Synthesis of Crown Ethers That Geometrically Orient Cations Relative to a Naphthalene π System. A Look at the Equilibration of Enantiomeric Conformations by "Rope-Skipping" Crown Ethers

Houston S. Brown,[1a] Chrysa P. Muenchausen, and Lynn R. Sousa*[1b]

Departments of Chemistry, Michigan State University, East Lansing, Michigan 48824, and Ball State University, Muncie, Indiana 47306

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A number of new naphthalene crown ethers were synthesized in moderate yield from the appropriate bis(halomethyl)naphthalenes and polyethylene glycols. The following crown ethers were synthesized: 2,3-naphtho-14-crown-4 (15%), 2,3-naphtho-17-crown-5 (19%), 2,3-naphtho-20-crown-6 (36%), 1,8-naphtho-15-crown-4 (20%), 1,8-naphtho-18-crown-5 (7%), 1,8-naphtho-21-crown-6 (38%), 1,2-naphtho-20-crown-6 (4%), 1,5-naphtho-22-crown-6 (14%), 1,5-naphtho-19-crown-5 (11%), 1,4-naphtho-22-crown-6 (9%), 1,3-naphtho-21-crown-6 (16%). These crown compounds form a series in which complexed cations perturb the naphthalene π system from different directions. Experimental evidence concerning the ease of equilibration of enantiomeric conformations by "rope-skipping" crown ethers is also reported. The equilibration of 1,5-naphtho-22-crown-6 enantiomeric conformations has about a 6.3-kcal energy of activation, while the corresponding barrier for 1,5-naphtho-19-crown-5 is greater than 21 kcal.

Crown ethers[2] have been used as synthetic agents which solubilize salts and increase anion activity,[2,3] as agents for the study of ion pairs,[2] as protective groups for aryl diazonium salts,[4] as complexers in molecular hosts which act as catalysts,[5] and as complexers which select on the basis of cation size, polarizability,[2] or absolute configuration.[6]

Crown ethers are also well suited for the study of interactions between the complexed cation and functional groups attached to the crown ring. We have recently reported on the interaction of the naphthalene system and cations complexed by crowns **3**, **6**,[7,8] and **9**.[9] Some of the studies[7,9] have focused on the response of naphthalene photoexcited states to complexed and therefore oriented alkali metal cations. Other work[8] has investigated field-induced π polarization of naphthalene by an oriented positive monopole (complexed cation) using ^{13}C NMR. X-ray studies of **6**, complexed **6**,[10] and complexed **3**[11] have given some indication of crown conformation as has ^{13}C NMR work. The synthesis of the crown ethers used in our previously published work will be presented in detail for the first time, and a number of new crown compounds will be described.

This report will also consider the conformational mobility of two "rope-skipping" crown ethers. Crowns such as 1,5-naphtho-22-crown-6 (**9**) and 1,5-naphtho-19-crown-5 (**8**) presumably exist most of the time in conformations with the polyether ring arching above the face of the naphthalene ring. If the polyether strand moves past the edge of the naphthalene system so that the polyether arch is under the ring, a new conformation results which is enantiomeric with the first. We wanted to determine what polyether ring size was required to make this enantiomer equilibrating "rope skipping" possible and to determine whether complexation of cations by the crown would greatly affect the rate of this conformational change.

Results and Discussion

Crown Synthesis. Although benzylic crowns have been reported a number of times,[12] naphthylic crown ethers are rare.[12,13] Our first synthesis of **3** and **6**[7] used the appropriate bis(hydroxymethyl)naphthalene and pentaethylene glycol ditosylate which were stirred together at room temperature with 2 equiv of potassium *tert*-butoxide in tetrahydrofuran with 10% dimethylformamide. The yields of **3** and **6** after chromatography and careful recrystallization were only 16 and 8%, respectively. Typically, crown ethers which are prepared from phenol derivatives are produced in better yields, owing to the increased nucleophilicity of the phenoxide ion over the benzylic alkoxide in the usual media.

A higher yield crown closure reaction for **3** and **6** involves the dropwise addition of an equimolar mixture of the appropriate bis(bromomethyl)naphthalene and pentaethylene glycol in dry tetrahydrofuran to a stirred refluxing slurry of potassium *tert*-butoxide in tetrahydrofuran. The yields of **3** and **6** after workup, alumina chromatography, and careful recrystallization are 35 and 38%, respectively.

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(1) (a) Current address: Packaging Systems Laboratory, 3M Center, St. Paul, MN. (b) To whom correspondence should be addressed at Ball State University.

