sistance is essentially ineffective, if operational at all. In fact, this pair of diols proved to be exemplary, displaying levels of stereochemical retention that exceed 90% *in opposite directions.*

When recourse was made to 4-C_6H_5 and 5-C_6H_5, similar high degrees of stereocontrol were no longer evident. However, as for the methoxyl pair, greater stereochemical preservation occurred with the axial alcohol 4-C_6H_5. Our results suggest that 5-C_6H_5 may represent a crossover point where ionization to give the tertiary carbocation begins to override the totally retentive mechanism.

The 2-methyl substituent exerts little stereochemical influence. Both 4-CH_3 and 5-CH_3 reproducibly provided a similar product distribution, slightly richer in the inverted ethers. Control experiments established that the product distribution in every instance is entirely kinetic and not thermodynamic.[13] The configurations of tetrahydrofurans **6** and **7** were independently corroborated by direct cyclization of **4** and **5** with *p*-toluenesulfonyl chloride in triethylamine.

We next probed the source of the resident ethereal oxygen in **6** and **7** by ^{18}O labeling of the tertiary hydroxyl substituent in each substrate. Incorporation of the isotope was achieved by hydrolysis[14] of the cyclohexanone dimethyl ketals in water enriched to the extent of 50% with ^{18}O. The levels of isotopic incorporation in the three ketones were determined by relative integration of the well-separated $^{13}C-^{16}O$ and $^{13}C-^{18}O$ signals in their 75-MHz natural-abundance carbon spectra.[15] Comparable measurements performed subsequently on the six diols revealed that no dilution of the isotopic concentrations had occurred.[16] In a series of duplicate experiments, the specifically C-1/^{18}O-labeled diols were dehydrated under acidic conditions as before. The results are compiled in Table II.

Although cyclization can occur through initial protonation and loss of either hydroxyl group, the 100% retention of ^{18}O observed during the 4-$OCH_3 \rightarrow$ 6-OCH_3 and 5-$OCH_3 \rightarrow$ 7-OCH_3 transformations establishes that the associative S_N processes depicted in **8** and **9** are decidedly dominant. Although we have no in-

8　　　　**9**　　　　**10**
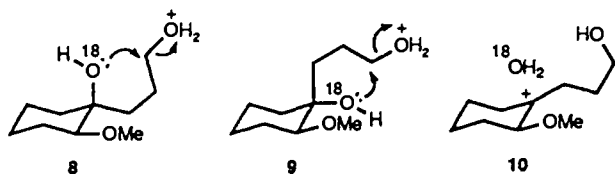
formation regarding the reacting conformation(s) of these diols, neighboring-group participation can operate from either chair arrangement. The higher percent of stereochemical retention achieved by 4-OCH_3 (and 4-C_6H_5) does suggest that an axial tertiary OH is perhaps better disposed to implement the S_N displacement than is its equatorial counterpart. The levels of residual ^{18}O that persist through the stereochemical inversion manifold of the methoxyl series are quite respectable. These data may reflect the tightness of the solvation shell in **10**[17] which prevents isotopically labeled water from escaping the vicinity of the carbocation as a consequence of its appreciable destabilization by electrostatic factors.

The gradual diminution in stereochemical control and isotopic retention as one progresses through the phenyl to the methyl analogues is best explained by a progressive attenuation of electron-withdrawing capacity at C-2, such that tertiary cyclohexyl

carbocation formation becomes increasingly more competitive with operation of the associative S_N process. However, increased incursion of the classical S_N1 process is not accompanied by full equilibration of the cations prior to hydration. This phenomenon, which is most evident in the matched methyl diastereomers, requires that these intermediates be unsymmetrically hydrated or captured at a rate faster than conformational ring inversion.

The remarkable departure from traditional chemical behavior made clear in this study prompts the advocacy of α-heteroatomic substitution as a useful tool for effecting highly stereocontrolled intramolecular reactions under seemingly improbable circumstances. One of the many conceivable applications of this strategy is illustrated in the ensuing report.[9]

Belted Spirocyclic Tetrahydrofurans: A New Class of Preorganized Ionophoric Polyethers. Molecular Structure, Conformation, and Binding to Alkali-Metal Atoms

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Nonmacrocyclic host molecules exhibit weaker cation-binding properties than coronands and cryptands unless their ligating oxygens are suitably preorganized for effective coordination.[2] These features can be found in select polyether antibiotics, e.g., monensin[3] and nonactin,[4] and in several totally synthetic tetrahydropyranoid podands.[5] Although interest in tetrahydrofuranyl building blocks has been high,[6] no attention has yet been accorded to poly(spiro ethers) of the type generalized by structures **1** and **2**. The effective binding capabilities of such host molecules are

