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Molecular Transformations of Unsaturated Thiacrown Ethers

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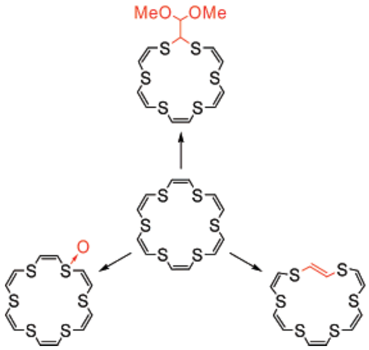

Unsaturated thiacrown ethers with 15, 18, and 21 members were oxidized to sulfoxides by the reaction with *m*-CPBA. The reaction with *t*-BuOCl at −20 °C also afforded sulfoxides, whereas the reaction at room temperature yielded cis−trans isomerized compounds. The cis−trans isomerized compound was also obtained by the photochemical reaction or by the reaction with NCS and NCP. Meanwhile, the reaction with NBS and NBP provided an acetal via 1,2-bridged bromonium intermediate.

Introduction

The chemistry of thiacrown ethers has been widely studied,[1,2] and they are of interest as possible metal-delivering agents.[1,3] Nanosized heteroatom/π multiple macrocycle systems attract special interest as molecular machines,[4] switches,[5] and electronics,[6] as well as for their topology.[7] We have recently reported the synthesis of unsaturated thiacrown ethers with cis geometry across the carbon−carbon double bonds[8] and their inclusion behavior toward silver[8,9] and mercury[10] ions and found that they

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(1) *Crown Compounds*: *Toward Future Applications*; Cooper, R. S., Ed.; VCH Publishers: New York 1992; Chapters 14 and 15.

(2) (a) Adam, R. D. *Acc. Chem. Res.* **2000**, *33*, 171. (b) Hill, S. E.; Feller, D. *J. Phys. Chem. A* **2000**, *104*, 652. (c) Alfimov, M. V.; Gromov, S. P.; Fedorov, Y. V.; Fedorova, O. A.; Vedernikov, A. I.; Churakov, A. V.; Kuz'mina, L. G.; Howard, J. A. K.; Bossmann, S.; Braun, A.; Woerner, M.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1999**, *121*, 4992. (d) Ito, T.; Takagi, Y.; Tsukube, H. *J. Mol. Catal. B* **1997**, *259.* (e) Ito, T.; Mitsukura, K.; Kanphai, W.; Takagi, Y.; Kihara, H.; Tsukube, H. *J. Org. Chem.* **1997**, *62*, 9165. (f) Alfimov, M. V.; Fedorov, Y. V.; Fedorova, O. A.; Gromov, S. S.; Hester, R. E.; Lednev, I. K.; Moore, J. N.; Oleshko, V. P.; Vedernikov, A. I. *J. Chem. Soc.*, *Perkin Trans. 2* **1996**, 1441. (g) Yamashita, K.; Kurita, K.; Ohara, K.; Tamura, K.; Nango, M.; Tsuda, K. *React. Polym.* **1996**, *31*, 47. (h) Hamed, M. M. A.; El-Nady, A. M.; Baker, M.; Mahmoud, M. R. *Phosphorus*, *Sulfur*, *Silicon* **1993**, *83*, 183.

(3) (a) Cooper, R. S. *Pure Appl. Chem.* **1990**, *62*, 1123. (b) Deutsch, E.; Hirth, W. *J. Nucl. Med.* **1987**, *28*, 1491. (c) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. *Prog. Inorg. Chem.* **1983**, *30*, *75*.

(4) (a) Balzani, V.; Credi, A.; Silvi, S.; Venturi, M. *Chem. Soc. Rev.* **2006**, *35*, 1135. (b) Balzani, M.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley-VCH: Weinheim , Germany, 2003.

(5) (a) Chiang, P.-T.; Cheng, P.-N.; Lin, C.-F.; Liu, Y.-H.; Lai, C.-C.; Peng, S.-M.; Chiu, S.-H. *Chem. Eur. J.* **2006**, *12*, 865. (b) Liu, Y.; Flood, A. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9150.

