CHEMISTRY LETTERS, pp. 675-678, 1983.

THE STRUCTURE OF HALOGEN ADDUCTS OF SOME SELENIDES AND A TELLURIDE IN SOLUTION STUDIED BY ^{1}H AND ^{13}C NMR SPECTROSCOPY. EVIDENCE FOR THE FORMATION OF A MOLECULAR COMPLEX OF SELENOXANTHONE WITH BROMINE

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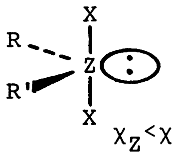
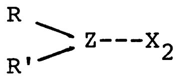
^{1}H and ^{13}C NMR chemical shifts of dimethyl selenide, selenoanisole, diphenyl selenide, phenoxyselenine, and phenoxytellurine and their chlorine, bromine, and iodine adducts have been measured to disclose the structure of the adducts in solution. The bromine adduct of selenoxanthone was found to have the structure of a molecular complex. The relative stability of selenuranes is discussed.

Selenides react with halogens or the O-O bond of peroxides to give selenuranes.[1)] The apical bonds in selenuranes thus formed are very polar and described as "three-center four-electron bonds".[2)] Since the stability of selenuranes is governed by the polarity of the apical bonds, the electronegative fluorine, chlorine, bromine, and oxygen atoms are considered to be a good ligand for the formation of selenuranes.[3)] Electronegativity of iodine is not larger than that of selenium and, therefore, selenides react with iodine to form molecular complexes.



$\chi_Z < \chi_X$



$\chi_Z > \chi_X$

Z,X	O	S	Se	Te	F	Cl	Br	I
χ	3.50,	2.44,	2.48,	2.01,	4.10,	2.83,	2.74,	2.21.

If the effective electronegativity of selenium in a selenide is modulated chemically increased by electron-withdrawing substituent(s), there is a chance of having an intermediate case; the selenide may form a molecular complex with bromine. We wish to report here such an instance.

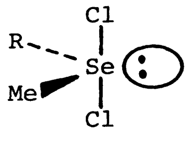
^{1}H and ^{13}C NMR chemical shifts of dimethyl selenide (1a), selenoanisole (2a), and diphenyl selenide (3a), and their chlorine, bromine, and iodine adducts (for example, 3b, 3c, and 3d, respectively) have been measured to see if the chemical shift data can be used as a criterion for differentiating between a selenurane and a molecular complex (Tables 1 and 2). ^{1}H and ^{13}C chemical shifts of the methyl groups in chlorine adducts (1b and 2b, respectively) of 1a and 2a are at ca. 1.6 and 39 ppm downfield from those of 1a and 2a, respectively. The chemical shifts of iodine adduct (1d) of 1a from those of 1a are ca. 0.5 and 8 ppm, respectively. The magnitude of the chemical shifts of the chlorine and iodine adducts from the selenides should be due to the formation of selenuranes and a molecular complex, respectively. The ring carbon chemical shifts in 2b are characterized by the large downfield shifts (ca. 9 and 6 ppm, respectively) of the C-1 and C-4 carbons from those of 2a.

A similar trend can be seen in the ring carbon chemical shifts of diphenyl selenides (Table 2). While large downfield shifts in C-1 and C-4 carbons are observed in 3b and 3c relative to 3a, those are small in 3d. The results suggest that 3b and 3c are selenuranes but 3d is a molecular complex in this solution (chloroform-d). It should be noted that the C-1 carbon chemical shifts of 3b and 3c from that of 3a are 11.4 and 8.0 ppm, respectively, but those of C-4 are 4.4 and 4.3 ppm, respectively. The former depends on the different electronegativity of halogens but the latter does not.$^{4)}$

Table 1. ^{13}C NMR chemical shifts of dimethyl selenides and selenoanisoles

Compound	H(Me)	C(Me)	C-1	C-2	C-3	C-4
1a	2.00	6.0				
1b	3.64	44.8				
1d	2.48	14.2				
2a	2.31	7.2	131.7	130.2	128.8	125.9
2b	3.90	45.7	141.0	128.5	129.9	131.7

Ppm from TMS in $CDCl_3$.

