

Synthesis, Characterization of Some New Heterocyclic Selenium Compounds Based on 3, 5-Naphtho-1-Seleoncylohexane

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Abstract

A new series of heterocyclic compounds derivative from 3, 5 – naphtho 1-selenocyclohexane have been prepared (i.e.: $C_{12}H_{10}SeX$; X=Cl, Br, I) and $C_{12}H_{10}SeRX$; R=CH₃; X=I)

The new compounds were characterized by elemental analysis, IR, NMR and molar conductance. Conductivity measurements of these compounds in DMSO solution indicated that they behave as weak electrolytes

Keywords: 3, 5-Naphtho-1-Seleoncylohexane

Introduction

The preparation, characterization and solution properties for heterocyclic tellurium and selenium had been described in previous paper [1-9].

3, 5- naphtho -1-tellurocyclohexane was studied firstly by Anderson et al [10] who studied the cyclic inversion that occurs in oxygen, sulphur, tellurium and selenium cyclic compounds.

Sign et al [11] was prepared 3, 5 - naphtho -1-tellurocyclohexane and 3, 5-Naphtho -1- selenocyclohexane from 1, 8 - bis (bromo methyl) naphthalene. Radhy [12] prepare charge transfer complexes with quinones

In the present work a new heterocyclic selenium compounds based on 3, 5 - naphtho -1-selenocyclohexane have been prepared and characterized by physical properties and spectroscopic methods.

Experimental

Physical measurements

Infrared spectra were recorded as KBr pellets in the range of 4000-200 cm^{-1} [pye-Unicam SP3-300s infrared spectrophotometer]. Elemental analysis was performed using EA-1108 Carlo-Erba elemental analyzer. ^1H NMR spectra were recorded in CDCl_3 or DMSO- d_6 solution containing TMS as internal standard using Joel EX-90 instrument. Melting points were determined by Gallen Kamp apparatus and were uncorrected. Conductivity measurements were done with a WTW conductivity meter LBR using a standard conductivity cell with constant of 0.8 cm^{-1} .

Synthesis

1, 8- bis (bromo methyl) naphthalene $\text{C}_{12}\text{H}_{12}\text{Br}$ (I)

A mixture of 2 gm (50m mole) of 1, 8- di methyl naphthalene and 6.4 gm (25m mole) N-bromo succinamide (N.B.S) with 0.25gm (1m mole) from benzoyl chloride in 40ml CCl_4 was heated to reflux for 5hr. A small quantity of pale yellow crystal was deposited from this reaction on cooling. The precipitate was washed with a small amount of water and recrystallized from benzene m.p. 165°C.

3, 5- naphtha-1- selenocyclohexane $\text{C}_{12}\text{H}_{10}\text{Se}$ (II)

To a well- stirred suspension of selenium (0.12gm) (1.59m mole) in water was added sodium borohydride 0.12gm (1.59m mole) in water (25ml) at room temperature. The selenium was consumed within 10 min. 1,8-bis (bromomethyl) naphthalene (0.59m mole) in toluene (25ml) was then added through a dropping funnel. After addition of phase transfer catalyst, tetrabutyl ammonium hydrogen sulphate (0.1gm) the temperature was raised to 60 °C and kept at 60°C for 8 hr. The organic layer was separated, washed with 5% aqueous sodium carbonate, then evaporated in vacuo to give an orange product. Recrystallisation from petroleum ether (40 – 60 °C) yielded orange crystals mp. 82°C (lit. [9]). 83.5 – 84.5°C.

1, 1-dibromo 3, 5-naphtha-1-selenocyclohexane $\text{C}_{12}\text{H}_{10}\text{Se Br}_2$ (III).

A solution of 3, 5-naphtha-1-selenocyclohexane 3 mmole in dry ether was treated drop wise with a solution of bromine 3 mmol in ether a white precipitate was formed immediately. The solution was evaporated and the residue was recrystallized from methanol to give white crystals (m.p. 202 – 204°C)

1, 1-dichloro-3, 5-naphtha-1-selenocyclohexane(IV).

