Reactions between Nucleophiles and Sulfonium Ions Containing Electron-withdrawing Substituents

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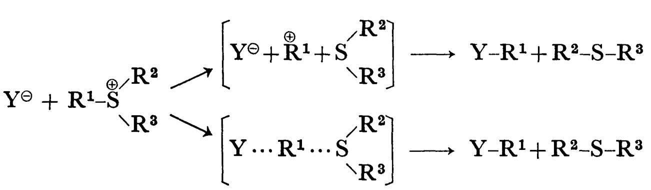
Sulfonium ions containing electron-withdrawing substituents are formed by the reactions between sulfonium ylides and suitable electrophiles. Reactivities of these sulfonium ions ($MeR\overset{+}{S}-CX(CO_2Me)_2$) with nucleophiles ($Y^-$) are investigated. The products found are those of 1) C-attack ($MeSR+YCX(CO_2Me)_2$), 2) Me-attack ($MeY+RSCX(CO_2Me)_2$) and 3) R-attack ($RY+MeSCX(CO_2Me)_2$). When R is (+)-2-octyl and Y^- is bromide ion, the RY found is (−)-2-octyl bromide with 59% optical purity. The mechanism of these reactions are discussed.

It has been shown that the reactions between trialkylsulfonium ions and nucleophiles yielding sulfides and alkylated nucleophiles have features different from ordinary S_N1, S_N2 or competitive S_N1-S_N2 reactions on carbon atoms.



In ordinary S_N2 reactions on carbon atoms (for instance, the leaving groups are halides), the relative reactivities of benzyl and methyl compounds are not much different from unity,[1] whereas benzylation predominates in the reaction of dimethyl-1-phenylethylsulfonium ion with nucleophiles.[2] When di-*t*-butylmethylsulfonium ion reacts with methyl sulfide, exclusive *t*-butylation takes place with no methylation accompanied.[3] Thus when sulfides are leaving groups, the behavior of the substitution are occasionally quite different from that with halides or ammonium ions as leaving groups. No comprehensive explanations have been proposed yet.

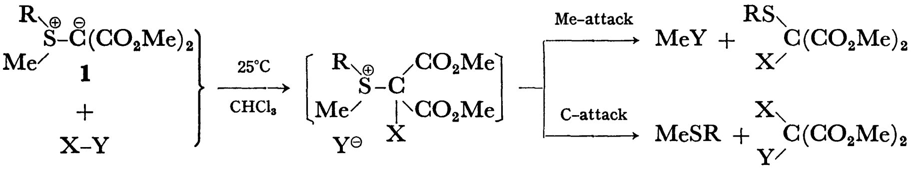
In an attempt to understand the reactions between sulfonium ions and nucleophiles, the reactivities of the sulfonium ions containing electron-withdrawing substituents have been investigated, and the results are described in this paper.

Results and Discussion

Sulfonium ions containing electron-withdrawing substituents were prepared by the reaction between sulfonium ylides and suitable electrophiles.

When sulfonium bis(methoxycarbonyl)methylide (**1**) was mixed in chloroform with Br–Br, Cl–Cl, PhS–Cl, PhS–Br, MeS–Br or H–Br, they reacted instantaneously at room temperature. Usually it was not possible to

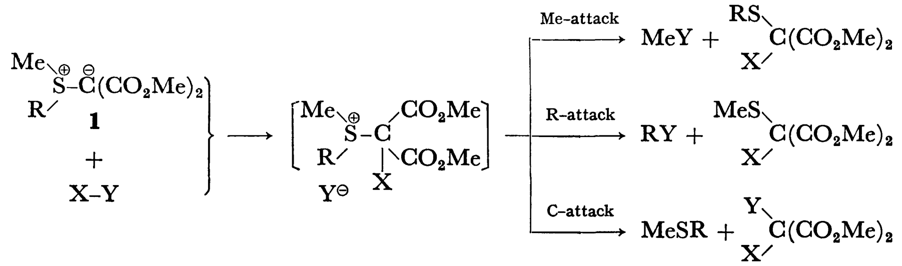
TABLE 1. REACTIONS OF SULFONIUM IONS WITH NUCLEOPHILES



