H_2SO_4 which was carefully added until vigorous reaction stopped. The Et_2O layer was separated, and the aqueous layer was extracted with Et_2O three times. The combined ether solution was washed with water and saturated NaCl solution and dried over anhydrous $MgSO_4$. Distillation at 85-90 °C (12 mmHg) gave 49.4 g (85% yield) of **5a**, a colorless liquid. The product was identical with an authentic sample prepared by another method.[3]

(*cis*-6-Methyltetrahydropyran-2-yl)ethyl Acetate (5b). Acetyl chloride (10.9 g, 0.139 mol) was added slowly to **5a** (20 g 0.139 mole) and dry pyridine (11.0 g, 0.139 mol) in an ice bath. The mixture was allowed to stand overnight, and then 100 mL of ice-water was poured into the flask. The organic layer was separated, and the aqueous layer was extracted three times with Et_2O. The combined Et_2O solution was washed with water and saturated NaCl solution and dried over anhydrous $MgSO_4$. Distillation at 103-106 °C (12 mmHg) gave 23.01 g (89%) of a colorless liquid, **5b**: IR (NaCl disk 2930 (s), 2850 (s), 1730 (s), 1440 (s), 1370 (s), 1240 (s), 1057 (s) cm^{-1}.

The ^1H NMR spectrum (*in parts per million relative to* Me_4Si) of each of the isomers is given below.

Isomer 1: 4.75-4.83 (m, 1 H), 3.39-3.47 (m, 1 H), 3.29-3.35 (m, 1 H), 2.05 (s, 3 H), 1.27-1.87 (m, 6 H), 1.22-1.25 (d, J = 6.60 Hz, 3 H), 1.15-1.18 (d, J = 6.60 Hz, 3 H).

Isomer 2: 4.86-4.96 (m, 1 H), 3.29-3.47 (m, 2 H), 2.07 (s, 3 H), 1.25-1.89 (m, 6 H), 1.21-1.23 (d, J = 6.60 Hz, 3 H), 1.16-1.18 (d, J = 5.9 Hz, 3 H).

For both isomers: mass spectrum, m/e 126 [$M^+ - 60$ (HOAc)]. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found (isomer 1): C, 64.40; H, 9.93. Found (isomer 2): C, 64.53; H, 9.86.

***cis*-2-(Vinylmethyl)tetrahydropyran (6).** The pyrolysis of the ester was carried out in the vapor phase at 450 °C. The acetate **5b** (15.2 g) in a 25-mL syringe was added at the speed of 10 mL/h to the top of a vertically mounted quartz tube (0.7 cm i.d. × 30 cm) packed with broken quartz and heated with a nichrome wire. The products were swept from the reaction column by a slow stream of N_2 and collected in a cold trap. The temperature was monitored by inserting a thermocouple between the wall of the column and nichrome wire. After pyrolysis, the products were neutralized with $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined Et_2O solution was washed with water and saturated NaCl solution and dried over anhydrous $MgSO_4$. After distillation at 45-47 °C (12 mmHg), 8.20 g (80%) of colorless liquid was collected: ^1H NMR ($CDCl_3$ with Me_4Si) 5.81-5.94 (m, 1 H), 5.19-5.28 (dt, 1 H, J = 17.2 Hz), 5.06-5.11 (dt, 1 H, J = 10.6 Hz), 3.79-3.86 (m, 1 H), 3.46-3.54 (m, 1 H), 1.21-1.85 (m, 6 H), 1.19-1.21 ppm (d, 3 H, J = 5.9 Hz); IR (NaCl disk) 2850 (s), 2925 (s), 1650 (w), 1680 (w), 1450 (m), 1380 (m), 1317 (m), 1240 (w), 1215 (w), 1164 (w), 1153 (w), 1090 (s), 1080 (s), 1048 (s), 1026 (m), 993 (m), 923 (w), 982 (w), 810 (w), 754 cm^{-1} (w); mass spectrum, m/e 126 (M^+). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.14; H, 11.32.

