Application of the Remote Photocyclization with a Pair System of Phthalimide and Methylthio Groups. A Photochemical Synthesis of Crown Ether Analogs[1]

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Based on the regioselective remote photocyclization of a pair system consisting of a phthalimide group and a methylthio group, a homologous series of N-substituted phthalimides (4) possessing a terminal sulfide function in the poly-ether side chain afforded, on irradiation, seven- to fifteen-membered crown ether analogs (5—7) in moderate yields.

Keywords——phthalimide derivative; crown ether analog; heteromeric cyclic ether; remote photocyclization; donor-acceptor pair system; extensive Norrish type II process

During the course of our systematic studies on imide photochemistry,[2] we found that phthalimides possessing a terminal sulfide function in their N-side chain undergo unusually facile photocyclization to give azathiacyclols.[3] We are now extending this type of reaction to a general synthesis of macrocycles on the basis of a regioselective remote photocyclization of a "pair system" which consists of, in this case, a phthalimide group and a methylthio group. With this particular pair of functional groups, macrocycles of up to 16-membered ring size,[4] cyclic peptide models of up to 21-membered ring size,[5] and macrolide derivatives of up to 27-membered ring size[6] have been synthesized. While the phthalimide ring is a good electron acceptor (A), the sulfide is a donor (D). Therefore it is assumed that the formation of a complex in the excited states may facilitate the reaction, suggesting the general working hypothesis that compounds possessing appropriate D-A pair groups, even when these are separated by a long chain, are capable of forming a new carbon-carbon bond on irradiation (Chart 1).[2,4-6] To determine the scope and limitations of this synthetic method, examination of a series of compounds with systematic structural variation in the connecting portion (X), which carries a donor and an acceptor group, was needed. We have already investigated the photocyclization
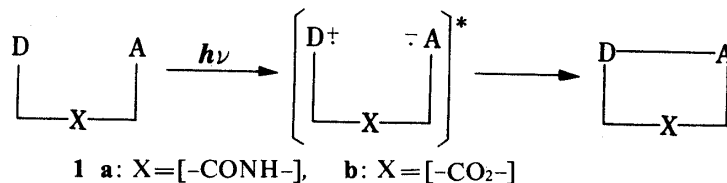

1 a: X=[-CONH-], b: X=[-CO$_2$-]

Chart 1

of phthalimides containing amide and ester bonds in a long side chain (1a—b).[4-6] In addition, we have preliminarily reported the results of the photolysis of such a pair system with poly-ether bonds as the connecting part.[7] In the present paper, we wish to present a full account of this photochemical synthesis of crown ether analogs.

A series of N-[(ω-methylthio)polyoxalkyl]phthalimides (4) was prepared by the following procedures. Condensation of phthalimide and dibromides [BrCH$_2$(CH$_2$OCH$_2$)$_n$CH$_2$Br; $n=1$—3] gave the ω-bromo compounds 3 in moderate yields. Replacement of the ω-bromo group of 3 with sodium methylsulfide also took place smoothly, giving the N-substituted

phthalimides **4**, which contain the terminal sulfide group and the ether groups in their side chain as a connecting part.   The assignment of these structures was made on the basis of elemental analyses and spectral properties.

