New Synthesis and Some Reactions of Vinyl Arenecarbodithioates. Wittig Reaction of (Triphenylphosphonio)methyl Arenecarbodithioate Iodides

Masaru ISHIDA, Koh-ichi KAGA, Hiroyuki SATO, Masato YOKOI, and Shinzi KATO*
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11
(Received November 29, 1985)

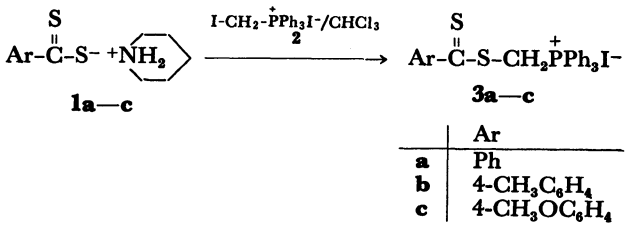
Wittig reaction of new phosphonium salts, (triphenylphosphonio)methyl arenecarbodithioate iodides, with variety of aldehydes gave the corresponding vinyl arenecarbodithioates in moderate to good yields. Reaction of the vinyl dithiocarboxylate with nucleophiles such as potassium alkoxide or alkanethiolate was investigated and found to give the thioacylated products in high yields. Ab initio molecular orbital calculations of the model compound, vinyl dithioformate, are also discussed.

During the investigation on dithiocarboxylic acid derivatives,[1] the dithiocarboxylic ester containing a double bond α to the sulfide sulfur has attracted our attention, because of the interest in the spectral and physical properties and the potential usefulness as synthetic intermediates. Recently, the following three methods have been reported for the synthesis of vinyl alkanedithioates, 1) base-catalysed rearrangement of allyl dithiocarboxylate;[2] 2) base-induced ring opening of 2-ylidene-1,3-dithiolanes;[3] and 3) addition reaction of dithiocarboxylic acid to acetylene derivatives.[4] However, for the synthesis of vinyl arenecarbodithioates **6**, no general method has been developed.

In our preliminary report,[5] we have described a convenient and general synthesis of the esters **6** via Wittig reaction of (triphenylphosphonio)methyl arenecarbodithioate iodides **3**[6,7] with various aldehydes. In the present paper, we report full details of our study on the preparation of vinyl arenecarbodithioates and their synthetic applications together with results of molecular orbital calculation of vinyl dithioformate, which provide the estimation of the reactivity and structure of **6**.

Results and Discussion

Synthesis of the Phosphonium Salts. The phosphonium salts **3** are easily prepared by addition of piperidinium arenecarbodithioates **1**[8] to a chloroform suspension of (iodomethyl)triphenylphosphonium iodide (**2**)[9] at room temperature (Table 1). The crude salts **3** dried in vacuo were pure enough to be subjected to the following reactions. The structures of **3** were confirmed on the basis of spectral data and elemental analyses. For example, the ^{1}H NMR spectrum of the phosphonium salt **3c** showed a doublet peak at δ 6.08 with a coupling constant of 8 Hz (J_{H-P}). The IR spectrum of **3c** showed an absorption at 1240 cm^{-1} due to thiocarbonyl stretching frequency. The UV spectrum exhibited an absorption band at 360 nm ($\log \varepsilon$=4.36) due to $\pi \rightarrow \pi^*$ transitions. At visible region, an absorption band was observed at 483 nm ($\log \varepsilon$=2.53) due to $n \rightarrow \pi^*$ transitions of thiocarbonyl moiety with the hypsochromic shift from that of methyl 4-methoxybenzenecarbodithioate.[10]



Scheme 1.

Table 1. Synthesis of (Triphenylphosphonio)methyl Arenecarbodithioate Iodide **3**

Product No.	Ar	Yield/%[a]
3a	Ph	53
3b	4-$CH_3C_6H_4$	77
3c	4-$CH_3OC_6H_4$	62

a) Isolated yield.

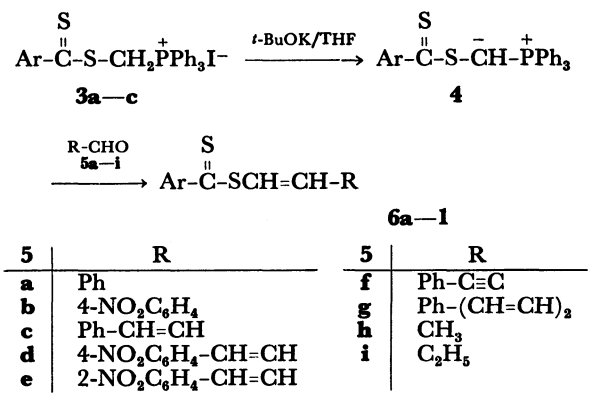
Synthesis of Vinyl Arenecarbodithioates. The Wittig reaction of the phosphonium salts **3** was carried out as follows. The salt **3** suspended in tetrahydrofuran (THF) was treated with an equimolar amount of potassium *t*-butoxide at −75 °C under argon atmosphere to give a deep purple solution of the ylide **4**.[11] Then, the aldehyde **5a**, **b**, **d**, or **e** was added to the solution and the mixture was gradually warmed to 0 °C (Method A). After workup, the corresponding vinyl arenecarbodithioates **6** were obtained in moderate to good yields. In the reaction with relatively inactive aldehydes **5c** and **f**—**i**, forcing conditions were required: The aldehyde **5** was added to the ylide solution at −30 °C and the reaction mixture was maintained at that temperature with stirring for 0.5—5 h (Method B). The cis/trans ratios of the products **6** seem to be dependent on the

Table 2. Synthesis of Vinyl Arenecarbodithioate **6**

Product No.	Ar	R	Yield/%[a]	Ratio[b] cis : trans
6a	Ph	4-$NO_2C_6H_4$	45 (A)	100 : 0
6b	4-$CH_3C_6H_4$	Ph	75 (A)	100 : 0
6c	4-$CH_3C_6H_4$	4-$NO_2C_6H_4$	89 (A)	100 : 0
6d	4-$CH_3OC_6H_4$	Ph	39 (A)	100 : 0
6e	4-$CH_3OC_6H_4$	4-$NO_2C_6H_4$	56[c] (A)	85 : 15
			69[c] (B)	50 : 50
6f	4-$CH_3OC_6H_4$	Ph-CH=CH	46[c] (B)	—
6g	4-$CH_3OC_6H_4$	4-$NO_2C_6H_4$-CH=CH	88[c] (A)	—
6h	4-$CH_3OC_6H_4$	2-$NO_2C_6H_4$-CH=CH	94[c] (A)	—
6i	4-$CH_3OC_6H_4$	Ph-C≡C	63[c] (B)	50 : 50
6j	4-$CH_3OC_6H_4$	Ph-$(CH=CH)_2$	55[c] (B)	—
6k	4-$CH_3OC_6H_4$	CH_3	65[c] (B)	40 : 60
6l	4-$CH_3OC_6H_4$	C_2H_5	28[c] (B)	50 : 50

a) Preparation methods are in parenceses; Method A; The reaction of the aldehyde and the ylide was carried out at −70°C, Method B; The reaction was carried out at −30 °C (See Experimental Section). b) Isomer ratios were determined on the basis of ^{1}H NMR. Those of the products **6f, g, h,** and **j** could not be determined, because of overlapping of olefin protons. c) Yield of a mixture of cis and trans isomers.

reaction conditions (Table 2). When the Wittig reaction of **3c** with 4-nitrobenzaldehyde was performed at −75 °C (Method A), **6e** was obtained as a 5:1 mixture of cis and trans isomers. While, under the conditions of method B, 1:1 mixture of *cis*-and *trans*-**6e** was obtained in 69% yield.