2-(*cis*-6-Methyltetrahydropyran-2-yl)ethanol (7). A solution of olefin **6** (2.50 g, 19.8 mmol) in 10 mL of dry THF was placed in a 50-mL three-necked flask equipped with a thermometer, a reflux condenser connected with a bubbler, and a dispersion tube connected with Tygon tubing to a 50-mL, three-necked flask serving as the diborane generator and equipped with a N_2 inlet and an Hg pressure equalizer. In the generator was placed 3 mL of boron trifluoride etherate in 3 mL of diglyme. Diborane was generated by the dropwise addition of 9 mL of 1 M solution of $NaBH_4$ in diglyme by using a syringe to the stirred BF_3 solution. The diborane was passed into the olefin solution (maintained at 20 °C) by applying a slight flow of dry N_2 through the generator. After addition of the $NaBH_4$ addition, the generator was heated 0.5 h at 70 °C and then disconnected from the hydroboration flask after cooling to room temperature. The excess hydride was decomposed by the addition of 1.5 mL of water. To the organoborane solution were added 3 mL of 3 N NaOH and 3 mL of 30% H_2O_2 dropwise at 30-50 °C. The reaction mixture was stirred for an additional hour, and then 30 mL of Et_2O was added. The organic phase was separated, and the aqueous phase was saturated with NaCl and then extracted twice with 15-mL portions of Et_2O. The combined extracts were washed twice with 15-mL portions of saturated NaCl solution and dried over anhydrous $MgSO_4$. After the evaporation of solvent, 2.3 g (80%) of a colorless liquid was collected at 112-115 °C (12 mmHg): ^1H NMR ($CDCl_3$ with Me_4Si) 3.77-3.79 (m, 2 H), 3.44-3.60 (m, 2 H), 3.17 (br, s, 1 H), 1.20-1.84 (m, 8 H), 1.15-1.17 ppm (d, 3 H, J = 5.9 Hz); IR (NaCl) 3400 (s), 2900 (s), 1450 (m), 1375 (m), 1325 (m), 1210 (m), 1155 (m), 1087 (s), 1050 (s), 1020 cm^{-1} (m); mass spectrum, m/e 144 (M^+). Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.38; H, 11.02.

(*cis*-6-Methyltetrahydropyran-2-yl)acetic Acid (1). (1) Pyridinium dichromate (4.73 g, 12.5 mmol) was added to **7** (0.513 g, 3.56 mmol) in 9.5 mL of dry DMF. The solution was stirred for 9 h at room temperature. Water (80 mL) was poured into the DMF solution, and the solution was extracted with Et_2O three times. The combined extracts were washed with water and saturated NaCl solution and dried over anhydrous $MgSO_4$. After the evaporation of solvent, the DMF and **1** were separated by column chromatography with anhydrous Et_2O as an eluent on silia gel. The acid was collected first and crystallized by evaporation of the solvent, giving acid **1**: 0.375 g (67%); mp 48-51 °C (uncor).

(2) To a solution of **7** (0.50 g, 3.47 mmol) in 10 mL of acetone was added the chromic acid oxidizing reagent (Jones reagent) at 20 °C until the characteristic orange color of the reagent persisted for 20 min. The mixture solution was stirred for 1 h, and the green salts were filtered and rinsed with acetone several times. Isopropyl alcohol was added to the acetone solution until the excess chromic acid was destroyed. The solution was neutralized with $NaHCO_3$ and the suspension was filtered. After evaporation of acetone, 10 mL of saturated NaCl solution was added, and the mixture was extracted with Et_2O three times. The combined extracts were washed with water and saturated NaCl solution and dried over anhydrous $MgSO_4$. After evaporation of ether solution **1** was collected: 0.424 g (77%); ^1H NMR ($CDCl_3$ with Me_4Si) 3.73-3.80 (m, 1 H), 3.51-3.59 (m, 1 H), 2.52-2.56 (q, 2 H), 1.24-1.87 (m, 6 H), 1.19-1.21 ppm (d, 3 H, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$ with Me_4Si) 22.02 (6 C), 23.20 (3 C), 30.86 (2 C), 32.86 (4 C), 41.31 (7 C), 74.13 (5 C), 74.80 (1 C), 173.91 ppm (8 C); IR (NaCl disk) 2400-3780 (br, s), 1720 (s), 1740 (s), 1440 (m), 1380 (m), 1300 (m), 1210 (m), 1185 (m), 1076 cm^{-1} (s); mass spectrum, m/e 158 (M^+). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.54; H, 9.05.

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Registry No. (±)-**1**, 82335-13-5; **4**, 1123-32-6; (±)-**5a** (isomer 1), 82335-14-6; (±)-**5a** (isomer 2), 82335-15-7; (±)-**5b** (isomer 1), 82280-94-2; (±)-**5b** (isomer 2), 82335-16-8; (±)-**6**, 82293-67-2; (±)-**7**, 82280-95-3.