(6) (a) Domagaa, S.; Wickowska, A.; Kowalski, J.; Rogowska, A.; Szydowska, J.; Daszkiewicz, B. K.; Bilewicz, R.; Woniak, K. *Chem. Eur. J.* **2006**, *12*, 2967. (b) Godt, A.; Duda, S.; Ünsal, Ö.; Thiel, J.; Härter, A.; Roos, M.; Tschierske, C.; Diele, S. *Chem. Eur. J.* **2002**, *8*, 5094.

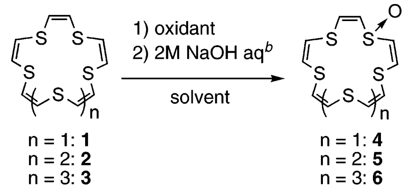
(7) (a) Bäuerle, P.; Ammann, M.; Wilde, M.; Götz, G.; Osteritz, E. M.; Rang, A.; Schalley, C. A. *Angew. Chem.*, *Int. Ed.* **2007**, *46*, 363. (b) Christensen, C. A.; Batsanov, A. S.; Bryce, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 10484. (c) Nakao, K.; Nishimura, M.; Tamachi, T.; Kuwatani, Y.; Miyasaka, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2006**, *128*, 16740. (d) Liu, Y.; Bonvallet, P. A.; Vignon, S. A.; Khan, S. I.; Stoddart, J. F. *Angew. Chem.*, *Int. Ed.* **2005**, *44*, 3050. (e) Yamaguchi, Y.; Yoshida, Z. *Chem. Eur. J.* **2003**, *9*, 5430.

(8) Tsuchiya, T.; Shimizu, T.; Kamigata, N. *J. Am. Chem. Soc.* **2001**, *123*, 11534.

(9) Tsuchiya, T.; Shimizu, T.; Hirabayashi, K.; Kamigata, N. *J. Org. Chem.* **2002**, *67*, 6632.

10.1021/jo701757s CCC: $40.75

TABLE 1. Oxidation of Unsaturated Thiacrown Ethers[a]



run	macrocycle	oxidant	recovered substrate (%)	sulfoxide yield (%)
1[c]	**1**	*m*-CPBA	22	**4**, 58
2[c]	**2**	*m*-CPBA	1	**5**, 65
3[c]	**3**	*m*-CPBA	7	**6**, 78
4[d]	**1**	*t*-BuOCl	10	**4**, 66
5[d]	**2**	*t*-BuOCl	5	**5**, 74
6[d]	**3**	*t*-BuOCl	3	**6**, 80

[a] All reactions were performed with macrocycle (0.2 mmol) and oxidant (0.2 mmol). [b] Except for runs 1−3. [c] Reactions were carried out in CH_2Cl_2 (15 mL) at rt for 2 h. [d] Reactions were carried out in MeOH (5 mL) and CH_2Cl_2 (10 mL) at −20 °C for 2 h.

showed selectivity for the number of metals included in their cavity. In addition, unsaturated thiacrown ethers were recently revealed to have inclusion ability toward endohedral metallofullerene.[11] Staeb and co-workers also reported the synthesis of thiacrown ethers possessing both saturated and unsaturated carbon−carbon bonds relevant to unsaturated thiacrown ethers, indicating that introduction of carbon−carbon unsaturated bonds to crown ethers has become of interest.[12] We report here the fundamental reactivity such as oxidation and cis−trans isomerization of the unsaturated thiacrown ethers. Introduction of a substituent to the unsaturated thiacrown ethers will also be reported.

Results and Discussion

Reaction of Unsaturated Thiacrown Ethers with *m*-CPBA and *t*-BuOCl. The reaction of 15-membered unsaturated thiacrown ether **1** with 1 equiv of *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 at rt gave sulfoxide **4** in 58% isolated yield (Table 1, run 1), and **1** was recovered in 22% yield. Both 18- and 21-membered unsaturated thiacrown ethers **2** and **3** also afforded sulfoxides **5** and **6** in 65% and 78% yields, respectively, by a similar reaction (Table 1, runs 2 and 3). On the other hand, the reactions of **1**−**3** with 1 equiv of *t*-BuOCl in MeOH/CH_2Cl_2 (1:2) at −20 °C formed yellow solutions. Treatment of the resulting solution with 2 M NaOH also yielded sulfoxides **4**−**6** in 66%, 74%, and 80% yields, respectively (Table 1, runs 4−6).

