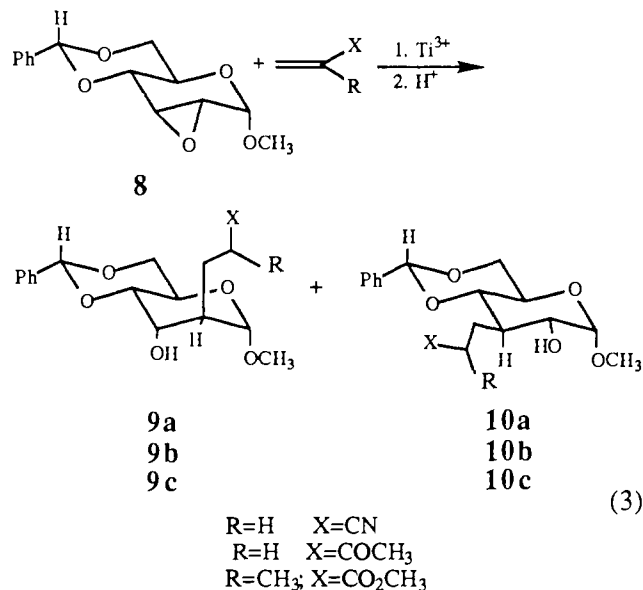
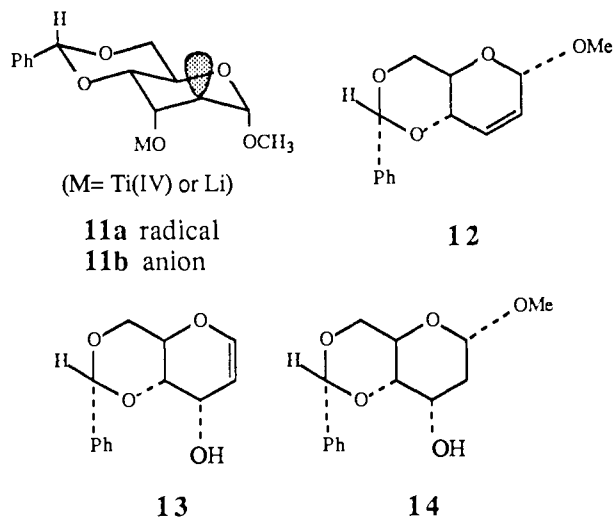


scheme represents a novel [3 + 3] annulation to prepare such lactones<sup>5</sup> from epoxides. The major lactone from epoxydecane and MMA can be prepared in overall 60% yield.

The functional group compatibility and some stereochemical questions are probed in the addition of acrylonitrile, MMA, and methyl vinyl ketone to the carbohydrate epoxide<sup>6</sup> shown in eq 3.



Depending on the reactivity of the acceptor, the initially formed radical (**11a**) participates in the addition reaction or is further reduced by Ti(3+) to the carbanion (**11b**). Elimination of the  $\beta$ -groups to give **12** and **13** or hydrogen atom transfer from some



substrates (methyl vinyl ketone for example) to give a reduction product **14** are the major side reactions in these cases. It should be noted that the relative amounts of axial versus equatorial bond formation in the radical **11a** are the same as those observed by Giese et al. in a related system.<sup>7</sup> Qualitatively, it appears that the regioselectivity of the ring opening is affected by the stereoelectronic stabilization of the incipient radical.<sup>8</sup> However, we

cannot rule out the possibility of a reversible ring opening followed by slow addition to the olefin.

The use of transition-metal-centered radicals for the generation of useful organic radicals may be broadly applicable in synthesis. Moreover, the reductive termination strategy for the reactions of these radicals illustrated here is only one of the possibilities. Reactions of the titanium enolate **4** with electrophiles may conceivably be used for its subsequent elaboration.<sup>9</sup> The compatibility of C<sub>p</sub>2TiCl with a variety of common functional groups and the ease with which epoxides<sup>10</sup> can be generated should make this an attractive method for the synthesis of polyfunctional molecules.

**Supplementary Material Available:** Details of isolation and characterization (IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS, elemental analysis) of products **1**, **7**, **9a**, **9b**, **9c**, **10a**, **10b**, **14** and those described in Table I (8 pages). Ordering information is given on any current masthead page.

(9) Reaction of an in situ generated C<sub>p</sub>2TiCl-enolate: Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664.

