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Pyrolysis of (2-Phenylethyl)phenylsulfonium Ylides

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In order to obtain information concerning the reaction mechanism of the pyrolysis of sulfonium ylides bearing a substituted phenyl group on the 2-position in the S-ethyl group of ethylphenylsulfonium ylide, (2-phenylethyl)phenylsulfonium bis(methoxycarbonyl)methylide (**1**) and dicyanomethylide (**2**) were subjected to pyrolysis in benzene. The reaction rates of **1** and **2** at 140°C were 6.0- and 3.2-times faster than those of ethylphenylsulfonium bis(methoxycarbonyl)methylide and dicyanomethylide, respectively. The activation parameters for **1** were $\Delta H^{\ddagger}=125\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger}=-3.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$, while those for **2** were $\Delta H^{\ddagger}=124\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger}=-2.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$. Substituent effects on the β-phenyl groups in **1** and **2** afforded positive Hammett ρ-values: $\rho=0.49$ ($\gamma=0.997$) and $\rho=0.26$ ($\gamma=0.993$), respectively.

From the obtained results, it was suggested that the pyrolysis proceeds through essentially a concerted intramolecular cis-elimination inclined toward a slightly carbanion-like type from an E1-like type by introducing a phenyl substituent at the 2-position of the ethyl group in the ethylphenylsulfonium ylide.

Though the E*i* reaction of sulfoxides[2—5] and sulfilimines[6,7] is generally regarded as being a concerted process, kinetic investigations using aryl alkyl sulfoxides and sulfilimines have revealed that electron-withdrawing substituents on the phenyl group accelerate the reaction, suggesting a polarization of the S–Cα bond and development of a partially negative charge on the sulfinyl group in the transition state. From these results, the development of a partially positive charge on the α-carbon atom has been assumed. However, in order to determine how the transition state deviates from the ideal concerted state, it is necessary to examine any substituent effect on the α- and β-position. Unlike in E2 reactions, the development of charge at the α- or β-carbon should be small, as discussed in a previous paper.[15] We have called the small deviated mechanisms the E1-like or carbanion-like type. Recently, we suggested that the transition state of the pyrolysis of 1-phenylethyl phenyl sulfoxide[15] deviates to E1-like, while that of 2-phenylethyl phenyl sulfoxide[10] is more carbanion-like, according to the results of the substituent effects on the 1-phenyl group and the 2-phenyl group, respectively.

Furthermore, from the results that acceleration by the 1-phenyl substituent on ethyl phenyl sulfoxides is larger than that by the 2-phenyl group, the E*i* reaction of alkyl aryl sulfoxides was suggested to essentially have a tendency to deviate to the E1-like type. Meanwhile, the transition state for the pyrolysis of sulfilimines is more the E1-like type[7] than that of the sulfoxides.[8,9] However, mechanistic investigations concerning the E*i* reaction of sulfonium ylides, which have an isoelectronic structure to sulfoxides and sulfilimines, have been very few.

In a previous paper,[1] the E*i* reaction of ethylphenylsulfonium bis(methoxycarbonyl)methylides suggested that the electronic structure of the transition state is an E1-like type, and that the reactivity of sulfonium ylides is similar to that of sulfoxides. However, in order to clarify the transition state for an E*i* reaction of sulfonium ylide, itself, it is necessary to further examine the details concerning the pyrolysis of (1- or 2-substituted ethyl)phenylsulfonium ylides.

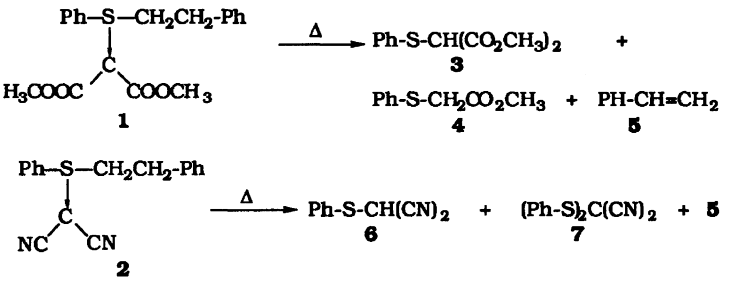
Thus, (2-phenylethyl)phenylsulfonium bis(methoxycarbonyl)methylides (**1**) and dicyanomethylides (**2**) were prepared and subjected to pyrolysis, and an investigation concerning the substituent effects on the phenyl groups was carried out in order to examine any change in the transition state to the carbanion-like type.

Results and Discussion

Reaction Products. Benzene solution of (2-phenylethyl)phenylsulfonium bis(methoxycarbonyl)methylide **1** and dicyanomethylide **2** were prepared in a sealed tube, and were immersed in an oil bath adjusted to the desired temperature in order to pyrolyzed. After removing the solvent, the formed products were isolated and identified as being dimethyl (phenylthio)malonate (**3**), methyl (phenylthio)acetate (**4**), and styrene (**5**) by comparing their ^{1}H NMR and IR spectra with those of authentic samples.

