

Bis(2,6-dimethoxyphenyl) sulfide, selenide and telluride, and their derivatives

Masanori Wada *, Shin-ichi Nobuki, Yoshinori Tenkyuu, Satoko Natsume,
Masahiro Asahara, Tatsuo Erabi

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama, Tottori 680-0945, Japan

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Abstract

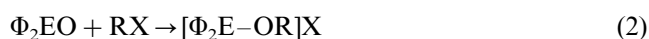
2,6-Dimethoxyphenyl derivatives of sulfur, selenium, and tellurium, such as $\Phi\text{EE}\Phi$, $\Phi_2\text{E}$, ΦSeH , $[\text{Me}\Phi_2\text{E}]\text{X}$ ($\text{X} = \text{MeSO}_4$, ClO_4), $\Phi_2\text{EO} \cdot x\text{H}_2\text{O}$, $[\Phi_2\text{EOH}]\text{ClO}_4$, $[\Phi_2\text{EOR}]\text{ClO}_4$ ($\text{R} = \text{Me}$, Et), $\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{EO}$ ($\text{E} = \text{S}$, Se) [$\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$; $\text{E} = \text{S}$, Se , Te] have been prepared, and their properties compared with common phenyl derivatives. The reaction rates of $\Phi_2\text{E}$ with dimethyl sulfate and butyl bromide increased in the order $\text{E} = \text{S} < \text{Se} < \text{Te}$, which were compared with those of Ph_3M and $\Phi_3\text{M}$, $\text{M} = \text{P} > \text{As} > \text{Sb}$. These reactivities are parallel with the electrochemical oxidation potentials reported for Ph_2E and with the first ionization potentials reported for Ph_3M . The rate of $\Phi_2\text{Te}$ was faster than that of Ph_3P and slightly faster than that of $\Phi_3\text{Sb}$. From the reactivity of $[\Phi_2\text{E-Me}]^+$ salts with nucleophiles, the $\text{E}^+ - \text{Me}$ bond strengths were estimated to increase in the order $\text{E} = \text{Se} < \text{S} < \text{Te}$. The reaction rates of $\Phi_2\text{EO}$ with dimethyl sulfate increased in the order $\text{E} = \text{S} < \text{Se} < \text{Te}$, and the respective rate of $\Phi_2\text{EO}$ was faster than that of $\Phi_2\text{E}$. The origins of these reactivities and bond strengths are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Sulfur; Selenium; Tellurium; 2,6-Dimethoxyphenyl; Onium; Reaction rate; Bond strength

1. Introduction

It is a basic chemical interest to compare the chemical and physical properties of compounds among elements as well as substituents. While a variety of comparisons have been reported among Group 15 and 16 elements, there are few works of comparison between the two groups. As part of our systematic investigation on the chemistry of 2,6-dimethoxyphenyl derivatives such as $\Phi_3\text{M}$ ($\text{M} = \text{P}$, As , Sb , Bi ; $\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$) [1,2], we attempted to study a series of its derivatives of Group 16 elements. 2,6-Dimethoxyphenyl derivatives of these elements in general have prominent properties such as odorless character, higher crystallinity and higher nucleophilicity than common phenyl derivatives [3,4]. In the present paper, we report

the details of preparations and some basic reactions of 2,6-dimethoxyphenyl derivatives (Scheme 1), and also compare the nucleophilic reactivities of $\Phi_2\text{E}$ and $\Phi_2\text{EO}$ ($\text{E} = \text{S}$, Se , Te) (Eqs. (1) and (2)) with those of Group 15 elements.



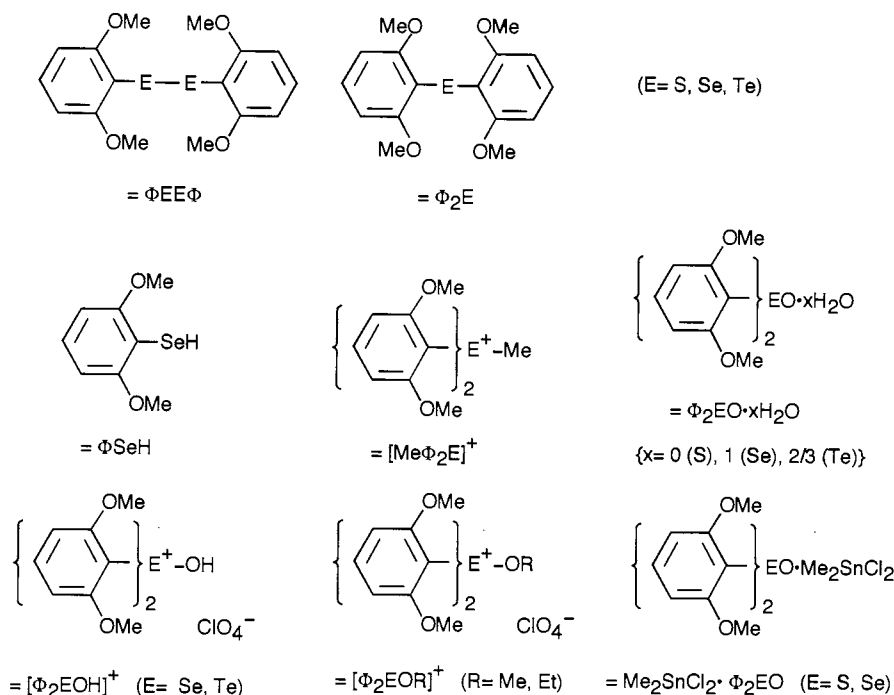
{ $\text{E} = \text{S}$, Se , Te ; $\text{RX} = (\text{MeO})_2\text{SO}_2$, BuBr , BuI }

2. Experimental

2.1. Physical measurements

^1H - and ^{13}C -NMR spectra were recorded for solutions in CDCl_3 using a JEOL model JNM-GX-270

* Corresponding author. Fax: +81-857-31-0881.



spectrometer. IR spectra were recorded for Nujol mull using a Shimadzu FTIR-4200 spectrophotometer. GC-MS spectra were recorded using a Shimadzu QP-5000 mass spectrometer. The ^1H - and ^{13}C -NMR spectral data are summarized in Tables 1 and 2, respectively.

