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New cyclic selenide. Synthesis, characterization and reactions of 2-methylselenolan *

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Abstract

Treatment of 1,4-dibromopentane with sodium selenide gave 2-methylselenolan (**1**), $C_5H_{10}Se$, as a yellow oil with an obnoxious odour. New derivatives of compound **1** ($C_5H_{10}Se(R)X$: $R = X = I$; $R = X = Br$; $R = X = Cl$; $R = CH_3$, $X = I$; $R = CH_3$, $X = BPh_4$; $R = C_6H_5$, $X = BPh_4$) have been prepared; ^1H NMR studies show the presence of *cis/trans* geometrical isomers.

Introduction

In previous papers [1–3] we have described the preparation and various spectroscopic, solid and solution properties of 2-methyl-1-telluracyclopentane derivatives. We have now extended our investigation to the selenium analogues. We now report the synthesis, characterization and spectroscopic properties of 2-methylselenolan, a hitherto unknown heterocyclic selenium compound, and its derivatives. Morgan and Burstall [4] prepared 2-methylselenane by heating poly(selenohexamethylene), poly[(diseleno)hexamethylene], or 1,8-diselenacyclotetradecane.

Experimental

Physical measurements

Infrared spectra as KBr discs in the range 4000–250 cm^{-1} were recorded on a Pye–Unicam SP3-300s spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-200 (200 MHz) instrument. Melting points were determined on Yanaco MP-S3 micro melting point apparatus and are uncorrected. Mass spectra were obtained with a Jeol JMS-DX mass spectrometer, equipped with JAM-3500 data processing system. Analysis for carbon and hydrogen was by the Analytical Service Unit, Institute for Chemical Research, Kyoto University, Japan.

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* This work was carried out at the Institute for Chemical Research, Kyoto University, Kyoto, Japan.

Synthesis

All preparations were carried out under purified nitrogen with carefuly dried solvents. Silica gel was used for column chromatography.

2-Methylselenolan (1). Sodium borohydride (1.51 g, 20 mmol) was added under nitrogen at room temperature to a suspension of selenium powder (1.58 g, 20 mmol) in ethanol (50 cm^3). The selenium was consumed within 30 min. 1,4-Dibromopentane (4.60 g, 20 mmol) was rapidly added to the stirred solution at room temperature and the mixture then refluxed for 3 h. After cooling, the solution was diluted with water (200 cm^3) and air was passed through it for 12 h. The mixture was extracted with diethyl ether (3 × 100 cm^3) and the extracts washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to give a viscous yellow oil, with a penetrating odour. The product was purified by column chromatography with hexane/ethyl acetate (10 : 1) as eluent to give compound **1** (2.32 g) as a yellow oil in 78% yield. Mass spectrum, *m/e* (relative intensity), 150(95) (M^+), 135(45), 122(10), 105(18), 69(100), 55(24), 41(100).

1,1-Diodo-2-methylselenolan (2). A mixture of 1,4-dibromopentane (4.60 g, 20 mmol), powdered selenium (1.58 g, 20 mmol) and sodium iodide (12.0 g, 80 mmol) in 2-methoxyethanol (100 cm^3) was stirred under gentle reflux for 4 h then cooled. Deionized water was added and the organic material extracted with ether (4 × 100 cm^3). The extract was evaporated to leave a red viscous oil which was subjected to column chromatography with hexane/ethylacetate (5 : 1) as eluant to give 2.17 g of compound **2** in 27% yield as a red viscous oil. Reduction of **2** with $NaBH_4$ gave compound **1** in good yield. Attempts to solidify this product were unsuccessful.

