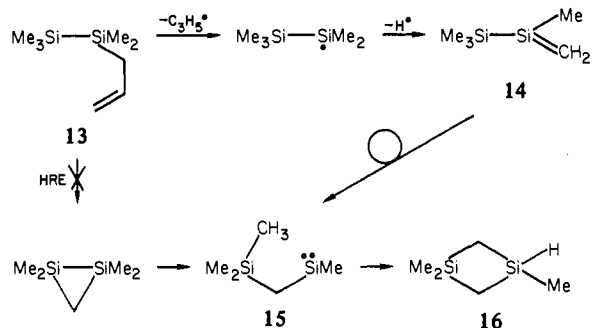


Scheme V



by Beckwith.¹⁵ However, we are unaware of any published studies on the cyclization of 4-pentenyl radicals.

It is interesting to note (Scheme IV) that ultimate formation of **2** from **10** could involve either endo closure of radical **11** or ring expansion of cyclobutylcarbiny radical **12**. Neither of these processes has precedent in carbon-radical chemistry.

Lastly, the elimination of the HRE mechanism presents a problem in the interpretation of the thermolysis results from allylpentamethyldisilane (**13**). We initially undertook the pyrolysis (840 °C, 10^{-3} torr)¹⁶ of **13** as a test for the necessity of C-H activation in the proposed HRE elimination. Thus, we predicted (Scheme V) and observed the formation of the major product, 1,1,3-trimethyl-1,3-disilacyclobutane (**16**, 18%).¹⁸ Key features in this route are the now precedented¹⁹ disproportionation of a methylsilicon radical to a silene (**14**) and the rearrangement of a silene (**14**) to a silylene (**15**). To our knowledge, this latter process has never before been observed or proposed. Silylene **15** has been generated before in our laboratory, and shown to cyclize to **16**.⁹ Experiments are currently under way to unambiguously generate silene **14** as well as radicals such as **11** and **12**.

Acknowledgment. We thank Dow Corning Corporation for partial support of this work.

(15) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482.

(16) Prepared in 71% yield from the coupling of chloropentamethyldisilene and allylmagnesium bromide; bp 80 °C (55 mmHg) [lit. bp 155 °C (760 mm)].¹⁷

(17) Chernyshev, E. A.; Tolstikova, N. G.; Ivashenko, A. A.; Zelenetskaya, A. A.; Leites, L. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1963**, 660.

(18) Also obtained in the pyrolysis of **13** were allyltrimethylsilane (5%), trimethylvinylsilane (2%) (possibly from α elimination of $Me_2Si\cdot$ and decomposition of $Me_2SiC_2H_5$, respectively, although both products could arise from addition of $Me_2Si\cdot$ to **13**), and **2** (10%, presumably from initial loss of methyl radical, perhaps with π assistance?).

(19) Tokach, S. K.; Koob, R. D., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 376. Cornett, B. J.; Choo, K. V.; Gaspar, P. P. *Ibid.* **1980**, *102*, 377. Gammie, L.; Safarik, I.; Strausz, O. P.; Roberge, R.; Sandorfy, C. *Ibid.* **1980**, *102*, 378.

Thomas J. Barton,* Stephanie A. Jacobi

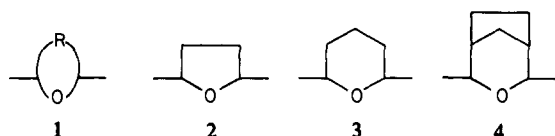
Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received September 2, 1980

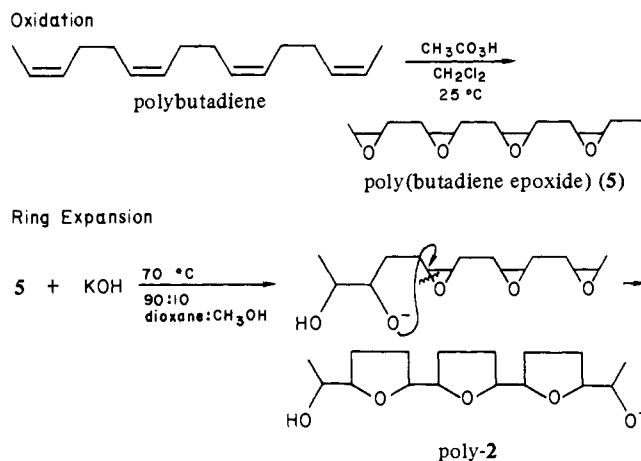
A New Family of Cation-Binding Compounds: threo- α,ω -Poly(cycloalkane)diyl

