# Synthesis and pectroscopic Studies of Some 1-Organo-1-halo-1-Selenocyclohexane Derivatives

**Dr. Ala'a I. Ayoob**
**The higher Inistitute for Teachers**
**MISURATA**

**د. علاء إسماعيل أيوب**
المعهد العالي لأعداد المعلمين مصراتة

**Abstract :**

A new series of heterocyclic selenium salts ($C_5H_{10}$ Se (RX) : R=X=Cl, Br, I or R=$CH_3$, $C_2H_5$, $C_3H_5$, X=I or R=$CH_3$, $C_2H_5$, Ph, X=$BPh_4$ or R=$C_2H_5$, $C_3H_5$, X=Br) have been prepared and characterized. The molar conductivies measured in DMSO or DMF indicate that these compounds are weak electrolytes and there is some ion pairing.

The H NMR spectra recorded in DMSO-d showed considerable stability towards reductive elimination reaction and do not interact with the solvent used. IR spectra are reported and discussed.

## Introduction :

Our previous investigation on organotellurium compounds showed that compounds derived from $C_4H_8OTe$ (RX) [1] or $C_{10}H_8O_3$ Te (RX) [2] and compound (2-$CH_3$)-$C_5H_9$-1-Te (RX) [3] are stable towards reductive-eliminatiom and do not interact with the solvent used.

Some work on the analogues organoselenium compounds had been previously carried out; the compounds $C_4H_8Se$ (RX) [4], $C_4H_8$ Ose (RX) [5], $C_{10}H_8O_3Se$ (RX) [6] and (2-$CH_3$)-$C_5H_9$ Se (RX) [7] have been prapared, but no details about their behaviour in solvents like DMF or DMSO were reported. Because of this and to inorder investigate such compounds, we report in the present work the synthesis and properties of new type of selenium compounds i.e $C_5H_{10}Se$ (RX) which is to the best of our knowledge have not been previously attempted.

## Experimenntal :

### General :

$^1$H NMR spectra were recorded on a Hitachi perkim-Elmer HR-60 MHz spectrometer with TMS as internal reference.

Solution conductivities were measured with a WTW conducticity meter LBR, using a standard conductivity cell with cell comstant of 0.0577.

IR spectra were recorded with KBr discs in the range 4000-200 cm on a Bechman TM spectrophotometer.

**Preparatiom of the comounds :**

1,1-diiodo-1-selenocyclohexane (Ia) :

This compound was prepared according to the following procedure.

Selenium dust (0.79g, 0.01 mol) was added to a mixture of 1,5-dibromo pnetane (1.23g, 0.01 mol) and sodium iodide (9g, 0.06 mol) in 2-butoxy ethanol (100 ml). The mixture was heated slowly with stirring for ca. 3hrs. until the colour became deep-red. The reaction mixture was filtered through celite while it is hot and solution was cooled to room temperature. Distilled water (200 ml) was then added to the solution. The yellow precipitate was filtered off, washed with water, then with alclhol, and recrystallized from ethanol to give off yellow crystals (Table 1).

1,1-dichloro-1-selenocyclohexane (II) :

This compound was prepared by a method similar to that reported by Al-Rubaie [8] from selanocyclohexane (2ml) and sulphonyl chloride (2ml). A white solid compound was formed on crystallization of the product from ethanol (Table 1).

1,1-dibromo-1-selenocyclohexane (IIIa) :

This white solid compound was prepared by treatment of bromine solution (2ml) in ether with selenocyclohexane (2ml) in ether. The solid was filtered off and recrystallized from ethanol as white crystals (Table 1).

1-methyl-1-iodo-1-selenocyclohexane (Ib) :

This was prepared by the stepwise addition of sodium borohydride ($NaBH_4$) ((0.76g, 0.02 mol) to a solutiom of (Ia) (0.403g, 0.01 mol) in ethanol (30ml) until the yellow colour of the solution had completely disappeared. The reaction mixture

was filtered through celite, and then distilled water (200 ml) was added. The product was extracted with ether (3 X 30 ml), and the etheral solution was dried over calcium chloride. To the dry etheral solution an exess of freshly distilled methyl iodide was added and the mixture allowed to stand for 2hrs. A white soled started to deposit, it was filtered off and recrystallized from ethanol as white crystals (Table 1).

Similarly the compounds Ib, Ic, Id and IIIb, IIIc were prepared from selenocyclohexane and the corresponding alkyl halide (Table 1).

1-methyl-1-selenocyclohexane tetraphenyl borate (Iva) :

This was prepared by heated a mixtre of (Ib) (0.291g, 0.01 mol) and sodium tetraphenyl borate ($NaBPh_4$) (3.42g, 0.01 mol) in ethanol under continuous stirreing for ca. 2hrs. The white solid was filtered off and recrystallized from a mixture of DMF/Water (1:3 ratio) to give IVa as white crystals (Table 1).

1-ethyl-1-selenocyclohexane tetraphenyl borate (Ivb) :

This was prepared by heated a mixture of (Ic) (0.305g, 0.01mol) and sodium tetraphenyl borate (3.42g, 0.01mol) in ethanol ynder continuous stirring for ca. 2hrs. The white solid was filtered off and recrystallized from a mixture of DMF/$H_2$o (1:3 ratio) to give Ivb as white crystals (Table 1).

