Synthesis and carbon-13 NMR analysis of some organoselenium compounds

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Abstract—Carbon-13 chemical shift assignments are reported for a series of 10 organoselenium compounds of the type PhSeL.

In the course of this study, hydroalumination and bromination of alkynylselenium compounds was performed for the first time, and compared with the rate of hydroalumination and bromination of the corresponding alkynylsilane.

The phenyl carbon shifts reflect ground state electron density changes. The selenium atom transmits electronic effects when the selenium atom acts as a link or bridge between two conjugative groups. For alkynylphenyl selenide, a polarization of charge within the triple bond occurs.

INTRODUCTION

Organoselenium compounds have become an important part of organic chemistry in recent years [1–4] (selenium has now also been found to occur in certain enzymes, amino acids and tRNA [5]). Thus, the carbon-13 chemical shift measurements of organoselenium compounds have become very important, as well as being interesting from the point of view of structure determination. However, there are a limited number of reports concerning the carbon-13 chemical shifts of organoselenium compounds. The most recent investigation involved ¹H and ¹³C chemical shift measurements for phenylvinyl ether, sulfides and selenides [6]. However, measurements were also carried out which provided further evidence concerning the relative position of Se on the transmission scale.

In this paper, we have synthesized a wide variety of organoselenium compounds of the type PhSeL (see Table 1). In addition, we report the ¹³C NMR spectra of these compounds and an analysis of the data in terms of substituent chemical shift effects (SCS) parameters.

EXPERIMENTAL

Nuclear Magnetic Resonance (¹H NMR) spectra were recorded on a JEOL JNM FX-100 spectrometer; chemical shifts are reported as δ values in parts per million (ppm) down-field from internal tetramethylsilane.

Natural abundance 13 C NMR spectra were recorded at 25 MHz using a JEOL JNM FX-100 instrument operating in the Fourier transform (FT) mode with a 10 mm tunable probe. All the spectra were recorded at ambient temperature, 26°C; the compounds were studied as 0.1 M solutions in CDCl₃. Chemical shift data of the 13 C NMR spectra were determined relative to TMS (0.0 ppm).

GLPC analyses were performed on a Pye Unicam series 304 chromatograph with an OV-1 glass column.

Diisobutylaluminium hydride (Fluka) was used as a 1 M solution in hexane. *n*-Butyllithium in hexane and bromine in carbon tetrachloride (Fluka) were used as 1 M solutions. All reactions were stirred magnetically and carried out under an atmosphere of nitrogen in oven-dried $(160^{\circ}C)$ glassware. Tetrahydrofuran and hexane solvents were distilled over sodium and benzophenone. Other solvents were distilled and dried prior to use.

Compounds 1 and 2 are commercially available. The synthesis of compounds 3, 4, 5, 6, 7 and 8 are known [7]. Compound 4 was prepared by oxidation of compound 3. Compounds 3, 5, 6, 7 and 8 were prepared by treatment of the corresponding lithium compounds with phenylselenyl chloride in THF at -78° C for 5 min. Compound 8 was prepared by hydroalumination of the corresponding alkyne compound [8]. Compound 9 was prepared by bromination of the corresponding alkyne compound [9].

Preparation of 1-(phenylselenyl)-1-pentene (8)

To 0.67 g (3 mol) of 1-(phenylselenyl)-1-pentyne in 3 ml of hexane was added drop-wise 3.6 ml of 1 M diisobutylaluminium hydride in hexane (3.6 mmol, 1.2 eq.) at room temperature for 15 min and then at 70°C for 24 h. Work-up and evaporation of solvents gave a residue which was chromatographed on 20 g of silica gel. Elution with hexane gave 0.54 g (2.4 mmol, 80% yield) of the desired product: i.r. (neat) 3070 (w, aromatic H), 2970 (s), 1590 (m, C=C), 1450 (s), 1100 (m) and 750 cm⁻¹ (s); H NMR (CDCl₃, internal TMS), δ CH₃, 0.95 (t); δ CH₂, 1.65 (m); δ CH₂, 2.73 (m); δ CH=, δ Ar-H, 7.31-7.60 (m) ppm. Found: C, 58.03; H, 6.24 C₁₁H₁₄Se requires C, 58.68; H, 6.22