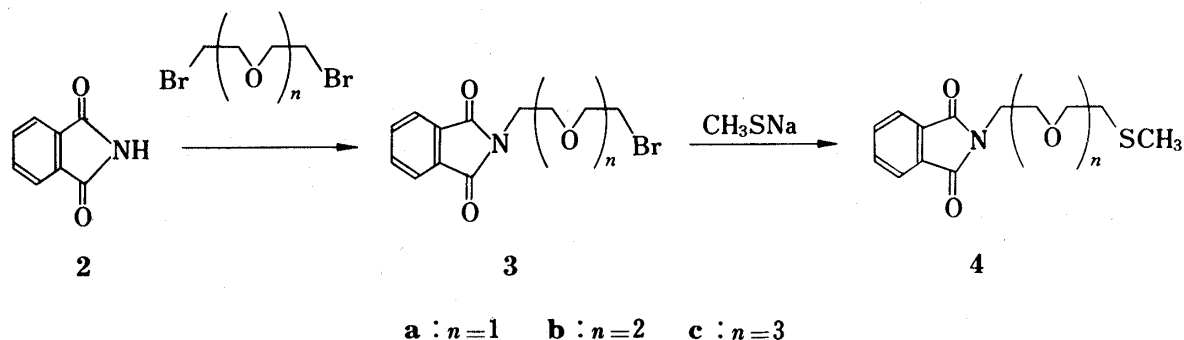

a : $n=1$ **b** : $n=2$ **c** : $n=3$

Chart 2

   Irradiation of the substrate **4a** with a 400W high pressure mercury lamp in 7.3 mM acetone solution in a stream of argon for 0.5 h afforded a mixture of medium-sized cyclols, which were separated into **5a** (74%) and **6a** (6%) by silica gel column chromatography.   The structural assignments were made on the basis of the following spectroscopic data.   The [1]H-nuclear magnetic resonance (NMR) spectrum of **5a** showed a new peak due to a methylene group at 3.1— 4.0 ppm (in *deuterio*-chloroform; CDCl₃) with other methylene protons in place of the original sulfide methyl group in **4a**, indicating that the cyclization had occurred at the terminal sulfide methyl group, and a singlet peak due to a hydroxy group appeared at 4.57 ppm, supporting the presence of a tertiary cyclol moiety.   The minor product **6a**, in which a sulfide methylene group
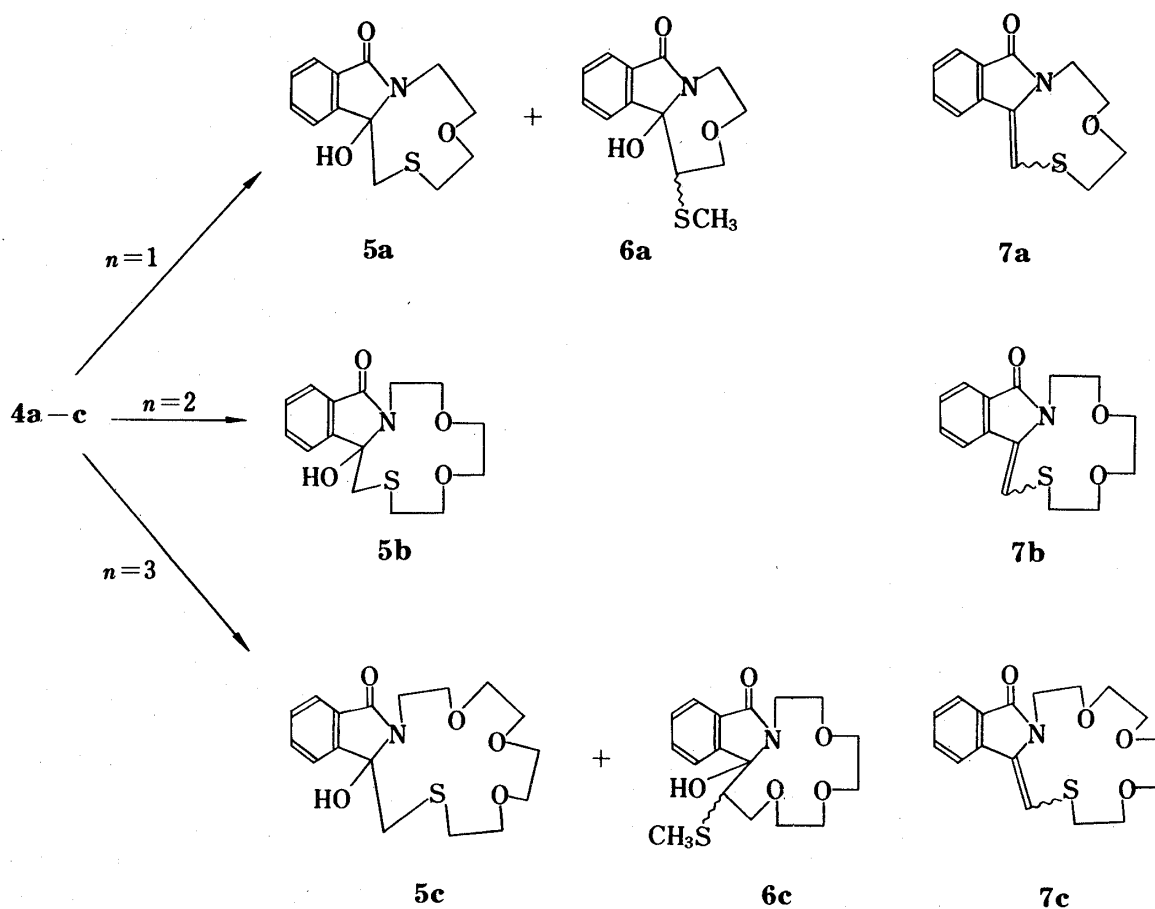

