Interactions between Sulfur Ylides and Electrophilic Monosulfides[1)]

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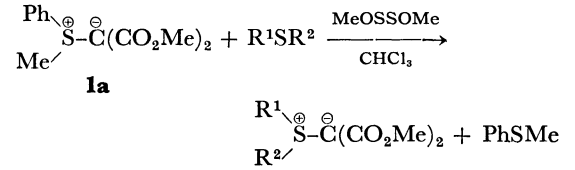
(Received August 3, 1978)

The catalytic activities of electrophilic monosulfides, Ar–S–R* (R* = CN, CF_3, OMe), for the transylidation reactions of sulfur ylide, $\mathrm{Ph(Me)\overset{\oplus}{S}{-}\overset{\ominus}{C}(CO_2Me)_2}$, with alkyl sulfides and pyridines were investigated. Among these monosulfides, methyl arenesulfenates reacted with dimethylsulfonium phenacylide (or dimethylsulfonium ethoxycarbonylmethylide) to give α-(arylthio)phenacylides (or α-(arylthio)ethoxycarbonylmethylides) and methanol. The ^{13}C-NMR spectra of several sulfur ylides and aryl thiocyanates were investigated in $CDCl_3$, and the presence of *S*-ylide–thiocyanate adduct intermediates was established.

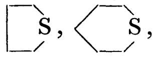
Electrophilic sulfides, $\overset{\delta-}{R^*}\leftarrow\overset{\delta+}{S}\rightarrow\overset{\delta-}{R^*}$ (R* = electron-withdrawing substituents), are very interesting compounds. We have previously reported that the disulfides containing electron-withdrawing substituents, $\overset{\delta-}{R^*}\leftarrow\overset{\delta+}{S}{-}\overset{\delta+}{S}\rightarrow\overset{\delta-}{R^*}$ (R* = OMe, CN, CF_3, and COPh), react as novel catalysts in several reactions of sulfur ylides.[2—5)] Particularly, in the presence of dimethoxy disulfide (R* = OMe), transylidation reactions take place smoothly at room temperature, as is shown below:[2)]

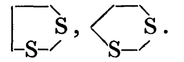


$$\mathrm{Ph(Me)\overset{\oplus}{S}{-}\overset{\ominus}{C}(CO_2Me)_2} + \mathrm{R^1SR^2} \xrightarrow[\mathrm{CHCl_3}]{\mathrm{MeOSSOMe}} \mathrm{R^1(R^2)\overset{\oplus}{S}{-}\overset{\ominus}{C}(CO_2Me)_2} + \mathrm{PhSMe}$$

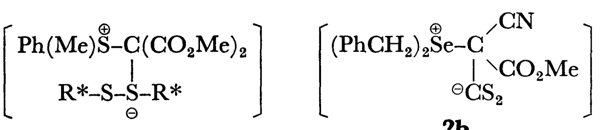
1a

R^1SR^2: Me_2S, MeSEt, MeSBu-*n*, MeSPr-*i*, $MeSC_8H_{17}$-2, $MeSCH_2Ph$, Et_2S, $MeSCH_2SMe$,





Tamagaki *et al.* reported that carbon disulfide acts as a catalyst for the transylidation reaction of selenonium ylide with alkyl sulfides.[6)] In both reactions, the formation of ylide-catalyst adducts (**2a** and **2b**) and the subsequent nucleophilic attack of alkyl sulfides on the adducts to afford the new ylides were postulated.[2,6)]

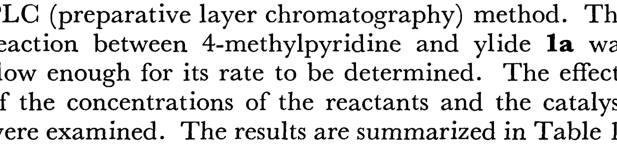


2a **2b**

Hitherto, the catalytic ability of the monosulfides for the transylidation reaction of sulfur ylides has not been investigated. Recently, we have found that the monosulfides containing electron-withdrawing substituents, Ar–S–R* (R* = CN, CF_3, and OMe), act as catalysts for the transylidation reaction of sulfur ylide **1a**. In this paper, we wish to report how to produce interaction between sulfur ylides and electrophilic monosulfides which act as catalysts on transylidation reactions.

