Pergamon

Tetrahedron 56 (2000) 8077–8081

TETRAHEDRON

One-Pot Synthesis of Cycloalkane Derivatives using Allyl Phenyl Sulfone and Epoxymesylate

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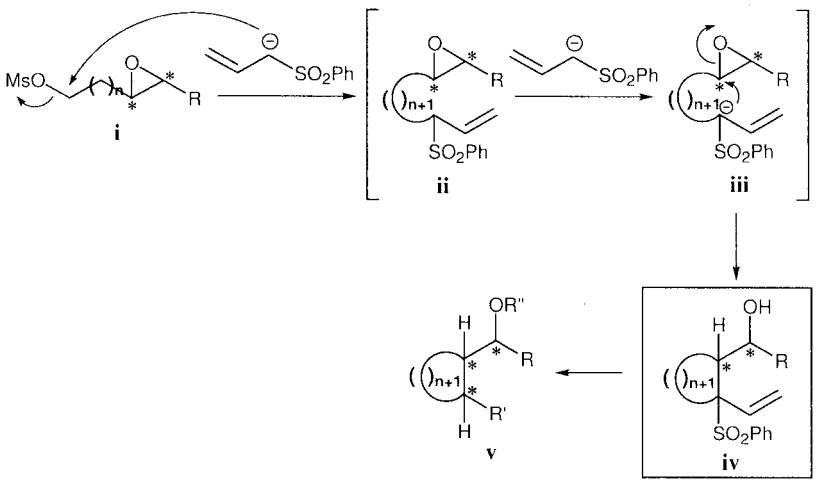
Received 17 July 2000; accepted 21 August 2000

Abstract—One-pot synthesis of cycloalkane derivatives using an anion of allyl phenyl sulfone and epoxymesylate is presented.

Sulfones are useful in the conduct of carbon–carbon bond-forming reactions and thus have found wide application in organic synthesis.[1] The anion prepared from allyl phenyl sulfone[2] and base, reacts with alkyl halide, epoxide, ketone or enone as a nucleophile mainly at the α position on an allyl group.[3] Allyl phenyl sulfone forms two carbon–carbon bonds at the α position to sulfone in the presence of 2 equiv. of base and electrophile. Reaction of allyl phenyl sulfone with a compound having two leaving groups, in the presence of 2 equiv. of base, should proceed through intermolecular alkylation followed by intramolecular alkylation to form cycloalkane at the α position of sulfone.[4]

In this study, examination was made of reaction of allyl phenyl sulfone and epoxymesylate **i** to give cycloalkane derivative **iv** through intermolecular and intramolecular alkylations (Scheme 1).[5] Various ring-size cycloalkane **iv** was obtained by alteration of the length of the methylene chain in epoxymesylate **i**.

The synthesis of cycloalkane **iv** using allyl phenyl sulfone and epoxymesylate **i** was found to involve the following uninterrupted continuous flow, so to speak, sequence: (1) anion of allyl phenyl sulfone reacts with epoxymesylate **i** to give epoxysulfone **ii**; (2) lithiation of epoxysulfone **ii** by an anion of allyl phenyl sulfone in situ gives anion **iii**; and (3) intramolecular alkylation of anion **iii** gives cycloalkane **iv**. Stereochemistry of the hydroxyl group and the methine adjacent the hydroxyl group in **iv** is dependent on stereochemistry of the epoxide in epoxymesylate **i**. The carbon chain at the vinyl group in cycloalkane **iv** is capable of elongation. Cycloalkane **iv** is easily converted to



Scheme 1.

Keywords: sulfones; cycloalkanes; epoxides; marine metabolites; eicosanoids.