Chart 3

is involved in the cyclization, showed peaks due to a sulfide methyl group and a hydroxy group at 2.16 and 4.75 ppm, respectively. The infrared (IR) signals of a hydroxy group and an amide group appeared at ν 3240 (OH) and 1680 (amide carbonyl) cm^{-1} in **5a** and at ν 3260 (OH) and 1670 (amide carbonyl) cm^{-1} in **6a**, respectively. All other spectral and analytical data were consistent with the structures **5a** and **6a**. In agreement with the assigned structure, the aza-oxathiacyclol **5a** was readily converted into the dehydrated product **7a** [NMR; at 6.36 ppm (1H, singlet, olefinic proton)] by treatment with p-toluenesulfonic acid.

Irradiation of the poly-ether phthalimides (**4b**—**c**) was performed in a similar manner (Table I). The expected cyclol **5b** (58%) was obtained as a single product from **4b**. From

TABLE I. Photoproducts from the Poly-ether Substrates (**4a**—**c**)

Substrates		Conditions				Products (yield)				
4	n	Weight Concentration Time g (mmol) (mM) (min)			**5** (%)	Ring size	mp (°C)	**6** (%)	Ring size	mp (°C)
4a	1	2.5 (9.4)	7.3	30	74	9	154—156	6	7	192—193
4b	2	2.0 (6.5)	5.0	70	58	12	143—144			
4c	3	2.0 (5.7)	4.4	45	35	15	98—99	24	13	127—130

4c, the fifteen-membered cyclol **5c** (35%) and thirteen-membered one **6c** (24%) were obtained as a result of carbon-carbon bond formation between the imide carbonyl group and the sulfide-methyl and -methylene groups, respectively. In the NMR spectrum (in $CDCl_3$) of **5c**, multiplet peaks at 3.22—4.28 ppm (accompanied by other methylene signals) due to a new methylene appeared instead of the methyl group signal in the substrate **4c**. The IR spectrum showed maxima at ν 3240 and 1670 cm^{-1} due to a hydroxy group and an amide carbonyl group, respectively, supporting the presence of the cyclol moiety. The molecular weight values determined by the vapor-pressure method[8] and by mass spectrometry (MS) were 343 and 353, respectively, both in agreement with the value for a monomeric structure (353). On treatment with p-toluenesulfonic acid, **5c** similarly afforded the dehydrated compound **7c** [NMR; at 6.65 ppm (1H, singlet, olefinic proton)]. The stereochemistry of these dehydrate derivatives (**7a**—**c**) has not yet been determined. In the NMR spectrum of the photoproduct **6c**, two singlet peaks due to the sulfide methyl groups appeared at 1.88 and 2.18 ppm. This crystal-
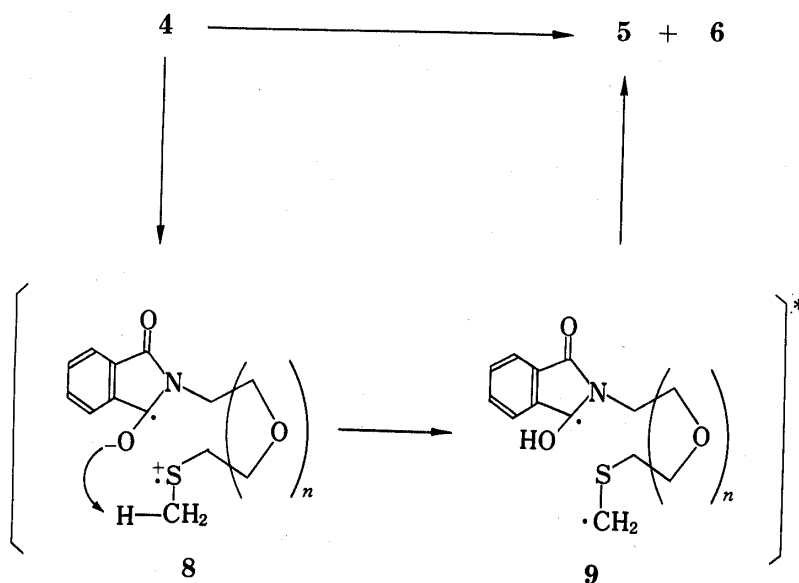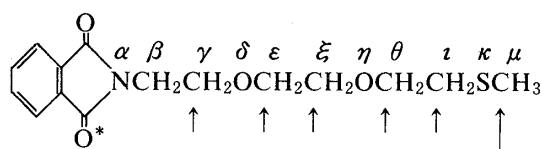
4 ⟶ **5** + **6**

