Remote Pummerer Reaction via Intermolecular Through-Space Interaction between Sulfonium and Sulfenyl Sulfur Atoms

Kenji Kobayashi,* Emiko Koyama, Kazuhiko Namatame, Toyokazu Kitaura, Chihiro Kono,
Mariko Goto, Takanobu Obinata, and Naomichi Furukawa*

*Department of Chemistry and Tsukuba Advanced Research Alliance Center, University of Tsukuba,
Tsukuba, Ibaraki 305-8571, Japan*

Received December 3, 1998

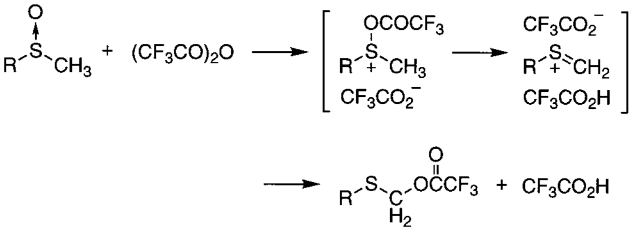
The remote Pummerer reaction of the mono-sulfoxide of *p*-bis(methylthio)-aromatic **1** is described. The reaction of **1** with $(CF_3CO)_2O$ in CH_2Cl_2 gave a mixture of the corresponding mono-Pummerer product **2**, the bis-Pummerer product **3**, and the bis-sulfide **4** in an *n*:1:1 ratio ($n \geq 2$). The 1:1 formation of **3** and **4** indicates an intermolecular interaction between sulfur atoms. The reaction with the deuterium-labeled **1-d_3** showed that the formation of **2** occurs at the sulfenyl as well as sulfinyl groups in **1a-d_3−1d-d_3**, in which the product ratio of **2-d_3**:**2-d_2** is in the range of 3.5−10. On the other hand, the Pummerer reaction of **1e-d_3** occurred preferably at the sulfinyl group in a usual manner. The reaction of a 1:1 mixture of the bis-sulfide **4** and the bis-sulfoxide **5** with $(CF_3CO)_2O$ also gave **2**, **3**, and **4** in a ratio similar to that for the reaction of **1**. The mechanism in the present remote Pummerer reactions is discussed in light of an intermolecular through-space interaction between the sulfonium and sulfenyl sulfur atoms, and a dithia dication dimer **B** and/or a bis(dithia dication) cyclic dimer **C** are proposed as intermediates.

Introduction

Although the study of a σ-bonded dithia dication formed by an intramolecular through-space interaction between bifunctional sulfur atoms in close proximity has attracted considerable attention in heteroatom chemistry,[1] such a bond formation via an intermolecular interaction has not been explored extensively.[2] Recently, Nenajdenko and co-workers reported the preparation and reactivity of a dithia dication which is generated from the combination of dimethyl sulfoxide, triflic anhydride, and dimethyl sulfide.[3] Such a formation of dithia dication by an intermolecular interaction would be worth pursuing from the viewpoint of molecular assembly, as well as organosulfur conducting materials.[4]

For the past decades, Pummerer rearrangement reactions have been widely studied in light of mechanistic interests and synthetic applications (Scheme 1).[5] Pummerer-type reactions via through-bond interactions are especially useful for the construction of cyclic aromatic compounds and quinones.[6] Kaji and co-workers reported the reaction of aryl methyl sulfoxide with dimethyl sulfide in the presence of $(CF_3CO)_2O$ to form aryl methyl sulfide and (trifluoroacetoxy)methyl methyl sulfide, in which a dithia dication is proposed as an intermediate.[7]

Scheme 1



Our attention has been focused on whether an intermolecular interaction of the sulfur atom of an acyloxysulfonium salt with a sulfur functional group essentially occurs in the course of Pummerer reaction[7−9] and on whether an intermolecular or through-bond interaction is more favorable. To this end, we have chosen the monooxide of *p*-bis(methylthio)-aromatic **1** as a model.[10] The two sulfur atoms in **1**, which are separated

---

(1) (a) Musker, W. K. *Acc. Chem. Res.* **1980**, *13*, 200−206. (b) Furukawa, N. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2571−2591 and references therein.

(2) For dithio dications by dimerization of sulfide radical cations, see: (a) Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.*, **1978**, *100*, 6416−6421. (b) Tamaoki, M.; Serita, M.; Shiratori, Y.; Itoh, K. *J. Phys. Chem.*, **1989**, *93*, 6052−6058.

(3) Nenajdenko, V. G.; Shevchenko, N. E.; Balenkova, E. S. *Tetrahedron* **1998**, *54*, 5353−5362.

(4) (a) Nakasuji, K.; Sasaki, M.; Kotani, T.; Murata, I.; Enoki, T.; Imaeda, K.; Inokuchi, H.; Kawamoto, A.; Tanaka, J. *J. Am. Chem. Soc.* **1987**, *109*, 6970−6975. (b) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55−58. (c) Heywang, G.; Roth, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 176−177. (d) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature*, **1994**, *371*, 141−143.

(5) (a) Oae, S.; Numata, T.; Yoshimura, T. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Ed.; John Wiley: New York, 1981; pp 571−672. (b) Lucchi, O. D.; Miotti, U.; Modena, G. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley: New York, 1991; Chapter 3, pp 157−184. (c) Grierson, D. S.; Husson, H. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 6, pp 909−947.

(6) (a) Jung, M. E.; Kim, C.; von dem Bussche, L. *J. Org. Chem.* **1994**, *59*, 3248−3249. (b) Kuethe, J. T.; Cochran, J. E.; Padwa, A. *J. Org. Chem.* **1995**, *60*, 7082−7083. (c) Kita, Y.; Takeda, Y.; Matsugi, M.; Iio, K.; Gotanda, K.; Murata, K.; Akai, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1529−1531. (d) Akai, S.; Takeda, Y.; Iio, K.; Takahashi, K.; Fukuda, N.; Kita, Y. *J. Org. Chem.* **1997**, *62*, 5526−5536.