Product **4** is considered to be generated by the decarboxylation of **3**. Meanwhile, in the pyrolysis of **2**, (phenylthio)malononitrile (**6**) and bis(phenylthio)malononitrile (**7**) and **5** were found in the reaction mixture from the ^{1}H NMR and MS spectra. Owing to considerable instability, product **6** could not be isolated, while product **7** was isolated and the structure was confirmed by means of the ^{1}H NMR, MS, and IR spectra, as well as elemental analysis. Product **7** is considered to result from a disproportionation reaction of **6**. The formation of product **5** was confirmed in the pyrolysis of **2** in acetonitrile by means of an HPLC analysis and the ^{1}H NMR spectrum (Scheme 1).

Kinetics. The pyrolysis of **1** and **2** was carried out in benzene in sealed tubes. The reaction rates of both **1** and **2** were determined by measuring the decreasing in-



Scheme 1.

tensities of IR absorptions at 1630 cm^{-1} and 2170 cm^{-1} due to the sulfonium ylides, respectively. All of the reactions were found to follow good first-order kinetics; the kinetic data obtained for both **1** and **2** are summarized in Tables 1 and 2, respectively, together with the results of substituent effects. The reaction rates of **1** and **2** were 6.2- and 3.2-times faster than those of ethylphenylsulfonium bis(methoxycarbonyl)methylide (**8**)[1] and dicyanomethylide (**9**),[11] respectively, while in the case of 2-phenylethyl phenyl sulfoxide the rate-enhancing of the β-phenyl group was 8.6-times.[10]

Activation Parameters. Arrhenius plots for the pyrolysis of both **1** and **2** afforded good straight lines, (r=0.999) respectively. The activation parameters for the Ei reaction of sulfoxides are usually in the range of 106—125 kJ for activation enthalpies and $-71\sim+30$ $J\,K^{-1}\,mol^{-1}$ for activation entropies.[2,4,5,8,10,15] The activation entropy of the slowest type of such simple sulfoxides as the phenyl propyl is very negative (-63 $J\,K^{-1}\,mol^{-1}$),[8] suggesting that the transition state is more rigid than the starting state, due mainly to cyclization. As discussed in a previous paper,[15] the activation entropy reflects the looseness of the transition state, which is attributed to an extension of the C–S bond and the progress of a proton transfer, though the latter contribution is small because of a cancellation of the contribution of looseness of the C–H bond due to the development of O–H bond formation. We have revealed the relation between the activation entropies and the pyrolytic mechanism of sulfoxides. As depicted in Table 3, the pyrolysis of 1-methylcyclohexyl phenyl sulfoxide[20] and 1-phenylethyl phenyl sulfoxide[15] has large activation entropies relative to the simple sulfoxide, and proceed via an E1-like mechanism activated by α-substituents. Meanwhile, the pyrolyses of 1-(p-nitrophenyl)ethyl phenyl sulfoxide[15] and 1,1-dimethyl-1-methoxycarbonylethyl phenyl sulfoxide[9] also have large activation entropies, and proceed via a transition state involving the conjugation of the α-aryl group with the developing Cα–Cβ π-electrons activated by α-electron withdrawing substituents. However, the activation entropies for the pyrolysis of 2-phenylethyl phenyl sulfoxide[10] and 2-metoxycarbonylethyl phenyl sulfoxide[9] are not very large, i.e., in the middle of that for the α-phenylethyl one and simple sulfoxides. The electron-withdrawing groups at the β-position acidify the β-proton to activate the proton transfer reducing the requirement of stretching the C–S bond; thus, the reaction proceeds via a carbanion-like mechanism.

On the other hand, the pyrolysis of ethylphenylsulfonium ylides **8**, **9**, and the present (2-phenylethyl)phenylsulfonium ylides **1** and **2** has large activation

Table 1. Substituent Effects on the Pyrolysis of (2-Phenylethyl)phenylsulfonium Bis(methoxycarbonyl)methylides (**1**)

Substituent X	Substituent Y	Temp °C	$k\times10^4$ s^{-1}	Activation parameters (X=Y=H, 140°C)
p-OCH_3	H	140	6.90±0.10	
p-CH_3	H	140	8.01±0.05	
H	H	130	3.71±0.05	$\Delta H^\ddagger=120.5\pm4.7$
H	H	140	9.40±0.23	$kJ\,mol^{-1}$
H	H	150	23.1 ±0.1	$\Delta S^\ddagger=-3.8\pm2.1$
p-Cl	H	140	11.2 ±0.1	$J\,K^{-1}\,mol^{-1}$
m-Cl	H	140	13.6 ±0.2	
p-NO_2	H	140	19.9 ±0.2	
H	p-OCH_3	140	7.34±0.10	
H	p-CH_3	140	7.93±0.2	
H	p-Cl	140	12.8 ±0.2	
H	m-Cl	140	14.7 ±0.2	
H	p-NO_2	140	33.2 ±0.4	

The reaction rate constants were calculated by a least-squares method and errors are standard deviations.