The crystal structures of **4** and **6** were determined by X-ray crystallographic analysis, as shown in Figure 1. The ORTEP drawings show that oxygen atoms of **4** and **6** are directed outside of the ring and the sulfur atoms are nearly coplanar. Three sulfur atoms of **4** are oriented to the inside of the ring (endodentate) in the crystalline state similar to the crystal structure of **1**.[8] The bond lengths and angles of **4** are almost normal. The bond length of S(1)−O(1) and angles of O(1)−S(1)−C(1) and O(1)−S(1)−C(10) of **4** are 1.50 Å and 106.5° and 105.9°, respectively, and the S−C and C═C bond lengths and the C−S−C and S−C−C angles of **4** (S−C: 1.74−1.77 Å; C═C: 1.33−1.34 Å; C−S−C: 99.5−106.6°; S−C−C: 121.7−132.0°) are almost the same as those of **1**.[4] The crystal structure of **6** shows that all of the sulfur atoms are endodentate, also similar to the crystal structure of **3**.[4] The bond lengths and angles of **6** are also almost normal [S(1)−O(1): 1.49 Å; O(1)−S(1)−C(1): 107.6°; O(1)−S(1)−C(14): 106.8°; S−C: 1.71−1.77 Å; C═C: 1.31−1.33 Å; C−S−C: 96.0−102.7°; S−C−C: 121.3−126.6°]. Thus, it is revealed that the conformations of **1** and **3** are approximately retained in the crystalline state even if they are oxidized to sulfoxides.

Meanwhile, the reaction of **2** with *t*-BuOCl *at room temperature* for 2 h induced a cis−trans isomerization of the olefin moiety, and sulfoxide **5** hardly formed. Compound **7** having one trans-double bond was isolated in 36% yield. This reaction also formed **8** and **9** having two trans-double bonds in 15% and 8% yields, respectively (Table 2, run 1).[13] A similar isomerization reaction proceeded even in the absence of treatment with bases (Table 2, run 2). The yields of these products hardly changed even if the reaction time was extended from 2 to 15 h (Table 2, run 3). However, cis−trans isomerization was inhibited by shortening the reaction time to 20 min, and oxidation product **5** was obtained preferentially (44% yield; Table 2, run 4). These results suggest that nucleophilic attack of the sulfur atom toward *t*-BuOCl initially occurs to form chlorosulfonium ion **10**, which is a precursor of the sulfoxide **5** (Scheme 1). In addition, the equilibrium would exist between **10** and **11** (**10** $\rightleftharpoons$ **11**) or among **10**, **2**, and **11** (**10** $\rightleftharpoons$ **2** $\rightleftharpoons$ **11**) and more stable **11** is considered to form gradually since cis−trans isomerized compound was obtained by elongation of the reaction time. Therefore, the reason why the reaction of **2** with *t*-BuOCl affords different products such as sulfoxide and cis−trans isomerized compounds by changing the reaction temperature between −20 °C and rt is that **10** is the kinetically controlled intermediate whereas **11** is the thermodynamically controlled one. On the other hand, the reaction of **1** with *t*-BuOCl at rt without base treatment obviously proved almost no reaction. This result indicates that 15-membered unsaturated thiacrown ether having a trans-double bond is thermodynamically less stable than the 18-membered one. A similar reaction of **3** was also examined; however, the reaction became complicated, and the products could not be isolated. However, compound **7** was also obtained by photochemical reaction of **2** in 49% conversion yield along with the formation of 1,4-dithiin by using a 450-W medium-pressure mercury lamp with a Pyrex filter (Scheme 2).

