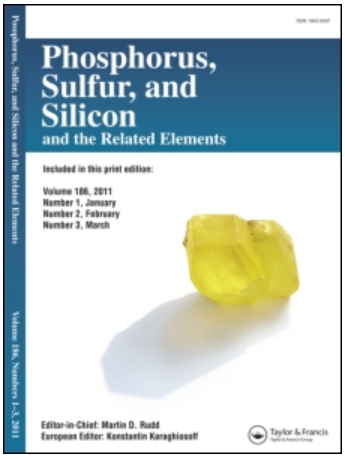

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LACTONIZATION REACTIONS OF (ω-CARBOXYALKYL)SULFONIUM SALTS

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LACTONIZATION REACTIONS OF (ω-CARBOXYALKYL)SULFONIUM SALTS

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The intramolecular cyclizations of sulfonium salts having an ω-carboxyalkyl group were investigated for the synthesis of five- to nine-membered lactones, and five- to seven-membered lactones were obtained in good yields from S-(ω-carboxyalkyl)thiolanium salts. The scope and limitations of the synthetic utility of the reaction are indicated by this study.

Key words: Lactonization reactions; (ω-carboxyalkyl)diphenylsulfonium salts; S-(ω-carboxyalkyl)thiolanium salts; medium-sized lactones; large-sized lactones; sulfur-containing lactones.

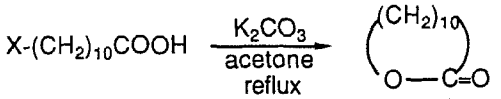
INTRODUCTION

The synthetic methods of macrocyclic lactones have been developed rapidly in the last two decades, since lactones are useful as perfumes and have biological activities.[1] Recently, much attention has been focused in the organic synthesis using sulfonium salts as alkylating reagents.[2] Bravo *et al.* reported the synthesis of optically active γ-lactones using sulfonium salts.[3] We have been interested in the use of sulfonium salts as alkylating reagents toward nucleophiles such as carboxylate anions, enolate ions of β-keto esters, phenols, amines, and thiolate ions.[4] Previously, we reported a useful method for the synthesis of large-sized lactones using (ω-carboxyalkyl)sulfonium salts.[5] In the reaction system, we supposed that the effective lactonization may be due to the electrostatic interaction between sulfonium ion and carboxylate anion which leads to regiospecific positioning of nucleophilic centers in close proximity to the sp^3 carbon atom adjacent to a sulfur atom. So, we investigated the effect of some leaving groups on the yields of cyclization and applied the intramolecular cyclization method using (ω-carboxyalkyl)sulfonium salts for the synthesis of medium-sized lactones. The scope and limitations of the synthetic utility of the reaction are indicated in this paper.

RESULTS AND DISCUSSION

Effect of Leaving Groups on the Yields of Cyclization

As a model case, we examined the effect of some leaving groups for the intramolecular cyclization of ω-functionalized undecanoic acid derivatives in acetone in the presence of potassium carbonate as a base under high-dilution conditions (Equation 1). (10-Carboxydecyl)diphenylsulfonium tetrafluoroborate and perchlorate gave markedly better yields than (11-p-tolylsulfonyloxy)undecanoic acid or 11-iodoun-



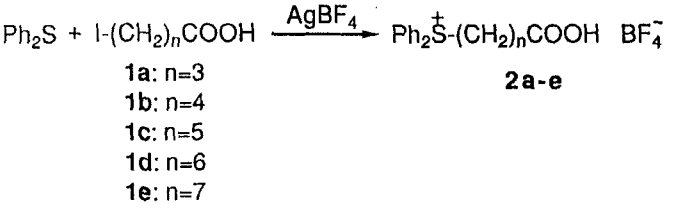
X	
TsO	48%
I	68
$Ph_2S^+(BF_4^-)$	85
$Ph_2S^+(ClO_4^-)$	87

(1)

decanoic acid.[6] The acceleration of intramolecular cyclization of (ω-carboxyalkyl)diphenylsulfonium salts can be accounted for by the electrostatic interaction between sulfur atom of the sulfonium ion and oxygen atom of carboxylate anion.[7]