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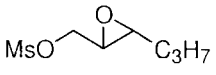
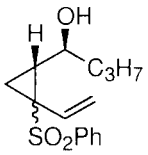
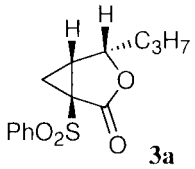
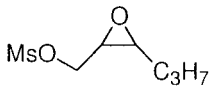
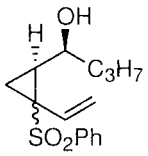
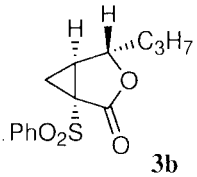
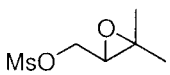
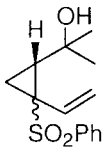
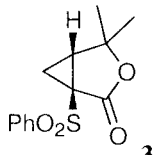
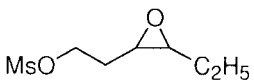
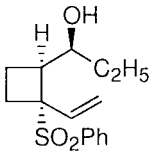
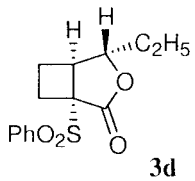
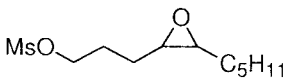
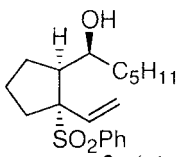
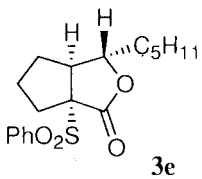
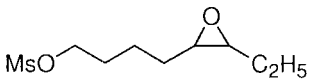
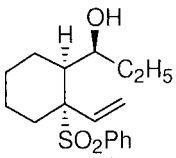
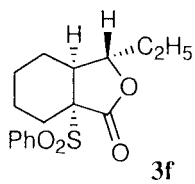
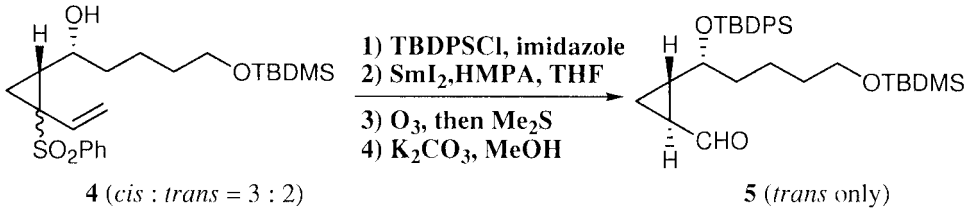
0040–4020/00/$ - see front matter
PII: S0040-4020(00)00728-6

Table 1. One-pot synthesis of cycloalkane derivative using allyl phenyl sulfone and epoxymesylate

Entry	Epoxide	Product	Yield[a)]	Lactone
1	 **1a**	 **2a** (*cis* : *trans* = 3 : 2)[b)]	96%	 **3a**
2	 **1b**	 **2b** (*cis* : *trans* = 3 : 2)[b)]	86%	 **3b**
3	 **1c**	 **2c** (*cis* : *trans* = 4 : 1)[b)]	92%	 **3c**
4	 **1d**	 **2d** (*cis* only)	47%	 **3d**
5	 **1e**	 **2e** (*cis* only)	91%	 **3e**
6	 **1f**	 **2f** (*cis* only)	82%	 **3f**

[a]Chemical yield was calculated based on epoxymesylate.
[b]The ratio of diastereomers was determined by ^{1}H NMR analysis.

cycloalkane **v** which has three consecutive chiral centers, by removal of the phenyl sulfonyl group. This study presents the one-pot synthesis of cyclopropane, cyclobutane, cyclopentane and cyclohexane using allyl phenyl sulfone and epoxymesylate. The anion of sulfone was prepared from allyl phenyl sulfone (2.4 equiv.) and ^{n}BuLi (2.3 equiv.) in THF at −78°C for 30 min. Epoxymesylate **1a** corresponding to **i** (n=0) (1.0 equiv.), prepared from the corresponding olefinic alcohol by epoxidation and mesylation in THF was then added at −78°C. The reaction mixture was warmed to room temperature over 5 h and stirred for 2 h to give cyclopropane derivative **2a** as epimeric mixtures in a 3:2 ratio with the sulfonyl group in 96% yield based on epoxymesylate **1a** (entry 1). The dianion of allyl phenyl sulfone,[6] prepared from allyl phenyl sulfone (1.2 equiv.) and ^{n}BuLi (2.4 equiv.) in THF, reacted with epoxymesylate **1a** (1.0 equiv.) to give cyclopropane derivative **2a** in 43% yield. The following all one-pot reactions were conducted under the above reaction conditions. Subsequent to separation of the epimeric mixtures **2a**, relative configurations of the major and minor products were determined by chemical conversions. The major product was ozonized and then subjected to Jones oxidation to give lactone **3a**. Thus, the relative configuration of two alkyl groups of **2a** major was determined to be *cis* configuration and that of two alkyl groups of **2a** minor was determined to be *trans* configuration. Relative configurations of other cycloalkane derivatives **2b–f** were determined based on similar chemical conversions of **2b–f** to lactone **3b–f**. Reaction of epoxymesylate **1b**, the epimer of **1a**, gave cyclopropane derivative **2b** as a mixture of diastereomers (3:2) in 86% yield (entry 2). Epoxymesylate **1c** was reacted with allyl phenyl sulfone to give cyclopropane derivatives **2c** as a mixture of diastereomers (4:1) in 92% yields (entry 3). Epoxymesylate