Chart 4

line product is probably mostly a mixture of two diastereoisomers of the thirteen-membered cyclol **6c** (in which the sulfide methylene group is involved) with respect to the relative configuration of the hydroxy group and sulfide methyl group. Namely, in one of the two possible isomers in **6c**, the sulfide methyl signal was shifted to higher field than that of the other isomer, due to the anisotropic shielding effects of the aromatic ring.[6]

Although the detailed mechanism of this remote photocyclization requires further study, this cyclization may be tentatively rationalized in terms of a rapid electron transfer followed by proton transfer from a radical-cation of the methylthio group with favorable entropy factors by virtue of charge-transfer complex formation in the excited state (Chart 4).[2,4]

Syntheses of macrocycles have recently attracted considerable attention in view of the important chemical and biological applications of naturally occurring and synthetic macrocycles.[9] Crown ethers and cryptands are well-known examples of synthetic macrocyclic ligands.[9a–g] Although many ground-state reactions for the construction of macrocycles are known,[10] much less information is available on photochemical syntheses of macrocycles.[11]

It is well known that an alkoxy group enhances the reactivity of the C–H bond adjacent to the excited carbonyl group in the Norrish type II processes.[12] In fact, we have observed that phthalimides with an ether moiety in their N-substituent undergo facile δ-hydrogen abstraction.[13] In the present cyclization (Chart 3), the substrates have several potentially reactive sites which the imide carbonyl could attack covalently. For example, compound **4b** has a six-carbon chain from γ to μ (Chart 5), with hydrogens (activated either by the adjacent oxygen or sulfur atoms) which could be abstracted by the excited imide carbonyl oxygen prior to the C–C bond formation. In view of the methodology of the photochemical syntheses of macrocycles, therefore, it is remarkable that the substrates **4** having many potentially reactive sites still undergo this remote cyclization selectively at the thiomethyl group. To estimate the efficiency of this remote reaction, the quantum yield was measured at 313 nm. The overall quantum yield for the formation of **5b** (in acetonitrile solution; 10 mM) was 0.006. It is worth noting that the quantum yield of the reaction is not very low, indicating[4,13] that this approach may provide a novel method for the synthesis of macrocyclic polyether derivatives: "photochemical synthesis of crown ethers". Heteromeric cyclic ethers thus prepared ranged up to a fifteen-membered ring **5c**, which is nearly equivalent in size to that of 15-crown-5.[9] Since the ligand capacity of crown-type compounds is highly dependent on the nature and arrangements of the hetero atoms,[9] "mixed" crowns such as compounds **5—7** represent a potentially interesting new family of compounds in the field of host-guest chemistry. The detailed mechanism of this remote photocyclization, including the regioselectivity is under investigation.

$$\alpha \quad \beta \quad \gamma \quad \delta \quad \varepsilon \quad \xi \quad \eta \quad \theta \quad \iota \quad \kappa \quad \mu$$
$$NCH_2CH_2OCH_2CH_2OCH_2CH_2SCH_3$$

4b

Chart 5

Experimental

All melting points were determined with a Yanagimoto capillary melting point apparatus (Model MP-1) and are uncorrected. IR spectra were recorded on a Hitachi IR-215 spectrophotometer. NMR spectra were determined on a JEOL JNM MH60 instrument in CDCl₃ (containing tetramethylsilane as an internal standard), unless otherwise specified. The chemical shifts are expressed in δ (ppm) values, coupling constants (J) are given in Hz and the following abbreviations are used; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. MS were measured on a Hitachi RMS-4 mass spectrometer. Molecular weights were measured with a Hitachi-Perkin-Elmer molecular weight measuring apparatus, Model 115 (vapor-pressure method).

