National Journal of Chemistry,2007, Volume 27 ,491-500 المجلة القطرية للكيمياء-2007-المجلد السابع والعشرون

Preparation and Spectroscopic Study of Some SelenoCyclo Pentane Derivatives

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(Received on 28/12/2006) **(Accepted for publication on 10/7 /2007)**

Abstract

A new series of cyclic selenium compounds of the type ($C_4H_8SeBrCO_2R$), derived from selenocyclopentane have been synthesized , where R = H; CH_3; C_2H_5; C_3H_7; $C(CH_3)_3$.

The conductivity measurements of their solutions in dimethyl sulphoxide (10^{-3}– 10^{-5}*M*), showed that the salts behave as (1 : 1) electrolyte and the conductivity decreases as the alkyl group of the carboalkoxymethyl derivatives is increased.

The I.R, ^{1}H-NMR and (C.H.N) data are reported and discussed below.

الخلاصة

تم تحضير مجموعة جديدة من مركبات السلينيوم الحلقية ذات الصيغة الجزيئية ($C_4H_8SeBrCO_2R$) والمشتقة من السلينوسايكلوبنتان حيث أن : R = H; CH_3; C_2H_5; C_3H_7; $C(CH_3)_3$. كما درست التوصيلية المولارية لمحاليل هذه المركبات وهي 1-برومو-1-كاربو الكوكسي مثيل-1-سلينوسايكلوبنتان في المذيب ثنائي مثيل أوكسيد الكبريت (DMSO) وبتراكيز تراوحت بين (10^{-3} – 10^{-5}) مولاري ، وقد أظهرت هذه النتائج إن محاليل هذه المركبات عبارة عن ألكتروليتات ضعيفة تقترب من القيمة (1 : 1) ألكتروليت.

شخصت المركبات المحضرة بوساطة أطياف الأشعة تحت الحمراء وبروتون الرنين النووي المغناطيسي وجهاز التحليل العنصري الدقيق (C.H.N) وتمت مناقشة النتائج على ضوء هذه التحاليل.

Introduction

Selenium is essential micro nutrient for animals and humans, although it was once known only for its toxicity(1). Selenium is a component of many enzymes and proteins in mammals(2). More recently, a large body of convincing evidence has indicated that Selenium act as a cancer preventative agent when given in pharmacological amounts(3-5). In addition, some of its compounds are used as antioxidants in some oil grease(6), and semi – conductives industry(7).

Very efforts were spent in recent years by the researchers to prepare many hetero cyclic compounds which have heterogeneous atom as one of the sixth group(8-14). Many selenium salts cyclic and acyclic are prepared(15-17) having the chemical formula of $[R_3M]^+[X]^-$ which means that these compounds have an ionic properties because of the existence of both of cation and anion.

Some researchers have already prepare some selenolanium salts of type trialkyl- (aryl) selenolanium halide(8,18). Selenolen is regarded as a good nucleophelic reagent because of the existence of the lone pairs of electron. Depending on this characters of the selenolan some selenolanium salts of the type of alkylacetyldibutyl selenolanium bromide are prepared from the reaction of dibutyl selenolan and alkyl bromo acetate(19).

The present work reports the synthesis of 1-bromo-1-carboalkoxy-1-seleno cyclopentane by the reaction of different bromo alkyl acetates ($BrCH_2CO_2R$) with cyclo selenolan.

Experimental

A- *Materials and Methods*

All chemicals are obtained from (Fluka, Merck and BDH), except of 1,1-di iodo selenolan $C_4H_8SeI_2$ which is prepared as described in the literature(16). The solvents used are purified by standard procedures. The melting points are determined on "P.D-303" APEL and uncorrected. Infrared spectra as CsI discs in the range of (4000 – 200 cm^{-1}) are recorded on a Pye – Unicam SP3 – 300 Spectrophotometer. ^1H– NMR spectra are recorded on SFOI 300 MHz instrument. Analysis for carbon and hydrogen are obtained with Micro analytical unit, 1108 C.H.N Elemental analyzer. Selenium ion concentrations are determined by Shimadzu – AA – 160 Atomic Absorption Flame Emission Spectrophotometer. Molar conductivity are measured by WTW – Conductivity Meter LBR.

