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Preparation and Decomposition of Potassium Alkalide−Lipophilic Crown Ether Complexes in Tetrahydrofuran

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Received June 20, 2002

Cyclohexano-15-crown-5, cyclohexano-18-crown-6, dicyclohexano-15-crown-5, and dicyclohexano-18-crown-6, but not dicylohexano-16-crown-5, in THF dissolve potassium metal to form dark blue potassium alkalide solutions at ambient temperature. On standing, the potassium alkalide complexes decompose and the solutions turn colorless at differing rates. Identification of the products provides insight into the decomposition mechanism.

Introduction

Since their discovery by Pedersen[1] in 1967, crown ethers have been used widely in organic synthesis,[2−5] biology, and medicine.[6] Due to the presence of several oxygen atoms, these cyclic molecules form complexes with metal cations, as well as with some organic compounds.[7] Some crown ethers dissolve alkali metals in ethereal or amine solvents to form deeply colored solutions in which metal cations are complexed by the crown ether and metal anions and small amounts of solvated electrons are present.[7,8] In addition to the theoretical interest in such solutions, they have also been employed as electron-transfer reagents in organic synthesis[9−15] as well as initiators for anionic polymerization.[11]

The metal solutions are stable only at low temperatures. Reactions taking place during the decomposition of K^-,K^+(18-crown-6) in THF were first described by Jedlinski, Stolarzewicz, and Grobelny[16] in 1986. Some years later, Dye[17] suggested that an important step in the decomposition may be deprotonation of methylene groups in the crown ether by electrons or metal anions leading to formation of hydrogen atoms and carbanions. Cauliez, Jackson, and Dye[18] investigated the decomposition of solvent-free, crystalline salts of M^-, $M'^+(C)_n$, where $(C)_n$ is a crown ether with $n = 1$ or 2, that earlier had been termed alkalides by Dye.[19] The salts decomposed at room temperature under inert atmosphere and several gaseous products (e.g., ethylene, ethane, and butane) were identified. Glymes were obtained when methyl iodide was used as a quenching agent. No other methylated products were observed. This ruled out the presence of carbanions in the reaction mixture. A different decomposition mechanism was proposed by Grobelny, Stolarzewicz, and Maercker from a study of $K^-,K^+(15\text{-crown-}5)_2$ decomposition in solution.[20] It was postulated crown ether ring opening by K^- resulted in an unstable organometallic intermediate that decomposed to ethylene and dipotassium tetraethylene glycoxide. In subsequent reactions, several side products were formed including those from solvent destruction.

Potassium anions were not formed in the presence of benzo-15-crown-5 or benzo-18-crown-6.[21] In these cases, slightly paramagnetic heterogeneous systems were obtained. GC−MS analysis after protonation identified mainly phenol (~70%) and benzene (~30%). It was postulated that initially formed aromatic radical anion

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10.1021/jo026086r CCC: $22.00

TABLE 1. Characterization of Potassium Alkalide−Crown Ether Solutions in THF

entry	crown ether	[K],[a] M	time for K^- decay,[b] h	complexation constant, log K_S, in MeOH[23]
1	15C5	0.19	24.0	3.43
2	CH15C5	0.15	15.0	3.58
3	DCH15C5[c]	0.14	11.5	NR[e]
4	18C6	0.40	1.5	6.08
5	CH18C6	0.40	1.5	5.89
6	DCH18C6[c]	0.40	1.5	5.97
7	DCH18C6[d]	0.40	1.5	5.69

[a] After a potassium mirror was exposed to a 0.20 M solution of the crown ether in THF for 25 min at 20 °C. [b] The solution was left at ambient temperature until the dark blue color faded. [c] Mixture of cis and trans isomers. [d] Mixture of cis-syn and cis-anti isomers. [e] NR = not reported.

intermediates decomposed with cleavage of the crown ether C−O bonds at the α- and β-positions.

In the present work, the preparation of potassium alkalide complexes with several lipophilic cyclohexano- and dicyclohexano-substituted crown ethers in THF was explored, and their decomposition at ambient temperature was investigated. Cyclohexano-15-crown-5 (CH15C5), cyclohexano-18-crown-6 (CH18C6), dicyclohexano-15-crown-5 (DC15C5), dicyclohexano-16-crown-5 (DCH16C5), and dicyclohexano-18-crown-6 (DCH18C6) are included in the study. Contrary to previously examined 15-crown-5 and 18-crown-6 in which all of the C−O bonds are equivalent, these macrocyclic polyethers possess different ethereal bonds that could be cleaved by K^-.

