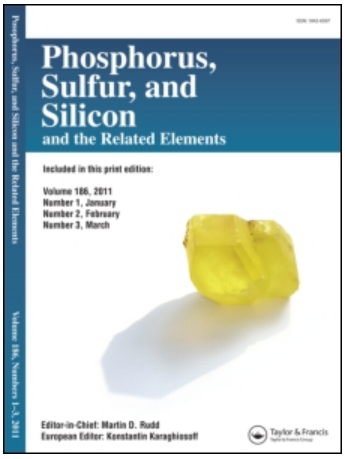

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SYNTHESIS OF OXOSULFONIUM SALTS BY THE OXIDATION OF SULFONIUM SALTS

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SYNTHESIS OF OXOSULFONIUM SALTS BY THE OXIDATION OF SULFONIUM SALTS

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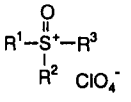
A general synthetic method for oxosulfonium salts by oxidation of sulfonium salts with sodium perbenzoate (or sodium *m*-chloroperbenzoate was developed. In case of the oxidation of aryldimethylsulfonium salts, the corresponding oxosulfonium salts (**1e–h**) were obtained in 64–91% yields. Diphenymethylsulfonium and triphenylsulfonium salts were also oxidized with sodium perbenzoate to afford the corresponding oxosulfonium salts (**1i** and **1j**) in 75 and 58% yields, respectively. Trialkylsulfonium salts such as trimethylsulfonium, dimethyloctylsulfonium, S-methylthiolanium, and *S*-methyl(pentamethylene)sulfonium salts, were also oxidized to the corresponding oxosulfonium salts (**1a–d**) in good yields. To clarify the reaction mechanisms, the oxidation of bicyclo[2.2.1]heptane-1-sulfonium salt (**5**) was investigated and found to afford oxosulfonium salt (**6**) in 50% yield. A reaction mechanism involving nucleophilic attack by perbenzoate anion on the cationic sulfur atom of sulfonium salt and giving an S—O sulfurane intermediate is proposed.

Key words: Oxosulfonium salts; oxidation of sulfonium salts; sodium perbenzoate; S—O sulfurane intermediate; bicyclo[2.2.1]heptane-1-sulfonium salt.

INTRODUCTION

Very little has been reported on the synthesis and reactions of oxosulfonium salts (**1**) except trimethyloxosulfonium iodide (**2**), which can be easily prepared by heating dimethyl sulfoxide and methyl iodide and is used as a source of dimethyloxosulfonium ylide (**3**).[1,2] Although methylation of dimethyl sulfoxide on sulfur is facile, this alkylation method of sulfoxides is not applicable for any other sulfoxides. For example, the reactions of dialkyl sulfoxides with alkyl iodide yield trialkylsulfonium salts as the main products under several conditions.[3] Alkyl aryl sulfoxides reacted very slowly with alkyl iodide in the presence of mercury(II) iodide on the sulfur atom even under severe conditions. Previously, we reported that ethylmethylphenyloxosulfonium salt (**1**: $R^1 = Me$; $R^2 = Et$; $R^3 = Ph$) was prepared by heating a mixture of ethyl phenyl sulfoxide, methyl iodide, and mercury(II) iodide.[3]



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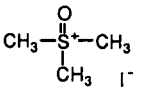

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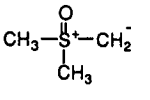

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† Author to whom all correspondence should be addressed.

It is fruitful to investigate the methods for synthesizing oxosulfonium salts containing various substituents by the oxidation of sulfonium salts. We describe here a general synthetic method for oxosulfonium salts by oxidation of sulfonium salts with perbenzoic acid under basic conditions.