4 (*cis* : *trans* = 3 : 2) **5** (*trans* only)

Scheme 2.

1d corresponding to **i** (n=1) reacted with allyl phenyl sulfone to afford cyclobutane derivative **2d** as the sole product in 47% yield (entry 4). Reactions of epoxymesylates **1e** and **1f** corresponding to **i** (n=2 and 3) with allyl phenyl sulfone gave cyclopentane derivative **2e** and cyclohexane derivative **2f** in 91 and 82% yields as the sole products, respectively (entries 5 and 6) (Table 1).

A *cis–trans* mixture of cyclopropane may undergo transformation to *trans*-cyclopropane by chemical conversions. The chemical transformation of a *cis–trans* mixture of cyclopropane **4** to *trans*-aldehyde **5** was previously reported to occur by protection of secondary hydroxyl group, removal of phenyl sulfonyl group, ozonolysis of vinyl group and isomerization of formyl group in the synthesis of marine eicosanoid constanolactone E (Scheme 2).[7]

The present results clearly demonstrate the one-pot synthesis of cycloalkane derivatives to be an effective means for the synthesis of natural products containing cyclopropane, cyclobutane, cyclopentane and cyclohexane derivative. Optically active cycloalkane derivative is produced by this reaction in that optically active epoxymesylate was found to be readily produced by asymmetric epoxidation. The synthesis of marine eicosanoid bacillariolides I–III by application of the present mode of synthesis to the optically active form is presented in the paper that follows the present one.[8]

Experimental

General experimental procedures

Melting points were measured on Yazawa BY-2 micro melting point apparatus and uncorrected. IR spectra were recorded with a Perkin–Elmer FT-IR 1710 spectrometer or JASCO FT-IR/620 spectrometer and ^{1}H and ^{13}C NMR spectra with a Varian Gemini-300. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane (TMS) as the internal standard (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad). EIMS was obtained with a Thermo Quest TSQ 700 spectrometer. High resolution EIMS (HREIMS) spectra were obtained with a VG Auto Spec E spectrometer. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh) or Merck silica gel 60 (230–400 mesh).

General procedure for the synthesis of epoxymesylate 1a–f. To a solution of olefinic alcohol (10.0 mmol) in $CHCl_3$ (10.0 mL) was added *m*CPBA (10.5 mmol) at 0°C and the mixture was stirred for 1 h at ambient temperature. After the usual work-up, the crude epoxide was obtained. The crude epoxide was used in the next reaction without purification. To a solution of the above crude product in 1,2-dichloroethane (10.0 mL) was added DMAP (12.0 mmol) and methanesulfonyl chloride (11.0 mmol) at 0°C. The mixture was stirred for 1 h at ambient temperature. After the usual work-up, chromatographic purification on silica gel gave epoxymesylate **1a–f** in 48–75% yield (2 steps).

1a. Colorless oil. IR (neat) 2960, 2937, 2875, 1360, 1176 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.97 (3H, t, J=7.1 Hz), 1.4–1.6 (4H, m), 2.91 (1H, m), 3.04 (1H, m), 3.07 (3H, s), 4.12 (1H, dd, J=11.9, 6.5 Hz), 4.48 (1H, dd, J=11.9, 3.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.5, 19.0, 33.2, 37.6, 54.7, 56.3, 70.0; EIMS (*m*/*z*): 177, 151, 99, 79.

1b. Colorless oil. IR (neat) 2938, 2877, 1359, 1173 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.99 (3H, t, J=7.2 Hz), 1.4–1.6 (4H, m), 3.09 (1H, m), 3.10 (3H, s), 3.26 (1H, m), 4.23 (1H, dd, J=11.5, 7.4 Hz), 4.46 (1H, dd, J=11.5, 3.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.3, 19.4, 29.3, 37.0, 52.8, 56.0, 68.3; EIMS (*m*/*z*): 151, 99, 79.

