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Reactions of Selenurane [10-Se-4 (C4)] with Alcohols, Thiols and Selenol. A Quest for Formation of a New σ-Selenurane [10-Se-4 (C3O)], [10-Se-4 (C3S)] or [10-Se-4 (C3Se)]

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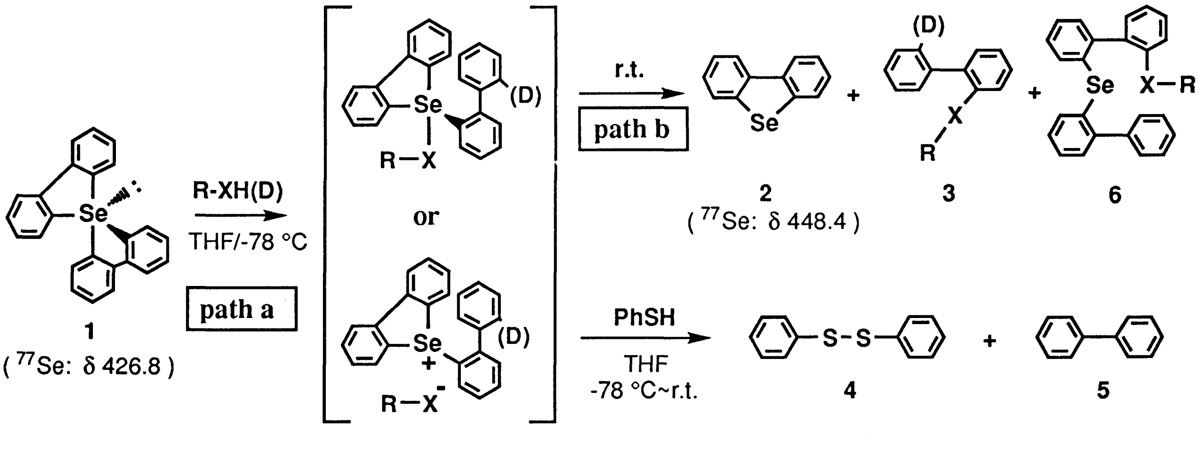
Bis(2,2'-biphenylylene)selenurane readily reacts with various alcohols, phenols, thiols and selenol to give ligand coupling or ipso-substitution products under mild conditions via a two-step mechanism involving a σ-selenurane [10-Se-4 (C3O)], [10-Se-4 (C3S)] and [10-Se-4 (C3Se)] or corresponding selenonium salts as intermediates.

Several stable σ-selenuranes bearing electronegative ligands such as oxygen or halogen atoms have been reported.1) However, those compounds having only carbon ligands [10-Se-4 (C4)] are unstable and undergo either ligand coupling reactions at room temperature2) or carbon-selenium bond cleavage to give the corresponding selenonium salts by acid and water. We have succeeded in the detection of tetraphenylselenurane and 2,2'-biphenylylene diphenylselenurane by NMR3) while bis(2,2'-biphenylylene)-selenurane (**1**) was first isolated by Hellwinkel.4) We have reported the results of the solution-state structure of selenurane **1**,5) but few studies on the reactivity have been reported. Here we present the results on the reactions of bis(2,2'-biphenylylene)selenurane **1** with various alcohols, phenols, thiols and selenols.



(**A**: ^{77}Se, δ 518.9; **B**: ^{77}Se, δ 505.3; **C**: ^{77}Se, δ 504.6, 287.8)

path a : Protonation
path b : Ligand Coupling or Ipso-Substitution Reaction

Scheme 1. [**A**: (X=O), **B**: (X=S) and **C**: (X=Se)].

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When one or two equimolar amounts of alcohols (ROH), thiols (RSH) and phenylselenol (PhSeH) were added to a solution of selenurane **1** in anhydrous THF under argon at -78 °C, the mixture became a yellow or red-orange solution. By elevating the temperature of the solution to room temperature, the solution turned colorless. After work-up the products were separated and their structures and yields were determined conventionally. The results are listed in Table 1. The reactions of **1** with alcohols and phenols gave solely the coupling products (**2**) and (**3**) in high yields while with an equimolar amount of thiols three coupling products **2**, **3** and **6** were obtained. Furthermore 2 eq. molars of PhSH gave not only **3** and **6** but also diphenyl disulfide (**4**) and biphenyl (**5**) in 30 and 28% yields, respectively. The reaction with methanol-*d* (MeOD) gave 2-deuterio derivative of compound **3**.$^{6)}$