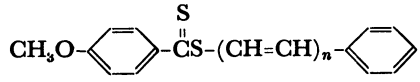


5	R	5	R
a	Ph	**f**	Ph-C≡C
b	4-$NO_2C_6H_4$	**g**	Ph-$(CH=CH)_2$
c	Ph-CH=CH	**h**	CH_3
d	4-$NO_2C_6H_4$-CH=CH	**i**	C_2H_5
e	2-$NO_2C_6H_4$-CH=CH		

Scheme 2.

Spectra of Vinyl Arenecarbodithioates. The typical spectra are exemplified by the vinyl dithiocarboxylate **6i**. The ^{1}H NMR spectrum of the crude **6i** showed two doublet peaks at δ 6.17 (J=10.0 Hz) and 6.29 (J=16.0 Hz) with an integration ratio of 1:1. The former resonance is due to the olefinic proton of *cis*-**6i** and the latter is due to that of *trans*-**6i**.[4] The geometrically pure samples were obtained from fractional recrystallization from methanol. The IR spectra of *cis*-and *trans*-**6i** showed C=S stretching absorptions at 1245 and 1240 cm^{-1}, respectively. The UV spectra of *cis*- and *trans*-**6i** showed absorption maxima due to $\pi\rightarrow\pi^*$ transitions of thiocarbonyl moieties at 362 (log ε=4.33) and 361 nm (log ε=4.41), respectively. In the visible spectra, the absorptions due to n→π^* transition were observed at 505 nm (*cis*-**6i**; log ε=2.41) and at 502 nm (*trans*-**6i**; log ε=2.51). It is noted that the wavelengths of the absorption maxima due to thiocarbonyl moieties of the vinyl dithiocarboxylates **6d, f,** and **j** (4-$CH_3OC_6H_4$-CS_2-$(CH=CH)_n$-Ph, n=1—3) are clearly dependent on the number of conjugated double bonds of enethiolate moieties (Table 3).

Table 3. The Absorption Bands of Electron Spectra with High Molar Absorptivities (log ε>4) of a Series of Vinyl Dithiocarboxylates **6d, f,** and **j**



Compound No.	n	Absorption [nm] (log ε)[a]		
6d	1			356(4.47)[b]
6f	2	296(4.44)	350(4.39)	400(4.31)[c]
6j	3		334(4.67)	418(4.43)[c]

a) CH_2Cl_2 as a solvent. b) n→π^* transition band of thiocarbonyl moiety of **6d** was observed at 503 nm (log ε=2.53). c) Other absorption maxima were not observed at visible region.

Reaction of Vinyl Dithiocarboxylates with Nucleophiles. Since the enethiolate moiety of the ester **6** can be considered as a good leaving group, the reaction of **6** with some nucleophiles such as potassium alkoxides and alkanethiolates was investigated.

A solution of **6e** in THF was added to a solution of equimolar amount of potassium methoxide in

methanol at 0 °C under nitrogen atmosphere. The resulting deep purple solution[12] was stirred for 2 h at that temperature and then quenched with phenacyl bromide to give *O*-methyl 4-methoxybenzenecarbothioate (**7a**) in 80% yield.[13] The counter part, potassium ethenethiolate **8**, was isolated as a vinyl sulfide **10a** in 84% yield. High yield formation of **10a** may suggest that the vinyl dithiocarboxylate **6** can be considered as a useful precursor of enethiolate **8**. In a similar manner, potassium phenolate was converted into *O*-phenyl 4-methoxybenzenecarbothioate (**7d**) in 77% yield.

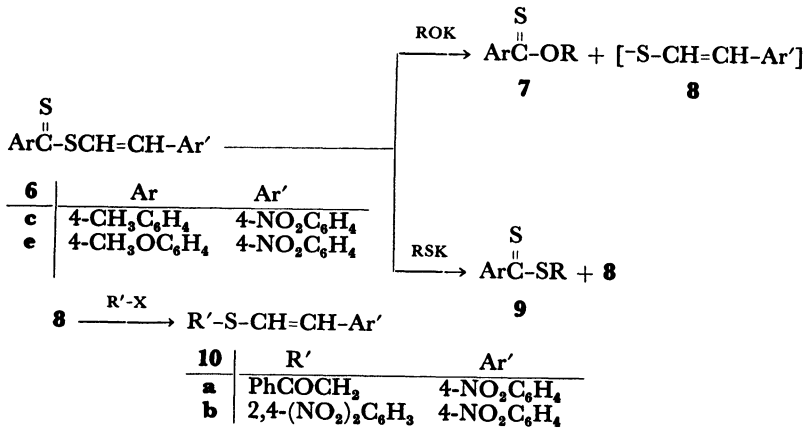
It is noteworthy that the reaction of **6e** with potassium 2-methyl-2-propanethiolate also gave *t*-butyl 4-methoxy-benzenecarbodithioate (**9c**) in 51% yield, which can not be prepared by esterification of piperidinium or alkali metal dithiocarboxylate with *t*-butyl bromide (Table 4).

The structural confirmation of the products **7**, **9**, and **10** were performed on the basis of the comparison of their spectra and physical properties with those of the authentic samples.[13–18]

Molecular Orbital Calculation. In order to estimate the reactivity and the structure of the vinyl dithiocarboxylates **6**, molecular orbital calculations were performed on the model compound, vinyl dithioformate (**11**). Two sets of the conformers, **11-I** and **11-II**, were optimized by the ab initio MO calculation with the minimal (STO-3G) basis set. The calculation of the total energy showed that the conformer **II** is more stable than the conformer **I** with the energy difference of 0.154 eV (14.9 kJ mol^{-1}) (Fig. 1).