Preparation of 1,2-dibromo-1-(phenylselenyl)-1-pentene (9)

To 1.12 g (5 mmol) of 1-(phenylselenyl)-1-pentyne in 10 ml carbon tetrachloride was added dropwise 6 ml of 1 M solution of bromine in carbon tetrachloride (1.2 equiv, 6 mol) at 12°C. The reaction mixture was stirred for 30 min at -12° C. At the end of this time, the resulting mixture was poured into a 10% sodium sulphite solution and extracted with hexane. After drying over sodium sulphate the solvent was removed by rotary evaporator to leave a residue which was chromatographed on 45 g of silica gel. Elution with hexane gave 1.57 g (4.1 mmol, 81% yield) of the desired product: i.r. (neat) 3070 (w, aromatic H), 2970 (s), 1585 (m, C=C), 1450 (s) and 750 cm⁻¹ (s); H NMR (CDCl₃, internal TMS) δ CH₃, 1.0 (t); δ CH₂, 1.4 (m); δ CH₂, 2.2 (t); δ Ar-H, 7.2-7.37 ppm. Found: C, 34.01; H, 3.20 requires C, 34.48; H, 3.14.

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No.	Compound		Cipso	c°	С ^в	°,	CH3	CH ₂	CH2	c,	C,	Others
-	PhSeCI	\$\$ \$44	131.56	133.79	129.33	130.04						
4	PhSeSePh	1770	130.85	131.45	129.10	127.63						
			-2.35	-2.95	- 0.60	0.87	c T					
r t i	PhSeCH ₃		133.81 5.31	-1.77	-0.42 -0.42	2.58	/.18					
	~											
4	PhSeCH ₃		0	130.27	127.04	134.03	29.72					
				- 1.77	1.46	-5.53						
NO.	PhSePh m0		0	132.80	129.15	127.10						
9	PhSe - O - OCH,		134.50	132.15	129.10	127.10						55.15 (OCH ₃); 159.69
			-6.00	-3.65	-0.6	1.4						(C _{1pw} , OCH ₃); 136.49 (m) 110.87 (C. Sa)
	0											115.06 (0)
2	PhSe 6 1 2		130.68 - 2.18	135.14 -6.64	129.04 0.54	128.16 0.34	47.57 (C ₆);	28.89(C ₅);	131.27(C ₂);	149.47(C ₃)	; 195.47(C=0)
	>											
90	PhSe-C ^a =C ⁿ -nPr		133.26	129.21	128.92	126.57	13.45	22.49	22.20	57.26	104.36	
9	PhSe <i>n</i> Pr		-4.76	-0.71	0.42	1.93						
			129.33	135.26	129.33	129.04	12.98	21.08	43.10	127.98	130.21	
	H H		-6.83	-6.76	-0.83	-0.54						
	PhSeBr											
01			132.32	129.15	129.15	128.92	13.71	22.61	33.18	120.29	125.45	
	Br nPr		3.82	-0.65	-0.65	-0.42						

*Chemical shift (δ) in ppm relative to TMS in CDCl₃; $\dagger \delta \Delta$ ppm SCS effect relative to benzene shift at 128.5 ppm. A negative value implies deshielding and 0, overlaps.

Table 1. Carbon-13 NMR data for some organoselenium compounds

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RESULTS AND DISCUSSION

Although the preparation of compounds 3, 4, 5, 6, 7 and 8 were known [7], the preparation of compounds 9 and 10 were done for the first time. Compound 9 was prepared via hydroalumination of the corresponding alkynylselenium compound. It was found that hydroalumination of the alkynylselenium compound is slow (70°C, 24 h) when compared with hydroalumination of the corresponding alkynylsilane [8] (40°C, 1 h). This is probably due to the coordination of aluminium with the electron pair of selenium and also to the electron withdrawing effect of selenium, as compared to silicon, which deactivates the triple bond towards electrophilic attack by aluminium. The synthesis was followed by GLPC (Pye Unicam series 304 chromatograph with OV-1 glass column).