2.2. Preparation of bis(2,6-dimethoxyphenyl) disulfide, diselenide and ditelluride

2.2.1. $\Phi\text{SS}\Phi$

A suspension of ΦLi was prepared from a 15% hexane solution of butyllithium (12.5 ml, 20 mmol), 1,3-dimethoxybenzene (2.6 ml, 20 mmol), and a catalytic amount of tetramethylethylenediamine (TMEDA) (0.1 ml) as described elsewhere [1]. To this suspension were added elemental sulfur (0.481 g, 15 mmol) and benzene (15 ml), and the mixture was stirred at room temperature (r.t.) for 15 h to give a brown suspension. Water (50 ml) was added to extract the precipitates of ΦSLi . To the aqueous solution was added 30% aqueous hydrogen peroxide (1.6 ml, 20 mmol) to give precipitates, immediately, which could be recrystallized from acetone to give light yellow crystals of $\Phi\text{SS}\Phi$ (7.1 ~ 5.2 mmol); m.p. 199–201°C (206–209 [5]); MS [m/z (rel. intensity)] 338 (100, M^+). Anal. Found: C, 56.60; H, 5.42; S, 18.88%. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$: C, 56.78; H, 5.36; S, 18.95%. The organic layer was dried under reduced pressure, and the residue was recrystallized from 2-propanol to give $\Phi_2\text{S}$ (0.31 mmol) (see below for the characterization).

2.2.2. $\Phi\text{SeSe}\Phi$

A suspension of ΦLi was prepared as mentioned above from 1,3-dimethoxybenzene (20 mmol), 15% hexane solution of butyllithium (20 mmol) and TMEDA (0.1 ml) under argon. To this suspension were added elemental selenium (15 mmol), dry lithium chloride (ca. 1 g) and dry tetrahydrofuran (30 ml), and the mixture was stirred at r.t. in the dark for 15 h to give a brown suspension. Water (50 ml) was added to extract the precipitates of ΦSeLi , the aqueous layer was treated with 30% aqueous hydrogen peroxide (1.6 ml, 20 mmol) as mentioned above, and the resultant precipitates could be recrystallized from methanol to give orange crystals of $\Phi\text{SeSe}\Phi$ (6.5 ~ 5.0 mmol); m.p. 146–147°C; MS [m/z (rel. intensity)] 434 and 432 (50, M^+), 138 (100). Anal. Found: C, 44.67; H, 4.26%. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{Se}_2$: C, 44.46; H, 4.20%. The organic layer was dried under reduced pressure, and the residue was recrystallized from diethyl ether to give $\Phi_2\text{Se}$ (0.34 mmol) (see below for the characterization).

2.2.3. $\Phi\text{TeTe}\Phi$

In an analogous manner to that mentioned above, a treatment of ΦLi suspension with elemental tellurium (15 mmol) in the presence of lithium chloride and tetrahydrofuran gave dark brown crystals of $\Phi\text{TeTe}\Phi$ (4.5 ~ 3.2 mmol), which could be recrystallized from methanol or toluene; m.p. 140–141°C; MS [m/z (rel. intensity)] 530 (20, M^+), 137 (100). Anal. Found: C, 36.24; H, 3.53%. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{Te}_2$: C, 36.29; H, 3.43%.

Table 1

¹H-NMR spectral data for 2,6-dimethoxyphenyl derivatives of sulfur, selenium and tellurium^a

Compounds	$\delta(4\text{-H})^b$	$\delta(3,5\text{-H})^c$	$\delta(2,6\text{-MeO})^d$	$\delta(\text{Others})$
$\Phi_2\text{S}$	7.13	6.49	3.72	
$\Phi_2\text{Se}$	7.14	6.48	3.68	
$\Phi_2\text{Te}$	7.17	6.46	3.64	
$\Phi\text{SS}\Phi$	7.23	6.51	3.69	
$\Phi\text{SeSe}\Phi$	7.22	6.51	3.71	
$\Phi\text{TeTe}\Phi$	7.18	6.48	3.75	
ΦSeH	7.11	6.54	3.87	2.02s[J(Se) 68 Hz, Se–H]
$\Phi_2\text{SO}$	7.27	6.53	3.78	
$\Phi_2\text{SeO} \cdot \text{H}_2\text{O}$	7.27	6.53	3.75	
$\Phi_2\text{TeO} \cdot (2/3)\text{H}_2\text{O}$	7.26	6.52	3.70	
$[\text{Me}\Phi_2\text{S}]\text{ClO}_4$	7.55	6.69	3.93	3.67s (Me–S)
$[\text{Me}\Phi_2\text{Se}]\text{ClO}_4$	7.49	6.66	3.84	3.57s (Me–Se)
$[\text{Me}\Phi_2\text{Te}]\text{ClO}_4$	7.44	6.61	3.77	3.06s (Me–Te)
$[\Phi_2\text{SeOH}]\text{ClO}_4^c$	7.62	6.77	3.97	
$[\Phi_2\text{TeOH}]\text{ClO}_4^c$	7.56	6.75	3.88	
$[\Phi_2\text{SOMe}]\text{ClO}_4$	7.70	6.77	3.92	4.12s (OMe)
$[\Phi_2\text{SeOMe}]_2\text{SO}_4$	7.46	6.63	3.82	3.72s (OMe)
$[\Phi_2\text{TeOMe}]_2\text{SO}_4$	7.44	6.65	3.79	3.64s (OMe)
$[\Phi_2\text{SOEt}]\text{ClO}_4$	7.69	6.76	3.92	4.41q[J(H) 7 Hz], 1.46t[J(H) 7 Hz]
$[\Phi_2\text{SeOEt}]_2\text{SO}_4$	7.45	6.62	3.81	4.10q[J(H) 7 Hz], 1.27t[J(H) 7 Hz]
$\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{SO}$	7.30	6.54	3.78	1.19s[J(¹¹⁹ Sn) 83.5 Hz, Me–Sn]
$\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{SeO}$	7.33	6.55	3.76	1.16s[J(¹¹⁹ Sn) 85.5 Hz, Me–Sn]

^a In CDCl₃; $\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$; s, singlet, t, triplet, q, quartet.^b Triplet with J_{HH} 8–9 Hz.^c Doublet with J_{HH} 8–9 Hz.^d Singlet.^e Measured in the presence of CF₃COOH (ca. 1 w/w%) to avoid deprotonation.