In ether was added slowly to a stirred solution of 3mmole from 3,5 naphtha-1-selenocyclohexane in the same solvent at room temperature. A white precipitation was formed immediately. The precipitate was washed with H_2O and recrystallized from ethanol to give a white crystal (m.p. 200–201°C)

1, 1-diodo-3, 5-naphthol-selenocyclohexane $\text{C}_{12}\text{H}_{10}\text{SeI}_2$ (V).

A solution of 3,5 naphtha-1-selenocyclohexane 1mmole in dry ether (10ml) was treated drop wise with a solution of iodine 0.39gm(1.5m mole) in ether. A white

precipitation was formed. The solution was evaporated and the residue was recrystallized from ethanol to give white crystal (m.p. 188-200°C)

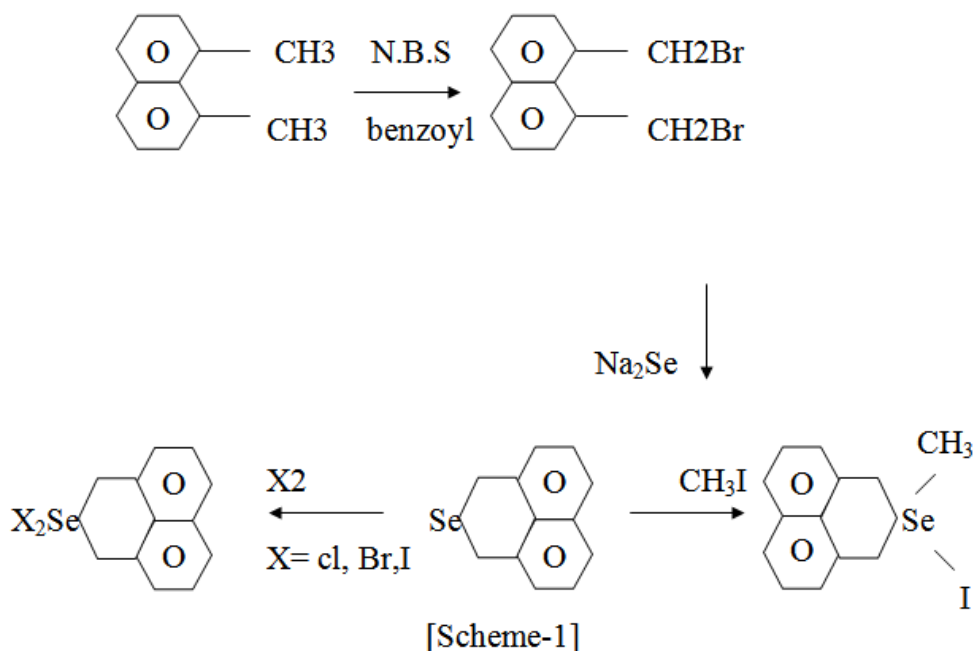
Iodo-1-methyl-3, 5-naphtho-1-selenocyclohexane C₁₃H₁₃SeI (VI).

3mmole of freshly distilled iodo methane was introduced with cyclic selenide 3mmole. Recrystallized from ethanol/H₂O (3/1) give white crystals of m.p. 170-173°C.

Result and discussion

This paper deals with the synthesis of 3, 5-naphtho-1-selenocyclo hexane (11) which was then converted to dihalo derivatives through the reaction with halogen in 70% yield. Its treatment with methyl iodide to form compound C₁₂H₁₀SeCH₃I(VI).

The synthesized compounds and their synthesis modes are show in Scheme (1).



All compounds are soluble in DMSO, their physical properties and elemental analysis is listed in table1.

The infrared spectra (KBr disk) a fall compounds show a weak to moderate band near 585 - 600 cm⁻¹ which characteristic of the C-Se stretching [7].

Two strong absorption, this first at 770- 780 cm⁻¹ owing to bending stretching of C-H and the second at 1620 – 1590 cm⁻¹ owing to aromatic stretching c=c Table (2).

In addition to these absorption peaks, there are a number of characterization absorption such Se-Br, Se-Cl and Se-I stretching at 620, 610 and 605 cm⁻¹ respectively.