Table 1. Reactions of Selenurane **1** with Alcohols, Thiols and Selenol

		Yield/%					
R-XH	eq.	2	3	4	5	6	R-XH
PhOH	1.0	97	89	-	-	-	-
PhOH	2.0	99	85	-	-	-	98
MeOH	1.0	87	86	-	-	-	-
EtOH	1.0	91	85	-	-	-	-
i-PrOH	1.0	71	65	-	-	-	-
t-BuOH	1.0	89	71	-	-	-	-
MeOD	1.0	88	86^{a}	-	-	-	-
PhSH	1.0	75	60	trace	trace	25	-
PhSH	2.0	70	50	30	28	20	-
t-BuSH	1.0	80	74	trace	trace	19	-
PhSeH	1.0	80	61	-	-	14	-

a) 2-Deuterio-2'-methoxybiphenyl.

In order to understand whether the reactions proceed via the formation of σ-selenurane, i.e., [10-Se-4 (C3O)] or [10-Se-4 (C3S)] or via selenonium salts, the ^{1}H, ^{13}C and ^{77}Se NMR spectra of the reaction of **1** with PhOH and PhSH were measured in situ at -20 °C.$^{7)}$ The ^{77}Se NMR signal of the selenurane **1** was observed at 426.8 ppm at -20 °C.$^{2)}$ On careful treatment of selenurane **1** in anhydrous THF solution with a half-equimolar amount of PhOH or PhSH at -20 °C, a new ^{77}Se NMR signal appeared at 518.9 ppm (**A**) or at 505.3 ppm (**B**) together with a signal of selenurane **1**. The ^{77}Se NMR signal of the solution containing a 1:1 or 1:2 ratio of selenurane **1** and PhSH or PhOH appeared only at the new signals corresponding to that of the intermediate **A** or **B**, and no other signals were observed at all at -20 °C. By elevating the temperature of this solution to 20 °C, the ^{77}Se NMR signal of intermediate **A** or **B** disappeared and was converted to that of the products; dibenzoselenophene (**2**) and 2-(2'-phenylthio)biphenyl-2"-biphenylselenide (**6**) at 20 °C (the chemical shifts of **2** and **6** were observed at 448.5 and 376.8 ppm in THF and $CDCl_3$ at 22 °C). The ^{1}H and ^{13}C chemical shifts of **A** or **B** were determined by the cross peaks observed in the two-dimensional HH and CH shift correlation (HH and CH COSY) NMR spectrum.$^{8,9)}$

The results demonstrate clearly that present reaction proceeds by the proton-initiated ring opening of selenurane **1** followed by the formation of intermediate **A** or **B**, from which the ligand coupling or ipso-substitution takes place as shown in Scheme 1. The question remains is whether the structure of the intermediate **A** or **B** is a hypervalent compound or an onium salt. Although the ^{77}Se chemical shifts of the intermediate are nearly identical to that of 2,2'-biphenylylene-2''-biphenylselenonium chloride (**7**) (^{77}Se; 508.4 ppm),9) it is reasonable to assume that the intermediates **A** and **B** possess the selenurane structures because the trend of these small ^{77}Se NMR chemical shifts agrees with that observed in the case of ^{125}Te NMR chemical shifts between the telluronium chloride and tellurane having one phenoxy ligand of which structure was confirmed by X-ray crystallographic analysis.10)

Furthermore, the reaction of selenurane **1** with selenophenol (PhSeH) was monitored by ^{77}Se NMR (Figure 1). On careful treatment of selenurane **1** in anhydrous THF solution with one equimolar amount of PhSeH at -50 °C, only one ^{77}Se NMR signal appeared at 504.6 ppm. By lowering the temperature to -110 °C, another broad signal of ^{77}Se NMR appeared at 287.8 ppm together with the signal at ppm in a 1 to 1 ratio. This ^{77}Se chemical shift was quite different from that of PhSeH (148.3 ppm) or PhSeNa (26.8 ppm). Though the ^{77}Se-^{77}Se coupling between selenium and selenium was not observed owing to the broadening of these peaks, the result suggests that the intermediate **C** should be the tetracoordinated selenurane in solution and the pseudorotations take place slowly in the NMR time scale at low temperature.5)