The frontier orbitals of the conformers are illustrated in Fig. 2. The HOMO of the conformer I is a nonbonding orbital of thiocarbonyl sulfur. Whereas HOMO of the conformer **II** is a π-allyl type orbital at carbodithioate moiety. Thus, the [3+2] cycloaddition reactions[19] with dienophiles at dithiocarboxy moiety may be expected. The LUMO is π^* orbital of thiocarbonyl moiety and the coefficient is largest at thiocarbonyl carbons in both of the conformers. These calculation are well-compatible with experimental results.

In summary, the first general synthesis of vinyl arenecarbodithioate **6** via Wittig reaction of (triphenylphosphonio)methyl arenecarbodithioate iodide **3** have been developed. Some reactions of the vinyl

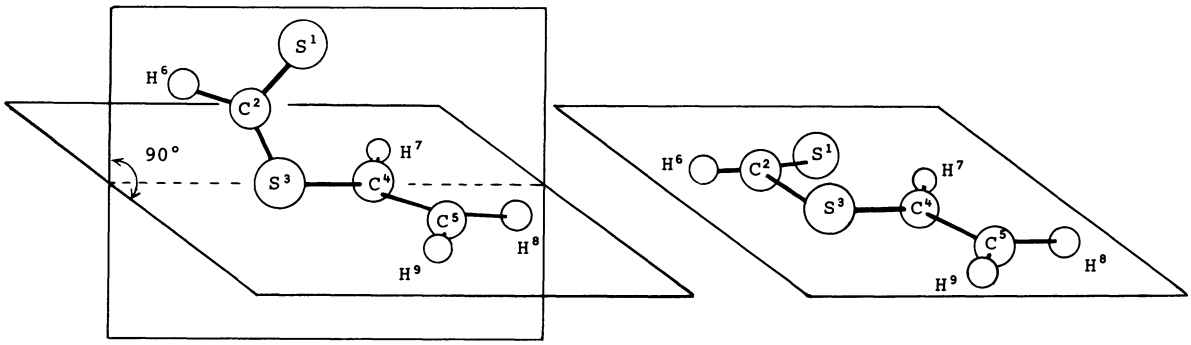


Scheme 3.

Table 4. Synthesis of *o*-Alkyl Thiobenzoates **7** and Dithiobenzoates **9** via the Reaction of Vinyl Arenecarbodithioate **6** with Alkoxides or Alkanethiolates

Product No.	Reagent No.	Ar	Nucleophile	Yield[a] %	[Byproduct[b] (Yield/%)]
7a	**6e**	4-$CH_3OC_6H_4$	CH_3-O$^-$K$^+$	80	[**10a** (84)]
7b	**6c**	4-$CH_3C_6H_4$	CH_3-O$^-$K$^+$	82	[**10b** (43)]
7c	**6e**	4-$CH_3OC_6H_4$	C_2H_5-O$^-$K$^+$	57	[**10a** (15)]
7d	**6e**	4-$CH_3OC_6H_4$	Ph-O$^-$K$^+$	77	[**10b** (43)]
9a	**6e**	4-$CH_3OC_6H_4$	C_2H_5-S$^-$K$^+$	81	[**10a** (75)]
9b	**6c**	4-$CH_3C_6H_4$	C_2H_5-S$^-$K$^+$	67	[**10b** (56)]
9c	**6e**	4-$CH_3OC_6H_4$	*t*-C_4H_9-S$^-$K$^+$	51	[**10a** (70)]
9d	**6e**	4-$CH_3OC_6H_4$	Ph-S$^-$K$^+$	46	[**10a** (82)]

a) Yield of isolated product. b) **10a**: Phenacyl 2-(4-nitrophenyl)vinyl sulfide, **10b**: 2,4-Dinitrophenyl 2-(4-nitrophenyl)vinyl sulfide.



11-I

Total energy = −24492.86 eV

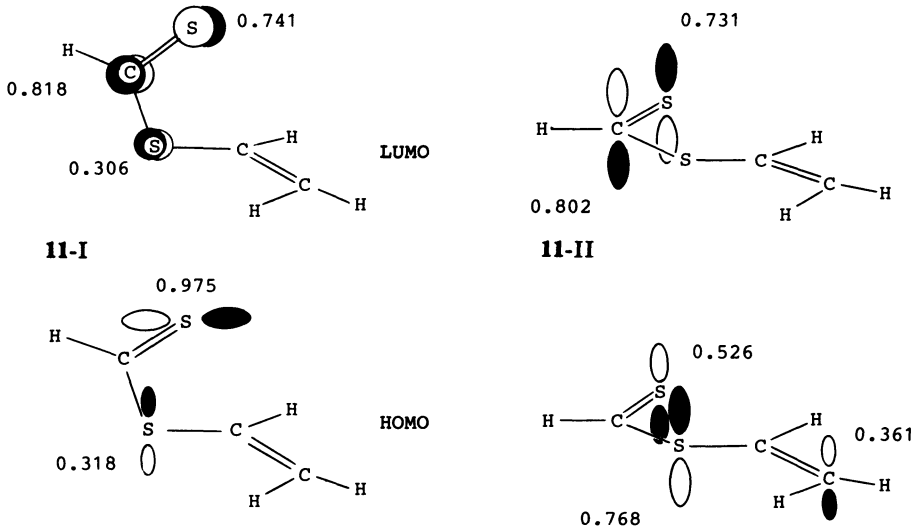
Bond length	[l/Å]	Bond angle	[ϕ/°]
S^1-C^2	1.582	S^1-C^2-S^3	130.0
C^2-S^3	1.760	S^1-C^2-H^6	122.2
C^2-H^6	1.102	S^3-C^2-H^6	107.7
S^3-C^4	1.779	C^2-S^3-C^4	101.6
C^4-C^5	1.309	S^3-C^4-C^5	123.1
C^4-H^7	1.086	S^3-C^4-H^7	116.6
C^5-H^8	1.083	C^5-C^4-H^7	120.4
C^5-H^9	1.083	C^4-C^5-H^8	122.2
		C^4-C^5-H^9	122.1
		H^8-C^5-H^9	115.7

11-II

Total energy = −24493.02 eV

Bond length	[l/Å]	Bond angle	[ϕ/°]
S^1-C^2	1.582	S^1-C^2-S^3	130.7
C^2-S^3	1.760	S^1-C^2-H^6	121.7
C^2-H^6	1.092	S^3-C^2-H^6	107.6
S^3-C^4	1.764	C^2-S^3-C^4	102.5
C^4-C^5	1.310	S^3-C^4-C^5	123.7
C^4-H^7	1.084	S^3-C^4-H^7	115.1
C^5-H^8	1.081	C^5-C^4-H^7	121.2
C^5-H^9	1.082	C^4-C^5-H^8	121.1
		C^4-C^5-H^9	123.0
		H^8-C^5-H^9	115.9

Fig. 1.