Sir:

α,ω -Poly(cycloalkane)diyl (**1**) constitutes a new generic family of polymers in which cyclic ether units are bonded together along the main chain. Specifically, separate polymers have been made which contain long segments of recurring 2,5-tetrahydrofurandiyl

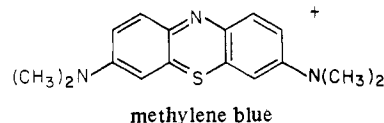


Scheme I



(**2**), 2,6-tetrahydropyrandiyl (**3**), and 2,4-bicyclo[3.2.1]-3-oxaoctanediyl (**4**) units.

Certain of these polymers bind cations in a manner similar to that of the crown ethers. However, unlike the crowns, whose complexing ability is determined to a large extent by the relative cation and macrocycle cavity dimensions,¹⁻³ a given **1** compound can effectively bind cations of widely varying sizes, e.g., Li^+ , Ba^{2+} , and methylene blue. Cation binding properties of **1** are partic-



ularly manifest when the average segment length of cyclic ether units is sufficient (at least 6 units) and the ring junctures are of three configuration.

The syntheses of polymers of **2**, **3**, and **4** involve the essentially complete oxidation⁴ and subsequent ring expansion of the oxiranes thus derived from the polymers of butadiene, cyclopentene,⁵ and norbornene,⁶ respectively. Scheme I gives the synthesis of poly-**2** by using Ameripol CB220 as starting material (B. F. Goodrich Co.), a poly butadiene of 100 000 mol wt having 98% *cis*-olefin and 2% pendant vinyl contents.

The following features characterize the overall synthesis of poly-**2**: (a) Assignment of all polymer functional groups can be made by ¹H and ¹³C NMR. (b) The complete conversion of main chain olefins to oxirane units is readily achieved under conditions which leave vinyl groups intact. (c) The rate-controlling step in the ring expansion reaction is the initiation step, which amounts to the random nucleophilic cleavage of an oxirane unit. (d) The propagation reaction which gives rise to poly-**2** segments is a chain reaction. (e) Termination of the reaction involves proton transfer when the propagating alkoxide ion encounters a "defect" unit, i.e., a separation of oxirane units by other than two or three carbon atoms.

Polymers having essentially all *cis*- and all *trans*-olefin configurations were used as precursors for **1** in separate experiments. Products derived from *cis* precursors were discovered to be effective complexing agents for a large variety of cations as measured by phase-transfer experiments of the type used to determine the binding efficiencies of crown ethers,² whereas those made from

(1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017-7036 (1967).

(2) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16-25 (1972).

(3) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351-384 (1974).

(4) The oxidation of diene polymers with peracids is the subject of a review article: E. M. Fettes, Ed., "High Polymers", Vol. 19, Chemical Reactions of Polymers, Interscience Publishers, New York, 1964, pp 152-172 (F. P. Greenspan).