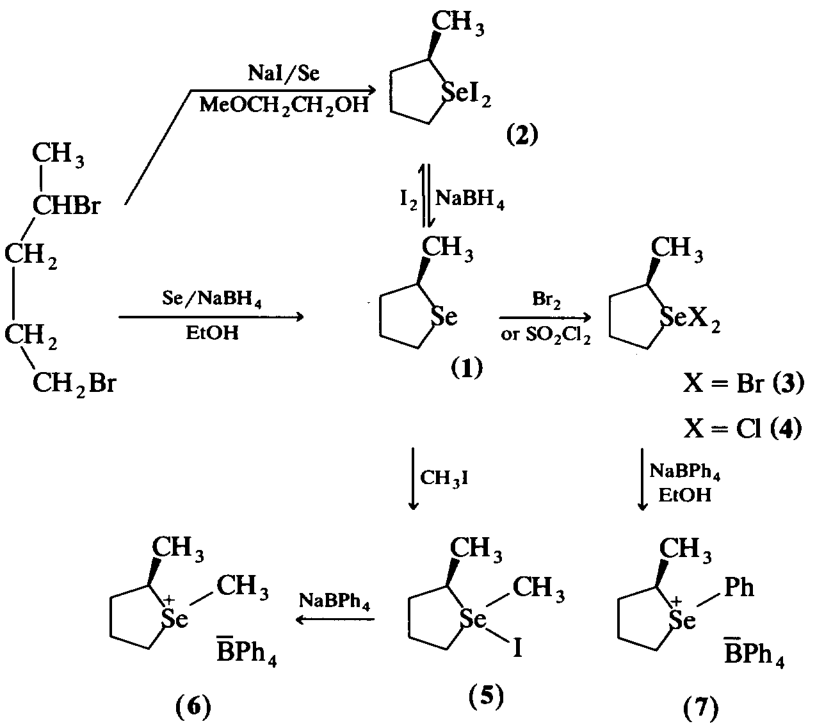
Compound **2** was also prepared by addition of iodine to an ethereal solution of 2-methylselenolan at -5°C.

1,1-Dibromo-2-methylselenolan (3). A solution of bromine in CCl_4 was added dropwise to 1.49 g (10 mmol) of 2-methylselenolan in CCl_4 (30 cm^3) until the colour of bromine persisted. The mixture was stirred for 5 h at room temperature and the solvent then evaporated to leave a pale yellow precipitate. Recrystallization from ethanol gave yellow needles (2.87 g, 93%). Mass spectrum, *m/e* (relative intensity) 312(2), (M^+), 231(25), 229(32), 150(51), 135(31), 69(100), 55(41), 41(100).

1,1-Dichloro-2-methylselenolan (4). This was prepared by a similar oxidation reaction involving thionyl chloride; the product was obtained in 85% yield after recrystallization from ethanol. Mass spectrum, *m/e* (relative intensity) 220(3) (M^+), 185(21), 150(55), 135(24), 105(10), 69(100), 55(18), 41(100).

1,2-Dimethylselenolanium iodide (5). To a stirred ethereal solution of $C_5H_{10}Se$ (1.49 g, 10 mmol) at room temperature under nitrogen was added an excess of iodomethane (10 cm^3). After 4 h the white precipitate was filtered off, washed with ether, dried *in vacuo* and recrystallized from ethanol (3 times) to give 1.87 g in 64% of **5**.

1,2-Dimethylselenolanium tetraphenylborate (6). A solution of **5** (0.58 g, 2 mmol) dissolved in 30 cm^3 of absolute ethanol was added with stirring to sodium tetraphenylborate (1.7 g, 5 mmol) in 30 cm^3 of the same solvent at room temperature. Precipitation occurred within 15 min but stirring was continued for 3 h, then the white product was filtered off and recrystallized from DMF/water to give 0.90 g (85%) of **6**. Mass spectrum, *m/e* (relative intensity) 484(0.6) (M^+), 319(1.2), 304(0.4), 242(64), 165(66), 164(100), 163(58), 154(26), 105(12), 91(39), 77(19), 69(18).



Scheme 1. Methods of preparation of new cyclic selenide and its derivatives.