1-phenyl-1-selenocyclohexane tetraphenyl borate (IVc) :

This was prepared by heating a mixture of (Ia) (0.403g, 0.01 mol) and $NaBPh_4$ (3.42g, 0.01 mol) in ethanol for ca. 2hrs. The white solid was filtered washed with water and ethanol, and recrystallized from DMF/H O (1:3 ratio) to give IVc as white crystals (Table 1).

**Result and Discussion :**

The compounds (Ib,c, II, IIIa-c and IVa-c) were prepared as white solids, their physical properaties are listed in Table 1.

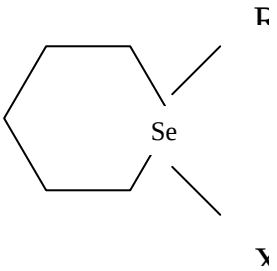
The IR spectral data for these compounds showed no unusual features. The V(Se-C(R) band was observed between 465-530 $cm^{-1}$ and V(Se-$C_{2,6}$) band was observed between 425-495 $cm^{-1}$.

The conductivities of each compound were obtained in both DMSO and DMF single concentration data ($10^{-3}$ M) and presented in Table 1. Each compound was examined over a range of concentration ($10^{-3}$ – $10^{-5}$ M). In each case no linear plots of molar conductivity ( M) against $\sqrt{C}$ were obtained indicating that an appreciable ion pairing between the cation (selenium site) and the anion exists but in DMSO at least, the value of ( M) (Table 1) nearly approach those sxpected for 1:1 electrolytes. It is clear from Table 1 that the conductivity value of compounds Ia, II and IIIa are less than those for the other compounds under investigation i.e $C_5H_{10}$-Se (RX). This could be attraibuted to either dimerization of the former compounds [10,11] or to inductive effect of the halogen in $C_5H_{10}$-Se ($X_2$) which are covaently value of the former compounds were founds to increase successively by icreasing the atomic number of the halogen i,e I>Br>Cl. This may be explained on the basis of differences in electronegativity of these halogens. Compounds IVa-c give a surprisingly low conductivity in DMSO and DMF (Table 1). This may be attributed to close contact between a selenium atom and one phenyl ring of the $BPh_4$ ion as observed by x-ray and molecular structure studies on analogous compound [13]. Some representative $^1H$ NMR data in DMSO are presented in Table 2. The methylene protons ($C_{2.6}$) showed triplents for compounds Ia, II, IIIa. However, replacement of one halogen by

an alkyl group covalently attached to the selenium atom showed a remarkable change in the methylene spectrum; it appeared as a multiplet complex single Table 2.

In the $^{1}H$ NMR spectrum of compound Ib, in DMSO, one singlet was observed at $\delta$=2.25 ppm. The position of the methyl group did not change after 24h, which may be attributed to the stability of this compound to reductive elimination [9,10]. No signal was observed at $\delta$ =2.07 ppm (due to the formation of $[(CH_3)_2 SO \ldots.CH_3]^+$ indicating that there is no reaction between the solute and solvent such as recently demonstrated for telluronium salts derived from phenoxatellurine [14]. The spectra of I-IV in DMSO were similary recorded but none of the salts studied showed reductive elimination of alkylhalides or reaction with DMSO.

Table 1: Physical properties of selenium compounds




| Comp. No. | X | R | M.P C | Yield % | IR data V $cm^{-1}$ C-H | C=C | Se-C(R) | Se-C | Conductivity M $Ohm^{-1}$ $C m^2$ $Mol^{-1}$ DMSO | DMF |
|---|---|---|---|---|---|---|---|---|---|---|
| Ia | I | I | 111-113 | 45 | 2870 | ----- | ----- | 425 | 22.5 | 38.3 |
| Ib | I | $CH_3$ | 185-187 | 75 | 2880 | ----- | 525 | 485 | 23.8 | 51.6 |
| Ic | I | $C_2H_5$ | 158-160 | 65 | 2875 | ----- | 520 | 485 | 26.3 | 52.8 |
| Id | I | $C_3H_5$ | 131-132 | 45 | 2890 | 1630 | 530 | 495 | 27.8 | 58.3 |
| II | CI | CI | 85-87 | 55 | 2870 | ----- | ----- | 465 | 12.1 | 21.4 |
| IIIa | Br | Br | 95-97 | 50 | 2885 | ----- | ----- | 450 | 19.3 | 30.6 |
| IIIb | Br | $C_2H_5$ | 142-143 | 60 | 2890 | ----- | 465 | 455 | 30.1 | 56.3 |
| IIIc | Br | $C_3H_5$ | 135-137 | 45 | 2915 | 1635 | 520 | 475 | 31.2 | 62.5 |
| Iva | $BPh_4$ | $CH_3$ | 195-197 | 60 | 3035 | ----- | 515 | 470 | 17.6 | 25.7 |
| Ivb | $BPh_4$ | $C_2H_5$ | 207-209 | 60 | 3035 | ----- | 480 | 465 | 18.1 | 26.1 |
| Ivc | $BPh_4$ | Ph | 215-217 | 65 | 3035 | ----- | ----- | 475 | 17.1 | 24.6 |

Molar conductivities were measurured for $10^{-2}$M solution of the compound

$[(C_2H_5)_4N] -Cl^-$ ; M 30(DMSO), 80(DMF) $ohm^{-1}$ $cm^2$ $mol^{-1}$

.