B- Preparations

1. Selenocyclopentane $C_4H_8Se^{(13)}$

1,1-Di iodo selenolan (7.78gm, 0.02mole) is dissolved in (100ml) of hot ethanol. The sodium borohydride (1.51gm, 0.02mole) is then added to the reaction mixture with stirring. After cooling the solution is diluted with water (150ml). The mixture is extracted with diethyl ether (3×100ml) and washed with water, and then dried with ($MgSO_4$), the solution is filtered off and concentrated by using rotatory evaporator, to give a viscous yellow oil.

2. 1-Bromo-1-carboxy methyl-1-selenocyclopentane

$C_4H_8SeBrCH_2CO_2H$

A solution of α-bromo acetic acid (0.01mole) is added to excess of cycloselenolan in ether solution a pale yellow crystals are formed, it is dried and recrystallized from ethanol to gave a yellow crystals.

3. 1-bromo-1-carbo methoxy methyl-1-seleno cyclopentane $C_4H_8SeBrCH_2CO_2CH_3$

It is prepared by treating α-bromomethylacetate (0.01 mole) with excess of cyclo- selenolan in its ether solution in the same method of compound (1). Yellowish white powder was obtained.

4. *1-bromo-1-carbo ethoxy methyl-1-selenocyclopentane*:

$C_4H_8SeBrCH_2CO_2C_2H_5$

It is prepared from adding α-bromo ethyl acetate (0.01mole) with excess of cyclo selenolan in its ether solution. The mixture was stirred for 3hr at (60°C), and the yellow precipitate then filtered off, washed with acetone and air dried. Recrystallization from ethanol to gave a pale yellow crystals.

5. 1-Bromo-1-carbopropoxy methyl-1-selenocyclopentane

$C_4H_8SeBrCH_2CO_2C_3H_7$

It is prepared by treating α-bromopropylacetate (0.01mole) with excess of cyclo- selenolan (0.01 mole) in ether. The mixture is heated at (50°C) with stirring for 5hr. the solution is cooled and the precipitate is collected, washed with acetone and air dried. Recrystallization from chloroform gives white crystals .

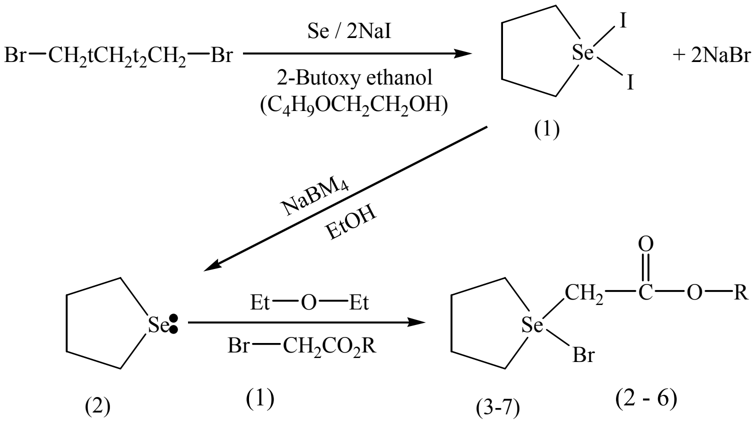
6. 1-Bromo-1-carbo(tre-.butoxy)methyl-1-selenocyclopentan

$C_4H_8SeBrCH_2CO_2C(CH_3)_3$

A solution of α-bromo t-Butyl acetate (0.01 mole) in (50 ml) ethanol is added with continuous stirring to a hot etheric solution of cycloselenolan (0.01 mole). The mixture was stirring for 3hr, the solution is filtered, the precipitate is washed by acetone and air dried. Recrystallized by ethanol to obtain a yellow crystals. Some physical properties and analytical data are summarized in Table.1.

Results and Discussion

The cycloselenolan contains selenium atom which has lone pair of electrons so it reacts easily with alkyl halide(15-18), depending on this quality of cycloselenolan a new heterocyclic selenolan compounds have been obtained by the reaction between cycloselenolan and α-bromoalkylacetate as the following scheme.1, presents



R = H ; CH_3 ; C_2H_5 ; C_3H_7 ; $C(CH_3)_3$

(2) (3) (4) (5) (6)

Scheme.1: Methods of preparation of new hetero cyclic selenium compounds

The accurate conclusions of elemental analysis (C.H.N), IR, and ^{1}H-NMR spectra for these compounds prove that their structures are correct as shown in the Tables 1, 2, and 3 respectively. The elemental analysis data of these compounds which summarized in Table.1, are consistent with the calculated results from the empirical formula of each compound.