Frontier Orbitals and Frontier Orbital Coefficients[a] of Vinyl Dithioformate **11**-I and II
a) Coefficients of 3p-atomic orbitals of sulfurs and 2p-atomic orbitals of carbons.

Fig. 2.

dithiocarboxylate **6** proved to be useful as thioacylating reagent of alkoxides and alkanethiolate and as a precursor of ethenethiolate anion.

Experimental

Melting points were determined using a Yanagimoto melting point apparatus and are uncorrected. The IR spectra were measured on a JASCO grating IR spectrometer IR-G. The UV and Vis spectra were measured on a Hitachi 124 spectrophotometer. The ^{1}H NMR spectra were recorded on Hitachi R-24 (60 MHz), Hitachi R-22 (90 MHz), and JEOL-JNM-GX 270 (270 MHz) with tetramethylsilane as an internal standard. Mass spectra were recorded on Hitachi RMU-6M mass spectrometer at an ionizing voltage of 20 eV. Elemental analyses were performed by Elemental Analysis Center of Osaka Univer-

sity.

Preperation of [4-Methoxy(thiobenzoyl)thiomethyl]triphenylphosphonium Iodide (3c): Typical Procedure: To a solution of (iodomethyl)triphenylphosphonium iodide (**2**, 2.65 g, 5 mmol) in methanol/dichloromethane (1:3, 450 mL), piperidinium 4-methoxybenzenecarbodithioate (**1c** 1.34 g, 5 mmol) was added at room temperature. The mixture was stirred for an hour. After removal of the solvent in vacuo, the residue was poured into dichloromethane (100 mL), washed with water (3×50 mL), and dried over anhydrous sodium sulfate. Addition of ethyl acetate (50 mL) to the extracts followed by condensation in vacuo to ca. 50 mL gave the salt **3c** as orange precipitates (1.815 g, 62%). Recrystallization from dichloromethane/ethyl acetate (2:1) gave analytically pure **3c**: Mp 202—205 °C; IR (KBr) 1250 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 360 nm (log ε=4.36), 483 nm (log ε=2.53); ^1H NMR ($CDCl_3$) δ=3.76 (3H, s, CH_3), 6.08 (2H, d, J=8 Hz, CH_2), 6.7 (2H, d, aromatic), 7.40—8.15 (17H, m, aromatic). Found: C, 55.43; H, 4.08%. Calcd for $C_{27}H_{24}OS_2PI$: C, 55.29; H, 4.12%.

[(Thiobenzoyl)thiomethyl]triphenylphosphonium Iodide (3a): Similarly to the synthesis of **3c**, from the salt **2** (2.65 g, 5.0 mmol) and piperidinium benzenecarbodithioate (**1a**, 1.19 g, 5.0 mmol) was obtained 1.46 g (53%) of the salt **3a**. Pure **3a** was recrystallized from dichloromethane/ethyl acetate (1:1): Mp 174—178 °C; IR (KBr) 1230 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 308 nm (log ε=4.37), 483 nm (log ε=2.34); ^1H NMR ($CDCl_3$*) δ=5.90 (2H, d, J=9 Hz, CH_2), 7.20—8.20 (20H, m, aromatic). Found: C, 56.09; H, 4.03%. Calcd for $C_{26}H_{22}S_2PI$: C, 56.13; H, 3.99%. *Containing 5% of DMSO-d_6.

[4-Methyl(thiobenzoyl)thiomethyl]triphenylphosphonium Iodide (3b): Similarly to the synthesis of **3c** from the salt **2** (2.65 g, 5.0 mmol) and piperidinium 4-methylbenzenecarbodithioate (**1b**, 1.27 g, 5.0 mmol) was obtaind 2.20 g (77%) of the salt **3b**. Pure **3b** was recrystallized from dichloromethane/ethyl acetate (1:1): Mp 179—182 °C; IR (KBr) 1240 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 321 nm (log ε=4.38), 487 nm (log ε=2.44); ^1H NMR ($CDCl_3$*) δ=2.42 (3H, s, CH_3), 5.85 (2H, d, J=9 Hz, CH_2); 7.20—8.15 (19H, m, aromatic). Found: C, 56.89; H, 4.19%. Calcd for $C_{27}H_{24}S_2PI$: C, 56.85; H, 4.24%. *Containing 5% of DMSO-d_6.

2-Phenylvinyl 4-Methoxybenzenecarbonditioate (6d): Typical Procedures (Method A): To the salt **3c** (0.587 g, 1.0 mmol) suspended in dry THF (30 mL) was added potassium t-butoxide (0.112 g, 1.0 mmol) under argon atmosphere at −75 °C. The mixture was stirred for 30 min. Then benzaldehyde (**5a**, 0.11 g, 1.0 mmol) was added and the mixture was gradually warmed to 0 °C within 3 h. The mixture was poured into water (50 mL), extracted with ether (3×50 mL), and the extract was dried over anhydrous sodium sulfate. After removal of the solvent, the residue was chromatographed on silica gel (benzene/hexane=1:10 as eluant) to give a red oil. After addition of ethanol, the oil was cooled at −20 °C to give 0.112 g (39%) of red crystalls of **6d**: Mp 49—50 °C; IR (KBr) 1245 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 356 nm (log ε=4.47), 503 nm (log ε=2.53); ^1H NMR ($CDCl_3$) δ=3.85 (3H, s, CH_3), 6.90 (1H, d, J=11 Hz, vinyl), 6.75—8.20 (10H, m, aromatic and vinyl); MS m/z, 286 (M^+). Found: C, 66.98; H, 4.98; S, 22.41%. Calcd for $C_{16}H_{14}OS_2$: C, 67.00; H, 4.93; S, 22.36%.

2-(4-Nitrophenyl)vinyl Benzenecarbodithioate (6a): Similarly to the synthesis of **6d**, from the salt **3a** (0.556 g, 1.0 mmol) and 4-nitrobenzaldehyde (**5b**, 0.15 g, 1.0 mmol) was obtained 0.14 g (45%) of **6a** as red crystals. Recrystallization from ethanol gave pure **6a**: Mp 135—138 °C; IR (KBr) 1225 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 328 nm (log ε=4.42), 512 nm (log ε=2.38); ^1H NMR ($CDCl_3$) δ=7.0 (1H, d, J=12 Hz, vinyl), 7.3—8.4 (10H, m, aromatic and vinyl); MS m/z, 301 (M^+). Found: C, 59.43; H, 3.75; N, 4.53%. Calcd for $C_{15}H_{11}NO_2S_2$: C, 59.78; H, 3.68; N, 4.65%.