(2) For some reviews of crown ether chemistry see: (a) R. M. Izatt and J. J. Christensen, Eds., "Progress in Macrocyclic Chemistry", Vol. 1, Wiley-Interscience, New York, 1979; (b) C. J. Pederson and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (c) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974); (d) D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974); (e) J.-M. Lehn, *Struct. Bonding (Berlin)*, 16 (1973); (f) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976).

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(6) D. J. Cram et al., *Pure Appl. Chem.*, **43**, 327 (1975).

(7) L. R. Sousa and J. M. Larson, *J. Am. Chem. Soc.*, **99**, 307 (1977).

(8) (a) L. R. Sousa and M. R. Johnson, *J. Am. Chem. Soc.*, **100**, 344 (1978); (b) L. R. Sousa, M. R. Johnson, and H. S. Brown, Second Symposium on Macrocyclic Compounds, Provo, UT, Aug 1978.

(9) Results with crown **9** were presented in part by J. M. Larson and L. R. Sousa, 174th National Meeting of the American Chemical Society, Chicago, IL, Aug 1977.

(10) D. L. Ward, H. S. Brown, and L. R. Sousa, submitted for publication.

(11) D. L. Ward, H. S. Brown, and L. R. Sousa, *Acta Crystallogr., Sect. B*, **33**, 3537 (1977).

(12) For a recent review, see D. N. Reinhoudt and F. DeJong in "Progress in Macrocyclic Chemistry", Vol. 1, R. M. Izatt and J. J. Christensen, Eds., Wiley-Interscience, New York, 1979, p 157.

(13) E. Weber and F. Vögtle, *Chem. Ber.*, **109**, 1803 (1976).

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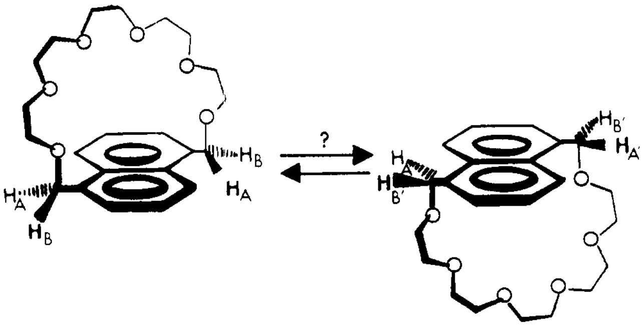
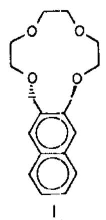


Figure 1. Equilibration of enantiomeric conformations of 1,5-naphtho-22-crown-6 (9).

The other crown-forming reactions with the appropriate bis(bromomethyl)naphthalene and polyethylene glycol gave the following compounds in the yields indicated: **1**, 15%; **2**, 19%; **4**, 20%; **5**, 7%; **8**, 11%; **9**, 14%; **10**, 9%; **11**, 16%. Crown **7** was synthesized in 4% yield from 1-(chloromethyl)-2-(bromomethyl)naphthalene, which in turn was prepared by *N*-bromosuccinimide bromination of 1-(chloromethyl)-2-methylnaphthalene. A convenient method of production of the known[14] bis(bromomethyl)naphthalenes used *N*-bromosuccinimide in carbon tetrachloride with catalysis by a sunlamp.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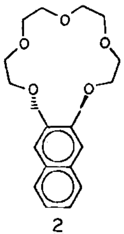
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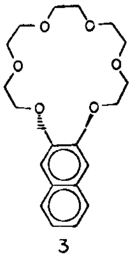
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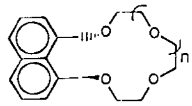
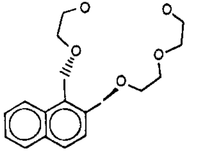

4, n=1
5, n=2
6, n=3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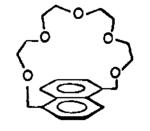
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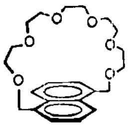
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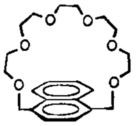
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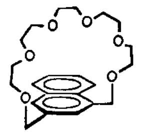
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The set of crown ethers described here provide for extensive testing of the way complexed ions interact with the naphthalene system. For example, the following aspects of geometry can be adjusted: (1) cation–naphthalene distance (**1**, **2**, and **3**; **4**, **5**, and **6**); (2) cation angular position in the modal plane of the naphthalene moiety (**3**, **6**, and **7**); (3) cation positioning at several points above the π face of the naphthalene (**8**, **9**, **10**, and perhaps **11**). The methylene groups are interposed next to naphthalene in each case to insulate the π system from the crown ether oxygens.