Compound 10 was prepared via bromination of the corresponding alkynylselenium compound at a rate similar to the bromination of the corresponding alkynylsilane [9] $(-12^{\circ}C, 15 \text{ min})$. This is probably due to the high reactivity of bromine.



¹³C chemical shifts for phenyl selenides are listed in Table 1 and are based on chemical shifts, intensity information, off-resonance decoupling and geometry of the substituents (in alkenyl selenide). Inspection of phenyl carbon chemical shifts indicates the additive nature of selenium-L on aryl carbons compared with benzene. The C_{ipso} resonances covered a range of over 7 ppm (down-field shift), more deshielding effects have been observed when L, an alkenyl group (compound 9), a down-field shift of the ortho resonances (0.6 to 7 ppm), and smaller down-field shifts of the meta position have been recorded (see Table 1). The para resonances covered a range of over 8 ppm, up-field and down-field of the benzene resonance depending on the nature of L. Thus, phenyl carbon shifts accurately reflect ground state electron density changes. Interestingly, when $L = phenyl, p(CH_3O)Ph$ -, substituent alkenyl group and alkynyl group, the effect of substituents on Cipso chemical shifts varies markedly. This result indicates the ability of the link atom (i.e. Se) to transmit electronic effects between conjugative groups. A similar effect has been reported for 4substituted phenylvinyl selenides [6].

The resonances for alkenyl carbons appear in the same regions as those for aromatic compounds (Nos 9 and 10, Table 1). Diamagnetic shifts resulting from the bromine at the carbons of attachment are observed (compound 10 compared with 9). Of particular interest are the assignments of C_a and C_{β} of the alkynyl selenide compound (8). Charge transfer and/or $(p \rightarrow d)_{\pi}$ bonding have been invoked to explain experimental results in studies of various organosilicon compounds [10]. It has been well established that ¹³C chemical shift data can yield insights into intramolecular changes in electron density patterns [11]. In a previous study [12], we provided new evidence for a significant $(p \rightarrow d)_{\pi}$ or equivalent interaction between silicon and alkynylic π systems in R-alkynyl trimethylsilanes. For (phenylalkynyl)trimethylsilane [10], a significant ground state contribution from the resonance form (I), explains the up-field shift of C_a and the down-field shift

$$\mathbf{R} - \dot{\mathbf{C}} = \mathbf{C} = \mathbf{\bar{S}i}(\mathbf{CH}_3)_3 \tag{I}$$

of C_{β} ($C_{\alpha} = 92.5$, $C_{\beta} = 104.4$ ppm). Similar effects have been observed for alkynyl phosphines and thioethyne compounds [13] (HC=C-P (sBu)₂, $C_{\alpha} = 83.2$, $C_{\beta} = 92.7$ ppm; HC=C-S-Et, $C_{\alpha} = 72.6$, $C_{\beta} = 81.4$ ppm).



However, S and Se are normally considered to have a similar electronegativity [14]. For alkynyl selenide, a polarization of charge within the triple bond occurs. The carbon-selenium bonding interaction is indicated by the ≥ 21 ppm deshielding of C_{β} relative analogous signal in 1-hexyne to the $C_a = 67.4,$ $(CH \equiv C - CH_2CH_2CH_2CH_3)$ C_s = 82.8 ppm). The up-field shift of the α alkynylic carbon by ≥ 10 ppm relative to C_a in 1-hexyne is expected because of the polarization of charge within the triple bond. Invocation of the resonance form (I) is analogous to the known shielding of the alkynylic carbon β to the oxygen atoms, explained by use of resonance forms such as (II) [13] $({}^{13}C_{\alpha} = 88, {}^{13}C_{\beta}$ = 28 ppm).

$$CH_3C \equiv C - O - CH_3 \leftrightarrow CH_3\overline{C} = C = O^+CH_3$$
 (II)

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