RESULTS AND DISCUSSION

Oxidation of Sulfonium Salts

The oxidations of sulfonium salts to the corresponding oxosulfonium salts by use of hydrogen peroxide were reported,[4,5] but the products were not isolated as pure substances. In an attempt to examine this route as a possible method for synthesis of oxosulfonium salts, several sulfonium salts were treated with 30% H_2O_2, 87% H_2O_2—CF_3CO_2H, $PhCO_3H$—CH_3CN, NaOBr, HNO_3, Cl_2—CH_3CO_2H and PhIO under various conditions, however, oxosulfonium salts were not obtained.[3] Trost *et al.* reported that the treatment of triaryl sulfonium salts with alkyllithium afforded biaryl and alkyl aryl sulfides.[6] To explain the interesting reactions, they proposed the four-coordinated sulfurane intermediate by the nucleophilic attack of alkyl anion to the cationic sulfur atom. On the basis of this study, we considered that peracid anion acts as a strong nucleophile and reacts with sulfonium salts to give the corresponding oxosulfonium salts.

When 100 ml of aqueous solution of sodium perbenzoate (6 mmol; 0.06 M; 1 M = 1 mol dm^{-1}) was reacted with 2 mmol of dimethylphenylsulfonium perchlorate at room temperature for 10 h, dimethylphenyloxosulfonium perchlorate (**1e**) was obtained in 40% yield. Several reaction conditions were examined to obtain **1e** in high yield, and the results are summarized in Table I. When the reaction was carried out using 50 ml of aqueous solution of sodium perbenzoate (6 mmol; 0.12 M), the yield of **1e** was improved to 74% (entries 1 and 2 in Table I). The oxidation of dimethylphenylsulfonium perchlorate with sodium *m*-

TABLE I

Oxidation of Dimethylphenylsulfonium Perchlorate with Sodium Perbenzoate

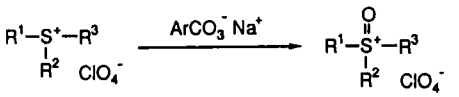
	Conditions			
Entry	Conc. of Oxidant (M)	pH	Temp (°C)	Yield of **1e** (%)
1	0.06	12.5	r.t.	40
2	0.12	12.5	r.t.	74
3	0.15[a]	13.0	r.t.	53
4	0.26[a]	13.0	r.t.	80
5	0.17	10.0	r.t.	40
6	0.17	13.0	r.t.	72
7	0.35	13.0	10	89
8	0.35	13.0	25	92
9	0.29	13.0	47	94

[a] Sodium *m*-chloroperbenzoate (3 molar equivalent to sulfonium salt) was used.

chloroperbenzoate (0.15 or 0.26 M) was found to afford **1e** in 53 or 80% yield, respectively. The effect of pH of the reaction media was also examined, and it was found that the yield of **1e** was decreased from 72 to 40% when pH was changed (entries 5 and 6). The reaction temperature affected the yield of **1e** a little in the range of 10–47°C (89–94%; Entries 7–9).

Synthesis of Oxosulfonium Salts

According to the best of the reaction conditions examined above, various oxosulfonium salts were prepared by the oxidation of corresponding sulfonium perchlorates with sodium perbenzoate (or sodium *m*-chloroperbenzoate) in aqueous solution at room temperature. The results are summarized in Table II.



As shown in Table II, trialkyloxosulfonium salts such as trimethyloxosulfonium (**1a**), dimethyloctyloxosulfonium (**1b**), *S*-methyloxothiolanium (**1c**), and *S*-methyl(pentamethylene)oxosulfonium salt (**1d**), were obtained in good yields from the corresponding sulfonium salts. The oxidation of aryldimethylsulfonium perchlorates afforded corresponding aryldimethyloxosulfonium perchlorates (**1e–h**) in 64–91% yields. Diphenylmethyloxosulfonium (**1i**) and triphenyloxosulfonium salts (**1j**) also were obtained in 75 and 58% yields, respectively. In case of the oxidation of benzylmethylphenylsulfonium perchlorate, *t*-butylethylmethylsulfonium perchlorate, and ethylmethylphenacylsulfonium perchlorate, the corresponding oxosulfonium salts could not be obtained and instead decomposition products were observed. It seems that carbon-sulfur bonds of the sulfonium salts which possess a benzyl or *t*-butyl group are easily broken in the basic media.