Crown Conformational Changes. "Rope-Skipping" by 1,5-Crowns. Crowns **8** and **9** are different from **1**–**7**, **10**, and **11** in that enantiomeric conformations such as those shown in Figure 1 can interconvert only if the ethyleneoxy strand can stretch past the naphthalene ring and arch across the opposite face of the π system. The other crowns may also perfer chiral conformations. For example, an X-ray structure determination of **6**[11] shows it to prefer chiral conformations in the solid state, as do **3**[10] and **6**[11] when complexing potassium thiocyanate. However, the enantiomeric conformations of **1**–**7**, **10**, and **11** are interconverted by relatively facile changes in the dihedral angles around the crown ring.

The Corey–Pauling–Koltun (CPK) model of crown **9** allows the six-oxygen ethyleneoxy strand to slip past the edge of the naphthalene system without much difficulty. Even the CPK model of crown **8** allows its five-oxygen ethyleneoxy strand to slip around to the other face of the naphthalene, but just barely. If the CPK model sizes reflect behavior at room temperature, the ethyleneoxy strand of crown **8** should be sweeping around the naphthalene faces slowly but measurably. Crown **9** might be expected to be "skipping" the strand rapidly. In both crowns **8** and **9**, the models show that the interconversion of enantiomeric conformations requires that the ethyleneoxy strand free any previously complexed cation. The polyethyleneoxy strand would in effect be wiped free of ions bound by more than two crown oxygens as it passes the edge of the naphthalene ring. Therefore, complexed ions might be expected to slow the turning of the ether strand if the rate of ion decomplexation is slower than the rate of rope skipping.

Experimental evidence of the extent of equilibration of the enantiomeric conformations of crowns **8** and **9** is given by the ^{1}H NMR signal(s) of the naphthylic hydrogens (H_A and H_B in Figure 1). When the ethyleneoxy strand is over a face of the naphthalene ring, one hydrogen (H_A) on each naphthalene carbon is directed in the general direction of the peri hydrogen, and the other (H_B) is directed out away from the naphthalene system. Rope skipping would interchange the situations of the A and B hydrogens.

The ^{1}H NMR spectrum of the six-oxygen 1,5-crown **9** shows a sharp singlet in the naphthylic region at room temperature. Assuming that H_A and H_B have different chemical shifts (see below), the ethyleneoxy strand is slipping past the naphthalene ring rapidly, as expected from inspection of CPK models. The five-oxygen 1,5-crown **8** has an AB quartet in the naphthylic region of its room-temperature NMR spectrum, indicating its equilibration is even slower than that predicted from CPK model work. In fact the AB quartet of **8** showed no sign of coalescence even when the spectrum was measured at 160 °C (see Figure 2). This implies that the free energy of activation for rope skipping of **8** is greater than 21 kcal/mol.

Low-temperature NMR spectra of crown **9** were measured to determine the free-energy barrier for equilibration of the enantiomeric conformations and are shown in Figure 3. The coalescence temperature was −134 °C (139 K), so the free energy of activation is about 6.3 kcal/mol. The reasonably low $\Delta G^{\ddagger}$ for rotation indicates that the dual requirements that the polyethyleneoxy strand slip past the naphthalene ring and that rotation about two C_{sp^2}–C_{sp^3} bonds take place (although probably not synchronously) do not add exorbitantly to the cost of rotating about one C_{sp^2}–C_{sp^3} bond. The barrier to rotation about the C_{sp^2}–C_{sp^3} bond in 2-methylpropene, for example, is 2.2 kcal/mol. The free-energy barrier at room temperature is likely to be even lower than 6.3 kcal/mol since the end-to-end length of polyethyleneoxy strands has been shown to decrease as the temperature is decreased.[15] Attempts to slow

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(14) W. Reid and H. Bodem, *Chem. Ber.*, 91, 1981 (1958).

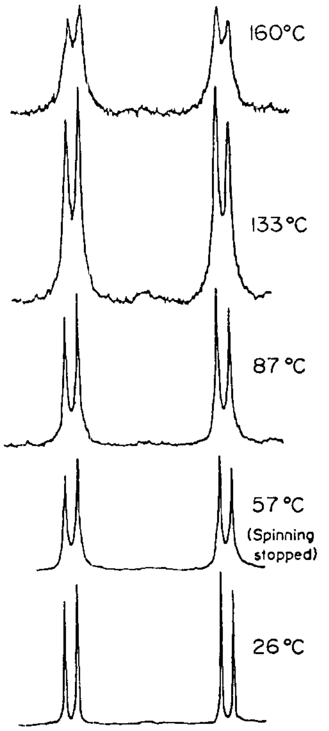

Figure 2. High-temperature ^{1}H NMR spectra of 1,5-naphtho-19-crown-5 (**8**), naphthylic region.

