2. Preparation of R₃—M (M = MgCl, Cu, Cu₃Li₃, Ag, Ag₃Li₃, ZnCl or ZnI₃)

The R₃—M compounds shown in Tables I and II were obtained by adding an appropriate amount of MgCl₂, CuBr, AgBr(LiBr), or ZnCl₂, respectively to R₃—Li (0.020 mole) in THF at −20°C (see under 1). Stirring at this temperature was continued for 15 min. Vinylzinc chloride (0.020 mole) was obtained by stirring a solution of H₂C=CH—MgBr (0.020 mole) with ZnCl₂ (0.020 mole) for 30 min at 0°C in THF (40 ml). The zinc compound HC=C—ZnCl (0.020 mole) was prepared by stirring, HC=C—MgCl (0.020 mole) with ZnCl₂ (0.020 mole) at 25°C, in THF (40 ml). The resulting solutions were used as such.

3. General procedure for the conversion of 1 and 4 into 2

To a stirred solution of R₃—M (0.020 mole: M = Li, MgCl, Cu, Ag or ZnCl; 0.010 mole: M = Cu₃Li₃, Ag₃Li₃ or ZnI₃) in THF (40 ml; Rs = HC=C—C≡C—I; 120 ml: Rs = HC=C—C≡C—I) were subsequently added, at −20°C, Pd[PPh₃]₄ (0.02 M solution in THF; for amounts see Tables I and II) and substrates 1 (0.020 mole) or 4 (0.020 mole). Stirring of the resulting mixture was continued for the periods and at the temperatures indicated in Tables I and II. The reaction mixture was poured into a saturated aqueous solution of NH₄Cl containing NaCN (~1 g) when M was Cu, Cu₃Li₃, Ag or Ag₃Li₃. The products were isolated by extraction with pentane (3 × 75 ml); after washing the combined extracts and drying with MgSO₄ the solvent was evaporated in vacuo. The residue was distilled; when R₃ was PhC≡C or HC≡C—C≡C, purification was performed by column chromatography (Al₂O₃ + 5% H₂O/hexane). Physical constants and characteristic spectroscopic data for allenes 2 are given in Table III.

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Preliminary Communications

A Molecular Cation Channel

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Abstract. A polymer of an isocyanide, [R-N=C<]n, has been synthesized in which R contains a benzo-18-crown-6 group. The crown ether rings are situated on top of each other and form channels which bind metal ions.

In this communication we report on the construction of a synthetic molecular cation channel. This system might serve as a model for a molecular channel in biological membranes. The model system is a polymer of an isocyanide. Polymers of isocyanides, called poly(iminomethylene) or poly(carbonimidoyls), [R-N=C<]n, are prepared from isocyanides by the catalytic action of nickel(II) salts. Their structure is very regular and rigid. The polymer chain is a tightly coiled helix with four repeating units per helical turn (Figure 1). Poly[a-phenylethyl-iminomethylene], Ia, has extensively been studied both by Millich and by us. In this polymer the side chains form four stacks which run parallel to the polymer helix axis. In these stacks the phenyl groups are situated on top of each other and are locked in this position by the tight structure of the polymer chain. If the phenyl groups are part of a crown ether ring system, like in Ib, these crowns are on top of each other and form four channels (Figure 2). Polymer Ibb was prepared as shown in Scheme 1. Starting material is 4-acetylbenezol-18-crown-
of the polymer amounted to $M_v = 15,000$, which corresponds to 40 repeating units. Copolymers of $\alpha$-phenylethyl isocyanide and crown ether containing isocyanide were prepared by reacting mixtures of the monomers with NiCl$_2$·6H$_2$O at 25-40°C. The binding properties of polymer $lb$ and a copolymer of $\alpha$-phenylethyl isocyanide towards metal ions and protonated amines were measured by the picrate extraction technique. Representative results are given in Figure 3. Reference compounds are 4-acetylbenzo-18-crown-6 and benzo-18-crown-6. The polymers are more effective in extracting cations than the reference compounds. In particular this is true for Rb$^+$ and Cs$^+$. These ions have large diameters and will be sandwiched between consecutive crown ether rings of the channels. The binding profiles of the homopolymer and the copolymer do not differ greatly. This phenomenon suggests that the copolymer largely is an alternating copolymer in which the crown ether rings are arranged just as in the homopolymer. In other words, the crown ether side chains and the $\alpha$-phenylethyl side chains are in separate stacks. The amphiphilic nature of polymer $lb$ (top and bottom are hydrophilic, outer mantle is lipophilic) makes this compound suitable for incorporation into vesicles, e.g. of the type recently prepared from synthetic surfactants, and for subsequent ion transport studies. Also, the average chain length of the polymer (4 nm) is of the same order of magnitude as the thickness of the bilayers of most vesicles (3-5 nm).

**References and Notes**

1. A solid state model of a $K^+$ channel has very recently been reported: J.F. Behr, M.L. Lehn, A.C. Dook and D. Monas, Nature 295, 526 (1982).
9. Woeilm W 200 neutral alumina, eluent diethyl ether-ethyl acetate, 1:1 v/v. Yield 80% of colorless oil: $^1$H NMR (CDCl$_3$) $\delta$ 1.62 (m, 3H, CH$_3$); 3.67 (s, 4H), 3.73 (s, 8H), 3.9 (m, 4H), 4.15 (m, 4H), crown ether protons; 4.74 (m, 1H, CH); 6.90 (s, 3H, ArH); IR (neat) 2138 cm$^{-1}$ (NC), 1260 and 1100 cm$^{-1}$ (CO).
10. Reddish glassy polymerization product was worked up by dissolving it in chloroform. The latter solution was extracted with water, concentrated to a smaller volume, and added dropwise to a well stirred mixture of diethyl ether- $n$-hexane (1:1, v/v). The flocky precipitate was filtered, washed with diethyl ether- $n$-hexane (1:1, v/v) and dried to give pale yellow polymer. Yield 1.0 g of yellow polymer; $[\eta]$ $0.17$ (toluene, 30°C); $M_v = 42,000$ (see Ref. 11); IR (KBr) 1625 cm$^{-1}$, 1580, 1455 (amides).

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