1c. Colorless oil. IR (neat) 2974, 1350, 1173 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.34 (3H, s), 1.37 (3H, s), 3.08 (1H, dd, J=7.0, 4.3 Hz), 3.08 (3H, s), 4.23 (1H, dd, J=11.7, 7.0 Hz), 4.43 (1H, dd, J=11.7, 4.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 18.7, 24.3, 37.7, 58.6, 59.8, 68.7.

1d. Colorless oil. IR (neat) 2973, 2881, 1354, 1176 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.06 (3H, t, J=7.7 Hz), 1.5–1.6 (2H, m), 1.85 (1H, m), 2.09 (1H, m), 2.95 (1H, dt, J=4.3, 6.3 Hz), 3.04 (3H, s), 3.07 (1H, dt, J=7.6, 4.3 Hz), 4.35–4.45 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 10.4, 21.1, 27.8, 37.3, 53.4, 58.1, 67.3; EIMS (*m*/*z*): 137, 97, 83.

1e. Colorless oil. IR (neat) 2958, 2860, 1354, 1176 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.87 (3H, t, J=6.9 Hz), 1.30 (4H, m), 1.46 (5H, m), 1.72 (1H, m), 1.85–2.0 (2H, m), 2.90 (2H, m), 2.99 (3H, s), 4.2–4.35 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.9, 22.5, 23.9, 26.1, 26.5, 27.6, 31.5, 37.2, 56.1, 57.0, 69.4; EIMS (*m*/*z*): 250 (M^+), 233, 207, 155.

1f. Colorless oil. IR (neat) 2970, 2877, 1353, 1176 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.03 (3H, t, J=7.5 Hz), 1.45–1.6 (6H, m), 1.62 (1H, m), 2.89 (2H, m), 3.00 (3H, m), 4.24 (2H, t, J=6.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 10.2, 20.7, 22.3, 26.7, 28.5, 36.8, 56.4, 57.7, 69.6; EIMS (*m*/*z*): 222 (M^+), 205, 193, 181, 165.

General procedure for the synthesis of cycloalkane 2a–f. To a solution of allyl phenyl sulfone (1.35 mmol) in THF (5.0 mL) was added BuLi (1.3 mmol, hexane solution) at −78°C. The mixture was stirred for 30 min at same temperature. A solution of epoxide **1a–f** (0.565 mmol) in THF (0.6 mL) was added to the resultant mixture and the reaction mixture was warmed to rt over 5 h and stirred for 2 h at ambient temperature. After the usual work-up, chromatographic purification on silica gel gave cycloalkane **2a–f** in 47–96% yield. The ratio of diastereomers was determined by ^{1}H NMR analysis.

2a major. Colorless solid. mp 131–133°C; IR (KBr) 3494, 2960, 2932, 2973, 1447, 1306, 1139 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.88 (3H, t, J=7.0 Hz), 1.2–1.7 (6H, m), 2.22 (1H, m), 3.14 (1H, m), 5.12 (1H, d, J=17.0 Hz), 5.37 (1H, d, J=10.4 Hz), 6.00 (1H, dd, J=17.0, 10.4 Hz), 7.52 (2H, m), 7.61 (1H, m), 7.79 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.9, 14.1, 18.3, 29.8, 39.6, 48.7, 70.3, 124.4, 128.0, 128.7, 128.8, 133.4, 137.9; EIMS (*m/z*): 280 (M^+), 195, 143, 125, 77; Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.35; H, 7.11.

2a minor. Colorless oil. IR (neat) 3471, 2959, 2934, 2873, 1634, 1586, 1448, 1307, 1141 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.96 (3H, t, J=7.0 Hz), 1.4–1.7 (5H, m), 1.96 (1H, m), 2.51 (1H, m), 4.38 (1H, m), 4.94 (1H, d, J=17.0 Hz), 5.14 (1H, d, J=10.3 Hz), 6.13 (1H, dd, J=17.0, 10.3 Hz), 7.53 (2H, m), 7.61 (1H, m), 7.82 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.9, 16.8, 18.6, 37.8, 39.9, 49.5, 67.5, 120.2, 128.5, 128.7, 132.7, 133.4, 139.3; EIMS (*m/z*): 280 (M^+), 195, 143, 125, 91; Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.05; H, 7.20.

