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2. Preparation of \( R^3 - M \) (\( M = \text{MgCl}, \text{Cu}, \text{Ag}, \text{AgLi}, \text{ZnCl} \) or \( \text{Zn}_2 \))

The \( R^3 - M \) compounds shown in Tables I and II were obtained by adding an appropriate amount of \( \text{MgCl}_2, \text{CuBr}, \text{AgBr}(\text{LiBr})_3 \) or \( \text{ZnCl}_2 \), respectively to \( R^3 - \text{Li} \) (0.020 mole) in THF at \(-20^\circ\text{C}\) (see under 1). Stirring at this temperature was continued for 15 min. Vinylzinc chloride (0.020 mole) was obtained by stirring a solution of \( \text{H}_2\text{C} = \text{CH} - \text{MgBr} \) (0.020 mole) with \( \text{ZnCl}_2 \) (0.020 mole) for 30 min at 0°C in THF (40 ml). The zinc compound \( \text{HC} = \text{C} - \text{ZnCl} \) (0.020 mole) was prepared by stirring, \( \text{HC} = \text{C} - \text{MgCl} \) (0.020 mole) with \( \text{ZnCl}_2 \) (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 \( R^3 - M \) (0.020 mole; \( M = \text{Li, MgCl, Cu, Ag or ZnCl} \); 0.010 mole; \( M = \text{CuLi}^\text{I}, \text{AgLi}^\text{I} \) or \( \text{Zn}^\text{I} \)) in THF (40 ml) were subsequently added, at \(-20^\circ\text{C}\), \( \text{Pd} [\text{PPh}_3]_4 \) (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 \( \text{NH}_4\text{Cl} \) (containing \( \text{NaCN} \) (1 g) when \( M \) was \( \text{Cu}, \text{CuLi}^\text{I}, \text{Ag or AgLi}^\text{I} \)). The products were isolated by extraction with pentane (3 x 75 ml); after washing the combined extracts and drying with \( \text{MgSO}_4 \) the solvent was evaporated in vacuo.

The residue was distilled; when \( R^3 \) was \( \text{PhC} = \text{C} - \text{C} = \text{C} \), purification was performed by column chromatography (Al2O3 + 5% \( \text{H}_2\text{O} \)/hexane). Physical constants and characteristic spectroscopic data for allenes 2 are given in Table III.

Acknowledgements

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We are indebted to drs. C. J. Elsevier for preparing the allene \( \text{PhCH} = \text{C} = \text{CH} - \text{CH} = \text{CH} \text{H}_2 \) and to prof. dr. H. J. T. Bos for critically reading the manuscript.

Preliminary Communications

A Molecular Cation Channel

A.J.M. van Beijnen, R.J.M. Nolte, J.W. Zwikker and W. Drenth

Laboratory for Organic Chemistry, University at Utrecht,
Croesestraat 79, 3502 AD Utrecht, The Netherlands

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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( \( \alpha \)-phenylethyliminomethylene), \( 1a \), 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 \( 1b \), these crowns are on top of each other and form four channels (Figure 2). Polymer \( 1b \) was prepared as shown in Scheme 1. Starting material is 4-acetylbenzo-18-crown-
of the polymer amounted to $M_w = 15,000$, which corresponds to 40 repeating units. Copolymers of α-phenylethyl isocyanide and crown ether containing isocyanide 3 were prepared by reacting mixtures of the monomers with NiCl$_2$.H$_2$O at 25-40°C. 12 The binding properties of polymer 1b and a copolymer of 3 and α-phenylethyl isocyanide towards metal ions and protonated amines were measured by the picrate extraction technique. 6,13 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 α-phenylethyl side chains are in separate stacks.

### References and Notes

1. A solid state model of a K$^+$ channel has very recently been reported: J.F. Behr, J.-M. Lehn, A.C. Dook and D. Monog, Nature 295, 526 (1982).


9. Woelm W 200 neutral alumina, eluent diethyl ether-ethyl acetate, 1:1 v/v. Yield 80% of colorless oil; $^1$H NMR (CDCl$_3$) δ 1.62 (m, 3H, CH$_3$); 3.67 (s, 4H), 3.73 (s, 4H), 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. The redish grayish 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-nc-hexane (1:1, v/v). The flocy precipitate was filtered, washed with diethyl ether-nc-hexane (1:1, v/v) and dried to give pale yellow polymer. Yield 75%; [n] = 11,000 (toluene, 30.00°C); $M_w = 15,000$ (see Ref. 11); IR (KBr) 1625 cm$^{-1}$ (NC), 1260 and 1100 cm$^{-1}$ (CO). Anal. Calcd. for C$_{42}$H$_{26}$NO$_6$: C, 62.45; H, 7.45; N, 3.83; O, 26.27. Found: C, 62.13; H, 7.19; N, 3.96; O, 26.72.


12. In a representative experiment 1.3 g (3.5 mmol) of 3 and 1.1 g (8.4 mmol) of α-phenylethyl isocyanide were heated with 3 mol % of NiCl$_2$.H$_2$O at 40°C for 5 days. The polymerization product was worked up as indicated for 1b. Yield 1.0 g of yellow polymer; [n] = 0.031 (toluene, 30.00°C); $M_w = 42,000$ (see Ref. 11); IR (KBr) 1625 cm$^{-1}$ (NC), 1260 and 1100 cm$^{-1}$ (CO). Anal. Calcd. for C$_{42}$H$_{26}$NO$_6$: C, 62.45; H, 7.45; N, 3.83; O, 26.27. Found: C, 62.13; H, 7.19; N, 3.96; O, 26.72.


14. Association constants of polymer 1b as measured by the procedure described in Ref. 13, and assuming 1:1 complexes are (picrate, $K_a \times 10^{-7}$ mol dm$^{-3}$): Li$^+$, <5; Na$^+$, 20; K$^+$, 300; Rb$^+$, 120; Cs$^+$, 90; NH$_4^+$, 55; MeNH$_3^+$, 3.4; β-ButNH$_3^+$, 0.70. 15. J.H. Millich, Acc. Chem. Res. 13, 7 (1980).

16. Calculated from the number of repeating units and the distance between these units (0.1 nm, from Ref. 2).

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