(7) Conductivities were measured at 9.5 GHz by a cavity perturbation method using compressed disks which were approximately 3 × 0.5 mm.[15]

(8) Calculated from the relationship $\mu_{eff} = 2.83 \sqrt{\chi T}$.

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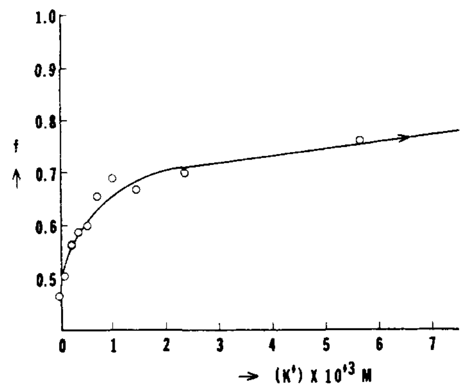
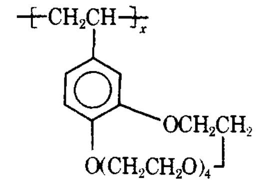


Figure 1. Plot of fraction, *f*, of picrate bound to P18C6 as a function of potassium chloride concentration.

Solute Binding and Catalytic Effects in Aqueous Solutions of Poly(vinyl crown ethers)

Sir:

Cation binding to macroheterocycles such as crown ethers and the effects of such compounds on the mechanism of ionic reactions have been extensively investigated in recent years,[1] When the ligands are attached as pendent groups to a polymer chain,[2] the resulting poly(crown ethers) behave as typical polycations in salt solutions of alkali and alkaline earth cations. In several instances the cation binding is distinctly different from that of the corresponding monomeric crown compounds, especially when effective complexation involves a cooperative effect of neighboring crown moieties.



We now wish to report that in aqueous solution the polymer poly(vinylbenzo-18-crown-6) (abbreviated here as P18C6) strongly interacts with neutral solutes and organic anions and that the binding can be regulated by the addition of crown complexable cations. The interaction was first observed spectrophotometrically with alkali picrates. Addition of P18C6 to a solution of sodium picrate in water induces a red shift of the main 354-nm picrate absorption band. At a large enough excess of polymer only one species is present with λ_m equal to 380 nm, the spectrum being identical with that of a crown separated picrate ion pair or of a free picrate ion in an aprotic solvent such as tetrahydrofuran.[3] The shift apparently results from a loss of water around the picrate anion as it becomes hydrophobically bonded to the tightly coiled poly(crown ether) (the intrinsic viscosity of P18C6 for M_n = 110000 is only 0.1, see ref 2a). Interaction of organic solutes in aqueous media has been reported for several natural and synthetic polymers, e.g., poly(vinylpyrrolidone),[4] bovine serum albumin,[5] and chemically modified polymers with apolar side chains.[6]

The rearranged form of the Langmuir isotherm[4,5] yields a straight line for sodium picrate, the minimum number of crown monomer units that can accommodate a picrate anion being 35. The first binding constant, K, was found to be 8.9×10^5 calculated on the basis of 10^5 g of polymer (a unit frequently used in the literature). Equilibrium dialysis measurements under a set of identical conditions gave 75% binding of picric acid to P18C6 and only 5% to poly(vinylpyrrolidone). Binding of Methyl Orange to P18C6 is comparable to that of picrate, implying that the poly(crown ether) is considerably more effective in binding this dye than is bovine serum albumin ($K = 5.4 \times 10^4$)[7] and comparable or better than some of the chemically modified synthetic polymers reported by Takagishi et al.[6] although the modified polyethylene imines reported by Klotz[7] are superior.

An interesting difference between P18C6 and other solute binding polymers concerns the presence of the cation binding crown unit which makes it possible to regulate the binding of organic anions by adding certain electrolytes. Potentiometric measurements of KCl in water in the presence of P18C6 yield a complex formation constant for K^+ of only 50 M^{-1}. Nevertheless, a sufficient amount of KCl considerably increases the binding of picrate to P18C6 as shown in Figure 1. For example, addition of 2×10^{-3} M KCl to a mixture of 5×10^{-4} M P18C6 and 10^{-5} M potassium picrate raises the fraction of bound picrate from 0.45 to about 0.70. The increase is found to be nearly proportional to the increase in the fraction of K^+ ions bound to P18C6. It is not surprising that salts of organic anions show a reverse effect, e.g., the tetraphenylboron anion easily expels the picrate anion from the polymer domain as demonstrated by the reappearance of the 354 nm absorption band of the picrate anion in water.

Many other solutes interact with P18C6 such as *p*-nitrophenol and its salts, phenolphthalein and chrysophenine, the binding of the latter dye being very strong. Dissociation equilibria can be affected when relatively weak electrolytes are involved. For example, a 5×10^{-5} M solution of sodium *p*-nitrophenolate contains approximately equal fractions of the phenolate anion (λ_m 400 nm) and the nondissociated *p*-nitrophenol (λ_m 318 nm, $K_a = 8 \times 10^{-8}$ M^{-1}). However, the anion spectrum disappears on addition of a small amount of P18C6, while the 318-nm band increases. Similarly, a phenolphthalein solution at pH 11.0 is decolorized on addition of P18C6, although the pH remains nearly unchanged. Preferential binding of the undissociated form of these compounds may cause the spectral shifts.