Results and Discussion

Transylidation. In the presence of aryl thiocyanates (Ar–S–CN), phenylmethylsulfonium bis(methoxycarbonyl)methylide **1a** reacted with 4-methylpyridine to give a new 4-methylpyridinium ylide in chloroform at room temperature.



In the absence of aryl thiocyanates, **1a** is very stable and shows no transylidation when it is mixed with pyridine at 35 °C. After the reaction was over, aryl thiocyanates were recovered from its solution by the PLC (preparative layer chromatography) method. The reaction between 4-methylpyridine and ylide **1a** was slow enough for its rate to be determined. The effects of the concentrations of the reactants and the catalyst were examined. The results are summarized in Table 1. The first-order rate constants calculated by assuming $-d[\mathbf{1a}]/dt=k[\mathbf{1a}]$ increased with the initial concentration of 4-methylpyridine; apparently the rate depends on 4-methylpyridine. The rates increased also with the

TABLE 1. RATES OF TRANSYLIDATION BETWEEN YLIDE **1a** AND 4-METHYLPYRIDINE IN $CDCl_3$ AT 35 °C

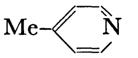
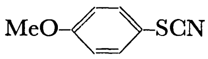
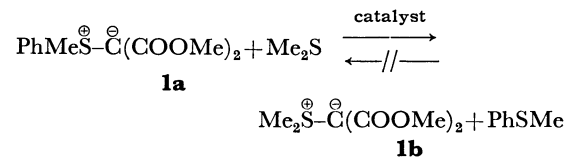
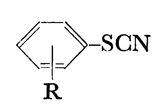
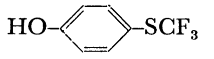
Reactants (mol/l)			First-order rate constants calcd from $-d[\mathbf{1a}]/dt=k[\mathbf{1a}]$ $10^5\times k$ (s^{-1})
$\mathrm{PhMe\overset{\oplus}{S}{-}\overset{\ominus}{C}(COOMe)_2}$ **1a**			
0.50	0.50	0.50	0.78
0.50	1.00	0.50	2.2
0.50	1.50	0.50	3.4
0.50	1.50	1.00	7.3
0.50	1.50	2.00	10

Table 2. Rates of transylidation of ylide **1a** with methyl sulfide in $CDCl_3$ at 35 °C[a)]



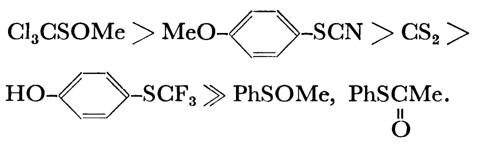
$$\underset{\mathbf{1a}}{\mathrm{PhMe\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(COOMe)_2}}+\mathrm{Me_2S}\underset{\not\longleftarrow}{\xrightarrow{\text{catalyst}}}\underset{\mathbf{1b}}{\mathrm{Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(COOMe)_2}}+\mathrm{PhSMe}$$

Catalyst		First-order rate constants calcd from $-d[\mathbf{1a}]/dt=k[\mathbf{1a}]$ $10^5\times k(s^{-1})$
None		No reaction
	R = p-MeO	4.6
	p-Me_2N	0.50
	p-Me	0.50
	p-Cl	0.32
		0.73
Cl_3CSOMe		Very fast[b)]
CS_2		2.3
PhSOMe		No reaction
PhSC(O)Me		No reaction

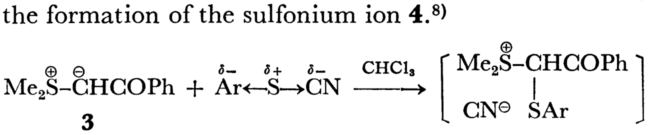
a) A mixture consists of **1a** (0.5 M), dimethyl sulfide (1.5 M), and a catalyst (2.0 M). b) 10 min after, the yield of **1b** was 70%.

initial concentration of p-methoxyphenyl thiocyanate.