Table 1: Analytical and physical properties for (II- VI) Compounds.

No.	Chemical formula	Colour	M.P. °C	Yield %	Anal. Found (cal.) %	
					C	H
II	C ₁₂ H ₁₀ Se	Orange	82	70	61.20 (61.81)	4.34 (4.32)
III	C ₁₂ H ₁₀ SeBr ₂	White	202 – 204	75	36.10 (36.67)	2.51 (2.56)
IV	C ₁₂ H ₁₀ SeCl ₂	White	200 – 201	70	47.47 (47.41)	2.29 (3.31)
V	C ₁₂ H ₁₀ SeI ₂	White	188 – 200	70	29.58 (29.59)	2.40 (2.06)
VI	C ₁₂ H ₁₀ SeCH ₃ I	White	170 - 173	75	41.60 (41.62)	3.42 (3.49)

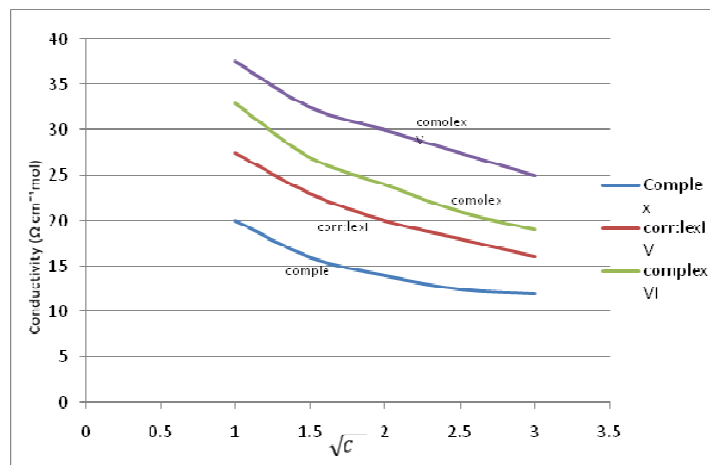
Table 2: I R and ¹H NMR for (II – VI) Compounds.

No.	Se – C	C = C	C - H _{ben}	δ (PPM)	SOLVENT
II	585	1580	780	4.3 {S, H (2,6)} 7.7 – 08 {M, H- Aromatic }	DMSO – d ₆ 2.15
III	585	1590	775	4.6 {S, H (2,6)} 7.2 – 8.1 {M, H- Aromatic }	CDCl ₃
IV	590	1580	770	4.8 {S, H (2,6)} 7.2 – 8.2 {M, H- Aromatic }	CDCl ₃
V	590	1620	770	4.5 {S, H (2,6)} 7.2 – 8 {M, H- Aromatic }	CDCl ₃
VI	600	1608	780	1.2 {S, CH ₃ } 5.23 {M, H (2,6) } 7.2 –8.2 {M, H- Aromatic }	DMSO-d ₆

¹H NMR spectra for compounds (II-VI) were measured in CDCl₃ and DMSO-d₆. These compounds C₁₂H₁₀SeX₂ in CDCl₃ solvent gave two types of bands: the first, a singlet signal related to methylene protons (2,6) and the second multiple signal at 7-8.2 ppm for aromatic protons. Table 2.

¹H NMR for C₁₂H₁₀SeCHI (VI) shows a quartet signal for methylene proton (2,6) at 5.23 ppm which are not equivalent as compared with C₁₂H₁₀Se and C₁₂H₁₀SeX₂ compounds. This results in agreement with C₁₂H₁₀TeX. [13] And C₁₂H₁₀TeX [14].

The molar conductivity for these compounds in DMSO as solvent with concentration between 10⁻⁴ – 10⁻⁵ molar were measured. When plots molar conductance (ohm⁻¹ cm⁻¹ mole) against square root of concentration for compounds, showed a typical behavior of weak electrolyte in DMSO solvent Fig.1 and this result agrees with previous studies [12, 15].



x	Complex	corr:lexIV	complex VI	complex V
1	20	27.5	33	37.5
1.5	16	23	27	32.5
2	14	20	24	30
2.5	12.5	18	21	27.5
3	12	16	19	25

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