

Figure 1. A view of the molecular structure of $[\text{Cu}(\text{dien})(\text{C}_7\text{H}_{10})]^+$, showing the atomic numbering scheme.

$[\text{Cu}(\text{dien})(\text{C}_7\text{H}_{10})]^+$. A perturbation or polarization of the C-H bond by an electrophilic metal atom, like Cu^+ , should be considered the earliest stage of a metal induced C-H activation.¹⁶ This norbornene bonding mode, when applied to norbornadiene-copper(I) interaction, would help in describing the specific copper(I)-norbornadiene bonding which predisposes this olefin toward photoassisted valence isomerization processes.⁶

Both the results by Gagné et al.¹ and those here reported seem to suggest that the five coordination may play an unexpected role in molecular activation processes promoted by copper(I) complexes.

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Supplementary Material Available: The final atomic parameters, bond distances, and angles within the BPh_4^- anion and the diethylenetriamine ligand, and a complete listing of factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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- A typical procedure is given for the preparation of the norbornene complex. To methanol (100 mL) containing dien (2 mL, 18.5 mmol), CuI (1.55 g, 8.14 mmol) was added. The copper dissolved completely when norbornene (1.2 g, 12.7 mmol) was added and gave a slightly blue solution. Sometimes the precipitation of very little blue solid, which was eliminated by filtration, was observed. By addition of NaBPh_4 (2.63 g, 7.69 mmol) to the solution, $[\text{Cu}(\text{dien})(\text{C}_7\text{H}_{10})]\text{BPh}_4$ was obtained as white crystalline solid (~46%). Calcd for $[\text{Cu}(\text{dien})(\text{C}_7\text{H}_{10})]\text{BPh}_4$ ($\text{C}_{35}\text{H}_{43}\text{N}_3\text{BCu}$): C, 72.47; H, 7.42; N, 7.25. Found: C, 72.21; H, 7.49; N, 7.38. The solid is only slightly stable in air. Its insolubility prevented NMR measurements. The magnetic susceptibility measurements in the solid state showed that $[\text{Cu}(\text{dien})(\text{C}_7\text{H}_{10})]\text{BPh}_4$ is diamagnetic: $\chi_M^{\text{cor}} = -360 \cdot 10^{-6}$ cgs units at 293 K. Norbornene is displaced by CO in methanol to give $[\text{Cu}(\text{dien})\text{CO}]\text{BPh}_4$.²
- All cited olefins gave isolable, rather thermally stable, microcrystalline complexes (yield in the range of 50–75%). Analytical data agree with the formulation given. For ethylene the stoichiometry was gas volumetrically controlled. Olefin can be replaced readily in the complex by CO and $\text{P}(\text{OC}_2\text{H}_5)_3$. Though stable in vacuo in the solid state, the complex containing ethylene loses it when in solution. The "practical" stability of the complex seems to increase along with the π acidity of the ligand, the greatest being found for L = DMM and DMFu. For these two complexes, which are yellow, the reaction with CO gives back the starting olefinic isomer. The IR spectra (Nujol) show that the CO groups (L = DMM and DMFu) are probably not directly involved in the coordination; in fact the absorptions due to these groups showed a shift to higher wave numbers of only 10–20 cm^{-1} with respect to the free ligand: ν_{CO} (L = DMM) 1730 (br s), cm^{-1} ; ν_{CO} (L = DMFu) 1740 (br s), cm^{-1} .
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- Computer programs used on a CYBER 7600 computer of the "Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale" (Bologna) were those of SHELX-76 system (G. M. Sheldrick, 1976, University of Cambridge, England).
- A difference Fourier map, calculated at $R = 0.070$, gave the approximate coordinates of 18 hydrogen atoms, including one at $\sim 2 \text{ \AA}$ from copper and bonded to C(17) in an approximately tetrahedral environment. The remaining hydrogen atoms were introduced in calculated positions and all hydrogens were subjected to a cycle of isotropic refinement down to $R = 0.048$. The position of H(17) was further confirmed by a final ΔF map computed at $R = 0.050$ without the contribution of this atom. Assuming C-H bond lengths of 1.08 Å and a sp^3 hybridization at C(17), the following values are calculated: Cu-H(17) 2.230 Å, Cu-H(17)-C(17) 109.0°. These values are still consistent with a Cu...H interaction, even if the model assumed in calculations is objectionable, the sp^3 configuration at C(17) being severely distorted: C(13)-C(17)-C(16) = 90.5(12)° instead of 109.5°.
- Bond distances and angles in the dien ligand are in good agreement with those of the monomeric cation $[\text{Cu}(\text{dien})\text{CO}]^+$.²
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Bromine Adsorbed on a Molecular Sieve: A Reagent for Selective Bromination