1　　　　　　**2**
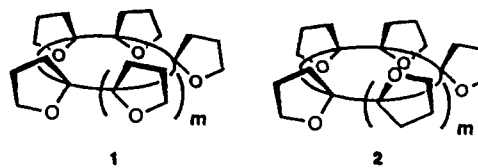
expected to be linked to the limiting conformational restrictions offered by the central belt and to the energy required to cluster the oxygens properly about the guest ion during complexation. Knowledge of the extent to which **2** and more extensively epim-

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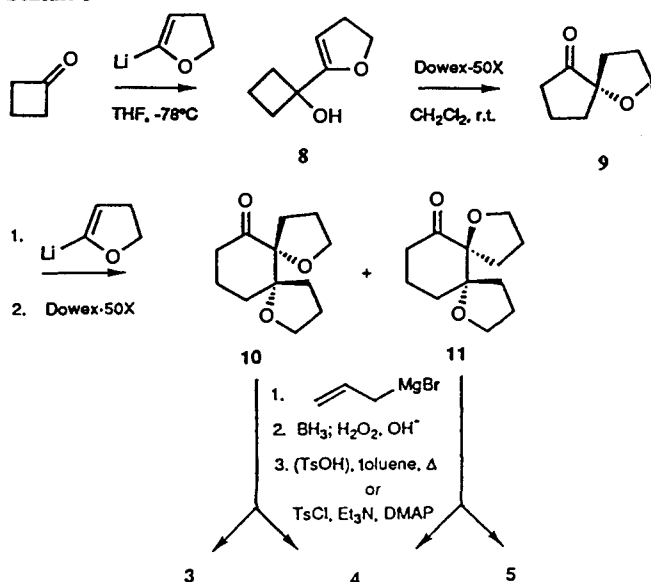(3) Pinkerton, M.; Steinrauf, L. K. *J. Mol. Biol.* **1970**, *49*, 533.
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5074   *J. Am. Chem. Soc., Vol. 113, No. 13, 1991*

Communications to the Editor

Scheme I

Scheme II

Table I. Extraction Equilibrium Constant K_{ex} (M^{-2} in $CDCl_3$ at 20 °C)

$$[M^+]_{aq} + [Pic^-]_{aq} + [host]_{org} \overset{K_{ex}}{\rightleftharpoons} [M^+Pic^-host]_{org}$$

compd	log K_{ex}		
	Li$^+$	Na$^+$	K$^+$
15-crown-5	2.29	4.03	3.49
	2.34	3.98	3.46
12-crown-4	2.11	2.20	2.33
	2.14	2.27	2.33
3	2.04	2.01	2.17
	2.08	1.94	1.96
5	1.91	1.94	2.04
	1.93	1.91	1.97
4	1.45	1.53	2.16
	1.20	1.53	1.96

erized stereoisomeric arrays exhibit modified levels of cation coordination could infuse valuable insight into future synthetic design.

In a program aimed at accessing these structural types, we have initially developed methodology amenable to the convenient preparation of the trispiro isomers 3–5 shown herein and have elucidated their solid-state conformational features. Furthermore, the binding properties of 3–5 have been compared to those of their previously unknown lower homologues 6 and 7.
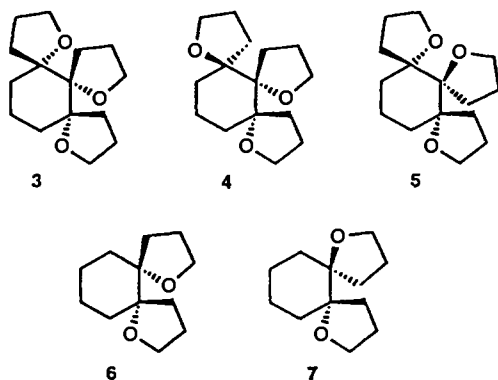
The synthesis of 3–5 began with the 1,2-addition of 5-lithio-2,3-dihydrofuran[7] to cyclobutanone (83%) in order to take advantage of an anticipated[8] regiocontrolled acid-catalyzed ring expansion of the resulting carbinol. As shown in Scheme I, stirring 8 with methanol-free Dowex-50X resin in CH_2Cl_2 at 20 °C for 20 h made 9 available in 95% yield.[9] Repetition of the two-step sequence on 9 gave rise to a chromatographically separable 1:1 mixture of 10 and 11 (88%). No stereoselectivity was observed during 1,2-addition of the α-lithio vinyl ether reagent to this chiral α-alkoxy ketone, despite the presence of a customarily powerful stereocontrol element (internal chelation) for directing the reaction course.[10] The pair of allylic alcohols proved too sensitive for chromatographic purification and was therefore used directly.

