hibit a doublet at τ 5–7 with the relative intensity corresponding to two methylene protons. Furthermore the downfield signals would occur with the relative intensities and multiplicities reflecting the presence of two and one vinyl protons in the C_4H_7 and C_5H_9 sulfinates, respectively.[7]

The generality of the above-described allylic rearrangement is supported by the behavior of the 2-butenyl derivatives of cyclopentadienyliron dicarbonyl, cyclopentadienylmolybdenum tricarbonyl, and cyclopentadienyltungsten tricarbonyl toward sulfur dioxide. The nmr spectra of all of the resulting sulfinates are consistent with the rearranged structure of the hydrocarbon moiety.[9]

We are currently examining insertion reactions between allyl metal complexes and substrates other than sulfur dioxide with a view to elucidating the scope of the rearrangement described herein.

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(7) This argument receives support from the recent isolation of $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ *via* the reaction of $Na[C_5H_5Fe(CO)_2]$ and sulfur dioxide with 1-chloro-3-methyl-2-butene. The proton magnetic resonance spectrum of the sulfinate exhibits doublets at τ 8.08 (CH_3) and 6.17 (CH_2) with the relative intensity ratio of 6:2, a sharp singlet at τ 4.68 (C_5H_5), and a complex signal at τ 4.30–4.95 ($CH{=}C$), in complete accord with the proposed allylic attachment.[8]

(8) R. L. Downs and A. Wojcicki, to be published.

(9) Although we cannot rule out the possibility that the "rearranged" allyl-S-sulfinato complexes result from the initial formation of the corresponding "normal" allyl sulfinates, which then rapidly undergo isomerization, there is evidence against such a sequence of events. The derivative $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ retains its identity after 4 hr of refluxing in liquid SO_2; a 3:1 mixture of the geometric isomers $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$ and $C_5H_5Fe(CO)_2SO_2C(CH_3)_2CH{=}CH_2$ becomes *ca.* 8:1 and 14:1 upon refluxing for 4 and 8 hr, respectively, in liquid sulfur dioxide. Thus, at least in this case, isomerization of the sulfinates does occur, *albeit* of the sterically more hindered $C_5H_5Fe(CO)_2SO_2C(CH_3)_2CH{=}CH_2$ to the less crowded $C_5H_5Fe(CO)_2SO_2CH_2CH{=}C(CH_3)_2$.

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Cyclic Polyethers and Their Complexes with Metal Salts

Sir:

Thirty-three cyclic polyethers, derived from aromatic vicinal diols and containing from 9 to 60 atoms including 3–20 oxygen atoms in the ring, have been synthesized. Some of these have been prepared in good yields without the use of a high-dilution technique. Fifteen of the compounds have been catalytically hydrogenated to the corresponding saturated cyclic polyethers.

Many of these cyclic polyethers have the unusual property of forming relatively stable complexes with alkali and alkaline earth metal ions. The more effective ligands are those containing 5–10 oxygen atoms, each separated from the next by 2 carbon atoms. This communication deals primarily with two examples of the six-oxygen compounds which are the most effective and versatile complexing agents: an aromatic compound derived from catechol, 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (I); and its hydrogenation product, a mixture of *cis–trans* isomers, 2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane (II).

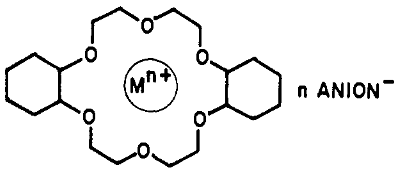

Figure 1. *o*-Benzo or 1,2-cyclohexyl polyethers.

The two cyclic polyethers form stable complexes with ionic compounds of Li, Na, NH_4, RNH_3, K, Rb, Cs, Ag(I), Ca, Sr, Ba, Cd, Hg(I), Hg(II), La(III), Tl(I), Ce(III), and Pb(II). The complexes are thought to be field valency compounds formed by ion–dipole interaction between the cation and the negative dipoles of the oxygen atoms of the polyether ring, as shown in Figure 1; the formation of stable ammonium complexes supports this interpretation. The "hole" in I and II, estimated to be 4 A in diameter, is large enough to accommodate any unsolvated or uncoordinated inorganic cation. The stoichiometry of the complexes is one molecule of polyether per single cation regardless of the valence.