Results and Discussion

Dissolution of Potassium by Lipophilic Crown Ethers in THF. DCH16C5 was found to be ineffective for the dissolution of potassium. After contact with a potassium mirror in THF, only a light blue solution developed and the color was quickly discharged. Apparently, the presence of a propylene bridge in the crown ether results in weak complexation of K^+. Therefore, the DCH16C5 system was excluded from further consideration.

On the other hand, contact of the potassium mirror with CH15C5, CH18C6, DCH15C5, and DCH18C6 in THF for 25 min at 20 °C produced dark blue solutions with high metal concentrations. Data for these systems, as well as some others described in the literature,[16,22,23] are presented in Table 1. As noted previously,[8] stability of the potassium alkalide-crown ether complexes, as measured by the length of time for K^- decay, increases with a decrease of the association constant for the K^+(C) complex. The most stable potassium solution at ambient temperature reported to date was obtained with 15-crown-5 (15C5).[22] In methanol, log $K_a = 3.43$ for complexation of K^+ by 15C5.[23] Markedly less stable was the potassium alkalide solution containing 18-crown-6 (18C6).[16] For complexation of K^+ by 18C6 in methanol, log $K_a = 6.08$.[23] It is worth noting that the potassium alkalide solution with cryptand C222 can be prepared only below −10 °C.[24] In methanol, log $K_a = 10.6$ was estimated for the K^+(C222) complex.[23]

Based upon the time required for discharge of the dark blue color resulting from K^-,[8] stability of the potassium alkalide solutions in THF decreases as the structure of the crown ether varies in the order: 15C5 > CH15C5 > DCH15C5 ≫ 18C6, CH18C6, DCH18C6. The total concentration of dissolved potassium (Table 1) indicates formation of $K^-,K^+(C)_2$ complexes with 15C5, CH15C5, andDCH15C5, but K^-,K^+(C) complexes with 18C6, CH18C6, and DCH18C6.

Decomposition Products from Potassium Alkalide Solutions of Lipophilic Crown Ethers in THF. All of the potassium alkalide solutions became colorless after some time at ambient temperature. The decomposition products were quenched with methyl iodide to provide volatile derivatives for analysis by GC−MS.

Anticipating the presence of cyclohexano-substituted glymes in the quenched reaction products, two cyclohexano-substituted tetraglymes and three cyclohexano-substituted pentaglymes were synthesized as summarized in Scheme 1. The key step in these syntheses was ring-opening of cyclohexene oxide by an alcohol or diol in the presence of catalytic NaH.[25]

GC−MS analysis of products from decomposition of $K^-,K^+(CH15C5)_2$ in THF after quenching with methyl iodide gave mainly two unsaturated hydrocarbons (cyclohexene and ethylene) and three glymes (tetraglyme and cyclohexano-substituted tetraglymes **4** and **6**) (Scheme 2). Thus, cleavage to varying degrees takes place at each of the C−O bonds in the crown ether. Cleavage of the polyether ring at the α-position gives an organometallic intermediate **9** that decomposes with reductive elimination of cyclohexene to form dipotassium tetraethylene glycoxide **10** (Scheme 2). Opening of the crown ether ring at the β- and/or γ-positions leads to organometallic compounds **11** and **12**, respectively. Elimination of ethylene gives a common dipotassium glycoxide **13**. A similar phenomenon is observed for scission of the C−O bond in the δ- and/or ϵ-positions to generate organometallic compounds **14** and **15**. Reductive elimination of ethylene produces the same dipotassium glycoxide **16**.

A similar situation was observed for decomposition of K^-,K^+(CH18C6) in THF to form cyclohexene, ethylene, and dipotassium glycoxides **17**−**20** (Scheme 3). After quenching with methyl iodide, pentaglyme and cyclohexano-substituted pentaglymes **5**, **7**, and **8** were obtained. Once again, cleavage is observed to take place at each of the C−O bonds in the crown ether.

