Electrophilic Sulfides(II) as a Novel Catalyst. V.[1a-d] Structure, Nucleophilicity, and Steric Compression of Stabilized Sulfur Ylides as Observed by ^{13}C-NMR Spectroscopy[2]

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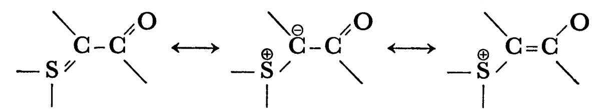
^{13}C chemical shifts and ^{13}C–H spin coupling constants (179.7 Hz) of the ylide carbons of two dialkylsulfonium phenacylides show that the ylide carbons are basically sp^2. Large upfield shifts (−9.5—−11.8 ppm) of carbonyl carbon signals (δ_C 181.7 and 179.2) of the ylides from those of the corresponding salts (δ_C 191.2 and 191.0) suggest significant contribution of a betaine structure. The ^{13}C-NMR spectrum of methylisopropylsulfonium phenacylide showed two non-equivalent methyl signals (δ_C 17.9 and 18.4) for the isopropyl group. Steric γ-effects on ylide carbon chemical shifts were observed with several alkylsulfonium bis(methoxycarbonyl)methylides and trialkylsulfonium salts.

The sulfonium ylides containing such electron-withdrawing substituents as carbonyl groups on their negatively charged carbon atoms are described by the canonical structure **a**—**c**.[3] The carbonyl stretching band of dimethylsulfonium phenacylide (**1a**) is observed at 1520 cm^{-1}, and this suggests that the contribution of **c** is important. In structure **c**, lone-pair electrons on the ylide carbon are considerably delocalized.[4] In fact, **1a** reacted as a zwitter ion and gave *O*-alkylation products.[5]



a   **b**   **c**

Recently, we studied the reactions of stable sulfonium ylides containing electron-withdrawing substituents on their ylide carbon atoms (COPh, COMe, COOMe, CN, *etc.*), and large differences were observed in the nucleophilic reactivity of ylide carbanions containing different electron-withdrawing substituents.

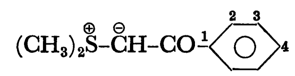
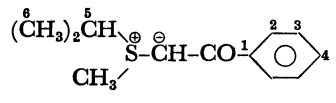
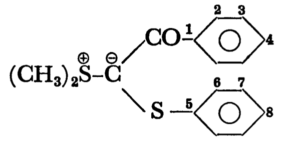
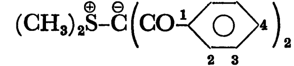
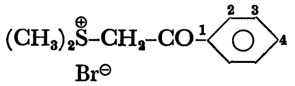
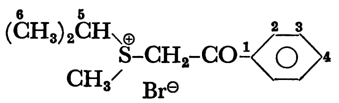
Carbon-13 chemical shifts provide some information on the electronic state of carbon atoms in molecules.[6] Some ^{13}C-NMR studies of phosphorus ylides have been reported,[7] but few ^{13}C-NMR studies have been reported on sulfonium ylides.

We measured the ^{13}C-NMR spectra of a series of sulfonium ylides containing electron-withdrawing substituents. The results are described in this paper and the nucleophilicity of these ylides is discussed.

Results and Discussion

sp^2-Carbanion and Betaine Structure. As is shown

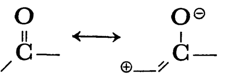
TABLE 1. CARBON-13 NMR CHEMICAL SHIFTS OF DIMETHYLSULFONIUM PHENACYLIDE (**1a**) AND RELATED COMPOUNDS[a)]