General Procedure for the Synthesis of 2-[(ω-Bromo)polyoxalkyl]-isoindole-1,3(2H)-dione [N-(ω-Bromo)-polyoxalkyl]-phthalimide) (3)————A mixture of phthalimide (85 mmol), a dibromide [BrCH₂(CH₂OCH₂)ₙCH₂Br; n=1—3][14] (170 mmol) and K₂CO₃ (85 mmol) in dimethylsulfoxide (DMSO) (70 ml) was stirred at room temperature for 10 days. The reaction mixture was poured into ice-water, acidified with conc. HCl and extracted

with CHCl₃. The extracts were washed with water, dried over Na₂SO₄ and concentrated *in vacuo*. The residue was chromatographed on silica gel to give the desired compounds.

2-(2-(2-Bromoethoxy)ethyl)-isoindole-1,3(2*H*)-dione (3a)————The residue was chromatographed (benzene:hexane:AcOEt=6:3:0.5) to give 13.2 g (52.1%) of **3a** as colorless needles from CH₂Cl₂-hexane, mp 77—79°C. IR ν_{max}^{Nujol}cm⁻¹: 1765, 1705, 1615. MS m/e: 297(M⁺), 190, 174, 173, 160. NMR (CDCl₃) δ: 7.50—8.00 (4H, m, arom protons), 3.60—4.05 (6H, m, 3×CH₂), 3.25—3.55 (2H, m, BrCH₂). *Anal.* Calcd for C₁₂H₁₂BrNO₃: C, 48.34; H, 4.06; N, 4.70; Br, 26.80. Found: C, 48.53; H, 4.19; N, 4.70; Br, 27.14.

2-(2-(2-(2-Bromoethoxy)ethoxy)ethyl)-isoindole-1,3(2*H*)-dione (3b)————The residue was chromatographed (benzene : AcOEt=9 : 1) to give 24 g (82.5%) of **3b** as a colorless oil. IR $\nu_{max}^{liq.}$cm⁻¹: 1770, 1710, 1610. MS m/e: 341 (M⁺), 262, 174, 173, 160. NMR (CDCl₃) δ: 7.60—8.00 (4H, m, arom protons), 3.20—4.10 (12H, m, 6×CH₂). *Anal.* Calcd for C₁₄H₁₆BrNO₄: C, 49.14; H, 4.71; N, 4.09; Br, 23.35. Found: C, 49.07; H 4.80; N, 3.99; Br, 23.34.

2-(2-(2-(2-(2-Bromoethoxy)ethoxy)ethoxy)ethyl)-isoindole-1,3(2*H*)-dione (3c)————The residue was chromatographed (benzene:AcOEt=9:1) to give 18.5 g (54%) of **3c** as colorless needles from ether–hexane, mp 54—55°C. IR ν_{max}^{Nujol}cm⁻¹: 1765, 1715, 1610. MS m/e: 386 (M⁺+1), 306, 174, 173, 160. NMR (CDCl₃) δ: 7.60—8.00 (4H, m, arom protons), 3.30—4.10 (16H, m, 8×CH₂). *Anal.* Calcd for C₁₆H₂₀BrNO₅: C, 49.76; H, 5.22; N, 3.63; Br, 20.69. Found: C, 49.99; H, 5.15; N, 3.70; Br, 20.29.

General Procedure for the Synthesis of 2-[ω-(Methylthio)polyoxalkyl]-isoindole-1,3(2*H*)-dione (*N*-[ω-(Methylthio)polyoxalkyl]-phthalimide) (4)————Sodium methyl sulfide (45 mmol) was added to a solution of **3** (30 mmol) in dimethylformamide (DMF) (80 ml) at 0°C under an argon atmosphere. After being stirred at 30°C for 2 days, the mixture was poured into ice-water, acidified with conc. HCl, and extracted with AcOEt. The combined extracts were washed with water, dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by recrystallization or column chromatography.