(7) (a) Tanikaga, R.; Nakayama, K.; Tanaka, K.; Kaji, A. *Chem. Lett.* **1977**, 395−396. (b) Drabowicz, J.; Oae, S. *Chem. Lett.* **1977**, 767−768.

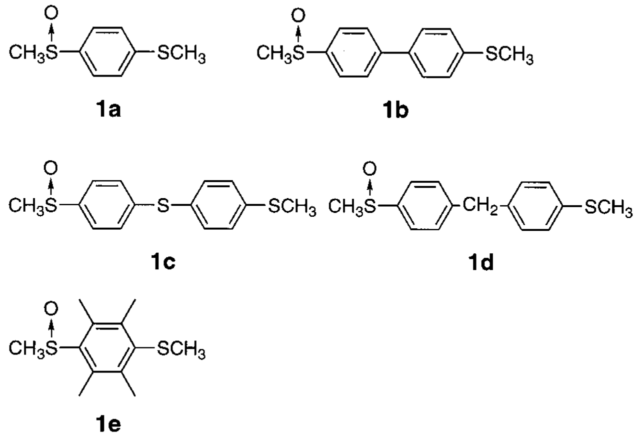
(8) For the reactions of sulfonium sulfur atoms with heteroatoms, see: (a) Tidwell, T. T. *Synthesis* **1990**, 857−870. (b) Reference 5a.

(9) For the reactions of sulfonium sulfur atoms with aromatic rings, see: Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819−5820.

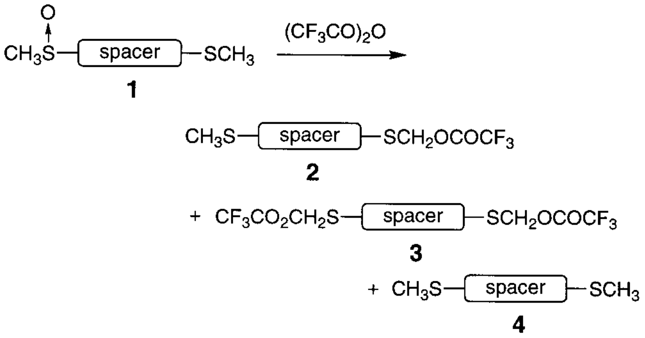
(10) For an intermolecular interaction between sulfur atoms in the oxygen atom migration reaction of **1a** mediated by CF_3CO_2H, see: Kobayashi, K.; Obinata, T.; Furukawa, N. *Chem. Lett.* **1997**, 1175−1176.

10.1021/jo982377h CCC: $18.00

Chart 1



Scheme 2



intramolecularly by aromatic spacers so as not to contact each other, may allow an intermolecular through-space or intramolecular through-bond interaction. We report here the remote Pummerer reaction, where an intermolecular interaction between the sulfur atom of acyloxysulfonium salt of **1** and the sulfenyl sulfur atom of a second molecule predominantly occurs to form a dithia dication prior to the Pummerer reaction and consequently leads to the Pummerer product at the sulfenyl moiety of **1**.

Results and Discussion

Remote Pummerer Reaction of Monooxide of *p*-Bis(methylthio)-Aromatic 1. The monooxides of *p*-bis(methylthio)-aromatics **1** (mono-sulfoxides) studied here are 1-(methylsulfinyl)-4-(methylthio)benzene (**1a**), 4-(methylsulfinyl)-4′-(methylthio)biphenyl (**1b**), [4-(methylsulfinyl)phenyl]-[4′-(methylthio)phenyl] sulfide (**1c**), [4-(methylsulfinyl)phenyl]-[4′-(methylthio)phenyl]-methane (**1d**), and 1-(methylsulfinyl)-4-(methylthio)-2,3,5,6-tetramethylbenzene (**1e**) (Chart 1).

When the mono-sulfoxide **1** was treated with 5 equiv of $(CF_3CO)_2O$ (TFAA) in CH_2Cl_2 at −20 °C to room temperature for 10 h under an Ar atmosphere, a mixture of the (trifluoroacetoxy)methylthio-methylthio-aromatic **2** (mono-Pummerer product), the bis[(trifluoroacetoxy)-methylthio]-aromatic **3** (bis-Pummerer product), and the bis-sulfide **4** was obtained exclusively as shown in Scheme 2. The totally isolated yields were more than 90%. The product ratio of the reaction under the standard conditions is summarized in Table 1.

Table 1. Reaction of Monooxide of *p*-Bis(methylthio)-Aromatic 1 with TFAA[a]

run	substrate	concn, mM	product ratio **2**:**3**:**4**	total yields, %
1	**1a**	70	12.8:1.0:0.9	94
2	**1b**	70	3.1:1.0:1.0	97
3	**1b**	1	2.9:1.0:1.0	97
4	**1c**	70	3.3:1.0:1.0	95
5	**1c**	1	3.2:1.0:1.4	97
6	**1d**	70	2.1:1.0:1.0	91
7	**1d**	1	2.4:1.0:0.7	97
8	**1e**	70	7.8:1.0:0.9	97

[a] Carried out in a ratio of **1**:TFAA = 1:5 in CH_2Cl_2 at −20 °C to room temperature for 10 h.

