CHEMISTRY LETTERS, pp. 1373-1376, 1989.

The γ-Gauche Effect in the Se-Ge(α)-C(β)-C(γ) System as Detected by ^{77}Se-NMR

Shuji TOMODA, Masakatsu SHIMODA, and Yoshito TAKEUCHI
Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

The steric compression effect (γ-effect) of γ-carbon on ^{77}Se chemical shift in mono- and diselenogermanes has been first evaluated by ^{77}Se NMR spectroscopy. The γ-gauche effect falls in the range between -59.1 and -13.6 ppm (upfield shift).

Systems involving heavy-atom elements, such as selenium and germanium, are of great interest because they may offer a unique opportunity to test the validity of the conventional concepts in organic chemistry which have been established chiefly on the basis of the property of compounds containing 2nd-row elements. Described herein is the first example of a remarkably strong γ-gauche effect of a carbon atom on the chemical shift of a selenium nucleus segregated from the γ-carbon via a carbon-germanium single bond.

In the course of our research project directed toward the photochemical generation of organogermylenes,[1a)] we prepared several dialkyl- or diphenylbis(phenylseleno)germanes (**1**). We have now extended the synthesis of **1** as shown in Table 1, which lists ^{77}Se and ^{13}C NMR chemical shifts for eight bis(phenylseleno)germanes (**1**) along with those for three phenylselenogermanes (**2**) as references.[1)] While the ^{13}C NMR data[2)] in Table 1 show no anomalies, several noteworthy features are apparent with respect to the chemical shift of ^{77}Se :

(1). On going from **1a** to **1c**, the ^{77}Se chemical shift decreases by about 19 ppm (18.5 ppm from **1a** to **1b** and 18.7 ppm from **1b** to **1c**). The significant upfield shift (ca. -19 ppm) upon replacement of a methyl group by a phenyl group is surprising in view of the prolonged distance in the heteroatom system.

(2). Introduction of an alkyl substituent in the methyl group of **1a** also causes an upfield shift of ^{77}Se chemical shift. The magnitude of this shift varies with the substituents introduced (**1d** through **1f**). The largest upfield shift is observed for **1d** (-50.8 ppm). Replacement of two methyl groups of **1a** by two propyl groups (**1e**) or two butyl groups (**1f**) causes somewhat smaller upfield shift (-37.7 and -39.4 ppm, respectively).

(3). Such a trend also holds true for cyclic cases (**1g** and **1h**), which show 13.6 and 31.8 ppm upfield shifts, respectively, relative to the chemical shift of the parent compound (**1a**). The magnitude of upfield shift for the five-membered ring (**1g**) is substantially lower than that for the germacyclohexane derivative (**1h**).

(4). Similar trend is also observed for monoselenogermanes (**2a**, **2b**, **2c**). Replacement of three methyl groups of **2a** by ethyl groups causes an upfield shift by -70.0 ppm (for **2b**) and replacement of all methyl groups in **2a** by phenyl rings causes -36.1 ppm (for **2c**) upfield shift. The magnitude of upfield shift per substitution for **2** are less than those observed for the case of diselenogermanes (**1**).

These observations may be explained at least in part in terms of the γ-gauche (steric compression) effect of the CH_2(alkyl) or $C(sp^2)$-H(aromatic) located at the γ-position with respect to the selenium atom. The first observation above is due to the γ-gauche effect of the ortho positions of the phenyl groups. Since replacement of a methyl by a phenyl in an aliphatic system causes an upfield ^{13}C chemical shift of only 1 ppm,[3)] the large negative value of the γ-effect of a phenyl group in the $C(\gamma)$-$C(\beta)$-$Ge(\alpha)$-Se^* system (-19 ppm for **1b** and **1c**; -36.1 ppm for **1c**) is surprising if one considers the prolonged distance between $C(\gamma)$ and Se^* compared with the corresponding distance in the homogeneous carbon system. Assuming that the γ-gauche effect is inversely proportional to the cubic of the distance between the γ-carbon and the observing nucleus,[3)] it is expected that the γ-effect in the heteroatom system (Se-Ge-C-C) should be attenuated approximately one half of that in an all-carbon system. Nevertheless the former system shows by far the larger upfield shift. This could be compensated in part by the chemical shift range of ^{77}Se nucleus which is about five times wider than that of ^{13}C,[4)] but this alone does not seem sufficient to explain the 19 ppm upfield shift. Introduction of two phenyl groups in **1a** causes 37.2 ppm upfield shift, suggesting that there exists an additivity in these cases (**1b** and **1c**: about 19 ppm upfield shift per phenyl).