X-ray structural analysis of **7** showed four crystallographically independent molecules, although they have similar structure, in the triclinic unit cell, and Figure 2 illustrates one of them. The bond lengths of S−C (1.71−1.77 Å) and C═C (1.30−1.34 Å), bond angles of C−S−C (100.6−107.0°) and S−C═C (119.3−134.7°), and torsion angles around the C═C bonds (*cis*-olefin: 0.8−4.8°; *trans*-olefin: 170.9−175.9°) exhibit the normal values indicating the strain-free structure.[14]

Reaction of 2 with NCS, NCP, NBS, and NBP. The reactions of **2** with other chlorinating reagents such as *N*-

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[10] Tsuchiya, T.; Shimizu, T.; Hirabayashi, K.; Kamigata, N. *J. Org. Chem.* **2003**, *68*, 3480.

[11] Tsuchiya, T.; Kurihara, H.; Sato, K.; Wakahara, T.; Akasaka, T.; Shimizu, T.; Kamigata, N.; Mizorogi, N.; Nagase, S. *Chem. Commun.* **2006**, 3585.

[12] (a) Staeb, T. H.; Gleiter, R.; Rominger, F. *Eur. J. Org. Chem.* **2002**, 2815. (b) Werz, D. B.; Staeb, T. H.; Benisch, C.; Rausch, B. J.; Rominger, F.; Gleiter, R. *Org. Lett.* **2002**, *4*, 339.

[13] Compounds **8** and **9** were identified by ^1H NMR, ^{13}C NMR, and EI-MS for the mixture of **8** and **9**. These data are described in the Experimental Section.

[14] Shimizu, T.; Iwata, K.; Kamigata, N.; Ikuta, S. *J. Chem. Res.* (*S*) **1997**, 38.

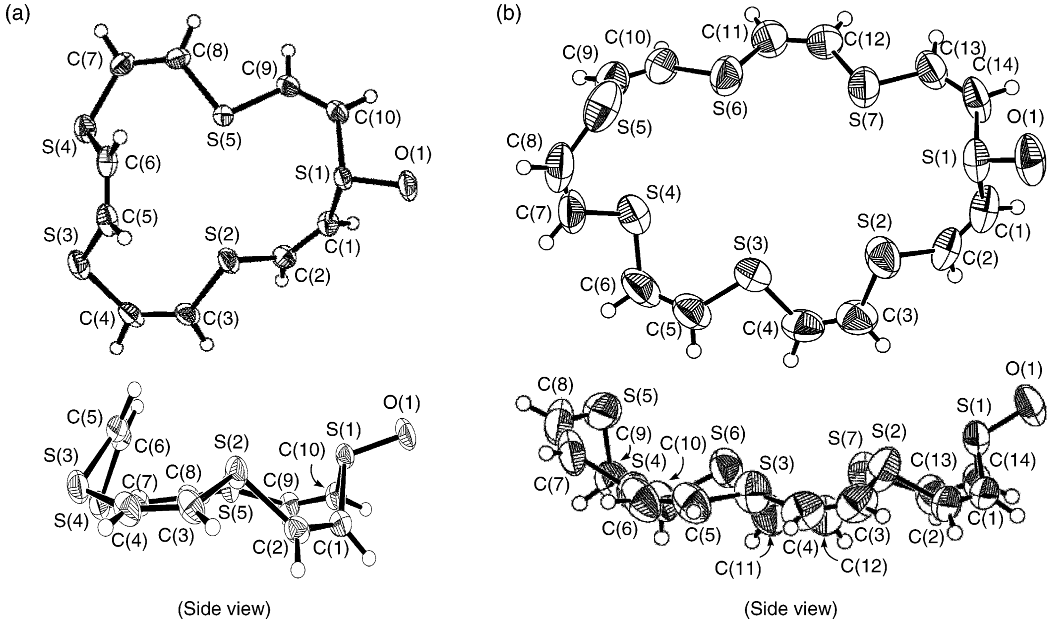
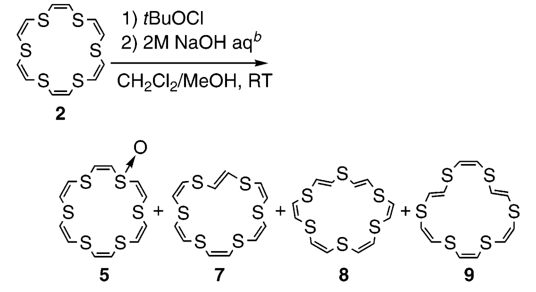