Compound	$\overset{\ominus}{C}H$ or CH_2	C=O	CH_3-$S^{\oplus}$	1	2 and 3	4	5	6, 7, and 8	Solvent
1a 	53.2 [J_{CH} 179.7]	182.3	28.7 [J_{CH} 142.6]	140.9	126.2; 127.8	129.3			$CDCl_3$
	56.6	180.1	28.4	140.9	125.8; 127.4	128.7			CD_3CN
	60.6	181.7	31.8	143.8	129.0; 130.5	131.8			DMSO-d_6
1b 	51.8 [J_{CH} 179.7]	182.3	24.2 [J_{CH} 142.6]	140.9	126.4; 127.8	129.2	46.1 [J_{CH} 144.5]	17.9; 18.4 [J_{CH} 128.9]	$CDCl_3$
	53.4 [J_{CH} 175.8]	179.2	23.9 [J_{CH} 140.7]	141.2	126.0; 127.4 [J_{CH} 160.2]	128.7	46.6	16.5; 17.7	DMSO-d_6
1c 	65.1	189.5	27.4	142.2	127.4; 127.7	128.8	140.5	124.2; 125.1	$CDCl_3$
1d 	88.2	190.9	26.9	141.9	127.4; 128.6	129.7			$CDCl_3$
1a′ 	52.6 [J_{CH} 146.5]	191.2	24.4 [J_{CH} 146.5]	134.8	128.4; 128.8 [J_{CH} 158.2]	133.8			DMSO-d_6
1b′ 	48.8 [J_{CH} 144.5]	191.0	19.7 [J_{CH} 146.5]	134.7	128.8 [J_{CH} 162.1]	133.9	45.2	17.1; 17.5 [J_{CH} 125]	DMSO-d_6
	b)	191.9	19.7 [J_{CH} 146.5]	135.8	129.0; 129.3 [J_{CH} 164.1]	133.5	46.2 [J_{CH} 146.5]	16.8; 17.5 [J_{CH} 123.1]	D_2O

a) δ_C, ppm from TMS(accurate to ±0.13 ppm); J_{CH}, Hz. b) Signal is not observable because of rapid H-D exchange in D_2O.

in Table 1, the ^{13}C–H coupling constant of the ylide carbon atom of dimethylsulfonium phenacylide (**1a**) as 179.7 Hz, and this shows that this carbon uses an sp^2 orbital in bonding with the hydrogen.[8] The coupling constant observed in **1a**′ (146.5 Hz) is that expected for sp^3-hybridized carbon bound to a sulfonium sulfur atom.[9] X-Ray studies of various ylides have shown that ylide carbons are basically trigonal planar and therefore sp^2 hybridized.[10]

Large upfield shifts (−9.5—−11.8 ppm) were observed when the carbonyl carbon signals (δ_C 181.7 and 179.2 in DMSO-d_6) of the ylides were compared with those of the corresponding salts (δ_C 191.2 and 191.0 in DMSO-d_6). This suggests an important contribution of betaine structure **c**, since similar upfield shifts were observed when ketones were compared with α,β-unsaturated ketones.[11]



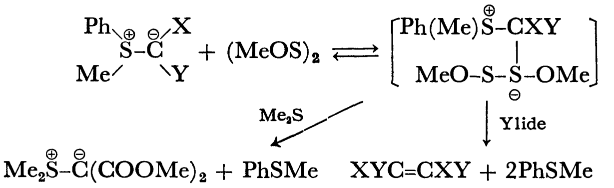
The chemical shifts of the ylide carbon of phenacylide (**1a**), which contains only one electron-withdrawing substituent, is dependent on kinds of solvent (δ_C 53.2 in $CDCl_3$ and 60.6 in DMSO-d_6). This suggests that the electrons are localized on its ylide carbon atom and that large nucleophilicity is expected.[12] The chemical shifts of ylides **1c** and **1d** containing two electron-withdrawing substituents (PhS and COPh) are found at fields lower than those of ylides **1a** and **1b**. Smaller nucleophilicity is expected for **1c** and **1d**.

Nucleophilicity of Disubstituted Sulfonium Ylides. Nucleophilicity of these disubstituted sulfonium ylides was compared by determining the rates of transylidation[1b,1d] and olefin formation[1c] in the presence of dimethoxy disulfide. The results are shown in Table 2. Clearly, the presence of acetyl groups decreases the reactivity toward both transylidation and olefin formation.

Carbon-13 chemical shifts of acetyl and methoxycarbonyl ylides are listed in Table 3. These chemical shifts are not solvent dependent. When Tables 2 and 3 are compared, it is clear that these order of reactivity of sulfonium ylides are parallel with the order of the chemical shifts of ylide carbon atoms.

Asymmetric Environment about Sulfur of Ylides. The tetrahedral nature of sulfur in disubstituted sulfonium ylides has been shown on the basis of ^1H-NMR spectra.[13] The appearance of the methylene group of the benzyl and ethyl substituents, respectively, as AB patterns in their ^1H-NMR spectra requires an asymmetric environment about sulfur.