2-(2-(2-(Methylthio)ethoxy)ethyl)-isoindole-1,3(2*H*)-dione (4a)————The crude product was recrystallized from AcOEt–hexane to give 2.81 g (70.3%) of **4a** as colorless needles, mp 84—85°C. IR ν_{max}^{Nujol}cm⁻¹: 1765, 1710, 1610. MS m/e: 265 (M⁺), 174, 160. NMR (CDCl₃) δ: 7.50—8.00 (4H, m, arom protons), 3.54—4.03 (6H, m, 3×CH₂), 2.61 (2H, t, J=6.7 Hz, SCH₂), 2.07(3H, s, SCH₃). *Anal.* Calcd for C₁₃H₁₅NO₃S: C, 58.86; H, 5.70; N, 5.28; S, 12.07. Found: C, 59.21; H, 5.80; N, 5.32; S, 12.06.

2-(2-(2-(2-(Methylthio)ethoxy)ethoxy)ethyl)-isoindole-1,3(2*H*)-dione (4b)————The crude product was chromatographed on silica gel (benzene:AcOEt=4:1) to give 5.6 g (60.4%) of **4b** as a colorless oil. IR $\nu_{max}^{liq.}$cm⁻¹:1765, 1710, 1610. MS m/e:309(M⁺), 174, 160. NMR (CDCl₃) δ: 7.60—8.00 (4H, m, arom protons), 3.50—4.05 (10H,'m, 5×CH₂), 2.61 (2H, t, J=6.7 Hz, SCH₂), 2.10 (3H, s, SCH₃). *Anal.* Calcd for C₁₅H₁₉NO₄S: C, 58.24; H, 6.19; N, 4.53; S, 10.35. Found: C, 58.50; H, 6.19; N, 4.51; S, 10.33.

2-(2-(2-(2-(2-(Methylthio)ethoxy)ethoxy)ethoxy)ethyl)-isoindole-1,3(2*H*)-dione (4c)————The crude product was chromatographed on silica gel (benzene:AcOEt=4:1) to give 9.04 g (85.4%) of **4c** as a colorless oil. IR $\nu_{max}^{liq.}$cm⁻¹: 1765, 1710, 1610. MS m/e: 353 (M⁺), 174, 160. NMR (CDCl₃) δ: 7.40—7.76 (4H, m, arom protons), 3.37—4.02 (14H, m, 7×CH₂), 2.65 (2H, t, J=6.8 Hz, SCH₂), 2.12 (3H, s, SCH₃). *Anal.* Calcd for C₁₇H₂₃NO₅S: C, 57.78; H, 6.56; N, 3.96; S, 9.06. Found: C, 58.19; H, 6.50; N, 3.96; S, 9.21.

General Procedure for the Irradiation————A solution of **4** [2.0—2.5 g (5.7—9.4 mmol)] in acetone (4.4—7.3 mM) was irradiated with a 400W high pressure mercury lamp at room temperature for 30—70 min in a stream of argon. After removal of the solvent *in vacuo*, the residue was subjected to silica gel column chromatography, followed by recrystallization of each fraction as appropriate (experimental details are given in Table I).