FIGURE 1. ORTEP drawings of (a) **4** and (b) **6** showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): (a) S(1)−O(1), 1.502(1); S(1)−C(1), 1.764(2); S(1)−C(10), 1.772(2); O(1)−S(1)−C(1), 106.48(10); O(1)−S(1)−C(10), 105.90(9); C(1)−S(1)−C(10), 99.52(10); (b) S(1)−O(1), 1.494(6); S(1)−C(1), 1.750(10); S(1)−C(14), 1.773(8); O(1)−S(1)−C(1), 107.6(4); O(1)−S(1)−C(14), 106.8(4); C(1)−S(1)−C(14), 96.0(5).

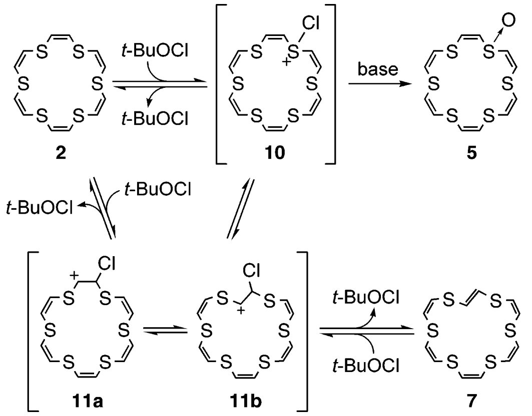
TABLE 2. Reactions of 2 with *t*-BuOCl at Room Temperature[a]



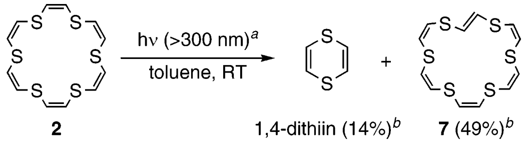
run	time (h)	NaOH (equiv)	recovered **2** (%)	yield (%)			
				5	**7**	**8**[c]	**9**[c]
1	2.0	2.0	30	trace	36	15	8
2	2.0		23		35	9	5
3	15.0	2.0	32	trace	33	19	10
4	0.3	2.0	25	44	6	trace	trace

[a] All reactions were performed with **2** (0.2 mmol) and *t*-BuOCl (0.2 mmol) in MeOH (5 mL) and CH_2Cl_2 (10 mL) at rt. [b] Except for run 2. [c] Determined by ^1H and ^{13}C NMR.

SCHEME 1. Reaction of 2 with *t*-BuOCl



SCHEME 2. Photochemical Reaction of 2



[a] Reaction was performed with **2** (0.2 mmol) in toluene (144 mL) for 20 min. [b]Conversion yield.

chlorosuccinimide (NCS) and *N*-chlorophthalimide (NCP) in CH_2Cl_2/MeOH also afforded cis−trans isomerized compound **7** after treatment with base although conversion efficiency was low (Table 3, runs 1 and 2). A similar isomerization reaction proceeded even in the absence of treatment with base (Table 3, run 3). The reaction mechanism is considered to be similar with that of *t*-BuOCl. However, when *N*-bromosuccinimide (NBS) and *N*-bromophthalimide (NBP) were applied for the reaction with **2** instead of NCS and NCP, acetal **12** was obtained in 44% and 76% yields, respectively. In the cases of the reactions with NBS and NBP, 1,2-bridged bromonium cation **13** is considered to form initially (Scheme 3), and carbocation **14** would be subsequently given via episulfonium ion. After that, by means of the base treatment, methoxide is considered to attack **14** twice yielding acetal **12**. The crystal structure of **12** was determined by X-ray analysis, as shown in Figure 3. ORTEP drawing of **12** shows that all sulfur atoms are endodentate and the bond lengths and angles are almost normal. The S(1)−C(11), S(6)−C(11), and C(11)−C(12) bond lengths and S(1)−C(11)−C(12), S(6)−C(11)−C(12), and S(1)−C(11)−S(6) angles are 1.82, 1.82, and 1.53 Å and 108.5°, 115.7°, and 113.9°, respectively, and other S−C and C═C bond lengths and the C−S−C and other S−C−C angles are similar to those of **2** (S−C: 1.73−1.76 Å; C═C: 1.30−1.33 Å; C−S−C: 100.5−103.3°; S−C−C: 122.4−125.1°).[8]