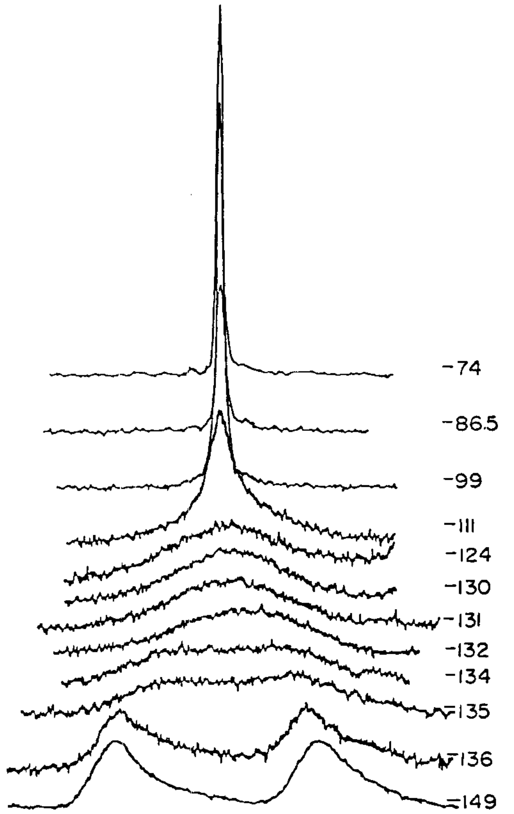

Figure 3. Low-temperature ^{1}H NMR spectra of 1,5-naphtho-22-crown-6 (**9**).

rope skipping by the addition of salts to crown **9** solutions were partially frustrated by the lack of solubility of salts at low temperatures and the relatively low complexation constants of **9** with most cations. No slowing of equilibration was observed when the ^{1}H NMR spectrum of **9** was measured with saturated potassium chloride in acetone-d_6 at −80 °C. Judging from ^{13}C NMR experiments in alcohol at room temperature which show complexation of **9** with this salt[16] and the fact that lower temperatures increase the complexation constant of this particular crown,[17] the cation should be complexed under the conditions of the experiment. The indication is that the rate of cation decomplexation is fast on the NMR time scale at −80 °C and thus does not affect the spectrum even though decomplexation might be slowing down the equilibration of the enantiomeric conformations.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. The ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer with deuteriochloroform (1538.2 Hz) as an internal standard. The ^{1}H NMR spectra were taken on a Varian T-60 spectrometer with tetramethylsilane as an internal standard, except high-resolution spectra, which were taken on a Bruker WH-180 multinuclear spectrometer, with a 10-mm proton insert. Low-temperature spectra (<−90 °C) were taken with 10 mg of the crown dissolved in 3 mL of dichlorodifluoromethane with 0.3 mL of deuterioacetone as a lock solvent and 0.1 μL of tetramethylsilane as an internal standard. High-temperature spectra (>35 °C) were taken with 10 mg of the crown dissolved in 3 mL of dimethyl-d_6 sulfoxide with 0.1 μL of tetramethylsilane as an internal standard. The mass spectra were taken on a Hitachi Perkin-Elmer RMU-6D spectrometer. Tetrahydrofuran was distilled from sodium benzophenone ketyl immediately before use. All reactions were done under nitrogen. Microanalyses were performed by Chemalytics, Inc., or Instranal Laboratory.

General Procedure for the Synthesis of Bis(bromomethyl)naphthalenes. Dimethylnaphthalene (10.0 g, 64.0 mmol) and recrystallized *N*-bromosuccinimide[18] (46.0 g, 258 mmol) in 250 mL of carbon tetrachloride were irradiated with a 200-W sunlamp. The reaction was greater than 90% complete (^{1}H NMR) in less than 30 min after noticeable conversion of the *N*-bromosuccinimide to succinimide started, even though the induction period was highly variable. The mixture was filtered, and the succinimide was extracted with hot carbon tetrachloride. Some of the dibromides were exceedingly soluble in carbon tetrachloride [e.g., the 2,3-bis(bromomethyl)naphthalene], but others (e.g., 1,4 and 1,5) required multiple extractions to separate all of the brominated product from the succinimide. The combined filtrate and extracts were evaporated to give 72–81% yields of the dibromide. The dibromides could be recrystallized from benzene–petroleum ether to remove traces of monobrominated and unbrominated material.