Various monosulfides were examined as regards their catalytic activity in this transylidation. Neither S-phenylthioacetate nor methyl benzenesulfenate was effective, methyl trichloromethanesulfenate and p-trifluoromethylphenol possessed a catalytic activity similar to that of aryl thiocyanate. Carbon disulfide also acted as catalyst in this transylidation (Table 2). The order of catalytic activity was:

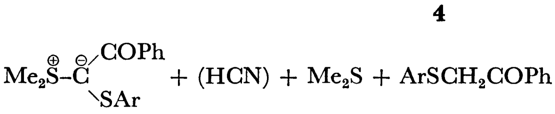


Reactions of Dimethylsulfonium Phenacylide 3 with Aryl Thiocyanates. It was found that p-chlorophenyl thiocyanate (Ar=p-Cl-C_6H_4) reacted very slowly with ylide **3** to give dimethylsulfonium α-(p-chlorophenylthio)phenacylide (31%), methyl sulfide (43%), and p-chlorophenyl phenacyl sulfide (40%) after 4 days. These reaction products can be explained by assuming the formation of the sulfonium ion **4**.[8)]



$$\underset{\mathbf{3}}{\mathrm{Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}HCOPh}}+\overset{\delta-}{\mathrm{Ar}}\leftarrow\overset{\delta+}{\mathrm{S}}\rightarrow\overset{\delta-}{\mathrm{CN}}\xrightarrow{\mathrm{CHCl_3}}\left[\begin{array}{c}\mathrm{Me_2\overset{\oplus}{S}\text{-}CHCOPh}\\ |\\ \mathrm{CN^{\ominus}\ \ SAr}\end{array}\right]$$

4

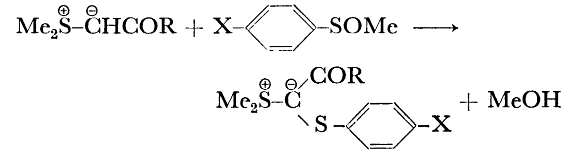


$$\mathrm{Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}}\begin{array}{l}\mathrm{COPh}\\ \mathrm{SAr}\end{array}+(\mathrm{HCN})+\mathrm{Me_2S}+\mathrm{ArSCH_2COPh}$$

Ar=p-Cl-C_6H_4	(31%)	(43%)	(40%)
p-Me-C_6H_4	(24%)	(45%)	(40%)
o-Cl-C_6H_4	(30%)	(40%)	(40%)

Reactions of the 3 and 5 Sulfur Ylides with Methyl Arenesulfenates. In contrast to aryl thiocyanates, methyl arenesulfenates, ArSOMe, did not act as catalysts for transylidation. However, they reacted instantaneously at room temperature with phenacylide **3** (or ethoxycarbonylmethylide **5**), which contains only one electron-withdrawing substituent, in chloroform and gave the sulfenylated products, dimethylsulfonium α-(arylthio)phenacylide[19)] (or α-(arylthio)ethoxycarbonylmethylide[19)]). The results are shown in Table 3.

Table 3. Reactions of sulfur ylides **3** and **5** with methyl arenesulfenates in $CHCl_3$ at room temperature

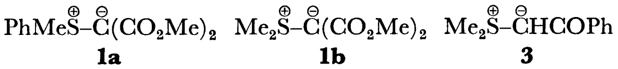


Ylide	R	X	Yield (%)[a)]	Mp (°C)	$\nu_{CO}(cm^{-1})$
3	Ph	H	75	138—140	1520
		Me	68	136—138	1520
		Cl	89	148—149	1520
5	OEt	H	42	126—127	1600
		Me	33	114—116	1600
		Cl	87	135—136	1600

a) Isolated yield.