1	R	X	Y	Products (mol%) Me-attack MeY	Me-attack (RS)XC(CO$_2$Me)$_2$	C-attack MeSR	C-attack XYC(CO$_2$Me)$_2$
1a	Me	Br	Br	94	99	0	0
		Cl	Cl	95	84	0	0
		H	Br	100	100	0	0
		PhS	Cl	84	85	0	0
		PhS	Br[a]	92	64	0	0
		MeS	Br[b]	(25)	0	75	84
1b	Ph	Br	Br	100	86	0	0
		Cl	Cl	100	88	0	0
		H	Br	34	34	66	66
		PhS	Cl	0	0	84	88
		PhS	Br[c]	(36)	0	65	97
		MeS	Br[d]	(20)	0	80	83

a) Since PhSBr contains about 36% of free bromine, 36% of Br(MeS)C(CO$_2$Me)$_2$ was produced from the reaction of free bromine. b) From the reaction of free bromine, methyl bromide (25%) was produced. c) From the reaction of free bromine, methyl bromine (36%) was produced. d) From the reaction of free bromine, methyl bromide (20%) was produced.

TABLE 2. REACTION OF DIALKYLSULFONIUM IONS WITH NUCLEOPHILES



1	R	X	Y	Products (mol%) Me-attack MeY[a)]	(RS)XCQ$_2$[b),c)]	R-attack RY[d)]	(MeS)XCQ$_2$[c),d)]	C-attack MeSR[a)]	XYCQ$_2$[b),c)]
1c	Et	Br	Br	56	66	(34)	34	0	0
1d	*n*-Bu			81	81	(19)	19	0	0
1e	*i*-Pr			19	28	(72)	72	0	0
1f	*sec*-C_8H_{17}			21	21	(79)	79	0	0
1g	$PhCH_2$			0	0	100	97	0	0
1h	$MeSCH_2$			0	0	100	95	0	0
1c	Et	Cl	Cl	57	63	(37)	37	0	0
1e	*i*-Pr			23	33	(67)	67	0	0
1g	$PhCH_2$			0	0	97	95	0	0
1h	$MeSCH_2$			0	0	100	100	0	0
1c	Et	PhS	Cl	52	56	(44)	44	0	0
1e	*i*-Pr			18	25	(75)	75	0	0
1g	$PhCH_2$			0	0	90	90	0	0
1h	$MeSCH_2$			0	0	100	100	0	0
1c	Et	H	Br	73	73	(11)	11	16	(16)
1d	*n*-Bu			68	68	(12)	12	20	(20)
1e	*i*-Pr			61	62	(13)	13	25	(25)
1g	$PhCH_2$			0	0	100	100	0	0
1h	$MeSCH_2$			0	0	100	100	0	0

a) Determined from its methyl singlet absorption. b) The CO_2Me (δ 3.77—3.86, broad singlet) absorptions of (RS)XCQ$_2$, (MeS)XCQ$_2$ and XYCQ$_2$ usually could not be resolved. The amount of (MeS)XCQ$_2$ was determined from its MeS singlet, and that of XYCQ$_2$ was estimated by assuming the equimolar formation of MeSR and XYCQ$_2$. Then the amount of (RS)XCQ$_2$ could be calculated. c) Q=CO_2Me. d) The amounts of $PhCH_2Y$ (or $MeSCH_2Y$) were determined from its singlet near 4.50 ppm. The amounts of other RY's were estimated from the assumption of equimolar formation of RY and (MeS)XCQ$_2$ (determined from its MeS singlet).

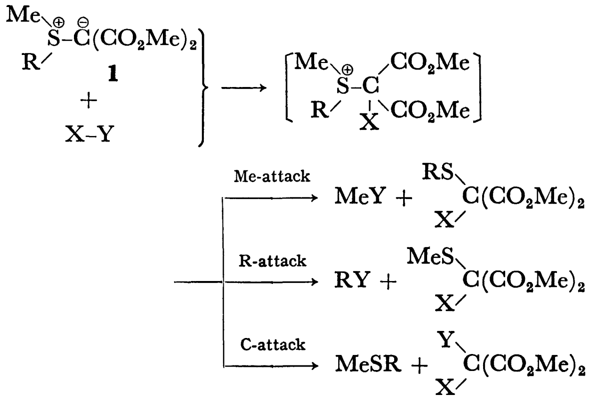
isolate the sulfonium salts. It was possible to isolate a white solid sulfonium salt from the reaction between **1a** (R=Me) and HBr; they decomposed when they were dissolved in chloroform and allowed to stand at room temperature for 5 hrs. The products of the reaction of **1a** (R=Me) and **1b** (R=Ph) with several electrophiles are listed in Table 1.

When R in **1** is an alkyl group, competitive S_N2 attacks on the methyl and alkyl groups are expected. Ylide **1** with various alkyl groups was allowed to react with X—Y, and the products are shown in Table 2.