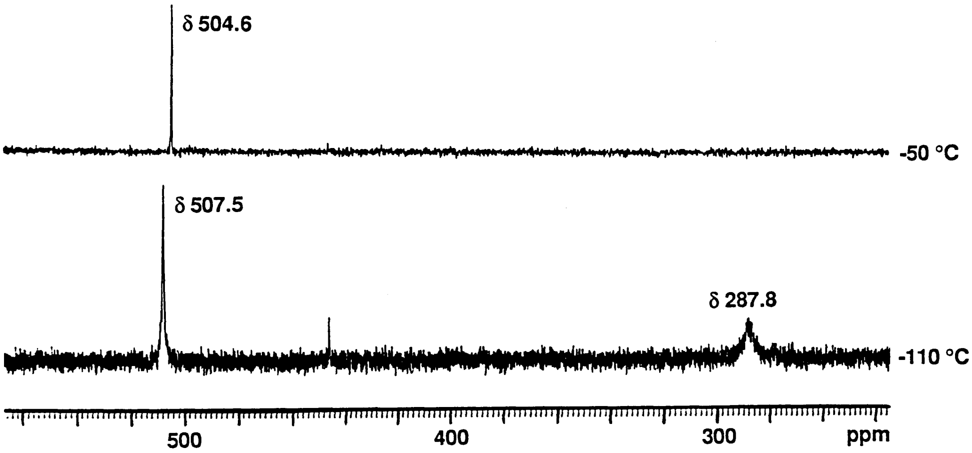

Fig. 1. ^{77}Se NMR spectra of the reaction of selenurane **1** with PhSeH.

Recently, we have reported that bis(2,2'-biphenylylene)sulfurane reacts readily with various alcohols and phenols to give the corresponding 2-alkoxy or 2-phenoxybiphenyls in high yields, and this reaction could be used as a possible reagent for detection of the OH group.11) Selenurane **1** may also serve as a useful reagent for trapping of active proton compounds. Further examination of the reactions of **1** with other reagents is in progress in this laboratory.

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References

1) H. J. Reich, *J. Am. Chem. Soc.*, **95**, 964 (1973); B. Dahlen and B. Lindgren, *Acta. Chem. Scand.*, **27**, 2218 (1973); D. G. Garratt and G. H. Schmid, *Can. J. Chem.*, **52**, 1026, 3599 (1974); B. Dahlen, *Acta. Cryst.*, **B30**, 647 (1974); D. B. Denny, D. Z. Denny, Ph. J. Hammond, and Y. F. Hsu, *J. Am. Chem. Soc.*, **103**, 2340 (1981); J. C. Martin, *Science*, **221**, 509 (1983).

2) S. Ogawa, S. Sato, and N. Furukawa, *Tetrahedron Lett.*, **33**, 7925 (1992).

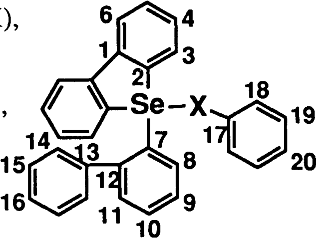
3) S. Ogawa, S. Sato, T. Erata, and N. Furukawa, *Tetrahedron Lett.*, **32**, 3179 (1991).

4) D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, **715**, 68 (1968).

5) S. Ogawa, S. Sato, T. Erata, and N. Furukawa, *Tetrahedron Lett.*, **33**, 1915 (1992).

6) All NMR spectra were recorded on a JEOL EX-270.

7) 2-Deuterio-2'-methoxybiphenyl ^{1}H NMR (270 MHz, CDCl$_3$, 22 °C) δ 3.80 (s, 3H, CH$_3$), 6.98-7.05 (m, 2H, ArH), 7.28-7.43 (m, 5H, ArH), 7.51-7.54 (m, 1H, ArH); ^{13}C NMR (68 MHz, CDCl$_3$, 22 °C) δ 55.5, 111.2, 120.8, 126.9, 127.8, 128.0, 128.6, 129.5, 130.9, 138.4, 156.4; MS (m/z): 185 (M$^+$), 170 (M$^+$-15).