Carbon-13 NMR Spectra of Ylide-catalyst Adducts. In order to obtain spectroscopic evidence for the formation of the sulfur ylide–electrophilic sulfides adducts, we investigated the carbon-13 NMR spectra of solutions of several sulfur ylides and aryl thiocyanates which are active catalysts. Carbon-13 chemical shifts provide some information on the electronic state of carbon atoms in molecules. The chemical shifts of disubstituted sulfur ylides, **1a** and **1b**, are little affected by solvents.[7)] On

Table 4. ^{13}C chemical shifts of ylide carbons of some sulfonium ylides[a)]



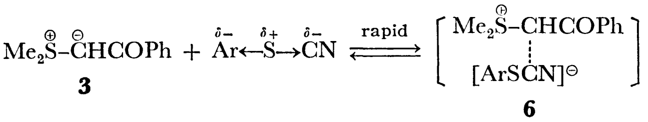
$$\underset{\mathbf{1a}}{\mathrm{PhMe\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(CO_2Me)_2}}\quad\underset{\mathbf{1b}}{\mathrm{Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(CO_2Me)_2}}\quad\underset{\mathbf{3}}{\mathrm{Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}HCOPh}}$$

Thiocyanate/Ylide (mol/mol)			$\overset{\ominus}{C}$ or $\overset{\ominus}{C}H$	Δδ[b)]	Solvent
None	**1a**		59.1	(0)	$CDCl_3$
None	**1a**		59.2	(0.1)	DMSO-d_6
MeO-C_6H_4-SCN	**1a**	(1/1)	59.1	(0)	$CDCl_3$
None	**1b**		58.6	(0)	$CDCl_3$
None	**1b**		58.4	(−0.2)	DMSO-d_6
MeO-C_6H_4-SCN	**1b**	(1/1)	58.7	(0.1)	$CDCl_3$
None	**3**		53.2	(0)	$CDCl_3$
None	**3**		60.6	(7.4)	DMSO-d_6
MeO-C_6H_4-SCN	**3**	(1/1)	54.2	(1.0)	$CDCl_3$
Me_2N-C_6H_4-SCN	**3**	(1/1)	53.8	(0.6)	$CDCl_3$
		(2/1)	54.4	(1.2)	$CDCl_3$
MeSCN	**3**	(1/1)	53.1	(0)	$CDCl_3$
		(5/1)	54.4	(1.2)	$CDCl_3$
		(10/1)	55.5	(2.3)	$CDCl_3$
		(15/1)	56.2	(3.1)	$CDCl_3$
		(23/1)	56.5	(3.3)	$CDCl_3$

a) δ_c, ppm from TMS (accurate to ±0.13).
b) $\Delta\delta=(\delta^{\mathrm{ArSCN}}_{\mathrm{CDCl_3}}-\delta^{\mathrm{none}}_{\mathrm{CDCl_3}})$.

the other hand, the chemical shifts of the ylide carbon of dimethylsulfonium phenacylide, **3**, which contains only one electron-withdrawing substituent and which acts as a reactive carbanion, are dependent on the kind of solvent (Table 4).

When ylide **3** and aryl thiocyanate are mixed in chloroform, the downfield shifts (0.6—3.3 ppm) of the ylide carbon of phenacylide **3** were observed. Though the values of the shifts of ylide carbon were small, the NMR data can be explained by assuming that the formation of the adduct **6** from the ylide **3** and aryl thiocyanate is reversible and rapid.



$$\overset{\oplus}{Me_2S}\text{-}\overset{\ominus}{C}HCOPh + \overset{\delta-}{Ar}\leftarrow\overset{\delta+}{S}\rightarrow\overset{\delta-}{CN} \xrightleftharpoons{\text{rapid}} \left[\begin{array}{c} Me_2\overset{\oplus}{S}\text{-}CHCOPh \\ \vdots \\ [ArSCN]^{\ominus} \end{array}\right]$$

3　**6**

By the formation of the dipole-dipole interaction complex **6**, the negative charge on the ylide carbanion is withdrawn toward the catalytic sulfide, and the nucleophilic attack of a sulfide (or a pyridine) on the sulfonium atom is facilitated.[5] Therefore, monosulfides possessing strongly electronegative substituents can act as the catalysts for transylidation.