The upfield shift in the alkyl series of diselenogermanes (**1d**, **1e** and **1f**) is much more significant (50.8, 37.7 and 39.4 ppm upfield shift, respectively), than in the cases involving phenyl group(s) (**1b** and **1c**). The magnitude of the shift is a little smaller for **1e** and **1f** than that for **1d** presumably because of the downfield shift due to the δ-effect of alkyl substitution at the γ-carbons. Considering that the ^{13}C γ-effect in an aliphatic system is-2 to -5 ppm,[4)] it is again apparent that the observed ^{77}Se γ-effects in **1d**,**1e**,**1f** are by far larger than we expect by taking into account both the chemical shift range difference between ^{13}C and ^{77}Se and the increase in non-bonded distance.

Similar trend is observed for the cyclic cases, **1g** and **1h**. Since the germacyclopentane ring in **1g** is more planar[1b)] than the germacyclohexane ring[5)], the observation that the ^{77}Se γ-effect in **1g** is much less effective (-13.6 ppm) than the corresponding value for **1h** (-31.8 ppm) is not unreasonable. Indeed a molecular model shows that the non-bonded distance between the γ-(ring) carbon and selenium is a little longer in **1g**(4.53 Å) than in **1h**(4.42 Å).[6)] The magnitude of the large upfield shift is however again not easily understood in terms of

Table 1. ^{77}Se and ^{13}C NMR Chemical Shifts of Bis(phenylseleno)germanes (**1**) and Phenylselenogermanes (**2**)$^{a)}$

1 or 2		^{77}Se NMR		^{13}C NMR						
				Se-Ge(α)-C(β)-C(γ)			Se-Ph$^{c)}$			
			Δδ(Se)$^{b)}$	C(β)	C(γ)$^{d)}$	C (other)	C(i)	C(o)	C(m)	C(p)
1a	$Me_2Ge(SePh)_2$	148.9	(0.0)	5.0			125.2	136.7	128.8	127.3
1b	$PhMeGe(SePh)_2$	130.4	(-18.5)	2.8 137.4	132.8	128.1 129.8	125.3	136.6	128.8	127.3
1c	$Ph_2Ge(SePh)_2$	111.7	(-37.2)	135.3	134.0	128.2 130.0	124.9	136.5	128.7	127.3
1d	$Et_2Ge(SePh)_2$	98.1	(-50.8)	13.1	9.1		125.2	136.7	128.8	127.3
1e	$nPr_2Ge(SePh)_2$	111.2	(-37.7)	18.7	17.0	23.2	125.4	136.6	128.8	127.2
1f	$nBu_2Ge(SePh)_2$	109.5	(-39.4)	20.5	13.5	25.4 27.1	125.4	136.6	128.8	127.3
1g	$c\text{-}C_4H_8Ge(SePh)_2$	135.3	(-13.6)	19.6	26.9		125.9	136.3	128.9	127.3
1h	$c\text{-}C_5H_{10}Ge(SePh)_2$	117.1	(-31.8)	21.5	25.8	28.9	125.3	136.6	128.8	127.3
2a	$Me_3GeSePh$	98.8	(0.0)	2.5			125.9	136.6	128.8	126.6
2b	$Et_3GeSePh$	28.8	(-70.0)	9.1	8.1		125.4	136.7	128.6	126.6
2c	$Ph_3GeSePh$	62.7	(-36.1)	135.3	134.8	128.3 129.6	125.1	136.6	128.6	126.9