2.3. Preparation of bis(2,6-dimethoxyphenyl)sulfide, -selenide, and -telluride

2.3.1. $\Phi_2\text{S}$

To a suspension of ΦLi , prepared as mentioned above from 1,3-dimethoxybenzene (35 mmol), 15% hexane solution of butyllithium (33 mmol), and TMEDA (0.1 ml), was added a solution of disulfur dichloride (0.8 ml, 10 mmol) in diethyl ether (45 ml) at 0°C under argon. The mixture was stirred at r.t. for 6 h, water (100 ml) was added, and the precipitates could be recrystallized from ethanol to give $\Phi_2\text{S}$ (8.4 ~ 5.6 mmol); m.p. 153–154°C; MS [m/z (rel. intensity)] 306 (100, M^+). Anal. Found: C, 62.72; H, 5.92%. Calc. for C₁₆H₁₈O₄S₁: C, 62.60; H, 5.91%. The aqueous layer was acidified using 6 M hydrochloric acid to give ΦSH (8.7 mmol) [5,6].

2.3.2. $\Phi_2\text{Se}$

To a suspension of ΦLi , prepared as mentioned above from 1,3-dimethoxybenzene (15 mmol), 15% hexane solution of butyllithium (15 mmol) and TMEDA (0.02 ml) under argon, was added a solution of $\Phi\text{SeSe}\Phi$ (5.90 g, 13.6 mmol) in benzene (30 ml). The mixture was stirred at r.t. for 15 h, water (30 ml) was added, and the mixture was heated to dissolve the precipitates. The organic layer was separated, the volatile materials

in this layer were removed under reduced pressure, and the residue could be recrystallized from diethyl ether to give light yellow crystals of $\Phi_2\text{Se}$ (9.2 mmol); m.p. 124–125°C; MS [m/z (rel. intensity)] 354 (100, M^+). Anal. Found: C, 54.11; H, 5.16%. Calc. for C₁₆H₁₈O₄Se₁: C, 54.40; H, 5.14%. The aqueous layer was acidified using 6 M hydrochloric acid to give ΦSeH (9.2 mmol) (see below).

2.3.3. $\Phi_2\text{Te}$

To a suspension of ΦLi , prepared as mentioned above from 1,3-dimethoxybenzene (6 mmol), 15% hexane solution of butyllithium (6 mmol) and TMEDA (0.1 ml) under argon, was added a solution of $\Phi\text{TeTe}\Phi$ (2.65 g, 5 mmol) in benzene (50 ml). The mixture was stirred at r.t. for 15 h, water (70 ml) was added, and the grey precipitates could be recrystallized from acetone to give light brown crystals of $\Phi_2\text{Te}$ (4.0 ~ 3.3 mmol); m.p. 191–192°C; MS [m/z (rel. intensity)] 404 (67, M^+), 77 (100). Anal. Found: C, 47.68; H, 4.66%. Calc. for C₁₆H₁₈O₄Te₁: C, 47.81; H, 4.51%. On standing the aqueous layer in air for 2 days, brown crystals of crude $\Phi\text{TeTe}\Phi$ (1.40 mmol) were obtained.

2.3.4. ΦSeH

The suspension of ΦLi was prepared as mentioned above in 80 mmol scale of butyllithium, to which was

added dry tetrahydrofuran (100 ml), lithium chloride (3.4 g), and elemental selenium (4.74 g, 60 mmol) under argon. The mixture was stirred in the dark at r.t. for 15 h to give a reddish–brown suspension. It was extracted with cold water (ca. 100 ml), and to the aqueous layer was added aqueous 6 M hydrochloric acid (21 ml). It was cooled at 0°C overnight to give orange crystals, which could be recrystallized from hexane to give ΦSeH (45 mmol); m.p. 58–59°C; IR 2320 cm^{-1} (Se–H). Anal. Found: C, 43.97; H, 4.52%. Calc. for $\text{C}_8\text{H}_{10}\text{O}_2\text{Se}_1$: C, 44.25; H, 4.64%.

2.4. Preparations of bis(2,6-dimethoxyphenyl) sulfoxide, selenoxide and telluroxide

2.4.1. $\Phi_2\text{SO}$

To a suspension of $\Phi_2\text{S}$ (0.612 g, 2 mmol) in acetic acid (5 ml) was added 30% aqueous hydrogen peroxide (0.22 ml), and the mixture was stirred at r.t. for 8 h. The resultant precipitates were washed with 1.5 M sodium hydroxide and then with water, and they were recrystallized from toluene to give $\Phi_2\text{SO}$ in 83–64% yield; m.p. 185–188°C (decomposed); IR 1050 cm^{-1} (S=O); MS [m/z (rel. intensity)] 306 (95, $\Phi_2\text{S}^+$), 151 (100). Anal. Found: C, 59.59; H, 5.86%. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{S}_1$: C, 59.61; H, 5.63%.