Sir:

In this communication we report a novel type of molecular sieve effect in which 5A zeolite crystals, saturated with bromine, are used as a reagent for the selective bromination of a terminal double bond. Although the novel adsorptive properties of molecular sieve zeolites have found widespread application in shape selective catalysis¹ and in separation processes,² previous applications in synthetic organic chemistry are limited to uses in esterification, ketalization, and other similar reactions as a means of selectively adsorbing the water which is formed during the reactions, in order to promote a favorable shift in the equilibrium.³ Molecular sieves have also been used as carriers for KMnO_4 but in this application the sieve func-

tions merely as a high area (nonselective) solid support. The possibility of using the shape selective feature of a molecular sieve adsorbent in order to influence directly the course of a noncatalytic reaction does not appear to have been previously examined.

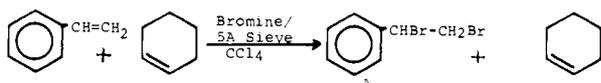
The surface of a zeolite crystal contains small pore openings giving access to somewhat larger cavities within the crystal. Structural details have been summarized by Breck.² Such a structure may be employed in two ways to modify the course of a chemical reaction. One possibility is to use the sieve to protect a functional group, thus allowing the reaction to occur selectively at another point in the molecule. This requires that the functional side chain be sufficiently strongly adsorbed so that the equilibrium concentration in the ambient fluid is very small, to minimize the competing homogeneous reaction.

Alternatively, the sieve may be used as a container for the reagent so that the desired reaction can occur only when the functional group of the reacting molecule can penetrate the sieve pore opening. Thus, in a complex molecule which contains functional groups such as a double bond, located both in a linear side chain which can penetrate the sieve and in a ring structure which cannot penetrate the sieve, a sterically selective reaction is in principle possible. This type of selectivity should apply equally to the case of a mixture of two compounds containing accessible and inaccessible centres. To achieve a high selectivity in such a process requires strong selective adsorption of the reagent (to minimize any homogeneous reaction) and relatively weak adsorption of the product (otherwise the reaction may be inhibited by formation of a strongly adsorbed monolayer of product).

The 5A-type molecular sieve is probably the most promising structure since the pore openings ($\sim 4.2 \text{ \AA}$) are sufficiently large to admit straight hydrocarbon side chains, but cyclic structures, branched chain hydrocarbons, and carboxylic acid groups are too large to enter. Of the other commonly available synthetic zeolites, types 3A and 4A are not useful because the pore opening is too small while the apertures of the X and Y zeolites are too large to provide the required shape selectivity, except possibly for very large molecules (see below).

In addition, the substrate must meet the necessary steric requirements and the constraints imposed by sorption equilibrium requirements for both reactant and substrate must also be fulfilled. We have selected, for initial investigation, the selective bromination of a side-chain double bond by bromine pre-adsorbed on 5A zeolite. Bromine, like the other halogens, is strongly adsorbed on molecular sieves,⁵ the course and mechanism of bromination reactions in homogeneous solution is well known, and the reaction is relatively rapid with easily identifiable products. Here we show that a 5A sieve, saturated with bromine, may be used as a selective brominating agent capable of differentiating between a double bond located in a sterically unhindered linear side chain and in an inaccessible position within an alicyclic ring.

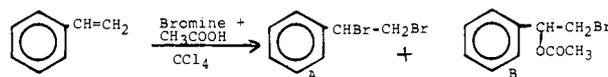
(i) As a simple model system we used a mixture of cyclohexene and styrene (approximately 67% cyclohexene, 33% styrene on a molar basis). In homogeneous solution these compounds are both brominated rapidly so that a mixture of α,β -dibromostyrene and dibromocyclohexene is obtained with 95% conversion of both reactants. However, when the cyclohexene-styrene mixture was treated with a 5A sieve, previously saturated with bromine, we obtained only α,β -dibromostyrene (in 95% yield) with no trace of dibromocyclohexene. (The total



quantity of adsorbed bromine present in this experiment was more than sufficient to brominate all the cyclohexene and styrene.) This result is exactly what is expected from steric

considerations since the side chain of the styrene molecule can penetrate through the window of the sieve whereas the double bond in cyclohexene is not accessible.