a) In ppm downfield from Me_2Se(^{77}Se) or TMS(^{13}C).
b) Δδ(Se) $= -\delta_{Me}$(**1a** or **2a**)$+\delta_R$(**1** or **2**) (Negative sign indicates an upfield shift.)
c) Assignments were made according to M. Baiwir, G. Llabres, A. Luxen, L. Christiaens, and J-L. Piette, Org. Magn. Reson., 22, 312 (1984).
d) Tentative assignment except **1d** and **2b.**

the chemical shift range difference between ^{13}C and ^{77}Se nuclei alone. An average γ-effect of a methyl carbon observed for 1,1,4-trimethyl-1-germacyclohexane (C-C-Ge-C system) is -1.9 ppm (^{13}C NMR).[5] Assuming the chemical shift range of ^{77}Se nuclei to be five times as wide as that of ^{13}C, the γ-effect in the C(γ)-C-Ge-Se system as observed by ^{77}Se NMR is expected to be -1.9 x 5 = -9.5 ppm. This value is less than the observed upfield shift of ^{77}Se for **1g** and **1h.** The large discrepancy between these values may indicate that the ^{77}Se nucleus is much more sensitive than ^{13}C with respect to the steric compression effect in the C-C-Ge-Se system.

In the phenylselenogermanes (**2a**, **2b** and **2c**), similar upfield shifts are observed in all cases, although their magnitude is a little less than those observed for the bis(phenylseleno) series (**1a** through **1d**). Thus **2b** shows up by 70.0 ppm higher than **2a** and **2c** appears higher by 36.1 ppm than **2a**. Again the γ-effect of methyl group is greater than that of phenyl group.

It is clear from the above arguments that the ^{77}Se γ-effect indeed exists in the C-C-Ge-Se system and its magnitude is by far greater than it is expected from the difference in the chemical shift range between ^{77}Se and ^{13}C nuclei. One possible explanation for this discrepancy is an additional upfield shift due to an atractive interaction between C-H and Se. We are continuing our research to evaluate the precise origin of this unusually large γ-effect in the diselenogermane systems. The results will be reported in due course.

This work is partially supported by grant-in-aid for Scientific Research on Priority Areas, "New Functionality Materials, Design, Synthesis and Control" sponsored by the Ministry of Education, Science and Culture (Nos. 62604522, and 63604520).

References

1) a) S. Tomoda, M. Shimoda, Y. Takeuchi, Y. Kajii, K. Obi, I. Tanaka, and K. Honda, J. Chem. Soc., Chem. Commun., 1988, 910; b) S. Tomoda, M. Shimoda, Y. Takeuchi, and Y. Iitaka, Chem. Lett., 1988, 535.

2) The NMR spectra of these new compounds, purified by preparative HPLC, were recorded at 22.50 MHz (^{13}C NMR) and 17.04 MHz (^{77}Se NMR) using a JEOL FX-90Q NMR spectrometer at ambient temperature. Solutions of 10-30% v/v in $CDCl_3$ with the egg-shape cell were used. Tetramethylsilane(TMS) as internal standard for ^{13}C NMR spectra and 50% v/v of dimethylselenide (Me_2Se) in $CDCl_3$ as external reference for ^{77}Se NMR spectra were used.

3) F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra," Heyden, London (1976), p.36.

4) W. Nakanishi, Y. Ikeda, and H. Iwamura, Org. Magn. Reson., 20, 117 (1982).

5) a) Y. Takeuchi, M. Shimoda, and S. Tomoda, Magn. Reson. Chem., 23, 580 (1985); b) Y. Takeuchi, M. Shimoda, K. Tanaka, S. Tomoda, K. Ogawa, and H. Suzuki, J. Chem. Soc., Parkin Trans. 2, 1988, 7.

6) The bond dictances are estimated by using the X-ray structure data for **1g** and the geometry of 1-germacyclohexane optimized by molecular mechanics calculation,[5b] in which two phenylseleno groups are placed at the germanium atom with the bond lengths and angles determined by X-ray analysis of **1g** (C-Ge 1.964 Å; C-Se 1.922 Å; Se-C-Se 101.7°).[1b]

(Received May 6, 1989)