

Synthesis and Characterization of Some New Heterocyclic Selenium Derivatives of 3,5-Naphtho-1-Seleoncyclohexane

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ABSTRACT

A new series of heterocyclic derivatives from 3,5-naphtho-1-selenocyclohexane have been prepared ($C_{12}H_{10}SeX$; $X=Cl, Br, I$) and $C_{12}H_{10}SeRX$; $R=CH_3$; $X=I$)

The new compounds were characterized by elemental analysis, IR, H^1NMR and molar conductance. Conductivity measurements of these compounds in DMSO solution indicated that they behave as weak electrolytes

INTRODUCTION

The preparation, characterization and solution properties of heterocyclic tellurium and selenium had been described previously [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.

Singh et. al. [11] have prepared 3,5-naphtho-1-tellurocyclohexane and 3,5-naphtho-1-selenocyclohexane from 1,8-bis (bromo methyl) naphthalene.

Radhy [12] prepared charge transfer complexes from quinines. 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

A) Physical measurements

All physical measurements were achieved in the University of Basrah. Infra-red spectra were recorded as KBr pellets in a range of $4000-400\text{ cm}^{-1}$ on a Pye-Uniecam SP300s infrared spectrophotometer. Elemental analysis were performed using EA-1108 Carlo-Erba elemental analyzer. H^1NMR spectra were recorded in $CDCl_3$ or DMSO- d_6 solution containing TMS as internal standard using Joel EX-90 instrument 100MHz. Melting points were



determined by Gallenkamp apparatus and were uncorrected. Conductivity measurements were done with a WTW conductivity meter LBR using a standard conductivity cell with a constant of 0.8 cm^{-1} .

B) Synthesis

1, 8- bis(bromo methyl)naphthalene $\text{C}_{12}\text{H}_{12}\text{Br}_2$ (I)

A mixture of (2 g, 50 mmol) of 1,8-dimethylnaphthalene and (6.4 gm, 25mmol) N-bromosuccinimide (NBS) with (0.25g ,1mmol) from benzoyl chloride in 40 ml CCl_4 was heated to reflux for 5 hrs. 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) [11]

To a well-stirred suspension of selenium (0.12 g) (1.59 mmol) in water, sodium borohydride (0.12 gm, 1.59 mmol) was added in water (25ml) at room temperature .The selenium was consumed with in 10 min. 1,8-bis (bromomethyl) naphthalene (0.59mmol) in toluene (25ml) was there added through a dropping funnel. After addition of a phase-transfer catalyst, tetrabutylammoniumhydrogensulphate (0.1 g) the temperature was raised to 60°C and kept at 60°C for 8 hrs. The organic layer was separated, washed with 5% aqueous sodium carbonate, then evaporated in vacuo to give an orange product. Recrystallization from petroleum ether ($40-60^\circ\text{C}$) yielded orange crystals mp. 82°C (lit. [9]). $83.5-84.5^\circ\text{C}$.

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 mmol) in dry ether was treated dropwise 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. $202-204^\circ\text{C}$)

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

In ether was added slowly to a stirred solution of (3 mmol) of 3,5-naphtho-1-selenocyclohexane in the same solvent at room temperature. A white precipitate was formed immediately. The precipitate was washed with water and recrystallized from ethanol to give a white crystal (m.p. $200-201^\circ\text{C}$)

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

A solution of 3,5-naphtho-1-selenocyclohexane (1 mmol) in dry ether (10 ml) was treated drop wise with a solution of iodine (0.39 g,1.5 mmol) in ether. A white precipitate was formed. The solution was evaporated and the residue was recrystallized from ethanol to give white crystals (m.p. $188-200^\circ\text{C}$).