Based upon the global C−O cleavage pattern observed for decomposition of potassium alkalide solutions of CH15C5 and CH18C6, the results found with DCH15C5 and DCH18C6 as the crown ether constituents were quite unexpected. Thus, decomposition of potassium alkalide complexes of DCH15C5 and DCH18C6 in THF (Schemes 4 and 5, respectively) gave only the products from rupture of the C−O bond between the carbon of the cyclohexane ring and the attached oxygen by K^-. Neither ethylene nor glymes substituted with two cyclohexano groups were observed after quenching with methyl iodide. It is

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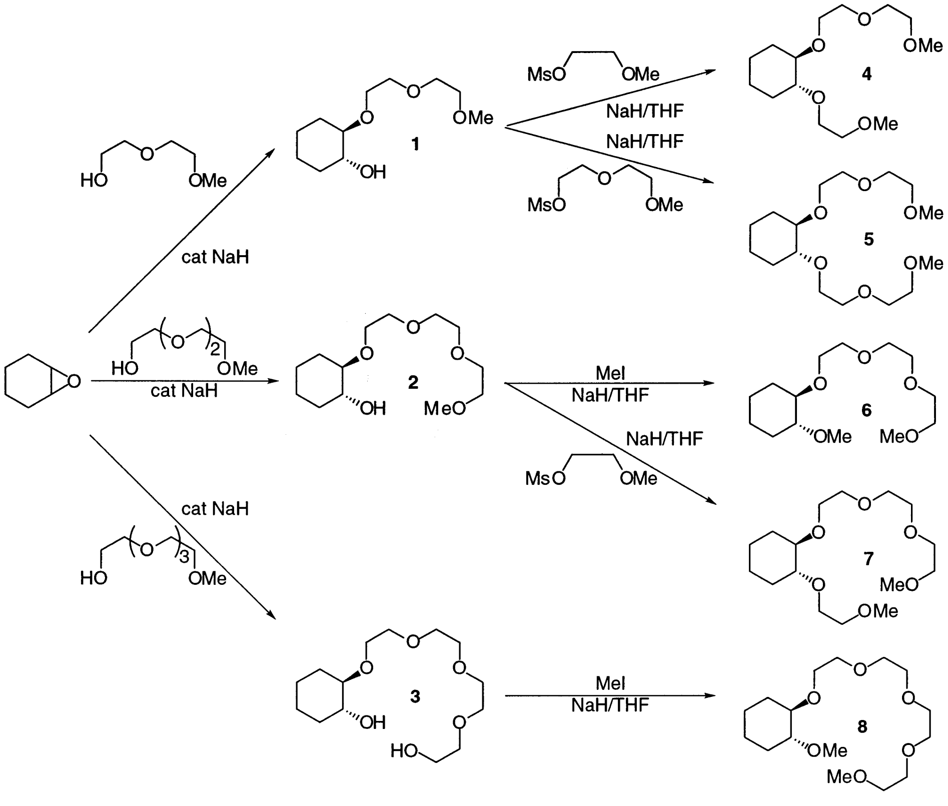
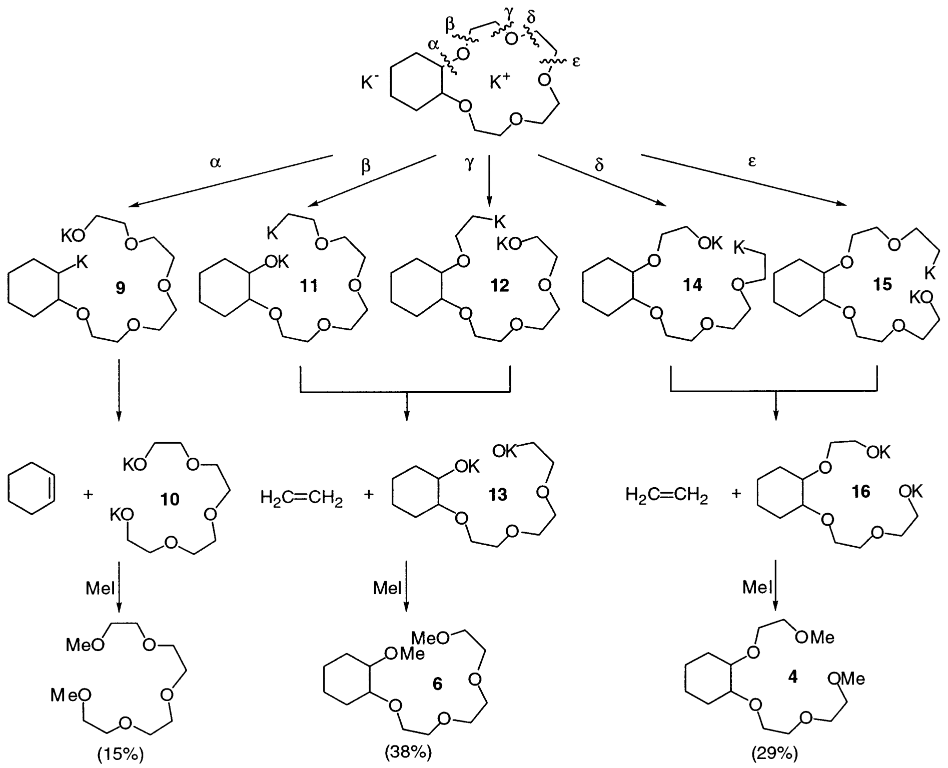
SCHEME 1