1-Phenyl-2-methylselenolanium tetraphenylborate (7). A solution of 1,1-dibrom-2-methyl-selenolan (0.62 g, 2 mmol) in 50 cm^3 of absolute ethanol was added with stirring to sodium tetraphenylborate (1.7 g, 5 mmol) in 30 cm^3 of the same solvent

Table 1

Analytical data for the new compound 1–7

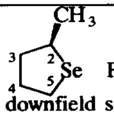
Compound	Colour	Melting point (°C)	Yield (%)	Anal. Found (calc.) (%) [a]	
				C	H
1	Yellow	Oil	78	40.28 (40.13)	6.69 (6.76)
2	Red	Viscous	96 [b], 27 [c]	14.23 (14.91)	2.01 (2.50)
3	Yellow	73–75	93	19.26 (19.44)	3.22 (3.26)
4	Pale yellow	52–54	85	27.24 (27.29)	4.45 (4.58)
5	White	165(vap) [d]	64	24.85 (24.76)	4.39 (4.50)
6	White	242(vap) [d]	85	74.52 (74.55)	6.85 (6.88)
7	White	186–188	76	77.13 (77.07)	6.52 (6.47)

[a] Calculated values are given in parentheses. [b] Produced by reaction of 1 with I_2. [c] Based on 1,4-dibromopentane charged. [d] Vaporized.

Table 2

^{1}H and ^{13}C NMR data for compounds 1–7 [a]

Compound	Solvent	Chemical shifts (ppm) and assignments [b]		J (Hz)	Cis / trans mixture ratio	^{13}C NMR (δ)
1	$CDCl_3$	1.73(d)	C_2–CH_3	6.6	0/100(0/100) [b]	
		1.87–2.16(m)	3-H			
		2.87–3.06(m)	4-H			
		3.38–3.74(m)	5-H			
		4.05–4.19(m)	2-H			
2	$CDCl_3$	1.57(d)	C_2–CH_3	7.0	0/100(0/100) [b]	
		1.70–1.83(m)	3-H			
		2.12–2.40(m)	4-H			
		3.32–3.42(m)	5-H			
		3.69–3.86(m)	2-H			
3	$CDCl_3$	1.88(d)	C_2–CH_3	6.8	0/100(0/100) [b]	17.43, 31.33, 40.18, 65.41, 76.75 [c]
		2.40–2.58(m)	3-H			
		2.66–2.79(m)	4-H			
		4.01–4.49(m)	5-H			
		4.58–4.76(m)	2-H			
4	$CDCl_3$	1.87(d)	C_2–CH_3	6.4	0/100(0/100) [b]	17.24, 30.85, 45.17, 62,32, 75.94 [c]
		2.42–2.47(m)	3-H			
		2.66–2.78(m)	4-H			
		3.95–4.20(m)	5-H			
		4.40–4.82(m)	2-H			
5	$CDCl_3$	1.45(d)	C_2–CH_3 *cis*	6.6	18/82(39/61) [b]	
		1.84(d)	C_2–CH_3 *trans*	7.2		
		2.15(s)	Se–CH_3 *cis*			
		2.71(s)	Se–CH_3 *trans*			
		2.17–3.04(m)	3-H			
		3.25–3.78(m)	4-H			
		3.95–4.30(m)	5-H			
		4.50–4.65(m)	2-H			
	DMSO-d_6	1.46(d)	C_2–CH_3 *cis*	6.6	18/82(39/61) [b]	
		1.59(d)	C_2–CH_3 *trans*	7.8		
		2.55(s)	Se–CH_3 *cis*			
		2.78(s)	Se–CH_3 *trans*			
		2.05–2.45(m)	3&4-H			
		3.30–3.71(m)	5-H			
		3.81–4.18(m)	2-H			
6	DMSO-d_6	1.39(d)	C_2–CH_3 *cis*	6.3	4/96(34/66) [b]	
		1.51(d)	C_2–CH_3 *trans*	8.3		
		2.58(s)	Se–CH_3 *cis*			
		2.62(s)	Se–CH_3 *trans*			
		1.70–2.35(m)	3&4-H			
		3.35–3.60(m)	5-H			
		3.71–4.03(m)	2-H			
		6.71–7.32(m)	Ar-H			
7	DMSO-d_6	1.68(d)	C_2–CH_3	6.3	0/100(0/100) [b]	
		1.90–2.32(m)	3&4-H			
		3.72–3.95(m)	5-H			
		4.05–4.30(m)	2-H			
		6.70–7.34(m)	Ar-H			
		7.53–7.94(m)	Ar-H			