Experimental

Materials. Sulfonium bis(methoxycarbonyl)methylide **1a** and **1b** were prepared by the copper sulfate-catalyzed decomposition of dimethyl diazomalonate in a large excess of sulfides.[9] The dimethylsulfonium ylides **3**[10a] and **5**[10b] were prepared by the methods described in the literature. Methyl trichloromethanesulfenate was obtained by the drop-by-drop addition of a CCl_4 solution of trichloromethanesulfenyl chloride (10 mmol; prepared by the reaction of carbon disulfide and chlorine; bp 148 °C) to a CCl_4 solution of methanol (12 mmol) and pyridine (12 mmol) at 0 °C. Cl_3CSOMe, bp 25 °C/5 mmHg; NMR ($CDCl_3$), $\delta=4.19$ (s, OMe). *p*-Methoxyphenyl thiocyanate (mp 33—35 °C (lit,[11] 33—34 °C), IR (KBr), 2180 cm^{-1} (ν_{SCN}); NMR ($CDCl_3$), $\delta=3.82$ (3H, s, OMe) and 6.82—7.55 (4H, q, aromatic-H)), *p*-dimethylaminophenyl thiocyanate (mp 73—74 °C (lit,[12] 73—74 °C); IR (KBr), 2160 cm^{-1} (ν_{SCN}); NMR; ($CDCl_3$), $\delta=2.96$ (6H, s, NMe_2) and 6.55—7.44 (4H, q, aromatic-H)), and *o*-chlorophenyl thiocyanate (bp 98—100 °C/4 mmHg (lit,[13] 160 °C/42 mmHg); IR (neat), 2190 cm^{-1} (ν_{SCN}) were prepared by the methods described in the literature. *p*-Tolyl thiocyanate (bp 92—96 °C/1 mmHg (lit,[14] 117—118 °C/20 mmHg); IR (neat), 2160 cm^{-1} (ν_{SCN})) and *p*-chlorophenyl thiocyanate (bp 101—105 °C/1 mmHg) were prepared by the reaction of formamide and sulfenyl chloride ArSCl (Ar=*p*-Me-C_6H_4, *p*-Cl-C_6H_4) in the presence of $SOCl_2$.[14] Methyl arenesulfenates ArSOMe (Ar-Ph, bp 50 °C/2 mmHg (lit,[15a] 54 °C/10 mmHg); NMR ($CDCl_3$), $\delta=3.70$ (3H, s, OMe) and 7.30 (5H, s, Ph); Ar=*p*-Me-C_6H_4, bp 55 °C/3 mmHg; NMR ($CDCl_3$), $\delta=2.34$ (3H, s, *p*-Me), 3.65 (3H, s, OMe) and 7.28 (4H, s, aromatic-H); and Ar=*p*-Cl-C_6H_4, bp 76—77 °C/3 mmHg; NMR ($CDCl_3$), $\delta=3.70$ (3H, s, OMe) and 7.29 (4H, broad s, aromatic-H) were synthesized by the drop-by-drop addition of an ether solution of the corresponding arenesulfenyl chlorides[15b] to an ether solution of methanol and triethylamine at 0 °C under a nitrogen atmosphere. *p*-(Trifluoromethylthio)phenol (mp 57—58 °C lit,[16] 57—58 °C)) was prepared by the reaction of phenol (0.94 g) and trifluoromethanesulfenyl chloride[17] (in a CCl_4 solution) at 0 °C in the presence of pyridine (0.8 g). *S*-Phenyl thioacetate (bp 82—84 °C/7 mmHg) was obtained by the condensation of thiophenol and acetyl chloride.[18] Carbon disulfide was of reagent grade and was used without purification.