TABLE II

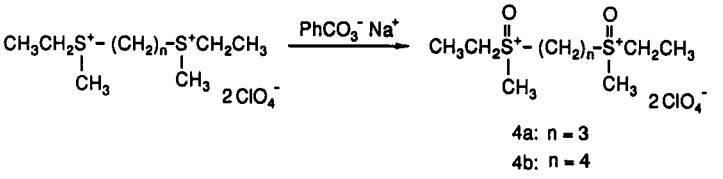
Yields of Oxosulfonium Salts (**1**)[a]

	R^1, R^2, and R^3 in **1**			Yield of **1**
	R^1	R^2	R^3	(%)
1a	CH_3	CH_3	CH_3	34
1b[b]	CH_3	CH_3	n-C_8H_{17}	50
1c	CH_3	$-(CH_2)_4-$		80
1d	CH_3	$-(CH_2)_5-$		88
1e	CH_3	CH_3	C_6H_5	66
1f[b]	CH_3	CH_3	p-$CH_3C_6H_4$	91
1g[b]	CH_3	CH_3	p-ClC_6H_4	64
1h	CH_3	CH_3	p-$CH_3OC_6H_4$	80
1i	CH_3	C_6H_5	C_6H_5	75
1j	C_6H_5	C_6H_5	C_6H_5	58

[a] Sulfonium salt (10 mmol) was added to 100 ml of 0.3 M aqueous solution (pH 13.0) of sodium perbenzoate (30 mmol) and the mixture was stirred at room temperature overnight.

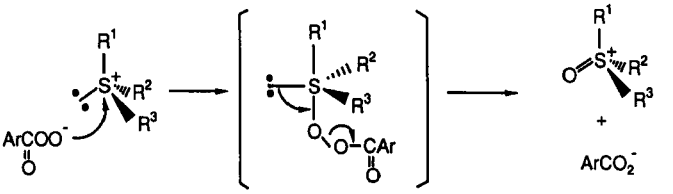
[b] Sodium *m*-chloroperbenzoate (3 equivalent to sulfonium salt) was used.

When perchlorate salts of 1,3-bis(ethylmethylsulfonio)propane was oxidized with sodium perbenzoate, perchlorate salts of 1,3-bis(ethylmethyloxosulfonio)-propane (**4a**) was obtained in 15% yield. Similarly, bisoxosulfonium salt (**4b**) was obtained in 32% yield by the oxidation of perchlorate salts of 1,4-bis(ethylmethylsulfonio)butane.



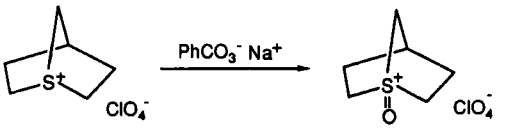
Mechanism

The oxidation of sulfonium salts with sodium perbenzoate in aqueous solution may proceed via an S—O sulfurane intermediate to afford an oxosulfonium salt by nucleophilic attack of perbenzoate anion on the cationic sulfur atom of the sulfonium salt as shown in Scheme 1.



SCHEME 1.

According to this mechanism, the oxidation will not be much affected by the structure of sulfonium salts and will be expected to proceed on sulfur atom at bridgehead position of sulfonium salt, because nucleophilic attack of peracid anion on the sulfur atom and elimination of benzoate anion proceed at the same side around the sulfur atom of the sulfonium salts. Then, the oxidation of bicyclo[2.2.1]heptane-1-sulfonium perchlorate (**5**) was carried out, and the corresponding oxosulfonium salt **6** was obtained in 50% yield. The formation of oxosulfonium salt **6** is accounted for by the attack of the peracid anion on the sulfur atom of the sulfonium salt **5** from the front side of the bicyclic ring. The result supports the mechanism described in Scheme 1.



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EXPERIMENTAL

Melting points were determined on a Yamato Model MP-21 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a JEOL FX-60 spectrometer using TMS as internal standard. Chemical shifts and coupling constants were recorded in δ (ppm) and Hertz units.

IR spectra were recorded on a Hitachi Model 260-10 spectrometer. No explosion hazard was encountered with the perchlorates under the following experimental procedures.