Table 2: $^{1}$H NMR (S PPm) for Selenocyclohexane Derivates.

| Comp | Chemical shift | (PPm) and assignment |
|---|---|---|
| Ia | 1.60-1.75 (m) | H ($C_{3,4,5}$) |
| | 3.35 (t) | H ($C_{2,6}$) |
| Ib | 1.55-2.00 (m) | H ($C_{3,4,5}$) |
| | 2.25 (s) | -$CH_3$ |
| | 3.35-3.65 (m) | H ($C_{2,6}$) |
| Ic | 1.40 (t) | Se-$CH_2CH_3$ |
| | 1.50-2.10 (m) | H ($C_{3,4,5}$) |
| | 2.50 (q) | Se-$CH_2$ |
| | 3.60-3.75 (m) | H ($C_{2,6}$) |
| Id | 1.50-2.18 (m) | H ($C_{3,4,5}$) |
| | 3.60-3.70 (m) | H ($C_{2,6}$) + Se-$CH_2$ (α) |
| | 5.15-5.35 (m) | CH (β) |
| | 5.55-6.25 (m) | CH (γ) |
| II | 1.50-2.18 (m) | H ($C_{3,4,5}$) |
| | 2.70 (t) | H ($C_{2,6}$) |
| IIIa | 1.55-1.85 (m) | H ($C_{3,4,5}$) |
| | 2.75 (t) | H ($C_{2,6}$) |
| IIIb | 1.35 (t) | Se-$CH_2CH_3$ |
| | 1.55-2.10 (m) | H ($C_{3,4,5}$) |
| | 2.45 (q) | Se-$CH_2$ |
| | 2.65-3.10 (m) | H ($C_{2,6}$) |
| IIIc | 1.55-2.20 (m) | H ($C_{3,4,5}$) |
| | 3.55-3.65 (m) | H ($_{2,6}$) + Se-$CH_2$ (α) |
| | 5.15-5.30 (m) | CH (β) |
| | 5.55-6.25 (m) | CH (γ) |
| Iva | 1.55-1.95 (m) | H ($C_{3,4,5}$) |
| | 2.20 (5) | -$CH_3$ |
| | 3.5503.60 (m) | H ($C_{3,6}$) |
| | 6.85-7.30 (m) | Ar-H |
| Ivb | 1.35 (t) | Se-$CH_2CH_3$ |
| | 1.50-2.15 (m) | H ($C_{3,4,5}$) |
| | 2.55 (q) | Se-$CH_2$ |
| | 3.30-3.55 (m) | H ($C_{2,6}$) |
| | 6.80-7.35 (m) | Ar-H |
| Ivc | 1.65-2.15 (m) | H ($C_{3,4,5}$) |
| | 3.50-3.65 (m) | H ($C_{2,6}$) |
| | 6.85-8.10 (m) | Ar-H |

* Downfield from internal TMS. Using DMSO-$d_6$ as a solvent.

+ Abbreviation: s,d,t,m means singlet, doublet triplet (with J=7 HZ) and multiplet, respectively,α, β, γ are for the allyt carbons $CH_2$-CH=$CH_2$, respectively.

**References :**

A.Z.AL-Rubaie, H.A.AL-Shirayda and A.I. Ayood, J. Organomet. Chem. , 134, 139 (1987).

A.I. Ayoob and T.A.K.AL-Allaf, Asian, J.Chem. in press (1991) and reference therein.

A.I. Ayoob and T.A.K.AL-Allaf, Asian, J, Chem. 38.3 (1991).

G.T. Morgan and F.H. Burstall J.chem. Soc. 1096 (1929).

C.S. Gibson and J.D.A. Johnson J.Chem. Soc. 266 (1931).

A.I.Ayoob, Accepted in J. of Education and science (1993).

A.I.Ayoob, Accepted in J. of Education and Science (1993.

A.Z.AL-Rubaie and H.A.AL-Shirayda, J. of Iraqi Chem. Soc. 87, 10 (1985).

A.Z. AL—Rubaie, W.R>McWhinnie, P.Granger and S. Chapelle, J.Organomet. Chem. 234, 287 (1982).

A.Z.AL-Rubaie, H.A.AL-Shirayda, P. Granger and S. Chapelle, J. Organomet. Chem. 287, 321 (1985).

J.D. McCullough, Inorg. Chem. 2669, 12(1973).

N.Zumbulyad and H.J.Gysling, J.Organomet. Chem. 138, 192 (1980).

R.H. Jones and T.A.Hamor, J.Organometal. Chem. 269, 11 (1984)

D.P. Rainville and R.A.Zingaro, inorg. Chim. Acta 86. 33 (1984).