Synthesis of Lactones from (ω-Carboxyalkyl)diphenylsulfonium Salts

(ω-Carboxyalkyl)diphenylsulfonium salts (**2a–e**) were prepared in 80–90% yields from diphenyl sulfide and ω-iodocarboxylic acids (**1a–e**) in the presence of silver tetrafluoroborate (Equation 2). S-(ω-Carboxyalkyl)thiolanium salts (**3a–e**) were

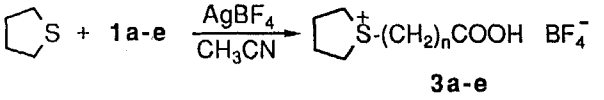


1a: n=3
1b: n=4
1c: n=5
1d: n=6
1e: n=7

2a-e

(2)

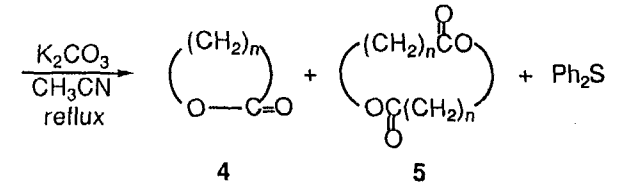
readily prepared in 90–100% yields from thiolane and **1a–e** in the presence of silver tetrafluoroborate in acetonitrile (Equation 3).



3a-e

(3)

The lactonization of (3-carboxypropyl)diphenylsulfonium tetrafluoroborate (**2a**; $n = 3$) (Equation 4) was carried out in acetonitrile in the presence of potassium carbonate as a base under high-dilution conditions to afford γ-butyrolactone (**4a**) (28%) and diolide (macrocyclic lactide) **5a** ($n = 3$) (2%). Similarly, sulfonium salts **2b–e** were cyclized under similar conditions, and the results are summarized in



4 **5**

(4)

TABLE I
Lactonization of sulfonium salts **2**

Sulfonium salt	Ring size of **4**	Yield[a]/%		
		4	**5**	Ph_2S
2a (n = 3)	5	**4a** 28	**5a** 2	65
2b (n = 4)	6	**4b** 26	**5b** 46	67
2c (n = 5)	7	**4c** 30	**5c** 6	82
2d (n = 6)	8	**4d** 18	**5d** 11	91
2e (n = 7)	9	**4e** 33	**5e** 12	84
2 (n = 10–14)[b]	12–16	85–92	0–11	86–97

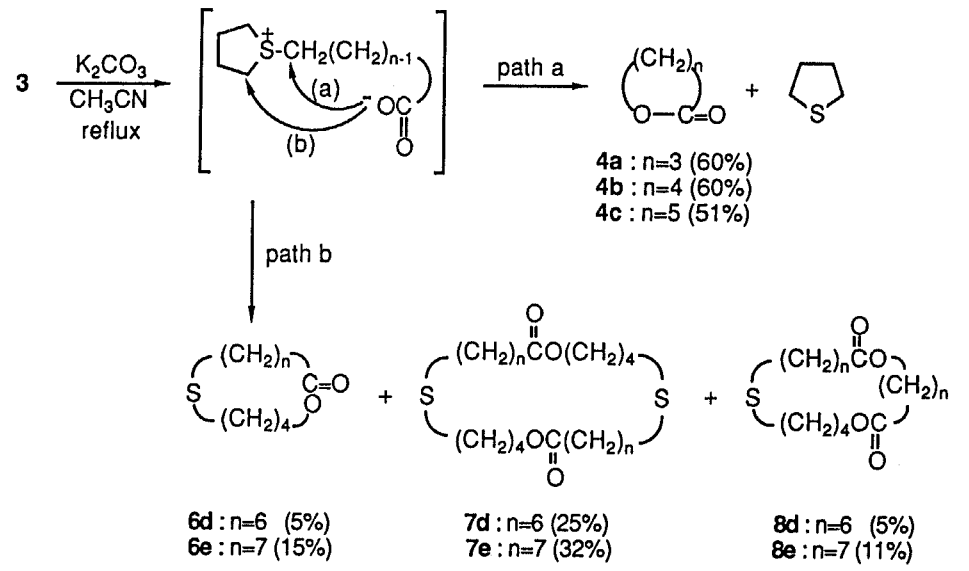
[a]Isolated yield.
[b]Reference 5.