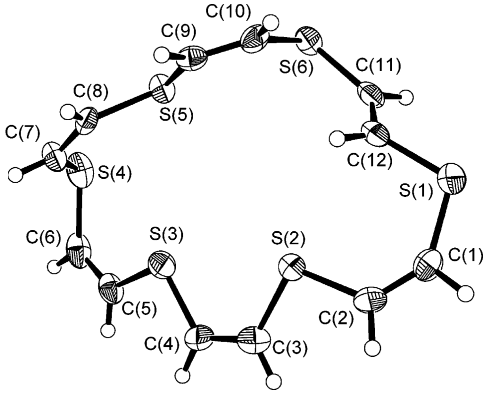
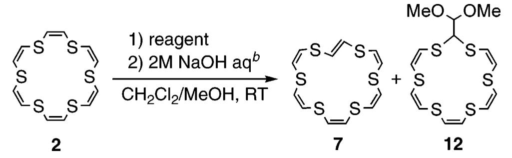


FIGURE 2. ORTEP drawing of **7** showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): S(1)−C(12), 1.738(5); S(6)−C(11), 1.750(6); C(11)−C(12), 1.324(7); S(1)−C(12)−C(11), 121.4(5); S(6)−C(11)−C(12), 128.9(5).

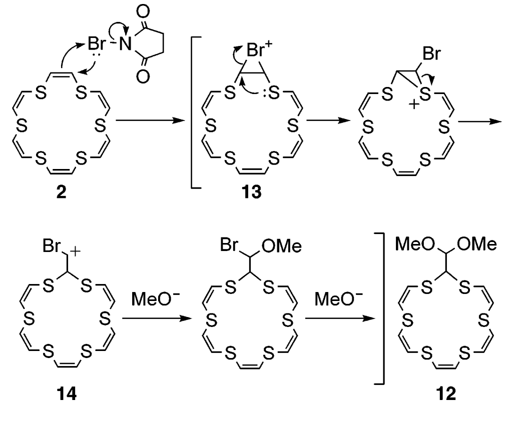
TABLE 3. Reactions of 2 with NCS, NCP, NBS, and NBP[a]



run	reagent	NaOH (equiv)	recovered **2** (%)	yield (%) **7**	yield (%) **12**
1	NCS	2.0	66	11	
2	NCP	2.0	63	9	
3	NCS		63	6	
4	NBS	2.0	49		44
5	NBP	2.0	15		76

[a] All reactions were performed with **2** (0.2 mmol) and reagent (0.2 mmol) in CH$_2$Cl$_2$ (10 mL) and MeOH (5 mL) at rt for 5 h. [b] Except for run 3.

SCHEME 3. Reaction of 2 with *N*-Bromosuccinimide (NBS)



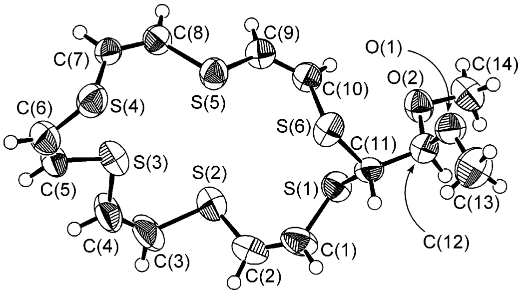


FIGURE 3. ORTEP drawing of **12** showing thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): S(1)−C(11), 1.817(8); S(6)−C(11), 1.823(9); C(11)−C(12), 1.53(1); O(1)−C(12), 1.406(9); O(1)−C(13), 1.41(1); O(2)−C(12), 1.415(9); O(2)−C(14), 1.42(1); C(12)−O(1)−C(13), 114.7(7); C(12)−O(2)−C(14), 111.7(7); S(1)−C(11)−S(6), 113.9(4); S(1)−C(11)−C(12), 108.5(9); S(6)−C(11)−C(12), 115.7(6); O(1)−C(12)−O(2), 107.9(7); O(1)−C(12)−C(11), 112.8(7); O(2)−C(12)−C(11), 108.3(7).