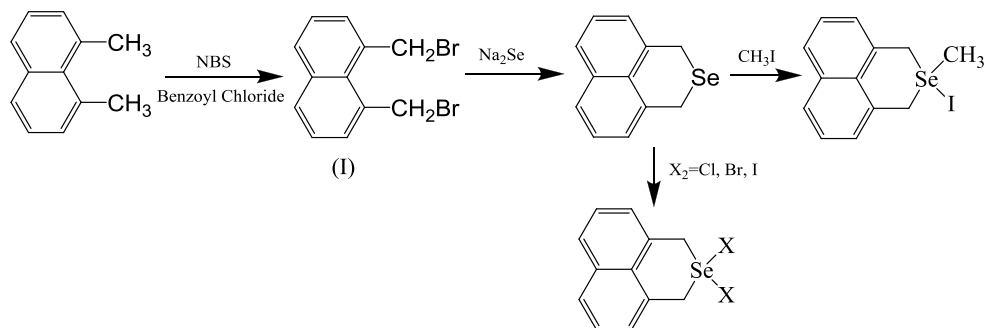
Iodo-1-methyl-3,5-naphtho-1-selenocyclohexane $\text{C}_{13}\text{H}_{13}\text{SeI}$ (VI).

(3 mmol) of freshly distilled iodomethane was introduced with cyclic selenide (3 mmol). Recrystallization from ethanol/water (3/1) gave white crystals of m.p. $170-173^\circ\text{C}$.

RESULT AND DISCUSSION

This paper deals with the synthesis of 3,5-naphtho-1-selenocyclo hexane (II) which was then converted to dihalo derivatives through the reaction with halogen in 70% yield. Its treatment with methyl iodide gave compound $\text{C}_{12}\text{H}_{10}\text{SeCH}_3\text{I}$ (VI).

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



All compounds are soluble in DMSO, their physical properties and elemental analysis are listed in Table (1).

The infrared spectra (KBr disk) of all compounds show a weak to moderate band near $585\text{-}600\text{ cm}^{-1}$ which characteristic of the C-Se stretching [7].

Two strong absorption bands: the first was at $770\text{-}780\text{ cm}^{-1}$ owing to bending stretching of C-H; and the second was at $1620\text{-}1590\text{ cm}^{-1}$ owing to aromatic stretching C=C Table(2).

In addition to these absorption bands, there is 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 compounds (II- VI).

No.	Chemical formula	Colour	M.P. °C	Yield %	Anal. Found (cal.) %	
					C	H
II	$\text{C}_{12}\text{H}_{10}\text{Se}$	Orange	82	70	61.20 (61.81)	4.34 (4.32)
III	$\text{C}_{12}\text{H}_{10}\text{SeBr}_2$	White	202 – 204	75	36.10 (36.67)	2.51 (2.56)
IV	$\text{C}_{12}\text{H}_{10}\text{SeCl}_2$	White	200 – 201	70	47.47 (47.41)	2.29 (3.31)
V	$\text{C}_{12}\text{H}_{10}\text{SeI}_2$	White	188 – 200	70	29.58 (29.59)	2.40 (2.06)
VI	$\text{C}_{12}\text{H}_{10}\text{SeCH}_3\text{I}$	White	170 - 173	75	41.60 (41.62)	3.42 (3.49)

^1H NMR spectra of compounds (II-VI) were measured in CDCl_3 and DMSO-d_6 . Compounds $\text{C}_{12}\text{H}_{10}\text{SeX}_2$ in CDCl_3 solvent gave two types of bands the first, 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 of $\text{C}_{12}\text{H}_{10}\text{SeCHI}$ (VI) shows a quartet signal for methylene proton (2,6) at 5.23 ppm which are not equivalent as compared with $\text{C}_{12}\text{H}_{10}\text{Se}$ and $\text{C}_{12}\text{H}_{10}\text{SeX}_2$ compounds. This result is in agreement with $\text{C}_{12}\text{H}_{10}\text{TeX}$ [13] and $\text{C}_{12}\text{H}_{10}\text{SeRX}$ [14].

Table (2): IR and ¹HNMR for (II–VI) compounds.