Compound I is prepared by treating 1 mole of catechol, 2 moles of sodium hydroxide, and 1 mole of bis(2-chloroethyl) ether in 1-butanol at reflux temperature (115°) for about 24 hr. The yield is 44–48%, and 1 mole (360 g) of product can be synthesized in a volume of 5 l. White fibrous crystals are obtained by crystallization from benzene; mp 164°; bp *ca.* 380–384° (769 mm). *Anal.* Calcd for $C_{20}H_{24}O_6$: C, 66.6; H, 6.7; mol wt, 360. Found: C, 66.3; H, 6.8; mol wt, 371. Compound I is readily soluble in methylene chloride and chloroform, and very little soluble in methanol and water. Its ultraviolet spectrum in methanol has a peak at 274 mμ (ϵ 5200). Its infrared spectrum shows no OH band but two strong, broad ether bands near 8.1 and 8.5 μ. Its nmr spectrum is consistent with the proposed structure: a multiplet 4.11 ppm downfield from TMS, area ratio 2.2, and a singlet, 6.92 ppm, area ratio 1.00. The good yield of I obtained without resorting to a high-dilution technique is unusual for an 18-membered ring. Possibly the sodium ions promote ring formation by properly orienting the reactants and the intermediate products through ion–dipole interaction.

Compound II is prepared by hydrogenating I in a stainless steel autoclave at 100° and 1600 psig using *p*-dioxane as solvent and ruthenium dioxide as catalyst. The product, free of alcoholic by-products, is obtained by chromatography with acid-washed alumina and *n*-heptane in 67% yield. *Anal.* Calcd for $C_{20}H_{36}O_6$: C, 64.5; H, 9.7; mol wt, 372. Found: C, 64.5; H, 9.6; mol wt, 378. The product is a mixture of isomers, melts between 30 and 56°, and boils at about 344° (769 mm). It is soluble in organic solvents including petroleum ether. Its solubility in water at 26° is 0.036 mole/l. and decreases with rising temperature. Its ultraviolet spectrum shows no significant absorption above 200 μ, and its infrared spectrum shows no OH band but a strong, broad ether band near 9 μ. Its nmr spectrum is consistent with the proposed structure: a multiplet 1.50 ppm downfield from TMS, area ratio 1.17, and a singlet, 3.67 ppm, area ratio 1.00.

Crystalline 1:1 complexes of I have been prepared with, for example, LiI_3, $NaNO_2$, KI, KCNS, NH_4CNS, CN_3NH_3CNS, RbCNS, CsCNS, $CaCl_2$, $Ba(OH)_2$, $CdCl_2$, $HgCl_2$, and $Pb(OAc)_2$. The potassium thiocyanate complex can be obtained as long, glistening crystals melting at 248–249°, considerably higher than the melting points of the components (172° for potassium thiocyanate). The ammonium thiocyanate complex melts at 187–189° (149° for ammonium thiocyanate). The analytical data on the complexes are satisfactory.[1]

The solubility of I in polar solvents is increased by the addition of soluble complexable salts. For example, the solubility of I in methanol at 30° (1.1 m-moles/l.) is increased to the following values by the presence of the salts at 25 m*M*: NaCNS, 23.6 m-moles/l., KF, 24.7; RbCNS, 25.6; $AgNO_3$, 22.2; $SrCl_2$, 17.9; and $BaCl_2$, 26.6. The complexes tend to be more soluble in organic solvents of high dielectric constant, but most are decomposed by water. All soluble, ionic compounds of the complexable elements form complexes in solvents, such as methanol, regardless of the anion.

Compound II, being a mixture of isomers, forms solid complexes with not so well-defined melting points, but always higher than the melting point of II itself. Some of its complexes, such as that of potassium triiodide, are stable to water. II has the useful property of solubilizing ionic compounds in aprotic solvents including aromatic hydrocarbons. The following are a few examples. Crystals of potassium permanganate are insoluble in benzene, but they begin to dissolve immediately after the addition of II and continue to dissolve until the concentration of permanganate exceeds 0.02 *M*. Crystals of palladous chloride are insoluble in *o*-dichlorobenzene, but when crystals of potassium chloride and II are added, they go into solution as the complex of II with K_2PdCl_4. The salts of many other alkali, alkaline earth, and transition metals have been solubilized by these two methods. A most interesting and useful complex is that of II with potassium hydroxide, which is soluble in toluene to over 0.3 mole/l. This solution saponifies the hindered esters of 2,4,6-trimethylbenzoic acid by the normal acyl–oxygen fission.