General Procedure for the Oxidation of Sulfonium Salts with Sodium Perbenzoate (or m-Chloroperbenzoate). An aqueous solution of sodium perbenzoate was prepared from benzoyl peroxide and sodium methoxide according to the literature.[7] The trialkylsulfonium and aryldialkylsulfonium perchlorates were prepared according to the modified methods described in the literature[8] by the reaction between the corresponding sulfide and alkyl iodide in the presence of silver perchlorate in acetonitrile. The sulfonium salt (10 mmol; one-third equivalent to sodium perbenzoate) was added to 100 ml of 0.3 M aqueous solution (pH 13.0) of sodium perbenzoate (30 mmol) with stirring, and the mixture was left at room temperature overnight. The resulting solution was acidified with 2 M HCl (1 M = 1 mol dm^{-1}), and benzoic acid precipitated was filtered off. The filtrate was evaporated to dryness, and the residue was washed with ether and extracted with acetone. The acetone extract was dried over anhydrous magnesium sulfate and evaporated to afford the oxosulfonium salt. Similarly, 30 mmol of *m*-chloroperbenzoic acid of Wako Chemicals was used in 150 ml of 0.2 M aqueous solution of sodium carbonate (30 mmol) for the oxidation of the sulfonium salt (10 mmol) at room temperature. The physical properties and spectral data of oxosulfonium salts (**1a–j**) are as follows.

Trimethyloxosulfonium Perchlorate (**1a**). Yield 34%; m.p. 281–282°C (MeOH); IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 4.10(s).

Dimethyloctyloxosulfonium Perchlorate (**1b**). Yield 50%; m.p. 89–90°C (acetone-ether); IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 0.70–1.83 (15H, m), 4.03 (6H, s), 4.07–4.45 (2H, m). Anal. Calcd for $C_{10}H_{23}ClO_5S$: C, 41.30; H, 7.97. Found: C, 41.37; H, 8.05.

Methyloxothiolanium Perchlorate (**1c**). Yield 80%; m.p. 147.5–149°C (acetone-ether); IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 2.50–2.85 (4H, m), 3.80–4.70 (4H, m), 4.20 (3H, s); ^{13}C NMR (D_2O) δ 25.08, 39.69, 54.38. Anal. Calcd for $C_5H_{11}ClO_5S$: C, 27.47; H, 5.07. Found: C, 27.57; H, 5.15.

Methyl(pentamethylene)oxosulfonium Perchlorate (**1d**). Yield 88%; m.p. 158–159°C (acetone); IR (KBr) 1200 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (DMSO-d_6) δ 1.49–1.89 (2H, m), 1.89–2.40 (4H, m), 3.77–4.18 (4H, m), 3.88 (3H, s); ^{13}C NMR (D_2O) δ 21.35, 22.08, 36.77, 50.08. Anal. Calcd for $C_6H_{13}ClO_5S$: C, 30.97; H, 5.63. Found: C, 31.14; H, 5.59.

Dimethylphenyloxosulfonium Perchlorate (**1e**). Yield 66%; m.p. 164.5–166°C (MeOH) (lit.[3] 158–159°C); IR (KBr) 1240 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 4.38 (6H, s), 8.00–8.70 (5H, m).

Dimethyl(p-tolyl)oxosulfonium Perchlorate (**1f**). Dimethyl-(*p*-tolyl)sulfonium perchlorate (3 g, 12 mmol) was oxidized with a 0.2 M aqueous solution of sodium *m*-chloroperbenzoate (180 ml, 36 mmol) and **1f** (2.9 g, 91%) was obtained: m.p. 172.5–174°C (MeOH); IR (KBr) 1240 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 2.55 (3H, s), 4.29 (6H, s), 7.72 and 8.16 (4H, AA'BB', J = 9.0 Hz). Anal. Calcd for $C_9H_{13}ClO_5S$: C, 40.23; H, 4.88. Found: C, 40.35; H, 4.84.

Dimethyl(p-chlorophenyl)oxosulfonium Perchlorate (**1g**). Yield 64%; m.p. 166.5–167°C (MeOH); IR (KBr) 1240 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 4.37 (6H, s), 7.95 and 8.34 (4H, AA'BB', J = 9.0 Hz). Anal. Calcd for $C_8H_{10}Cl_2O_5S$: C, 33.23; H, 3.49. Found: C, 33.26; H, 3.50.