In conclusion, the oxidation reaction of unsaturated thiacrown ethers **1**−**3** with *m*-CPBA and *t*-BuOCl was examined. In the case of the reaction of **2** with *t*-BuOCl, cis−trans isomerized compound **7** was alternatively formed at rt while the oxidized product **5** was obtained at −20 °C. The cis−trans isomerized compound **7** was also obtained by the reaction of **2** with NCS and NCP at rt; however, the reactions with NBS and NBP gave acetal **12**. It is demonstrated that the reactions with NBS and NBP are a convenient method for introducing the substituent to **2**. This is an important stepping stone to introducing the new function into the unsaturated thiacrown ether and developing future material as well as catalytic and biological applications by using the agent.

Experimental Section

(*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13-Pentathiacyclopentadeca-2,5,8,11,14-pentaene 1-oxide (4): mp 147.0−148.5 °C (colorless prisms, dec); ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.28 (s, 2H), 6.42 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 7.9 Hz, 2H), 6.83 (d, J = 7.9 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 122.3, 125.4, 131.6, 132.6, 135.0; IR (KBr) ν_{max} 3436, 3010, 1532, 1281, 1019 (S═O), 815, 691, 651; MS (EI) *m/z* 306 (M$^+$, 0.2%), 290 (C$_{10}$H$_{10}$S$_5$$^+$, 3.1%), 116 (C$_4H_4S_2$$^+$, 100%). Anal. Calcd for C$_{10}$H$_{10}$OS$_5$: C, 39.18; H, 3.29. Found: C, 39.16; H, 3.26.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene 1-oxide (5): mp 193.5−194.5 °C (colorless prisms, dec); ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.35 (d, J = 7.7 Hz, 2H), 6.60 (d, J = 8.9 Hz, 2H), 6.80 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 118.6, 121.6, 125.2, 129.4, 132.2, 136.1; IR (KBr) ν_{max} 3448, 3029, 3000, 1548, 1524, 1282, 1018 (S═O), 815, 722, 698, 666, 522; MS (EI) *m/z* 364 (M$^+$, 0.3%), 348 (C$_{12}$H$_{12}$S$_6$$^+$, 3.5%), 116 (C$_4H_4S_2$$^+$, 100%). Anal. Calcd for C$_{12}$H$_{12}$OS$_6$: C, 39.53; H, 3.32. Found: C, 39.46; H, 3.23.

(*Z*,*Z*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16,19-Heptathiacycloheneicosa-2,5,8,11,14,17,2-heptaene 1-oxide (6): mp 161.0−162.5 °C (colorless prisms, dec); ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.28 (d, J = 8.0 Hz, 2H), 6.29 (d, J = 8.3 Hz, 2H), 6.35 (s, 2H), 6.42 (d, J = 8.3 Hz, 2H), 6.43 (d, J = 8.9 Hz, 2H), 6.47 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 120.3, 122.0, 124.0, 124.8, 128.3, 130.2, 136.1; IR (KBr) ν_{max} 3014, 1551, 1531, 1282, 1035 (S═O), 805, 696, 649; MS (EI) *m/z* 422 (M$^+$, 0.2%), 406 (C$_{14}$H$_{14}$S$_7$$^+$, 2.8%), 116 (C$_4H_4S_2$$^+$, 100%). Anal. Calcd for C$_{14}$H$_{14}$OS$_7$: C, 39.78; H, 3.34. Found: C, 39.97; H, 3.34.