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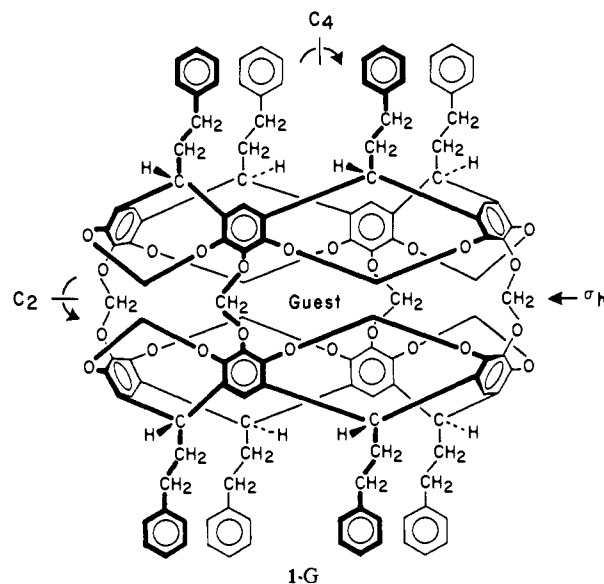
### Carcerand Interiors Provide a New Phase of Matter<sup>1</sup>

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Earlier papers reported the synthesis and properties of a non-collapsible molecular cell (a carcerand) whose interior was occupied by various components of the medium to give a mixture of carceplexes whose separation and study were inhibited by their insolubility.<sup>2,3</sup> Here we report three new soluble carceplexes (**1-G**) which differ only in their imprisoned guests.



The syntheses involved **2** (prepared from resorcinol and dihydrocinamaldehyde, 69%),<sup>4</sup> bromination (NBS) of which gave

(5) For a related free-radical approach to  $\delta$ -lactones, see: Kozikowski, A.; Nieduzak, T. R.; Scripko, J. *Organometallics* **1982**, *1*, 675.

(6) Sugar epoxide **8** is very sensitive toward both nucleophiles and electrophiles. See, for example: Tsuda, N.; Yokota, S.; Kudo, T.; Mitsunobu, O. *Chem. Lett.* **1983**, 289.

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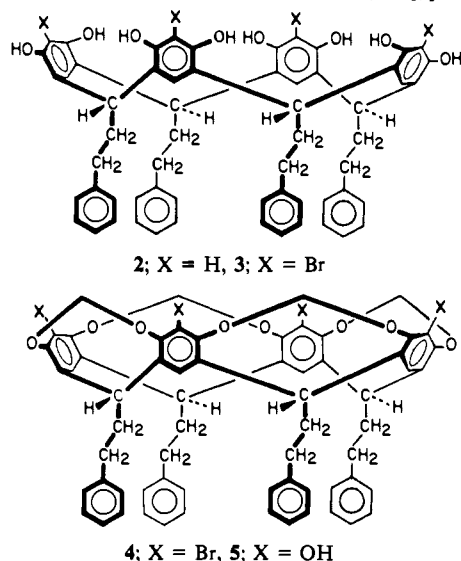
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tetrabromide **3**<sup>5,6</sup> (58%). Treatment of **3** with  $\text{CH}_2\text{ClBr}-\text{K}_2\text{CO}_3-\text{DMA}$  gave cavitand **4**<sup>5,6</sup> (52%), whose crystal structure was normal.<sup>7</sup> Metalation of **4** in THF with  $(\text{CH}_3)_3\text{CLi}$  at  $-78$



$^\circ\text{C}$  and quenching the organometallic formed with  $(\text{CH}_3\text{O})_3\text{B}$  gave the arylboron intermediate, which was oxidized with  $\text{H}_2\text{O}_2-\text{NaOH}$  ( $-78^\circ\text{C}$ ) to produce tetrol **5**<sup>6</sup> (53% overall). Shell closures of **5** to give **1-G** were conducted under high dilution conditions in purified dry  $(\text{CH}_3)_2\text{SO}$ ,  $(\text{CH}_3)_2\text{NCOCH}_3$ , or  $(\text{CH}_3)_2\text{NCHO}$  solutions at  $60-100^\circ\text{C}$  with  $\text{Cs}_2\text{CO}_3$  as base and  $\text{CH}_2\text{ClBr}$  (large excesses) being added by syringe pump (3 days). Products **1** ( $(\text{CH}_3)_2\text{SO}$ ), **1** ( $(\text{CH}_3)_2\text{NCOCH}_3$ ), and **1** ( $(\text{CH}_3)_2\text{NCHO}$ ) were purified by chromatography on silica gel- $\text{CHCl}_3/\text{hexane}$  and crystallization ( $\text{CHCl}_3/\text{CH}_3\text{CN}$ ) to give carceplexes in 61%, 54%, and 49% yields, respectively. Analysis of each for C, H, O, and N or S was within 0.20% of theory. Summed analyses were 99.73-99.90% of theory. Each carceplex's mass spectrum gave substantial peaks at masses corresponding to **1-G**.<sup>8,9</sup> Attempts to shell close **5** failed in  $(\text{CH}_2)_5\text{NCHO}$ , a solvent too large for incarceration (CPK molecular model examination). A reaction run in 99.5  $(\text{CH}_2)_5\text{NCHO}-0.5(\text{CH}_3)_2\text{NCOCH}_3$  (mol %) gave a 10% yield of **1** ( $(\text{CH}_3)_2\text{NCOCH}_3$ ). A run in equimolar  $(\text{CH}_3)_2\text{NCOCH}_3-(\text{CH}_3)_2\text{NCHO}$  gave 10% of **1** ( $(\text{CH}_3)_2\text{NCOCH}_3$ )/**1** ( $(\text{CH}_3)_2\text{NCHO}$ ) = 5.3. These two complexes were separated chromatographically, showing that the guests "communicate" with their host's environment. Models of **1** ( $(\text{CH}_3)_2\text{NCOCH}_3$ ) can barely be assembled, whereas the guest in **1** ( $(\text{CH}_3)_2\text{NCHO}$ ) is liberally housed. Apparently, appropriately sized guests template the shell closures, the product composition being determined in the transition state for completing the second or third interhemispheric bridge.