Dimethyl(p-methoxyphenyl)oxosulfonium Perchlorate (**1h**). Yield 80%; m.p. 164–165°C (MeOH); IR (KBr) 1225 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 4.03 (3H, s), 4.30 (6H, s), 7.42 and 8.26 (4H, AA'BB', J = 9.0 Hz). Anal. Calcd for $C_9H_{13}ClO_6S$: C, 37.93; H, 4.60. Found: C, 38.19; H, 4.50.

Diphenylmethyloxosulfonium Perchlorate (**1i**). Diphenylmethylsulfonium perchlorate was prepared from 10 fold excess of diphenyl sulfide and methyl iodide in the presence of silver perchlorate: m.p. 77–79°C (MeOH); ^{1}H NMR (acetone-d_6) δ 3.95 (3H, s), 7.55–8.20 (10H, m). The sulfonium salt (5 g, 17 mmol) was oxidized with 167 ml of 0.3 M aqueous solution of sodium perbenzoate (50 mmol) to give 3.9 g (75%) of diphenylmethyloxosulfonium perchlorate (**1i**): m.p. 128–130°C (MeOH); IR (KBr) 1240 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (acetone-d_6) δ 4.78 (3H, s), 7.65–8.45 (10H, m). Anal. Calcd for $C_{13}H_{13}ClO_5S$: C, 49.29; H, 4.14. Found: C, 49.59; H, 4.24.

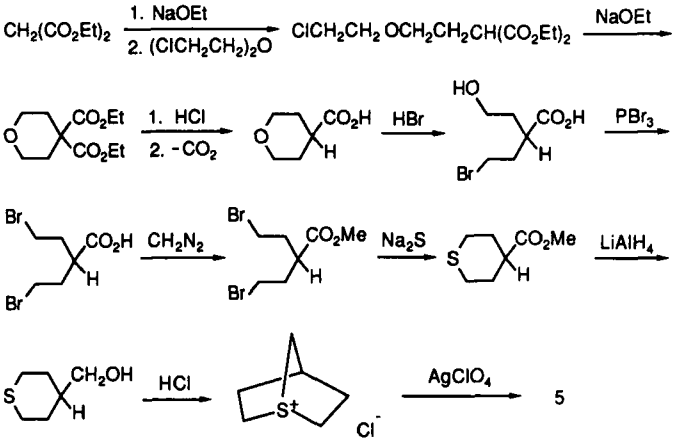
Triphenyloxosulfonium Perchlorate (**1i**). Triphenylsulfonium perchlorate was prepared according to the literature:[9] m.p. 190–192°C (MeOH); ^{1}H NMR (acetone-d_6) δ 7.75–8.05. The sulfonium salt (2 g,

5.5 mmol) was oxidized with 85 ml of 0.2 M aqueous solution of sodium perbenzoate (17 mmol) to give 1.2 g (58%) of triphenyloxosulfonium perchlorate (**1j**): m.p. 251–252°C (MeOH); IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^1H NMR (acetone-d_6) δ 7.95–8.35 (m). Anal. Calcd for $C_{18}H_{15}ClO_5S$: C, 57.07; H, 3.99. Found: C, 57.27; H, 3.98.

Perchlorate Salt of 1,3-*Bis*(*ethylmethyloxosulfonio*)*propane* (**4a**). 1,3-Bis(ethylthio)propane (b.p. 120°C/7 mmHg) (10 g, 61 mmol), which was prepared by the reaction between 1,3-dibromopropane and sodium ethanethiolate in methanol, was methylated with methyl iodide (50 g, 0.35 mol) in the presence of silver perchlorate (61 mmol) in acetonitrile (50 ml), and 16.2 g (81%) of perchlorate salt of 1,3-bis(ethylmethylsulfonio)propane was obtained: ^1H NMR (acetone-d_6) δ 1.56 (6H, t, J = 7.2 Hz), 2.35–2.90 (2H, m), 3.12 (6H, s), 3.62 (4H, q, J = 7.2 Hz), 3.67 (4H, q, J = 7.2 Hz); ^{13}C-NMR (D_2O) δ 9.01, 20.29, 22.64, 37.50, 39.61. The sulfonium perchlorate (2 g, 5 mmol) was oxidized with 120 ml of 0.25 M aqueous solution of sodium perbenzoate (30 mmol) to afford 0.3 g (15%) of perchlorate salt of 1,3-bis(ethylmethyloxosulfonio)propane: IR (KBr) 1220 cm^{-1} ($\nu_{S=O}$); ^1H NMR (DMSO-d_6) δ 1.50 (6H, t, J = 7.2 Hz), 2.60–2.90 (2H, m), 3.94 (6H, s), 3.70–4.50 (8H, m); ^{13}C NMR (DMSO-d_6) δ 4.63, 7.58, 34.58, 45.62, 47.16. Anal. Calcd for $C_9H_{22}Cl_2O_{10}S_2$: C, 25.47; H, 5.21. Found: C, 25.38; H, 5.21.