Scheme 3

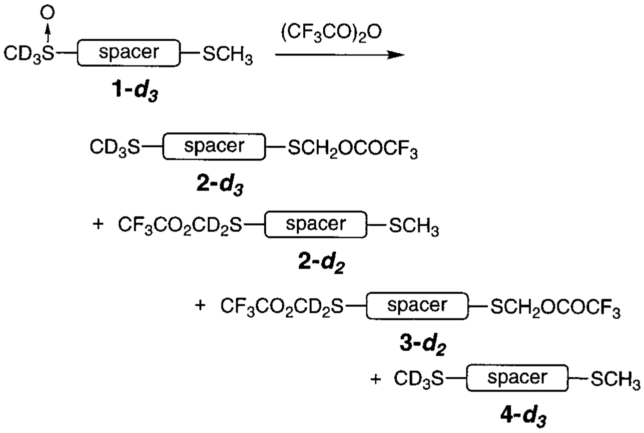


Table 2. Reaction of Deuterium-Labeled 1 with TFAA[a]

run	substrate	product ratio **2-*d*₃**:**2-*d*₂**:**3-*d*₂**:**4-*d*₃**
1	**1a-*d*₃**	3.5:1.0:—[b]:—[b]
2	**1b-*d*₃**	5.0:0.5:1.0:0.8
3	**1c-*d*₃**	3.6:0.7:1.0:1.0
4	**1d-*d*₃**	2.3:0.5:1.0:0.8
5	**1e-*d*₃**	2.0:4.3:1.0:1.0

[a] Carried out in a ratio of $\mathbf{1}\text{-}d_3$:TFAA = 1:5 in CH_2Cl_2 at −20 °C to room temperature for 10 h. [b] Not available.

In all cases, the ratio of the bis-Pummerer product **3** to the bis-sulfide **4** is constantly 1:1, although the yield of the mono-Pummerer product **2** is higher than those of **3** and **4**. The formation of **3** and **4** could be attributed to an intermolecular reaction. The ratio of **3** to **2** relatively increases with increasing the spacer length. The product ratio resulting from **1d** with the methylene bridge is similar to those obtained for **1b** and **1c** having π-conjugate spacers. In all cases, the ratio of **2**, **3**, and **4** is almost independent of the concentration of **1** at least in the range of 1−70 mM.

Deuterium-Labeled Experiment. The Pummerer reaction of trideuteriomethylsulfinyl-methylthio-aromatic **1-*d*₃** with TFAA was conducted (Scheme 3). The totally isolated yields of the (trifluoroacetoxy)methylthio-trideuteriomethylthio-aromatic **2-*d*₃**, the (trifluoroacetoxy)-dideuteriomethylthio-methylthio-aromatic **2-*d*₂**, the (trifluoroacetoxy)dideuteriomethylthio-(trifluoroacetoxy)-methylthio-aromatic **3-*d*₂**, and the trideuteriomethylthio-methylthio-aromatic **4-*d*₃** were almost the same as those for unlabeled ones (ca. 90% yield). The product ratio of **2-*d*₃**:**2-*d*₂**:**3-*d*₂**:**4-*d*₃** is shown in Table 2.

It is noted that the ratio of the mono-Pummerer products, **2-*d*₃**:**2-*d*₂**, from **1a-*d*₃**−**1d-*d*₃** is significantly large and in the range of 3.5−10. In general, the Pummerer reaction should proceed at the methylsulfinyl group, but not at the methylsulfenyl group. In the present

Scheme 4

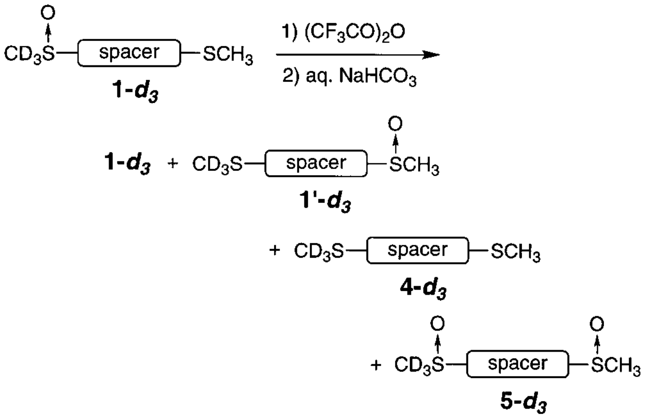


Table 3. Quick Quench of the Reaction Mixture of Deuterium-Labeled 1 and TFAA with Aqueous NaHCO$_3$[a]

run	substrate	temp, °C	time, s	product ratio **1-d_3:1′-d_3:4-d_3:5-d_3**
1	**1a-d_3**	−15	5	1.0:1.0:0.2:0.2
2	**1b-d_3**	−25	900	1.0:1.1:0.8:0.2
3	**1c-d_3**	−15	5	1.0:1.0:0.5:0.3
4	**1d-d_3**	−15	10	1.0:0.9:0.7:0.3

[a] Carried out in a ratio of **1-d_3**:TFAA = 1:5 in CH$_2$Cl$_2$.

reaction, this is not the case. The above results unambiguously indicate that the formation of **2** occurs at both groups in **1** which are located at the remote position by the intervention of spacers. In marked contrast, the product ratio of **2e-d_3**:**2e-d_2** from **1e-d_3** as a sterically hindered analogue of **1a** was 0.47. This result indicates that a normal Pummerer reaction at the sulfinyl group dominates in **1e**.

Quench at the Initial Stage of the Reaction. We turned our attention to the initial stage of the present Pummerer reaction. When the reaction of the deuterium-labeled mono-sulfoxide **1-d_3** with TFAA in CH$_2$Cl$_2$ at −15 °C was quickly quenched with aqueous NaHCO$_3$ in 5−900 s, a mixture of **1-d_3**, the methylsulfinyl-trideuteriomethylthio-aromatic **1′-d_3**, **4-d_3**, and the trideuteriomethylsulfinyl-methylsulfinyl-aromatic **5-d_3** was obtained exclusively instead of Pummerer products as shown in Scheme 4. The product ratio of **1-d_3**:**1′-d_3**:**4-d_3**:**5-d_3** is listed in Table 3.