Transylidation. The NMR spectra were determined by means of a Hitachi NMR spectrometer R-20B (60 MHz). A $CDCl_3$ solution of ylide **1a** (0.5 M), dimethyl sulfide (1.5 M), and a catalyst (2.0 M) was placed in an NMR tube at 35 °C, and the intensity changes of the signals of the original ylide, **1a**, the new ylide, **1b**, and the new sulfide, PhSMe, were followed. After the original ylide, **1a**, had completely disappeared, hexane was added to the reaction mixture. The ylide crystals thus precipitated were filtered and recrystallized from methanol. The melting points, IR, and NMR spectra of the ylide obtained were identical with those reported in the literature.[9] The results are listed in Table 2.

Carbon-13 NMR Measurement. The ylide **3** and thiocyanate were dissolved in $CDCl_3$ (usually 100—150 mg/cm^3) containing 1—5% tetramethylsilane as a reference. Solutions were examined in 10-mm tubes using a JEOL-FX-60 NMR spectrometer in the Fourier transform mode. Several hundred transients were typically accummulated with an acquisition time of 3.0 s. The line positions were determined automatically by computer software. The results are shown in Table 4.

Reactions of Sulfur Ylide 3 with Aryl Thiocyanates in Chloroform. (a) A chloroform (7 ml) solution of ylide **3** (0.90 g, 5.0 mmol) was mixed with *p*-chlorophenyl thiocyanate (0.86 g, 5.0 mmol) at room temperature. After 90 h the NMR spectra of the reaction mixture showed the presence of dimethyl sulfide ($\delta=2.10$, s; 43%) and $\underline{Me}_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(p\text{-}Cl\text{-}C_6H_4S)COPh$ ($\delta=2.55$, s; 31%). The low-boiling fractions from the mixture were trapped in liquid nitrogen, and the presence of Me_2S was shown by NMR spectroscopy ($\delta=2.11$, s). When CCl_4 was added to the residue, the ylide crystals were precipitated; mp 148—149 °C. The CCl_4 solutions were concentrated *in vacuo*, and the residue was chromatographed by preparative thick-layer chromatography on silica gel, using a 2: 1 mixture of hexane–ether as an eluent; the yellowish crystals ($R_f=0.41$) thus obtained were found to be *p*-Cl-$C_6H_4SCH_2COPh$ (0.52 g, 0.20 mmol; 40%); mp 81—82 °C; IR (KBr), 1680 cm^{-1} (ν_{CO}); NMR ($CDCl_3$), $\delta=4.25$ (2H, s, S-CH_2-CO) and 7.26—8.0 (9H, m, aromatic-H). *p*-Chlorophenyl phenacyl sulfide was prepared independently by the reaction of phenacyl bromide and sodium *p*-chlorophenylmethanethiolate in methanol, and its physical data (mp, NMR and IR spectra) were identified with the above product. (b) Similarly, a chloroform (7 ml) solution of ylide **3** (0.90 g, 5.0 mmol) was mixed with *p*-tolyl thiocyanate (0.75 g, 5.0 mmol) at room temperature. After 6 days, the NMR spectra of the reaction mixture showed the presence of methyl sulfide ($\delta=2.10$, s; 45%) and $\underline{Me}_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(p\text{-}Me\text{-}C_6H_4S)COPh$ ($\delta=2.54$, s; 24%). When CCl_4 was added to the residue, the ylide crystals (mp 136—138 °C) were precipitated. The CCl_4 solutions were concentrated *in vacuo*, and the residue was chromatographed by preparative thick-layer chromatography on silica gel, using a 2: 1 mixture of hexane–ether as an eluent; the oil ($R_f=0.50$) thus obtained was found to be *p*-Me-C_6H_4S-CH_2COPh (0.48 g, 0.20 mmol; 40%); IR (neat), 1680 cm^{-1} (ν_{CO}); NMR ($CDCl_3$), $\delta=2.28$ (3H, s, *p*-Me), 4.20 (2H, s, S-CH_2-CO) and 7.17—8.0 (9H, m, aromatic-H). *p*-Tolyl phenacyl sulfide was prepared independently by the reaction of phenacyl bromide and *p*-tolyl mercaptane sodium salt on methanol, and its spectral data (IR and NMR) were identified with the above product. (c) A chloroform (5 ml) solution of ylide **3** (1.0 g, 6.6 mmol) was mixed with *o*-chlorophenyl thiocyanate (1.12 g, 6.6 mmol) at room temperature. After 70 h, the NMR spectra of the reaction mixture showed the presence of dimethyl sulfide (δ=2.06, s; 40%) and $\underline{Me_2}\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(o\text{-}Cl\text{-}C_6H_4\text{-}S)COPh$ (δ=2.52, s; 30%). The low-boiling fractions from the mixture were trapped in liquid nitrogen, and the presence of Me_2S was shown by NMR spectroscopy (δ=2.11, s). The high-boiling fractions were chromatographed by preparative thick-layer chromatography on silica gel, using a 2: 1 mixture of hexane–ether as an eluent; the white crystals (R_f=0.25) thus obtained were found to be $o\text{-}Cl\text{-}C_6H_4SCH_2COPh$ (0.69 g, 2.6 mmol; 40%); mp 91.5—92.5 °C; IR (KBr), 1680 cm^{-1} (ν_{CO}); NMR ($CDCl_3$), δ=4.30 (2H, s, $S\text{-}CH_2\text{-}CO$) and 7.0—8.0 (9H, m, aromatic-H). Found: C, 63.26; H, 4.44%. Calcd for $C_{14}H_{11}OClS$: C, 63.99; H, 4.22%.