Perchlorate Salt of 1,4-*Bis*(*ethylmethyloxosulfonio*)*butane* (**4b**). Yield 32%; IR (KBr) 1210 cm^{-1} ($\nu_{S=O}$); ^1H NMR (DMSO-d_6) δ 1.50 (6H, t, J = 7.2 Hz), 1.90–2.30 (4H, m), 3.88 (6H, s), 4.06 (4H, m) 3.70–4.30 (4H, m).

Preparation of Bicyclo[2.2.1]*heptane*-1-*sulfonium Perchlorate*[10] (**5**). Sulfonium salt **5** was prepared according to the following procedure as shown in Scheme 2.



SCHEME 2.

Reaction procedures, typical physical properties, and spectral data of key intermediates are as follows.

Diethyl Tetrahydropyran-4,4-*dicarboxylate*. In a 500 ml round bottomed flask equipped with a mechanical stirrer and a reflux condenser, was placed 210 ml of ethanol. After evolution of hydrogen gas had ceased by adding 18.4 g (0.8 mol) of sodium metal, 64 g (0.4 mol) of diethyl malonate was added dropwise with stirring at room temperature. To this solution, 57.2 g (80.4 mol) of β,β'-dichloroethyl ether was added, and the mixture was left at room temperature overnight and refluxed for additional 24 h. Ethanol was removed from the reaction mixture, and 240 ml of water and 4 ml of 3% HCl were added. The oil separated was extracted with ether and the ether solution was dried over anhydrous magnesium sulfate and concentrated. The residue was distilled under reduced pressure to give diethyl tetrahydropyran-4,4-dicarboxylate: b.p. 107–108°C/4 mmHg; yield 47 g (51%); ^1H NMR ($CDCl_3$) δ 1.27 (6H, t, J = 6.8 Hz), 2.00 (4H, t, J = 5.3 Hz), 3.57 (4H, t, J = 5.3 Hz), 4.16 (4H, q, J = 6.8 Hz).

1,5-Dibromopentane-3-carboxylic Acid. A mixture of 47 g (0.2 mol) of the diester and 156 ml of 10% HCl in a 300 ml round bottomed flask was refluxed overnight. Ethanol and water were evaporated under reduced pressure, and the residue was cooled in a refrigerator to give solid tetrahydropyran-4,4-dicarboxylic acid, which was recrystallized from ether-hexane: yield 31.4 g (88%); m.p. 171°C. In a 100 ml round bottomed flask, 15.3 g (88 mmol) of dicarboxylic acid was heated at slightly above temperature than melting point (171°C) in oil bath to give 8.6 g (75%) of tetrahydropyran-4-carboxylic acid: m.p. 89–90°C (acetone). In a 20 ml pressure-proof glass tube 4 g (31 mmol) of tetrahydropyran-4-carboxylic acid and 15 g of 48% HBr aqueous solution were placed. HBr gas (evolved from P_2O_5-48% HBr aqueous solution) was bubbled through the solution cooled to 0°C. The tube was sealed and heated at 100°C in oil bath for 12 h. The reaction mixture was poured into water, and the oil separated was extracted with chloroform. The extracts were dried over anhydrous magnesium sulfate and concentrated to give 4.9 g (69%) of 3-carboxy-5-bromopentanol. The alcohol (15.1 g, 72 mmol) was placed in a 100 ml round bottomed flask, and PBr_3 (19.5 g, 72 mmol) was added dropwise at room temperature with stirring by magnetic stirrer. After the mixture was heated for 1 h, water was added carefully with ice cooling. The solid product was filtered and recrystallized from hexane to give 1,5-dibromopentane-3-carboxylic acid: yield 13.6 g (69%); m.p. 57–59°C; ^{1}H NMR (CCl_4) δ 1.90–2.55 (4H, m), 2.60–3.20 (1H, m), 3.44 (4H, t, J = 6.8 Hz), 11.64 (1H, s).