2-Phenylvinyl 4-Methylbenzenecarbodithioate (6b): Similarly to the synthesis of **6d**, from the salt **3b** (0.571 g, 1.0 mmol) and benzaldehyde (**5a**, 0.11 g, 1.0 mmol) was obtained 0.20 g (75%) of **6b** as red crystals: Mp 50—51 °C; IR (KBr) 1245 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 328 nm (log ε=4.32), 503 nm (log ε=2.40); ^1H NMR ($CDCl_3$) δ=2.35 (3H, s, CH_3), 6.95 (1H, d, J=11.3 Hz, vinyl), 7.10—8.20 (10H, m, aromatic and vinyl); MS m/z, 270 (M^+). Found: C, 70.82; H, 5.23; S, 23.51%. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22; S, 23.68%.

2-(4-Nitrophenyl)vinyl 4-Methylbenzenecarbodithioate (6c): Similarly to the synthesis of **6d**, from the salt **3b** (0.571 g, 1.0 mmol) and 4-nitrobenzaldehyde (**5b**, 0.15 g, 1.0 mmol) was obtained 0.28 g (89%) of **6c**. Recrystallization from ethanol gave pure **6c**: Mp 122—128 °C; IR (KBr) 1255 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 332 nm (log ε=4.43), 507 nm (log ε=2.34); ^1H NMR ($CDCl_3$) δ=2.35 (3H, s, CH_3), 6.92 (1H, d, J=11.3 Hz, vinyl), 7.05—8.40 (9H, m, aromatic and vinyl); MS m/z, 315 (M^+). Found: C, 61.12; H, 4.15%. Calcd for $C_{16}H_{13}NO_3S_2$: C, 60.93; H, 4.15%.

2-(4-Nitrophenyl)vinyl 4-Methoxybenzenecarbodithioate (6e): Similarly to the synthesis of **6d**, from the salt **3c** (0.586 g, 1.0 mmol) and 4-nitrobenzaldehyde (**5b**, 0.151 g, 1.0 mmol) was obtained 0.186 g (56%) of **6e**. Recrystallization from methanol gave pure **6e** as orange needles (cis/trans=5:1): Mp 166—168 °C; IR (KBr) 1225 (C=S) cm^{-1}. UV and Vis (CH_2Cl_2) 367 nm (log ε=4.58), 504 nm (log ε=2.57); ^1H NMR ($CDCl_3$) δ=3.89 (3H, s, CH_3), 6.98 (0.8H, d, J=11.0 Hz, vinyl), 7.06 (0.2H, d, J=16.5 Hz, vinyl), 6.80—7.20 (2H, m, aromatic), 7.77 (0.8H, d, J=11.0 Hz, vinyl), 8.03 (0.2H, d, J=16.5 Hz, vinyl), 7.20—8.40 (6H, m, aromatic); MS m/z, 331 (M^+). Found: C, 57.95; H, 4.00; N, 4.21; S, 19.19%. Calcd for $C_{16}H_{13}NO_3S_2$: C, 57.99; H, 3.95; N, 4.23; S, 19.32%.

4-(4-Nitrophenyl)-1,3-butadienyl 4-Methoxybenzenecarbodithioate (6g): Similarly to the synthesis of **6d**, from the salt **3c** (0.586 g, 1.0 mmol) and 4-nitrocinnamaldehyde (**5d**, 0.177 g, 1.0 mmol) was obtained 0.32 g (88%) of the dithiocarboxylate **6g**. Recrystallization from dichloromethane/ethanol (2:1), gave pure **6g** as red crystals: Mp 192—194 °C; IR (KBr) 1245 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 365 nm (log ε=4.55), 513 nm (log ε=2.96); ^1H NMR ($CDCl_3$) δ=3.90 (3H, s, CH_3), 6.65—8.20 (12H, m, aromatic and olefinic); MS m/z, 357 (M^+). Found: C, 60.24; H, 4.32; N, 3.67; S, 17.73%. Calcd for $C_{18}H_{15}NO_3S_2$: C, 60.48; H, 4.23; N, 3.92; S, 17.94%.

4-(2-Nitrophenyl)-1,3-butadienyl 4-Methoxybenzenecarbodithioate (6h): Similarly to the synthesis of **6d**, from the salt **3c** (0.586 g, 1.0 mmol) and 2-nitrocinnamaldehyde (**5e**, 0.177 g, 1.0 mmol) was obtained 0.33 g (94%) of the sulfide **6h** as red crystals. Recrystallization from dichoromethane/ethanol gave pure **6h**: Mp 96—100 °C; IR (KBr) 1250

(C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 361 nm (log ε=4.52), 491 nm (log ε=2.72); ^1H NMR ($CDCl_3$) δ=3.85 (3H, s, CH_3), 6.5—8.3 (12H, m, aromatic and olefinic); MS *m/z*, 357 (M^+). Found: C, 60.35; H, 4.22; N, 3.98; S, 17.65%. Calcd for $C_{18}H_{15}NO_3S_2$: C, 60.48; H, 4.23; N, 3.92; S, 17.94%.

2-(4-Nitrophenyl)vinyl 4-Methoxybenzenecarbodithioate (6e): Typical Procedure (Method B): To the salt **3c** (0.587 mg, 1 mmol) suspended in 40 mL of dry THF was added potassium *t*-butoxide (0.112 g, 1 mmol) at −30 °C [Dry Ice/carbontetrachloride-chloroform (50:1)]. The solution was stirred for 30 min. Then, 4-nitrobenzaldehyde (**5b**, 0.151 g, 1 mmol) was added to the resulting deep purple solution of the ylide. The reaction mixture was gradually warmed to 0 °C with stirring within 3 h. After usual workup, was obtained 0.228 g (69%) of vinyl dithiocarboxylate **6e** as a mixture of cis and trans isomers (1:1). The ratio of the isomers was determined on the basis of ^1H NMR.

4-Phenyl-1,3-butadienyl 4-Methoxybenzenecarbodithioate (6f): Similarly to the synthesis of **6e** (Method B), from the salt **3c** (0.587 g, 1.0 mmol) and cinnamaldehyde (**5c**, 0.132 g, 1.0 mmol) was obtained 0.145 g (46%) of **6f** as red crystals. Recrystallization from methanol gave pure **6f**: Mp 95—97 °C; IR (KBr) 1250 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 296 nm (log ε=4.44), 350 nm (log ε=4.39), 400 nm (log ε=4.31); ^1H NMR ($CDCl_3$) δ=3.90 (3H, s, CH_3), 6.70—8.20 (13H, m, aromatic and olefinic); MS *m/z*, 312 (M^+).