Table 2

^{13}C -NMR spectral data for 2,6-dimethoxyphenyl derivatives of sulfur, selenium and tellurium^a

Compounds	δ^b
$\Phi_2\text{S}$	112.2, 160.1, 104.2, 128.1, 56.2
$\Phi_2\text{Se}$	109.2, 160.0, 104.2, 128.4, 56.1
$\Phi_2\text{Te}$	96.2, 161.3, 103.6, 129.2, 56.0
$\Phi\text{SS}\Phi$	114.0, 161.2, 103.8, 130.9, 56.0
$\Phi\text{SeSe}\Phi$	109.6, 160.9, 103.8, 130.7, 56.1
$\Phi\text{TeTe}\Phi$	90.6, 162.1, 103.4, 130.5, 56.1
ΦSeH	107.4, 156.7, 104.0, 126.3, 56.2
$\Phi_2\text{SO}$	120.8, 159.2, 104.6, 131.9, 56.2
$\Phi_2\text{SeO} \cdot \text{H}_2\text{O}$	119.2, 160.2, 104.7, 132.3, 56.2
$\Phi_2\text{TeO} \cdot (2/3)\text{H}_2\text{O}$	– ^c , 162.2, 104.6, 132.6, 56.1
$[\text{Me}\Phi_2\text{S}]\text{ClO}_4$	– ^c , 160.3, 105.3, 136.3, 57.0; 27.2 (Me–S)
$[\text{Me}\Phi_2\text{Se}]\text{ClO}_4$	– ^c , 159.8, 105.4, 135.0, 56.8; 24.4 (Me–Se)
$[\text{Me}\Phi_2\text{Te}]\text{ClO}_4$	– ^c , 161.7, 105.0, 134.8, 56.6; 7.9 (Me–Te)
$[\Phi_2\text{SOMe}]\text{ClO}_4$	103.3, 160.4, 105.4, 138.9, 57.3; 63.6 (OMe)
$[\Phi_2\text{SeOMe}]\text{SO}_4$	110.4, 160.0, 105.3, 135.6, 56.8; 54.5 (OMe)
$[\Phi_2\text{TeOMe}]\text{SO}_4$	– ^c , 161.7, 105.3, 135.6, 56.7; 54.5 (OMe)
$[\Phi_2\text{SOEt}]\text{ClO}_4$	103.8, 160.3, 105.4, 138.7, 57.3; 74.5, 15.5 (OEt)
$[\Phi_2\text{SeOEt}]\text{SO}_4$	110.7, 160.2, 105.3, 135.4, 56.8; 63.5, 15.1 (OEt)
$\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{SO}$	– ^c , 159.4, 104.9, 132.5, 56.3; 11.1 (Me–Sn)
$\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{SeO}$	116.1, 160.1, 105.0, 133.3, 56.4; 13.6 (Me–Sn)

^a In CDCl_3 ; $\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$.

^b In the order of C(1), C(2,6), C(3,5), 2,6-MeO; and others.

^c The C(1) resonance could not be observed.

2.4.2. $[\Phi_2\text{SeOH}]\text{ClO}_4$ and $\Phi_2\text{SeO} \cdot \text{H}_2\text{O}$

To a suspension of $\Phi_2\text{Se}$ (0.708 g, 2 mmol) in acetic acid (20 ml) was added 30% aqueous hydrogen peroxide (0.28 ml) to give an orange solution. It was diluted with water (100 ml), and 60% aqueous perchloric acid (0.32 ml) was added to give white crystals of $[\Phi_2\text{SeOH}]\text{ClO}_4$ in 87–79% yield after recrystallization from ethanol; m.p. 139°C (decomposed **explosively, Caution!**); IR 3340 (OH), 1100 (ClO_4) cm^{-1} . This salt (0.470 g, 1 mmol) was suspended in 1 M sodium hydroxide (5 ml) for 0.5 h, and the resultant solution was extracted with dichloromethane (30 ml), from which white crystals of $\Phi_2\text{SeO} \cdot \text{H}_2\text{O}$ were obtained in 87–71% yield; m.p. 164–166°C. Anal. Found: C, 49.39; H, 5.19. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{Se} \cdot \text{H}_2\text{O}$: C, 49.62; H, 5.21%.

2.4.3. $[\Phi_2\text{TeOH}]\text{ClO}_4$ and $\Phi_2\text{TeO} \cdot (2/3)\text{H}_2\text{O}$

To a suspension of $\Phi_2\text{Te}$ (0.804 g, 2 mmol) in acetic acid (10 ml) was added 30% aqueous hydrogen peroxide (0.30 ml) to give a colorless solution. It was diluted with water (40 ml), and 60% aqueous perchloric acid (0.40 ml) was added to give light yellow crystals of $[\Phi_2\text{TeOH}]\text{ClO}_4$ in 88–83% yield after recrystallization from ethanol; m.p. 143°C (decomposed **explosively, Caution!**); IR 3480 (OH), 1100 (ClO_4) cm^{-1} . This salt (0.518 g, 1 mmol) was treated in 1 M sodium hydroxide as mentioned above to give white crystals of $\Phi_2\text{TeO} \cdot (2/3)\text{H}_2\text{O}$ in 71% yield; m.p. 193–195°C. Anal. Found: C, 44.50; H, 4.49. Calc. for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{Te} \cdot (2/3)\text{H}_2\text{O}$: C, 44.70; H, 4.53%.

2.5. Preparations of methyl-bis(2,6-dimethoxyphenyl)-sulfonium, -selenonium and -telluronium salts

2.5.1. $[\text{Me}\Phi_2\text{S}]\text{X}$ ($\text{X} = \text{MeSO}_4, \text{ClO}_4$)

To a mixture of $\Phi_2\text{S}$ (1.53 g, 5 mmol) and 1,2-dichloroethane (0.4 ml) was added dimethyl sulfate (0.5 ml, 5 mmol), and the mixture was heated at 55°C overnight. The resultant suspension was washed with diethyl ether (25 ml \times 3) and by benzene (35 ml) to leave white solid of $[\text{Me}\Phi_2\text{S}]\text{MeSO}_4$ in 89% yield, m.p. 119–127°C; IR 1255 cm^{-1} (MeSO_4).