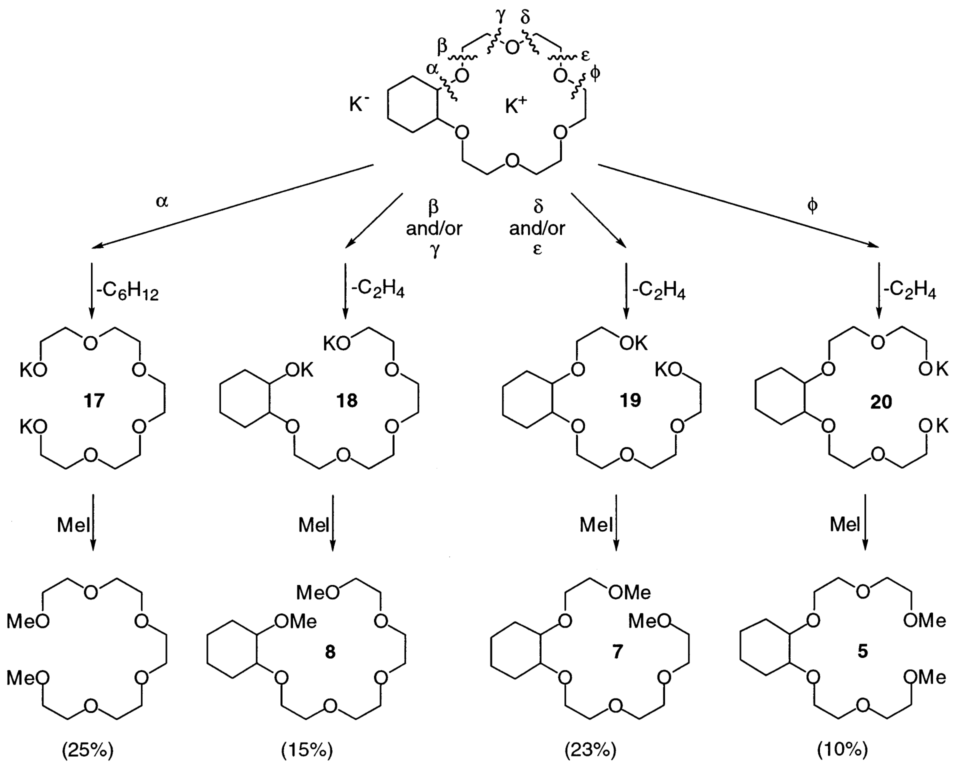
SCHEME 2[a]