The results shown in Tables 1 and 2 can be summarized as follows. The ylides and electrophiles react and form sulfonium ions and anions $Y^{\ominus}$, which further react in three different ways (namely, Me-attack, R-attack and C-attack).

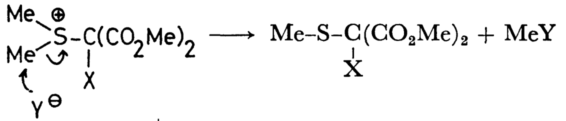
The course of the reaction depends upon the structure of the sulfonium ion (R and X) and the nucleophile $Y^{\ominus}$.

1) When R is Me, methyl attack of $Y^{\ominus}$ predominates

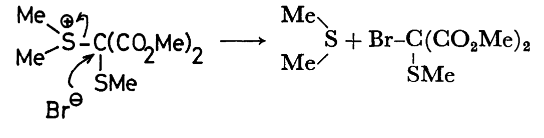


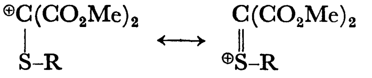
except one case, in which X is MeS.

When X is MeS, Me_2S group easily leaves from $Me_2\overset{\oplus}{S}-C(SMe)(CO_2Me)_2$; it is known that R—S groups can stabilize the adjacent carbonium ion by resonance effect as shown below.[4)]



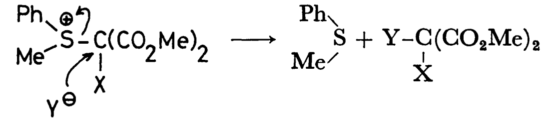
X	Br	Cl	H	PhS	PhS
Y	Br	Cl	Br	Cl	Br





When X is PhS, such resonance effect is not great enough to help the elimination of Me_2S.

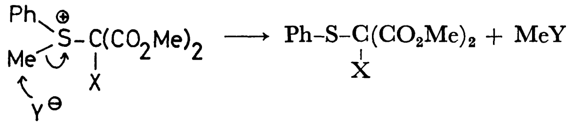
2) When R is Ph, and X is MeS or PhS, the elimination of PhSMe and the apparent C-attack of $Y^{\ominus}$ predominate.



X	PhS	PhS	MeS
Y	Cl	Br	Br

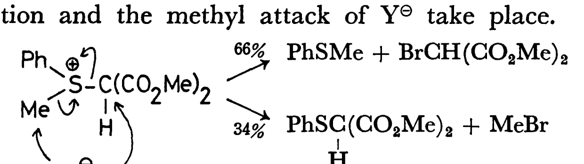
Apparently PhSMe is a better leaving group than Me_2S,⁵⁾ and even when X is PhS (a poorer resonance-stabilizing group), the elimination of PhSMe takes place readily.

3) When X is Br or Cl, the main reaction is methyl attack of $Y^{\ominus}$ and RSMe elimination is not observed.



It is reasonable that the carbon atom containing three electron-withdrawing groups (two CO_2Me's and one halogen) does not allow the RSMe elimination resulting in the formation of a carbonium ion.

4) When R=Ph and X=H, both the RSMe elimination and the methyl attack of $Y^{\ominus}$ take place.

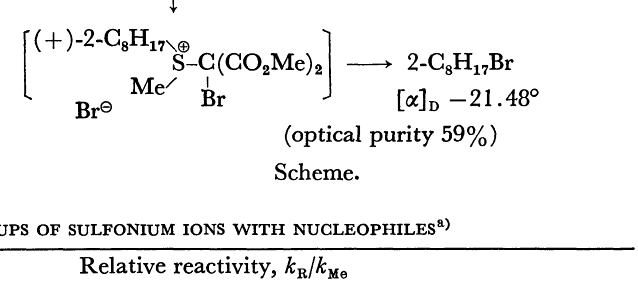


It is interesting to note that when one of the substituents is benzyl or methylthiomethyl group, the reaction is exclusive benzylation or methylthiomethylation of the nucleophile with no accompanying methylation. The ratio between the yields of methylated and alkylated products are calculated and summarized in Table 3. They are quite different from what are expected for ordinary S_N2 reactions on carbon. For instance, the relative reactivities of alkyl bromides with bromide anion in acetone at 25 °C are Me 1.0, Et 0.013, *i*-Pr 0.0086, and $PhCH_2$ 1.0.⁶⁾ The remarkable feature in the results shown in Table 3 is that the reactivity of methyl group is comparable to that of ethyl group, smaller than that of isopropyl group, and far smaller than that of benzyl group.