To an aqueous solution of $[\text{Me}\Phi_2\text{S}]\text{MeSO}_4$ (0.5 mmol/10 ml) was added 60% aqueous perchloric acid (a slight excess), and the resultant precipitates were recrystallized from ethanol or water to give colorless crystals of $[\text{Me}\Phi_2\text{S}]\text{ClO}_4$ in 48% yield; m.p. 202°C (decomposed); IR 1100 and 625 cm^{-1} (ClO_4). Anal. Found: C, 48.27; H, 4.94%. Calc. for $\text{C}_{17}\text{H}_{21}\text{Cl}_1\text{O}_8\text{S}_1$: C, 48.52; H, 5.03%.

2.5.2. $[\text{Me}\Phi_2\text{Se}]\text{X}$ ($\text{X} = \text{MeSO}_4, \text{ClO}_4$)

To a mixture of $\Phi_2\text{Se}$ (1.76 g, 5 mmol) and 1,2-dichloroethane (1 ml) was added dimethyl sulfate (0.7 ml, 7 mmol), and the mixture was stirred overnight. It

was washed with diethyl ether (10 ml \times 3) to leave a white solid of $[\text{Me}\Phi_2\text{Se}]\text{MeSO}_4$ in quantitative yield, as characterized by ^1H - and ^{13}C -NMR spectra; m.p. 120–123°C (decomposed); IR 1255 cm^{-1} (MeSO_4).

To an aqueous solution of $[\text{Me}\Phi_2\text{Se}]\text{MeSO}_4$ (0.5 mmol/5 ml) was added 60% aqueous perchloric acid (a slight excess), and the resultant precipitates were recrystallized from ethanol or water to give colorless crystals of $[\text{Me}\Phi_2\text{Se}]\text{ClO}_4$ in 56% yield; m.p. 166–167°C (decomposed); IR 1100 and 625 cm^{-1} (ClO_4). Anal. Found: C, 43.69; H, 4.59%. Calc. for $\text{C}_{17}\text{H}_{21}\text{Cl}_1\text{O}_8\text{Se}_1$: C, 43.65; H, 4.53%.

2.5.3. $[\text{Me}\Phi_2\text{Te}]\text{X}$ ($\text{X} = \text{MeSO}_4, \text{ClO}_4$)

In an analogous manner to those mentioned above using $\Phi_2\text{Te}$, both $[\text{Me}\Phi_2\text{Te}]\text{MeSO}_4$ and $[\text{Me}\Phi_2\text{Te}]\text{ClO}_4$ were prepared as colorless crystals in 78 and 63% yields, respectively. $[\text{Me}\Phi_2\text{Te}]\text{MeSO}_4$, m.p. 126–131°C (decomposed); IR 1255 cm^{-1} (MeSO_4). $[\text{Me}\Phi_2\text{Te}]\text{ClO}_4$ (recrystallized from ethanol), m.p. 211–213°C (decomposed); IR 1100 and 625 cm^{-1} (ClO_4). Anal. Found: C, 39.34; H, 4.08%. Calc. for $\text{C}_{17}\text{H}_{21}\text{Cl}_1\text{O}_8\text{Te}_1$: C, 39.54; H, 4.10%.

2.6. Preparations of alkoxy-bis(2,6-dimethoxyphenyl)-sulfonium, -selenonium and -telluronium salts

2.6.1. $[\Phi_2\text{SOMe}]\text{ClO}_4$

A mixture of $\Phi_2\text{SO}$ (1 mmol), 1,2-dichloroethane (0.2 ml), and dimethyl sulfate (0.1 ml) was heated at 60°C for 1.5 h. It was washed with diethyl ether repeatedly (5 ml \times 3) and was extracted with water (15 ml). Perchloric acid (1 M, 1.5 ml) was added at 0°C to form white precipitates, which were recrystallized from ethanol to give crystals of $[\Phi_2\text{SOMe}]\text{ClO}_4$ in 54–41% yield; m.p. 135–139°C (decomposed); IR 1100 cm^{-1} (ClO_4). This compound was characterized by ^1H - and ^{13}C -NMR spectra, since recrystallization resulted in partial hydrolysis to give $[\Phi_2\text{SOH}]\text{ClO}_4$.

2.6.2. $[\Phi_2\text{SeOMe}]_2\text{SO}_4$

A mixture of $\Phi_2\text{SeO}\cdot\text{H}_2\text{O}$ (1 mmol), 1,2-dichloroethane (0.2 ml) and dimethyl sulfate (0.2 ml) was stirred at r.t. for 1 h to give a clear solution. It was washed with diethyl ether repeatedly (5 ml \times 3) to give brown crystals of $[\Phi_2\text{SeOMe}]_2\text{SO}_4$ in 74% yield; m.p. 118–121°C (decomposed). This compound was characterized by ^1H - and ^{13}C -NMR spectra, since recrystallization resulted in partial hydrolysis to give $[\Phi_2\text{SeOH}]\text{ClO}_4$.

In essentially analogous manners to those above, the following compounds were obtained using dialkyl sulfate at 60°C or at r.t.

2.6.3. $[\Phi_2\text{TeOMe}]_2\text{SO}_4$

Yield 64%; m.p. 124–126 °C (decomposed).

2.6.4. $[\Phi_2\text{SOEt}]\text{ClO}_4$

Yield 60–48%; m.p. 121–123 °C (decomposed).

2.6.5. $[\Phi_2\text{SeOEt}]_2\text{SO}_4$

Yield 75%; m.p. 120–123 °C (decomposed).

2.7. Formation of dimethyltin dichloride complexes of bis(2,6-dimethoxyphenyl) sulfoxide, selenoxide and telluroxide

2.7.1. $\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{SO}$

To a solution of Me_2SnCl_2 (1 mmol) in toluene (50 ml) was added $\Phi_2\text{SO}$ (2 mmol), and the mixture was stirred for 5 min to give white precipitates of the 1:2 adduct in 61% yield; m.p. 189–190°C (decomposed). Anal. Found: C, 47.12; H 4.94%. Calc. for $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{O}_{10}\text{S}_2\text{Sn}_1$: C, 47.24; H4.90%. The 1:2 adduct was obtained even though the ratio of Me_2SnCl_2 and $\Phi_2\text{SO}$ was varied to 1:1 or 2:1.