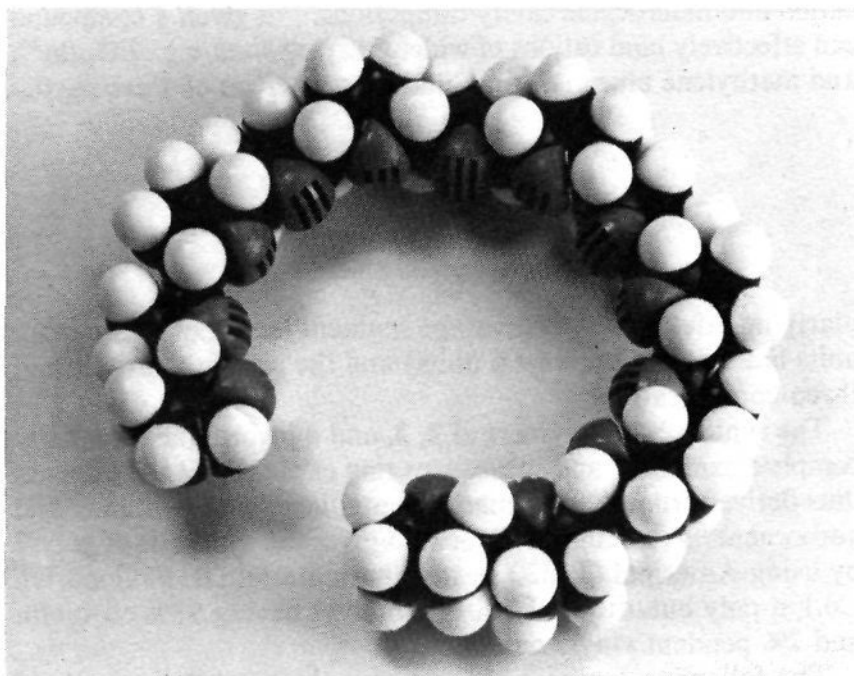
(5) N. Calderon, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C7**, 105-159 (1972).

(6) K. J. Ivin, D. T. Laverty, and J. J. Rooney, *Makromol. Chem.*, **178**, 1545-1560 (1977).

Table I. Phase Transfer of Picrate Salts at 25 °C^a

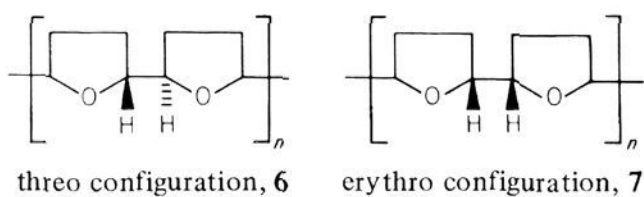
cation	complexing agent	salt transferred, %
Li ⁺	18-crown-6	63
	poly-6 ^b	37
K ⁺	18-crown-6	74
	dibenzo-18-crown-6	11
	poly-6 ^b	53
	poly-7 ^c	0
	poly-3(threo) ^d	58
Ba ²⁺	poly-3(erythro) ^d	0
	poly-4(threo) ^d	9
	poly-6 ^b	67
	18-crown-6	2
	poly-6 ^b	83
methylene blue ^e	18-crown-6	2
	poly-6 ^b	83

^a [Salt] in water = 0.025 g/L; [complexing agent] in CHCl₃ = 2.5 g/L. ^b Sample contained 77% of 6 units recurring in long segments. (Remainder consisted largely of segments of oxirane units.) ^c Sample contained 65% of 7 units recurring in long segments. ^d Samples were the indicated structures (i.e., >90%). ^e Dye extractions were performed by using equal solution volumes of methylene blue (0.1 mg in water) and complexing agent (140 mg in CHCl₃).

Figure 1. Segment of poly-6 (*cis*-2-units).

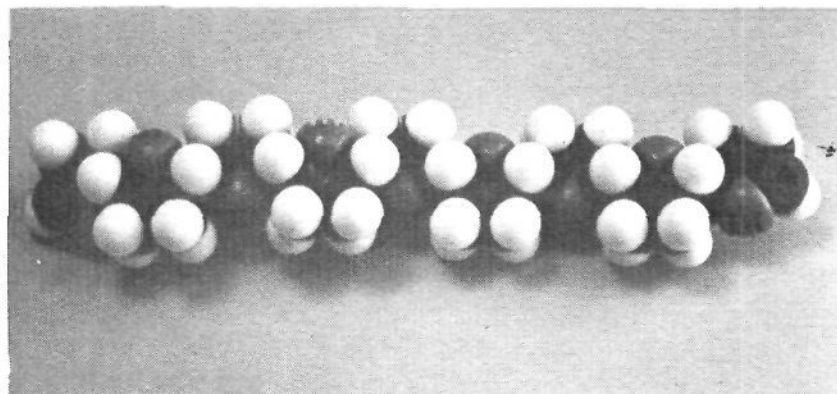
the *trans* precursors were found to be completely ineffective (Table I).