Distinction between 10 and 11 was achieved by X-ray crystallographic analysis of the more polar isomer 10. The cyclohexanone ring of 10 adopts that chairlike conformation in which the flanking C–O bond is projected equatorially. This orientational preference does not conform to expectations based on the minimization of electrostatic interactions[11,12] and may stem from a combination of factors including the desirability of projecting the vicinal pair of ether oxygen–carbon bonds into a gauche relationship.

The subsequent elaboration of 3–5 was achieved by "capping" the carbonyl groups in 10 and 11 as described in the accompanying report.[13] The initial involvement of allylmagnesium bromide led to improved stereoselectivity, presumably due in part to the more effective chelating abilities of Mg^{2+} relative to Li^+.[14] It is relevant, however, that the response of these diastereomers differs to a notable degree (11, anti:syn = 6:1; 10, anti:syn = 3:2).[15]

The diols produced subsequently were cyclized under both acidic and basic conditions. Acid catalysis eventuated in operation of the associative S_N reaction[13] in every instance, retention of stereochemistry being manifested in excess of 95% in all four cyclizations. Since 4 is the only trispiro tetrahydrofuran that can be produced from either ketone precursor, its stereochemical assignment is unequivocal. The solid-state structures of ionophores 3 and 5 were determined by X-ray analysis. While the three sequential oxygens in 3 adopt an equatorial–axial–equatorial arrangement, an all-equatorial alignment is adopted by 5. A rationalization of these conformational preferences will be advanced in the full paper.

The dispiro ethers 6 and 7 were prepared in comparable fashion from alcohol 12 (Scheme II).[8] Like 10 and 11, 13 exhibits a preference for anti attack (anti:syn = 5:1). The meso character of 6 was revealed by its simplified six-line ^{13}C NMR spectrum.

The binding capabilities of 3–7 toward lithium, sodium, and potassium picrate have been assessed by means of Cram's ex-

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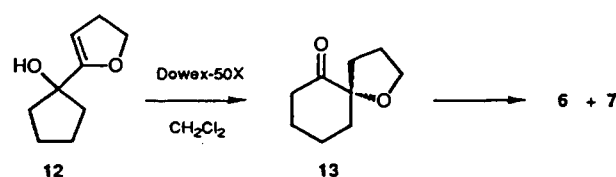(11) (a) Eliel, E. L.; Allinger, N. L.; Angyal, S. Y.; Morrison, C. A. *Conformational Analysis*; Interscience: New York, 1965; pp 460–469. Lambert, J. B. In *The Conformational Analysis of Cyclohexenes, Cyclohexadienes, and Related Hydroaromatic Compounds*; Rabideau, P., Ed.; VCH: Weinheim, 1989; Chapter 2.

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(15) Anti C–C bond formation corresponds to nucleophilic attack from the equatorial direction in that conformer carrying an adjacent equatorial C–O bond.

traction method[16a] and quantified in terms of extraction equilibrium constants (K_{ex}).[16b] As shown in Table I, the spiro furans exhibit coordinative abilities toward alkali-metal cations that are quite respectable for the limited number of oxygen atoms available for binding. Although **3** is expectedly the best ligand of its subset, with K_{ex} values approaching those of 12-crown-4 (four coordination sites), the precise geometry of the bridging oxygens in these complexes (1,3-diaxial as in A or diequatorial as in B) has yet to be established. Inversion of the *central* oxygen atom as in **5**
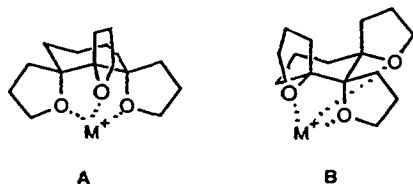
is less detrimental to ion complexation than inversion of a *terminal* binding site (see **4**). This finding, when linked to the response of **6**, suggests that the host:guest stoichiometric ratio may be >1 in these circumstances. Whatever the case, the promise offered by completely spherical ligands of type **1** and **2** appears high.

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Poly(phosphazophosphazenes): A New Class of Inorganic Polymers with Short-Chain Branching

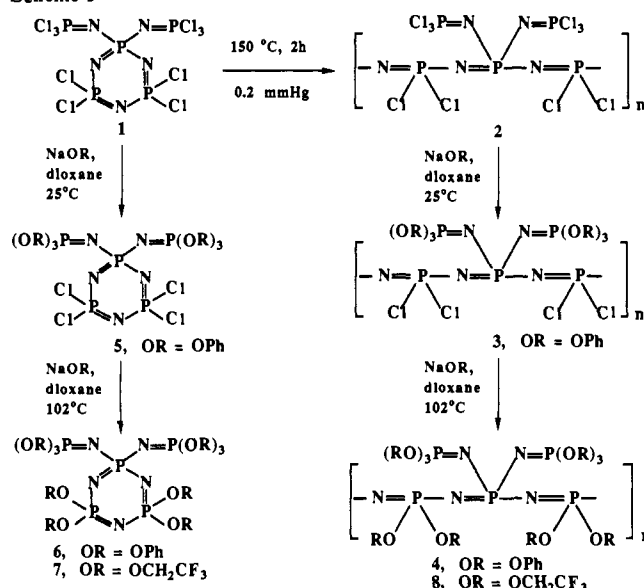Dennis C. Ngo, J. Steven Rutt, and Harry R. Allcock*