2.7.2. $\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{SeO}$

To a solution of $\Phi_2\text{SeO}\cdot\text{H}_2\text{O}$ (1.5 mmol) in 2-propanol (10 ml) was added Me_2SnCl_2 (1 mmol), and the mixture was stirred for 1 h to give white precipitates, which were recrystallized from ethanol to give white crystals of the 1:2 adduct in 73% yield; m.p. 195–197°C. Anal. Found: C, 42.46; H 4.36%. Calc. for $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{O}_{10}\text{Se}_2\text{Sn}_1$: C, 42.62; H 4.42%.

2.8. Rate measurement

Reaction rates were determined by conductimetry for solutions containing Ar_nE or Ar_nEO (0.01 M) in Table 3 and alkyl halide or dimethyl sulfate (0.20–0.80 M) in acetonitrile in a boiling chloroform bath at 61.2°C. Correlation coefficients were greater than 0.9998 except for very fast reactions (Ph_3Sb , $\Phi_2\text{TeO}$). The results are summarized in Table 3. 2,6-Dimethoxyphenyl derivatives of Group 15 elements in Table 3 were prepared as described elsewhere [1,6].

3. Results and discussion

3.1. Preparation and properties of 2,6-dimethoxyphenyl chalcogenides

2,6-Dimethoxyphenyllithium, ΦLi , is easily prepared as a suspension by the reaction of 1,3-dimethoxybenzene and butyllithium in the presence of a catalytic amount of tetramethylethylenediamine [1]. In contrast to phenyllithium, ΦLi is poorly soluble in hydrocarbons and diethyl ether, and its reactivity is often very poor.

Table 3
Rate constants for the reactions, Eqs. (1) and (2)

RX	Ar _n E or Ar _n EO	k ₂ (1 mol ⁻¹ s ⁻¹) ^a	Relative rate <i>r</i>	
(MeO) ₂ SO ₂	Φ ₂ S	9.23 × 10 ⁻⁵	1.0	0.99992
	Φ ₂ Se	1.13 × 10 ⁻³	12.2	0.99992
	Φ ₂ Te	3.13 × 10 ⁻²	339	0.99998
	Ph ₃ P	7.72 × 10 ⁻³	83.6	0.99994
	Ph ₃ As	2.20 × 10 ⁻⁴	2.4	0.99998
	Ph ₃ Sb	1.63 × 10 ⁻⁴	1.8	0.99920
	Φ ₃ Sb	2.61 × 10 ⁻²	283	0.99986
	Φ ₂ SO	1.39 × 10 ⁻³	15	0.99996
	SeO · H ₂ O	4.47 × 10 ⁻²	484	0.99987
	Φ ₂ TeO · (2/3)H ₂ O	Too fast	>1000	
	BuBr	Φ ₂ Te	(1.7 × 10 ⁻³) ^b	
Ph ₃ P		3.52 × 10 ⁻⁵		0.99995
Φ ₃ PO		(4.3 × 10 ⁻⁵) ^b		0.99999
Φ ₃ AsO		5.63 × 10 ⁻³		0.99992
Φ ₃ SbO ^c		2.78 × 10 ⁻³		0.99997
BuI	Φ ₂ Te	(1.1 × 10 ⁻²) ^b		0.99997

^a By conductimetry for solutions containing Ar_nE (or Ar_nEO) (0.01 M) and RX (0.20–0.80 M) in acetonitrile, at 61.2°C; $k_{\text{obs}} = k_2[\text{Ar}_n\text{E}][\text{RX}]$; $\Phi = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$.

^b The reaction attained equilibrium.

^c See the manuscript for the reaction.

In fact, while it reacted with elemental sulfur in hexane–benzene to give the suspension of ΦSLi, it reacted with neither elemental selenium nor with tellurium under the analogous conditions or even in THF, although 2,4,6-trimethoxyphenyllithium has been reported to react with elemental tellurium [7].

However, it was found incidentally that the reactions proceeded in the presence of lithium chloride in THF to give ΦSeLi or ΦTeLi. Magnesium chloride or iodide was also effective in place of lithium chloride. The role of these inorganic salts is not clear at present, but it is expected that they form double salts with LiΦ to make them soluble in the solvent. The reagents ΦELi (E = S, Se, Te), thus prepared, could be oxidized in water using hydrogen peroxide to give bis(2,6-dimethoxyphenyl) dichalcogenides, ΦEEΦ (E = S, Se, Te), as light yellow (S), orange (Se) or dark brown (Te) crystals with much higher melting points than diphenyl dichalcogenides, PhEPh. These dichalcogenides, ΦEEΦ, are thermally stable, and the GC-MS spectra showed clearly the parent peaks, M⁺.

A reaction of LiΦ with disulfur dichloride gave bis(2,6-dimethoxyphenyl) sulfide, Φ₂S, and 2,6-dimethoxybenzenethiol, ΦSH. Bis(2,6-dimethoxyphenyl) selenide, Φ₂Se, was prepared by the reaction of LiΦ with ΦSeSeΦ, which formed 2,6-dimethoxybenzeneselenol, ΦSeH, as the by-product. Bis(2,6-dimethoxyphenyl) telluride, Φ₂Te, was prepared by the reaction of LiΦ with ΦTeTeΦ, where the expected by-product, ΦTeH, was air-sensitive to be oxidized to

ΦTeTeΦ. While all the diphenyl chalcogenides, Ph₂E (E = S, Se, Te), are liquid at r.t., all of Φ₂E are crystalline with higher melting points than 120°C. These chalcogenides Φ₂E are also thermally stable, and the GC-MS spectra also showed clearly the parent peaks, M⁺.