The following compounds were prepared as described above. 2,3-Bis(bromomethyl)naphthalene: 81% yield; mp 145–146 °C; ^{1}H NMR ($CDCl_3$) δ 4.77 (s, 4 H), 7.15–7.7 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 30.88, 127.08, 127.60, 130.63, 133.19, 133.66. 1,4-Bis(bromomethyl)naphthalene: 72% yield; mp 190–191 °C; ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 4 H), 7.3–8.1 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 31.05, 124.50, 126.76, 127.14, 131.53, 134.85. 1,5-Bis(bromomethyl)naphthalene: 78% yield; mp 213.5–214 °C; ^{1}H NMR ($CDCl_3$) δ 4.87 (s, 4 H), 7.1–8.3 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 31.46, 125.29, 125.94, 128.03, 134.08. 1,3-Bis(bromomethyl)naphthalene: 76% yield; mp 116–116.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.50 (s, 2 H), 4.77 (s, 2 H), 7.2–8.1 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 30.86, 33.10, 123.53, 126.65, 127.06, 128.29, 128.75, 129.25, 130.51, 133.68, 134.11, 134.46. 1-(Chloromethyl)-2-(bromomethyl)naphthalene: 78% yield; mp 130–131.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.83 (s, 2 H), 5.08 (s, 2 H), 7.08–8.07 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 30.52, 37.99, 123.48, 126.47, 127.21, 127.49, 128.59, 129.93, 131.50, 131.65, 133.60, 134.45.

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(15) (a) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965). (b) For an application to crown ethers, see G. R. Newkome, A. Nayak, F. Fronczek, T. Kawato, H. C. R. Taylor, L. Meade, and W. Mattice, *J. Am. Chem. Soc.*, **101**, 4472 (1979).

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(18) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).

1,8-Bis(bromomethyl)naphthalene. The dimethyl ester of 1,8-naphthalenedicarboxylic acid was prepared by the method of Geissman and Morris[19] from the 1,8-naphthalic anhydride (Aldrich). The dimethyl ester was reduced with lithium aluminum hydride (Alfa Ventron) in tetrahydrofuran to the corresponding diol in quantitative yield.[20] 1,8-Bis(hydroxymethyl)naphthalene was then brominated by the method of Bergmann and Szmuszkovicz[21] to give 1,8-bis(bromomethyl)naphthalene: mp 130–131 °C; ^{1}H NMR ($CDCl_3$) δ 5.22 (s, 4 H), 7.20–7.80 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 35.43, 123.91, 127.27, 130.11, 131.26, 131.63, 134.30.

General Procedure for the Synthesis of the Crowns. A solution of the appropriate polyethylene glycol (10 mmol) and bis(halomethyl)naphthalene (10 mmol) in 150 mL of dry THF was added dropwise to a refluxing tetrahydrofuran slurry of potassium *tert*-butoxide (2.36 g, 21 mmol in 500 mL of THF) over a 6-h period under a dry nitrogen atmosphere. The slurry was stirred at reflux another 4 h before filtration through a diatomaceous earth pad and subsequent washing of the solid with tetrahydrofuran. Solvent was removed from the filtrate under vacuum, and the resulting yellow oil was chromatographed on a quartz column with alumina (400 g, Fisher neutral alumina with Lumilux[22] added) eluted with dichloromethane–methanol (200:1). The first band eluted which was observable on the column by using a 375-nm lamp gave a yellow-brown oil. Some of the fractions of this band crystallize from ether–pentane and can be recrystallized from cyclohexane except as otherwise noted.

2,3-Naphtho-14-crown-4 (1) was prepared as above except that lithium *tert*-butoxide (1.67 g, 21 mmol) and triethylene glycol (1.44 g, 10 mmol) were used: yield 460 mg (15.2%); mp 86–88 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 4 H), 3.73 (s, 8 H), 4.87 (s, 4 H), 7.13–7.68 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.27, 70.00, 71.37, 71.46, 125.72, 127.46, 132.83, 134.89; IR ($CHCl_3$) 3000, 2850 (s), 1550, 1450, 1350, 1300, 1250, 1125 (s), 1025 (w), 975, 925, 900, 875, 800 cm^{-1}; mass spectrum, *m*/*e* 302.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.77; H, 7.40.