Methyl Pentamethylenesulfide-4-carboxylate. To 50 ml of ethereal solution of diazomethane, which was prepared from 6 g (58 mmol) of *N*-nitrosomethylurea, was added 1,5-dibromopentane-3-carboxylic acid (13.6 g, 50 mmol). After evolution of the nitrogen gas had ceased, excess diazomethane was decomposed with 1N HCl. The ether layer was dried over anhydrous magnesium sulfate, and concentrated. The residue was distilled under reduced pressure to give methyl 1,5-dibromopentane-3-carboxylate: yield 9.7 g (68%); b.p. 111–115°C/6 mmHg; ^{1}H NMR (CCl_4) δ 1.85–2.55 (4H, m), 2.55–3.10 (1H, m), 3.36 (4H, t, J = 6.8 Hz), 3.68 (3H, s). In a 500 ml round bottomed three-necked flask equipped with a mechanical stirrer, a reflux condenser, and two dropping funnels, 200 ml of ethanol was heated at gentle reflux. Then, the dibromide (53.5 g, 186 mmol) and a solution of sodium sulfide (49 g, 205 mmol) in 83 ml of hot water were added simultaneously over the period of 3 h with stirring. After the mixture was heated at reflux with stirring for additional 2 h, ethanol was removed under reduced pressure, and the residue was diluted with water. The oil separated was extracted with ether, and the ether layer was dried over anhydrous magnesium sulfate and concentrated. The residue was distilled under reduced pressure to give methyl pentamethylenesulfide-4-carboxylate: yield 12.1 g (41%); b.p. 76°C/6 mmHg; ^{1}H NMR (CCl_4) δ 1.60–2.45 (5H, m), 2.45–2.80 (4H, m), 3.67 (3 H, s).

To a slurry of lithium aluminum hydride (7.3 g; 0.19 mol) in ether under reflux, the ester (12.1 g, 76 mmol) was added dropwise, and the mixture was refluxed for 4 h. The excess lithium aluminum hydride was decomposed with acetic acid. Water was added to the reaction mixture, and the ether layer separated was washed with aqueous solution of K_2CO_3, and dried over anhydrous K_2CO_3. The ether was removed under reduced pressure to give pentamethylenesulfide-4-carbinol: yield 6 g (60%). The alcohol (6 g, 45 mmol) was treated with 40 ml of 37% hydrochloric acid at room temperature for 24 h with stirring and then heated at 50°C for 2 h. After removal of water, bicyclo[2.2.1]heptane-1-sulfonium chloride was obtained: yield 6.8 g (100%); ^{1}H NMR (D_2O) δ = 2.00–2.40 (4H, m), 3.30–3.70 (7H, m). The sulfonium salt **5** was obtained from the above sulfonium chloride by treatment with silver perchlorate in water, removal of silver chloride, and evaporation of solvent: m.p. 255°C (dec) (MeOH); ^{1}H NMR (D_2O) δ 1.95–2.36 (4H, m), 3.30–3.70 (7H, m).

Oxidation of Bicyclo[2.2.1]heptane-1-sulfonium Perchlorate (**5**). Sulfonium salt **5** (1.0 g, 5 mmol) was oxidized with 50 ml of 0.2 M aqueous solution of sodium perbenzoate (14 mmol) to afford bicyclo[2.2.1]heptane-1-oxosulfonium perchlorate: yield 0.54 g (50%); m.p. 208–210°C (dec) (water); IR (KBr) 1260 cm^{-1} ($\nu_{S=O}$); ^{1}H NMR (D_2O) δ 2.30–2.85 (4H, m), 3.10–3.50 (1H, m), 3.85–4.45 (6H, m). Anal. Calcd for $C_6H_{11}ClO_5S$: C, 31.24; H, 4.82, S, 13.90. Found: C, 31.10; H, 4.74; S, 14.12.

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