In all cases, the ratio of **1-d_3**:**1′-d_3** is approximately 1:1.[10] The total yields of **1-d_3** and **1′-d_3** are higher than those of **4-d_3** and **5-d_3**. The facts of a 1:1 formation of **1-d_3** and **1′-d_3**, as well as no formation of the Pummerer products, show that at the initial stage of the reaction an intermolecular or intramolecular interaction of the sulfonium with the sulfenyl sulfur atoms is much more favorable than the abstraction of an α-proton of the sulfonium group leading to the Pummerer products.

Remote Pummerer Reaction of Bis-Sulfide 4 with Bis-Sulfoxide 5. In the presence of TFAA (5 equiv), the bis-sulfide **4** itself completely remained unchanged, whereas the bis-sulfoxide **5** afforded only the bis-Pummerer product **3** quantitatively. On the other hand, as shown in Scheme 5, the reaction of a 1:1 mixture of **4** and **5** with 5 equiv of TFAA exclusively gave a mixture of the mono-Pummerer products **2**, **3**, and **4** (total yields are more than 88%). The product ratio obtained here is summarized in Table 4.

Scheme 5

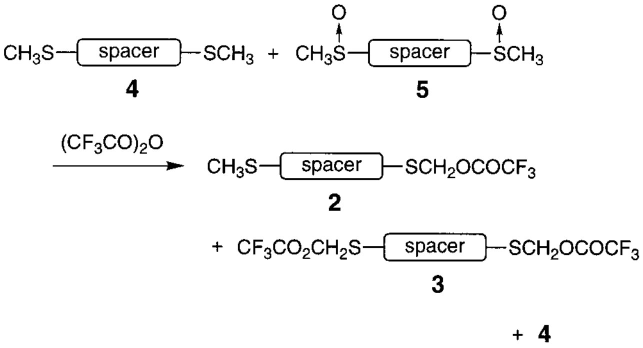
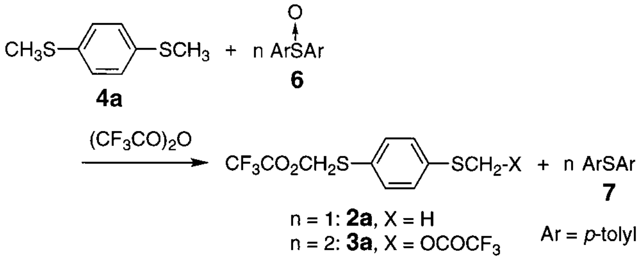


Table 4. Reaction of a 1:1 Mixture of Bis-Sulfide 4 and Bis-Sulfoxide 5 with TFAA[a]

run	substrates	product ratio **2**:**3**:**4**	total yields, %
1	**4a** + **5a**	13.2:1.0:0.9	97
2	**4b** + **5b**	2.5:1.0:1.0	95
3	**4c** + **5c**	3.2:1.0:1.1	91
4	**4d** + **5d**	2.3:1.0:1.1	88

[a] Carried out in a ratio of **4**:**5**:TFAA = 1:1:10 in CH$_2$Cl$_2$ at −20 °C to room temperature for 10 h.

Scheme 6

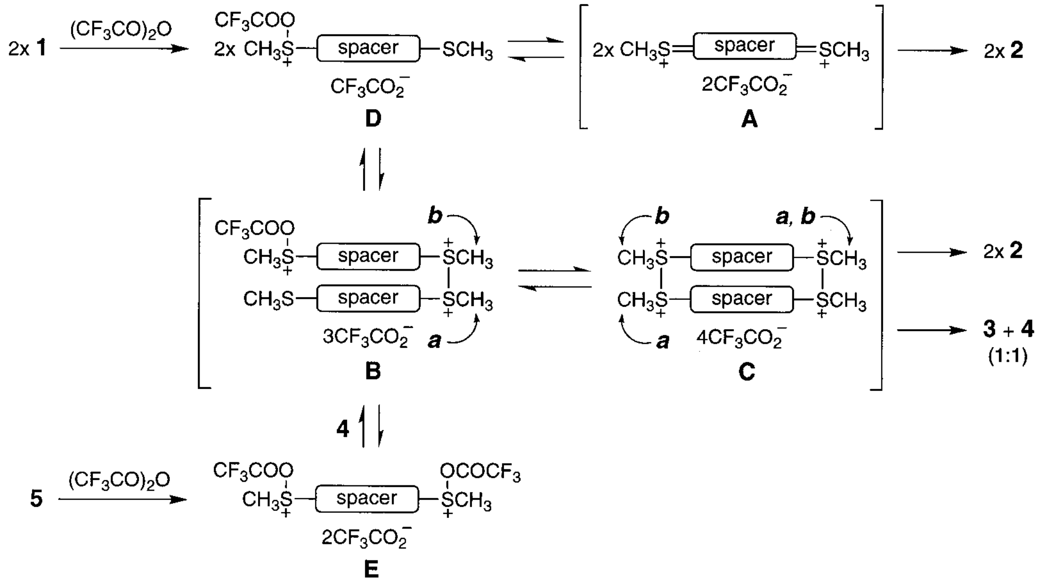


It is noteworthy that the product ratios for the reactions of **4a**−**d** with **5a**−**d** are **2a**−**d**:**3a**−**d**:**4a**−**d** = *n*:1:1 (*n* ≥ 2) and are similar to those for the reactions of the mono-sulfoxides **1a**−**d**, respectively. The product ratios were also approximately independent of the concentration of the substrates. These results strongly suggest that the reactions shown in both Schemes 2 and 5 proceed via the same intermediate.