2,3-Naphtho-17-crown-5 (2) was prepared as above except that lithium *tert*-butoxide (1.67 g, 21 mmol) and tetraethylene glycol (1.67 g, 10 mmol) were used: yield 652 mg (18.8%); mp 51.0–53.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.58 (s, 10 H), 3.70 (s, 10 H), 4.8 (s, 4 H), 7.15–7.73 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.69, 70.43, 70.71, 70.96, 71.14, 125.71, 126.85, 127.44, 132.63, 134.69; IR ($CDCl_3$) 2850 (s), 1550, 1450, 1350, 1300, 1250 (w), 1100 (s), 980, 950, 890, 810 (s) cm^{-1}; mass spectrum, *m*/*e* 346.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.58; H, 7.36.

2,3-Naphtho-20-crown-6 (3) was prepared as above with pentaethylene glycol (2.39 g, 10 mmol): yield 1.39 g (35.6%); mp 58.0–58.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.63 (s, 12 H), 3.68 (s, 8 H), 4.78 (s, 4 H), 7.13–7.77 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.80, 70.67, 71.31, 125.72, 127.35, 127.57, 132.63, 134.55; IR ($CHCl_3$) 3000, 2850–2825 (s), 1470 (w), 1450 (w), 1350, 1075–1150 (s) cm^{-1}; mass spectrum, *m*/*e* 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.65; H, 7.89.

1,8-Naphtho-15-crown-4 (4) was prepared as above except that lithium *tert*-butoxide (1.67 g, 21 mmol) and triethylene glycol (1.44 g, 10 mmol) were used: yield 619 mg (20.5%); mp 77.0–77.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 4 H), 3.80 (s, 8 H), 5.17 (s, 4 H), 7.28–7.77 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.74, 70.19, 71.09, 73.13, 124.79, 128.17, 129.43, 134.74, 135.33; IR ($CHCl_3$) 3010, 2860 (s), 1600 (w), 1450, 1350, 1290, 1240, 1100, 1000 (w), 960, 940, 875, 800 (s) cm^{-1}; mass spectrum, *m*/*e* 302.

Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.72; H, 7.47.

1,8-Naphtho-18-crown-5 (5) was prepared as above except that lithium *tert*-butoxide (1.67 g, 21 mmol) and tetraethylene glycol (1.94 g, 10 mmol) were used: yield 239 mg (6.9%); mp 69.5–70.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 8 H), 3.72 (s, 8 H), 5.03 (s, 4 H), 7.22–7.70 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 70.00, 70.19, 70.66, 77.16, 124.73, 129.01, 129.68, 130.69, 134.21; IR ($CHCl_3$) 3000, 2850, 1720 (w), 1600 (w), 1450, 1350, 1300, 1250 (w), 1100 (s), 1000, 940 (w), 880, 800 (s) cm^{-1}; mass spectrum, *m*/*e* 346.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.49; H, 7.47.

1,8-Naphtho-21-crown-6 (6) was prepared as above with pentaethylene glycol (2.39 g, 10 mmol): yield 1.50 g (38.4%); mp 53.5–55.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 12 H), 3.78 (s, 8 H), 5.17 (s, 4 H), 7.35–7.87 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.30, 70.43, 70.58, 124.62, 129.90, 130.19, 131.11, 133.91, 135.51; IR ($CHCl_3$) 3050 (w), 1460, 1350, 1125 (s), 1090 (s), 840, 820 cm^{-1}; mass spectrum, *m*/*e* 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.77; H, 7.79.

1,2-Naphtho-20-crown-6 (7) was prepared as above except that pentaethylene glycol (2.39 g, 10 mmol) and 1-(chloromethyl)-2-(bromomethyl)naphthalene (2.70 g, 10 mmol) were used: yield 172 mg (4.4%); mp 58.0–58.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 12 H), 3.65 (s, 8 H), 4.44 (s, 2 H), 5.05 (s, 2 H), 7.33–8.22 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 65.82, 69.52, 69.82, 70.72, 70.98, 71.25, 124.69, 125.49, 126.16, 127.23, 127.89, 128.11, 128.47, 132.16, 133.39, 135.06; IR ($CDCl_3$) 3000, 2860 (s), 1460, 1450, 1350, 1300, 1250, 1100 (s), 815 cm^{-1}; mass spectrum, *m*/*e* 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.84; H, 7.79.