Table.1: Some physical properties and analytical data of the prepared compounds

R	Color	Melting point (°C)	Yield %	Anal. Found (Calc.)%		
				C	H	Se
H	Yellow	122 - 124	87	26.29 (26.64)	4.04 (4.24)	28.81 (28.39)
CH_3	Yellowish - white	89 - 91	91	29.18 (28.81)	4.55 (4.39)	27.41 (26.88)
C_2H_5	Pale yellow	136 - 138	78	31.81 (31.35)	5.00 (4.76)	26.14 (25.54)
C_3H_7	White	223 - 225	82	34.19 (34.69)	5.42 (5.11)	24.98 (25.59)
$C(CH_3)_3$	Yellow	211 - 213	72	36.38 (35.89)	5.80 (5.56)	23.92 (23.41)

IR Spectra

Through studying IR spectra for 1-bromo-1-carboalkoxyl methyl-1-selenocyclo- pentane compounds, it is noticed that the absorption of carbonyl group is less than that of esters which absorbs in 1735 cm^{-1}. This difference is justified under the existence of mutual interference between oxygen atom of carbonyl group and selenium atom. The absorption of carbonyl group in compound (2) is less than of the absorption of the other compounds because of hydrogen bonding as well as inductive effect of the alkoxy group.

The IR spectra of all compounds show two weak bands in the range of 570–585 cm^{-1} which may due to ν_S ($C_{2,5}$─Se) and broad bands characteristic of ν_S (Se─C_{alkyl}) at 605– 620 cm^{-1} .These are agree with the previous studies(15,17,20). IR spectra show strong bands characteristic of ν_S (CO) group at 1710–1725 cm^{-1} and weak bands characteristic of ν_S (Se─Br) were located at 325–340 cm^{-1}. Relevant IR data are presented in Table.2.

Table.2: Characteristic IR absorption bands of 1-bromo-1-carboalkoxymethyl-1-selenocyclopentane ($C_4H_8SeBrCH_2CO_2R$)

R	ν_{as} (C—O—C)	ν(C—O—C)	ν(C═O)	ν(C—H)$_{aliph}$	ν(Se—Br)	ν(Se—C$_{alkyl}$)	ν(Se—C$_{2,5}$)
H	1260	1100	1710	2950	335	605	570
CH_3	1250	1105	1720	2945	340	620	580
C_2H_5	1265	1150	1720	2950	330	615	575
C_3H_7	1270	1100	1715	2955	335	610	585
$C(CH_3)_3$	1285	1150	1725	2950	325	615	570

A representative example for these spectra are given in Figs. 1 and 2.

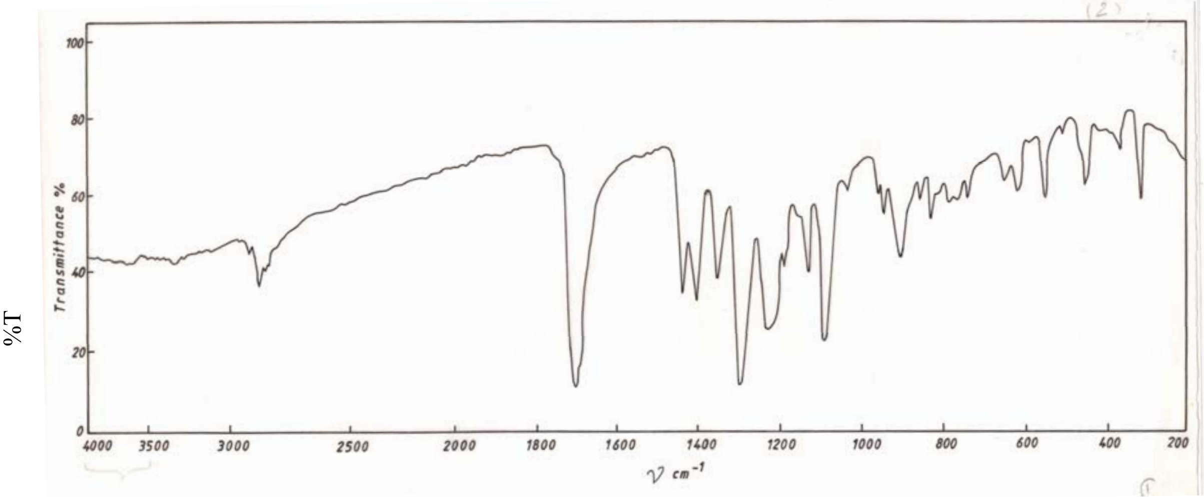


Fig.1: IR spectrum of 1-Bromo-1-carboxymethyl-1-selenocyclopentane $C_4H_8SeBrCH_2CO_2H$