(ii) In the homogeneous liquid phase bromination of styrene in the presence of acetic acid it has been shown that a mixture of products A and B is obtained.⁶ This is because the inter-



mediate bromonium ion is accessible to attack by both the bromide and acetate anions. When styrene (in solution in carbon tetrachloride with a small amount of acetic acid) was added to a solution of bromine, also in carbon tetrachloride, the reaction product contained 80% dibromostyrene (A) and 20% bromoacetate (B), a result similar to that obtained by Rolston and Yates.⁶ When the styrene-acetic acid mixture, in the same proportion as in the previous experiment, was treated with the 5A molecular sieve, previously saturated with bromine, only α,β -dibromostyrene (A) was obtained with no trace of product B, indicating that the bromination reaction must take place inside the cavity of the sieve where the acetate ion cannot penetrate.

These experiments show clearly the possibility of using bromine pre-adsorbed on 5A zeolite as a specific reagent for the bromination of terminal double bonds or double bonds in an aliphatic side chain where the stereochemistry permits penetration of the sieve window. In both reactions it was observed that the reaction rate using the brominated zeolite as reagent is very slow compared with the homogeneous liquid phase bromination reaction. This is to be expected since only the outside surface of the crystals is involved and each pore mouth can accommodate only one styrene molecule at a time. In any application of this method it is therefore desirable to use very small crystals to maximize the external surface.

The key role of the sieve window dimension was demonstrated by blank experiments carried out with 3A, 4A, and 13X zeolites. The 3A and 4A sieves showed no adsorption of bromine from the solution, and their presence had no noticeable effect on the bromination of the cyclohexene-styrene mixture. (A mixture of α,β -dibromostyrene and 1,2-dibromocyclohexane was obtained in 95% yield.) The 13X sieve adsorbed bromine from the carbon tetrachloride solution, but the resulting reagent showed no selectivity in the bromination reaction.

A typical reagent was prepared as follows: 300 g of 5A molecular sieve powder ($\sim 0.7\text{-}\mu\text{m}$ crystals) was dehydrated at 400°C in a current of helium and transferred to a 2.0-L round-bottom flask; 1 L of carbon tetrachloride, dried over P_2O_5 , was then added to the mixture and the resultant suspension was stirred for 3 h; 3.0 g of liquid bromine was then added and the mixture was stirred for a further 24 h when the Br_2 color had disappeared.

A typical experimental procedure is as follows. The required amount of reagent was prepared as described above and reactants were added (e.g., 180 g of reagent in carbon tetrachloride, 0.3 g of styrene, and 0.5 g of cyclohexene). The reaction mixture was stirred for 3 days and then filtered. The residual sieves were washed with excess of dry CCl_4 and the filtrate was carefully evaporated to dryness under reduced pressure at room temperature. Products were separated by the chromatography of the residue on silica gel column. (E.g., in this case α,β -dibromostyrene was obtained in 95% yield. No trace of dibromocyclohexene was found in the product.) Structures of the products were confirmed by NMR, IR, mass spectrum, and melting point.

Acknowledgment. The initial suggestion that it might be possible to utilize the shape selective feature of a molecular

sieve adsorbent to influence the course of an organic reaction was due to Dr. Z. Valenta (Department of Chemistry, U.N.B.) to whom we are also grateful for several helpful discussions during the course of this work.

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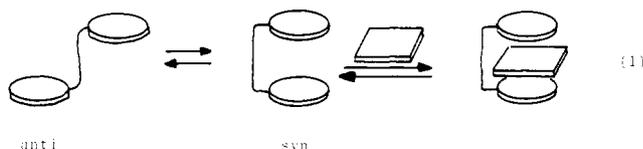
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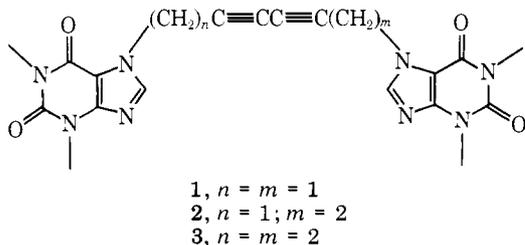
Molecular Tweezers: A Simple Model of Bifunctional Intercalation

Sir:

We have synthesized several bifunctional derivatives of caffeine¹⁻⁷ and wish to report here that they appear to show the expected exponential increase in association constants anticipated for formation of "sandwich" π -system hydrophobic complexes (eq 1). We refer to these molecules as "molecular



tweezers". These molecules, 1-3, possess two of the three characteristics expected to enhance complexation of aromatic molecules in aqueous solution. (1) The rigid diyne unit prevents self-association⁸ of the two caffeine moieties. (2) The caffeine-caffeine distance in the syn conformation, ~ 7 Å, is proper for insertion of a π system between the rings. The third structural feature, a rigid syn conformation, is not met.