TABLE 2. TRANSYLIDATION[1b,1d] AND OLEFIN FORMATION[1c] OF SULFONIUM YLIDES IN THE PRESENCE OF DIMETHOXY DISULFIDE IN $CDCl_3$ AT 35 °C



	Ylide		Transylidation[a)] half life, $\tau_{1/2}$ (min)	Olefin formation[b)] First-order rate constant calculated from $-d[Ylide]/dt=k[Ylide]$ $10^5\times k$ (s^{-1})
	X	Y		
2f	COOMe	COOMe	7	0.8
3b	COMe	COOMe	400	no reaction
4b	COMe	COMe	700[c)]	no reaction

a) Mixture consists of ylide (0.5 mmol), Me_2S (0.6—0.8 mmol), and $(MeOS)_2$ (0.2—0.3 mmol), except in the case of **4b**. b) Mixture consists of ylide (0.85 mol/l) and $(MeOS)_2$ (1.36 mol/l). c) Mixture consists of ylide **4b** (0.5 mmol), Me_2S (6.5 mmol), and $(MeOS)_2$ (0.3 mmol).

We examined the ^1H-NMR spectrum of methylisopropylsulfonium penacylide (**1b**), since asymmetric environment of isopropylsulfonium ylides has not been reported in the literature. Two methyl signals were observed at δ_H 1.32 (d, J=6.6 Hz) and 1.36 (d, J=6.6 Hz). The ^{13}C-NMR spectrum of **1b** also showed two methyl signals at δ_C 17.9 and 18.4, and that of **2d** showed two methyl signals at δ_C 18.4 and 18.8 for the isopropyl group.

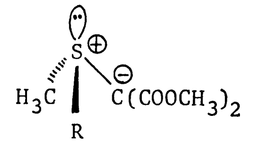
γ-Effect Observed in Sulfonium Compounds. In the system of sulfonium bis(methoxycarbonyl)methylides (**2a**—**2h**), effects of a bulky substituent on ^{13}C chemical shifts were investigated. The results are listed in Table 4. Clearly, the presence of a bulky substituent on the sulfur atom causes an upfield shift of the ylide carbon signal. This shift is not due to a simple inductive effect but due to steric compression through space (γ-effect).[14] It can be assumed that the inductive effect of the diethyl group of diethyl sulfonium ylide **2g** is similar to that of the pentamethylene group of pentamethylenesulfonium ylide **2h**. However, the chemical shift of the ylide carbon of **2g** was smaller than that of **2h** by −7.0

TABLE 3. CARBON-13 NMR CHEMICAL SHIFTS OF DISUBSTITUTED SULFONIUM YLIDES[a)]

	Compound	$C^{\ominus}$	C=O		CH_3–$S^{\oplus}$	OCH_3	CH_3	Solvent
			ester	keto				
2a	$(CH_3)_2\overset{\oplus}{S}-\overset{\ominus}{C}(COOCH_3)_2$	58.6	166.6		27.6	50.7		$CDCl_3$
		58.4	165.6		27.1	49.7		DMSO-d_6
3a	$(CH_3)_2\overset{\oplus}{S}-\overset{\ominus}{C}\begin{smallmatrix}COOCH_3\\ COCH_3\end{smallmatrix}$	73.5	166.4	191.8	26.6	50.2	29.8	$CDCl_3$
		73.4	166.0	189.9	26.0	49.9	29.7	DMSO-d_6
4a	$(CH_3)_2\overset{\oplus}{S}-\overset{\ominus}{C}(COCH_3)_2$[b)]	87.6		190.3	26.7		30.1	$CDCl_3$

a) δ_C, ppm from TMS (accurate to ±0.13). b) **4a** is insoluble in DMSO-d_6.

TABLE 4. ^{13}C CHEMICAL SHIFTS OF YLIDE CARBONS OF SOME SULFONIUM YLIDES[a)]



Compound	R	$C^{\ominus}$	$\Delta\delta$[b)]	$H_3C\text{-}S^{\oplus}$	$\Delta\delta$[b)]
2a	CH_3	58.6	0	27.7	0
2b	CH_3CH_2[c)]	55.7	−2.9	25.9	−1.7
2c	$CH_3CH_2CH_2CH_2$[d)]	56.2	−2.4	26.7	−1.0
2d	$(CH_3)_2CH$[e)]	53.5	−5.1	24.4	−3.3
2e	$C_6H_5CH_2$[f)]	57.4	−1.2	24.7	−3.0
2f	C_6H_5[g)]	59.1	+0.5	27.1	−0.5