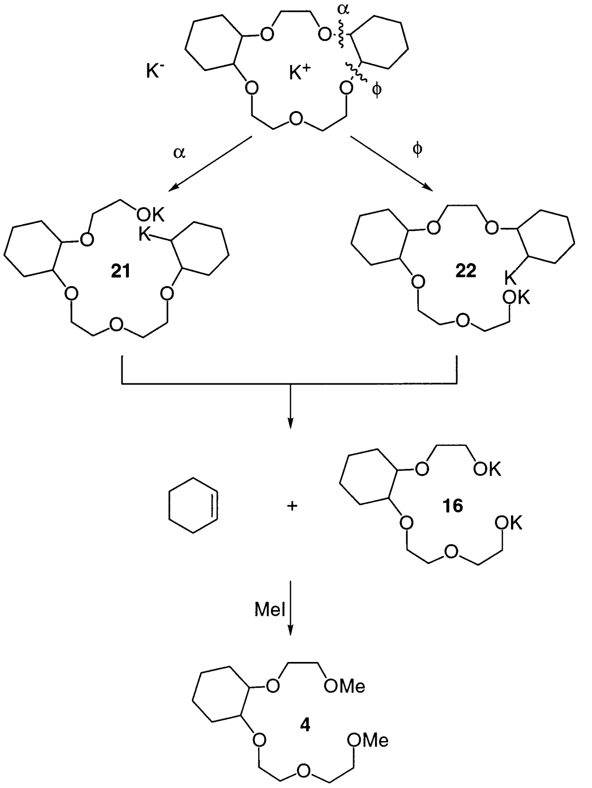
[a] The second crown ether molecule in the complex with K^+ is omitted.

noteworthy that these are the first instances in which ethylene was not observed as a product from decomposition of potassium alkalide solutions of a crown ether. Since decomposition of potassium alkalide solutions of dicyclohexano-24-crown-8 is reported to produce ethylene,[26] the reason for this unusual behavior in the decomposition of DCH15C5 and DCH18C6 is not immediately apparent.

SCHEME 3



SCHEME 4[a]



[a] The second crown ether molecule in the complex with K^+ is omitted.

In decompositions of the potassium alkalide solutions of the four lipophilic cyclohexano- and dicyclohexano-substituted crown ethers, several minor side products were also formed. However, they were not identified due to their low yields.

Conclusions

Self-decomposition of potassium alkalide solutions of cyclohexano- and dicyclohexano-substituted crown ethers in THF is initiated by attack of K^- on the C−O bond of the crown ether. For cyclohexano-substituted crown ethers with 15- and 18-membered rings, all of the C−O bonds are subject to cleavage. Unexpectedly, for analogous dicyclohexano-substituted crown ethers, K^- ruptures only the C−O bonds that link the cyclohexano substituent to the crown ether framework.

These findings, as well as results from the literature,[20] reveal that the precise decomposition mechanism depends on the identity of the crown ether. However, an organometallic intermediate does take part in each process.

Experimental Section

General Considerations. GC−MS analysis of liquids were performed on a 30-m fused silica capillary column DB-5 in a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. Diethylene glycol was used as an internal standard. The gaseous components were determined with a Chromatron GCHF chromatograph at ambient temperature on a 2-m metal column filled with modified alumina. NMR spectra were recorded in deuteriochloroform with a Varian Unity INOVA spectrometer (499.7 MHz for ^1H and 125.7 MHz for ^{13}C) at 23 °C or with a Varian VXR-300 spectometer (300 MHz for ^1H and 75 MHz for ^{13}C) at 20 °C. Chemical shifts (δ) are expressed in ppm downfield from TMS.

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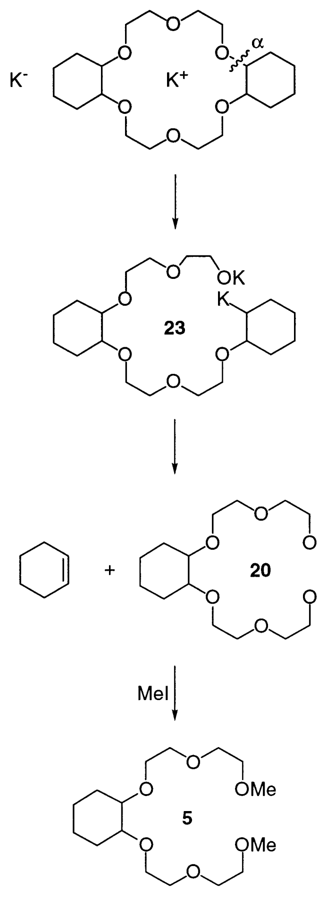
SCHEME 5



Infrared spectra were measured with a Perkin-Elmer 1600 or BIO-RAD FTS-40A FTIR spectophotometer.