2b major. Colorless solid. mp 94–95°C; IR (KBr) 3516, 2959, 2873, 1636, 1448, 1305, 1138 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.90 (3H, t, J=7.2 Hz), 1.05 (1H, t, J=6.2 Hz), 1.3–1.65 (4H, m), 1.70 (1H, dd J=9.8, 5.7 Hz), 1.84 (1H, br s), 2.23 (1H, m), 3.04 (1H, m), 5.13 (1H, d, J=17.1 Hz), 5.39 (1H, d, J=10.2 Hz), 6.12 (1H, dd, J=17.1, 10.2 Hz), 7.50 (2H, m), 7.60 (1H, m), 7.82 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.9, 14.0, 18.5, 30.6, 39.0, 48.3, 70.3, 124.6, 128.0, 128.6, 128.7, 133.2, 137.9; EIMS (*m/z*): 280 (M^+), 263, 195, 143, 125, 77; Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.23; H, 7.17.

2b minor. Colorless oil. IR (neat) 3530, 2959, 2871, 1634, 1447, 1288, 1186, 1139 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.95 (3H, t, J=7.2 Hz), 1.4–1.7 (6H, m), 1.81 (1H, dd, J=7.7, 5.5 Hz), 2.82 (1H, d, J=3.0 Hz), 4.24 (1H, m), 5.04 (1H, d, J=17.0 Hz), 5.10 (1H, d, J=10.2 Hz), 5.90 (1H, dd, J=17.0, 10.2 Hz), 7.54 (2H, m), 7.63 (1H, m), 7.85 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 14.2, 17.5, 18.9, 38.2, 39.2, 49.3, 69.5, 77.4, 120.7, 128.9, 132.6, 133.6, 139.0; EIMS (*m/z*): 280 (M^+), 263, 195, 143, 125; Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 63.97; H, 7.20.

2c major. Colorless oil. IR (neat) 3359, 2969, 1585, 1283, 1141 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.31 (3H, s), 1.34 (3H, s), 1.49 (1H, dd, J=7.4, 5.3 Hz), 1.61 (1H, dd, J=10.3, 5.3 Hz), 2.30 (1H, dd, J=10.3, 7.4 Hz), 5.04 (1H, dd, J=17.3, 1.0 Hz), 5.44 (1H, d, J=10.4 Hz), 6.14 (1H, dd, J=17.3, 10.4 Hz), 7.51 (2H, m), 7.62 (1H, m), 7.78 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 12.1, 30.3, 30.4, 34.2, 48.2, 69.2, 125.5, 128.7, 128.7, 129.0, 133.4, 137.8; EIMS (*m/z*): 266 (M^+), 251, 195, 124, 72; HREIMS: Calcd for $C_{14}H_{18}O_3S$ (M^+) 266.0977: Found: 266.0975.

2c minor. Colorless oil. IR (neat) 3467, 2979, 1634, 1286, 1142 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.37 (3H, s), 1.44 (1H, dd, J=9.6, 5.6 Hz), 1.64 (3H, s), 1.65 (1H, dd, J=9.6, 8.8 Hz), 2.07 (1H, dd, J=8.8, 5.6 Hz), 4.84 (1H, d, J=17.0 Hz), 5.12 (1H, d, J=10.3 Hz), 6.19 (1H, dd, J=17.0, 10.3 Hz), 7.51 (2H, m), 7.62 (1H, m), 7.82 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 15.4, 30.6, 31.0, 47.3, 50.8, 67.4, 119.6, 128.8, 133.5, 133.5, 139.0; EIMS (*m/z*): 266 (M^+), 251, 195, 143, 124, 72; HREIMS: Calcd for $C_{13}H_{15}O_3S$ (M^+-CH_3) 251.0742: Found: 251.0738.