Reaction of Diaryl Sulfoxide with Bis-Sulfide. The reactions of **4a** with 1 and 2 equiv of bis(*p*-tolyl) sulfoxide **6** in the presence of 5 equiv of TFAA quantitatively gave the mono-Pummerer product **2a** and the bis-Pummerer product **3a**, respectively, together with the bis(*p*-tolyl) sulfide **7** (Scheme 6). This result shows an intermolecular interaction of the sulfonium intermediate formed by **6** and TFAA with the methylsulfenyl group of **4a**, leading to the Pummerer product.[7a] Furthermore, this indicates that when 1 equiv of **6** was used, the mono-Pummerer product **2a** formed at the initial stage does not react with the sulfonium intermediate during the course of the reaction.

Intramolecular Through-Bond vs Intermolecular Through-Space Interactions between Sulfonium and Sulfenyl Sulfur Atoms. The reaction of the mono-sulfoxide **1** with TFAA affords the bis-Pummerer product **3** and the bis-sulfide **4** in a 1:1 ratio, as well as the mono-Pummerer product **2** (Scheme 2), and the reaction of a 1:1 mixture of **4** and the bis-sulfoxide **5** with TFAA produces **2** in addition to **3** and **4** (Scheme 5). These results clearly indicate the mechanism including an

Scheme 7



intermolecular through-space interaction between the sulfonium and the sulfenyl sulfur atoms. The favorable formation of **2-*d*$_3$** more than **2-*d*$_2$** in the reaction of the deuterium-labeled **1-*d*$_3$** also indicates an intramolecular through-bond and/or intermolecular interactions between sulfur atoms (Scheme 3). Furthermore, the quenching experiment at the initial stage of the reaction shows that intramolecular and/or intermolecular interactions of the sulfonium with the sulfenyl sulfur atoms are much more favorable than the abstraction of an α-proton of the sulfonium group leading to the Pummerer products (Scheme 4).

On the basis of these observations, the following three types of intermediates are envisaged in the present reactions as shown in Scheme 7: a dithiaquinodimethane-like dication (**A**), a dithia dication dimer (or oligomer) (**B**),[3,7a] and a bis(dithia dication) cyclic dimer (**C**).[10] At this stage, these intermediates have not been detected even at −40 °C. The mono-sulfoxide **1** and the bis-sulfoxide **5** react with TFAA to form the trifluoroacetoxysulfonium salt **D** and bis-sulfonium salt **E**, respectively.[11] An intramolecular through-bond interaction between the sulfonium and the sulfenyl sulfur atoms in **D** would afford intermediate **A**. The abstraction of an α-proton of **A** by trifluoroacetate followed by the addition of trifluoroacetate to the resulting methylenesulfonium salt would give only the mono-Pummerer product **2**. On the other hand, the nucleophilic attack by the sulfenyl sulfur atom of one **D** on the sulfonium sulfur atom of the other **D** and by those of **4** on those of **E** via an intermolecular through-space interaction would produce intermediates **B** and/or **C**, respectively. The abstraction of an α-proton of **B** and/or **C** by trifluoroacetate from side ***a*** would give two molecules of **2**, whereas the proton abstraction from side ***b*** would afford the bis-Pummerer product **3** and the bis-sulfide **4** in the 1:1 ratio.

Coexistence of two reaction pathways, where the mono-Pummerer product **2** results from the intermediate **A** and the bis-Pummerer product **3** and the bis-sulfide **4** arise from the intermediates **B** and/or **C**, is not plausible, because the ratio of **2** to **3** in the present Pummerer reaction is independent of the concentration of **1** as shown in Table 1. Otherwise this ratio would increase with a decrease in the concentration of **1** when the intermediate **A** is dominant in the reaction. It is also decisive that the product ratio of **2**, **3**, and **4** for the reaction of **1** with TFAA is similar to that for the reaction of a 1:1 mixture of **4** and **5** and that the 1:1 formation of **3** and **4** is invariable in all cases presented here (Tables 1 and 4). The most plausible mechanism which could fit all the results described above should involve the intermediates **B** and/or **C**, but not **A**.[12]

Further evidence for the proposed mechanism comes from the following two types of experiments. First, the reaction of **1d-*d*$_3$**, in which an intramolecular through-bond interaction is not available due to the insulation of π-conjugation by the methylene bridge, gave the ratio of **2d-*d*$_3$**:**2d-*d*$_2$** = 4.6 in the mono-Pummerer products, which is in the range of those from **1a-*d*$_3$**−**1c-*d*$_3$** having π-conjugate spacer (runs 4 vs 1, 2, and 3 in Table 2). Second, the reaction of **1e-*d*$_3$** as a sterically hindered analogue of **1a** gave the ratio of **2e-*d*$_3$**:**2e-*d*$_2$** = 0.47, which is in marked contrast to that obtained from **1a-*d*$_3$** (runs 5 vs 1 in Table 2). This result shows that a normal Pummerer reaction at the sulfinyl group dominates in **1e** probably due to disadvantage of an intermolecular through-space interaction between sulfur atoms by a steric hindrance of the methyl groups at the 2,6-positions of the aromatic ring. This result also indicates that an intramolecular through-bond interaction between sulfur atoms is essentially unfavorable.

Conclusion

We have demonstrated that the remote Pummerer-type reaction proceeds via an intermolecular through-

---

[11] The trifluoroacetoxysulfonium salt **D** and the bis-sulfonium salt **E** were detected at −40 °C by the ^{1}H NMR spectra of the reaction mixture of **1** or **4** and **5** with TFAA in CDCl$_3$. The signals of the mono-sulfoxide **1** and the bis-sulfoxide **5** in the ^{1}H NMR instantaneously disappeared when added TFAA to them, and those of **D** and **E** appeared, respectively. The chemical shifts of methylsulfonium groups of **D** and **E** are shifted downfield by ca. 0.3 ppm relative to those of methylsulfinyl groups of **1** and **5**, respectively.