Table 2. Substituent Effects on the Pyrolysis of (2-Phenylethyl)phenylsulfonium Dicyanomethylides (**2**)

Substituent X	Substituent Y	Temp °C	$k\times10^4$ s^{-1}	Activation parameters (X=Y=H, 140°C)
p-OCH_3	H	120	1.76 ±0.02	
p-CH_3	H	120	1.92 ±0.02	
p-Cl	H	120	2.55 ±0.03	
H	H	110	0.785±0.004	$\Delta H^\ddagger=123.5\pm0.5$
H	H	120	0.785±0.004	$kJ\,mol^{-1}$
H	H	130	5.69 ±0.03	$\Delta S^\ddagger=-2.5\pm0.8$
H	H	140	14.3 ±0.2	$J\,K^{-1}\,mol^{-1}$
m-Cl	H	120	3.01 ±0.02	
H	p-OCH_3	120	1.85 ±0.02	
H	p-CH_3	120	1.94 ±0.02	
H	p-Cl	120	2.55 ±0.04	
H	m-Cl	120	2.64 ±0.01	

Table 3. The Relative Rates and Kinetic Parameters of the Pyrolysis of Sulfoxides and Sulfonium Ylides

Substrate	Solvent	Temp °C	Rate constant $k\times10^5$ s^{-1} (X=Y=H)	Relative rate (X=Y=H)	$\Delta H^\ddagger$ kJ mol^{-1} (X=Y=H)	$\Delta S^\ddagger$ J K^{-1} mol^{-1} (X=Y=H)	ρ_X (Y=H)	ρ_Y (X=H)	Mechanism	Ref.
$PhS(O)CH_2CH_3$	Dioxane	100	0.165[a)]	1	105	−77	—		—	15
$XC_6H_4S(O)CH_2CH_2CH_3$	PhOPh	100	0.268[a)]	1.62	108	−63	0.51		E1-like	8
	Dioxane	100	18.6	113	118	−2	0.87		E1-like	20
threo- $XC_6H_4S(O)CH(CH_3)C_6H_4Y$	Dioxane	100	43.5	264	113	−6	0.64	−0.39 (*p*-OMe-*m*-OMe)	E1-like	15
								0.13 (*m*-OMe-*p*-NO_2)	Conjugated	15
$XC_6H_4S(O)C(CH_3)_2COOEt$	Dioxane	100	963[a)]	5840	106	1	0.69		Conjugated	9
$XC_6H_4S(O)CH_2CH_2C_6H_4Y$	Dioxane	100	1.41	8.55	106	−45	0.32	0.76	Carbanion-like	10
$XC_6H_4S(O)CH_2CH_2CN$	Dioxane	100	33.0	200	—	—	−0.49		Carbanion-like	10
$PhS(O)CH_2CH_2COOCH_3$	Dioxane	100	47.7	289	104	−30	—		Carbanion-like	9
$XC_6H_4SCH_2CH_3$ (**8**) ↓ $C(CO2Me)$	C_6H_6	140	15.6	1	135	−2	0.40		E1-like	1
$XC_6H_4SCH_2CH_2C_6H_4Y$ (**1**) ↓ $C(CO_2Me)$	C_6H_6	140	94.0	6.0	120±5	−4±2	0.49		Carbanion-like	
$XC_6H_4SCH_2CH_3$ (**9**) ↓ $C(CN)_2$	C_6H_6	140	44.9	1	129	1	0.42		E1-like	11
$XC_6H_4SCH_2CH_2C_6H_4Y$ (**2**) ↓ $C(CN)_2$	C_6H_6	140	143	3.2	124±1	−3±1	0.26		Carbanion-like	

a) The rate constants are calculated by Arrhenius equation from the data at other temperatures.

entropies, suggesting that the transition state of the sulfonium ylides is considerably loose. However, it is impossible to distinguish the deviation of the mechanism from the data of only the activation parameters.

Substituent Effects. The substituent effects for the pyrolysis of **1** and **2** were also studied in benzene. Hammett plots for the substituents on both the *S*-phenyl and β-phenyl groups of **1** and **2** are shown in Figs. 1 and 2, respectively. As is apparent from these results, log *k* nicely correlates with the σ-values, showing positive slopes for both the *S*-phenyl (X-side; ρ_X) and β-phenyl substituent (Y-side; ρ_Y) of **1** and **2**.

A plot for the derivatives having a *p*-NO_2 substituent on the β-phenyl group was found to deviate from the Hammett straight correlation, suggesting that the result is due to a strong electron-withdrawing action of the *p*-NO_2 group. However, since *p*-nitrostyrene and dimethyl (phenylthio)malonate were isolated and identified by the ^1H NMR and IR spectra as products for the pyrolysis of the *p*-NO_2 derivative, the reaction mechanism was regarded as being the same as that of the other substituents. Though the Hammett plot using σ^- values gives a straighter line than the present plot, the deviation for the *p*-nitro group should be attributed to the change of the transition state to a more carbanion-like type in view of the change of mechanism of the E*i* reaction of 1-(substituted phenyl)ethyl phenyl sulfoxides,[5)] which shows the V-shape Hammett plot. On the other hand, the pyrolysis of **2** also gave similar ρ_X and ρ_Y-values.