THF (POCH) was purified by a reported method.[8] Potassium (Aldrich) was distilled under high vacuum. The crown ethers were dried at 50 °C under high vacuum for several hours before use. CH15C5, CH18C6, and *cis*-DCH18C6 were obtained from Aldrich. DCH18C6 (a mixture of cis and trans isomers) was purchased from Merck.

The GC−MS and NMR spectra of tetraethylene glycol dimethyl ether[12] and pentamethylene glycol dimethyl ether[27] are reported in the literature.

Complete GC−MS data for dicyclohexano-15-crown-5, dicylohexano-16-crown-5, **4**, and **6**−**8** are available as Supporting Information.

Dicyclohexano-15-crown-5.[1c] A mixture of 8.26 g (2.61 mmol) of dibenzo-15-crown-5,[1a] 1.6 g of glacial acetic acid, and 0.75 g of 5% rhodium on alumina catalyst in 200 mL of 1-BuOH was reacted under hydrogen (700 psi) at 110 °C for 2 h in a Parr pressure reactor. The mixture was cooled to room temperature, and the hydrogen pressure was released. While being flushed with nitrogen, the reactor was opened and another 0.75 g of catalyst was added. After hydrogenation for 2 h, a third catalyst addition was made in the same manner. After another 2 h, the mixture was filtered through Celite and the 1-BuOH was evaporated in vacuo. The residue was passed through a short column of alumina with dichloromethane as eluent to give 7.00 g (81%) of DCH15C5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00−2.05 (m, 16H), 3.15−3.95 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.4, 27.4−27.9, 67.7, 68.5, 70.9, 77.2−77.9. IR (neat): 1103 (CO) cm^{-1}. MS: *m*/*e* 328 (M$^+$).

Dicyclohexano-16-crown-5.[1c] Hydrogenation of dibenzo-16-crown-5[1a] under similar conditions gave a 70% yield of DCH16C5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.10−2.04 (m, 18H), 3.10−3.90 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): 21.6−22.6, 27.1−28.3, 30.9−31.4, 66.2, 67.7, 68.4, 70.6, 71.2, 75.9, 76.7, 77.8, 78.2. IR (neat): 1111 (CO) cm^{-1}. MS: *m*/*e* 342 (M$^+$).

***trans*-2-[2-(Methoxy)ethoxy]ethoxycyclohexanol (1).** Under nitrogen, a mixture of 2-[2-(methoxy)ethoxy]ethanol (12.50 g, 100 mmol) and 95% NaH (0.26 g, 10 mmol, 0.1 equiv) was heated at 80 °C until a homogeneous solution was obtained. The temperature was raised to 110 °C, and cyclohexene oxide (10.20 g, 103 mmol) was added. The mixture was stirred at 110 °C for 4 h and cooled to room temperature. Vacuum distillation (160−170 °C/0.4 Torr) gave 10.60 g (49%) of **1**. Anal. Calcd for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.51; H, 10.44. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14−1.31 (m, 4H), 1.67−1.73 (m, 2H), 1.98−2.04 (m, 2H), 3.04−3.09 (m, 1H), 3.39 (s, 1H), 3.40−3.46 (m, 1H), 3.49 (d, 1H, J = 1.2 Hz), 3.54−3.57 (m, 2H), 3.58−3.63 (m, 1H), 3.65−3.70 (m, 4H), 3.85−3.89 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.0, 24.4, 29.8, 32.2, 59.0, 68.5, 70.4, 70.7, 71.9, 73.9, 84.8. IR (neat): 3453 (OH); 1101, 1039 (CO) cm^{-1}.

***trans*-2-(10-Methoxy-1,4,7-trioxanonyl)cyclohexanol (2).** By the same procedure, cyclohexene oxide and $MeOCH_2(CH_2OCH_2)_3CH_2OH$ were reacted to provide **2** in 52% yield after vacuum distillation (180 °C/0.8 Torr). Anal. Calcd for $C_{13}H_{26}O_5$: C, 59.52; H, 9.99. Found: C, 59.67; H, 10.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16−1.28 (m, 4H), 1.67−1.73 (m, 2H), 1.98−2.04 (m, 2H), 3.03−3.08 (m, 1H), 3.38 (s, 1H), 3.41,−3.45 (m, 1H), 3.49 (d, 1H), J = 1.5 Hz), 3.55−3.56 (m, 2H), 3.58−3.63 (m, 1H), 3.64−3.69 (m, 4H), 3.85−3.89 (m, 1H). ^{13}C NMR (126 MHz): δ 24.0, 24.4, 29.9, 32.2, 59.0, 68.6, 70.48, 70.54, 70.8, 71.9, 73.9, 84.8. IR (neat): 3443 (OH); 1103, 1049 (CO) cm^{-1}.