4-Phenyl-1-buten-3-ynyl 4-Methoxybenzenecarbodithioate (6i): Similarly to the synthesis of **6e** (Method B), from the salt **3c** (1.173 g, 2.0 mmol) and 3-phenyl-2-propynal (**5f**, 0.26 g 2.0 mmol) was obtained 0.39 g (63%) of red crystals of **6i** as a mixture of cis and trans isomers (1:1). Fractional recrystallization from dichloromethane/methanol gave geometrically pure samples: *cis*-**6i**: red crystals: Mp 69—73 °C; IR (KBr) 1240 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 294 nm (log ε=4.19), 362 nm (log ε=4.33), 505 nm (log ε=2.41); ^1H NMR ($CDCl_3$) δ=3.87 (3H, s, CH_3), 6.17 (1H, d, *J*=10 Hz, vinyl), 7.70 (1H, d, *J*=8Hz, vinyl), 6.8—8.2 (9H, m, aromatic); MS *m/z*, 310 (M^+). Found: C, 69.56; H, 4.38%. Calcd for $C_{18}H_{14}OS_2$: C, 69.65; H, 4.55%. *trans*-**6i**: orange crystals: Mp 125—127 °C; IR (KBr) 1240 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 293 nm (log ε=4.33), 361 nm (log ε=4.41), 502 nm (log ε=2.51); ^1H NMR ($CDCl_3$) δ=3.87 (3H, s, CH_3), 6.29 (1H, d, *J*=16 Hz, vinyl), 7.65 (1H, d, *J*=16 Hz, vinyl), 6.8—8.1 (9H, m, aromatic); MS *m/z*, 310 (M^+). Found: C, 69.68; H, 4.36%. Calcd for $C_{18}H_{14}OS_2$: C, 69.65; H, 4.55%.

6-Phenyl-1,3,5-hexatrienyl 4-Methoxybenzenecarbodithioate (6j): Similarly, from the salt **3c** (1.17 g, 2.0 mmol) and potassium *t*-butoxide (0.235 g, 2.0 mmol) was prepared 2.0 mmol of the ylide. Then, 5-phenyl-2,4-pentadienal (**5g**, 0.316 g, 2.0 mmol) was added at −30 °C and the reaction mixture was stirred at that temperature for 5 h. After usual workup, 0.369 g (55%) of **6j** was obtained as red crystals. Recrystallization from hot methanol gave pure **6j**: Mp 169—170 °C; IR (KBr) 1245 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 334 nm (log ε=4.67), 418 nm (log ε=4.43); ^1H NMR ($CDCl_3$) δ=3.83 (3H, s, CH_3), 6.33—8.13 (15H, m, aromatic and olefinic); MS *m/z*, 338 (M^+). Found: C, 70.80; H, 5.38%. Calcd for $C_{20}H_{18}OS_2$: C, 70.97; H, 5.36%.

1-Propenyl 4-Methoxybenzenecarbodithioate (6k): Similarly to the synthesis of **6j**, from the salt **3c** (0.587 g, 1.0 mmol) and acetaldehyde (**5h**, 0.04 g, 0.9 mmol) was obtained 0.132 g (65%) of **6k** as a red oil (cis/trans=3:2). Analytically pure sample was obtained by preparative TLC (R_f=0.6, dichloromethane/hexane=2:3): IR (neat) 1235 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 347 nm (log ε=3.72), 500 nm (log ε=1.71); ^1H NMR* ($CDCl_3$) δ=1.89 (1.8H, dd, *J*=1.5 and 7.0 Hz, CH_3), 1.97 (1.2H, dd, *J*=1.5 and 6.6 Hz, CH_3), 3.85 (3H, s, CH_3), 6.16 (0.4H, qd, *J*=6.6 and 15.6 Hz, vinyl), 6.16 (0.6H, qd, *J*=7.0 and 9.52 Hz, vinyl), 6.8—7.0 (2H, m, aromatic), 6.84 (0.4H, qd, *J*=1.2 and 15.6 Hz, vinyl), 7.02 (0.6H, qd, *J*=1.2 and 9.5 Hz, vinyl), 8.0—8.2 (2H, m, aromatic); MS *m/z*, 224 (M^+). Found: C, 58.68; H, 5.68%. Calcd for $C_{11}H_{12}OS_2$: C, 58.90; H, 5.39%. *270 MHz

1-Butenyl 4-Methoxybenzenecarbodithioate (6l): Similarly to the synthesis of **6j**, from the salt **3c** (0.587 g, 1.0 mmol) and propanal (**5i**, 0.06 g, 1.0 mmol) was obtained 0.066 g (28%) of **6l** as a red oil (cis/trans=1:1). Analytically pure sample was obtained by preparative TLC (R_f=0.8, dichloromethane/hexane=2:3): IR (neat) 1235 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 345 nm (log ε=4.13), 498 nm (log ε=2.14); ^1H NMR* ($CDCl_3$) δ=1.07 (1.5H, t, *J*=7.7 Hz, CH_3), 1.13 (1.5H, t, *J*=7.3 Hz, CH_3), 2.2—2.4 (2H, m, CH_2), 3.85 (3H, s, CH_3), 6.07 (0.5H, td, *J*=7.3 and 9.5 Hz, vinyl), 6.20 (0.5H, td, *J*=6.6 and 15.8 Hz, vinyl), 6.86 (0.5H, td, *J*=1.5 and 15.8 Hz, vinyl), 6.8—6.9 (2H, m, aromatic), 7.00 (0.5H, td, *J*=1.5 and 9.5 Hz, vinyl), 8.0—8.2 (2H, m, aromatic); MS *m/z*, 238 (M^+). Found: C, 60.42; H, 6.18%. Calcd for $C_{12}H_{14}OS_2$: C, 60.47; H, 5.92%. *270 MHz-NMR

***O*-Methyl 4-Methoxybenzenecarbothioate (7a): Typical Procedures:** A solution of the dithiocarboxylate **6e** (0.083 g, 0.25 mmol) in 50 mL of dry THF was added dropwise at −70 °C to a solution of potassium methoxide (0.028 g, 0.24 mmol) in methanol (10 mL). The reaction mixture was warmed to 0 °C and the resulting deep purple solution (Vis; λ_{max}=493 nm) was stirred at 0 °C for 20 min. Then, to the enethiolate generated phenacyl bromide (0.05 g, 0.25 mmol) in 10 mL of methanol was added and stirred for 10 min. The mixture was quenched by addition of 5 drops of concentrated hydrochloric acid. The color of the solution turned to pale red then to yellow. After removal of the solvent, the residue was diluted with 50 mL of dichloromethane and washed with water (3×30 mL) and dried over anhydrous sodium sulfate. After concentration, the residue was purified by preparative TLC (hexane/dichloromethane=2:1 as eluant) gave 0.036 g (80%, R_f=0.63) of **7a** as yellow crystals together with 0.063 g (84%, R_f=0.11) of phenacyl 2-(4-nitrophenyl) vinyl sulfide (**10a**)[6] as pale yellow crystals. **7a**: Mp 43.5—45 °C [lit, mp 47 °C,[13a] 45 °C,[13a]]; IR (KBr) 1250 (C=S) cm^{-1}; ^1H NMR (CD_3COCD_3) δ=3.87 (3H, s, CH_3), 4.24 (3H, s, CH_3), 6.9—8.15 (4H, m, aromatic) [lit,[13a] ^1H NMR (CD_3COCD_3) δ=3.89 (3H, s, CH_3), 4.27 (3H, s, CH_3), 7.0—8.22 (4H, m, aromatic)]; MS *m/z*, 182 (M^+).