The 360 MHz  $^1\text{H}$  NMR spectra of **1-G** were taken, and all protons were assigned making use of comparisons with the spectra of **4** and appropriate heteronuclear-decoupling experiments involving  $^{13}\text{C}$  NMR spectra taken in  $\text{CDCl}_3$ . The guests' protons in  $\text{CDCl}_3$  all shifted upfield by 1-4 ppm from their normal positions, consistent with their enforced proximity to the arene-shielding zone.<sup>10</sup> Careful proton signal integrations<sup>11</sup> established

the **1-G** samples to be >95-98% one-to-one complexes. When heated to reflux for 12 h, a solution of **1** ( $(\text{CH}_3)_2\text{SO}$ ) in  $(\text{CH}_3)_2\text{NCHO}$  failed to undergo guest exchange. Apparently, guests can enter or depart the carceplexes only by covalent bond making or breaking processes.

Molecular model (CPK) examination of **1-G** indicates that the host's cavity has a long  $C_4$  axis and four, much shorter,  $C_2$  axes as well as four  $\sigma_v$  and one  $\sigma_h$  planes. Models also suggest that  $(\text{CH}_3)_2\text{NCHO}$  and  $(\text{CH}_3)_2\text{SO}$  are loosely held in the cavity, whereas  $(\text{CH}_3)_2\text{NCOCH}_3$  is incorporated only when its long axis matches that of its host. Experimentally, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the three carceplexes provide the following conclusions: (1) Incarcerated  $(\text{CH}_3)_2\text{NCHO}$  rotates about the host's short and long axes rapidly on the  $^1\text{H}$  NMR time scale, even at  $-38^\circ\text{C}$  ( $\text{CDCl}_3$ ). (2) Incarcerated  $(\text{CH}_3)_2\text{NCOCH}_3$  rotation about the host's long axis is fast, and those about the short axes are slow on the  $^1\text{H}$  NMR time scale, even at  $175^\circ\text{C}$  ( $\text{C}_6\text{D}_5\text{NO}_2$ ). (3) Incarcerated  $(\text{CH}_3)_2\text{SO}$  rotations about all axes are fast above  $2^\circ\text{C}$  but slow about the short axes below  $2^\circ\text{C}$  on the  $^1\text{H}$  NMR time scale ( $\text{CDCl}_3$ ). (4) The orders of rates of rotation about the C-N bond of amide guests vary with phase changes as follows ( $\text{C}_6\text{D}_5\text{NO}_2$  solvent when present): for  $(\text{CH}_3)_2\text{NCHO}$ , vacuum > interior phase > solution; for  $(\text{CH}_3)_2\text{NCOCH}_3$ , vacuum > solution > interior phase.

These carceplexes represent a new state of matter whose interiors are new phases (guest plus vacuum in varying proportions). Their guest mobility with respect to host and their physical properties are subject to molecular level manipulation. Several potential applications of carceplexes to material science problems are envisioned and are being examined.

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## Fluid Electrolyte Solutions for Electrochemistry at Near Liquid Nitrogen Temperatures

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This paper reports the discovery of three remarkable solvent mixtures that extend the useable range of electrochemical voltammetry in fluid electrolyte solutions to temperatures that approach the boiling point of liquid nitrogen. There have been no improvements in low-temperature fluid electrolyte solutions<sup>1</sup> since the classical work of Van Duyn and Reilly<sup>2</sup> in 1972 in which they utilized propionitrile/butyronitrile mixtures containing tetraalkylammonium salts to obtain a low-temperature voltammetric limit of 155 K. As part of an ongoing effort<sup>3</sup> to develop the

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