***trans*-2-(12-Hydroxy-1,4,7,10-tetraoxadodecyl)-1-cyclohexanol (3).** By the same procedure, cyclohexene oxide and tetraethylene glycol (3 equiv) gave **3** in 25% yield after vacuum distillation (170 °C/0.4 Torr). Anal.Calcd for $C_{14}H_{28}O_6$: C, 57.51; 9.65. Found: C, 57.35; H, 9.54. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13−1.26 (m, 4H), 1.65−1.68 (m, 2H), 1.98−2.00 (m, 2H), 3.03−3.07 (m, 1H), 3.43 (br s, 2H), 3.81−3.83 (m, 1H), 4.01 (d, 1H, J = 1.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.0, 24.3, 29.7, 32.1, 61.51, 61.52, 68.4, 70.2, 70.36, 70.39, 70.5, 70.6, 73.7, 84.6. IR (neat): 3416 (OH), 1096 (CO) cm^{-1}.

***trans*-2-[[2-Methoxy)ethoxy]ethoxy]-1-[(2-methoxy)ethoxy]cyclohexane (4).** Under nitrogen, **1** (3.30 g, 15.0 mmol) and 95% NaH (0.43 g, 18 mmol) were refluxed for 0.5 h. A THF solution of $MsOCH_2CH_2OMe$ (2.70 g, 18 mmol) was added via syringe pump during a 1-h period, and the mixture was refluxed overnight. After the mixture was cooled to room temperature, Et_2O was added, and the solution was washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was chromatographed on alumina with hexanes−EtOAc (10:1) as eluent to give 1.87 g (45%) of **4**. Anal. Calcd for $C_{16}H_{32}O_6$: C, 60.84; H, 10.21. Found: C, 61.08, 10.24.. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13−1.32 (m, 4H), 1.62−1.67 (m, 2H), 1.96−2.00 (m, 2H), 3.17−3.24 (m, 2H), 3.37 (s, 3H), 3.38 (s, 3H), 3.48−3.57 (m, 4H), 3.63−3.67 (m, 4H), 3.71−3.79 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.55, 23.59, 30.2, 30.3, 58.87, 58.92, 69.21, 69.29, 70.3, 70.9, 71.9, 72.4, 81.97, 82.01. IR (neat): 1106 (CO) cm^{-1}. MS: *m*/*e*: 277 (M$^+$).

***trans*-1,2-Bis[[2-(methoxy)ethoxy]ethoxy]cyclohexane (5).** By the same procedure, **1** and $MsOCH_2(CH_2OCH_2)_2CH_2OMe$ were reacted to form the crude product. Vacuum distillation (130−133 °C/0.4 Torr) gave a 50% yield of **5**. Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07. Found: 59.62; H, 10.11. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15−1.19 (m, 2H), 1.21−1.26 (m, 2H), 1.63−1.64 (m, 2H), 1.95−1.97 (m, 2H), 3.17−3.22 (m, 2H), 3.37 (s, 6H), 3.51−3.55 (m, 4H), 3.60−3.67 (m, 8H). 3.73−3.75 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.6, 30.3, 59.0, 70.4, 71.0, 72.0, 81.9. IR (neat): 1106 (CO) cm^{-1}. MS *m*/*e* (rel intens): 321 (0.5, M$^+$), 200 (4), 186 (6), 142 (16), 141 (22), 121 (13), 103 (50), 87 (12), 81 (34), 59 (100), 45 (76).