The relative reactivities of phenylmethylalkylsulfonium perchlorates with iodide anion in acetone at 50 °C are Me 1.0, Et 0.20, *n*-Pr 0.16, and *i*-Pr 0.05, and apparently these reactions involve S_N2 attack on the sulfonium alkyl groups.⁷⁾

Table 3 shows that benzyl and methylthiomethyl are far more reactive than methyl group. These results suggest that these reactions may involve an S_N1-like process. In the reactions of **1** with hydrogen bromide, however, the reactivity of isopropyl group is smaller than that of methyl group. Thus, *sec*-alkyl groups are more reactive than methyl group only when the α atom in X is a hetero atom such as Br, Cl or S.

Reversible bond-formation between sulfonium sulfur atom and an anion is a possible process, since evidence for the formation of a tetracovalent sulfur intermediate from a sulfonium ion and chloride ion has been presented,⁸⁾ and many examples of tetracovalent sulfur intermediates were described in a recent review.⁹⁾ In an attempt to elucidate the mechanism of these reactions, a sulfonium ylide with optically active (+)-2-C_8H_{17}



Scheme.

TABLE 3. RELATIVE REACTIVITIES OF ALKYL GROUPS OF SULFONIUM IONS WITH NUCLEOPHILES[a]

Sulfonium ion	Nucleophile	Relative reactivity, k_R/k_{Me}						
		Me	Et	*n*-Bu	*i*-Pr	*sec*-C_8H_{17}	$PhCH_2$	$MeSCH_2$
$MeRS^{\oplus}$-$BrC(CO_2Me)_2$	$Br^{\ominus}$	(1.0)	0.61	0.23	3.79	3.76	∞	∞
$MeRS^{\oplus}$-$ClC(CO_2Me)_2$	$Cl^{\ominus}$	(1.0)	0.65	—	2.91	—	∞	∞
$MeRS^{\oplus}$-$(PhS)C(CO_2Me)_2$	$Cl^{\ominus}$	(1.0)	0.85	—	4.17	—	∞	∞
$MeRS^{\oplus}$-$HC(CO_2Me)_2$	$Br^{\ominus}$	(1.0)	0.15	0.18	0.21	—	∞	∞

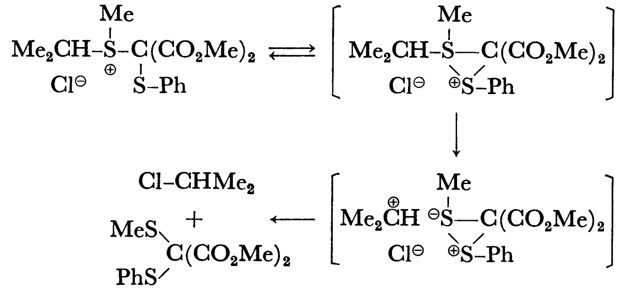
a) Relative reactivities are the ratio RY/MeY, calculated from Table 2.

group (**1f′**) was prepared and its reaction with bromine was examined according to the Scheme shown.

The reactivity of 2-C_8H_{17} group is about 4 times that of methyl group. The results of optical measurements show that the main course of the reaction is the inversion at the asymmetric carbon accompanied by some racemization.

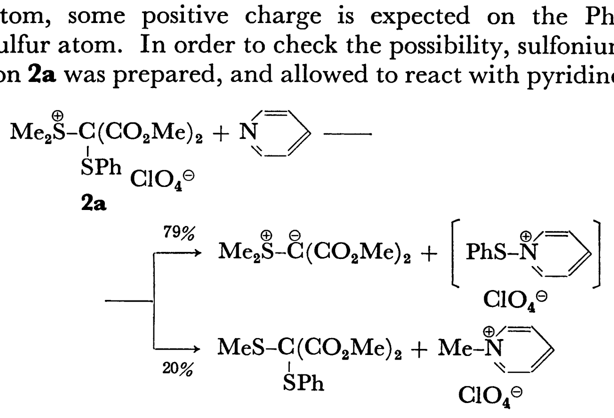
If a sulfurane intermediate is produced by the bond-formation between the sulfonium sulfur atom and bromide ion, the collapse of the sulfurane should yield (+)-2-C_8H_{17}-Br with retention of configuration. The optical data show that such sulfurane intermediates are probably not formed in the reaction between **1f′** and bromine.

It is of interest that $k_{i\text{-Pr}}$ is smaller than k_{Me} in the reactions between MeRS$^\oplus$—Ph $ClO_4^\ominus$ and $I^\ominus$,[7] and $k_{i\text{-Pr}}$ is greater than k_{Me} in the reactions between MeRS$^\oplus$—CX-$(CO_2Me)_2$ and $Y^\ominus$ only when the α atom in X is a hetero atom. One possible explanation is the formation of the following intramolecular sulfurane.