[12] An another intermediate from a reaction of the sulfonium salt **D** with **1** might be formed. However, this is not the case, because at the initial stage of the present reaction **1** was completely consumed by TFAA and **D** was instantaneously produced.[11]

space interaction between the sulfonium and the sulfenyl sulfur atoms which is much more favorable than an intramolecular through-bond interaction and the abstraction of an α-proton of the sulfonium group leading to the Pummerer product. The results presented here may provide for the understanding of the electric conductivity mechanisms of materials bearing sulfur functionalities.[4,13,14]

Experimental Section

General. ^{1}H NMR spectra were recorded at 270 or 400 MHz, and ^{13}C NMR spectra were taken at 67.5 or 100 MHz. High-resolution mass spectra (HRMS) were recorded at 70 eV by electron impact. Preparative HPLC was performed on a Japan Analytical Industry Co., Ltd., model LC-908. Dichloromethane and THF were distilled from CaH_2 and sodium−benzophenone ketyl, respectively, under N_2. Trifluoroacetic anhydride (TFAA) was purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

Preparation of Bis-Sulfide 4. To a solution of the *p*-dibromo- or *p*-diiodo-aromatic (10.0 mmol) in dry THF (50 mL) at −78 °C under an Ar atmosphere was added a solution of *n*-BuLi in hexane (1.6 M, 13.8 mL, 22.0 mmol). After stirring for 10 min, dimethyl disulfide (2.0 mL, 22.0 mmol) was added at −78 °C. The resulting mixture was allowed to warm to room temperature overnight, pored into water, and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of solvents, the residue was subjected to column chromatography on silica gel to give **4**.

1,4-Bis(methylthio)benzene (4a):[15a] yield 72%; mp 78−79 °C; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 6H), 7.02 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 16.4, 127.6, 135.1; MS *m/z* 170 (M^+).

4,4′-Bis(methylthio)biphenyl (4b):[15a] yield 91%; mp 185−186 °C; ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 6H), 7.31, 7.49 (ABq, J = 8.4 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 15.9, 127.0, 127.1, 137.3, 137.5; MS *m/z* 246 (M^+).

Bis[4-(methylthio)phenyl] sulfide (4c):[16] yield 42%; mp 86−87 °C; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 6H), 7.18, 7.24 (ABq, J = 8.5 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 15.8, 127.1, 131.4, 132.1, 137.7; MS *m/z* 278 (M^+).

Bis[4-(methylthio)phenyl]methane (4d):[15b] yield 82%; mp 55−56 °C; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 6H), 3.89 (s, 2H), 7.09, 7.19 (ABq, J = 8.1 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 16.1, 40.8, 127.0, 129.4, 135.8, 138.0; MS *m/z* 260 (M^+).

1,4-Bis(methylthio)-2,3,5,6-tetramethylbenzene (4e): yield 54%; mp 157−158 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 6H), 2.52 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 18.9, 19.8, 136.5, 138.8; MS *m/z* 226 (M^+).

Preparation of Monooxide of *p*-Bis(methylthio)-Aromatic 1 and Bis-Sulfoxide 5. To a solution of **4** (4.0 mmol) in CH_2Cl_2 (400 mL) at −20 °C was added dropwise a solution of *m*-CPBA (707 mg, 4.1 mmol) in CH_2Cl_2 (400 mL) over a period of 10 h. The resulting mixture was stirred at −20 °C for 12 h. The reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine and dried over $MgSO_4$. After evaporation of solvent, the residue was subjected to column chromatography on silica gel to give **1** and **5**.

1-(Methylsulfinyl)-4-(methylthio)benzene (1a): yield 79%; mp 101−102 °C; ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H), 2.71 (s, 3H), 7.36, 7.56 (ABq, J = 8.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 15.2, 44.0, 124.0, 126.3, 141.6, 143.1; MS *m/z* 186 (M^+).

1,4-Bis(methylsulfinyl)benzene (5a): yield 10%; mp 129−130 °C; ^{1}H NMR ($CDCl_3$) δ 2.78 (s, 6H), 7.82 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 44.0, 124.5, 149.2; MS *m/z* 202 (M^+).

4-(Methylsulfinyl)-4′-(methylthio)biphenyl (1b): yield 56%; mp 170−171 °C; ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H), 2.77 (s, 3H), 7.35, 7.54 (ABq, J = 8.4 Hz, 4H), 7.71 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 15.6, 44.0, 124.1, 126.8, 127.5, 127.7, 136.3, 138.9, 143.4, 144.3; MS *m/z* 262 (M^+).

4,4′-Bis(methylsulfinyl)biphenyl (5b): yield 20%; mp 132−133 °C; ^{1}H NMR ($CDCl_3$) δ 2.79 (s, 6H), 7.76 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 44.0, 124.2, 128.2, 142.6, 145.5; MS *m/z* 278 (M^+).

[4-(Methylsulfinyl)phenyl]-[4′-(methylthio)phenyl] sulfide (1c): yield 63%; mp 66−67 °C; ^{1}H NMR ($CDCl_3$) δ 2.51 (s, 3H), 2.71 (s, 3H), 7.25, 7.40 (ABq, J = 8.4 Hz, 4H), 7.29, 7.51 (ABq, J = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 15.3, 43.8, 124.2, 126.9, 127.9, 128.4, 134.2, 140.2, 142.5, 142.8; MS *m/z* 294 (M^+).

Bis[4-(methylsulfinyl)phenyl] sulfide (5c): yield 21%; mp 92−93 °C; ^{1}H NMR ($CDCl_3$) δ 2.75 (s, 6H), 7.49, 7.61 (ABq, J = 8.4 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 43.9, 124.5, 131.6, 138.7, 145.0; MS *m/z* 310 (M^+).

[4-(Methylsulfinyl)phenyl]-[4′-(methylthio)phenyl]methane (1d): yield 46%; mp 41−42 °C; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H), 2.71 (s, 3H), 3.99 (s, 2H), 7.10, 7.33 (ABq, J = 8.2 Hz, 4H), 7.21, 7.56 (ABq, J = 8.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 15.8, 41.0, 43.8, 123.7, 126.8, 129.3, 129.7, 136.2, 136.8, 143.1, 144.4; MS *m/z* 276 (M^+).