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***trans*-2-(10-Methoxy-1,4,7-trioxanonyl)cyclohexyl methyl ether (6).** By the same procedure, **2** and MeI (3.9 equiv) were reacted to give the crude product. Vacuum distillation (120 °C/0.4 Torr) gave **6** in 37% yield. Anal. Calcd for $C_{12}H_{22}O_5$: C, 60.84; H, 10.21. Found: C, 61.20; H, 10.23. ^1H NMR (500 MHz, $CDCl_3$): δ 1.12−1.29 (m, 4H), 1.59−1.63 (m, 2H), 1.92−1.98 (m, 2H), 3.04−3.08 (m, 1H), 3.14−3.19 (m, 1H), 3.35 (S, 3H), 3.40 (s, 3H), 3.51−3.54 (m, 2H), 3.58−3.67 (m, 8H), 3.68−3.72 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.36, 23.43, 29.4, 29.9, 57.3, 59.0, 69.0, 70.4, 70.6, 70.9, 71.9, 81.7, 82.5. IR (neat): 1103 (CO) cm^{-1}. MS: *m*/*e* 277 (M^+).

***trans*-1,2-Bis[[2-(methoxy)ethoxy]ethoxy]cyclohexane (7).** By the same procedure, **2** and $MsOCH_2(CH_2OCH_2)_2$-CH_2OMe were reacted to give the crude product. Vacuum distillation (140−150 °C/0.4 Torr) provided a 45% yield of **7**. Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07. Found: C, 59.87; H, 10.07. ^1H NMR (500 MHz, $CDCl_3$): δ 1.14−1.32 (m, 4H), 1.64−1.66 (m, 2H), 1.97−1.99 (m, 2H), 3.12−3.24 (m, 2H), 3.38 (s, 3H), 3.39 (s, 3H), 3.49−3.57 (m, 4H), 3.61−3.70 (m, 8H), 3.71−3.79 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.66, 23.69, 30.4, 58.98, 59.03, 69.3, 69.4, 70.5, 70.6, 71.0, 71.9, 72.5, 82.1. IR (neat): 1106 (CO) cm^{-1}. MS: *m*/*e* 321 (M^+).

***trans*-2-(12-Methoxy-1,4,7,10-tetraoxadodecyl)-1-cyclohexyl methyl ether (8).** By the same procedure, **3** and MeI (3 equiv) were reacted to produce the crude product. Vacuum distillation (150−160 °C/0.4 Torr) gave a 38% yield of **8**. Anal. Calcd for $C_{16}H_{32}O_6$: C, 59.97; H, 10.07. Found: C, 60.18; H, 9.97. ^1H NMR (500 MHz, $CDCl_3$): δ 1.17−1.32 (m, 4H), 1.62−1.66 (m, 2H), 1.95−2.01 (m, 2H), 3.07−3.11 (m, 1H), 3.17−3.21 (m, 1H), 3.38 (s, 3H), 3.43 (s, 3H), 3.54−3.57 (m, 2H), 3.61−3.69 (m, 12H), 3.71−3.75 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.4, 23.5, 29.5, 30.0, 57.4, 59.0, 69.1, 70.50, 70.53, 70.57, 70.61, 71.9, 91.7, 82.6. IR (neat): 1103 (CO) cm^{-1}. MS: *m*/*e* 321 (M^+).

Preparation and decomposition of potassium alkalide-crown ether complexes in THF. Using a reported procedure,[8] dark blue potassium alkalide solutions were prepared by dissolution of a potassium mirror through contact with a 0.20 M solution of the crown ether in THF for 25 min at 20 °C. After being filtered through a glass frit, the solution was allowed to stand at ambient temperature until its blue color faded. After addition of MeI to the colorless solution, the quenched reaction solution was analyzed by GC−MS, GC, and NMR spectroscopy. The methylated decomposition products were identified by matching their mass spectra, retention times, and ^1H and ^{13}C NMR spectra, respectively, with those of authentic compounds.

Acknowledgment. We are indebted to Dr. K. Skutil for analysis of the gaseous reaction products. This work was supported in part by the Committee of Scientific Research in Poland (Project No. 3 TO9A 097 18). The work performed at Texas Tech University was supported by The Welch Foundation (Grant No. D-775). The US National Science Foundation is thanked for Grant No. CHE-9808436, which was used to purchase the Varian Unity INOVA NMR spectrometer at TTU.

Supporting Information Available: Complete MS data for DC15C5, DC16C5, **4**, and **6**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026086R