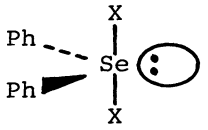


	1b	2b
R	Me	Ph

Table 2. ^{13}C NMR chemical shifts of diphenyl selenides

Compound	C-1	C-2	C-3	C-4
3a	131.0	132.8	129.2	127.2
3b	142.4	131.2	129.7	131.6
3c	139.0	132.4	129.8	131.5
3d	133.8	132.6	129.5	128.2
3d + $2I_2$	134.6	132.4	129.6	128.8

Ppm from TMS in $CDCl_3$.



	3b	3c
X	Cl	Br

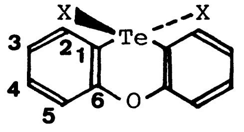
$Ph_2Se{-}{-}{-}I_2$

3d

Table 3. ^{13}C NMR chemical shifts of phenoxytellurines

Compound	C-1	C-2	C-3	C-4	C-5	C-6
4a	103.9	135.1	125.2	128.7	118.9	155.2
4b	119.2	133.8	124.5	133.2	118.9	151.1
4c	115.2	134.4	124.7	133.2	118.8	151.5
4d	109.4	135.3	124.9	132.9	118.7	152.4

Ppm from TMS in DMSO-d_6.



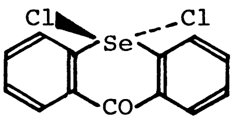
	4b	4c	4d
X	Cl	Br	I

The characteristic C-1 and C-4 carbon chemical shifts due to the formation of trigonal bipyramidal adducts are further confirmed by examination of the halogen adducts of a telluride because tellurides are known to react with iodine to form tellururanes.3) ^{13}C NMR chemical shifts of halogen adducts of phenoxytellurine (4a) are collected in Table 3. The downfield shifts of C-1 carbons in the chlorine, bromine, and iodine adducts (4b, 4c, and 4d, respectively) of 4a from that of 4a are 15.1, 11.3, and 5.5 ppm, respectively. A minor but opposite effect of halogens on the chemical shifts is observed in C-2 and C-6 carbons. On the other hand, the downfield shifts of C-4 in 4b, 4c, and 4d from that of 4a are 4.5, 4.5, and 4.2 ppm, respectively. From the above results, we note that the structure of halogen adducts of selenides can be represented by ^{13}C chemical shifts of the C-1 and C-4 carbons.

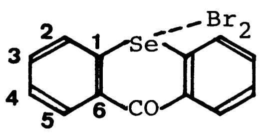
Table 4. ^{13}C NMR chemical shifts of selenoxanthones[a)]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C=O
5a	134.9	128.1	132.0	126.6	131.2	130.8	181.7
5b	142.7	128.5	134.7	132.7	132.1	128.7	179.8
5c	b)	128.3	132.1	126.7	131.4	b)	b)
5d	134.8	128.2	132.1	126.7	131.3	130.8	181.8

a) Ppm from TMS in $CDCl_3$. b) Unobserved due to broadning.



5b

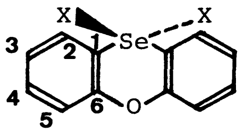


5c

Table 5. ^{13}C NMR chemical shifts of phenoxyselenines

Compound	C-1	C-2	C-3	C-4	C-5	C-6
6a	116.2	129.3	124.9	128.1	118.6	152.9
6b	120.6	129.2	125.7	134.3	119.9	147.6
6c	116.9	129.8	126.0	134.1	119.9	148.1
6d	115.3	129.4	125.0	128.6	118.7	152.6

Ppm from TMS in $CDCl_3$.