Table I. The yields of five- to nine-membered lactones **4** (n = 3–7) were moderate (18–33%), although macrocyclic lactones **4** (n = 12–16) were obtained in high yields (85–92%) as we reported previously.[5]

Generally, it is difficult to synthesize medium-sized ring compounds including lactones, and seven- to nine-membered lactones have not been prepared by the cyclization of ω-halocarboxylic acids.[6] Kellogg *et al.* reported that the cyclization of ω-halocarboxylic acid **1c** (n = 5) in the presence of Cs_2CO_3 in N,N-dimethylformamide (DMF) afforded only diolide **5c** (n = 5) without the formation of seven-membered lactone **4c** (n = 5).[6c] On the other hand, the present methods provided seven- to nine-membered lactones **4c–e** by intramolecular cyclization using sulfonium salts though the yields were not excellent. These cyclization methods have advantage for the synthesis of medium-sized lactones due to the electrostatic interaction between sulfur atom of the sulfonium ion and oxygen atom of the carboxylate anion.[7] For the reason that the total yields of lactones **4** and diolides **5** were lower than that of diphenyl sulfide produced as leaving group in our reaction system, β-elimination may be occurring as a side reaction,[8] although we failed to isolate the corresponding β-elimination product.

Synthesis of Lactones from S-(ω-Carboxyalkyl)thiolanium Salts

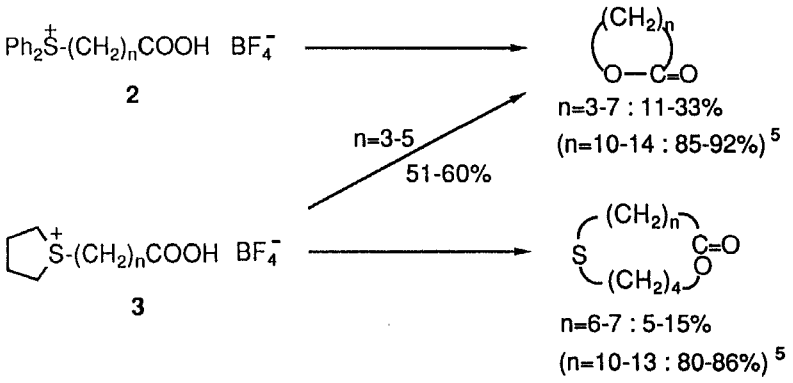
Interestingly, Eliel *et al.*[9] reported that alkylation of nucleophiles with S-alkylthiolanium salts occurred preferentially on the α-methylene carbon of the five-membered ring. In the case of intramolecular cyclization of thiolanium salts **3**, carboxylate anion formed from **3** may attack on two kind of carbons; one is the side chain's methylene carbon atom (Scheme I, path a) and the other is the α-methylene carbon atom of the five-membered ring (Scheme I, path b). We synthesized S-(ω-carboxyalkyl)thiolanium tetrafluoroborates (**3a–e**) and examined their intramolecular cyclization (Scheme I). The intramolecular cyclization of S-(ω-carboxyalkyl)thiolanium salts (**3a–c**; n = 3–5) gave five- to seven-membered lactones **4a–c** in good yields (51–60%) without the formation of sulfur-containing lactones **6**. Whereas, in the case of sulfonium salts **3d,e** (n = 6,7) having a longer CH_2-chain, sulfur-containing lactones **6d,e** were formed in low yields (5–15%) (via path b), together with the moderate amounts of diolides **7** (25–32%) and **8** (5–11%). In the intramolecular cyclization of S-(ω-carboxyalkyl)thiolanium salts (**3**; n = 10–



SCHEME I

13) giving large-membered lactones, we reported that the carboxylate anion attacks selectively on the α-methylene carbon atom of the five-membered ring (via path b).[5] This difference in regioselectivity of intramolecular cyclization of thiolanium salts **3** is of interest and depends on the numbers of n in the CH_2-chain in the carboxyalkyl group of **3**. If the carboxylate anions of **3b,c**, having a shorter CH_2-chain, attack selectively on the α-methylene carbon atom of the five-membered ring (via path b), the intramolecular cyclization has to proceed via eight- or nine-membered transition state which is generally an unfavorable ring system.