Bis[4-(methylsulfinyl)phenyl]methane (5d): yield 23%; oil; ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 6H), 4.10 (s, 2H), 7.35, 7.60 (ABq, J = 8.2 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 41.4, 43.9, 123.9, 129.9, 143.4, 143.7; MS *m/z* 292 (M^+).

1-(Methylsulfinyl)-4-(methylthio)-2,3,5,6-tetramethylbenzene (1e): yield 72%; mp 181−182 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3H), 2.56 (s, 6H), 2.58 (s, 6H), 2.89 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 15.9, 18.7, 18.8, 38.5, 133.9, 134.3, 140.0, 140.4; MS *m/z* 242 (M^+).

Preparation of 1-d_3. To a solution of **1** (1.0 mmol) in dry THF (10 mL) at room temperature under an Ar atmosphere was added a solution of sodium (90 mg, 3.9 mmol) in methanol-*d* (2.0 mL, 49 mmol). The resulting mixture was stirred at room temperature for 24 h, quenched with 1 M HCl, and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of solvents, the residue was subjected to column chromatography on silica gel to give **1-d_3**. In all cases, the deuterium contents were more than 95%.

Reaction of Monooxide of *p*-Bis(methylthio)-Aromatic 1 with TFAA. Typical Procedure (Scheme 2, Table 1, Run 2). To a solution of **1b** (100 mg, 0.38 mmol) in dry CH_2Cl_2 (6 mL) at −20 °C under an Ar atmosphere was added TFAA (270 μL, 1.91 mmol). The mixture was allowed to warm to room temperature for 10 h, and saturated aqueous $NaHCO_3$ was added to quench the reaction. The aqueous layer was quickly extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of solvent, an analytically pure mixture of **2b**, **3b**, and **4b** was obtained (134 mg), and the ratio was determined to be **2b**:**3b**:**4b** = 3.1:1.0:1.0 by the integration of the ^{1}H NMR spectrum. The separation of the mixture was performed with preparative HPLC eluted with $CHCl_3$.

1-[(Trifluoroacetoxy)methylthio]-4-(methylthio)benzene (2a): oil; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3H), 5.55 (s, 2H), 7.20, 7.40 (ABq, J = 7.8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 15.3, 73.1, 114.2 ($^1J_{CF}$ = 283.9 Hz), 126.7, 128.3, 132.8, 140.3, 156.8 ($^2J_{CF}$ = 42.9 Hz); MS *m/z* 282 (M^+); HRMS calcd for $C_{10}H_9F_3O_2S_2$ 281.9996, found 282.0025.

---

[13] The conductivity of oligothiophenes results from a π-dimer of the radical cation, as well as a π-conjugation of polarons/bipolarons. (a) Hill, M. G.; Penneau, J.-F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106−1113. (b) Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113−1118. (c) Miller, L. L.; Mann, K. R. *Acc. Chem. Res.* **1996**, *29*, 417−423. (d) Graf, D. D.; Duan, R. G.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 5888−5899.

[14] The 1,2,4,6-chalcogenatriazinyl radicals and the diradical benzo-1,2:4,5-bis(1,3,2-dithiazolyl) form dimers having chalcogen−chalcogen bonds, respectively. (a) Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 7745−7749. (b) Barclay, T. M.; Cordes, A. W.; de Laat, R. H.; Goddard, J. D.; Haddon, R. C.; Jeter, D. Y.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Patenaude, G. W.; Reed, R. W.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2633−2641.

[15] (a) Engman, L.; Hellberg, J. S. E. *J. Organomet. Chem.* **1985**, *296*, 357−366. (b) Streitwieser, A., Jr.; Vorpagel, E. R.; Chen, C.-C. *J. Am. Chem. Soc.* **1985**, *107*, 6970−6975.

[16] Tsuchida, E.; Yamamoto, K.; Nishide, H.; Yoshida, S.; Jikei, M. *Macromolecules* **1990**, *23*, 2101−2106.

1,4-Bis[(trifluoroacetoxy)methylthio]benzene (3a): oil; ^{1}H NMR (CDCl$_3$) δ 5.62 (s, 4H), 7.46 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 72.0, 114.2 ($^1J_{CF}$ = 284.1 Hz), 132.1, 133.5, 156.8 ($^2J_{CF}$ = 42.7 Hz); MS *m/z* 394 (M$^+$); HRMS calcd for $C_{12}H_8F_6O_4S_2$ 393.9768, found 393.9743.

4-[(Trifluoroacetoxy)methylthio]-4′-(methylthio)biphenyl (2b): mp 107−108 °C; ^{1}H NMR (CDCl$_3$) δ 2.53 (s, 3H), 5.64 (s, 2H), 7.32, 7.50 (ABq, *J* = 8.4 Hz, 4H), 7.55 (d, *J* = 2.6 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 15.6, 72.7, 114.3 ($^1J_{CF}$ = 283.9 Hz), 126.7, 127.2, 127.6, 131.4, 132.2, 136.5, 138.4, 140.9, 156.8 ($^2J_{CF}$ = 43.0 Hz); MS *m/z* 358 (M$^+$); HRMS calcd for $C_{16}H_{13}F_3O_2S_2$ 358.0309, found 358.0319.

4,4′-Bis[(trifluoroacetoxy)methylthio]biphenyl (3b): oil; ^{1}H NMR (CDCl$_3$) δ 5.65 (s, 4H), 7.57 (s, 8H); ^{13}C NMR (CDCl$_3$) δ 72.5, 114.3 ($^1J_{CF}$ = 283.9 Hz), 127.9, 132.2, 132.4, 140.2, 156.9 ($^2J_{CF}$ = 43.0 Hz); MS *m/z* 470 (M$^+$); HRMS calcd for $C_{18}H_{12}F_6O_4S_2$ 470.0081, found 470.0106.