New Hydronium Ion-Crown Ether Complexes[1]

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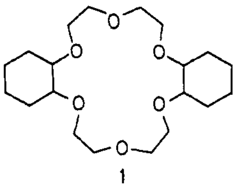
In 1972, Izatt et al.[2] reported the precipitation of 1:1 complexes of *cis-syn-cis*-dicyclohexano-18-crown-6, 1, and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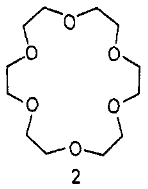
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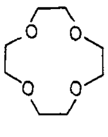
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[1] This research was supported by Grant D-775 from the Robert A. Welch Foundation.

Table I. Hydronium Ion–Crown Ether Complexes

complex	mp, °C	yield, %[a]	elemental analysis, %			
			calcd		found	
			C	H	C	H
(H_3O^+)(18-crown-6)(PF_6^-)	131–132	71	33.65	6.36	33.62	6.15
(H_3O^+)(18-crown-6)(ClO_4^-)	168–169	70	37.65	7.11	37.79	7.26
(H_3O^+)(18-crown-6)(BF_4^-)	140–142	70	38.94	7.35	39.06	7.12
(H_3O^+)(18-crown-6)(I^-)	107–108 dec	71	35.13	6.63	35.19	6.82
(H_3O^+)(18-crown-6)(Br_3^-)	111–114	96	27.55	5.20	27.79	5.33
$(HNO_3 \cdot H_2O)_2$(18-crown-6)	55–56	65	33.80	7.09	34.05	7.16
(H_3O^+)(12-crown-4)$_2(PF_6^-)$	98–99	75	37.21	6.83	37.02	6.88

[a] Based upon the crown ether.

$H_3O^+ClO_4^-$ or $H_3O^+PF_6^-$ when an excess of the respective acid was added to an aqueous solution of the crown ether. These stable, crystalline complexes were characterized by elemental analysis and infrared spectroscopy. No complexes could be isolated with *cis-anti-cis*-dicyclohexano-18-crown-6 presumably because the complexes were too water soluble. In subsequent work, Izatt and co-workers[3] utilized these solubility differences for the separation of the cis isomers of dicyclohexano-18-crown-6.

Although other researchers[4–6] have explored the complexation of inorganic and organic acids by crown ethers and the uses[5,6] of such complexes, no further reports of hydronium ion–crown ether complexes have appeared. Presumably this is due to an inability to extend the synthetic method of Izatt et al.[2] to the more hydrophilic, unsubstituted crown ethers such as 18-crown-6, **2**. We have developed an alternative synthetic method for the preparation of hydronium ion–crown ether complexes and now report this method as well as the effects of polyether and anion variation upon the stoichiometry and properties of resultant hydronium ion–crown ether complexes.

Results and Discussion

Hydronium ion–crown ether complexes with 18-crown-6, 15-crown-5, or 12-crown-4 as the crown ether components are prepared by adding an excess of a concentrated aqueous[7] acid to a CH_2Cl_2 solution of the crown ether. After a short, vigorous agitation, the organic layer is separated and dried. The CH_2Cl_2 solution is reduced in volume followed by the addition of Et_2O, which precipitates the complex. The complex is filtered, washed with Et_2O,[8] and dried. Neither excess acid nor uncomplexed crown ether contaminates the complex.

Variation of the Anion. The influence of anion variation upon the synthetic method and the properties of the hydronium ion–crown ether complexes was probed with use of 18-crown-6, **2**, as the crown ether component. Stable, nonhygroscopic, solid complexes with a stoichiometry of $(H_3O^+)(\mathbf{2})(X^-)$ were obtained in 70% yields when $X^- = PF_6^-, ClO_4^-, BF_4^-$, or I^- and in almost quantitative yield when $X^- = Br_3^-$.[9] Elemental analysis and yield data for these complexes are collected in Table I.

Compared with those of 18-crown-6, the ^1H NMR absorptions of crown ether protons in the complexes are shifted downfield by 0.15–0.20 ppm, and new absorptions for the hydronium ion protons appear in the region 9–12 ppm.[10] Exact integration for 1:1 complexes are found. Infrared (IR) spectra of these complexes in Nujol shown broad absorptions in the region 3600–1600 cm^{-1} with weak maxima at approximately 3200, 2800, 2200, and 1700 cm^{-1} [2,11] and characteristic splitting of the C–O–C stretching absorption of 18-crown-6 (1100 cm^{-1}) into bands at 1140 and 1090 cm^{-1}.