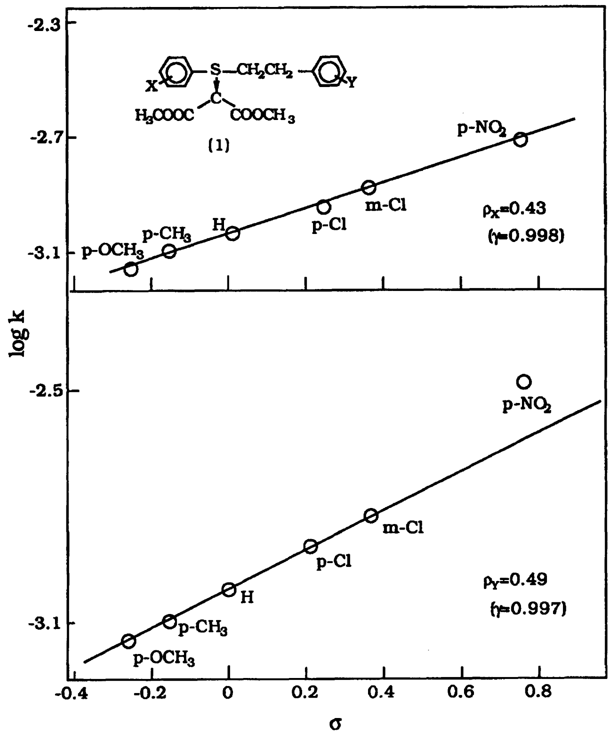


Fig. 1. Hammett relations for the pyrolysis of (2-phenylethyl)phenylsulfonium bis(methoxycarbonyl) methylides (**1**).

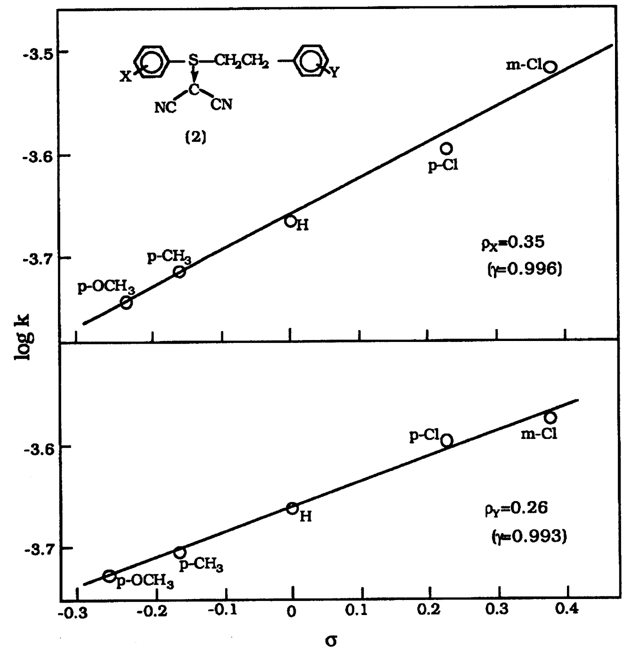
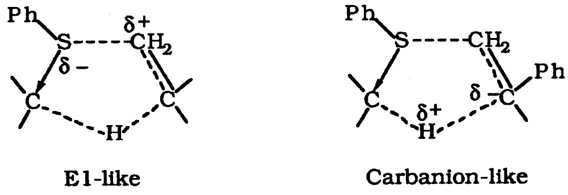


Fig. 2. Hammett relations for the pyrolysis of (2-phenylethyl)phenylsulfonium dicyanomethylides (**2**).

In the pyrolysis of *S*-ethyl-*S*-phenyl-*N*-tosylsulfilimines as a related substrate, it has been reported that a substitution of the phenyl group on the 1-position of the ethyl group accelerates the reaction by 10^3 times, while substitution on the 2-position promotes it by only 1.5-fold. This observation is thought to be due to a change in the transition state from a concerted cis-elimination (an ideal type) to an E1-like type;[7,13,14] the pyrolysis of sulfilimines essentially has a tendency that the mechanism deviates to the E1-like type. On the other hand, in the pyrolysis of (phenyl substituted)ethyl phenyl sulfoxides, it has been suggested that although 1-phenyl substitution on the ethyl group makes the transition state a nearly E1-like type,[15] the 2-phenyl group changes the transition state to a carbanion-like type.[10,15]

For the pyrolysis of **1** and **2**, the mechanism is considered to be essentially an ideal cis-elimination, because of the small difference between the ρ-values of both the X-side and the Y-side in the substrate and the small rate-enhancing effect of the β-phenyl group. The rather small rate-enhancing effect (6.0- and 3.2-times for **1** and **2**, respectively) of the β-phenyl group might not be sufficient to propose the nearly carbanion-like mechanism, since an E1cB reaction should show a large rate enhancement due to the β-phenyl group.

However, the substituent effects on the β-phenyl group showed a positive Hammett correlation, suggesting that the negative charge on the β-carbon atom is developing in the transition state, i.e., a carbanion-like mechanism (Scheme 2). The outstanding traits for the pyrolysis of **1** and **2** are that the ρ_X-value is relatively small, similar to that of the 2-phenylethyl phenyl sulfoxide;[10] further, the ρ_X values for both **1** and **2** are very similar to those for **8** and **9**. Meanwhile, for pyrolysis of the 2-phenylethyl phenyl sulfoxides,[10] the rate-enhancing effect of the β-phenyl group is 8.6-times compared to ethyl phenyl sulfoxide at 100°C, and the substituent effect on the *S*-phenyl group shows smaller ρ-values ($\rho=+0.32$) than that of phenyl propyl sulfoxide; instead, the effect on the β-phenyl group reveals a large positive one (+0.76). As compared with these observations, it is likely that the reactivity of sulfonium ylides is similar to that of sulfoxides, and that the tendency of the transition state for **1** and **2** lying to a carbanion-like type is smaller than that of the corresponding 2-phenylethyl phenyl sulfoxide.[10]



Scheme 2.