*Reactions of Sulfur Ylides **3** and **5** with Methyl Arenesulfenates in Chloroform.* (a) A chloroform (5 ml) solution of ylide **3** (0.5 g, 2.8 mmol; $Me_2\overset{\oplus}{S}\text{-}$, δ=2.85, s) was mixed with PhSOMe (0.39 g, 2.8 mmol) at room temperature. The NMR spectra of the reaction mixture showed the presence of a new ylide, $Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(SPh)COPh$ (δ=2.54, s), and MeOH (δ=3.38, s). The removal of the solvent *in vacuo* at 25 °C gave white solids. Yield, 0.75 g (75%); recrystallized from benzene; mp 138—140 °C (lit,[19)] 136 °C); IR (KBr), 1520 cm^{-1} (ν_{CO}). (b) A chloroform (5 ml) solution of ylide **5** (1.0 g, 6.8 mmol; $Me_2\overset{\oplus}{S}\text{-}$, δ=2.74, s) was mixed with PhSOMe (0.95 g, 6.8 mmol) at room temperature. The NMR spectra of the reaction mixture showed the presence of a new ylide, $Me_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(SPh)CO_2Et$ (δ=2.53), and MeOH (δ=3.40, s). The removal of the solvent *in vacuo* at 25 °C gave white solids. Yield, 0.72 g (42%); mp 126—127 °C (lit,[19c)] 126—127 °C); IR (KBr), 1600 cm^{-1} (ν_{OC}). Similarly, various α-(arylthio)phenacylides (or α-(arylthio)ethoxycarbonylmethylides) were obtained by the reactions of ylides **3** (or **5**) with methyl *p*-toluenesulfenate and methyl *p*-chlorobenzenesulfenate. The results are listed in Table 3. The products were identified by means of their NMR and IR spectra.

*The Determination of the Rate of the Transylidation of Ylide **1a** with 4-Methylpyridine (or Dimethyl Sulfide).* A $CDCl_3$ solution of **1a** and a suitable amount of a catalyst and 4-methylpyridine (or dimethyl sulfide) were mixed in a NMR tube. After nitromethane (0.79 mmol; δ=4.33 ppm) had been added as the internal standard, more $CDCl_3$ was added with a microsyringe so that the total volume became 800 μl. The disappearance of **1a** was followed by observing the decrease in $Ph\underline{Me}\overset{\oplus}{S}\text{-}$ (δ=3.20 ppm).

This work was supported in part by a Grant-in-Aid for Scientific Research from Ministry of Education (No. 274160).

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