{4-[(Trifluoroacetoxy)methylthio]phenyl}-[4′-(methylthio)phenyl] sulfide (2c): mp 84−85 °C; ^{1}H NMR (CDCl$_3$) δ 2.50 (s, 3H), 5.57 (s, 2H), 7.17, 7.36 (ABq, *J* = 8.2 Hz, 4H), 7.23, 7.36 (ABq, *J* = 8.2 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 15.3, 72.7, 114.2 ($^1J_{CF}$ = 283.6 Hz), 126.9, 129.0, 129.3, 130.1, 132.5, 133.6, 138.9, 139.5, 156.7 ($^2J_{CF}$ = 42.9 Hz); MS *m/z* 390 (M$^+$); HRMS calcd for $C_{16}H_{13}F_3O_2S_3$ 390.0030, found 390.0035.

Bis{4-[(trifluoroacetoxy)methylthio]phenyl} sulfide (3c): oil; ^{1}H NMR (CDCl$_3$) δ 5.61 (s, 4H), 7.31, 7.42 (ABq, *J* = 7.9 Hz, 8H); ^{13}C NMR (CDCl$_3$) δ 72.3, 114.2 ($^1J_{CF}$ = 283.5 Hz), 131.7, 131.9, 132.0, 132.4, 156.8 ($^2J_{CF}$ = 43.0 Hz); MS *m/z* 502 (M$^+$); HRMS calcd for $C_{18}H_{12}F_6O_4S_3$ 501.9802, found 501.9813.

{4-[(Trifluoroacetoxy)methylthio]phenyl}-[4′-(methylthio)phenyl]methane (2d): oil; ^{1}H NMR (CDCl$_3$) δ 2.45 (s, 3H), 3.93 (s, 2H), 5.56 (s, 2H), 7.09, 7.19 (ABq, *J* = 8.2 Hz, 4H), 7.16, 7.40 (ABq, *J* = 8.1 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 16.0, 40.9, 73.0, 114.2 ($^1J_{CF}$ = 284.1 Hz), 127.0, 129.4, 129.9, 130.1, 132.3, 136.1, 137.2, 141.9, 156.9 ($^2J_{CF}$ = 42.9 Hz); MS *m/z* 372 (M$^+$); HRMS calcd for $C_{17}H_{15}F_3O_2S_2$ 372.0466, found 372.0479.

Bis{4-[(trifluoroacetoxy)methylthio]phenyl}methane (3d): oil; ^{1}H NMR (CDCl$_3$) δ 3.98 (s, 2H), 5.58 (s, 4H), 7.17, 7.42 (ABq, *J* = 8.2 Hz, 8H); ^{13}C NMR (CDCl$_3$) δ 41.0, 72.9, 114.3 ($^1J_{CF}$ = 283.7 Hz), 129.9, 130.4, 132.3, 141.2, 156.8 ($^2J_{CF}$ = 42.7 Hz); MS *m/z* 484 (M$^+$); HRMS calcd for $C_{19}H_{14}F_6O_4S_2$ 484.0238, found 484.0247.

1-[(Trifluoroacetoxy)methylthio]-4-(methylthio)-2,3,5,6-tetramethylbenzene (2e): mp 57−58 °C; ^{1}H NMR (CDCl$_3$) δ 2.20 (s, 3H), 2.54 (s, 6H), 2.60 (s, 6H), 5.42 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 18.9, 19.8, 20.2, 73.8, 114.3 ($^1J_{CF}$ = 283.8 Hz), 131.5, 138.6, 139.3, 139.4, 156.9 ($^2J_{CF}$ = 42.5 Hz); MS *m/z* 338 (M$^+$); HRMS calcd for $C_{14}H_{17}F_3O_2S_2$ 338.0622, found 338.0614.

1,4-Bis[(trifluoroacetoxy)methylthio]-2,3,5,6-tetramethylbenzene (3e): mp 110−111 °C; ^{1}H NMR (CDCl$_3$) δ 2.56 (s, 12H), 5.43 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 20.3, 73.5, 114.3 ($^1J_{CF}$ = 283.5 Hz), 133.4, 140.0, 156.9 ($^2J_{CF}$ = 41.9 Hz); MS *m/z* 450 (M$^+$); HRMS calcd for $C_{16}H_{16}F_6O_4S_2$ 450.0394, found 450.0416.

Reaction of a 1:1 Mixture of Bis-Sulfide 4 and Bis-Sulfoxide 5 with TFAA. Typical Procedure (Scheme 5, Table 4, Run 4). To a solution of **4d** (110 mg, 0.42 mmol) and **5d** (123 mg, 0.42 mmol) in dry CH_2Cl_2 (10 mL) at −20 °C under an Ar atmosphere was added TFAA (600 μL, 4.23 mmol). The mixture was allowed to warm to room temperature for 10 h, and saturated aqueous $NaHCO_3$ was added to quench the reaction. The aqueous layer was quickly extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation of solvent, an analytically pure mixture of **2d**, **3d**, and **4d** was obtained (272 mg), and the ratio was determined to be **2d**:**3d**:**4d** = 2.3:1.0:1.1 by the integration of the ^{1}H NMR spectrum. The separation of the mixture was performed with preparative HPLC eluted with $CHCl_3$.

Acknowledgment. This work was supported in part by grants-in-aid from the Ministry of Education, Science, Sports and Culture, Japan (No. 09239103) and University of Tsukuba (TARA project fund).

Supporting Information Available: Copies of ^{1}H NMR spectra for compounds **1a**−**1e**, **2a**−**2e**, **3a**−**3e**, **4a**−**4e**, and **5a**−**5d**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO982377H