Unlike sulfoxides, the activation entropies for the pyrolysis of **1**,**2**,**8**,**9** are all large. The electron-withdrawing methoxycarbonyl and cyano groups on the carbanion carbon may contribute to the looseness of the C–S bond in the transition state. No difference in the activation entropies between **8**,**9** and **1**,**2** can be attributed to the slightness of the effect of the β-phenyl group on the E*i* reaction of the sulfonium ylides, in spite of the change of the transition state from E1-like to carbanion-like.

From a comparison between **1** and **2**, it was found that the rate-enhancing effect of the β-phenyl group for **1** is ca. 2-times larger than that of **2**, as a trend. Further, the substituent effects on the phenyl groups for **1** showed Hammett ρ-values of $\rho_X=0.43$ and $\rho_Y=0.49$, while the ρ-values for **2** were $\rho_X=0.35$ and $\rho_Y=0.26$. These results apparently show that the pyrolysis of sulfonium dicyanomethylides tends to proceed through a more E1-like transition state than that of bis(methoxycarbonyl)methylides, although the transition state is an almost ideal type cis-elimination.

As described above, the pyrolysis behavior of alkylarylsulfonium ylides is similar to that of ethyl phenyl sulfoxide, which change from an E1-like to a carbanion-like type cis-elimination by 2-phenyl substitution on the ethyl group of the substrate.[15] Summarizing the observations obtained in this work, the alkylarylsulfonium ylides proceed through essentially an E1-like type concerted five-membered cyclic transition state, while substitution of the phenyl group on the β-position in the alkyl group changes to an ideal type nearing a carbanion-like type; the effect is smaller than that seen in the pyrolysis of sulfoxide.

Experimental

General. All of the melting points are uncorrected.

The IR spectra were taken on a JASCO-810 spectrometer. The ^{1}H NMR spectra were recorded with a Hitachi R-24B spectrometer in $CDCl_3$ or CD_3CN using TMS as an internal standard. GC analyses were carried out using a Hitachi 163 gas-chromatograph with FID and a stainless DEGS column.

The peak areas were measured by a Yanaco SYSTEM-1100 integrator.

The MS spectra were taken with a JEOL-JMS-D 300 mass spectrometer.

All of the reactions were monitored by TLC (Wako Pure Chemical Industries Ltd., Wakogel B-5, or Merck, Kieselgel 60 GF), and the substrates and products were separated by column chromatography using Merck Kieselgel 60 silicagel or Merck Aluminumoxid 60 aktiv basisch. Elemental analyses were carried out at the Chemical Analysis Center of the Toyama Medical and Pharmaceutical University. The computations were performed on an NEC PC-9801-F computer. All of the reagents used were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., Ltd., or Aldrich Chemical Co. The reagents and solvents used were purified by general methods.

Product Analysis. A benzene solution of (2-phenylethyl)phenylsulfonium bis(methoxycarbonyl)methylide (**1**), (9.32×10^{-2} mol dm^{-3}) was prepared in a sealed tube, which was immersed in a silicone oil bath adjusted to 150°C. After 3 h, the solution was distilled under reduced pressure to remove the solvent. The residue was separated by silica-gel column chromatography using hexane, benzene, and chloroform as the eluents. From the ^{1}H NMR and IR spectral data, dimethyl (phenylthio)malonate, methyl (phenylthio)acetate, and the unreacted strating material were identified by comparing the spectra with those of authentic samples.

Dimethyl (Phenylthio)malonate: ^{1}H NMR ($CDCl_3$, TMS) δ=7.50—7.10 (m, 5H, $-C_6H_5$), 4.55 (s, IH, $-CH\langle$), 3.65 (s, 6H, $-(CO_2CH_3)_2$); IR (neat) 1741 cm^{-1} (C=O), bp 148—151°C/14 mmHg (1mmHg=133.322 Pa).

Methyl (Phenylthio)acetate: ^{1}H NMR ($CDCl_3$, TMS) δ=7.60—6.80 (m, 5H, $-C_6H_5$), 3.61 (s, 3H, $-CO_2CH_3$), 3.55 (s, 2H, $-CH_2-$); IR (neat) 1739 cm^{-1} (C=O).

The pyrolysis of [2-(*p*-nitrophenyl)ethyl]phenylsulfonium bis(methoxycarbonyl)methylide (5.1×10^{-4} mol) was also carried out in the same way. *p*-Nitrostyrene, one of the products, was isolated in 92% yield.

(2-Phenylethyl)phenylsulfonium dicyanomethylide (**2**), (7.2×10^{-4} mol) was thermally decomposed under similar pyrolysis conditions to those for **1**. Bis(phenylthio) malononitrile (**7**) was isolated from mixtures containing **7**, 2-(phenylthio)malononitrile (**6**), and an unreacted substrate. Product **6** was not isolated, since it is unstable, but was identified by measuring ^{1}H NMR and GCMS of the reaction mixture. Product **7** was then confirmed from the spectra of ^{1}H NMR, MS and IR, and elementary analysis.

Bis(phenylthio)malononitrile (7): ^{1}H NMR ($CDCl_3$, TMS) δ=7.5—8.0 (m, 10H, $-C_6H_5$); IR (KBr) 1685 cm^{-1}; Anal. Found: C, 63.90; H, 3.73; N, 9.67%. Calcd for $C_{15}H_{10}N_2S_2$: C, 63.80; H, 3.57; N. 9.92%. Mp 51.0—52.0°C; MS *m/z* 282.