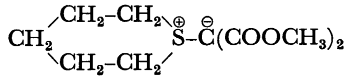
a) δ_C, ppm from TMS in $CDCl_3$ (accurate to ±0.13 ppm). b) $(\delta_C^R - \delta_C^{CH_3})$. c) CH_2 (α) 36.8, CH_3 (β) 9.53, C=O 167.1, and OCH_3 50.7. d) CH_2 (α) 42.6, CH_2 (β) 26.2, CH_2 (γ) 21.6, CH_3 (δ) 13.7, C=O 167.2, and OCH_3 51.0. e) CH (α) 46.0, CH_3 (β) 18.4 and 18.8, C=O 167.4, and OCH_3 50.9. f) CH_2 (α) 48.2, aromatic-C 129.3 and 130.3, C=O 167.1, and OCH_3 51.0. g) Aromatic-C 129.3, 130.5 and 132.3, C=O 166.4, and OCH_3 50.7.

ppm.

$$(CH_3CH_2)_2\overset{\oplus}{S}\text{-}\overset{\ominus}{C}(COOCH_3)_2$$

δ_C 52.0

2g



δ_C 59.0

2h

In the system of sulfonium phenacylides, **1a** and **1b**, a similar γ-effect was observed, which was shown in Table 1.

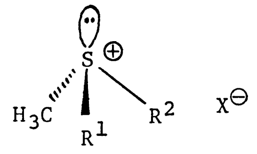
Table 5 shows the upfield shifts observed for some simple sulfonium salts possessing bulky substituents such as isopropyl and *t*-butyl groups. Such upfield shifts are found even in the sulfonium salts containing the electron-withdrawing phenacyl group (**1a′** and **1b′**), CH_2COPh.

As shown in Tables 4 and 5, large upfield shifts were observed for the ylide and methyl carbon signals when an isopropyl group was the substituent (**2d**, **5b**, **1b′**, and **5e**).

Experimental

Materials. The dimethylsulfonium ylides (**1a**,[4)] **1d**,[15)] **3a**,[16)] and **4a**[16)]) were prepared by the methods described in the literature. The phenylmethylsulfonium ylides (**2f**, **3b**, and **4b**) were synthesized by copper-catalyzed decomposition of diazo compounds in large excess sulfides.[17)] **1c** was obtained by reaction between **1a** and methyl benzenesulfenate in chloroform at room temperature (75% yield, mp 136—137 °C (lit,[18)] 136 °C)).[19)] Sulfonium bis(methoxycarbonyl)methylides (**2a**—**c**, **2g**, and **2h**) were prepared by catalytic decomposition of methyl diazomalonate in excess sulfide in the presence of dialkoxy disulfide at room temperature.[1a)] **2d** and **2e** were obtained by transylidation between **2f** and methyl isopropyl sulfide (or methyl benzyl sulfide) in chloroform in the presence of dimethoxy dusilfide at room temperature.[1b)] **2d**: mp 76—77 °C; IR (KBr), 1640 and 1700 cm^{-1} (ν_{CO}); ^1H-NMR ($CDCl_3$), δ=1.33 (d, J=7.2 Hz), 1.45 (d, J=7.2 Hz) (6H, $(CH_3)_2C$), 2.86 (3H, s, $CH_3\text{-}\overset{\oplus}{S}$), 3.78 (6H, s, $COOCH_3$) and 3.90—4.35 (1H, m, CH). Found: C, 49.43; H, 7.34%. Calcd for $C_9H_{16}O_4S$: C, 49.08; H, 7.32%. Methylisopropylsulfonium phenacylide (**1b**) was prepared by deprotonation of salt (**1b′**) with 10% aqueous sodium hydroxide. **1b**: mp 108—109 °C; IR (KBr), 1520 cm^{-1} (ν_{CO}); ^1H-NMR ($CDCl_3$), δ=1.32 (d, J=6.6 Hz), 1.36 (d, J=6.6 Hz) (6H, $(CH_3)_2C$), 2.85 (3H, s, $CH_3\text{-}\overset{\oplus}{S}$), 3.8—4.3 (2H, m, CH and $\overset{\ominus}{C}H$) and 7.25—7.86 (5H, m, C_6H_5); ^1H-NMR (DMSO-d_6), δ=1.25 (d, J=6.6 Hz), 1.30 (d, J=6.6 Hz) (6H, $(CH_3)_2C$), 2.71 (3H, s, $CH_3\text{-}\overset{\oplus}{S}$), 3.20—3.60 (1H, m, CH), 4.30 (1H, s, $\overset{\ominus}{C}H$) and 7.25—7.80 (5H, m, C_6H_5). Found: C, 68.90; H, 7.77%. Calcd for $C_{12}H_{16}OS$: C, 69.21; H, 7.74%. The sulfonium