Association constants were determined by phase partitioning⁹ of the tweezer ($\sim 10^{-4}$ M) between ethylene dichloride (EDC) and aqueous pH 7 potassium phosphate buffer containing varying concentrations of 2,6-dihydroxybenzoate (DHBA) or 1,3-dihydroxy-2-naphthoate¹⁰ (DHNA). From EDC-buffer partition coefficients of the tweezers and the above experiment one may calculate an "apparent" association constant

$$K_A^{\text{app}} = [\text{bound tweezer}] / [\text{acid}][\text{free tweezer}]$$

One may then relate K_A^{app} algebraically to various possible binding schemes as a function of the concentration of the

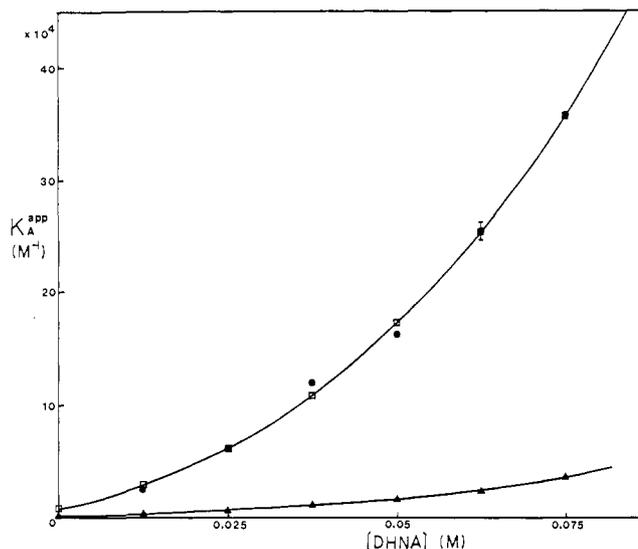


Figure 1. Calculated and experimental K_A^{app} vs. [DHNA] plot for 3 and potassium 1,3-dihydroxy-2-naphthoate in pH 7 phosphate buffer: ●, experimental points; ▲, calculated using $K_1 = 296 \text{ M}^{-1}$, $K_2 = 16.7 \text{ M}^{-1}$, $K_3 = 0$; □, calculated using $K_1 = 296 \text{ M}^{-1}$, $K_2 = 47.5 \text{ M}^{-1}$, $K_3 = 10 400 \text{ M}^{-1}$ (see Table II).

DHBA or DHNA salt and the various association constants. From the behavior of theophylline derivatives 4 and 5 one may calculate a best fit association constant (K_3 below) for the formation of a stacking complexes. We use the necessity of invocation of a large K_3 as evidence *pro* or *con* for the hypothesis.

Complexation of the simple theophylline derivative 4 and 5 with DHNA follows eq 2 closely (correlation coefficient > 0.99):

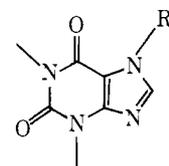
$$K_A^{\text{app}} = K_1 + K_1 K_2 [\text{DHNA}]$$



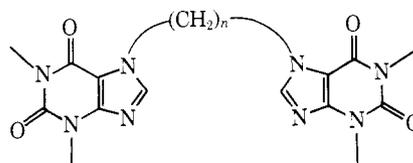
Values of K_1 and K_2 for 4 and 5 complexing with several acids are in Table I and are consistent with literature values.³ For tweezers 1-3 one may relate K_A^{app} to K_1 , K_2 , K_3 , and [DHNA] by the equation

$$K_A^{\text{app}} = 2K_1 + (2K_1 K_2 + K_1)^2 [\text{C}] + 2K_1^2 K_2 [\text{C}]^2 + K_1^2 K_2^2 [\text{C}]^3 + K_3 (1 + K_2 [\text{C}])^2 \quad (3)$$

Here K_1 and K_2 are as defined above and represent single and



4, $R = \text{CH}_2\text{C}\equiv\text{CH}$
5, $R = \text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$



6, $n = 8$
7, $n = 10$