All of Φ₂E (E = S, Se, Te) reacted with dimethyl sulfate in dichloroethane to give the onium salts, [MeΦ₂E]MeSO₄, which were soluble in water and could be converted to the perchlorates for pure isolation.

It has long been known that the nucleophilic reaction rates of Group 15 compounds, R₃M, with alkyl halides decrease in the order M = (N <) P > As > Sb [8–10], which is parallel with the first ionization potential in photoelectron spectra of Ph₃M (M = P, 7.37; As, 7.60; Sb, 7.80 eV) [11], as well as with the Brønsted basicity [12,13], the dipole moment [8,9], and the Lewis basicity to boron Lewis acids in gas-phase (calorimetry, et al.) [14,15]. In contrast, little work has been reported on the comparison of nucleophilic reaction rates of Ph₂E, probably due to their poor nucleophilicities. It has been reported that the reaction of Ph₂Se with bromine is slower than that of Ph₂Te [16]. Due to the higher nucleophilicity of Φ₂E than Ph₂E, we could observe the rates of reaction between Φ₂E and dimethyl sulfate by conductimetry, which clearly increased in the order E = S < Se < Te with a relative ratio of 1:12:339 (Table 3). We also confirmed that the rates of reaction between Ph₃M and dimethyl sulfate decreased in the order M = P > As > Sb with a relative ratio of 83.6:2.4:1.8, the rate of Φ₃Sb is faster than that of Ph₃P, and that the rate of Φ₂Te is faster than that of Ph₃P and slightly faster than that of Φ₃Sb (Table 3). With butyl bromide, the reaction of Φ₂Te also is faster than Ph₃P, but it attained equilibrium. The reaction of Φ₂Te with butyl iodide was very fast, but it also attained equilibrium. Of special interest is the reversed reactivities between Group 15 and 16 derivatives.

When [MeΦ₂S]MeSO₄ was treated with potassium iodide in water, Φ₂S began to precipitate immediately. An analogous reaction was observed for [MeΦ₂Se]MeSO₄ with potassium iodide to give Φ₂Se. In order to see the relative reactivity and/or stability, a 1:1 mixture of [MeΦ₂S]MeSO₄ and [MeΦ₂Se]MeSO₄ was treated in water with a half equimolar amount of potassium iodide, and Φ₂Se was obtained almost selectively. Treatments of [MeΦ₂Se]MeSO₄ with piperidine and triethylamine also resulted in very fast demethylations to give Φ₂Se, and treatments with aqueous sodium hydroxide and aqueous sodium bromide resulted in slow and partial demethylations. When [MeΦ₂Te]MeSO₄ was treated with aqueous potassium iodide, anion exchange gave precipitates of [MeΦ₂Te]I. The ¹H-NMR spectrum of [MeΦ₂Te]I in chloroform-*d*₁, however, showed a partial decomposition to give Φ₂Te and iodomethane. These observations suggest that the

$E^+ - Me$ bond strengths of $[\Phi_2EMe]^+$ increase in the order $E = Se < S < Te$, which is consistent with the order of equilibrium constant observed for reactions between Ph_2E ($E = S, Se$) and methyl iodide [17,18]. The equilibrium constant of reactions between R_3M ($M = P, As, Sb$) and methyl iodide decreases in the order $M = P > As > Sb$ [17,18], which suggests that the $[R_3M - Me]^+$ bond strength decreases in the order $M = P > As > Sb$.

While $[Me\Phi_2Te]I$ in solution gave equilibrium mixtures containing Φ_2Te and iodomethane, $[Me\Phi_3Sb]I$ was stable in solution. This indicates that the $\Phi_3Sb^+ - Me$ bond is stronger than the $\Phi_2Te^+ - Me$ bond as well as the $Me - I$ bond.

Oxidation potentials of Ph_2E (electrochemical E_0/V vs. NHE = 1.56 (S), 1.38 (Se), 0.95 (Te)) [19], $Me(4-RC_6H_4)E$ [19,20], Me_2E [20], $MePhE$ [20,21], and $\Phi EE\Phi$ [22] have been reported to decrease in the order $E = S > Se > Te$, while those of phenoxachalcogenides, $C_{12}H_8OE$ [23], and chalcathrenes, $C_{12}H_8E_2$ [24,25], studied both by photoelectron spectroscopy and semiempirical MO calculation, have been reported by somewhat different orders such as $Se > S > Te$. The former order ($S > Se > Te$) parallels the rate order of reactions between Φ_2E and dimethyl sulfate ($S < Se < Te$), while the latter parallels the $E^+ - Me$ bond strength order of $[\Phi_2E - Me]^+$ ($Se < S < Te$).

Thus, the reactivity orders of Φ_2E and Ar_3M are found to be parallel with the oxidation potentials reported for Ph_2E and Ph_3M , respectively. There then arises the question, why the oxidation potential orders of Ph_2E and Ph_3M reverse the respective element orders? Based on electronegativity consideration, the oxidation potential of Group 15 elements is expected to decrease in the order $P > As > Sb$, the reverse order of experimental observation [11].

Essentially in an analogous manner to that explained for the oxidation potentials [11], we also explain the reactivity order $P > As > Sb$ by the fact that the three phenyl groups compensate the electronegativity of M enough to increase the nucleophilicity of the non-bonded electron pair in the order.

The other question is why the bond strength order ($Se < S < Te$) is not parallel with the element order. At present, we have no appropriate explanation and further works are in progress.