TABLE 5. ^{13}C CHEMICAL SHIFTS OF METHYL CARBONS OF SOME SULFONIUM SALTS[a)]



Compound	R^1	R^2	$H_3C\text{-}S^{\oplus}$	$\Delta\delta$[b)]	C_α	C_β	X	Solvent
5a	CH_3	CH_3	27.7	0			I	D_2O
5b	CH_3	$(CH_3)_2CH$	22.0	−5.7	47.1	16.9	I	D_2O
5c	CH_3	$(CH_3)_3C$	24.4	−3.2	43.1	24.4	I	D_2O
5d	CH_3CH_2	CH_3CH_2	21.3	−6.4	35.6	8.4	I	D_2O
5e	$(CH_3)_2CH$	$(CH_3)_2CH$	15.6	−12.1	44.2	17.1; 18.9	I	D_2O
5f	CH_3CH_2	$(CH_3)_3C$	17.0	−10.6	32.1	9.5 (ethyl)	BF_4	D_2O
					43.5	24.8 (*t*-butyl)		
5a	CH_3	CH_3	26.1	0			I	DMSO-d_6
1a′	CH_3	$C_6H_5COCH_2$	24.4	−1.7	52.6 (phenacyl)		Br	DMSO-d_6
1b′	$(CH_3)_2CH$	$C_6H_5COCH_2$	19.7	−6.4	48.8 (phenacyl)		Br	DMSO-d_6
					45.2	17.1; 17.5 (isopropyl)		

a) δ_C, ppm from TMS as external standard in D_2O (accurate to ±0.08 ppm). b) $(\delta_C^{R^1,R^2} - \delta_C^{(CH_3)_2})$.

salts (**1a′** and **1b′**) were prepared by reaction between sulfides and phenacyl bromide in benzene at room temperature. **1b′**: mp 110—111 °C; IR (KBr), 1670 cm^{-1} (ν_{CO}); ^{1}H-NMR (DMSO-d_6), δ=1.55 (6H, d, J=6.6 Hz, $(CH_3)_2C$), 2.99 (3H, s, CH_3–$\overset{\oplus}{S}$), 4.09 (2H, s, CH_2) and 7.50—8.20 (5H, m, C_6H_5). The dialkylmethylsulfonium salts (**5a**—**e**) were obtained by direct reaction of the alkyl sulfides and methyl iodide. **5e**; ^{1}H-NMR (D_2O), δ=1.57 (d, J=6.6 Hz), 1.61 (d, J=6.6 Hz) (12H, $(CH_3)_2C$), 2.82 (3H, s, CH_3–$\overset{\oplus}{S}$) and 3.90 (2H, m, CH). **5f** was prepared by ethylation of methyl *t*-butyl sulfide with $(C_2H_5)_3O^{\oplus}\,BF_4^{\ominus}$).

Measurement. The ylides were dissolved in $CDCl_3$, CD_3CN and DMSO-d_6 (usually 100—150 mg/cm^3) containing 1—5% tetramethylsilane as reference. The sulfonium salts also were dissolved in D_2O (usually 100—150 mg/cm^3). Solutions were examined in 10-mm tubes using JEOL-FX-60 NMR spectrometer in the Fourier transform mode. Several hundred to several thousand transients were accumulated typically with acquisition times of 1.0 to 5 s, with 3.0 s being normal for coupling constant measurements. Line positions were determined automatically by computer software. The results are listed in Tables 1, 3, 4, and 5.

Transylidation and Olefin Formation. Transylidation and olefin formation of sulfonium ylides (**2f**, **3b**, and **4b**) in the presence of dimethoxy disulfide in $CDCl_3$ at 35 °C are described in the literature.[1b,c] The results are listed in Table 2.

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