3,4,6,9,1b-Hexahydro-13b-hydroxy-1*H*-[1,4,7*a*]oxathiazonino[6,7-a]isoindol-9-one (5a) and 1,2,4,5,7,11b-Hexahydro-11b-hydroxy-1-methylthio[1,4]oxazepino[5,4-*a*]isoindol-7-one (6a)————The residue was purified by column chromatography (AcOEt : benzene : hexane=6 : 2.5 : 1.5) to give **5a** and **6a**. The more polar compound was recrystallized from ethanol–AcOEt–hexane to give 1.84 g (73.6%) of **5a** as colorless needles, mp 154—156°C. Molecular weight, calcd 265; found 251 (in MeOH). IR ν_{max}^{Nujol}cm⁻¹: 3240, 1685, 1675 (sh), 1665 (sh), 1615, 1600. MS m/e:266(M⁺+1), 247, 174, 160, 74. NMR (CDCl₃) δ: 7.30—7.70 (4H, m, arom protons), 4.57 (1H, s, OH), 3.10—4.00 (8H, m, 4×CH₂), 2.36 (2H, t, J=5 Hz, SCH₂CH₂O). *Anal.* Calcd for C₁₃H₁₅NO₃S: C, 58.86; H, 5.70; N, 5.28; S, 12.06. Found: C, 59.19; H, 5.77; N 5.32; S, 11.99. The less polar compound was recrystallized from ethanol–AcOEt–hexane to give 0.14 g (5.6%) **6a** as colorless prisms, mp 192—193°C. Molecular weight, calcd 265; found 256 (in MeOH). IR ν_{max}^{Nujol}cm⁻¹: 3260, 1670, 1610, 1590. MS m/e: 266 (M⁺+1), 74. NMR (CDCl₃) δ: 7.89 (1H, d, J=4 Hz, arom proton), 7.24—7.64 (3H, m, arom protons), 4.75 (1H, s, OH), 3.20—4.20 (6H, m, 3×CH₂), 2.93 (1H, dd, J=5 Hz, J=3 Hz, SCH), 2.16 (3H, s, SCH₃). *Anal.* Calcd for C₁₃H₁₅NO₃S: C, 58.86; H, 5.70; N, 5.28; S, 12.06. Found: C, 58.85; H, 5.76; N, 5.19; S, 11.93.

12,16b-Dihydro-16b-hydroxy[1,4]dioxa[7]thia[10]azacyclododecano[9,10-*a*]isoindol-12-one(5b)————The crude product was purified by column chromatography (AcOEt : benzene=3 : 2) to give 1.16 g (58%) of **5b** as colorless prisms from AcOEt–ether–hexane, mp 143—144°C. Molecular weight, calcd 309; found 299 (in MeOH). IR ν_{max}^{Nujol}cm⁻¹: 3300, 1670, 1615. MS m/e: 310 (M⁺+1), 309 (M⁺), 174, 160, 75, 74. NMR (CDCl₃) δ: 7.30—8.00 (4H, m, arom protons), 6.05 (1H, s, OH), 3.25—4.34 (10H, m, 5×CH₂), 2.74—3.14 (4H, m, 2×SCH₂). *Anal.* Calcd for C₁₅H₁₉NO₄S: C, 58.24; H, 6.19; N, 4.53; S, 10.35. Found: C, 58.23; H, 6.17; N, 4.47; S, 10.46.

15,19b-Dihydro-19b-hydroxy[1,4,7]trioxa[10]thia[13]azacyclopentadecano[12,13-*a*]isoindol-15-one (5c)

and 13,17b-Dihydro-17b-hydroxy-1-methylthio[1,4,7]trioxa[10]azacyclotridecano[11,10-*a*]isoindol-113-one (6c)————The crude products were purified by column chromatography (AcOEt : benzene=4 : 1) to give the desired compounds. The more polar compound was recrystallized from AcOEt–isopropyl ether to give 0.69 g (34.5%) of 5c as colorless needles, mp 98—99°C. Molecular weight, calcd 353; found 343 (in MeOH). IR ν_{max}^{Nujol}cm^{-1}: 3240, 1670, 1610. MS *m/e*: 354 (M$^+$+1), 353 (M$^+$), 336, 335, 174, 75, 74. NMR (CDCl$_3$) δ: 7.36—7.92 (4H, m, arom protons), 5.63 (1H, s, OH), 3.22—4.28 (16H, m, 8×CH$_2$), 2.46—3.10 (2H, m, SCH$_2$CH$_2$O). *Anal.* Calcd for C$_{17}$H$_{23}$NO$_5$S: C, 57.78; H, 6.56; N, 3.96; S, 9.06. Found: C, 57.88; H, 6.48; N, 3.92; S, 8.95. The less polar compound was recrystallized from AcOEt–isopropyl ether to give 0.48 g (24%) of 6c as colorless prisms, mp 127—130°C. Molecular weight, calcd 353; found 345 (in MeOH). IR ν_{max}^{Nujol}cm^{-1}: 3280, 1700, 1685, 1610. MS *m/e*: 354 (M$^+$+1), 353 (M$^+$), 336, 335, 280, 174, 74. NMR (CDCl$_3$) δ: 7.36—7.92 (4H, m, arom protons), 5.66 and 6.08 (1H, s, OH, for diastereo-mixture), 3.18—4.66 (15H, m, CH and 7×CH$_2$), 1.88 and 2.18 (3H, s, SCH$_3$, for diastereo-mixture). *Anal.* Calcd for C$_{17}$H$_{23}$NO$_5$S: C, 57.78; H, 6.56; N, 3.96; S, 9.06. Found: C, 57.90; H, 6.54; N, 3.84; S, 8.95.