8) **A**: ^{1}H NMR (270 MHz, THF-d$_8$, -20 °C) δ 6.22 (t, J=7.6 Hz, 1H, 20-ArH), 6.52 (d, J=7.6 Hz, 2H, 18-ArH), 6.83 (t, J=8.1 Hz, 1H, 9-ArH), 6.87 (t, J=7.6 Hz, 2H, 19-ArH), 7.00 (t, J=8.1 Hz, 1H, 10-ArH), 7.29 (t, J=8.1 Hz, 1H, 11-ArH), 7.30 (t, J=7.6 Hz, 2H, 4-ArH), 7.36 (d, J=8.1 Hz, 1H, 12-ArH), 7.51 (t, J=7.6 Hz, 1H, 16-ArH), 7.52 (t, J=7.6 Hz, 2H, 5-ArH), 7.54 (t, J=7.6 Hz, 2H, 15-ArH), 7.86 (bd, 2H, 3-ArH), 8.04 (d, J=7.6 Hz, 2H, 14-ArH), 8.04 (d, J=7.6 Hz, 2H, 6-ArH); ^{13}C NMR (68 MHz, THF-d$_8$, -20 °C) δ 112.3 (C20), 120.4 (C18), 124.8 (C6), 126.2 (C9), 129.5 (C19), 129.8 (C16), 129.9 (C10), 130.2 (C15), 130.5 (C4), 131.4 (C14), 131.6 (C11), 132.1 (C3), 132.3 (C12), 132.8 (C5), 137.7 (C13), 138.9 (C8), 140.0 (C1), 140.9 (C2), 142.1 (C7), 169.7 (C17).

B: ^{1}H NMR (270 MHz, THF-d$_8$, -20 °C) δ 6.72 (t, J=7.3 Hz, 1H, 20-ArH), 6.79 (d, J=8.1 Hz, 1H, 9-ArH), 6.95 (t, J=7.3 Hz, 2H, 19-ArH), 7.01 (t, J=8.1 Hz, 1H, 10-ArH), 7.30 (t, J=7.6 Hz, 2H, 4-ArH), 7.32 (t, J=8.1 Hz, 1H, 11-ArH), 7.39 (d, J=8.1 Hz, 1H, 12-ArH), 7.45 (d, J=7.3 Hz, 2H, 18-ArH), 7.48 (t, J=7.6 Hz, 2H, 5-ArH), 7.58 (t, J=7.3 Hz, 1H, 16-ArH), 7.63 (t, J=7.3 Hz, 2H, 15-ArH), 7.92 (d, J=7.6 Hz, 2H, 6-ArH), 8.01 (bd, 2H, 3-ArH), 8.44 (d, J=7.3 Hz, 2H, 14-ArH); ^{13}C NMR (68 MHz, THF-d$_8$, -20 °C) δ 120.4 (C20), 124.9 (C6), 126.5 (C9), 128.1 (C19), 130.1 (C10), 130.2 (C16), 130.4 (C4), 130.4 (C15), 131.2 (C14), 131.9 (C3), 131.9 (C11), 132.5 (C12), 133.1 (C5), 134.6 (C18), 137.7 (C13), 138.4 (C8), 140.2 (C1), 141.0 (C7), 141.4 (C2), 158.4 (C17).

9) **7**: ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.90 (d, J=7.8 Hz, 1H, 9-ArH), 7.19 (dd, J=7.8, 8.8 Hz, 1H, 10-ArH), 7.43 (t, J=8.8 Hz, 1H, 11-ArH), 7.44 (t, J=7.6 Hz, 2H, 4-ArH), 7.45 (d, J=8.8 Hz, 1H, 12-ArH), 7.59 (t, J=7.3 Hz, 1H, 16-ArH), 7.65 (t, J=7.6 Hz, 2H, 5-ArH), 7.69 (t, J=7.3 Hz, 2H, 15-ArH), 7.92 (d, J=7.6 Hz, 2H, 6-ArH), 8.06 (d, J=7.6 Hz, 2H, 3-ArH), 8.24 (d, J=7.3 Hz, 2H, 14-ArH); ^{13}C NMR (68 MHz, CDCl$_3$) δ 124.0 (C6), 126.0 (C9), 129.6 (C16), 129.8 (C10), 129.8 (C15), 130.5 (C4), 130.5 (C14), 131.9 (C3), 131.9 (C11), 132.1 (C12), 133.0 (C5), 134.5 (C13), 134.8 (C8), 138.1 (C1), 141.0 (C2), 142.2 (C7); ^{77}Se NMR (51 MHz, CDCl$_3$) δ 508.4. See; X-ray crystallographic analysis of triphenylselenonium salt : R. V. Mitchan, B. Lee, K. B. Mertes, and R. F. Ziolo, *Inorganic Chemistry*, **18**, 3498 (1979); P. Ash, Jung-S. Lee, D. D. Titus, K. B. Mertes, and R. F. Ziolo, *J. Organomet. Chem.*, **135**, 91 (1977).

10) S. Sato, N. Kondo, and N. Furukawa, Submitted.

11) N. Furukawa, Y. Matsunaga, and S. Sato, *SYNLETT*, **1993**, 655.

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