In conclusion, the intramolecular cyclization of sulfonium salts **2** and **3** having an ω-carboxyalkyl group is an interesting method for the synthesis of lactones: (1)



SCHEME II

The cyclization of (ω-carboxyalkyl)diphenylsulfonium salts **2** (n = 3–7, 10–14) afforded the five- to sixteen-membered lactones, although the yields were moderate in the case of **2a–e** (n = 3–7) because β-elimination may be occurring as a side reaction. (2) Sulfur-containing lactones via ring-expansion reactions were obtained from S-(ω-carboxyalkyl)thiolanium salts **3** (n = 6, 7, 10–13) having a longer CH_2-chain. In the case of thiolanium salts **3a–c** (n = 3–5), having a shorter CH_2-chain, thiolane acted as a good leaving group to afford five- to seven-membered lactones in good yields (Scheme II).

EXPERIMENTAL

Melting points were determined on a Yamato MP-21 apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Proton magnetic resonance spectra were recorded on a JEOL PMX 60SI (60 MHz) spectrometer. Mass and high-resolution mass spectra were determined with a JEOL JMX-DX300 mass spectrometer with JEOL JMA 5000 mass data system at an ionizing voltage of 70 eV. GLPC were recorded on a Hitachi G-3000 with 10% SE-30 1-m column. Column chromatography was performed with Wako gel C-200 (Wako Pure Chemical Ind.). Thin-layer chromatography was performed on 0.25-mm silica gel (Merck $60F_{254}$). Acetonitrile was distilled from calcium hydride and stored over molecular sieves 4A (Wako Pure Chemical Ind.).

4-Bromobutyric acid, 5-bromovaleric acid, 6-bromohexanoic acid, 7-bromoheptanenitrile, 8-bromooctanoic acid, 11-bromoundecanoic acid, thiolane, γ-butyrolactone, δ-valerolactone, and 6-hexanolide from Aldrich Chemical Co. were used without purification.

ω-Iodocarboxylic acids **1a–e** were prepared quantitatively by treatment of the corresponding ω-bromocarboxylic acids with KI (3 equiv.) in boiling acetone for 6 h.

1a (n = 3): mp 28–29°C; ^{1}H NMR ($CDCl_3$) δ = 1.90–2.67 (4H, m), 3.25 (2H, t, J = 6.5 Hz), and 11.0 (1H, br s); IR (KBr) 3500–2500 (OH) and 1720 cm^{-1} (CO).
1b (n = 4): mp 53–54°C; ^{1}H NMR ($CDCl_3$) δ = 1.68–2.20 (4H, m), 2.43 (2H, t, J = 6.5 Hz), 3.22 (2H, t, J = 6.5 Hz), and 9.40 (1H, br s); IR (KBr) 3300–2300 (OH) and 1680 cm^{-1} (CO).
1c (n = 5): mp 40–41°C; ^{1}H NMR ($CDCl_3$) δ = 1.42–2.08 (6H, m), 2.37 (2H, t, J = 6.5 Hz), 3.14 (2H, t, J = 6.5 Hz), and 11.0 (1H, br s); IR (KBr) 3300–2300 (OH) and 1690 cm^{-1} (CO).
1e (n = 7): mp 37°C; ^{1}H NMR ($CDCl_3$) δ = 1.13–2.10 (10H, m), 2.17–2.57 (2H, m), 3.16 (2H, t, J = 6.5 Hz), and 11.0 (1H, br s); IR (KBr) 3400–2400 (OH) and 1687 cm^{-1} (CO); MS m/z 271 (M^+ + 1), 253, 169.

7-Iodoheptanoic acid (**1d**; n = 6) was prepared by the reaction of 7-bromoheptanenitrile with 57%-hydriodic acid in AcOH under reflux conditions for 1 day.[10] After distillation of hydriodic acid and AcOH, the residue was extracted with ether. The combined extracts were washed with aqueous $Na_2S_2O_3$, dried over Na_2SO_4, and concentrated. Recrystallization from ether-hexane gave **1d** (n = 6) as colorless crystals: 91% yield; mp 42–45°C; ^{1}H NMR ($CDCl_3$) δ = 1.05–2.11 (8H, m), 2.21–2.54 (2H, m), 3.16 (2H, t, J = 6.7 Hz), and 11.3 (1H, br s); IR (KBr) 3300–2200 (OH) and 1689 cm^{-1} (CO); MS m/z 257 (M^+ + 1), 239, 169.