1,5-Naphtho-19-crown-5 (8) was prepared as above except that tetraethylene glycol (1.94 g, 10 mmol) and lithium *tert*-butoxide (1.67 g, 21 mmol) were used: yield 391 mg [11.3% after molecular distillation (110 °C at 0.05 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 3.33 (s, 4 H), 3.42 (s, 4 H), 3.45 (s, 4 H), 3.52 (s, 2 H), 4.83 (dd, 4 H, J_{AA} = 12 Hz, $\Delta\delta_{AB}$ = 60 Hz), 7.1–7.4 (br m, 4 H), 7.7–8.1 (br m, 2 H); ^{13}C NMR ($CDCl_3$) δ 68.87, 69.53, 69.76, 69.96, 71.81, 124.77, 125.33, 127.25, 132.35, 134.07; IR (neat) 3075 (w), 3050 (w), 3025 (w), 1750, 1710 (w), 1600 (w), 1540, 1460, 1360, 1300, 1250, 1110 (s), 1050, 950, 875, 800 (s) cm^{-1}; mass spectrum, *m*/*e* 346.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.73; H, 7.61.

1,5-Naphtho-22-crown-6 (9) was prepared as above with pentaethylene glycol (2.39 g, 10 mmol): yield 544 mg (14.2%); mp 55.0–56.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.08 (s, 4 H), 3.25 (s, 8 H), 3.52 (s, 8 H), 4.70 (s, 4 H), 7.37–8.10 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 68.75, 69.69, 70.00, 70.21, 71.64, 124.90, 126.68, 132.00, 134.04; IR ($CHCl_3$) 2975, 2945 (s), 2900 (s), 2865 (s), 1500, 1405, 1290, 1175 (s), 1100, 1035, 825 cm^{-1}; mass spectrum, *m*/*e* 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.87; H, 7.71.

1,4-Naphtho-22-crown-6 (10) was prepared as above with pentaethylene glycol (2.39 g, 10 mmol): yield 359 mg (9.2%); mp 71.5–72.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 4 H), 3.42 (s, 8 H), 3.60 (s, 8 H), 4.97 (s, 4 H), 7.1–8.2 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.99, 70.46, 70.55, 70.75, 124.07, 125.15, 125.48, 131.40, 133.61; IR ($CHCl_3$) 2990, 2850 (s), 1600 (w), 1450 (w), 1350, 1300 (w), 1100 (s), 975, 870, 800 (s) cm^{-1}; mass spectrum, *m*/*e* 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.72; H, 7.54.

1,3-Naphtho-21-crown-6 (11) was prepared as above with pentaethylene glycol (2.39 g, 10 mmol): yield 632 mg [16.2% after molecular distillation (120 °C at 0.05 mmHg)]; ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 12 H), 3.65 (s, 8 H), 4.63 (s, 2 H), 4.97 (s, 2 H), 7.30–7.98 (br m, 6 H); ^{13}C NMR ($CDCl_3$) δ 69.21, 69.50, 69.79, 70.09, 70.48, 70.69, 71.13, 73.25, 123.32, 125.71, 125.83, 126.22, 126.58, 126.80, 128.30, 133.41, 134.08, 135.25; IR ($CHCl_3$) 3000, 2860 (s), 1700, 1450, 1350, 1290, 1240, 1100 (s), 940, 875, 800 cm^{-1}; mass spectrum, *m*/*e* 390.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.41; H, 7.63.

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Registry No. 1, 72939-28-7; 2, 72939-29-8; 3, 61899-30-7; 4,

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[22] Lumilux is the brand name for a fluorescent indicator used in UV-254 adsorbants and is currently marketed by Brinkmann Instruments.

72939-30-1; **5**, 72939-31-2; **6**, 61899-31-8; **7**, 72939-32-3; **8**, 72939-33-4; **9**, 66393-66-6; **10**, 72939-34-5; **11**, 72939-35-6; 2,3-bis(bromomethyl)naphthalene, 38998-33-3; 1,4-bis(bromomethyl)naphthalene, 58791-49-4; 1,5-bis(bromomethyl)naphthalene, 21646-18-4; 1,3-bis(bromomethyl)naphthalene, 36015-77-7; 1-(chloromethyl)-2-(bromomethyl)naphthalene, 72953-44-7; 1,8-bis(bromomethyl)naphthalene, 2025-95-8; 2,3-dimethylnaphthalene, 581-40-8; dimethyl 1,8-naphthalenedicarboxylate, 10060-33-0; 1,8-bis(hydroxymethyl)naphthalene, 2026-08-6; 1,4-dimethylnaphthalene, 571-58-4; 1,5-dimethylnaphthalene, 571-61-9; 1,3-dimethylnaphthalene, 575-41-7; 1,2-dimethylnaphthalene, 573-98-8; triethylene glycol, 112-27-6; tetraethylene glycol, 112-60-7; pentaethylene glycol, 4792-15-8.