3,4,6,7-Ttrahydro-9*H*-[1,4,7]oxathiazonino[6,7-*a*]isoindol-9-one (7a) [A Typical Procedure for the Dehydration of (5)]————A solution of 5a [130 mg (0.49 mmol)] and *p*-toluenesulfonic acid-3H$_2$O [13 mg (0.06 mmol)] in CH$_2$Cl$_2$ (13 ml) was refluxed for 40 min. After removal of the solvent *in vacuo*, the residue was recrystallized from AcOEt–isopropyl ether after column chromatography (AcOEt : benzene=1 : 1) to yield 115 mg (95%) of 7a as colorless needles, mp 155—156°C. IR ν_{max}^{Nujol}cm^{-1}: 1710, 1610, 1590. MS *m/e*: 247 (M$^+$), 188, 89. NMR (CDCl$_3$) δ: 7.3—8.00 (4H, m, arom protons), 6.36 (1H, s, olefinic proton), 4.83 (2H, m, NCH$_2$), 3.70—4.20 (4H, m, 2×OCH$_2$), 2.72 (2H, t, *J*=4.7Hz, SCH$_2$). *Anal.* Calcd for C$_{13}$H$_{13}$NO$_2$S: C, 63.15; H, 5.30; N, 5.67; S, 12.95. Found: C, 63.18; H, 5.22; N, 5.54; S, 12.83.

12*H*-[1,4]Dioxa[7]thia[10]azacyclododec[8]eno[9,10-*a*]isoindol-12-one (7b)————The reaction was processed in a manner similar to that described above. The product was recrystallized from AcOEt–hexane after column chromatography (AcOEt : hexane=3 : 2) to yield 170 mg (90.3%) of 7b as yellow needles, mp 142—144°C. IR ν_{max}^{Nujol}cm^{-1}: 1680, 1620. MS *m/e*: 291 (M$^+$), 258, 188. NMR (CDCl$_3$) δ: 7.23—8.20 (5H, m, arom and olefinic protons), 3.40—4.20 (10H, m, 5×CH$_2$), 3.04 (2H, t, SCH$_2$). *Anal.* Calcd for C$_{15}$H$_{17}$NO$_3$S: C, 61.85; H, 5.88; N, 4.81; S, 10.98. Found: C, 61.75; H, 5.88; N, 4.85; S, 11.04.

15*H*-[1,4,7]Trioxa[10]thia[13]azacyclopentadec[11]eno[12,13-*a*]isoindol-15-one (7c)————The reaction was processed in a manner similar to that described above. The product was recrystallized from CH$_2$Cl$_2$–hexane after column chromatography (AcOEt : hexane=4 : 1) to yield 137 mg (96.5%) of 7c as colorless needles, mp 137—138°C. IR ν_{max}^{Nujol}cm^{-1}: 1690, 1620, 1580. MS *m/e*: 335 (M$^+$), 302, 188, 172, 170. NMR (CDCl$_3$) δ: 8.20 (1H, d, d, *J*=6.0 and 1.9 Hz arom proton), 7.35—7.90 (3H, m, arom protons), 6.65 (1H, s, olefinic proton), 3.50—4.20 (14H, m, 7×CH$_2$), 3.03 (2H, t, *J*=6.4 Hz, SCH$_2$). *Anal.* Calcd for C$_{17}$H$_{21}$NO$_4$S: C, 60.88; H, 6.31; N, 4.18; S, 9.54. Found: C, 60.93; H, 6.29; N, 4.25; S, 9.54.

References and Notes

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