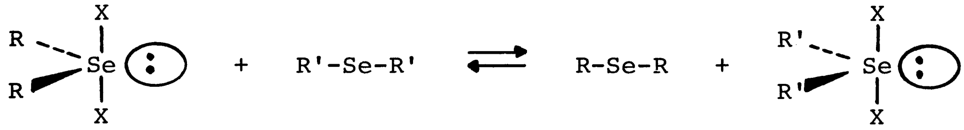
	6b	6c
X	Cl	Br

^{13}C NMR chemical shifts of selenoxanthone (5a) and the chlorine, bromine, and iodine adducts5) (5b, 5c, and 5d, respectively) are given in Table 4. The C-1 and C-4 carbons in 5b are shifted downfield by 7.8 and 6.1 ppm, respectively, from those of 5a showing the formation of a selenurane in contrast to those of 5d which is a molecular complex. Now, the structure of the bromine adduct (5c) should be discussed.

Since the chemical shift values of C-4 as well as C-2, C-3, and C-5 carbons are almost the same as those of 5d (and 5a) which must be a molecular complex, and different from those of 5b which is a selenurane. Electronegativity of the selenium atom in 5a must be higher than those of the same atom in simple selenides such as **3a** because of the neighboring electron-withdrawing carbonyl group. If electronegativity of bromine is not enough higher than that of selenium in **5a**, a stable selenurane may not be formed.

The cyclic structure in **5c** is not necessarily responsible for the formation of the molecular complex because phenoxyselenine (**6a**) reacts with bromine to form a stable selenurane (**6c**).6) ^{13}C NMR chemical shifts of **6a**, **6c**, and the chlorine and iodine adducts (**6b** and **6d**, respectively) of **6a** are collected in Table 5. The downfield shifts of C-4 in **6b**, **6c**, and **6d** from that of **6a** are 6.2, 6.0, and 0.5 ppm, respectively, which shows that **6c**, as well as **6b**, is a selenurane7) irrespective of the cyclic structure.

A selenide reacts with another selenide dichloride to form a new set of the selenide dichloride and selenide if the new selenide dichloride is more stable than the old.1a) The order of stability in the selenurane formation was obtained



as **5b** < **3b** < **1b** by application of the ligand exchange reaction. The results are in accord with the idea of the effective electronegativity discussed above.

This work was supported by the Joint Studies Program (1982) of the Institute for Molecular Science and by the Grant-in-Aids for Scientific Research from the Ministry of Education, Science, and Culture (No. 57740266).

References

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2) I. C. Paul, J. C. Martin, and E. F. Perozzi, J. Am, Chem. Soc., 94, 5010 (1972).

3) N. C. Baenziger, R. E. Bucklen, R. J. Maner, and T. D. Simpson, J. Am. Chem. Soc., 91, 5749 (1969).

4) For the interpretation of ^{13}C chemical shifts see, N. Inamoto and S. Masuda, Kagaku no Ryoiki, 33, 105 (1979).

5) **5b**: pale yellow prisms; mp(dec) 205 – 220 °C. Found: C, 47.07; H, 2.24%. Calcd for $C_{13}H_8Cl_2OSe$: C, 47.30; H, 2.44%.
5c: red needles. This compound was decolorized at ca. 125 °C and melted at 188 – 190 °C. The melting point should be compared with that of **5a** (191 – 192 °C8)). Found: C, 37.31; H, 1.56%. Calcd for $C_{13}H_8Br_2OSe$: C, 37.27; H, 1.92 %. NMR data of **5d** were obtained using a 1 : 1 mixture of **5a** and iodine.

6) H. D. K. Drew, J. Chem. Soc., 1928, 511.

7) Although the C-1 carbon chemical shift of **6c** is only at 0.7 ppm downfield from that of **6a**, it may be a reflection of the structure of **6a** and **6c**.

8) R. Lesser and R. Weiss, Ber., 47, 2523 (1914).

(Received March 4, 1983)