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Most polyphosphazenes are prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, at 250 °C to high molecular weight poly(dichlorophosphazene), $[NPCl_2]_n$,[1] followed by replacement of the chlorine atoms in the polymer by organic groups.[2] These organophosphazene polymers are essentially linear and often have a symmetric structure that generates microcrystallinity.

Here we report a method for the introduction of molecular asymmetry and materials free volume at the polymerization stage to yield a new series of polyphosphazenes. *gem*-Bis(trichlorophosphazo)tetrachlorocyclotriphosphazene (**1**) undergoes an unusual low-temperature, ring-opening polymerization to form a high molecular weight poly(phosphazophosphazene) (**2**) (Scheme I). This is the first example of a phosphazene polymer with well-defined short-chain branching. Polymer **2** can act as a macromolecular intermediate in selected cases and can be converted to hydrolytically stable, branched-structure poly(organophosphazenes).

Air-sensitive crystals of **1**[3] were placed in an airless flask, and the entire apparatus was evacuated through a vacuum line. Under

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Scheme I

a dynamic vacuum, the flask and its contents were heated at 150 °C for 2 h with stirring. The molten **1** was slowly converted to an immobile gel. This was soluble in dichloromethane. The spectra of both **1** and **2** consisted of A_2B_2C spin systems (Figure 1). Upfield chemical shift changes in the ^{31}P NMR spectra were detected for polymer **2** relative to trimer **1**. This observation is similar to the polymerization of other cyclotriphosphazenes such as $(NPCl_2)_3$.[1] The close similarity of the spectra suggested that polymerization did not result in a side-unit rearrangement or loss of the geminal trichlorophosphazo side groups. Integration of the NMR peaks of **2** relative to **1** indicated a 50–60% conversion of trimer to polymer. No intermediate species or side products were detected from the NMR spectra.

Trimer **1** was removed from polymer **2** by extraction with heptane to yield an air-sensitive, colorless polymer. Further characterization of **2** was accomplished by replacement of the chlorine atoms by reaction with sodium phenoxide in dioxane (Scheme I). Similar substitutions with trimer **1** were also explored as model reactions.

Treatment of solutions of **2** in dioxane with *excess* sodium phenoxide at 25 °C resulted in the facile formation of the partially substituted, but hydrolytically stable, polymer **3** (Scheme I), which was isolated by precipitation into water and hexane as a white, film-forming elastomer. The elasticity of the polymer is maintained when the polymer is stored under an inert atmosphere. Evidence for the structure of **3** was provided by the ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy and elemental analysis.[4] Despite the presence of excess sodium phenoxide, steric hindrance by the bulky, geminal triphenoxyphosphazo side groups appeared to prevent replacement of the main-chain P–Cl bonds of **3** at 25 °C and also retarded hydrolysis of the protected P–Cl bonds. This regioselective substitution by sodium phenoxide at 25 °C promises to allow a precisely controlled side-group incorporation for poly(organophosphazenes) prepared by the reaction of **2** with nucleophiles.

The residual P–Cl bonds in **3** were replaced by treatment with excess sodium phenoxide at 102 °C in dioxane for 7 days in the presence of tetra-*n*-butylammonium bromide as a phase-transfer agent to form **4**. This polymer was also isolated by precipitation into water and hexane as a white, film-forming material (Scheme I). The structure was confirmed by ^{31}P, ^{13}C, and ^{1}H NMR

(4) Characterization data for **3**: ^{31}P NMR (A_2BC_2 spin system, $\delta_A = -29$ ppm, $\delta_B = -30$ ppm, $\delta_C = -35$ ppm); ^{13}C NMR ($\delta = 121, 125, 130, 151$ ppm); ^{1}H NMR (m, $\delta = 6.8-7.4$ ppm). Elemental anal. Calcd: C, 46.70; H, 3.24; N, 7.57; Cl, 15.35. Found: C, 47.06, H, 3.79; N, 6.99; Cl, 14.81.
(5) Characterization data for **5**: ^{31}P NMR (A_2BC_2 spin system, $\delta_A = 14$ ppm, $\delta_B = -19$ ppm, $\delta_C = -28$ ppm); ^{13}C and ^{1}H NMR same as for **3**; mass spectrum calcd 925, found 925.