(Phenylthio)malononitrile (6): ^{1}H NMR ($CDCl_3$, TMS) δ=4.62 (m, CH); MS *m/z* 174.

Preparation of (2-Phenylethyl)phenylsulfonium Ylides. (2-Phenylethyl) phenylsulfonium bis(methoxycarbonyl)methylides (**1**)[16,17] were prepared by treating 2-phenylethyl phenyl sulfide (5.0 g) with an equivalent amount of dimethyl diazomalonate[16] in the presence of copper powder (0.5 g) in benzene (20 ml) at 110°C. After the color of the reaction mixture changed from light yellow-green to brown, the solvent was evaporated. The residue was purified by silica-gel column chromatography using chloroform as an eluent, and the oily material was recrystallized from ether-methanol.

(2-Phenylethyl)phenylsulfonium dicyanomethylides (**2**)[19] were prepared by treating 2-phenylethyl phenyl sulfide (5.0 g) with an equivalent tetracyanoethylene oxide (TCNEO)[18] in ether-THF at a room temperature for 1 d, and the solvent was removed. The residue was separated by basic alumina-column chromatography using 1,2-dichloroethane and acetonitrile as eluents followed by silica-gel column chromatography with chloroform. The oily substance was recrystallized from ether-methanol to obtain the desired product. Similarly, the (2-arylethyl)phenyl- and aryl(2-phenylethyl)sulfonium ylides were prepared by using the corresponding sulfides, which were synthesized by treating substituted thiophenols with 2-arylethyl bromides followed by the usual work-up process.

(2-Phenylethyl)(substituted phenyl)sulfonium Bis(methoxycarbonyl)methylides (1). ***p*-OCH$_3$:** ^{1}H NMR ($CDCl_3$, TMS) δ=7.38 (q, 4H, $-C_6H_4-$), 7.32 (s, 5H, $-C_6H_5$), 4.90—2.80 (m, 4H, $-CH_2CH_2-$), 3.87 (s, 3H, $-OCH_3$), 3.75 (s, 6H, $-(CO_2CH_3)_2$); IR (KBr) 1670, 1655 (C=O), 1330 cm^{-1} (C–O). Anal. Found: C, 63.77; H, 5.78%, Calcd for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92%. Mp 88.5—90.5°C.

***p*-CH$_3$:** ^{1}H NMR ($CDCl_3$, TMS) δ=7.45 (q, 4H, $-C_6H_4-$), 7.35 (s, 5H, $-C_6H_5$), 4.90—2.70 (m, 4H, $-CH_2CH_2-$), 3.73 (s, 6H, $-(CO_2CH_3)_2$), 2.40 (s, 3H, $-CH_3$); IR (KBr) 1670, 1650 (C=O), 1330 cm^{-1} (C–O). Anal. Found: C, 66.59; H, 6.14%, Calcd for $C_{20}H_{22}O_4S$: C, 67.02; H, 6.19%. Mp 123.3—124.0°C; MS *m/z* 358.

H: ^{1}H NMR ($CDCl_3$, TMS, ppm) δ=7.70—6.90 (m, 10H, $-C_6H_5$, $-C_6H_5$). 4.65—2.80 (m, 4H, $-CH_2CH_2-$), 3.70 (s, 6H, $-(CO_2CH_3)_2$); IR (KBr) 1685, 1640 (C=O), 1320 cm^{-1} (C–O). Anal. Found: C, 66.45; H, 5.90%. Calcd for $C_{19}H_{20}O_4S$: C, 66.26; H, 5.8%; Mp 119.5—121.0°C; MS *m/z* 344.

***p*-Cl:** ^{1}H NMR ($CDCl_3$, TMS) δ=7.55 (d, 4H, $-C_6H_4-$), 7.33 (s, 5H, $-C_6H_5$), 4.80—2.70 (m, 4H, $-CH_2CH_2-$), 3.70 (s, 6H, $-(CO_2CH_3)_2$); IR (KBr) 1675, 1650 (C=O), 1330 cm^{-1} (C–O). Anal. Found: C, 60.08; H, 5.05%. Calcd for $C_{19}H_{19}ClO_4S$: C, 60.23; H, 5.05%. Mp 112.8—113.8°C; MS *m/z* 378.

***m*-Cl:** ^{1}H NMR ($CDCl_3$, TMS) δ=7.80—7.05 (m, 9H, $-C_6H_5$, $-C_6H_4-$), 4.85—2.85 (m, 4H, $-CH_2CH_2-$), 3.70 (s, 6H, $-(CO_2CH_3)_2$); IR (KBr) 1630 (C=O), 1320 cm^{-1} (C–O). Anal. Found: C, 60.28; H, 5.03%. Calcd for $C_{19}H_{19}ClO_4S$: C, 60.23; H, 5.05%. Mp 133.0—134.0°C.

***p*-NO$_2$:** ^{1}H NMR ($CDCl_3$, TMS) δ=8.05 (q, 4H, $-C_6H_4-$), 7.30 (s, 5H, $-C_6H_5$), 4.90—2.85 (m, 4H, $-CH_2CH_2-$), 3.72 (s, 6H, $-(CO_2CH_3)_2$); IR (KBr) 1690, 1620 (C=O), 1345 (NO_2) 1330 cm^{-1} (C–O). Anal. Found: N, 3.62; C, 58.62; H, 4.89%. Calcd for $C_{19}H_{19}NO_6S$: N, 3.60; C, 58.60; H, 4.92%. Mp 126.0—128.0°C; MS *m/z* 389.