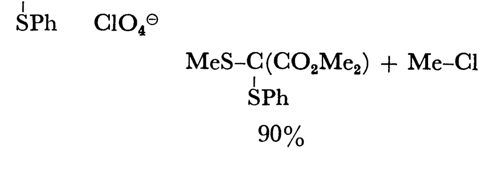
A similar intramolecular sulfurane has been proposed between a sulfonium ion and the neighboring nitro group.[10]

If the PhS group interacts with the solfonium sulfur atom, some positive charge is expected on the PhS sulfur atom. In order to check the possibility, sulfonium ion **2a** was prepared, and allowed to react with pyridine.

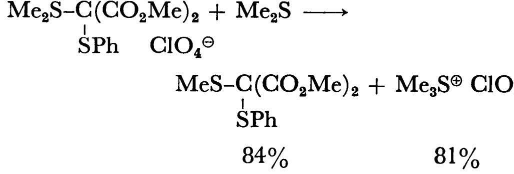


The product of the nucleophilic attack of pyridine on the PhS sulfur atom was found in 79% yield. These results suggest that the PhS sulfur atom has a partial positive charge in agreement with the above hypothesis.

Reactions of **2a** with $Cl^\ominus$ or Me_2S gave the results consistent with those shown in Table 1.



$$\underset{\text{SPh}\quad ClO_4^\ominus}{Me_2\overset{\oplus}{S}\text{-}C(CO_2Me)_2} + Ph_4As^\oplus\,Cl^\ominus \longrightarrow \underset{\text{SPh}}{MeS\text{-}C(CO_2Me_2)} + Me\text{-}Cl \quad 90\%$$



$$\underset{\text{SPh}\quad ClO_4^\ominus}{Me_2\overset{\oplus}{S}\text{-}C(CO_2Me)_2} + Me_2S \longrightarrow \underset{\text{SPh}}{MeS\text{-}C(CO_2Me)_2} + Me_3S^\oplus\,ClO_4^\ominus \quad 84\% \quad 81\%$$

The results of the reaction between optically-active **1f′** and Br_2 may be rationallized by assuming some elongation of the R-S$^\oplus$ bond, development of positive charge on R, and the attack of $Br^\ominus$ taking place mainly from the backside.

Ōki and Kobayashi studied the reaction between (+)-α-phenylpropyl methyl sulfide and methanesulfenyl chloride, and found that $Cl^\ominus$ attacked the intermediate sulfonium ion, PhEtC*H—S$^\oplus$Me(SMe), forming (−)-PhEtCH—Cl with 70% inversion and 30% racemization.[11]

Experimental

Materials. Sulfonium bis(methoxycarbonyl)methylides **1a**—**h** were prepared by copper salts-catalyzed decomposition of dimethyl diazomalonate in large excess sulfides[12] and by transylidation.[13] Benzenesulfenyl chloride (bp 50 °C/2 mmHg) was synthesized by the methods described in the literature.[14] Benzenesulfenyl bromide (or methanesulfenyl bromide) was prepared by mixing equimolar amounts of phenyl disulfide (or methyl disulfide) and bromine in carbon tetrachloride. Sulfonium salt **2a** was prepared by dropwise addition of a CCl_4 solution of benzenesulfenyl chloride (1.45 g, 10 mmol) to a nitromethane solution of **1a** (1.94 g, 10 mmol) and silver perchlorate (2.07 g, 10 mmol) at 0 °C. Yield, 3.6 g (90%); recrystallized from ethanol; mp 105—106 °C; IR (KBr), 1740 cm^{-1} (ν_{CO}); NMR (DMSO-d_6), δ 7.60 (5H, s, PhS), 3.93 (6H, s, CO_2Me) and 3.20 (6H, s, $Me_2\overset{\oplus}{S}$-). Found: C, 38.26; H, 4.25%. Calcd for $C_{13}H_{17}O_8ClS_2$: C, 38.96; H, 4.27%. This salt partially decomposed when it was allowed to stand at room temperature for several days.