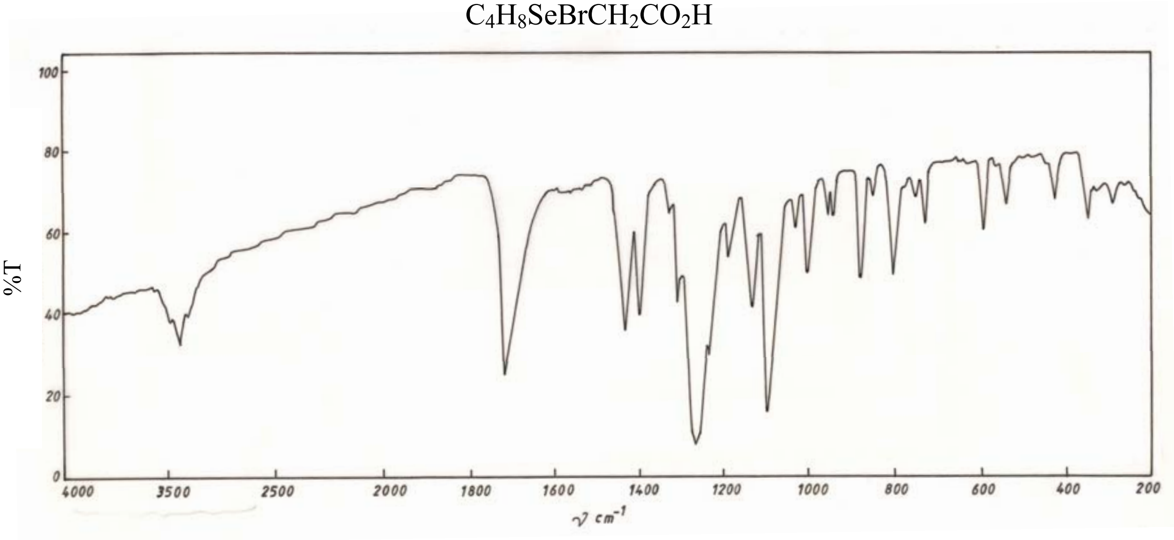


Fig.2 : IR spectrum of 1-bromo-1-carbomethoxymethyl-1-selenocyclopentane $C_4H_8SeBrCH_2CO_2CH_3$

^{1}H-NMR Spectra

The ^{1}H-NMR spectra of the compounds were obtained in d_6 – DMSO at room temperature using TMS as reference. The ^{1}H-NMR data and assignments of the compounds are presented in Table.3. The signals are identified through chemical shift, intensity, and their frequencies(15-21).

All these compounds show two identical signals at the chemical shift of δ = 2.6 – 3.7 ppm, and δ = 1.8 – 2.8 ppm, which are related to the (2 , 5) and (3 , 4) methylene ring protons respectively.

Table.3: ^{1}H-NMR data for the 1-bromo-1-carboalkoxymethyl-1-selenocyclo-pentane $C_4H_8SeBrCH_2CO_2R$

R	Assignment	Chemical shifts (ppm) TMS = 0 ppm
H	$H_{(2,5)}$	3.1 – 3.7 complex over lapping
	$H_{(3,4)}$	2.2 – 2.5 complex over lapping
	Se─CH_2	2.7 (s)
	O─H	8.3 (s)
CH_3	$H_{(2,5)}$	3.1 – 3.4 complex over lapping
	$H_{(3,4)}$	2.4 – 2.8 complex over lapping
	Se─CH_2	3.7 (s)
	O─CH_3	4.1 (s)
C_2H_5	$H_{(2,5)}$	3.2 – 3.5 complex over lapping
	$H_{(3,4)}$	2.4 – 2.7 complex over lapping
	Se─CH_2	3.4 (s)
	O─CH_2	4.2 – 4.5 (q)
	CH_2─CH_3	1.4 – 1.7 (m)
C $(CH_3)_3$	$H_{(2,5)}$	2.6 – 2.9 complex over lapping
	$H_{(3,4)}$	1.8 – 2.1 complex over lapping
	Se─CH_2	3.4 (s)
	$C(CH_3)_3$	1.5 (s)

A representative examples of their spectra are given in Figs.3, and 4.