Preparation of (ω-carboxyalkyl)diphenyl sulfonium salts **2**. In a round-bottomed flask were placed **1a–e** (10 mmol) and silver tetrafluoroborate (11 mmol); this was cooled in an ice bath. Phenyl sulfide (18.6 g, 100 mmol) was added dropwise over 5 min and then the ice bath was removed. The mixture was stirred for 3 days at room temperature in the dark. The reaction mixture was passed through a silica gel short column and eluted with acetone. After removal of solvent, the residue was washed with ether. The crude products obtained were purified from acetone-ether to yield sulfonium salts **2** in 80–90% yields.

2a (n = 3): oil; ^{1}H NMR (acetone-d_6) δ = 1.70–3.00 (4H, m), 4.00–4.60 (2H, m), and 7.50–8.30 (11H, m); IR (neat) 3600–2700 (OH), 1710 (CO), and 1070 cm^{-1} (BF_4^-).
2b (n = 4): oil; ^{1}H NMR (acetone-d_6) δ = 1.50–2.10 (4H, m), 2.20–2.50 (2H, m), 4.20–4.60 (2H, m), 7.00 (1H, br s), and 7.50–8.20 (10H, m); IR (neat) 3600–2500 (OH), 1720 (CO), and 1060 cm^{-1} (BF_4^-).
2c (n = 5): oil; ^{1}H NMR (acetone-d_6) δ = 1.50–2.10 (6H, m), 2.27 (2H, t, J = 6.0 Hz), 4.33 (2H, t, J = 6.0 Hz), and 7.70–8.30 (11H, m); IR (neat) 3600–2700 (OH), 1710 (CO), and 1070 cm^{-1} (BF_4^-).
2d (n = 6): oil; ^{1}H NMR (acetone-d_6) δ = 1.27–1.99 (8H, m), 2.13–2.50 (2H, m), 4.17–4.60 (2H, m), 7.56–7.88 (6H, m), 7.98–8.39 (4H, m), and 9.60 (1H, br s); IR (neat) 3675–2400 (OH), 1726 (CO), and 1064 cm^{-1} (BF_4^-).

2e (n = 7): oil; ^{1}H NMR (acetone-d_6) δ = 1.15–1.98 (10H, m), 2.02–2.57 (2H, m), 4.06–4.60 (2H, m), 7.53–7.83 (6H, m), 7.95–8.29 (4H, m), and 9.33 (1H, br s); IR (neat) 3650–2400 (OH), 1704 (CO), and 1066 cm^{-1} (BF_4^-).

Preparation of S-(ω-carboxyalkyl)thiolanium salts **3**. In a round-bottomed flask, cooled in an ice bath, were placed **1** (10 mmol) and silver tetrafluoroborate (11 mmol). Thiolane (11 mmol) in CH_3CN (15 ml) was added dropwise over 5 min and then the ice bath was removed. The mixture was stirred for 3 days at room temperature in the dark. The reaction mixture was worked up as described for the preparation of **2** to yield **3** in 90–100% yields.

3a (n = 3): oil; ^{1}H NMR (acetone-d_6) δ = 1.80–2.80 (8H, m), 3.10–3.70 (6H, m), and 9.10 (1H, br s); IR ($CHCl_3$) 3700–2700 (OH), 1710 (CO), and 1040 cm^{-1} (BF_4^-).
3b (n = 4): oil; ^{1}H NMR (acetone-d_6) δ = 1.50–2.10 (4H, m), 2.20–2.70 (6H, m), 3.00–3.80 (6H, m), and 8.30 (1H, br s); IR ($CHCl_3$) 3600–2700 (OH), 1710 (CO), and 1050 cm^{-1} (BF_4^-).
3c (n = 5): oil; ^{1}H NMR (acetone-d_6) δ = 1.50–2.10 (6H, m), 2.20–2.70 (6H, m), 3.10–3.80 (6H, m), and 7.80 (1H, br s); IR ($CHCl_3$) 3600–2700 (OH), 1700 (CO), and 1050 cm^{-1} (BF_4^-).
3d (n = 6): oil; ^{1}H NMR (acetone-d_6) δ = 1.31–1.93 (8H, m), 2.17–2.54 (6H, m), 3.04–3.83 (6H, m), and 9.67 (1H, br s); IR (neat) 3700–2400 (OH), 1728 (CO), and 1047 cm^{-1} (BF_4^-).
3e (n = 7): oil; ^{1}H NMR (acetone-d_6) δ = 1.00–1.93 (10H, m), 2.17–2.53 (6H, m), 3.06–3.78 (6H, m), and 9.21 (1H, br s); IR (neat) 3700–2700 (OH), 1704 (CO), and 1059 cm^{-1} (BF_4^-).

