CHEMISTRY LETTERS, pp. 1353-1356, 1981.

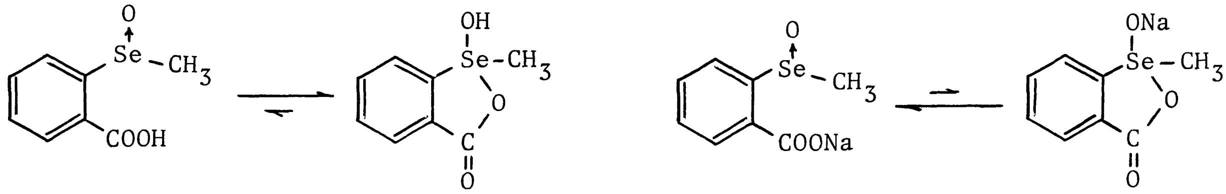
ON THE STRUCTURE OF 2-CARBOXYPHENYL METHYL SELENOXIDE AND ITS SODIUM SALT IN SOLUTION STUDIED BY ^{1}H, ^{13}C, AND ^{77}Se NMR SPECTROSCOPY

Warō NAKANISHI, Sigekazu MATSUMOTO, Yoshitsugu IKEDA,
Tadashi SUGAWARA,* Yuzo KAWADA,* and Hiizu IWAMURA*

Department of Chemistry, Faculty of Education, Wakayama University,
Masago-cho, Wakayama 640, and *Division of Applied Molecular Science,
The Institute for Molecular Science, Myodaiji, Okazaki 444

^{1}H, ^{13}C, and ^{77}Se NMR spectra of 2-carboxyphenyl methyl selenoxide, its sodium salt, and the related compounds have been measured to disclose their structures in solution. The results show that the carboxylic acid has the cyclic selenurane structure, while the salt is an acyclic selenoxide. The ^{77}Se chemical shifts and $^{1}J(^{77}Se-^{13}C)$ values are proposed to be particularly useful in distinguishing the two structures.

Since the carboxyl group in the neighborhood of the Se-O bond can act as a fourth ligand to form a selenurane, it has been a standing puzzle in organoselenium chemistry whether 2-carboxyphenyl methyl selenoxide (**1**) would be present as selenoxide **1a** or cyclic selenurane **1b**. Dahle'n has shown by X-ray crystallography that **1** has the ring closed selenurane structure with longer Se-O bonds.$^{1)}$ Trend has reported, however, that **1** shows the ^{77}Se chemical shift characteristic of selenoxide **1a** in D_2O solution.$^{2)}$ We have reexamined the structure of **1** in methanol-d_4 by NMR spectroscopy and found that **1** should be represented as cyclic selenurane **1b** in this solution. Sodium salt **2** has acyclic structure **2a**.



1a **1b** **2a** **2b**

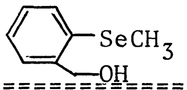
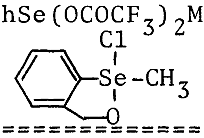
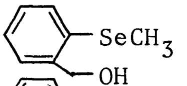
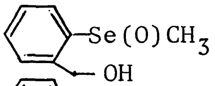
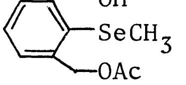
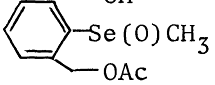
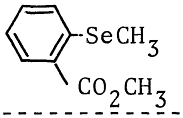
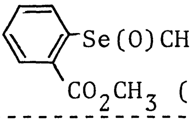
^{77}Se chemical shifts referred to dimethyl selenide (**3**) are given in Table I.$^{3)}$ When these data and some related data in the literature$^{2)}$ are examined, we note that the chemical shifts for selenuranes and selenoxides are in the range 488 ~ 794 and 822 ~ 852 ppm, respectively. The observed ^{77}Se chemical shift of **1** is just intermediate between the two. Formation of selenuranes from selenoanisole (**4**) causes downfield shifts within the range 286 ~ 536 ppm depending on electronegativity of the apical ligands (see Table II). In one case, a 639 ppm downfield shift is observed where the selenurane formation is accompanied by cyclization. On the

Table I. ^{77}Se NMR Chemical Shifts[a)]

Compound	No.	δ[b)]	δ[c)]	Compound	No.	δ[b)]	δ[c)]
MeSeMe	(3)	0	0	$PhSeCl_2Ph$		586	
PhSeMe	(4)	202	202[2)]	$PhSe(OBz)_2Me$	(9)	672	663[2)]
2-COOH	(5)	272	265[2)]	1		799[e)]	814[2)f)]
2-COOMe	(6)	265		2		830[e)]	
2-COONa	(7)	225[d)]		PhSe(O)Me	(10)	832	830[2)]
PhSePh			402[6)]	11		852	
2-COOH		470		PhSe(O)Ph		863	
2-COOMe		469					
2-COONa		435[d)]					

a) Ppm in $CDCl_3$ unless otherwise stated. b) This work. c) Lit. d) In 50% aqueous methanol. e) In Methanol. f) In D_2O.

Table II. ^{77}Se NMR Chemical Shift Differences[a)]

Compound	δ	Compound	δ	$\Delta\delta$[b)]
PhSeMe	202	$PhSeCl_2Me$	488[2)]	286
		$PhSe(OAc)_2Me$	658[2)]	456
		$PhSe(OBz)_2Me$	672, 663[2)]	470, 461
		$PhSe(OBu^t, Cl)Me$	718[2)]	516
		$PhSe(OCOCF_3)_2Me$	738[2)]	536
	155[2)]		794[2)]	639
	155[2)]		822[2)]	667
	163[2)]		816[2)]	653
PhSeMe	202	PhSe(O)Me	832, 830	630, 628
	265	 (11)	852	587
5	272, 265[2)]	1	799, 814[2)]	527, 549
7	225	2	830	605

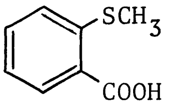
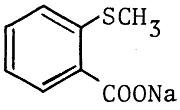
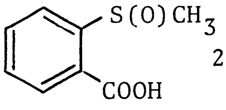
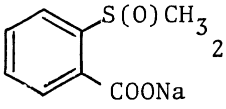
a) Chemical shifts in ppm are referred to MeSeMe. b) See text.