(*E*,*Z*,*Z*,*Z*,*Z*,*Z*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (7): mp 132.0−133.0 °C (colorless prisms from acetone); ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.29 (d, J = 8.4 Hz, 2H), 6.30 (s, 2H), 6.35 (d, J = 7.9 Hz, 2H), 6.42 (s,2H), 6.43 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 7.9 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 120.3, 121.5, 122.4, 124.5, 129.7, 131.2; IR (KBr) ν_{max} 3021, 1537, 1284, 919, 841, 793, 680; UV (CH$_3$CN) λ_{max} 270 (ϵ 3.2 × 10^4) nm; MS (EI) *m/z* 348 (M$^+$, 4%), 116 (C$_4$H$_4$S$_2$$^+$, 100%). Anal. Calcd for C$_{12}$H$_{12}$S$_6$: C, 41.34; H, 3.47. Found: C, 41.08; H, 3.43.

(*E*,*Z*,*Z*,*Z*,*Z*,*E*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (8): ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.27 (d, J = 14.6 Hz, 2H), 6.30 (d, J = 8.2 Hz, 2H), 6.31 (d, J = 7.9 Hz, 2H), 6.34 (d, J = 14.6 Hz, 2H), 6.52 (d, J = 7.9 Hz, 2H), 6.61 (d, J =

8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.7, 119.3, 122.3, 123.7, 131.7, 133.5; MS (EI) *m*/*z* 348 (M^+, 14%), 116 ($C_4H_4S_2{}^+$, 100%).

(*E*,*Z*,*Z*,*Z*,*E*,*Z*)-1,4,7,10,13,16-Hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (9): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (d, $J = 8.2$ Hz, 2H), 6.22 (d, $J = 14.7$ Hz, 2H), 6.24 (d, $J = 14.7$ Hz, 2H), 6.27 (s, 2H), 6.45 (s, 2H), 6.85 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 114.8, 120.8, 122.4, 124.1, 125.8, 138.3; MS (EI) *m*/*z* 348 (M^+, 14%), 116 ($C_4H_4S_2{}^+$, 100%).

2-Dimethoxymethyl-(*Z*,*Z*,*Z*,*Z*,*Z*)-1,3,6,9,12,15-hexathiacycloheptadeca-4,7,10,13,16-pentaene (12): mp 127.5−128.5 °C (colorless prisms); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50 (s, 6H), 4.25 (d, $J = 4.5$ Hz, 1H), 4.65 (d, $J = 4.5$ Hz, 1H), 6.29 (d, $J = 8.3$ Hz, 2H), 6.37 (d, $J = 8.1$ Hz, 2H), 6.43 (d, $J = 8.1$ Hz, 2H), 6.50 (s, 2H), 6.52 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.9, 57.4, 106.9, 122.1, 122.8, 126.0, 126.4, 128.9; IR (KBr) ν_{max} 3019, 2924, 2829, 1541, 1524, 1347, 1284, 1203, 1122, 1074, 816, 670; MS (EI) *m*/*z* 410 (M^+, 0.3%), 116 ($C_4H_4S_2{}^+$, 100%). Anal. Calcd for $C_{14}H_{18}O_2S_6$: C, 40.94; H, 4.42. Found: C, 40.91; H, 4.30.

X-ray Structure Determination. Data from X-ray diffraction were collected by a Rigaku RAXIS-RAPID imaging plate two-dimensional area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) to 2θ max of 55.0°. All of the crystallographic calculations were performed by using the SHELXL 97 software package. The crystal structure was solved by the direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. The experimental details including data collection, data reduction, and structure solution and refinement as well as the atomic coordinates and B_{iso}/B_{eq} anisotropic displacement parameters have been deposited in the Supporting Information.

Supporting Information Available: Typical procedure for the reactions of **1**−**3** with *t*-BuOCl, the reaction of **2** with NCS, NCP, CBS, and NBP, and photochemical reaction of **2**; ^{1}H and ^{13}C NMR spectra of **4**−**7** and **12** and X-ray crystallographic details including CIF file for **4**, **6**, **7**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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