The anion binding and subsequent dehydration by P18C6 was demonstrated kinetically by following the decomposition of potassium 6-nitrobenzisoxazole-3-carboxylate in water in the presence of P18C6. The decarboxylation of the anion is known to be very solvent sensitive,[8] i.e., slow in water and increasingly faster in aprotic media such as ben-

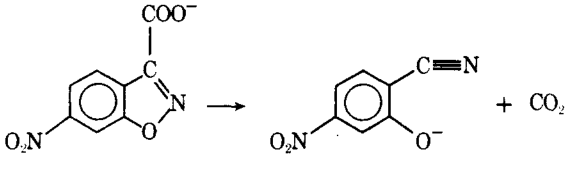


Table I. Decomposition of 6-Nitrobenzisoxazole-3-carboxylate in Water in the Presence of Poly(vinylbenzo-18-crown-6) (concentration of carboxylate $2 \times 10^{-4} M$; $T = 25°C$)

Ratio of crown to carboxylate	Ratio of salt to carboxylate	10^5k, sec^{-1}
0	—	0.4
2	—	11
2	10:1 NaCl	16
2	10:1 KCl	45
5	—	45
20	—	111
50	—	198

zene, acetone, and dimethyl sulfoxide. We observed that the decomposition of this carboxylate is significantly accelerated by addition of P18C6. The reaction is first order up to at least 80% decomposition. The pertinent rate constants are given in Table I. The carboxylate, on binding to P18C6 apparently is partially dehydrated causing the acceleration. The binding is weaker than that found for picrates, since the rate constant continues to go up even at concentrations of P18C6 as high as 0.05 *M*.

At a crown to carboxylate ratio of 50 the first-order rate constant is of the same order of magnitude as that found in benzene (using tetramethylguanidine as base the value in benzene was found to be 4.8×10^{-3} sec^{-1}, see ref 8). Complexable cations will further enhance the rate, as shown in Table I. Addition of KCl converts the poly(crown ether) into a polycation, resulting in a significant rate enhancement as more carboxylate is now attracted electrostatically to the polymer domain. Binding of Na^+ to P18C6 is known to be weaker than that of K^+, hence the effect of added NaCl is less pronounced. The behavior of P18C6 in some respects resembles the micellar catalysis of this decarboxylation reaction with cationic soap[9] although in the latter case electrostatic effects play a more important role and the effects of added electrolyte are different. Other types of reactions are presently being investigated, including the catalytic behavior of copolymers containing crown moieties.

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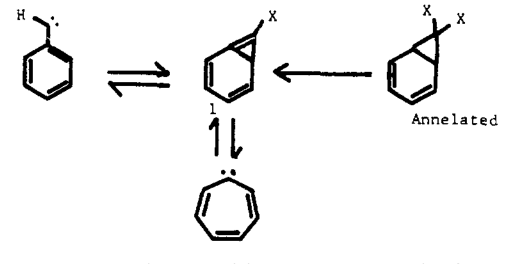
Formation of a Bicyclo[4.1.0]heptatriene by Intramolecular Addition of a Carbene to a Carbon–Carbon Triple Bond[1]

Sir:

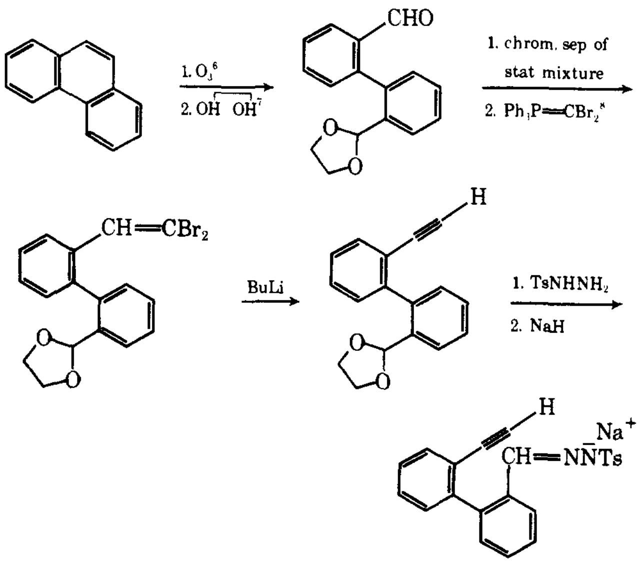
Bicycloheptatrienes (**1**), tautomers of benzcyclopropenes, have been postulated as intermediates in both the interconversion of aryl and aromatic carbenes[2] and the base induced dehydrohalogenation of gem-dihalocyclopropanes.[3] Although to date no direct evidence has been obtained for the parent hydrocarbon—although it is probably an intermediate in the interconversion of phenylcarbene and cycloheptatrienylidene[4]—there has been reported rather convincing evidence for its intermediacy in both mono- and dibenzannelated systems.[2] At this time, we would like to report evidence for the generation of dibenzbicycloheptatriene **7** from the intramolecular addition of a carbene to a carbon–carbon triple bond.



Schemes I and II describe the synthesis and chemistry of the carbene precursor **2**.[5] A study of the carbene that would result from nitrogen expulsion from the presumed diazoalkane **3** was severely complicated by the tendency of the diazoalkane to add to the triple bond to give the 1*H*-pyrazole **5**. For example, pyrolysis of **2** in benzene at 125° gave **5** in essentially quantitative yield. It was found, however, that 1*H*-pyrazole formation could be modestly suppressed[9] by lowering the temperature and, at −110°, photolysis of the tosylhydrazone salt **2** in a mixture of butadiene and dimethyl ether did, in fact, give a low but reproducible yield (5 ± 1%) of the adduct (**8**) expected from reaction of the bicycloheptatriene with the diene.[11,12] Photolysis of the tropone tosylhydrazone salt[13] **11** in the presence of butadiene gave the same adduct (30%), thus supporting the bicycloheptatriene as an intermediate in both reactions.

Photolysis of **2** at −110° also gave 11% of the ether **13**[14]

Scheme I



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