***O*-Methyl 4-Methylbenzenecarbothioate (7b):** Similarly to the synthesis of **7a**, a solution of the dithiocarboxylate **6c** (0.079 g, 0.25 mmol) in 40 mL of THF was treated with potassium *t*-butoxide (0.028 g, 0.25 mmol) in methanol (10 mL). In this case, the enethiolate generated was quenched by 2,4-dinitrochlorobenzene (0.051 g, 0.25 mmol). After usual workup, the residue was purified by preparative TLC (hexane/dichloromethane=1:1 as eluant) to give 0.034 g (82%, R_f=0.75) of **7b** as yellow oil together with

0.043 g (43%, R_f=0.05) of **10b**. **7b**: IR (neat) 1230 (C=S) cm^{-1}; ^1H NMR (CD_3COCD_3) δ=2.38 (3H, s, CH_3), 4.24 (3H, s, CH_3), 7.20—8.02 (4H, m, aromatic) [lit,[13a] ^1H NMR (CD_3COCD_3) δ=2.34 (3H, s, CH_3), 4.27 (3H, s, CH_3), 7.24—8.12 (4H, m, aromatic)]; MS *m/z*, 166 (M^+). The IR spectrum was well consistent with that of the authentic sample.[15] **10b**: Mp 153—158 °C; IR (KBr) 1330, 1510 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.73 (1H, d, *J*=10.5 Hz, vinyl), 7.20 (1H, d, *J*=10.5 Hz, vinyl), 7.6—7.9 (m, 3H, aromatic), 8.2—8.3 (m, 2H, aromatic), 8.43 (1H, dd, *J*=2.5 and 8.8 Hz, aromatic), 9.05 (1H, d, *J*=2.5 Hz, aromatic); MS *m/z*, 347 (M^+).

***O*-Ethyl 4-Methoxybenzenecarbothioate (7c):** Similarly to the synthesis of **7a**, the dithiocarboxylate **6e** (0.165 g, 0.5 mmol) was treated with potassium *t*-butoxide (0.056 g, 0.5 mmol) in ethanol (30 mL). After similar workup, the residue was purified by preparative TLC (ether/hexane=1:5 as eluant) to give 0.056 g (57%, R_f=0.45) of **7c** as yellow crystals together with 0.023 g (15%, R_f=0.1) of **10a**. **7c**: Mp 26—26.5 °C [lit,[16] mp 28—30 °C]; IR (KBr) 1220 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.49 (3H, t, *J*=7.2 Hz, CH_3), 3.87 (3H, s, CH_3), 4.69 (2H, q, *J*=7.2 Hz, CH_2), 6.9—8.2 (4H, m, aromatic); MS *m/z*, 196 (M^+).

***O*-Phenyl 4-Methoxybenzenecarbothioate (7d):** Similarly to the synthesis of **7b**, a solution of the dithiocarboxylate **6e** (0.083 g, 0.25 mmol) in 40 mL of THF was added dropwise at 20 °C to a solution of potassium phenoxide prepared from potassium *t*-butoxide (0.028 g, 0.25 mmol) and phenol (0.024 g, 0.25 mmol) in 10 mL of THF. The enethiolate generated was quenched by 2,4-dinitrochlorobenzene (0.05 g, 0.25 mmol) in 10 mL of THF. After similar workup, the residue was purified by preparative TLC (hexane/dichloromethane=1:1) to give 0.047 g (77%, R_f=0.47) of **7d** as pale yellow crystals together with 0.035 g (43%, R_f=0.04) of 2,4-dinitrophenyl 2-(4-nitrophenyl)vinyl sulfide (**10b**). **7d**: Mp 111—112 °C (recrystallized from methanol); IR (KBr) 1260 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.88 (3H, s, CH_3), 6.80—8.40 (9H, m, aromatic); MS *m/z*, 244 (M^+). Found: C, 68.35; H, 4.85%. Calcd for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.95%.

Ethyl 4-Methoxybenzenecarbodithioate (9a): Typical Procedures: A solution of the dithiocarboxylate **6e** (0.083 g, 0.25 mmol) in THF (40 mL) was added dropwise to a solution of potassium ethanethiolate (0.25 mmol) prepared from potassium *t*-butoxide (0.028 g, 0.25 mmol) and ethanethiol (4 mL) in THF (10 mL) at −70 °C. The reaction mixture was stirred at that temperature for 1 h, then gradually warmed to −10 °C within 1 h. After standing for additional 1 h phenacyl bromide (0.05 g, 0.25 mmol) was added. After usual workup, the residue was purified by preparative TLC (hexane/dichloromethane=2:1 as eluant) to give 0.043 g (81%, R_f=0.48) of **9a** as reddish orange crystals, together with 0.056 g (75%, R_f=0.10) of **10a**. **9a**: Mp 20—21 °C [lit,[16] mp 22—25 °C]; IR (neat) 1235 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (3H, t, *J*=7.5 Hz, CH_3), 3.45 (2H, q, *J*=7.5 Hz, CH_3), 3.80 (3H, s, CH_3), 6.75—8.10 (4H, m, aromatic); MS *m/z*, 212 (M^+).

Ethyl 4-Methylbenzenecarbodithioate (9b): Similarly to the synthesis of **9a**, the dithiocarboxylate **6c** (0.079 g, 0.25 mmol) was treated with potassium ethanethiolate (0.025 g, 0.25 mmol) in ethanol (10 mL). The enethiolate generated was quenched by 2.4-dinitrochlorobenzene (0.05 g, 0.25 mmol). After usual workup, the residue was purified by preparative TLC (hexane/dichloromethane=1:1) to give 0.030 g (67%; R_f=0.80) of **9b** as a red oil, together with 0.044 g (56%; R_f=0.05) of **10b**. **9b**: IR (neat) 1230 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.33 (3H, t, *J*=7.5 Hz, CH_3), 2.30 (3H, s, CH_3), 3.32 (2H, q, *J*=7.5 Hz, CH_2), 7.13 (2H, m, aromatic), 7.90 (m, 2H, aromatic) [lit,[17] ^1H NMR ($CDCl_3$) δ=1.3 (3H, t), 2.3 (3H, s), 3.3 (2H, q), 7.2 (2H, m), 7.9 (2H, m)]; MS *m/z*, 196 (M^+).