[2-(Substituted phenyl)ethyl]phenylsulfonium Bis(methoxycarbonyl) methylides (1). ***p*-OCH$_3$:** ^{1}H NMR ($CDCl_3$, TMS) δ=7.85—7.30 (m, 5H, $-C_6H_5$), 7.30—6.70 (m, 4H, $\mathrm{-C_6H_4-}$), 4.75—2.80 (m, 4H, $\mathrm{-CH_2CH_2-}$), 3.80 (s, 3H, $\mathrm{-OCH_3}$), 3.70 (s, 6H, $\mathrm{-(CO_2CH_3)_2}$); IR (KBr) 1625 (C=O), 1315 cm^{-1} (C–O). Anal. Found: C, 64.32; H, 5.92%. Calcd for $\mathrm{C_{20}H_{22}O_5S}$: C, 64.15; H, 5.92%. Mp 91.8—92.8°C; MS m/z 374.

p-CH$_3$: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.90—7.35 (m, 5H, $\mathrm{-C_6H_5}$), 7.10 (s, 4H, $\mathrm{-C_6H_4-}$), 4.70—2.70 (m, 4H, $\mathrm{-CH_2CH_2-}$), 3.70 (s, 6H, $\mathrm{-(CO_2CH_3)_2}$), 2.37 (s, 3H, $\mathrm{-CH_3}$); IR (KBr) 1630 (C=O), 1320 cm^{-1} (C–O). Anal. Found: C, 66.68; H, 6.11%. Calcd for $\mathrm{C_{20}H_{22}O_4S}$: C, 67.02; H, 6.19%. Mp 108.5—110.5°C; MS m/z 358.

p-Cl: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.90—7.35 (m, 5H, $\mathrm{-C_6H_5}$), 7.25 (d, 4H, $\mathrm{-C_6H_4-}$), 4.85—2.80 (m, 4H, $\mathrm{-CH_2CH_2-}$), 3.72 (s, 6H, $\mathrm{-(CO_2CH_3)_2}$); IR (KBr) 1638 (C=O), 1320 cm^{-1} (C–O). Anal. Found: C, 60.25; H, 5.05%. Calcd for $\mathrm{C_{19}H_{19}ClO_4S}$: C, 60.23; H, 5.05%. Mp 116.0—117.0°C; MS m/z 378.

m-Cl: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.90—6.90 (m, 9H, $\mathrm{-C_6H_5}$, $\mathrm{-C_6H_4-}$), 5.00—2.80 (m, 4H, $\mathrm{-CH_2CH_2-}$), 3.70 (s, 6H, $\mathrm{-(CO_2CH_3)_2}$); IR (KBr) 1625 (C=O), 1320 cm^{-1} (C–O). Anal. Found: C, 60.32; H, 4.99%. Calcd for $\mathrm{C_{19}H_{19}ClO_4S}$: C, 60.23; H, 5.05%. Mp 130.0—132.0°C; MS m/z 378.

p-NO$_2$: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=8.95—7.20 (m, 9H, $\mathrm{-C_6H_5}$, $\mathrm{-C_6H_4-}$), 5.05—2.90 (m, 4H, $\mathrm{-CH_2CH_2-}$), 3.70 (s, 6H, $\mathrm{-(CO_2CH_3)_2}$); IR (KBr) 1625 (C=O), 1345 ($\mathrm{NO_2}$), 1320 cm^{-1} (C–O). Anal. Found: N, 3.59; C, 58.70; H, 4.81%. Calcd for $\mathrm{C_{19}H_{19}NO_6S}$: N, 3.60; C, 58.60; H, 4.92%. Mp 132.5—133.5°C.

(2-Phenylethyl)(substituted phenyl)sulfonium Dicyanomethylides (2). **p-OCH$_3$:** ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.70—6.80 (m, 9H, $\mathrm{-C_6H_5}$, $\mathrm{-C_6H_4-}$), 3.85 (s, 3H, $\mathrm{-OCH_3}$), 4.30—2.80 (m, 4H, $\mathrm{-CH_2CH_2-}$); IR (neat) 2190, 2170 cm^{-1} (C≡N).

p-CH$_3$: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=8.80—6.70 (m, 9H, $\mathrm{-C_6H_5}$, $\mathrm{-C_6H_4-}$), 4.10—3.00 (m, 4H, $\mathrm{-CH_2CH_2-}$), 2.60 (s, 3H, $\mathrm{-CH_3}$); IR (KBr) 2190, 2170 cm^{-1} (C≡N). Anal. Found: N, 9.79; C, 73.83; H, 5.48%. Calcd for $\mathrm{C_{18}H_{16}N_2S}$: N, 9.58; C, 73.98; H, 5.52%. Mp 130.0—131.5°C; MS m/z 292.