[a] Assignment as illustrated. Peak assignments are based on integrations, multiplicity and structure, taking account of downfield shift for the trans form [1,3,9]. [b] Data from ref. 3 are given in parentheses for comparison. [c] Signals in $CDCl_3$ spectra.

at room temperature. Precipitation occurred within 5 min, but the mixture was stirred for 5 h and the white precipitate then filtered off. Recrystallization from acetonitrile yielded white crystals in 76% yield. Mass spectrum, *m/e* (relative intensity), 319(0.4), 304(7.5), 242(75), 165(75), 164(100), 163(70), 105(15), 91(41), 77(11), 69(11).

Results and discussion

The new heterocycle **1** has been obtained by reaction between sodium selenide and 1,4-dibromopentane or by reduction of the readily accessible diiodide **2** (Scheme 1). Compound **1** can be readily oxidized to its dihalo derivatives with I_2, Br_2 or SO_2Cl_2 as the oxidants. Oxidative addition of iodomethane to **1** gave the corresponding methylselenonium salt (**5**). Furthermore, the reaction of $NaBPh_4$ with compounds **3** and **5** gave compounds **7** and **6**, respectively (Scheme 1). Use of the reaction of **3** with $NaBPh_4$ to form a Se–C bond as described here appears to offer a general and expedient method for making organoselenium compounds; such an approach is well established for making organotellurium compounds [5].

Reaction of 1,4-dibromopentane with selenium powder and sodium iodide (or reaction of **1** with iodine) gave a red viscous compound which from its elemental analysis and ^1H NMR and IR spectroscopic data, is judged to be **2**. It is well known [6–8] that selenium heterocycles can form charge-tansfer complexes with iodine, and we have shown that a similar charge-transfer complex (*i.e.* $C_5H_{10}Se(I_2)$) can be formed. Reduction of **2** with $NaBH_4$ afforded the cyclic selenide (**1**); the dibromo derivative **3** of this product was prepared. Analytical data for all compounds are given in Table 1.

The IR spectra of all the compounds show two bands in the range 605–585 cm^{-1} due to ν_{as}(C–Se) and ν_s(C–Se). The ^1H NMR data in $CDCl_3$ or DMSO-d_6 for all the new compounds are presented in Table 2. The ^1H NMR spectra of compounds **5** and **6** show the presence of *cis/trans* geometrical isomers, with the *trans*-configuration as the major species. The data in Table 2 show that the size of the organic group has a large effect on the stereochemistry of the product. In sharp contrast to the tellurium analogue, the *cis/trans* ratio was found to depend on the nature of the counter anion (see Table 2).

In the mass spectra of compounds **1**, **3**, **4**, **6** (but not **7**) the parent ion was observed, but at low relative intensity. The ions $C_5H_9^+$ (for **1**, **3** and **4**) and $BC_{12}H_9$ (for **6** and **7**) have high relative intensities. The mass spectra of **6** and **7** show the ion $C_5H_{10}Se(Ph)_2^+$ to be present. The analogous ion has been observed with telluronium salts containing the tetraphenylborate anion [10].

In general, the spectra are closely similar to those of analogous heterocyclic selenium compounds [11,12].

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