***t*-Butyl 4-Methoxybenzenecarbodithioate (9c):** Similarly to the synthesis of **9a**, a solution of the dithiocarboxylate **6e** (0.083 g, 0.25 mmol) in THF (40 mL) was treated with potassium 2-methyl-2-propanethiolate (0.032 g, 0.25 mmol) in THF (10 mL). After usual workup, the residue was purified by preparative TLC (hexane/dichloromethane=2:1 as eluant) to give 0.031 g (51%, R_f=0.55) of **9c** as reddish orange crystals, together with 0.052 g (70%, R_f=0.12) of **10a**. **9c**: Mp 37.5—39.5 °C; IR (KBr) 1240 (C=S) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.65 (9H, s, CH_3), 3.80 (3H, s, CH_3), 6.75—8.25 (4H, m, aromatic); MS *m/z*, 240 (M^+). All of the spectra were well consistent with those of authentic sample.[1c]

Phenyl 4-Methoxybenzenecarbodithioate (9d): Similarly to the synthesis of **9a**, the dithiocarboxylate **6e** (0.083 g, 0.25 mmol) was treated with potassium benzenethiolate (0.037 g, 0.25 mmol) in ethanol (10 mL). After usual workup, the residue was purified by preparative TLC (ether/hexane=2:1 as eluant) to give 0.03 g (46%; R_f=0.36) of **9d** as red crystals, together with 0.061 g (82%; R_f=0.07) of **10a**. **9d**: Mp 79.5—83.0 °C [lit,[18] mp 83 °C]; IR (KBr) 1240 (C=S) cm^{-1}; UV and Vis (CH_2Cl_2) 361 nm (log ε=4.23), 511 nm (log ε=2.27); ^1H NMR ($CDCl_3$) δ=3.80 (3H, s, CH_3), 6.75—8.25 (4H, m, aromatic), 7.4 (5H, s, aromatic); MS *m/z*, 260 (M^+).

We wish to acknowledge associate Prof. Dr. Satoshi Inagaki of Gifu University for his valuable advices on molecular orbital calculation. The calculation was carried out on a Hitachi computer of Institute for Molecular Science.

References

1) a) S. Kato, K. Sugino, Y. Matsuzawa, T. Katada, I. Noda, M. Mizuta, M. Goto, and M. Ishida, *Liebigs Ann. Chem.*, **1981**, 1798; b) S. Kato, S. Yamamoto, K. Ando, K. Itoh, M. Mizuta, and M. Ishida, *Z. Naturforsch.*, **37b**, 739 (1982); c) S. Kato, H. Shibahashi, T. Katada, T. Takagi, I. Noda, M. Mizuta, and M. Goto, *Liebigs Ann. Chem.*, **1982**, 1229; d) M. Ishida, H. Nakanishi, and S. Kato, *Chem. Lett.*, **1984**, 1961; e) M. Ishida, H. Nakanishi, and S. Kato, *Phosphorous and Sulfur*, **22**, 135 (1985); f) S. Kato, M. Goto, R. Hattori, K. Nishiwaki, M. Mizuta, and M. Ishida, *Chem. Ber.*, **118**, 1668 (1985).

2) M. Schoufs, J. Meijer, P. Vermeer, and L. Brandsma, *Synthesis*, **1978**, 439.

3) M. Saquet and T. Thuillier, *Tetrahedron Lett.*, **21**, 2165 (1980).

4) G. Levesque and A. Mahjour, *Tetrahedron Lett.*, **21**, 2247 (1980).

5) M. Ishida, H. Sato, and S. Kato, *Synthesis*, **1982**, 927.

6) S-(Triphenylphosphonio)methyl arenecarbothioate bromide was also prepared by us; M. Ishida, T. Iwata, M.

Yokoi, K. Kaga, and S. Kato, *Synthesis*, **1985**, 632.

7) The corresponding oxygen analogues, [1-(aryl- and alkylcarbonyl)oxyalkyl]phosphonium salts, were recently reported; E. Ander, T. Gassner, and A. Stankowiak, *Chem. Ber.*, **118**, 124 (1985).

8) S. Kato, T. Mitani, and M. Mizuta, *Int. J. Sulfur Chem.*, **8**, 359 (1973).

9) H. Hellmann and J. Bader, *Tetrahedron Lett.*, **1961**, 724.

10) a) J. Fabian, S. Scheithauer, and R. Mayer, *J. Prakt. Chem.*, **311**, 45 (1969); b) R. Mayer, E. Schinke, P. Rosmuss, and S. Sheithauer, *J. Prakt. Chem.*, **321**, 767 (1970).

11) We have previously reported the corresponding acylated salt; [$ArCS_2$-CH(CO-Ph)$\overset{+}{P}Ph_3$] $ArCS_2^-$; S. Kato, S. Imamura, and M. Mizuta, *Int. J. Sulfur Chem.* [A] **2**, 283 (1972).

12) The deep purple color (λ_{max}=493 nm) of the reaction mixture can be ascribed to the formation of potassium 2-(4-nitrophenyl)ethenethiolate (**8**), because the quite similar deep purple solution is formed from the reaction of *S*-[2-(4-nitrophenyl)vinyl] methoxybenzenecarbothioate (4-$CH_3OC_6H_4$-COS-CH=CH-$C_6H_4NO_2$(4-)) with potassium methoxide; See Ref. 6.

13) a) E. O. Fischer and S. Riedmüller, *Chem. Ber.*, **107**, 915 (1974); b) O. Exner, V. Jehlicka, and A. Ohno, *Collection Czechoslov. Chem. Commun.*, **36**, 2157 (1970).

14) a) W. Schroth, *Tetrahedron Lett.*, **1965**, 195; b) L. Brandsma, *Rec. Trav. Chim.*, **89**, 593 (1970); c) M. G. Missakian, R. Ketcham, and A. R. Martin, *J. Org. Chem.*, **39**, 2010 (1974).

15) T. Katada, S. Kato, and M. Mizuta, *Chem. Lett.*, **1975**, 1037.

16) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Chem. Ber.*, **96**, 2671 (1963).

17) J. Perregaard, I. Thomsen, and S.-O. Lawesson, *Bull. Chem. Soc. Belg.*, **86**, 321 (1977).

18) H. Viola, S. Scheithauer, and R. Mayer, *Chem. Ber.*, **101**, 3517, (1968).

19) V. N. Drozd and O. A. Popova, *Tetrahedron Lett.*, **1979**, 4491.