Not all complexable salts, however, can be solubilized even in the better aprotic solvents. Salts of high crystal lattice energy, such as potassium fluoride, sulfate, nitrate, phosphate, and carbonate, do not form complexes in aprotic solvents, and neither can these complexes be isolated as solids from protic solvents, such as methanol.

A detailed paper on the cyclic polyethers and their complexes with metal salts is being prepared for publication.

[1] Crystalline etherates of the alkali metal salts have not been common heretofore. Two ($[Na(CH_3OCH_2CH_2OCH_2CH_2OCH_3)_2][Ta(CO)_6]$ and $[K(CH_3OCH_2CH_2OCH_2CH_2OCH_3)_3][Mo(CO)_5I]$) are mentioned by F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 318.

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Observation of Helix–Coil Transition Using Nuclear Magnetic Resonance Halogen Ion Probe Technique

Sir:

Recent work has shown that nuclear magnetic resonance of halide ions may be a valuable tool for investigating the gross physical characteristics and specific chemical reactivities of large biological molecules in solution.[1] This note reports an observation of the well-substantiated helix–coil transition in synthetic poly-L-glutamate using ^{35}Cl resonance, and thus illustrates a direct application of wide-line nmr to the study of macromolecular structure. The ^{35}Cl line width is usually determined by quadrupole relaxation so that in the extreme narrowing limit the line width for a nucleus of spin $^3/_2$ is given by eq 1, where $\Delta\nu$ is the

$$\Delta\nu = \frac{2\pi}{5}(e^2qQ)^2\tau_c \tag{1}$$

full line width in cycles per second at half-height, q is the electric field gradient at the nucleus with quadrupole moment Q, τ_c is the correlation time for molecular rotation, and the asymmetry parameter has been neglected.[2] In aqueous sodium chloride solutions the chloride ion is symmetrically solvated producing a field gradient at the nucleus close to zero and a line width of about 16 cps. If, however, the quadrupolar chlorine nucleus can be found at environmentally different sites in solution, the line width will depend on the relative concentration of each site, the values of $(e^2qQ)^2$ and τ_c associated with each site, as well as the frequency with which the ^{35}Cl nucleus samples the various sites. In the case where exchange of the chloride is fast with respect to $1/\pi\Delta\nu$, a single composite line is observed with the line width given by

$$\Delta\nu = (\Delta\nu_a)P_a + (\Delta\nu_b)P_b \tag{2}$$

where $\Delta\nu_a$ and $\Delta\nu_b$ are the contributions to the line width associated with sites a and b, while P_a and P_b are the probabilities that the chlorine is at site a and b, respectively.[3]

When a 2 *M* sodium chloride solution is made 10^{-3} *M* in mercuric chloride, the $^{35}Cl^-$ resonance is broadened to 34 cps. The effect is explained by the rapid exchange of chloride ions in solution with the covalent chlorine associated with the $HgCl_4^{2-}$ complex; thus, eq 2 correctly describes the line width. Since a similar effect is observed with species of the type RSHgCl in sodium chloride solutions, where R is almost any organic molecule, the mercury atom provides a convenient label for investigating changes in the correlation time of the molecule to which it is attached.[1]

In aqueous solutions of low pH, poly-L-glutamate acquires a helical structure while at higher pH the randomly coiled form predominates. The transition from the helical to the randomly coiled structure has been investigated as a function of pH using measurements of optical rotation, viscosity, per cent ionization, optical rotatory dispersion, and the infrared spectrum.[4,5] In solutions of low salt concentration the

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[1] T. R. Stengle and J. D. Baldeschwieler, *Proc. Natl. Acad. Sci. U. S.*, 55, 1020 (1966).

[2] A. Abragam, "The Principles of Nuclear Magnetism," The Clarendon Press, Oxford, 1961, p 314.

[3] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).