General procedure of intramolecular cyclization. To a stirred suspension of K_2CO_3 (831 mg, 6 mmol) in refluxing acetonitrile (100 ml) was added sulfonium salt (2 mmol) in acetonitrile (100 ml) over 1.5 days. After the mixture was refluxed for additional 12 h, the solution was cooled to room temperature, diluted with ether (100 ml), and passed through a silica-gel short column (ca. 10 cm). The solvent was removed, and the residue was chromatographed on silica gel (hexane-ether) to give pure products. The lactones **4a–c** (n = 3–5) were identified by the comparison of ^{1}H NMR, IR, mass spectral data, and retention time of GC with the authentic lactones from Aldrich Chemical Co., and bisolides **5a–c** (n = 3–5) were determined by GC-MS measurement. The following lactones, **4d,e** and **5d,e** were characterized by ^{1}H NMR, IR, and mass spectral data.

4d (n = 6): 18% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.39–2.05 (8H, m), 2.39–2.67 (2H, m), and 4.18–4.50 (2H, m); IR (neat) 1722 cm^{-1} (CO); MS m/z 128 (M^+), 100, 98.
4e (n = 7): 33% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.17–2.00 (10H, m), 2.10–2.47 (2H, m), and 4.13–4.43 (2H, m); IR (neat) 1735 cm^{-1} (CO); MS m/z 142 (M^+), 124, 112.
5d (n = 6): 11% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.33–1.95 (16H, m), 2.27–2.53 (4H, m), and 3.95–4.23 (4H, m); IR (neat) 1726 cm^{-1} (CO); MS m/z 256 (M^+), 197, 183.
5e (n = 7): 12% yield; Mp 86–88°C (colorless needles); ^{1}H NMR ($CDCl_3$) δ = 1.12–1.98 (20H, m), 2.07–2.63 (4H, m), and 3.99–4.29 (4H, m); IR (KBr) 1727 cm^{-1} (CO); MS m/z 284 (M^+), 265, 197.

Sulfur-containing lactones **6d** (n = 6), **6e** (n = 7), and diolides **7,8** were also determined by ^{1}H NMR, IR, and mass spectral data.

6d (n = 6): 5% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.13–2.07 (12H, m), 2.26–2.72 (6H, m), and 3.94–4.30 (2H, m); IR (neat) 1725 cm^{-1} (CO); MS m/z 216 (M^+), 187, 157; HRMS, Calcd for $C_{11}H_{20}O_2S$: 216.1184. Found: 216.1148.
6e (n = 7): 15% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.16–2.07 (14H, m), 2.27–2.77 (6H, m), and 4.06–4.35 (2H, m); IR (neat) 1726 cm^{-1} (CO); MS m/z 230 (M^+), 171, 157; HRMS, Calcd for $C_{12}H_{22}O_2S$: 230.1340. Found: 230.1345.
7d (n = 6): 25% yield; mp 63–65°C (colorless crystals); ^{1}H NMR ($CDCl_3$) δ = 1.17–2.03 (24H, m), 2.17–2.80 (12H, m), and 3.99–4.30 (4H, m); IR (KBr) 1727 cm^{-1} (CO); MS m/z 432 (M^+), 303, 217; HRMS, Calcd for $C_{22}H_{40}O_4S_2$: 432.2368. Found: 432.2426.
8d (n = 6): 5% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.13–2.03 (20H, m), 2.15–2.71 (8H, m), and 3.97–4.26 (4H, m); IR (neat) 1727 cm^{-1} (CO); MS m/z 344 (M^+), 285, 217; HRMS, Calcd for $C_{18}H_{32}O_4S$: 344.2021. Found: 344.2006.
7e (n = 7): 32% yield; mp 47–49°C (colorless crystals); ^{1}H NMR ($CDCl_3$) δ = 1.05–2.03 (28H, m), 2.16–2.71 (12H, m), and 3.90–4.30 (4H, m); IR (KBr) 1728 cm^{-1} (CO); MS m/z 461 (M^+ + 1), 318, 231; HRMS, Calcd for $C_{24}H_{44}O_4S_2$: 460.2859. Found: 460.2898.
8e (n = 7): 11% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 1.13–1.97 (24H, m), 2.14–2.71 (8H, m), and 3.97–4.27 (4H, m); IR (neat) 1725 cm^{-1} (CO); MS m/z 373 (M^+ + 1), 313, 231; HRMS, Calcd for $C_{20}H_{36}O_4S$: 372.2334. Found: 372.2288.