3.2. Preparation and properties of bis(2,6-dimethoxyphenyl) sulfoxide, selenoxide and telluroxide

Treatment of Φ_2S with hydrogen peroxide in acetic acid resulted in the precipitation of the oxide, Φ_2SO . In contrast, Φ_2SeO and Φ_2TeO , thus prepared, are highly soluble, and treatment of the aqueous solutions with perchloric acid gave precipitates of $[\Phi_2EOH]ClO_4$

(**Caution!: these salts are explosive.**) When these salts were treated with aqueous sodium hydroxide, we obtained the oxides as the hydrates, $\Phi_2SeO \cdot H_2O$ and $\Phi_2TeO \cdot (2/3)H_2O$. The precise formulations of these oxides are not known at present. Organometal (or -metalloid) oxides of heavier elements (Sn, Sb, Te, I) are apt to take polymeric structures or they dissolve in forms of hydroxide [26–30]. The GC spectrum of Φ_2SO showed that it partially decomposed to Φ_2S during the measurement, and mass spectrum of Φ_2SO showed strong peak due to Φ_2S^+ . Both $\Phi_2SeO \cdot H_2O$ and $\Phi_2TeO \cdot (2/3)H_2O$ also decomposed during the GC measurements completely to Φ_2Se and Φ_2Te , respectively.

Treatments of Φ_2EO ($E = S, Se, Te$) with dialkyl sulfate in 1,2-dichloroethane resulted to give their alkoxonium salts, $[\Phi_2EOR]X$ ($R = Me, Et$). The reactions of Φ_2EO were faster than those of Φ_2E and the rates increased also in the order $E = S < Se < Te$ (Table 3). The order may be related with the basicity or the $E - O$ bond polarity of Φ_2EO ($\Phi_2E^+ - O^-$). In contrast, an unusual order of reactivity was observed for the reaction of Φ_3MO with butyl bromide; $M = P < As \geq Sb$ (Table 3). The reactivity orders except for the position of Sb paralleled with the electronegativity orders of these Group 15 and 16 elements, respectively, where the $M - O$ and $E - O$ bond polarities of $\Phi_3M^+ - O^-$ and $\Phi_2E^+ - O^-$ must increase in the reverse order to electronegativity. The pK_a values of Ph_3MO and Ph_2EO have been studied in water, and the Brønsted basicity increases in the order of $Ph_2SO < Ph_3PO < Ph_2SeO < Ph_3AsO$ [31]. The basicity and the dipole moment of R_3MO and/or R_2EO also have been known to increase in the parallel orders of $M = P < As < Sb$ and $E = S < Se < Te$, which are the reverse orders of $M - O$ or $E - O$ bond dissociation energy [1,32–34]. Analogous orders have been observed for the basicity, $S \sim Se < P < As < Sb$, and the nucleophilicity, $P < S < Se < As < Sb$, of $Ph_nM = C_5Ph_4$ [35]. The rates of deuterium exchange of $[(CH_3)_4M]^+$ and $[(CH_3)_3E]^+$ decrease in the orders of $M = (N) < P > As > Sb$ and $E = S > Se > Te$, respectively, which must reflect the Brønsted basicity orders of the intermediate ylides [36]. The poorer reactivity of Φ_3SbO than Φ_3AsO with butyl bromide is tentatively attributed to the polymeric property of the former [1].

While we obtained 1:1 adducts of Φ_3PY ($Y = O, S$) with dimethyltin dichloride even though Φ_3PY was used in excess [2], both Φ_2SO and $\Phi_2SeO \cdot H_2O$ formed 2:1 adducts with dimethyltin dichloride even though the ratio of Φ_2SO and Me_2SnCl_2 was varied to 1:1 or 1:2. However, $\Phi_2TeO \cdot (2/3)H_2O$ reacted with dimethyltin dichloride to give complex mixtures. Most probably $\Phi_2TeO \cdot (2/3)H_2O$ reacted as a Brønsted base to form partial hydrolysis product of dimethyltin dichloride.

3.3. H- and ^{13}C -NMR spectra

The ^1H -NMR spectra of Φ -derivatives (Table 1) show a triplet due to 4-protons, a doublet due to 3,5-protons and a very sharp singlet due to 2,6-methoxy protons. In general, as expected, cationic compounds showed the resonances at lower magnetic field than neutral compounds. The 4-proton resonance shifts, in general, to higher magnetic fields in the order $\text{E} = \text{S} < \text{Se} < \text{Te}$ with exceptions for $\Phi_2\text{E}$ and $\text{Me}_2\text{SnCl}_2 \cdot 2\Phi_2\text{EO}$. The 3,5-proton resonance is less sensitive to the change of E, but it also shifts in the order. 2,6-Methoxy proton resonance is the most sensitive to E and also shifts, in general, in the order with an exception for $\Phi\text{EE}\Phi$. The methyl proton resonance, as well as the carbon resonance, of $[\text{Me}\Phi_2\text{E}]\text{ClO}_4$ also is sensitive to E and shifts to a higher magnetic field in the order $\text{E} = \text{S} < \text{Se} < \text{Te}$. These results of chemical shift are not in accord with the well-known electronegativity order of chalcogenides, $\text{S} \leq \text{Se} > \text{Te}$. There is, however, a possibility that the true electronegativity order is $\text{S} > \text{Se} > \text{Te}$, which explains the general trend of the proton chemical shifts. In contrast, the proton resonances for Φ -derivatives of Group 15 elements have been observed somewhat in the reverse order expected from the electronegativity, $\text{M} = \text{P} > \text{As} > \text{Sb} > \text{Bi}$ [1].

The coupling constant ($J_{119_{\text{Sn}}}$) observed for $\text{SnMe}_2\text{Cl}_2 \cdot 2\Phi_2\text{EO}$ is larger for $\text{E} = \text{Se}$ than S, suggesting that $\Phi_2\text{SeO}$ is a stronger Lewis base than $\Phi_2\text{SO}$ toward dimethyltin dichloride [2].

The ^{13}C -NMR spectra of Φ -derivatives (Table 2) show five resonances due to the Φ -group. The *ipso*-carbon, C(1), resonance of the Φ -group is often too weak to be observed, but it shifts to a higher magnetic field in the order $\text{E} = \text{S} < \text{Se} < \text{Te}$ for $\Phi\text{EE}\Phi$ and $\Phi_2\text{E}$. However, it shifts in the order $\text{S} > \text{Se}$ for $[\Phi_2\text{EOR}]\text{X}$. The other four resonances due to the Φ -group are far less sensitive to the change of E.

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