Table III. ^{1}H and ^{13}C NMR Data of Organoselenium Compounds

Compound	Solvent	$\delta_{C\underline{\underline{H}}_3}$ a)	$\delta_{\underline{\underline{C}}H_3}$ a)	δ_{C_i} a,b)	$J_{\underline{\underline{Se}}\underline{\underline{C}}H_3}$ c,d)	$J_{\underline{\underline{Se}}C\underline{\underline{H}}_3}$ c,e)	$J_{\underline{\underline{C}}\underline{\underline{H}}_3}$ c,d)
CH_3SeCH_3	$CDCl_3$	2.00	6.0	-----	60.4	10.1	140.6
$C_6H_5SeCH_3$	$CDCl_3$	2.31	7.2	131.7	63.8	11.0	141.9
5	CD_3OD	2.09	6.0	139.3	68.2	14.4	140.0
6	CD_3OD	2.25	5.9	139.9	68.2	14.4 (15.0$^{f)}$)	140.5
7	CD_3OD	2.16	5.9	139.7	66.9	14.4	139.7
$C_6H_5Se(Cl_2)CH_3$	$CDCl_3$	3.98	45.7	141.0	61.0	10.9	149.0
$C_6H_5Se(OBz)_2CH_3$	$CDCl_3$	3.73	35.8	138.9	64.5	10.1	146.8
$C_6H_5Se(O)CH_3$	$CDCl_3$	2.82	36.1	139.6	76.9	12.2	143.7
11	CD_3OD	2.78	38.1	145.1	80.6	11.7	144.4
1	CD_3OD	3.17	40.2	138.5	65.1	9.5	147.3
2	CD_3OD	2.80	40.0	144.1	81.4	11.2	143.6

a) Chemical shifts in ppm are referred to TMS. b) The ipso carbon of the phenyl rings. c) J values are in hertz. d) $\leq \pm$ 1.0 Hz. e) $\leq \pm$ 0.2 Hz. f) Proton undecoupled ^{77}Se NMR measurement.

Table IV. ^{1}H and ^{13}C NMR Data of Related Organosulfur Compounds

Compound	δ_{CH_3} a)	δ_{CH_3} a)	δ_{C_i} a,c)	J_{CH_3} b)
	2.44	15.4	144.5	138.8
	2.41	15.9	139.4 (138.7)	138.5
	2.87	44.3	150.0	140.2
	2.91	44.7	147.8	140.0

a) Ppm from TMS in CD_3OD. b) In Hz. c) The ipso carbon with respect to S of the phenyl rings.

other hand, the downfield shifts due to formation of methyl phenyl selenoxides are in the range 587 ~ 667 ppm depending on the nature of the 2-substituents. In these respects, the observed 527 ppm downfield shift of 1 from 5 is more consistent with structure 1b. Similarly, the structure of 2 should be 2a.

Structures 1b and 2a are further confirmed by comparing their ^{1}H and ^{13}C NMR chemical shifts and ^{77}Se-^{13}C and ^{77}Se-^{1}H coupling constants with those of related compounds (Table III). We note that many of these parameters are related to the structural difference between selenoxides and selenuranes. First of all, one-bond couplings between ^{77}Se and ^{13}C, $^{1}J(^{77}\text{Se}-^{13}\text{C})$, are in the range 61 ~ 65 Hz for selenuranes and 77 ~ 81 Hz for selenoxides. The observed 65.1 Hz of 1 and 81.4 Hz of 2 are in the typical regions of selenuranes and selenoxides, respectively. Secondly, two-bond coupling constants between ^{77}Se and ^{1}H appear to be larger by 1 ~ 2 Hz for selenoxides. The methyl hydrogens attached to the selenoxy group are somewhat more shielded than in selenuranes. These two parameters are again consistent with structures 1b and 2a.

In order to rule out the effects of the salt formation on the NMR parameters, ^{1}H and ^{13}C data are compiled for related 2-methylthio- and 2-methylsulfinylbenzoic acids and their sodium salts (Table IV). As in one pair of selenium compounds 5 and 7, the effect of the change from the carboxyl to carboxylate group appears to be neglected in evaluating the data in Table III.

We conclude that the driving force for the selenurane formation in 1 is not necessarily crystal packing in solid,[1,2] but its advantageous free energy of formation (even in solution).[4] Selenuranes are known to be stabilized by strong electronegative ligands at the apical positions.[5] The oxygen anion of 2b may not be enough to stabilize the selenurane structure because of the electron rich character of the ligand.

This work was supported by the Joint Studies Program (1980 ~ 1981) of the Institute for Molecular Science.

References

1) B. Dahle'n, Acta Crystallogr., B 29, 595 (1973).
2) J. E. Trend, Ph.D. Thesis, Wisconsin Univ. (1976).
3) Measured on a Varian FT-80A spectrometer at 15.2 MHz.
4) It is beyond the scope of this work to determine the possible contribution of minor structures 1a and 2b.
5) N. C. Baenzinger, R. E. Buckles, R. J. Maner, and T. D. Simpson, J. Am. Chem. Soc., 91, 5749 (1969).
6) M. Lardon, J. Am. Chem. Soc., 92, 5063 (1970).

(Received July 17, 1981)