General procedure of intramolecular cyclization of ω-functionalized undecanoic acid derivatives. To a stirred suspension of potassium carbonate (831 mg, 6 mmol) in refluxing acetone (100 ml) was added ω-functionalized undecanoic acid derivative (2 mmol) in acetone (100 ml) over 1.5 days. After the

mixture was refluxed for additional 12 h, the solution was cooled to room temperature, diluted with ether (100 ml), and passed through a silica-gel short column (ca. 10 cm). The solvent was removed and the residue was chromatographed on silica gel (hexane-ether) to give pure products.

Oxacyclododecan-2-one[6a] was characterized by ^{1}H NMR, IR, and mass spectral data: ^{1}H NMR ($CDCl_3$) δ = 1.33–1.91 (16H, m), 2.26–2.63 (2H, m), 4.07–4.23 (2H, m); IR (neat) 1734 cm^{-1} (CO); MS *m/z* 185 (M^+ + 1), 166, 148.

11-Iodoundecanoic acid was prepared by treatment of 11-bromoundecanoic acid with KI (3 equiv.) in boiling acetone for 3 h. Recrystallization from ether-hexane yielded pure acid as colorless crystals: 98% yield; mp 65°C; ^{1}H NMR ($CDCl_3$) δ = 1.30–1.92 (16H, m), 2.22–2.47 (2H, m), 3.17 (2H, t, *J* = 6.6 Hz), 11.6 (1H, br s); IR (KBr) 3460–2770 (OH), 1695 cm^{-1} (CO).

(11-*p*-Tolylsulfonyloxy)undecanoic acid was prepared by the reaction of 11-hydroxyundecanoic acid with *p*-toluenesulfonyl chloride in pyridine at room temperature for 2 h: 26% yield; oil; ^{1}H NMR ($CDCl_3$) δ = 0.97–2.00 (16H, m), 2.13–2.55 (5H, m), 3.85–4.18 (2H, m), 7.26 and 7.69 (4H, ABq, *J* = 7.7 Hz), and 9.97 (1H, br s); IR (neat) 3500–2400 (OH), 1708 (CO), 1600 (Ar), 1358, 1175 cm^{-1} (SO_2); MS *m/z* 338 (M^+ – 18), 183, 173. 11-Hydroxyundecanoic acid was prepared by hydrolysis of 11-hydroxyundecanoic lactone, oxacyclododecan-2-one,[6a] in 95% yield: mp 65–66°C (lit.,[11] mp 66–67°C); ^{1}H NMR ($CDCl_3$) δ = 1.00–1.93 (16H, m), 2.17–2.53 (2H, m), 3.47–3.80 (2H, m), 7.06 (2H, s).

(10-Carboxydecyl)diphenylsulfonium tetrafluoroborate: 87% yield; oil; ^{1}H NMR (acetone-d_6) δ = 1.08–2.00 (16H, m), 2.13–2.47 (2H, m), 4.03–4.47 (2H, m), 7.47–7.80 (6H, m), 7.90–8.20 (4H, m), 8.77 (1H, br s); IR (neat) 3700–2400 (OH), 1728 (CO), 1057 cm^{-1} (BF_4^-).

(10-Carboxydecyl)diphenylsulfonium perchlorate: 90% yield; oil; ^{1}H NMR (acetone-d_6) δ = 1.27–3.20 (18H, m), 4.38 (2H, t, *J* = 7.0 Hz), 7.25–7.80 (6H, m), 7.98–8.20 (4H, m), 9.73 (1H, br s); IR (neat) 3600–3000 (OH), 1710 (CO), 1080 cm^{-1} (ClO_4^-).

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