H: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.65 (s, 5H, $\mathrm{-C_6H_5}$), 7.35 (s, 5H, $\mathrm{-C_6H_5}$), 4.00—3.00 (m, 4H, $\mathrm{-CH_2CH_2-}$); IR (KBr) 2190, 2180 (C≡N). Anal. Found: N, 9.97; C, 73.46; H, 5.11%. Calcd for $\mathrm{C_{17}H_{14}N_2S}$: N, 10.06; C, 73.35; H, 5.07%. Mp 102.0—103.5°C; MS m/z 278.

p-Cl: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.60 (s, 4H, $\mathrm{-C_6H_4-}$), 7.30 (s, 5H, $\mathrm{-C_6H_5}$), 4.00—2.90 (m, 4H, $\mathrm{-CH_2CH_2-}$); IR (KBr) 2200, 2170 cm^{-1} (C≡N). Anal. Found: N, 8.89; C, 65.49; H, 4.18%, Calcd for $\mathrm{C_{17}H_{13}N_2SCl}$: N, 8.95; C, 65.27; H, 4.19%. Mp 92.0—93.8°C; MS m/z 312.

m-Cl: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=8.00—7.10 (m, 9H, $\mathrm{-C_6H_5}$, $\mathrm{-C_6H_4-}$), 4.00—3.00 (m, 4H, $\mathrm{-CH_2CH_2-}$); IR (KBr) 2200, 2170 cm^{-1} (C≡N). Anal. Found: 8.70; C, 64.95; H, 4.14%, Calcd for $\mathrm{C_{17}H_{13}N_2SCl}$: N, 8.95; C, 65.27; H, 4.19%. Mp 121.5—123.0°C.

[2-(Substituted phenyl)ethyl]phenylsulfonium Dicyanomethylides (2). **p-OCH$_3$:** ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.60 (s, 5H, $\mathrm{-C_6H_5}$), 7.30—6.70 (m, 4H, $\mathrm{-C_6H_4-}$), 3.90—2.90 (m, 4H, $\mathrm{-CH_2CH_2-}$), 3.20 (s, 3H, $\mathrm{-OCH_3}$); IR (KBr) 2190, 2175 cm^{-1} (C≡N). Anal. Found: N, 8.89; C, 70.36; H, 5.21%. Calcd for $\mathrm{C_{18}H_{16}N_2OS}$: N, 9.08; C, 70.10; H, 5.23%. Mp 90.5—92.0°C; MS m/z 308.

p-CH$_3$: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.60 (s, 5H, $\mathrm{-C_6H_5}$), 7.40—6.90 (m, 4H, $\mathrm{-C_6H_4-}$), 4.00—2.90 (m, 4H, $\mathrm{-CH_2CH_2-}$), 2.35 (s, 3H, $\mathrm{-CH_3}$); IR (KBr) 2195, 2190 cm^{-1} (C≡N). Anal. Found: N, 9.54; C, 74.26; H, 5.51%. Calcd for $\mathrm{C_{18}H_{16}N_2S}$: N, 9.58; C, 73.94; H, 5.52%. Mp 106.5—107.5°C; MS m/z 292.

p-Cl: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=7.70 (s, 5H, $\mathrm{-C_6H_5}$), 7.50—7.70 (m, 4H, $\mathrm{-C_6H_4-}$), 4.00—3.00 (m, 4H, $\mathrm{-CH_2CH_2-}$); IR (KBr) 2200 cm^{-1} (C≡N). Anal. Found: N, 8.80; C, 65.63; H, 4.09%. Calcd for $\mathrm{C_{17}H_{13}N_2SCl}$: N, 8.95; C, 65.27; H, 4.19%. Mp 96.0—97.0°C.

m-Cl: ^{1}H NMR ($\mathrm{CDCl_3}$, TMS) δ=8.00—6.80 (m, 9H, $\mathrm{-C_6H_5}$, $\mathrm{-C_6H_4-}$), 3.90—2.80 (m, 4H, $\mathrm{-CH_2CH_2-}$); IR (KBr) 2190, 2160 cm^{-1} (C≡N). Anal. Found: N, 8.96; C, 65.66; H, 4.17%. Calcd for $\mathrm{C_{17}H_{13}N_2SCl}$: N, 8.95; C, 65.27; H, 4.19%. Mp 85.5—86.0°C; MS m/z 312.

Kinetics. A precooled 10 ml solution of sulfonium ylides **1** or **2** (7.5×10^{-2} or 10^{-3} mol dm^{-3} respectively) in an anhydrous solvent was prepared and divided into a number of 1 ml sealed ampoules, which were immersed in a constant-temperature silicone oil bath (±0.05°C). At appropriate time intervals, the ampoules were taken out and frozen in an ice bath to stop the reaction. The reaction rate was then measured by following the decreasing absorbance at IR 1630 and 2170 cm^{-1} due to the carbonyl group of **1** and the cyano group of **2**, using with 0.1 mm- and 1.0 mm-thick liquid fixed cells, respectively. When other solvents than benzene were employed, the solvents were exchanged with benzene and the reaction rate was then measured. The rate constants were calculated by a least-squares method using the 6—8 points accumulated during the first 60% completion of the reaction. When the data were plotted as $\ln\,[(A_0-A_\infty)/(A_t-A_\infty)]$ vs. time (where A_0 is the initial absorbance of sulfonium ylide, A_t is the absorbance of the ylide at a particular time, and A_∞ is the absorbance of the ylide at infinite time), a good linear correlation was observed, suggesting that the kinetics are of first-order.

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