Reactions of Ylides 1a or 1b with Bromine. (a) When Br_2 (1.65 g, 10.3 mmol) was added to a chloroform (18 g) solution of **1a** (1.97 g, 10.0 mmol), they reacted instantaneously, and the solution turned from red to colorless. The ylide carbonyl absorptions (1630 and 1670 cm^{-1}) were replaced by the ester absorption (1730 cm^{-1}). The amounts of the products were determined by NMR spectroscopy with nitromethane as an internal standard. The low-boiling fractions from the mixture were trapped in liquid nitrogen, and the presence of MeBr was shown by NMR (δ 2.62, s). The high-boiling fractions were chromatographed (Florisil), and the oils obtained from the benzene eluate were found to be Br(MeS)C$(CO_2Me)_2$ (2.54 g, 9.9 mmol, 99%; IR (neat), 1740 cm^{-1} (ν_{CO}); NMR (CCl_4), δ 3.86 (6H, s, CO_2Me) and 2.22 (3H, s, MeS). Found: C, 27.76; H, 3.68%. Calcd for $C_6H_9O_4BrS$: C, 27.29; H, 3.44%). (b) A mixture of a $CHCl_3$ (10 g) solution of **1b** (1.25 g, 5.0 mmol) and Br_2 (0.80 g, 5.0 mmol) gave MeBr (δ 2.62, s) and Br(PhS)C$(CO_2Me)_2$ (liquid, 1.37 g, 0.43 mmol, 86%; IR (neat), 1740 cm^{-1} (ν_{CO}); NMR (CCl_4), δ 7.30—7.60 (5H, m, PhS) and 3.76 (6H, s, CO_2Me). Found: C, 41.26; H, 3.56%. Calcd for $C_{11}H_{11}O_4BrS$: C, 41.40; H, 3.47%).

Reactions of Ylides 1a or 1b with Chlorine. (a) The reaction between a $CHCl_3$ (10 g) solution of **1a** (1.0 g, 5.14 mmol) and a CCl_4 solution of Cl_2 (0.42 g, 6.0 mmol) was exothermic and instantaneous, and gave MeCl (δ 3.0, s) and Cl(MeS)C-$(CO_2Me)_2$ (liquid, 0.92 g, 4.34 mmol, 84%; IR (neat), 1740

cm^{-1} (ν_{CO}); NMR ($CDCl_3$), δ3.88 (6H, s, CO_2Me) and 2.25 (3H, s, MeS). Found: C, 32.75; H, 3.82%. Calcd for $C_6H_9O_4ClS$: C, 32.82; H, 4.13%).

(b) In a similar manner, a mixture of a $CHCl_3$ (19 g) solution of **1b** (2.61 g, 10.3 mmol) and a CCl_4 solution of Cl_2 (0.78 g, 11.0 mmol) gave MeCl (δ 2.97, s) and $Cl(PhS)C(CO_2Me)_2$ (liquid, 2.49 g, 9.09 mmol, 88%; IR (neat), 1740 cm^{-1} (ν_{CO}); NMR (CCl_4), δ 7.30—7.60 (5H, m, PhS) and 3.68 (6H, s, CO_2Me). Found: C, 48.17; H, 3.92%. Calcd for $C_{11}H_{11}O_4ClS$: C, 48.10; H, 4.04%). Methyl phenyl sulfide (PhSMe, δ 2.49, s) was not found.

Reactions of Ylides 1a or 1b with Benzenesulfenyl Chloride. (a) When PhSCl (1.60 g, 11.1 mmol) was added to a chloroform (15 g) solution of **1a** (1.98 g, 10.3 mmol), they reacted instantaneously, and the solution turned from red to colorless. The amounts of the products were determined by NMR spectroscopy with nitromethane as an internal standard. From the low-boiling fraction trapped in liquid nitrogen, methyl chloride was identified by NMR (δ 2.97, s). The high-boiling fraction solidified at room temperature, and recrystallization from benzene yielded white crystals of $MeS(PhS)C(CO_2Me)_2$. 2.51 g (8.77 mmol, 85%): mp 71—72 °C; IR (KBr), 1730 cm^{-1} (ν_{CO}); NMR (CCl_4), δ 7.30 (5H, s, PhS), 3.64 (6H, s, CO_2Me) and 2.15 (3H, s, MeS). Found: C, 50.52; H, 4.93%. Calcd for $C_{12}H_{14}O_4S_2$: C, 50.33; H, 4.93%.

(b) In a similar manner, a mixture of a $CHCl_3$ (9 g) solution of **1b** (1.75 g, 6.87 mmol) and PhSCl (1.01 g, 7.0 mmol) gave PhSMe (from hexane eluates; 0.71 g, 5.75 mmol, 84%), $Cl(PhS)C(CO_2Me)_2$ (oil from benzene eluates; 1.66 g, 6.05 mmol, 88%).