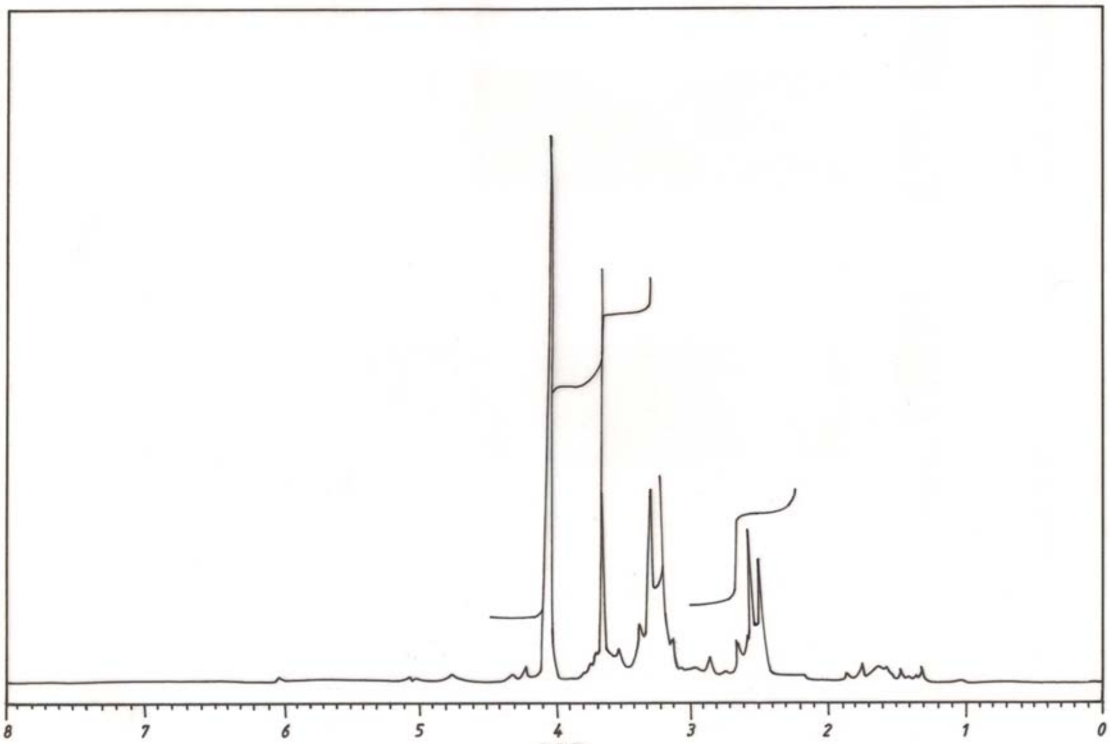


Fig.3 : ^{1}H-NMR spectrum of 1-Bromo-1-carboxymethyl-1-selenocyclopentane

$C_4H_8SeBrCH_2CO_2H$

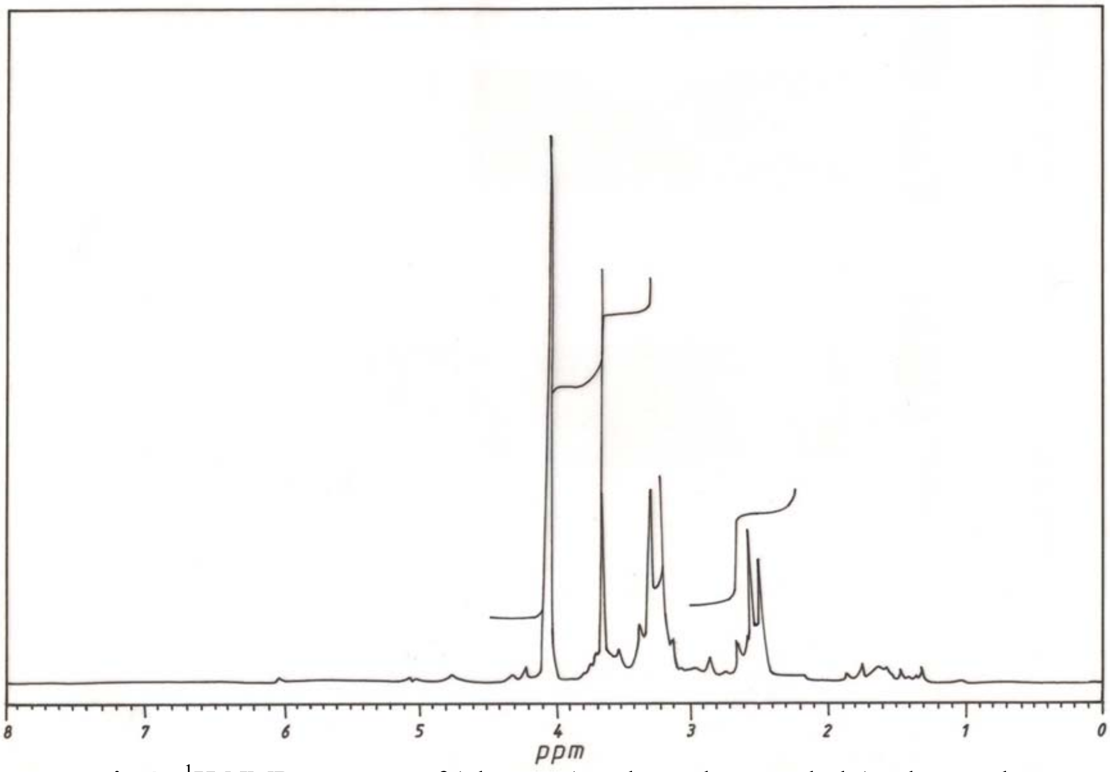


Fig.4 : ^{1}H-NMR spectrum of 1-bromo-1-carbomethoxymethyl-1-selenocyclopentane

$C_4H_8SeBrCH_2CO_2CH_3$

Molar Conductivity

The measured molar conductance's (Λm) of the selenolanium salts in (10^{-3} - 10^{-5} M) of DMSO solution, for identifying the ionic nature of these salts, as well as determining the effect of alkyl group volume.

The values of Λ_m for these salts at 10^{-3} M means that these salts are weak And this is related to the large positive ion volume which leads to limiting its motion in the solution. While the Λ_m of compound (2) is disagree with order electrolytes(15-22). They are represented in Table.4 and Fig. 5. They showed the plots of Λ_m against $(conc)^{½}$ showed a marked curvature for each of these salts, this is a typical of 1:1 electrolyte, this is in favor with the literature and the Λ_m values decrease with the increment of the alkyl group volume according to the following order;

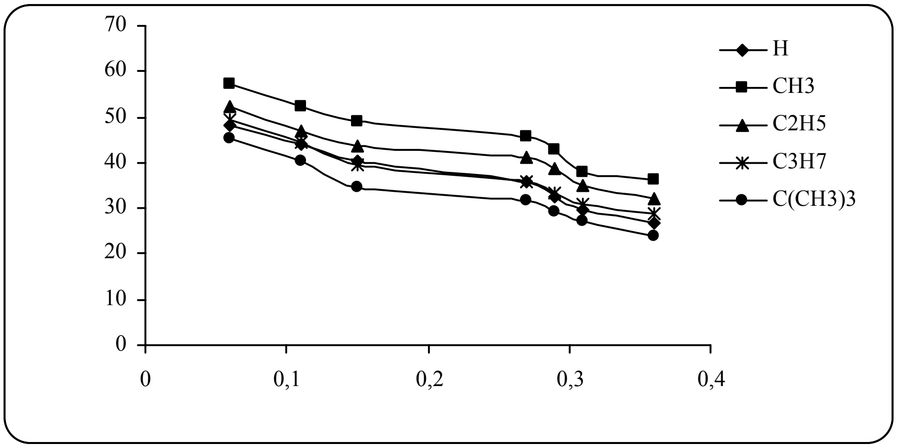
$-CH_3 > -C_2H_5 > -C_3H_7 > -C(CH_3)_3$

mentioned above because of the hydrogen bond existence which decrease the Λ_m value(16,17), Table.4.

Table.4: Conductivity data of 1-bromo-1-carbalkoxymethyl-1-selenocyclopentane ($C_4H_8SeBrCH_2CO_2R$)

R	Molar conductance Λ_m $ohm^{-1}.cm^{-2}.mol^{-1}$ (10^{-3} M, DMSO)*
H	26.73
CH_3	36.31
C_2H_5	32.03
C_3H_7	28.64
$C(CH_3)_3$	23.96

*10^{-3} M solutions Et_4NCl, (DMSO) 30. $ohm^{-1}.cm^2.mol^{-1}$



$\sqrt{c} \times 10^{-1} M$

Fig.5: Molar conductance of 1-bromo-1-carboalkoxy-1-selenocyclopentane

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