2d. Colorless oil. IR (neat) 3517, 2963, 1634, 1585, 1289, 1140 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.96 (3H, t, J=7.4 Hz), 1.28 (1H, m), 1.46 (1H, m), 1.55 (1H, m), 1.99 (2H, m), 2.67 (1H, m), 3.31 (1H, dd, J=18.2, 10.1 Hz), 3.46 (1H, ddd, J=10.1, 7.5, 3.2 Hz), 5.10 (1H, d, J=17.3 Hz), 5.42 (1H, d, J=10.7 Hz), 6.20 (1H, dd, J=17.3, 10.7 Hz), 7.49 (2H, m), 7.61 (1H, m), 7.74 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 9.3, 18.9, 22.1, 26.2, 45.2, 70.5, 71.4, 121.6, 128.6, 129.5, 133.7, 135.3; EIMS (*m/z*): 282 (M^+), 251, 222, 200, 143, 121, 81; HREIMS: Calcd for $C_{15}H_{22}O_3S$ (M^+) 282.1290: Found: 282.1263.

2e. Colorless oil. IR (neat) 3494, 2956, 1633, 1585, 1284, 1161, 1137 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.89 (3H, t, J=6.7 Hz), 1.2–1.85 (12H, m), 1.92 (1H, m), 2.21 (1H, m), 2.86 (1H, m), 3.54 (1H, m), 4.98 (1H, d, J=17.3 Hz), 5.40 (1H, d, J=10.9 Hz), 6.48 (1H, dd, J=17.3, 10.9 Hz), 7.49 (2H, m), 7.62 (1H, m), 7.81 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 14.0, 22.4, 22.6, 24.5, 29.5, 32.0, 32.3, 36.0, 51.3, 70.3, 76.9, 121.5, 128.3, 130.5, 131.8, 133.7, 135.2; EIMS (*m/z*): 336 (M^+), 265, 242, 143, 123, 95; HREIMS: Calcd for $C_{14}H_{17}O_3S$ ($M^+-C_5H_{11}$) 265.0898: Found: 265.0903.

2f. Colorless oil. IR (neat) 3467, 2937, 1586, 1284, 1147, 1126 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.05 (3H, t, J=7.3 Hz), 1.1–2.0 (10H, m), 2.47 (1H, dt, J=12.1, 3.6 Hz), 4.40 (1H, br d, J=9.4 Hz), 4.98 (1H, d, J=17.7 Hz), 5.54 (1H, d, J=11.0 Hz), 6.19 (1H, dd, J=17.7, 11.0 Hz), 7.49 (2H, m), 7.61 (1H, m), 7.78 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 11.0, 21.8, 24.4, 25.6, 26.8, 30.5, 48.6, 72.1, 72.2, 122.8, 129.1, 130.9, 133.5, 135.3; EIMS (*m/z*): 279, 200, 143, 108; HREIMS: Calcd for $C_{15}H_{19}O_3S$ ($M^+-C_2H_5$) 279.1055: Found: 279.1054.

General procedure for the synthesis of lactone 3a–f. A cold (−78°C) solution of cycloalkane **2a–c major** or **2d–f** (0.32 mmol) in CH_2Cl_2 (2.0 mL) and MeOH (2.0 mL) was treated with ozone until blue color persisted for more than 4 h. Excess ozone was removed by an argon flow. The reaction mixture was treated with excess Me_2S (9.73 mmol), allowed to warm slowly to rt over 2 h, stirred for 8 h at this temperature and concentrated under reduced pressure. The residue was diluted with Et_2O, washed with H_2O and saturated aqueous NaCl, dried over anhydrous

$MgSO_4$ and concentrated under reduced pressure to give crude hemiacetal for use in the reaction below without purification.

To a cold (0°C) solution of the above hemiacetal in acetone (3.0 mL) was added Jones reagent, followed by stirring for 1.5 h and treatment with 2-propanol. After stirring for 15 min, the reaction mixture was diluted with Et_2O, washed with H_2O, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give lactone **3a**–**f** in 70–90% yield (2 steps).

3a. Colorless solid. mp 74–75°C; IR ($CHCl_3$) 2962, 1779, 1326, 1156, 1088 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 0.94 (3H, t, J=7.2 Hz), 1.4–1.6 (5H, m), 2.03 (1H, dd, J=8.6, 5.4 Hz), 3.12 (1H, ddd, J=8.6, 5.4, 4.5 Hz), 4.62 (1H, m), 7.57 (2H, m), 7.67 (1H, m), 8.05 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.7, 16.3, 18.5, 30.1, 33.8, 47.0, 77.3, 129.1, 134.3, 138.2, 167.3; EIMS (*m/z*): 280 (M^+), 237, 216, 209, 188; Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75. Found: C, 59.90; H, 5.79.

