shaped cavitand **10** was prepared (34%) by treating **5** with 4 equiv of 2,3-dichloro-1,4-diazanaphthalene and excess KOH in $HCON(CH_3)_2$. The reaction produced **10**·$HCON(CH_3)_2$[10] which when recrystallized from $CHCl_3$ gave **10**·$1.3CHCl_3$.[10] Although the solvates failed to liberate their solvent at 100 °C and 10^{-5} mmHg, their mass spectra gave an M^+ peak for **10** alone.

Molecular models of **10** indicate that its base of four benzene rings and four nine-membered rings form an enforced concave inner surface to which are attached the four diazanaphthalenes. These diazanaphthalene groups resemble flaps that can occupy either axial (*a*) or equatorial (*e*) positions. In the *aaaa* conformer (**10a**), the four flaps occupy planes perpendicular to the plane of the eight oxygens, whose unshared electron pairs face outward. The C_{4v} symmetry of this conformer is visible in **10a**, viewed from its open face. In models, the α hydrogens of the adjacent 1,4-diazanaphthalenes touch one another to provide a continuous concave inner surface. The void is large enough to engulf one model of [2.2]paracyclophane (inward faces shaved) or ten models of water.

When the four flaps are moved to the *e* position to give the *eeee* conformer (**10b**), the methine hydrogens of the CH_3CH groups are forced into the faces of the diazanaphthalenes. To minimize this strain, the flaps rotate, the unshared electron pairs of four of the eight oxygens face inward, and the bowl deforms into a trough by elongating in one dimension and narrowing in the other. The two benzene rings that form the sides of the trough occupy parallel planes, and each of their basal aryl protons becomes wedged between their flanking methyl groups. This conformer (**10b**) possesses C_{2v} symmetry. Structures intermediate between the *aaaa* and *eeee* conformers appear less stable.

The 500-MHz ^1H NMR spectrum of **10** in $CDCl_3$–CS_2 does not change from 30 to 45 °C, exhibits sharp signals for all protons, and is consistent with a structure of C_{4v} symmetry. The spectrum changes dramatically and continuously as the temperature is lowered from 30 to −53 °C, but changes little from −53 to −62 °C. The signals at intermediate temperatures are broad and show coalescence between 25 and −5 °C. The $\Delta G^\ddagger$ for the conformational changes involved is about 10 kcal mol^{-1}. The well-defined methine quartet at 45 °C moves from δ 5.67 to 3.92 at −62 °C and broadens. The two benzene proton singlets at δ 8.04 (H^c) and 7.27 (H^b) at 45 °C shift, and each divides into two singlets respectively found at 7.38 and 7.28, and at 7.21 and 6.41 when the temperature is lowered to −62 °C. The protons of the naphthalene ring at 45 °C exhibit a symmetrical AA′BB′ splitting pattern, which at −62 °C divided into two doublets and two triplets, which are interpreted as an ABCD spectrum. Thus the spectrum from −50 to −62 °C is consistent with a structure of C_{2v} symmetry.[12]

The spectra, coupled with conformations suggested by model examination, correlate to provide these interpretations: (1) The 30 to 45 °C spectrum is explained by **10** assuming the *aaaa* conformation (**10a**), which has C_{4v} symmetry. In **10a**, the four methine protons are more distant from the faces of the diazanaphthalene rings than in **10b**. This proton at δ 5.67 occurs at lower field than the methine protons of **7** (4.96) or the methine protons in the conformationally mobile tetraacetate of **5** (4.23).[9a] (2) The −52 to −62 °C spectrum is explained by **10** occupying

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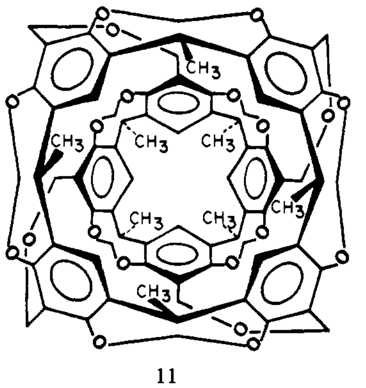
the *eeee* conformation of **10b** (C_{2v} symmetry). The marked upfield shift of the methine signal from δ 5.67 to 3.92 as the temperature is lowered correlates with the methine protons moving into the shielding cone of the naphthalene rings as the latter occupy the *e* positions. (3) Although all protons shift between 30 and −50 °C, above 30 and −50 °C their signals do not change. The spectra above 30 °C show no detectable ($<5\%$) C_{2v} conformer, and that below −50 °C shows no detectable ($<2\%$) C_{4v} conformer. Thus the conversion of the *aaaa* to the *eeee* conformer is favored by >3 kcal mol^{-1} as the temperature is lowered. Molecular models provide a definitive prediction that **10a** is less strained than **10b**. Although **10a** and **10b** possess molecular surfaces of equal magnitude, in solution, the more *extended surfaces* of **10b** must contact and orient more solvent molecules than the more *confined surfaces* of **10a**. These contacts are expected to be enthalpy stabilizing but entropy destabilizing for both systems.[13] In the conversion **10b** → **10a**, some collected and oriented solvent molecules are liberated. At low enough temperatures, **10b** is the more stable conformer in solution because its more favorable enthalpy of solvation overrides the sum of the unfavorable *TS* of solvation and the greater strain energy of this conformer. As the temperature increases, the unfavorable *TS* cancels more of the favorable enthalpy until the free energy of solvation no longer overrides the greater strain energy of **10b**. Above this temperature, **10a** dominated in the equilibrating mixture, since its stability in solution does not depend as much as that of **10b** on its free energy of solvation. To our knowledge, **10** is quite unique in providing conformations that present so widely differing opportunities for solvation.