Reactions of Ylides 1a or 1b with Benzenesulfenyl Bromide. (a) A mixture of a $CHCl_3$ (14 g) solution of **1a** (1.95 g, 10.0 mmol) and a CCl_4 (6 g) solution of PhSSPh (1.1 g, 5.0 mmol) and bromine (0.8 g, 5.0 mmol) reacted instantaneously, and gave MeBr (δ 2.64, s) and MeS (PhS) C $(CO_2Me)_2$ (1.83 g, 6.4 mmol, 64%; mp 71—72 °C).

(b) A mixture of a $CHCl_3$ (10 g) solution of **1b** (2.54 g, 10.0 mmol) and a CCl_4 (10 g) solution of PhSSPh (1.1 g, 5.0 mmol) and bromine (0.8 g, 5.0 mmol) gave PhSMe (δ 2.49, from hexane eluates; 0.81 g, 6.50 mmol, 65%) and $Br(PhS)C(CO_2Me)_2$ (oil from benzene eluates; 3.09 g, 7.70 mmol, 97%).

Reactions of Ylides 1a or 1b with Methanesulfenyl Bromide. (a) In a similar manner, a mixture of a $CHCl_3$ (10 g) solution of **1a** (1.92 g, 10 mmol) and a CCl_4 (9 g) solution of MeSSMe (0.42 g, 5.0 mmol) and bromine (0.8 g, 5.0 mmol) reacted instantaneously, and gave Me_2S (δ 2.10, s, 75%), MeBr (δ 2.64, s, 25%; produced from the reaction of free bromine) and $Br(MeS)C(CO_2Me)_2$ (oil from benzene eluates; 2.24 g, 8.40 mmol, 84%).

(b) A mixture of a $CHCl_3$ (10 g) solution of **1b** (1.90 g, 10 mmol) and a CCl_4 (8 g) solution of MeSSMe (0.42 g, 0.5 mmol) and bromine (0.8 g, 5.0 mmol) gave PhSMe (δ 2.49, s; from hexane eluates; 1.0 g, 8.0 mmol, 80%), MeBr (δ 2.64, s, 20%; produced from the reaction of free bromine) and $Br(MeS)C(CO_2Me)_2$ (oil from benzene eluates; 2.21 g, 8.30 mmol, 83%).

Reactions of Ylides 1a or 1b with Hydrogene Bromide. (a) When hydrogene bromide gas was bubbled through a $CHCl_3$ solution of **1a**, its NMR spectrum showed the formation of a sulfonium salt ($Me_2\overset{\oplus}{S}$–, δ 3.42, s). Evaporation of the solvent yielded white solids (NMR ($CHCl_3$), δ 4.01 (6H, s, CO_2Me) and 3.42 (6H, s, $Me_2\overset{\oplus}{S}$–)). When they were dissolved in $CHCl_3$ and allowed to stand for 5 hr at room temperature, the NMR spectrum showed the quantitative formation of MeBr (δ 2.63, s) and $\underline{Me}SCH(CO_2Me)_2$ (δ 2.25, s).

(b) When a CCl_4 solution of hydrogen bromide was added to a $CHCl_3$ solution of **1b**, they reacted instantaneously, and it was not possible to isolate the sulfonium salt. The amounts of MeBr (δ 2.62, s, 34%) and $PhS\underline{Me}$ (δ 2.46, s, 66%) were determined by use of nitromethane as an internal standard.

Reactions of Ylides 1c—h with Halogens, PhSCl or HBr. The $CDCl_3$ solutions of Ylides **1c**—**h** (0.7—1.0 mmol) and X—Y (0.8—1.1 mmol) containing nitromethane (internal standard, 50 μl, 0.79 mmol) were let to react in NMR tubes at 25 °C, and the amounts of the reaction products were determined from their singlet methyl absorption by NMR spectroscopy (see Table 2); $\underline{Me}$-Br (δ 2.62—2.64), $\underline{Me}$-Cl (2.90—2.98), $\underline{Me}SEt$ (2.05—2.12), $\underline{Me}SBu$-*n* (2.07), $\underline{Me}SPr$-*i* (2.10), $\underline{Me}SC_8H_{17}$-*sec* (1.99), $\underline{Me}SCH_2Ph$ (1.92), $\underline{Me}SCH_2$-$S\underline{Me}$ (2.10), $Br(\underline{Me}S)C(CO_2Me)_2$ (2.23), $Cl(\underline{Me}S)$ $C(CO_2Me)_2$ (2.23), $\underline{Me}S(PhS)C(CO_2Me)_2$ (2.19—2.20) and $\underline{Me}SCH(CO_2Me)_2$ (2.25).