No.	Se–C cm ⁻¹	C=C cm ⁻¹	C–H _{ben} cm ⁻¹	δ (ppm)	Solvent
II	585	1580	780	4.30 s (H _{2,6}) 7.70–8.00 (H _{aromatic})	DMSO-d ₆ 2.15
III	585	1590	775	4.60 s (H _{2,6}) 7.20–8.10m(H _{aromatic})	CDCl ₃
IV	590	1580	770	4.80 s (H _{2,6}) 7.20–8.20m(H _{aromatic})	CDCl ₃
V	590	1620	770	4.50 {S, H (2,6)} 7.20–8.00m (H _{aromatic})	CDCl ₃
VI	600	1608	780	1.20 {S, CH ₃ } 5.23 {M, H (2,6)} 7.20–8.20m (H _{aromatic})	DMSO-d ₆

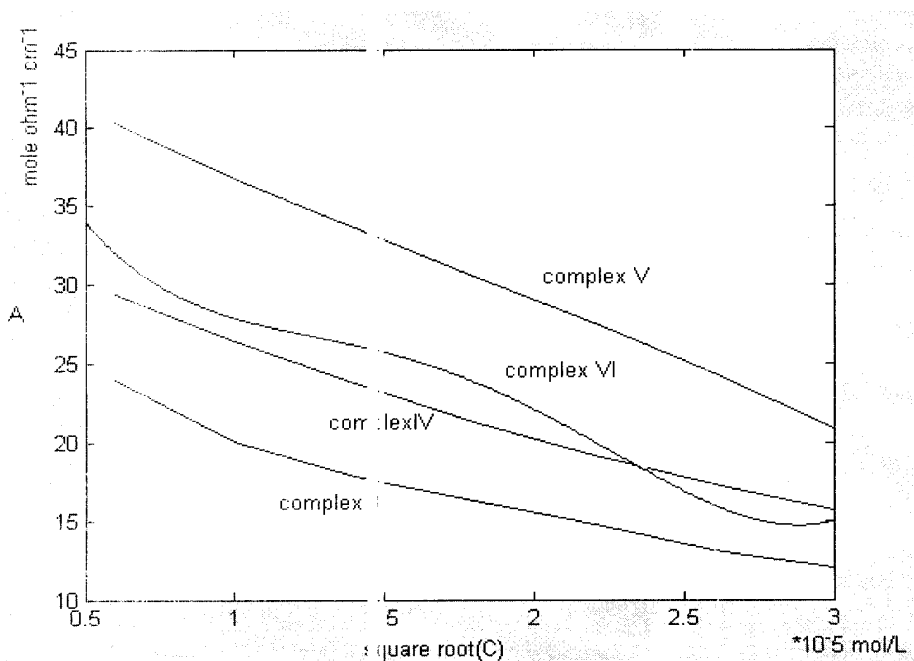


Figure (1): Molar conductivity versus square root of concentration.

The molar conductivity for these compounds in DMSO as solvent with concentration between 10⁻⁴–10⁻⁵ molar were measured. The plots of molar conductance (ohm⁻¹ cm² mole⁻¹) against square root of concentration for compounds showed a typical behavior of weak electrolyte in DMSO solvent (Fig.1) and this result is in agreement with previous studies [12-15].

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تحضير وتشخيص بعض مشتقات السلينيوم غير المتجانسة الجديدة 3,5-Naphtho-1-Seleoncylohexane لـ

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ملخص

في هذه الدراسة تم تحضير سلسلة جديدة من مشتقات المركب 3,5-naphtho -1- selenocyclohexane و هي $C_{12}H_{10}SeRX$; $R=CH_3$; $X=I$ و $C_{12}H_{10}SeX$; $X=Cl, Br, I$. وقد شخّصت هذه المركبات باستخدام التحليل العنصري الدقيق (CHN) واطياف الأشعة تحت الحمراء (IR) واطياف الرنين النووي المغناطيسي (H^1 -NMR). واثبتت التوصيلية المولارية في مذيب ثنائي مثيل سلفوكسايد (DMSO) بان المركبات عبارة عن الكتروليتات ضعيفة.