Although convincing ^1H NMR evidence for the formation of $(H_3O^+)(\mathbf{2})(Cl^-)$ and $(H_3O^+)(\mathbf{2})(Br^-)$ in about 20% yields was obtained, these complexes were not further characterized since the former melted at room temperature and the latter was found to be very hygroscopic. No complex could be isolated from sulfuric acid and 18-crown-6 presumably due to the high solubility of the complex in the aqueous phase.[12] Hydronium ion–crown ether complexes with organic anions such as trifluoroacetate and *p*-toluenesulfonate could not be prepared by use of our experimental method due to the high solubility of the parent acids in the organic phase.

After recrystallization from $CHCl_3$–Et_2O, the solid that is formed in 65% yield by treating a CH_2Cl_2 solution of 18-crown-6 with a 3-fold excess of concentrated HNO_3 is a nonhygroscopic, stable complex at room temperature and atmospheric pressure.[13] Elemental analysis (table), integration of the ^1H NMR spectrum for the complex in $CDCl_3$ (absorptions at 3.72 and 9.58 ppm), titration for H^+, and ion chromatographic analysis for NO_3^- are all consistent with a stoichiometry of one molecule of crown ether to two hydronium ions (i.e., a 1:2 complex).[14] Although the IR spectrum of this complex in Nujol shows broad absorptions in the region 3600–1600 cm^{-1}, it differs from those of the other solid hydronium ion complexes of 18-crown-6 in that it exhibits strong absorptions at 3400 and 1650 cm^{-1} (water absorptions) and no splitting of the C–O–C stretching absorption of the crown ether at 1100 cm^{-1}. Physical studies of the combination of water and nitric acid[15–17] have demonstrated the importance of covalent (nitric acid monohydrate) as well as ionic (hydronium nitrate) forms. The differences in IR spectra and stoichiometry between the complex formed from nitric acid

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(6) Fernando, L. A.; Miles, M. L.; Bowen, L. H. *Anal. Chem.* **1980**, *52*, 1115–1119.

(7) Use of an organic phase and concentrated aqueous acid minimizes loss of the hydrophilic crown ether and the hydronium ion–crown ether complex to the aqueous phase.

(8) The uncomplexed crown ethers are soluble in Et_2O.

(9) Bromine is added to a vigorously agitated mixture of concentrated aqueous HBr and 18-crown-6 in CH_2Cl_2.

(10) The chemical shift for the hydronium ion protons is concentration-dependent.

(11) Giguere, P. A.; Turrell, S. *Can. J. Chem.* **1976**, *54*, 3477–3482.

(12) The volume of the aqueous acid phase increased noticeably after shaking with a solution of 18-crown-6 in CH_2Cl_2.

(13) Under high vacuum the complex decomposes and melts.

(14) A 1:2 complex is also isolated from equimolar amounts of nitric acid and 18-crown-6.

(15) Savoire, R.; Giguere, P. A. *J. Chem. Phys.* **1964**, *41*, 2698–2705.

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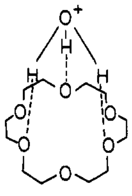
and other solid hydronium ion complexes of 18-crown-6 suggest that the former may involve nitric acid hydrate species rather than hydronium ions. Most probably the two nitric acid monohydrate molecules sandwich a molecule of 18-crown-6. Although an X-ray crystal structure would provide the essential structural information for further clarification, our attempts to grow suitable crystals of this complex have been unsuccessful.

Variation of the Polyether. So that requirements of the polyether component for the formation of solid hydronium ion-polyether complexes could be probed, three unsubstituted crown ethers and several glymes were examined by using concentrated aqueous HPF_6 as the acid component.

As was described previously, the complex formed from 18-crown-6 is a nonhygroscopic, sharp-melting solid with a stoichiometry of $(H_3O^+)(\mathbf{2})(PF_6^-)$. From 15-crown-5, a hygroscopic solid with mp 88–91 °C was isolated. However, integration of the ^1H NMR spectrum for this solid and the results of elemental analysis were both inconsistent with either a uniform 1:1 or 2:1 (two crown ether molecules and one hydronium ion) complex. From 12-crown-4, **3**, a nonhygroscopic complex with mp 98–99 °C and a stoichiometry of $(H_3O^+)(\mathbf{3})_2(PF_6^-)$, was obtained (table). For this complex, the ^1H NMR absorption of the crown ether protons shifts downfield by 0.08 ppm from that of **3**, and the absorption for the hydronium ion protons appears at 9–12 ppm[10] with the exact integration for a 2:1 complex. The IR spectrum of this complex in Nujol exhibits broad absorption in the region of 3600–1600 cm^{-1} and C-O-C stretching vibrations at 1140, 1070, and 1040 cm^{-1} (compared with 1120 and 1100 cm^{-1} for **3**).