*Synthesis of (+)-2-Octylmethylsulfonium Bis(methoxycarbonyl)-methylide (**1f′**).* (—)-2-Octyl bromide was prepared from the reaction between (+)-2-octanol (purchased from Fluka, $[\alpha]_D$ +11°) (15 g) and PBr_3 (34.8 g) below +5 °C; yield, 13.8 g (62.6%); bp 55 °C/3 mmHg (lit,[15] 61 °C/3 mmHg); $[\alpha]_D^{26.6}$ −36.62° (*c* 8.36, 95% ethanol) (lit,[15] $[\alpha]_D^{25}$ −34.25°).

(+)-2-Octyl methyl sulfide was prepared from the reaction between (—)-2-octyl bromide (11.1 g) and sodium methylmercaptide (20% aq solution, 42 g) in ethanol; yield, 75.0%; bp 84—85.5 °C/10 mmHg; $[\alpha]_D^{26.5}$ +8.78° (*c* 11.8, $CHCl_3$).

Ylide **1f′** was not obtained by copper-catalyzed decomposition of methyl diazomalonate in the sulfide.[12] Therefore, it was prepared by transylidation.[13] A chloroform (11.5 g) solution of **1b** (3.04 g), (+)-2-octyl methyl sulfide (6.0 g) and dimethoxy disulfide (1.3 g; a catalyst) was kept at 40 °C. After 4 days, its NMR spectrum showed the complete disappearance of **1b**. Sulfides and the catalyst were distilled off under reduced pressure at 55 °C/3 mmHg, and the NMR spectrum of the residual oil showed that it is ylide **1f′**; yield, 2.5 g (72%); IR (neat), 1620 and 1670 cm^{-1} (ν_{CO}); NMR ($CDCl_3$), δ 3.74 (6H, s, CO_2Me), 2.88 (3H, s, $Me\overset{\oplus}{S}$–) and 0.88—1.44 (16H, m, 2-octyl group); $[\alpha]_D^{28.2}$ −28.64° (*c* 10.5, $CHCl_3$).

Reactions of Ylide 1f′ with Bromine. A CCl_4 (13.8 g) solution of Br_2 (1.38 g, 8.62 mmol) was added drop by drop to a $CHCl_3$ (21 g) solution of **1f′** (2.5 g, 8.62 mmol). The completion of the reaction was ascertained by the IR spectrum (ν_{CO}, 1730 cm^{-1}). The NMR spectrum showed the formation of 2-octyl bromide (79.3%) and methyl bromide (20.7%). After the reaction mixture was concentrated under reduced pressure, the residue was subjected to column chromatography (Florisil), and the *n*-hexane eluates yielded 2-octyl bromide. Its purity was checked by gas chromatography. $[\alpha]_D^{25.2}$ −21.48° (*c* 5.96, 95% ethanol).

Reactions of Sulfonium Ion 2a with Nucleophiles. (a) A nitromethane solution of **2a** (1.0 mmol) and tetraphenylarsonium chloride (2.0 mmol) was heated at 50 °C for 5 min. After evaporation, the NMR spectrum of the residue (soluble in CCl_4) showed the presence of $MeS(PhS)C(CO_2Me)_2$ (δ 2.20, s, MeS; 90%).

(b) A DMSO-d_6 solution of **2a** (1.0 mmol) and methyl sulfide (1.5 mmol) was placed in an NMR tube at 25 °C. After 4 days, the amounts of trimethylsulfonium salt (δ 2.89, s, $Me_3\overset{\oplus}{S}$; 81%) and $MeS(PhS)C(CO_2Me)_2$ (δ 2.17, s, MeS; 84%) were determined by NMR spectroscopy.

(c) A DMSO-d_6 solution of **2a** (1.0 mmol) and pyridine (2.0 mmol) was placed in an NMR tube at 25 °C. After 2 hr, the amounts of **1a** (δ 2.88, s, $Me_2\overset{\oplus}{S}$–; 79%) and $MeS(PhS)C(CO_2Me)_2$ (δ 2.17, s, MeS; 20%) were determined by NMR spectroscopy.

Reaction of Ylide **1e** *with Methanesulfenyl Chloride.* In an NMR tube a $CDCl_3$ solusion of **1e** (1.0 mmol) and a CCl_4 solution of MeSCl were mixed. Rapid reaction took place, yielding MeSPr-*i* and $Cl(MeS)C(CO_2Me)_2$ quantitatively. The NMR spectrum showed the absence of isopropyl chloride.

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