3b. Colorless solid. mp 138.5–141°C; IR ($CHCl_3$) 3026, 1777, 1328, 1157, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 0.93 (3H, t, J=7.3 Hz), 1.4–1.6 (5H, m), 2.17 (1H, dd, J=8.8, 5.2 Hz), 2.89 (1H, dd, J=8.8, 5.2 Hz), 4.31 (1H, t, J=6.2 Hz), 7.60 (2H, m), 7.69 (1H, m), 8.05 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 13.6, 17.2, 19.6, 30.9, 37.9, 46.4, 78.7, 129.1, 134.3, 138.1, 167.3; EIMS (*m/z*): 280 (M^+), 237, 216, 209, 188, 141; Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75. Found: C, 59.76; H, 5.73.

3c. Colorless solid. mp 136.5–137°C; IR ($CHCl_3$) 3034, 1777, 1327, 1291, 1152, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 1.36 (3H, s), 1.40 (3H, s), 1.52 (1H, t, J=5.5 Hz), 2.11 (1H, dd J=8.6, 5.5 Hz), 2.88 (1H, dd, J=8.6, 5.5 Hz), 7.59 (2H, m), 7.68 (1H, m), 8.05 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 18.4, 23.5, 29.0, 36.0, 48.1, 81.5, 129.1, 134.3, 138.1, 166.8; EIMS (*m/z*): 266 (M^+), 251, 202, 109; Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30. Found: C, 58.62; H, 5.35.

3d. Colorless solid. mp 93–93.5°C; IR ($CHCl_3$) 2948, 1767, 1311, 1153, 1087 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 0.99 (3H, t, J=7.4 Hz), 1.61 (1H, m), 1.82 (1H, m), 2.01 (1H, m), 2.17 (1H, m), 2.49 (1H, m), 2.85 (1H, ddd, J=12.2, 10.9, 8.8 Hz), 3.55 (1H, dd, J=9.3, 6.7 Hz), 4.26 (1H, t, J=7.3 Hz), 7.56 (2H, m), 7.71 (1H, m), 7.92 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 9.6, 21.4, 26.3, 27.8, 41.0, 67.5, 86.8, 128.9, 130.1, 134.5, 171.3; EIMS (*m/z*): 280 (M^+), 251, 216, 173, 139; Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75. Found: C, 59.97; H, 5.76.

3e. Colorless oil. IR (neat) 2934, 1768, 1356, 1147, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 0.90 (3H, t, J=7.1 Hz), 1.25–1.7 (6H, m), 1.7–1.9 (2H, m), 1.96 (1H, m), 2.0–2.15 (2H, m), 2.29 (1H, ddd, J=13.0, 12.5, 6.7 Hz), 3.27 (1H, dd, J=7.2, 4.1 Hz), 3.98 (1H, ddd, J=10.2, 6.0, 4.3 Hz), 7.58 (2H, m), 7.71 (1H, m), 7.94 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 14.0, 22.5, 24.9, 25.5, 31.3, 34.5, 35.4, 35.5, 47.4, 79.3, 85.6, 128.8, 130.7, 134.5, 135.7, 172.1; EIMS (*m/z*): 336 (M^+), 295, 279, 272, 179; HREIMS: Calcd for $C_{18}H_{24}O_4S$ (M^+) 336.1395: Found: 336.1389.

3f. Colorless solid. mp 123.5–124°C; IR ($CHCl_3$) 2945, 1768, 1308, 1135, 1082 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 1.01 (3H, t, J=7.4 Hz), 1.39 (1H, m), 1.5–2.0 (7H, m), 2.09 (1H, m), 2.23 (1H, m), 3.05 (1H, br t, J=7.3 Hz), 4.21 (1H, ddd, J=11.6, 8.0, 3.6 Hz), 7.58 (2H, m), 7.68 (1H, m), 8.00 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 9.7, 19.1, 21.3, 26.2, 26.6, 39.4, 69.3, 80.9, 128.7, 131.1, 134.4, 134.7, 171.6; EIMS (*m/z*): 308 (M^+), 244, 167; Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.32; H, 6.54. Found: C, 62.32; H, 6.49.

Acknowledgements

This work was supported in part by a grant-in-aid for Scientific Research (Grant No. 05771939, 07772112 and 11771395) from the Ministry of Education, Science, Sports and Culture of Japan.

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