Thus, the stoichiometry of hydronium ion-crown ether complexes is found to be highly dependent upon the size of the crown ether. For 18-crown-6, the geometry allows the pyramidal hydronium ion to hydrogen bond with three alternate oxygens of the crown ether and thereby form a stable 1:1 complex, **4**. Similar arrangements have been proposed for the complexation of ammonium and monoalkylammonium ions by this crown ether.[18] On the other hand, it seems most reasonable that the 2:1 complex with 12-crown-4 exists as a sandwich complex of the cation between two molecules of **3** similar to those reported for $(Na^+)(\mathbf{3})_2(Cl^-)\cdot 5H_2O$,[19] $(Na^+)(\mathbf{3})_2(OH^-)\cdot 8H_2O$,[20] and $(Mn^{2+})(\mathbf{3})_2(Br_3^-)_2$.[21] Such an arrangement would allow the hydronium ion to hydrogen bond with two alternate oxygens of one crown ether molecule and one oxygen of the second molecule of **3**, as is illustrated in **5**. The geometry for 15-crown-5 is intermediate between that for 18-crown-6 and 12-crown-4. Therefore, the formation of an ill-defined hydronium ion-crown ether complex with neither 1:1 nor 2:1 stoichiometry is not unreasonable.



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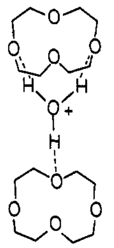

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An attempt to prepare solid hydronium ion-polyether complexes from acyclic polyethers (glymes) met with limited success. By use of the series of glymes from diglyme through heptaglyme, concentrated aqueous HPF_6 as the acid component, and ^1H NMR to determine the stoichiometry, it was found that only triglyme, tetraglyme, and pentaglyme formed well-defined complexes. Of these 1:1 complexes, only that obtained from tetraglyme was a solid (mp 54–57 °C, 52% yield), whereas those formed by triglyme and pentaglyme were oils. Since both tetraglyme and 15-crown-5 contain five ether oxygen atoms, the formation of a complex with definite stoichiometry only from the former suggests that the greater flexibility of the acyclic polyether allows for better complexation with the hydronium ion.

Experimental Section

^1H NMR spectra were recorded in $CDCl_3$ by using a Varian 360 spectrometer and tetramethylsilane as the internal standard. Infrared spectra were measured with a Beckman Acculab 8 spectrophotometer. Ion chromatography was conducted on a Dionex 16 ion chromatograph. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

Materials. 18-Crown-6, 15-crown-5, 12-crown-4, tetraglyme, triglyme, and diglyme were obtained from Aldrich Chemical Co. and were used directly. Heptaglyme, hexaglyme, and pentaglyme (all acquired from Parish Chemical), dichloromethane (MC & B Omnisolve), HPF_6 (65%, Alfa), HBF_4 (37–40%, Spectrum Chemical), $HClO_4$ (70%, Baker), HI (47%, MC & B), and HBr (48%, MC & B) were used as received.

Procedure. To 1.1 mmol of the crown ether in 4 mL of CH_2Cl_2 in a Pyrex or polyethylene test tube is added 1.5–2.2 mmol[22] of the concentrated aqueous acid. The contents of the test tube are shaken with a vortex mixer for 2 min, and the organic layer is separated and dried with anhydrous magnesium sulfate. The volume of the CH_2Cl_2 solution is reduced to 2 mL in vacuo at room temperature. Addition of anhydrous Et_2O (5 mL) precipitates[23] the complex, which is filtered, washed with anhydrous Et_2O (5 mL), and air-dried.

Registry No. (H_3O^+)(18-crown-6)(PF_6^-), 82280-97-5; (H_3O^+)(18-crown-6)(ClO_4^-), 82280-98-6; (H_3O^+)(18-crown-6)(BF_4^-), 82024-63-3; (H_3O^+)(18-crown-6)(I^-), 82280-99-7; (H_3O^+)(18-crown-6)(Br_3^-), 82281-01-4; $(HNO_3\cdot H_2O)_2$(18-crown-6), 82281-02-5; (H_3O^+)(12-crown-4)$_2(PF_6^-)$, 82281-03-6.

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[22] When the crown ether is 12-crown-4, 3.3 mol of the concentrated acid is used.

[23] If precipitation of the complex is slow, it may be hastened by partial removal of the solvents in vacuo with no external heating.

Acyl Hypobromite: An Intermediate in the Alcohol-Silver Salt-Bromine Reaction

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The reaction of alcohols with bromine and silver salts has been the subject of many papers[2] with particular interest in the role of the solvent,[3] the reaction conditions,[4]

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