Of the four cavitands, **7** and **10** crystallize only with, and **8** and **9** only without, solvent of crystallization. Molecular models of **7** and **10** are unable to fill their rigid cavities intermolecularly. These compounds crystallize only as solvates. Models of **8** and **9** are able to fill their cavities intermolecularly. These compounds do not form solvates. This correlation strongly suggests that solvent parts fill the cavities of **7** and **10** since voids are rarely encountered in crystal lattices. In spite of many attempts, crystals of **7** and **10** suitable for structure determination have not yet been grown.

This investigation has demonstrated that cavitands with large internal surfaces can be designed and readily prepared. When their molecular models cannot fit together intermolecularly to fill their enforced cavities, they crystallize only as solvates. One of the four cavitands contains mobile flaps whose conformations are governed by a balance between strain and solvation effects. Cycle **9** is the key intermediate in a projected synthesis of closed surface cavitand **11**, whose molecular model is unstrained and whose cavity is large enough to imprison models of compounds as large as C_6H_6, $(CH_2)_4O$, and $(CH_3CH_2)_2O$ or seven molecules of H_2O.



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Supplementary Material Available: Experimental procedures for compounds **6**, **7**, **8**, **9**, and **10** (3 pages). Ordering information is given on any current masthead page.

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Transients Generated upon Photolysis of Colloidal TiO_2 in Acetonitrile Containing Organic Redox Couples

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Received May 3, 1982

Increasing recognition of the importance of photoinduced electron-transfer reactions in synthetically useful transformations has led to an intense investigation of various methods for sensitization of redox reactions of organic substrates. One such method sure to enjoy future prominence involves the use of semiconductor powders as photocatalysts responsive in the visible and ultraviolet regions. Despite several recent reports outlining efficient photoinduced redox reactions of organic substrates, little firm evidence is available regarding the mechanisms of such reactions, particularly in nonaqueous solvents. This deficiency has prompted us to investigate the identity of transients formed upon irradiating colloidal TiO_2 particles in nonaqueous solvents in the presence of organic redox systems, a medium which simultaneously incorporates the heterogeneity of the powder-catalyzed reactions and the possibility for spectroscopic analysis of mechanistically relevant transients. Although semiconductor band theory predicts that photocatalyzed oxidations or reductions could occur with donors or acceptors whose redox potentials lie within the range between the valence and conduction bands of the metal oxide, little evidence for organic radical ion intermediates generated in this way from neutral precursors has yet been reported. We describe here transient spectra that affirm the occurrence of semiconductor-mediated electron transfer and demonstrate the involvement of radical ions, the first such data reported for organic redox couples in nonaqueous solvents.

Acetonitrile suspensions of colloidal TiO_2 were prepared by controlled hydrolysis[1] of titanium tetraisopropoxide, a route parallel to that reported by Graetzel[2] in aqueous solution. A preparation was considered successful if it exhibited the following properties: optical transparency, high absorbance near 350–360 nm, ability to photocatalyze the oxidative cleavage of 1,1-diphenylethylene,[3] and resistance to significant precipitation for at least 24 h. Although the required water could be provided from several sources (wet trifluoroethanol, glacial acetic acid, concentrated hydrochloric or perchloric acids), the latter two reagents were found to give the best results consistently.

In a typical experiment, such a colloidal suspension was made 0.01 M in *trans*-stilbene or 1×10^{-4} M in methyl viologen. The resulting mixture was excited with a laser pulse (third harmonic of a Q-switched Nd:YAG laser (355 nm)), and the formation of transient spectra was monitored by using a previously described apparatus.[4] The time-resolved transient spectra obtained in the presence of stilbene (Figure 1) corresponded closely to those reported for the *trans*-stilbene radical cation.[5,6] Although the broad absorption between 550 and 700 nm is not yet explained, a second band at 695 nm has been reported for the stilbene radical cation in viscous media.[6]

The shape and intensity of this spectrum are unaffected by dissolved oxygen, since identical results are obtained while bubbling oxygen or nitrogen through the solution. A rough estimate for

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