Oxirane formation involves *cis* addition but can occur from either face of the four coplanar carbons in which the double bond is centered. Base-catalyzed oxirane ring opening occurs with inversion of configuration.⁷ Application of these stereochemical generalizations provides two important conclusions regarding the nature of the chiral centers in poly-1 structures. (1) The cyclic ether units formed from either *cis*- or *trans*-alkenes can have either meso- or *dl*-like configurations. (2) All *cis*-alkenes lead only to ring junctures having threo configuration, while all *trans*-alkenes produce only ring junctures of erythro configuration. Poly-2 structures having these ring juncture configurations are shown.



CPK molecular models were used to construct long segments of 6 and 7. Examination of these showed the 6 chains, regardless of *cis* or *trans* configuration of individual rings, can readily assume flexible, coiled conformations in which the steric crowding of

(7) J. D. Roberts, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, 1964, p 414.

Figure 2. Segment of poly-7 (*cis*-2-units).

methylene hydrogens of the THF ring strongly favor the inward orientation of oxygen atoms, an arrangement similar to that of a crown ether (Figure 1).⁸ Unlike the crowns, however, 6 can form helical conformers in which the principal degrees of freedom involve variations in pitch and cavity size. It is possible that 6 binds cations of widely varying sizes so effectively because it is capable of adapting its conformation to optimize its multidentate coordination with a given cation.

In contrast, models of 7 showed that steric crowding of methine hydrogens tends to favor an extended chain conformation in which the oxygen atoms alternate direction along a linear chain (Figure 2). Possible conformers of 7 seem to present no reasonable geometry for multidentate coordination of oxygens with any cation. Only minor effects on the chain flexibilities of 6 and 7 resulted from varying the ratio of *cis*- to *trans*-THF units.

We are now studying the solution properties of these materials to gain more information on the effect of complex formation on polymer conformation.

Acknowledgment. We are grateful to A. R. Katritzky and R. A. Newmark for their considerable help in understanding the chemistry of these new compounds.

(8) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **11**, 8-14 (1978).

William J. Schultz, Margaret C. Etter
Alphonsus V. Pocius, Samuel Smith*

Central Research Laboratories, 3M Company
St. Paul, Minnesota 55144

Received August 11, 1980

Further Characterization of the Oxidation and Spin States of Iron in the Nitrogen-Bridged Metalloporphyrin μ -Nitrido-bis[(5,10,15,20-tetraphenylporphyrinato)iron]

Sir:

The nitrogen-bridged metalloporphyrin (TPPFe)₂N is the only known μ -nitrido complex bridging two first-row transition-metal ions.¹⁻³ Consequently, considerable efforts have been directed toward determining the structure of the complex and the physical properties of the two metal centers. These include Mössbauer and EPR spectroscopy,² X-ray crystallography,⁴ electrochemical studies,⁵ and X-ray photoelectron spectroscopy.⁶ These studies have resulted in conflicting views on the oxidation and spin states of the two iron atoms in the complex. It was originally proposed on the basis of Mössbauer studies² that the two iron atoms are

(1) Abbreviations used: μ -nitrido-bis[(5,10,15,20-tetraphenylporphyrinato)iron], (TPPFe)₂N; μ -oxo-bis[(5,10,15,20-tetraphenylporphyrinato)iron], (TPPFe)₂O; electron paramagnetic resonance, EPR.

(2) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747-1752.

(3) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339-345.

(4) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623-6628.

(5) Kadish, K. M.; Cheng, J. S.; Cohen, I. A.; Summerville, D. A. *ACS Symp. Ser.* **1977**, No. 38, Chapter 5.

(6) Kadish, K. M.; Bottomley, L. A.; Brace, J. G.; Winograd, N. *J. Am. Chem. Soc.* **1980**, *102*, 4341-4344.