Notes

Photochemistry of α-Diazo Thioesters: Migratory Aptitude of Sulfur vs. Oxygen in the Photochemical Wolff Rearrangement

V. Georgian,* S. K. Boyer, and B. Edwards

Department of Chemistry, Tufts University, Medford, Massachusetts 02155

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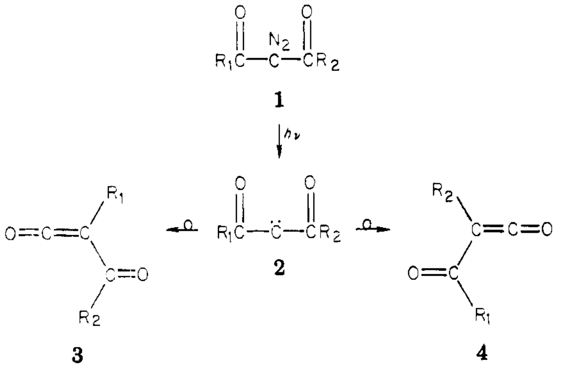
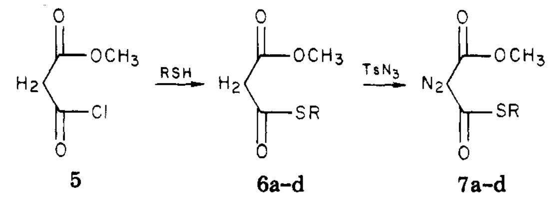
It has been shown that unsymmetrically substituted 2-diazo-1,3-dicarbonyl compounds **1** undergo a competitive rearrangement in which either R_1 or R_2 may migrate with concomitant elimination of nitrogen.[1]



The relative migration tendencies of various groups where R_1 or R_2 = C, O, or N have been studied,[2] and it has been suggested that sulfur might exhibit an enhanced migratory capacity owing to the greater participative ability of covalent sulfur than that of nitrogen or oxygen.[3] In connection with our work on the synthesis of β-lactams[4a,b] we have investigated the photochemical behavior of a series of diazo compounds of type **1**, in which R_1 and R_2 are oxygen and sulfur, respectively. We have found that these compounds rearrange with remarkable ease and specificity to yield ketenes resulting from the selective migration of sulfur. This result contrasts markedly with analogous rearrangements involving mixed esters, keto esters, and ester amides which lack specificity and proceed in low yields.[3]

Results and Discussion

A series of diazo thioesters (**7a–d**) were readily prepared from (methoxycarbonyl)acetyl chloride (**5**).[7] Thus **5** was



a, R = Me; b, R = Ph; c, R = allyl; d, R = *tert*-butyl

caused to react with the corresponding mercaptan (**a–d**) in anhydrous ether at 0 °C upon addition of pyridine to yield the methyl [[alkyl(and aryl)thio]carbonyl]acetates **6**. Diazo functionalization of **6** with tosyl azide according to known procedures[8] gave the diazo thioesters **7** in good yield.

The diazo thioesters **7a–d** were independently dissolved in wet benzene and irradiated with a 450-W Hanovia lamp equipped with a Pyrex filter. The reactions were monitored by IR and irradiated until the diazo band at 2140 cm^{-1} had completely disappeared. Removal of the benzene and distillation of the resulting residues produced in each case a single isolated product resulting from the selective migration of sulfur. These products **12**, as well as our preferred mechanism for their formation, are shown in Scheme I below. The structures of these photolysis products were confirmed via independent synthesis and comparison of IR and NMR spectra.

It is possible that an intermediate sulfonium ylide **9** may account for the overall selectivity of the reaction. Such an ylide would result from an intramolecular bond formation between the singlet carbene **8** and the electron pair on sulfur. Such carbene–sulfur interactions are precedented,[3] however, not in cases where other heteroatoms might compete with sulfur. The factors controlling the relative migration of various alkoxy or amido radicals are not understood, and the lack of correspondence between theoretical expectations and experimental results has been summarized and commented upon previously.[3a] In the

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(5) (a) For a review of references, see: W. A. Noyes, Jr., and I. Unger, *Pure Appl. Chem.*, **9**, 461 (1964). Irrespective of disagreement as to quantum yield determinations and secondary reaction mechanisms for the decarbonylation of ketene to ethylene and carbon monoxide, Ross and Kistiakowsky[5b] showed that it is efficient at 313 nm but immeasurably slow at 366 nm. Acetone displays its UV cutoff at 330 nm, thus protecting the ketene derivative, but permitting sufficient absorption by diazo thioester **7a**. (b) W. F. Ross and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 1112 (1934).

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